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# Upgrading and desulfurization of heavy oils by supercritical water

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**Abstract.** Supercritical water upgrading (SCWU) of heavy oils reduces sulfur content and decreases average molecular weight, without rejecting carbon as coke products. Despite many years of industrial and academic scrutiny, many fundamental questions remain in the field: intrinsic reaction rates and mechanisms; the role of water; the need for catalysts; the importance of phase behavior and mixing. In 2009, MIT initiated a SCWU research program aimed at improving the understanding of the relevant physical, chemical, and catalytic phenomena. This overview summarizes the work performed at MIT within the historical context of SCWU with a particular focus on new kinetic rate measurements and modeling, reaction mechanism analysis, catalyst investigation, and combined mass/heat transport modeling of hydrocarbon/water mixtures. Kinetic rate measurements showed that sulfide decomposition during SCWU is consistent with a radical chain reaction pathway. Mechanistic studies and product distribution analysis identified that sulfide decomposition likely occurs via thioaldehyde and aldehyde intermediates and that water plays important roles in thioaldehyde hydrolysis (as a reactant) and aldehyde decarbonylation (as a catalyst). Catalytic investigation found that ZnO has potential to improve sulfur removal during SCWU, without addition of molecular hydrogen. Mixing studies revealed the complex dynamic processes that occur when hydrocarbons are injected into near or supercritical water. The article concludes with a summary of research needs and thoughts on the future of SCWU.

## 1. Introduction.

Near and supercritical water (SCW), collectively termed hydrothermal water (HTW) in this review, have been successfully used for carbonization, gasification, liquefaction, and upgrading of hydrocarbon resources including crude oils (with a specific emphasis on heavy oils and heavy fractions),[1-14] microalgae,[15-21] lignocellulosic biomasses,[22-26] and wastes.[25,27] Although HTW requires elevated pressures compared to some competitive technologies, it has potential advantages in terms of process intensity, process energy balance, water recovery, and product distribution. In terms of process intensity, HTW is performed at higher densities than

gas-phase pyrolysis reactions, thereby affording potential throughput benefits as well as enhanced heat and mass transport. For process energy balance, performing reactions in a dense water phase means that feedstocks, many of which are naturally available in a wet form, need not be dried prior to processing. Moreover, heat recovery can be performed in compact and efficient liquid-liquid heat exchangers, thereby further improving system energy balance. Finally, water recovery is made easier since much of the water lost during dry processing of wet feedstocks can be contained; for HTW processing, the water is not evaporated, eliminating the need for costly water-condenser operations. In terms of product distribution, high-temperature processing in a water-rich environment reduces carbon lost to coking [8] – and a growing body of work suggests that water may instead donate hydrogen to the carbon resource, further improving the quality and yield of liquid products.[28-30]

Despite these advantages, HTW technologies have yet to achieve sustained commercial success. In December 2013, a group of experts met in Campinas, Brazil to discuss the commercial potential and challenges facing the supercritical fluid (SCF) and HTW communities. Biofuel processing was one of five focused panels; talks were presented on topics ranging from high-pressure gas-to-liquids technologies (presented by Karlsruhe Institute of Technology) to the use of supercritical carbon dioxide for bio-diesel purification (Federal University of Paraná). As part of this panel, the Massachusetts Institute of Technology (MIT) group presented an update on their work on supercritical water upgrading (SCWU) of heavy oils. In this overview, we summarize the MIT group's work on SCWU and use this as an opportunity to share with the broader community some thoughts on future research priorities.

## **2. HTW Technologies and the Water Phase Diagram.**

Manipulation of phase behavior during SCWU is likely a key aspect of the technology. SCWU is performed at temperatures that allow for rapid reaction rates without entering into a reaction regime that favors rapid gas formation. Figure 1 superimposes temperature/pressure ranges for HTW processes over the phase diagram of water. Water's triple point and critical point are shown in the phase diagram; the HTW technologies are typically performed in a narrow window just greater than the vapor-liquid co-existence curve or, for SCF conditions, at pressures slightly in excess of water's critical pressure (221 bar). Increasingly reactive conditions are encountered as temperature is increased while holding pressures greater than water's vapor pressure. On the time scale of hours and in the 150-200 °C range, hydrothermal carbonization (HTC) converts water-soluble and water in-soluble carbon fractions into insoluble carbonaceous solids.[31-34] On the time-scale of minutes or tens of minutes, hydrothermal liquefaction (HTL) converts feedstocks including lignocellulosic biomass or lipid-rich microalgae into an energy-rich bio-oil [15,35,36]. SCWU, the primary focus of this review, converts sulfur-rich heavy oils into lighter sweeter oils on the time scale of minutes and at temperatures ranging from 300-500 °C. At these conditions, reaction rates are appropriate for a large-volume product (upgraded crude oil), while minimizing gas and solid by-products. Accordingly at the higher temperature conditions used

for SCW-gasification (SCWG), hydrocarbons break down into a mixture of H<sub>2</sub>, CO, and methane on the time scale of minutes.[37-43]

Comparing Figure 1 with the temperature-varying properties of water near its critical point is instructive. At room temperature, water is a polar solvent characterized by a high dielectric constant (78) and ion product of  $1 \times 10^{-14}$ . Figure 2 shows even for the mildest of the HTW processes described in Figure 1 (i.e., HTC), the solvent and ionization properties of water differ substantially from those at room temperature. HTC, HTL, and SCWU are all performed at conditions where water's ionization constant differs substantially from ambient values (Figure 2a) and the dielectric constant is more similar to an organic solvent (Figure 2b). Therefore, while reaction chemistry remains dominated by temperature conditions for most HTW processes, an ample literature suggests that water's physical properties can play important roles in many cases.[44] As temperature is increased through HTC to SCWG, the relative importance of hydrolysis and other reaction types that require acid/base catalysis or that proceed via highly polar transition states gradually declines, whereas purely temperature driven reaction types, including radical chemistries, will gradually increase in importance.[45-47] Accordingly, SCWU is performed under conditions centered on the transition from dominance by ionic pathways (HTC and HTL) to dominance by radical pathways (SCWG).

### **3. SCWU Research at MIT.**

MIT initiated studies on SCWU in early 2009. The basic goal was a fundamental study on the use of HTW for the reduction of molecular weight and removal of sulfur from heavy, sour oils. The SCWU research effort built on the foundation of supercritical water oxidation (SCWO) and supercritical carbon dioxide studies that had been performed at MIT as far back as the 1970s.[45,48-57] The hallmark of the SCWO studies was a broad focus on range of fundamental chemical and physical phenomena, including reaction rate measurements, reaction mechanism elucidation by coupling experimental measurements with quantum chemical methods, corrosion studies, and experimental and modeling phase behavior studies.[48,49,52] Like the SCWO work that came before it, the SCWU program at MIT sought to integrate four specific thrusts: 1) experimental rate measurements,[4] 2) quantum chemical calculations and reaction mechanism investigation,[28] and 3) performance and stability of catalyst activity, specifically in the absence of added hydrogen:[58] 4) transport and mixing simulations.[59,60] As explained below, each of these areas was intended to close an existing gap in the literature. Herein, we report on progress in these four areas and conclude with some thoughts on future R&D priorities.

#### **3.1 Reaction Kinetics.**

A major focus of early SCWU work has been heteroatom removal. Due to its abundance in crude oil, sulfur removal has been a specific focus. Spanning the 1980s and 1990s, Katritzky and Siskin performed a well-known series of experiments probing the reactivity of a wide range of sulfur compounds in HTW.[61-66] Although Katritzky and Siskin reported reactivity for

many compounds, their batch-mode experiments did not afford an opportunity for high-precision kinetic rate mechanisms. Patwardhan et al.[4] recently reported kinetic rate measurement for SCWU of several representative sulfur compounds using a continuously-fed stirred tank reactor operating at 235 bar. Figure 3 provides representative data for hexyl sulfide (HS) and dibenzylsulfide (DBS) decomposition. In Figure 3a, conversion is plotted as a function of residence time for HS and DBS at several different reaction temperatures and several distinct feed concentrations. As expected, reaction temperature and the molecular structure of the sulfur compound both strongly influence its decomposition rate. However, beyond these general statements, the data in Figure 3a do not show direct evidence for underlying unifying mechanisms.

To make sense of the underlying trends, Patwardhan et al.[4] hypothesized the free-radical mechanism shown in Figure 4. Thus, the rate law takes the form:

$$Rate = -k_4[R \cdot][R_2S] = -k_4 \left\{ \frac{(k_1+k_2)}{k_t} \right\}^{1/2} [R_2S] = k_{effective}[R_2S] \quad (1)$$

and the Damköhler number ( $Da$ ), which is the ratio of the importance of reaction rates to bulk residence time in this instance, is defined by:

$$Da = \frac{k_{eff} F_{in}^{1/2} (1-X)^{3/2}}{V^{1/2} X} \quad (2)$$

notable for its inclusion of the feed sulfur concentration ( $[R_2S]_0$ ) to the  $\frac{1}{2}$  power through the definition of the conversion,  $X$ :

$$X = \frac{[R_2S]_0 - [R_2S](t)}{[R_2S]_0} \quad (3)$$

Plotting the sulfur compound conversion data using this definition of  $Da$  (Figure 4b) and fitting the effective rate constant  $k_{effective}$  at a given temperature for a given compound collapses the entire data set onto a single curve. Patwardhan et al. (2013) went on to show that Arrhenius plots of the fit rate constants were linear, yielding activation energies of  $40 \pm 1$  kcal/mol for HS and  $36 \pm 1$  kcal/mol for DBS. In both cases, best-fits of the logarithm of the pre-exponential factor were approximately  $25 \pm 3$ , indicating that all of the data in Figure 3 could be described by 4 parameters (two activation energies and two pre-exponential factors), all of which fall within reasonable ranges.

### 3.2 Reaction Mechanisms.

At the onset of the MIT studies of the SCWU process, the underlying chemical mechanisms were incompletely understood and based entirely on rationalizations of observed product distributions. Given that SCWU conditions span the critical point (Figure 1) where many relevant

physicochemical properties vary from liquid-like to gas-like (Figure 2), deciphering SCWU chemical mechanisms is particularly challenging. Specific knowledge gaps included: the relative importance of pyrolytic radical reaction pathways compared to hydrolytic or ionic pathways; the role of water; the coke reduction mechanism(s) responsible for the reduced coke product observed for SCWU relative to other high-temperature upgrading chemistries.

The MIT approach to address these questions was a combined experimental-theoretical study. Much of the work has focused on the reaction chemistry and product distributions obtained from alkyl sulfide decomposition with a focus on comparisons of SCW versus pyrolysis conditions.[28] Figure 5 shows representative product distribution data obtained for decomposition of HS in a high-temperature batch reactor (400 °C and >230 bar).[28] Under pyrolysis conditions in the absence of water, the primary HS decomposition products were *n*-hexane, hexanes, and hexanethiol. In the previous section, we showed that Patwardhan et al.[4] were able to explain a wide range of sulfide decomposition kinetics using a pyrolysis radical chain reaction mechanism, making the pyrolysis product distributions entirely expected. In contrast, Figure 5 provides HS decomposition product distribution data obtained for SCW conditions that are much more surprising. Specifically, HS decomposition produces pentane and a combination of CO and CO<sub>2</sub>, unexpected reaction products if the reaction indeed proceeds entirely through radical mechanisms. Moreover, the incorporation of oxygen in the reaction products clearly implicates a direct reactive role of water, since water is the only source of oxygen in the reaction mixture. Based on these observations, Kida et al.[28] surmised that water participates in the overall mechanism to convert C<sub>6</sub> intermediates into a mixture of C<sub>5</sub> and C<sub>1</sub> products, implying a C-C bond breaking event.

To understand the unexpected formation of pentanes, Kida et al.[28] undertook an extensive intermediate reactivity and quantum calculation study. Reactivity and product distribution products of putative intermediates were measured for the alkyl thiol, aldehyde, carboxylic acid, and thiocarboxylic acid. Of these, only the aldehyde exhibited decomposition rates fast enough to be consistent with a reactive intermediate and only the aldehyde decomposed primarily via a C-C bond break pathway. Based on these insights, Kida et al.[28] calculated the energetics for the pathway shown in Figure 6. After initial bond breaking occurs, the sulfur bearing product forms the thioaldehyde (compound 3 in Figure 6). The thioaldehyde is highly reactive and – in the absence of water – would self-polymerize. In the presence of water, the thioaldehyde instead forms first the germinal mercaptoalcohol (compound 4) via pericyclic addition of water to the C=S bond and then the aldehyde (compound 5). Conversion of the germinal mercaptoalcohol to the aldehyde takes place via the water-stabilized transition state labeled D in Figure 6; quantum calculations indicate that the water catalysis effect on this reaction is a 200-fold rate increase. Once the aldehyde is formed, formation of the C<sub>5</sub> and C<sub>1</sub> products is facile, as evidenced by the low barriers of reactions E and F. Although Figure 6 shows an overall increase in enthalpy associated with the reaction, calculated entropies are sufficient to push the reaction to the right in SCW.

The model encapsulated in Figure 6 offers insight into the outstanding questions that the MIT sought to answer. First, Figure 6 shows that water plays two separate roles in the overall mechanism: 1) as a reactant to intercept the highly reactive thioaldehyde to produce the germinal mercaptoalcohol and 2) as a catalyst to increase the conversion of the germinal mercaptoalcohol to produce the aldehyde. Both roles are crucial for the overall mechanism. Kida et al.[28] showed that water can play a role as a reductant in SCWU, reducing the need for molecular hydrogen. Second, the combined work of Kida et al.[28] and Patwardhan et al.[4] describe a combined mechanism of sulfur compound decomposition, consisting of both radical reactions which are responsible for initial disappearance rates and hydrolytic reactions which contribute to the observed product distribution. Finally, hydrolysis of the thioaldehyde likely explains at least part of water's ability to reduce coking. In the absence of water, the oil-phase reaction products of HS pyrolysis were a dark brown, suggestive of the presence of coke or coke precursors that eluded gas chromatography detection due to their low volatility. Oil-phase products produced under SCW conditions were clear and pale yellow, consistent with the diminished formation of coke products. Quantitatively, the improved mass balance obtained for SCW conditions (>90% at all reaction times) compared to pyrolysis conditions (as low as 65% after 30 min) is attributable to coke suppression by water. Based on these findings, water seems to play a role in short circuiting one coke formation pathway. In all likelihood, coke formation proceeds via multiple pathways, presumably involving formation of aromatic rings as an intermediate step, and continued work is merited for elucidating water's role in other coke formation pathways.

### 3.3 Catalysis.

Vogelaar et al.[67] published an influential report on the use of SCW for gasoil desulfurization, concluding that both added molecular hydrogen and desulfurization catalyst were required for decomposition of the cyclic aromatic sulfur compounds that are known to be the most recalcitrant sulfur carriers present in petroleum fractions. Following this work, the SCWU field largely focused attention on molecular weight, density, and viscosity reduction. As part of their HS and DBS kinetic study, Patwardhan et al.[4] performed decomposition rate tests on several cyclic and aromatic sulfur compounds. Table 1 summarizes the results, showing that the cyclic aromatic sulfur compounds (e.g., thiophene and dibenzothiophene) are stable when held for 30 minutes in SCW at 400 °C. Quantum calculations revealed that the strength of the H-C bond adjacent to the sulfur atom was a determining feature of sulfur compound stability.  $\Delta H$  for abstraction of this H ranged from 86.4 to 94 kcal mol<sup>-1</sup> for compounds which decomposed at least 16% under these reaction conditions. Diphenyl sulfide – which lacks a hydrogen atom on the adjacent carbon atom – was stable while  $\Delta H$  for hydrogen abstraction from the aromatic heterocycle thiophene was calculated to be 119 kcal mol<sup>-1</sup>, indicating a much stronger C-H bond in this compound. This C-H bond strength argument is therefore consistent with radical chain reaction mechanism described in Figure 4.

Motivated by the Vogelaar et al.[67] and Patwardhan et al.[4] studies and informed by the roles of water elucidated by the Kida et al.[28] study, Ates et al.[58] studied sulfur compound decomposition in the presence of catalysts but without addition of molecular hydrogen. Similar work has been performed by the Tohoku group, who used CO and formic acid and Mo-based catalysts for in situ generation of hydrogen,[11] and Furimsky[68], who studied the use of noble metals. Ates et al.[58] studied the SCWU use of inexpensive materials – namely MoS<sub>2</sub>, Mo<sub>2</sub>O<sub>3</sub>, and ZnO – and did not use any auxiliary chemicals aside from water alone, which is similar to a very recent report using metallic Zn for bitumen SCWU.[3,14] Three materials were selected as a desulfurization catalyst (MoS<sub>2</sub>), a sulfur adsorbent material (ZnO), and a material that would behave as a sulfur adsorbent and be converted into a catalyst (Mo<sub>2</sub>O<sub>3</sub>). Figure 7 contains sulfur-selective chromatograms obtained for analysis of Arabian Heavy (AH) crude oil, AH treated in a SCW batch reactor for 30-min at 400 °C, and AH treated with MoS<sub>2</sub> in a SCW batch reactor for 30-min at 400 °C. The analysis of the AH feed indicates the presence of a manifold of benzothiophene (BT) and DBT compounds. Interestingly, the relative proportions of specific BT and DBT compounds shift after non-catalytic SCW treatment and, even more interestingly, a new manifold of substituted thiophenes appears. For the MoS<sub>2</sub>-SCW treated AH, the BT and DBT content is modulated but the thiophene compounds are suppressed. Due to its low volatility, only about 20-30% of the sulfur content of AH can be analyzed using standard GC techniques. Therefore, a hypothesis consistent with Figure 7 is that SCW promotes decomposition of large, non-volatile sulfur-bearing compounds into BT and thiophenic compounds, which then remain stable. MoS<sub>2</sub>-SCW treatment causes decomposition of large sulfur-bearing molecules, but the presence of the desulfurization catalyst causes further decomposition of the thiophenes as evidenced by the sulfur selective chromatograms in Figure 7.

In addition to activity tests, Ates et al.[58] performed post-reaction catalyst characterization tests which included x-ray diffraction spectrometry, x-ray photoelectron spectroscopy, temperature programmed oxidation, and electron microscopy. The characterization tests confirmed that the MoS<sub>2</sub> was stable morphologically and chemically. ZnO and Mo<sub>2</sub>O<sub>3</sub> surfaces converted into the sulfide forms (>60%) but the bulk remained primarily as oxides (<20% bulk sulfidation). In addition, the Mo<sub>2</sub>O<sub>3</sub> underwent a morphological change from micron-size plates to nanoflowers. Carbonaceous deposits, possibly due to coke formation, were present on all of the catalyst surfaces and coke formation on catalysts in SCW conditions merits further investigation.

### **3.4 Transport and Phase Behavior.**

As suggested by Figures 1 and 2, phase behavior remains an important variable for many processes that utilize a component near its critical point. For HTL processes, the elevated temperature and pressure conditions make experimental measurements particularly challenging. Early work in this area was pioneered by E.U. Franck[69-71] and Erwin Brunner, at BASF AG, and largely published posthumously by Thies and Gerhard Schneider.[72] These data were collected using a high-pressure view cell equipped with a sapphire window to observe regions of phase co-existence. As such, their work was focused on identification of VLE boundaries and



critical points.[72] The data sets include many binary mixtures of hydrocarbons (alkanes and aromatic) and water; the critical behavior of all binary mixtures was classified as either “type II” or “type III”, following the classification system recommended by van Konynenburg and Scott.[73] In addition to binary systems, several multi-component mixtures were also studied. Accordingly, Pisoni et al.[74,75] presented generalized methods for computing ternary critical end lines that may be of use in SCWU applications. Progress notwithstanding, major gaps that persist in the literature are the phase and transport behavior of complex mixtures and composition of different phases under equilibrium conditions. Recent work in Alberta University [76,77] has demonstrated a new x-ray technique for identification of VLE co-existence using Athabasca bitumen as a realistic, multi-component feed. Consistent with earlier reports, the Athabasca bitumen was found to exhibit type III critical behavior.[76] Similar efforts are required to understand the transport behavior of complex mixtures near water’s pure component critical point.

The MIT SCWU work focused their efforts to address a second gap related to phase behavior – mixing rates of hydrocarbons and water near the pure component critical point. Given the limited work on SCW mixing phenomena, a particular focus of the MIT work has been on modeling simplified 1-D mixing of hydrocarbon droplets injected into an excess SCW reservoir. Both binary hydrocarbon-water[59] and ternary hydrocarbon-hydrocarbon-water mixing have been studied.[60] By their very nature, 1-D mixing studies must be restricted to modeling the diffusional mixing. However, since the final steps in mixing will be dominated by diffusion under any circumstances, these simplified studies represent a logical starting point for more complex studies of the coupling of fluid flow with heat and mass diffusion. Moreover, given the paucity of reliable transport data for complex mixtures containing hydrocarbons and water near its critical point, the 1-D mixing studies provide a way to judge the quality of the existing transport data and correlation methods.[59,60] One objective of this work, documented in more detail by Dabiri et al.,[59] was to assemble as single unified model all of the phase behavior and transport sub-models required for SCW simulations.

An important result reported by Dabiri et al.[59] is that the hydrocarbon droplet heats via thermal diffusion more rapidly than mixing occurs via mass diffusion. Because coking rates involve bimolecular condensation reactions, the differential between heating and mass dispersion rates suggests that oils injected into SCW may have the strongest coking tendencies immediately after injection. Dabiri et al.[59] found that holding the SCW temperature greater than the mixture upper critical solution temperature was an effective way to reduce the differential between heating and dispersion rates.

As demonstrated by Kida et al.,[28] the constituents of a complex mixture will likely exhibit different phase behaviors and coking tendencies. As a result, complex dynamic behavior are expected even for the 1-D model problem. The work of Wu et al.,[60] which focused on mixing of hydrocarbon-hydrocarbon mixtures with SCW, provides a test case to develop understanding of more complex multi-component mixtures. Figure 8 provides representative results for the

dynamic response of a 2-component hydrocarbon droplet consisting of toluene and decane injected into SCW reservoirs held at temperatures ranging from 305 to 350 °C. At the lowest temperature, both hydrocarbon components exhibit only partial miscibility with SCW. As a result at 305 °C, the droplet radius increases for all hydrocarbon compositions due to absorption of water. At both 330 °C and 350 °C, toluene is fully miscible with SCW but decane is only partially miscible. As a result, droplets injected into SCW at these conditions can either grow monotonically (for low toluene concentrations) or grow and then shrink (for higher toluene concentrations). The balance between these two behavior types depends on both the SCW reservoir temperature and the droplet composition, as Figure 8 describes.

#### **4. Future Needs**

SCWU continues to hold promise as a technology for environmentally responsible conversion of heavy oil resources into fuels and chemicals. As described by Ates et al.,[58] SCWU has the most potential as a pre-treatment technology to convert heavy, high-sulfur content oils into lighter, lower sulfur feeds prior to further refining. Figure 7 shows that a catalytic-SCWU process can be used for simultaneous cracking of large sulfur bearing molecules and decomposition of the resulting thiophene fragments. Unlike other sulfur rejection technologies which reduce oil sulfur content at the cost of coke formation, SCWU inhibits coke formation, thereby maximizing carbon yields. Moreover, Kida et al.[28] provide a concrete example of water acting as a reductant, thereby explaining the use of SCW as a hydrogen-free desulfurization technology. Due to the high costs of hydrogen associated with standard desulfurization technologies, SCWU may have an important role in reducing hydrogen requirements and thereby decreasing refining costs. Many challenges remain to realize this potential.

**4.1 Mechanistic and Kinetic Studies of Catalytic Reactions.** Removal of DBT compounds remains an expensive process in petroleum refining. As demonstrated previously in the literature,[67] DBT compounds are stable at industrially relevant timescales under SCWU conditions. However, Kida et al.[28] showed that water can be used without the addition of other promoters as a reductant and Ates et al.[58] show that water in the presence of a catalyst can be used to decompose DBT without the addition of other reducing agents. Unfortunately, the conversion results reported by Ates et al.[58] are insufficient for an economically viable commercial process. To make catalytic-SCWU commercially relevant, an improved understanding of the catalytic mechanism is required. Engineering studies, in situ spectroscopy, and computational studies need to be pursued in parallel to elucidate the relevant chemical phenomena of sulfur compound adsorption/desorption and C-S bond reduction.

**4.2 Identification of Cost-Effective Catalysts with High Activity and Stability.** Mechanistic studies will make possible identification of SCWU catalysts that exhibit high activity – follow-on application studies are needed to confirm the stability of these catalysts in SCWU, their regenerability characteristics, and their resistance to coking. Because the reactors used for

SCWU may prove to be more capital intensive than standard desulfurization reactors, an emphasis should be placed on the use of inexpensive catalysts with favorable regeneration characteristics over many cycles. Continuous flow tests will be required to obtain the necessary time-on-stream performance data.

**4.3 Improved Understanding of the Chemistry of Heavy Components.** At present, SCWU has been limited by the inability of GC techniques to analyze more than about 30% of heavy oil sulfur content; for heavy fractions (e.g, vacuum gas oil) or bitumen feeds, this fraction would further reduced according to their vapor pressures. Moreover, the chemical modeling techniques reported by Kida et al.[28] for mechanism elucidation become cost prohibitive for molecules containing 30 or more heavy atoms. Therefore, improved analysis methods are required for characterizing heavy oil feeds and products. Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FTICR-MS) is a powerful analytical tool for achieving mass resolution required for composition analysis of heavy oils[78-81] and for this reason the method holds promise for improving current understanding of SCWU. In addition, new methods for sulfur speciation analysis, including chelation chromatography,[82] are required to complement FTICR-MS and to provide cost effective analytical capabilities available within university and industry laboratories. For computational techniques, surrogate molecules must be identified that capture the relevant chemical phenomena but at acceptable computational expense. Additionally, approximate chemical mechanisms must be developed to explain the complex chemical dynamics associated with coking – similar to parallel work to model the combustion formation of soot.

**4.4 Fluid Mixing Modeling and Validation Studies.** Dabiri et al.[59] and Wu et al.[60] provide guidance on SCWU mixing phenomena that has yet to be validated experimentally. Additionally, data are required to develop accurate transport property correlations for multi-component mixtures containing a substantial water component near its critical point. New experiments and new experimental methods are required for direct visualization of SCWU mixing. Moreover, to date the MIT group has focused on 1-D systems. New SCWU mixing simulations are required for realistic engineering systems, at relevant Reynolds' numbers, and in the presence of phase boundaries. Specific challenges include quantifying the contributions of inertial, viscous, and buoyancy forces, phase behavior phenomena, and temperature-pressure varying properties at different operating conditions. In turn, these computational fluid dynamics studies will need guidance and validation from parallel experiments.[83,84] To date, transport modeling has relied on properties estimated using correlations for one or two-component mixtures.[59,60]

**4.5 Multi-physics Modeling of Complex Mixtures.** Many different physical and chemical phenomena play important roles in SCWU. Moreover, crude oil contains many thousands of components, making phase behavior and mixing studies of whole crude oil formidable. New methods are required for modeling phase behavior of multi-component mixtures – for example, development of robust, predictive equations of state and realistic pseudo-components that can be used to describe phase behavior in the vicinity of the critical point. Even with improved

equations of state, the chemical models demonstrated by Kida et al.[28] require too many explicit compounds for practical large-scale simulations. Reduced-order reaction models (both of homogeneous and heterogeneous chemical reactions) are required that can be coupled with phase behavior models. Finally, phase behavior and reaction models need to be integrated with mixing models, starting with 1-D systems and progressing to more relevant engineering geometries. The objective of these tasks will be providing a tool kit for rationale design of mixing systems, reactors, and heat exchangers for SCWU processes.

**4.6 Process Studies on Handling of Waste Streams.** To date, the majority of reported studies on SCWU have focused on characterizing the effects of the process on the oil. However, SCWU by-products that include a sulfur-rich gas stream, a solid coke stream, and the water stream itself. Additionally, depending on process conditions and the physical properties of the oil, it may be possible that emulsions consisting of water and oil phases may be produced.[4] Typically, in oil refinery operations, sulfur gases are formed as H<sub>2</sub>S and converted to sulfur via the Claus process. Presumably, the SCWU gas product can be handled in the same fashion. Process level work is required to confirm. As for the coke product, SCWU produces lower amounts of coke than similar pyrolysis process. Moreover, the SCWU coke has an unusual morphology compared to the pyrolysis coke.[8] Efforts should be placed on evaluating the effectiveness of the SCWU coke as an adsorbent, catalyst support, or even energy storage material. For emulsions, the MIT experience has been that centrifugation removes the majority of organic compounds present in the water phase produced after SCWU. However, the composition of the water phase has not been carefully studied nor have energy efficiency or process studies been performed to determine the energy input required to recycle the water or to purify it before release. Similarly, the formation of stable water/oil or oil/water emulsions should be studied so that process conditions can be tuned to avoid their formation.

**4.7 Improved Process Data and Economic Models.** To date, published SCWU studies have focused on batch-mode operation and/or experiments with model compounds. Continuous flow experiments with real feeds are needed to develop economic models for SCWU scale-up. Emphasis should be placed on total system operation, including SCWU reactors, downstream refining, separation processes, and heat recovery. Hybrid processes where SCWU is used as a pre-treatment step should be designed, built, and operated to obtain the data necessary for accurate economic forecasts. These demonstration tests should be designed to resolve outstanding questions regarding optimal heat exchanger design, time-on-stream catalyst performance and in-stream regeneration, and SCW corrosion. Early patents on down-hole SCWU[85] should be re-investigated, applying the knowledge gained from fundamental and process studies. High capital costs can be offset if SCWU can be performed in the pressurized geological environment. This is particularly true for unconventional, highly viscous resources that would benefit from in situ viscosity reduction.

**4.8 Continuing Integration with other SCW Communities.** As described in Figure 1, SCWU fits within the broader spectrum of HTW energy technologies. Continued and deeper

collaboration between researchers in the sub-fields shown in Figure 1 will help identify solutions to common problems; share common process, analytical, and computational resources, and provide better research direction for the community as a whole. Community workshops, joint review papers, scientist exchanges, and informal collaborations are some approaches for forging collaborations that can be competitive for industrial and government support.

## **5. Future Outlook**

Petroleum and other fossil resources will continue to play a crucial role in the global energy mix for many years to come. Clearly, the use of fossil fuels carries many environmental burdens, spanning exploration, production, refining, and power generation via combustion. At the refinery, hydrogen use and the energy costs associated with its production represent one of the chief environmental and economic costs. To the extent to which SCWU can reduce hydrogen consumption, SCWU can play a role in the environmentally benign and economical conversion of fossil resources to fuels and chemicals. The main advantage of SCWU is simultaneous hydrocarbon molecular weight reduction and sulfur removal – a benefit that does not come at the expense of carbon rejection. However, existing petroleum resources have percent levels of sulfur and modern fuels requirements stipulate fuel sulfur levels on the order of 10 ppm<sub>w</sub>. SCWU alone will not likely achieve the required sulfur levels of refined fuels. Therefore, the future of SCWU is not likely as a stand-alone technology, but as a sub-unit within the refinery – much as hydrodesulfurization, fluidized catalytic cracking, and hydroisomerization are currently used. Combining SCWU with other emerging desulfurization and upgrading technologies has potential. For example, oxidative desulfurization (ODS) is effective at removing the thiophenic compounds that evade SCWU. ODS has long been limited by the oxidant requirements. SCWU might be used as an oxidant and hydrogen free pre-treatment applied to crude oils prior to ODS, thereby greatly reducing refinery hydrogen requirements. Recently published economic models[86] suggest that ODS can be cost competitive with existing desulfurization processes. Integration with SCWU should make the SCWU-ODS process even more economically attractive. As increasingly heavy and sulfur-rich feeds are produced, complimentary technologies which reduce the burden on existing refinery processes will become increasingly favorable. This will be particularly crucial for environmentally responsible and economic production of un-conventional resources for which existing refinery processes are poorly optimized.

A major challenge will be convincing industry that capital investments will be profitable. As it is currently configured, the petroleum industry is highly profitable and most of the required refining infrastructure already exists. In the projected future of limited new refinery installations, economical retro-fitting of existing refineries, use of SCWU as an on-site pre-treatment, or down-hole SCWU all provide opportunities to advance the technologies. Realizing these opportunities will require improved fundamental understanding and continuing process scale research that de-risk SCWU capital investments and permit optimized design of SCWU sub-units. Continued progress toward commercial SCWU processes will require sustained

industrial and governmental funding. Already, many important fundamental and engineering questions have been resolved – many more remain as outlined in Section 4.

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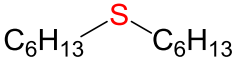

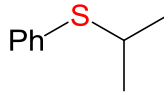
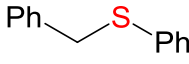
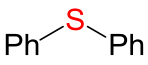

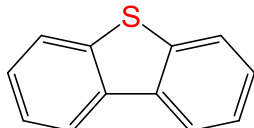


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**Table 1.** Reactivity of Model Sulfur Compounds in SCW.

Structure	Compound	Conversion (GC-FID)	% S removal (Horiba-XRF)
	Hexyl sulfide	31	25
	Tetrahydrothiophene	16	16
	Isopropyl phenyl sulfide	31	30
	Benzyl phenyl sulfide	97	22
	Dibenzyl sulfide	81	60
	Diphenyl sulfide	0	<5
	Thiophene	3	<5
	Dibenzothiophene	3	3-5

Performed in a CSTR reactor held at 400°C, 235 bar, 1000 rpm agitation rate, hydrocarbon:water feed ratio at room temperature 1:1 v/v, 31 minute residence time.

All uncertainties are estimated to be  $\pm 5\%$  based on the results of repeated runs.

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**Figure 1.** Phase diagram of water superimposed with different HTW technologies. HTC = hydrothermal carbonization, HTL = hydrothermal liquefaction, SCWU = supercritical water upgrading, c-SCWG = catalytic supercritical water gasification, and nc-SCWG = non-catalytic supercritical water gasification.

**Figure 2.** Dielectric constant (a) and ion product of water (b) as a function of temperature at 250 bar. Modified with permission from *Journal of Supercritical Fluids*. [60] Copyright, Elsevier, 2012.

**Figure 3.** Kinetics of model sulfur compound decomposition in SCW measured in a CSTR: a) conversion plotted as a function of bulk residence time and b) conversion plotted as a function of  $Da$  as given in Figure 4. HS = hexyl sulfide and DBS = dibenzylsulfide. All experiments performed at 235 bar. Reprinted with permission from Supercritical Water Desulfurization of Organic Sulfides Is Consistent with Free-Radical Kinetics, *Energy & Fuels* 27 (2013) 6108-6117. [4] Copyright 2013 American Chemical Society.

**Figure 4.** Hypothesized radical chain reaction used to explain data shown in Figure 3b. [4]

**Figure 5.** Hexyl sulfide decomposition products obtained under SCW and pyrolysis conditions: 400 °C, >230 bar. Reprinted courtesy of *Physical Chemistry and Chemical Physics*. [28] Copyright, The Royal Society of Chemistry, 2014.

**Figure 6.** Calculated energetics of the decomposition of hexyl sulfide in SCW. A key intermediate is the thio-aldehyde (shown as compound “3”) and the key transition states (labeled as “c” and “d”) are the water-stabilized thiol compounds. Reprinted courtesy of *Physical Chemistry and Chemical Physics*. [28] Copyright, The Royal Society of Chemistry, 2014.

**Figure 7.** Sulfur selective GC chromatograms of Arabian Heavy (AH), AH treated for 30 min in SCW at 400 °C, and AH treated for 30 in SCW at 400 °C in the presence of 10 wt% MoS<sub>2</sub>. Reprinted courtesy of *Applied Catalysis B: Environmental*. [58] Copyright Elsevier 2014.

**Figure 8.** Transient response of the radius of a hydrocarbon droplet (initially cool at radius  $R_0$ ) immersed in a water reservoir held at different temperatures. Line colors indicate the temperature of the water reservoir and solid/dash/dot indicates the initial mass fraction of the hydrocarbon droplet that is toluene (the remainder being dodecane). Reprinted with permission from *Journal of Supercritical Fluids*. [60] Copyright, Elsevier, 2012.

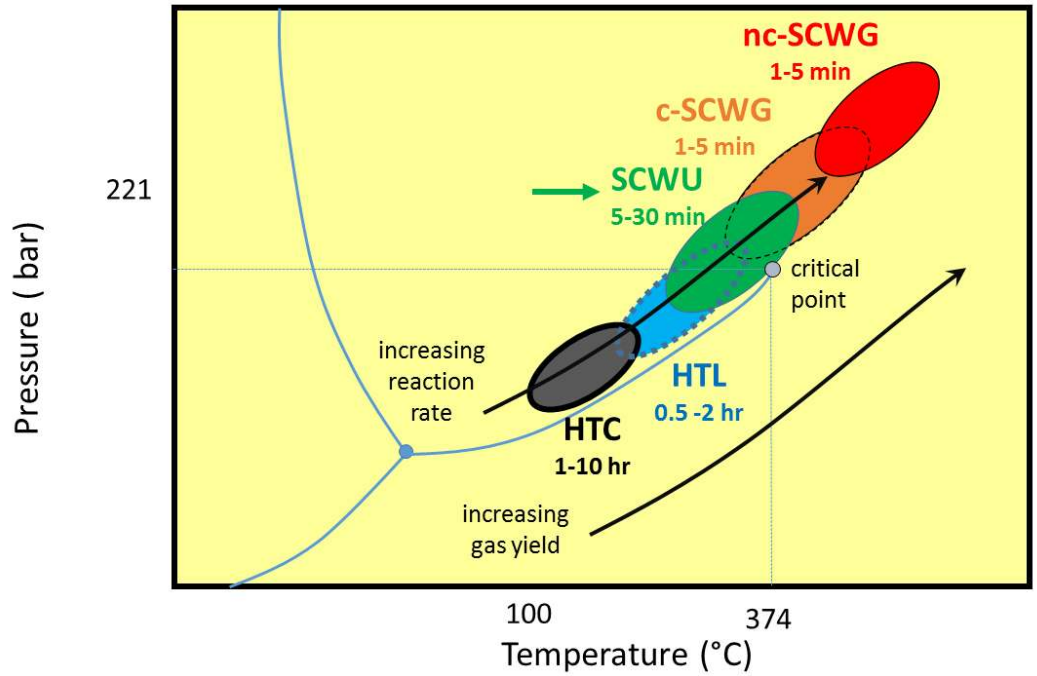
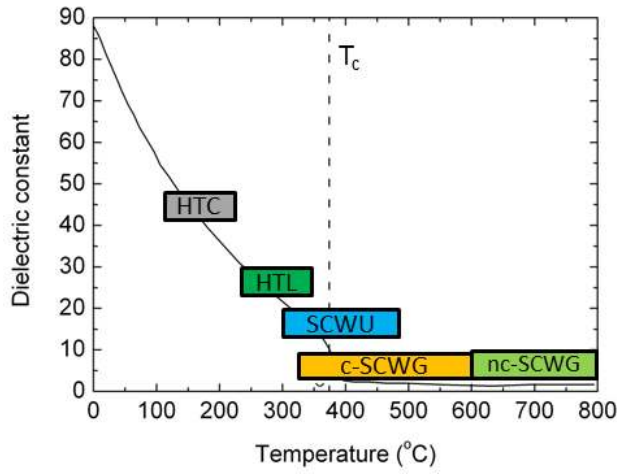
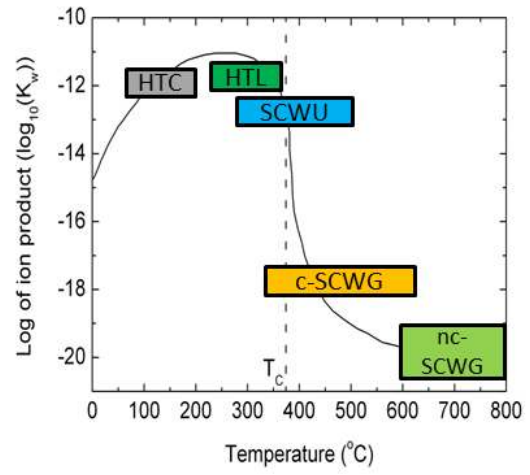


Figure 1.

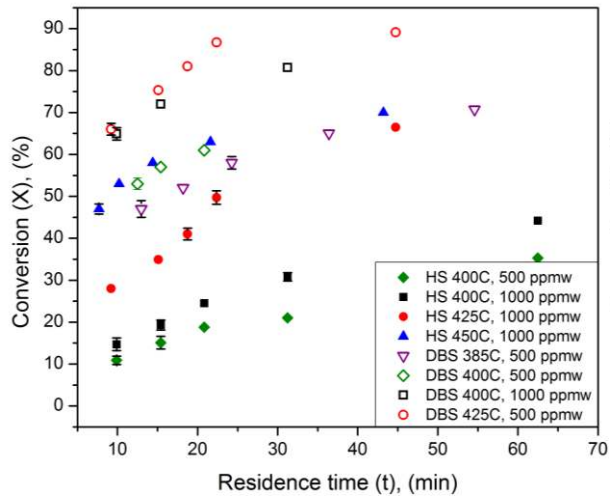


(a)

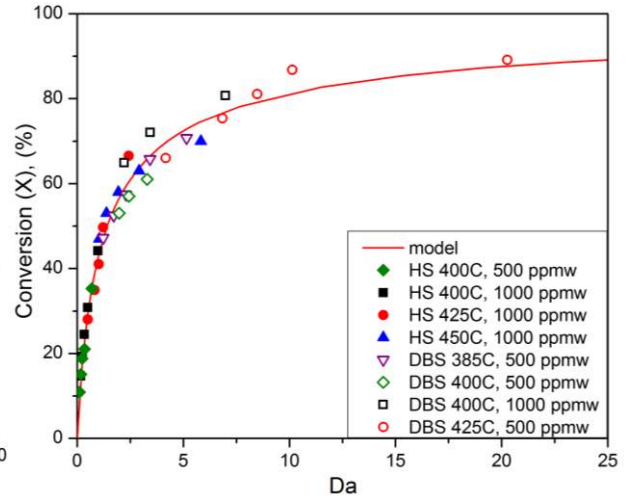


(b)

Figure 2.



(a)

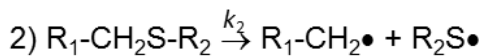
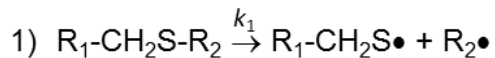


(b)

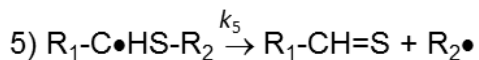
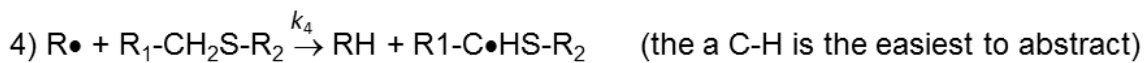
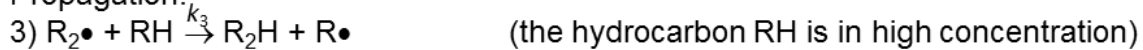
Figure 3.



Initiation: (C-S breakage)

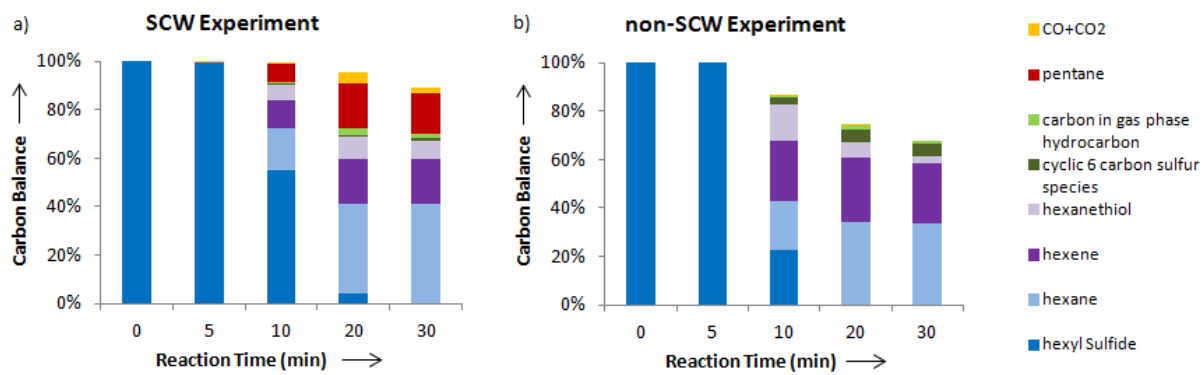


Propagation:



And radical-radical re-combination as the termination step with rate constant  $k_t$

**Figure 4.**



**Figure 5.**

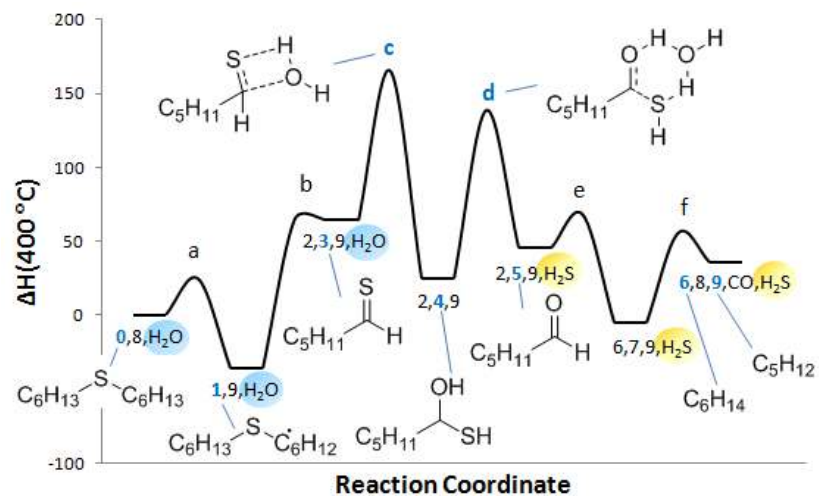
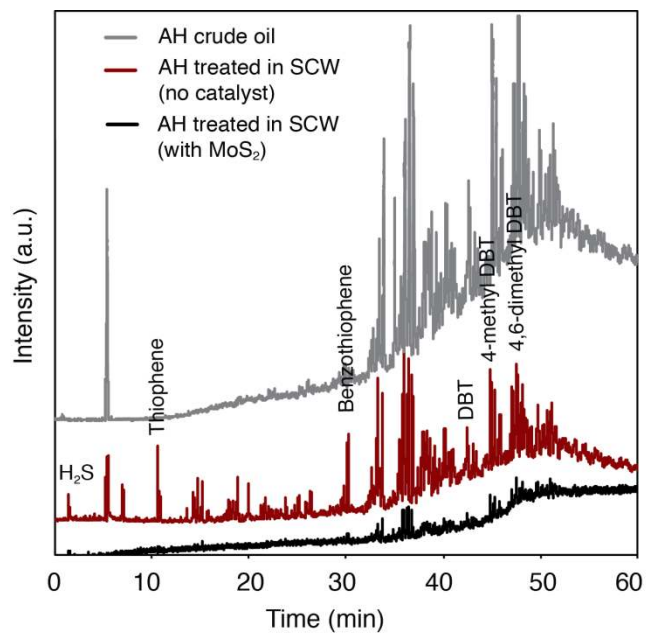


Figure 6.



**Figure 7.**

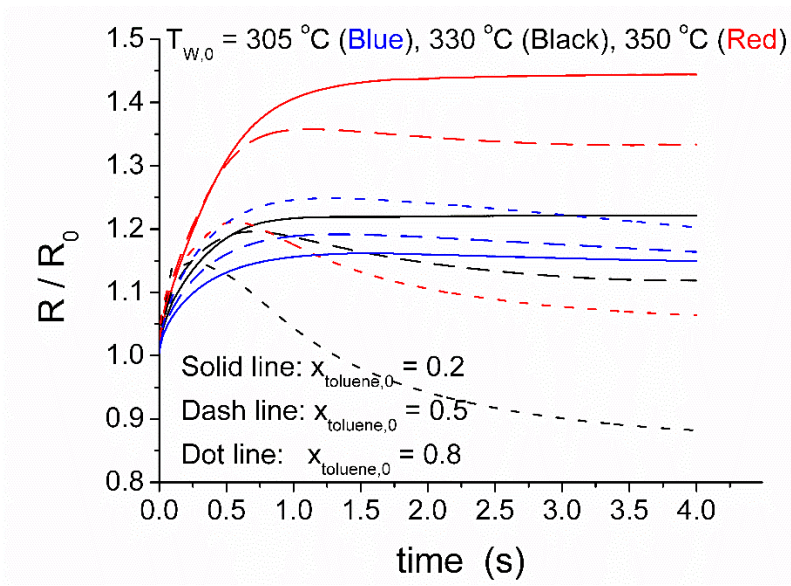


Figure 8.