공학박사 학위논문

Desulfurization mechanism of hexyl sulfide and hexanethiol in supercritical water

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화학생물공학부

강 지 문

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이 논문을 공학박사 학위논문으로 제출함

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강지문

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2020 년 2 월

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Abstract

Desulfurization mechanism of hexyl sulfide and hexanethiol in supercritical water

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Nowadays, the production of heavy crude oil has increased significantly as the cost for production are decreasing with technology developments and the conventional light crude oil are being depleted. Despite these increases in the production of heavy crude oil, it is very challenging to utilize. Heavy crude oil has heavy molecular compositions such as asphaltenes and high sulfur contents ranging from 2 to 5 wt%. Not only can heavy crude oil cause severe problems in the existing refinery process such as fouling, corrosion of pipe, catalyst deactivation, and water-oil emulsion in desalter, but also it can produce a large amount of sulfur dioxide in the combustion process due to its high sulfur content, which can have serious environmental impacts such as acid rain and lowering the pH of soil and freshwater bodies. Heavy oil needs upgrading process with removing impurities such as sulfur and heavy metals.

Supercritical water (SCW, Tc= 647.5 k, Pc=22.05 MPa) is regarded as a promising technology to upgrade the heavy oil. SCW has a high diffusivity with favorable transport properties, a high dissociation constant (K_w) generating high H+ concentration, and a low relative dielectric constant dissolving the organic compounds with low polarity. SCW has been very effective in the decomposition of hydrocarbons, the inhibition of coke formation and even the desulfurization in the upgrading of heavy oil. Despite the high sulfur content in heavy oil, however, the mechanisms of desulfurization in SCW still remain unclear.

In this study, desulfurization of hexyl sulfide and hexanethiol using supercritical water (SCW) was investigated by combining experimental and computational methods to study the desulfurization of alkyl sulfides and thiols in SCW. Desulfurization was conducted for 0 ~ 30 min at 400 °C using thermal decomposition and SCW decomposition (24.7 ~ 25.6 MPa), and the reaction pathways were built using the automated Reaction Mechanism Generator (RMG) and Gaussian 09.

In the experimental results, thermal decomposition and SCW decomposition showed considerable differences in the products composition. C6-hydrocarbons (hexane, hexene) were main products in the thermal decomposition, whereas C5-hydrocarbon (pentane) in addition to C6-hydrocarbons were main products with higher alkane to alkene ratio. Also, in thermal decomposition, aromatic sulfur compounds including thiophenes and alkyl-thiacycloalkanes were found, but in SCW decomposition, thiophenes were not detected and alkyl-thiacycloalkanes were detected in a relatively small amount.

To investigate the reactions pathways in the thermal decomposition of hexyl sulfide and hexanethiol, detailed kinetic models were set using automated reaction mechanism generation software (RMG) and corrected through various works of literature and experimental results. The thermal decomposition of hexyl sulfide and hexanethiol is a hydrogen-deficient process with the formation of thiophene formation and the low ratio of hexane to hexene. The reactions pathways in SCW decomposition were investigated by the quantum chemistry calculations with density functional theory using Gaussian 09 to study the role of water in SCW decomposition. In SCW decomposition, water played the major roles: H-transfer catalyst in the unimolecular decomposition of hexanethiol, reactants in the decomposition of hexylthioaldehyde, and even catalyst in the decomposition of hexylthioaldehyde. These computational results support the experimental results that SCW decomposition effectively removes sulfur in hexyl sulfide and hexanethiol as low molecular sulfur compounds while thermal decomposition produces high molecular sulfur compounds such as thiophenes and alkyl-thiacycloalkanes with hydrogen deficient process.

These results suggest that the removal of sulfur in SCW decomposition is more efficient than thermal decomposition in the decomposition of alkyl sulfides and alkyl thiol. In SCW, water can act as a H-transfer catalyst in the unimolecular decomposition of alkyl thiol to eliminate sulfur as a H_2S gas, and it also acts as reactants in the decomposition of alkyl thioaldehyde, the major intermediate compound of alkyl sulfide and alkyl thiol, to eliminate sulfur as a H_2S, CO, and CO_2 gas by providing H source and O source as well as acts as catalyst. In contrast, aromatic sulfur compounds such as thiophenes are produced due to the hydrogen deficiency in thermal decomposition. These experimental and computational studies would present a reliable guide to the various mechanisms of organosulfur compounds in thermal decomposition and SCW decomposition with a deeper understanding of the role of water. It can give great help in the upgrading of heavy oil which contains a large amount of sulfur with the optimization of process design for the SCW upgrading.

Keyword: supercritical water, thermal decomposition, desulfurization, sulfides, thiols

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1. Introduction

The demand for energy continues to increase worldwide and it is expected that more energy will be needed to run human life in the coming future [1]. Over the past 100 years, the main sources of energy in the world has been fossil fuels. In recent years, the use of renewable energy has been drawing attention to reduce the dependence on fossil fuels. Despite the efforts to increase the use of renewable energy, fossil fuels still dominate the energy market. The petroleum still remains to be the largest source of energy consumption not only in the United States but also around the world [2].

However, limited conventional oil reserves are not enough to meet the demands of oil. According to data published in the Energy Information Administration in 2016, the amount of commercially available light crude oil has declined for 2015, and 2016, leading to rising oil prices [3]. The production of commercially available light crude oil has already reached its peak. Therefore, in order to meet the required amount of petroleum, there are considerable demands for heavy crude oil such as heavy oil, extra heavy oil, shale oil, and oil sands, which are relatively rich in reserves [4]. As the cost for production has decreased with technology developments and the conventional light crude oil resources has been depleted, the production of heavy crude oil has increased significantly [5].

Despite these increases in the production of heavy crude oil, it is very challenging to utilize. Heavy crude oil has heavy molecular compositions such as asphaltenes and high sulfur contents ranging from 2 to 5 wt%. [6]. Not only can heavy crude oil cause severe problems in the existing refinery process such as fouling, corrosion of pipe, catalyst deactivation, and water-oil emulsion in desalter, but also it can produce a large amount of sulfur dioxide in the combustion process due to its high sulfur content, which can have serious environmental impacts such as acid rain and lowering the pH of soil and freshwater bodies [7]. It needs upgrading process with removing impurities such as sulfur and heavy metals.

Thermal decomposition, which is also referred to as pyrolysis, has been one of the conventional heavy oil upgrading methods by which complex heavy hydrocarbon molecules are broken into lighter hydrocarbon molecules by means of heat. The decomposition of heavy hydrocarbons takes place due to the limited thermal stability of chemical bonds of materials, which allows them to be disintegrated by using the heat. Thermal decomposition is known to not only reduce the viscosity of heavy crude oil but also to remove the impurities including sulfur and heavy metals with low cost, so it has been the most widely used for heavy crude oil upgrading. However, thermal decomposition has the fatal disadvantage of producing by-products such as coke with the low yield of light oil [8]. To solve these problems, catalytic pyrolysis, which is usually conducted at high temperature over special catalysts, were also widely studied and applied to the oil industry. Compared with conventional thermal decomposition, catalytic pyrolysis can not only reduce reaction temperature and energy cost but also allow one to flexibly adjust product distribution [9].

Supercritical water (SCW, T_c= 647.1 K, P_c=22.06 MPa) has been regarded as a promising technology to remove the chemical wastes for decades. SCW has a high diffusivity with favorable transport properties and has a low relative dielectric constant with low polarity dissolving the organic compounds. Also, it is excellent in stabilizing radicals. SCW participates in the reaction of decomposing the large molecules as a reaction medium, solvent, reactant or even catalyst [10]. Recently, SCW is attracting attention as a reaction solvent for upgrading heavy oil despite the enormous energy and equipment costs required for high temperatures and pressures. From the enormous studies, SCW has been reported to have two benefits in the upgrading of heavy oil; decomposition of hydrocarbons and inhibition of coke formation [11-21]. SCW has an excellent effect on the decomposition of hydrocarbons. Many studies showed that upgrading in SCW increases the light hydrocarbon with a higher H/C ratio and decreases the heavy hydrocarbon such as asphaltene [11-13, 15, 17-18, 22]. High molecular hydrocarbons in SCW are decomposed into low-molecular hydrocarbons through various radical reactions such as β-scission, H-abstraction, and C-C cleavage [13-14]. SCW participates in these reactions as a catalyst, stabilizing radicals or even reactant [11, 13, 19-20]. Also, upgrading in SCW effectively reduces the coke formation when compared with thermal decomposition [12-13, 15, 18, 21]. SCW can dissolve the heavy oil with a pseudo-single phase [21]. Since the oil and water form a pseudo-single phase above the critical point, high molecular compounds such as asphaltene are dispersed in SCW preventing the high molecular compounds from aggregating to form coke.

As SCW finds significant success in the upgrading of heavy oil, many attempts have been made to upgrade various types of heavy oils using supercritical fluids with the detailed kinetics and mechanisms [23-26]. But the removal mechanism of sulfur, which occupies a high proportion in many heavy oils, has been questionable. Generally, most heavy crude oil has sulfur levels in the range of 1.0–2.0 wt% and even some have sulfur levels >4 wt% [7]. It has been reported that sulfur in heavy oil exists as a bridge between core segments such as thiols, sulfides, disulfides and heterocycles such as thiophene [27]. Many studies showed that SCW can reduce the sulfur content of heavy oil, but it was also known that the removal of sulfur contents is closely related to the molecular structure of sulfur compounds. Depending on their molecular structure, the different sulfur compounds showed varying reactivity under the SCW environment [12, 14, 16]. The aliphatic sulfur compounds including thiols, sulfides, and disulfides cleave easily in SCW, while the aromatic sulfur compounds including thiophenes are difficult to be reduced. Sulfur removal in aliphatic sulfur compounds occurs well only with supercritical water, but sulfur removal in thiophene requires a desulfurization catalyst [11, 14, 16]. For example, the dibenzothiophene was effectively desulfurized only when the NiMo/Al_2O_3 catalyst was used [11]. However, SCW is a chemically aggressive environment, which can rapidly de-activate many catalysts. The industrially widely used catalysts have an extremely short lifespan in SCW, which makes it difficult to introduce SCW process using catalyst [28]. Therefore, understanding the desulfurization mechanisms in SCW is necessary to design and manufacture the catalysts for the desulfurization reactions in SCW.

Several studies have been conducted to study the desulfurization mechanism in SCW. To explain the formation of alkenes in the decomposition of octyl sulfide, the radical mechanism which does not involve water was proposed [29]. In the other study, it was claimed that the free-radical mechanism is the main mechanism in the reaction of benzyl phenyl sulfide [30]. Nowadays, quantum chemistry calculations have been widely used to predict the various reaction mechanisms at the molecular level. They also have been used to predict the desulfurization reactions in SCW. In the study of isopropylthiobenzene decomposition in SCW, three possible decomposition paths in SCW were suggested using quantum chemistry calculations [31]. Both experiments and theories were combined to study the sulfide decomposition in SCW using quantum chemistry calculations and a multi-step reaction sequence for hexyl sulfide reacting with SCW was suggested [32].

Recently, detailed reaction networks were proposed for the desulfurization of hexyl sulfide in the presence or absence of both SCW and hexadecane using the automated Reaction Mechanism Generator(RMG) where rate coefficients are derived from quantum chemical calculations [33]. RMG is an automatic chemical reaction mechanism generator that constructs kinetic models composed of elementary chemical reaction steps using a general understanding of how molecules react [34]. Detailed kinetic models based on the flux analysis with RMG calculation were generally in accord with experimental results and they clearly showed the reaction pathway with the amount of major product changes over time, but some clear discrepancies persisted with high uncertainty; significant differences were observed in the products such as hexanethiol, pentane and thiophenes [33]. Several limitations for utilizing RMG disturbed the detailed reaction networks of hexyl sulfide. It can cover only the decomposition reactions in which the weight of molecules decreases, but not the molecular weight growth reactions. Also, RMG cannot suggest the reaction path of the cyclic sulfides so the reaction of cyclic sulfides should be suggested through computational chemistry programs such as Gaussian. As the most of the water participating reactions form cyclic transition state which RMG cannot directly present, water participating reaction pathway was only limited to the reaction *via* the thiodaldehyde intermediate that was presented in the previous study [32]. Due to these limitations of the RMG, the proposed reaction model for the hexyl sulfide decomposition in SCW had several limitations.

In this study, experimental and computational studies for hexyl sulfide and hexanethiol, which is a major intermediate product of hexyl sulfide decomposition and one of the common thiols, were conducted to investigate the desulfurization of alkyl sulfides and thiols using thermal decomposition and SCW decomposition. Experiments for desulfurization were conducted for 0 ~ 30 min at 400 °C using thermal decomposition and SCW decomposition (24.7 ~ 25.6 MPa). In-depth analysis of products for hexyl sulfide and hexanethiol using gas chromatography was conducted, and the composition of products included thiols, sulfides, disulfides, thiophenes, and alkyl-thiacyloalkanes to investigate various kinds of possible sulfur compounds including cyclic sulfides, which is important to understand the formation of aromatic sulfides. The mechanisms of thermal decomposition were proposed using the theoretical studies with RMG, and the effect of water in the SCW decomposition was evaluated using the Gaussian 09 with the search of SCW participating reaction.

2. Background

2.1. Heavy crude oil

2.1.1. The needs for utilizing heavy crude oil

The demand for energy continues to increase due to industrial development and urbanization. It is expected that more energy will be needed to run human life in the coming future, and new problems such as resource depletion and energy economy are expected to become more prominent. The total amount of energy used in 2014 is three times the amount used in 1950, and energy consumption has been steadily increasing [1].

Over the past 100 years, the main source of energy in the world has been fossil fuels. Nowadays, the use of renewable energy is drawing attention in recent years to reduce dependence on fossil fuels. However, despite efforts to increase the use of renewable energy, fossil fuels still dominate the energy market. According to energy sources consumed in the United States from 1776 to 2017 in Figure 2.1., renewable energy which includes hydroelectricity, biomass, and other renewables such as wind and solar, accounts for 11.3%. Although it is the highest rate since 1930, the proportion of fossil fuels used in 2017 is close to 81%. Considering that the share of coal in fossil fuels has dropped by almost 40% since 2005, the use of petroleum is still increasing, and the petroleum is the largest source of energy consumption in the United States [2].

But limited oil reserves are not enough to follow human dependence on oil. According to data published in the Energy Information Administration in 2016 in

Figure 2.2., the amount of commercially available light crude oil has declined for 2015, and 2016, leading to rising oil prices [3]. In fact, diesel prices in the US are $ 3.20 per gallon as of Nov 26, 2018, an increase of 68 cents over the previous year. Therefore, in order to meet the required amount of petroleum, the demands for heavy crude oil such as heavy oil, extra heavy oil, shale oil, and oil sands, which are relatively inexpensive and rich in reserves compared to light crude oil, are increasing [4].

Although the reserves of heavy crude oil exceeded the reserves of existing heavy crude oil, the development of heavy crude oil was limited due to technical limitations such as mining technology and utilization technology and lack of economic efficiency [5]. However, with technological development and exhaustion of conventional light crude oil resources, the production of heavy crude oil is increasing as the prices of oil continue to rise and profitability of heavy crude oil production is secured. Heavy crude oil costs much cheaper than traditional light crude oil, so it is of great economic value. In addition, heavy crude oil is mainly developed in Canada, West Africa, and South America, so that utilizing the heavy crude oil can reduce the supply dependence on crude oil from the Middle East and strengthen energy security in Korea [35].

2.1.2. Challenges for utilizing heavy crude oil

The grade and transaction price of crude oil are determined by the API gravity (American Petroleum Institute gravity) value. The API gravity is based on the density in the liquid phase and determined by this equation.

$$API\ gravity = \frac{141.5}{specific\ gravity\ at\ 15.6°C} - 131.5$$

Heavy crude oil is crude oil with API gravity of 22.3 degrees or less. Heavy crude oil has much higher viscosity and density than conventional crude oil, and it contains a large amount of impurities such as sulfur, heavy metals (V, Ni, Fe, Na, Ca) and high molecular weight substances such as asphaltenes [36]. The properties of conventional light crude (West Texas Intermediate) and major heavy crude oil including Arabian heavy oil, Athabasca sands bitumen and Alberta bitumen are compared in Table 2.1. It shows that heavy oil has higher density, sulfur and nitrogen content, heavy metals content, and asphaltene content than conventional crude oil with large differences.

In the existing refinery process, heavy crude oil can cause problems such as fouling, corrosion of pipe, and catalyst deactivation, and water-oil emulsion in desalter. Also, heavy crude oil produces a large amount of sulfur dioxide in the combustion process due to its high sulfur content, which can have serious environmental impacts such as acid rain and lowering the pH of the soil and freshwater bodies [6, 37]. The removal of sulfur from oil is consequently one of the central conversion requirements in most refineries and the price (and processing cost) of crude oil is influenced by its sulfur content [38]. It must be upgraded through additional pretreatment.

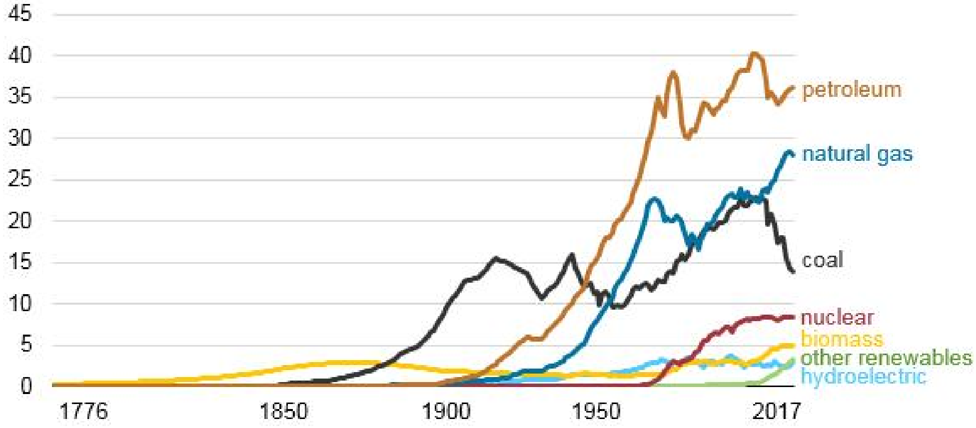


Figure 2.1. Energy consumption in the United States (1776-2017) [2]

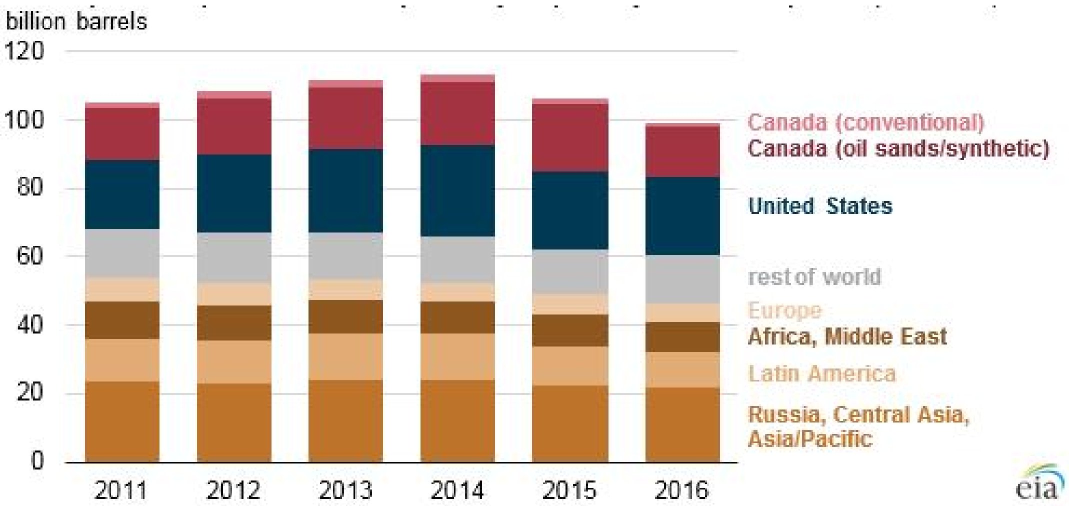


Figure 2.2. Global proved liquids reserves reported by 67 publicly traded companies (2011-2016) [4]

Table 2.1. Properties of West Texas intermediate, Arabian heavy oil, Athabasca bitumen, and Alberta bitumen

	Gravity, API	Sulfur	Nitrogen	Iron	Vanadium	Nickel	Asphaltene
		(wt%)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(wt%)
West Texas intermediate	40.8	0.3	800	23	1.6	1.6	0.1
Arabian heavy oil	21.9	3.2	1210	96.1	34	2.7	3.9
Athabasca ㅠ itumen	7.9	4.9	4000	126.3	222	87	17.5
Alberta bitumen	11	4.6	3740	117.8	182	65	16

2.2. Supercritical water

2.2.1. Supercritical fluids

Supercritical fluids are defined as 'the fluids above the critical temperature and pressure'. The temperature, pressure and molar volume at the critical point are critical constants, expressed as the critical temperature (T_c), the critical pressure (P_c), and the critical molar volume (V_c), respectively. At the temperature slightly below the critical temperature, the gas condenses to a liquid and the interface between the gas and the liquid can be seen. Above the critical temperature, the densities of the two phases become identical and the distinction between the gas and the liquid disappears. [39].

Supercritical fluids have unique properties that distinguish them from conventional fluids. In general, the physical properties of fluids are determined by the kind of molecules and intermolecular interactions. The incompressible liquid fluid hardly changes its intermolecular distance, so it is difficult to expect a large change in physical properties. However, when the pressure is changed near the critical point, many physical properties such as density, viscosity, diffusion coefficient, and polarity are continuously changed from the state close to the gas to the state close to the liquid continuously. Supercritical fluid changes from gaslike to liquidlike as the pressure is increased, and its thermodynamic properties change in the same way. Close to the critical temperature, this change occurs rapidly over a small pressure range [39].

Supercritical fluid technology utilizes the advantages of supercritical fluids such as rapid heat and mass transfer, dissolution power similar to organic solvent, low viscosity, and fast permeability to micropores due to the high diffusion coefficient. It has attracted attention as an innovative technology that can solve technical difficulties such as low efficiency, low quality, low speed, environmental pollution in processes such as distillation, crystallization, absorption, adsorption, drying, and washing [40].

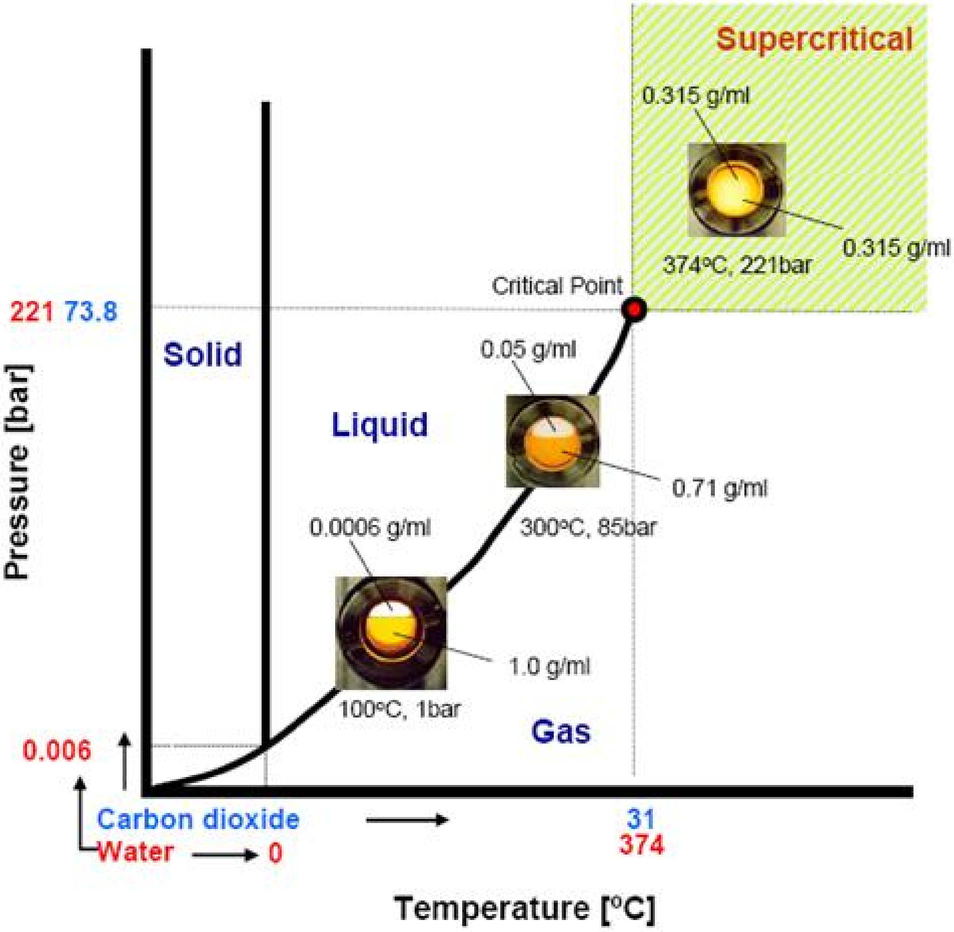


Figure 2.3. The state of supercritical water and critical points in T-P diagram

2.2.2. The characteristics of supercritical water

Supercritical water (SCW, T_c=374.3 ℃, P_c=22.1 MPa) is water with higher temperature and pressure than the critical point (374.3 ℃, 22.1MPa). Figure 2.4. shows the characteristics of water before and after the critical temperature. SCW has low viscosity close to gas state and high density close to the liquid state.

Supercritical water has properties very different from those of ambient liquid water. The dielectric constant is very low, and the number and persistence of hydrogen bonds are both diminished. At a constant pressure of 250 bar, the dielectric constant of water is 80 at room temperature and water is good to dissolve polar materials. However, with a rise in temperature, the dielectric constant near the critical point is 10, which is similar to hexane. Therefore, the supercritical water behaves like an organic solvent and can dissolve many organic compounds, completely mixing with alkane. Moreover, gases are also miscible in SCW so employing an SCW reaction environment provides an opportunity to conduct chemistry in a single fluid phase that would otherwise occur in a multiphase system under more conventional conditions. The single supercritical phase reaction medium allows higher concentrations of reactants to be attained, as well as no interphase mass transport processes to hinder reaction rates [10].

The ion product, or dissociation constant (K_w) for SCW is about 3 orders of magnitude higher than ambient liquid water. Accordingly, in addition to SCW being an excellent solvent for organic compounds, it can also boast a higher H+ and OH- ion concentration than liquid water under certain conditions. Therefore, SCW is an effective medium for acid- and base-catalyzed reactions of organic compounds. In fact, the dissociation of water near the critical point generates a sufficiently high H+ concentration that some acid-catalyzed organic reactions proceed without any added acid, but as one exceeds the critical point, K_w decreases dramatically. For example, K_w is about 9 orders of magnitude lower at 600 °C and about 250 atm than it is at ambient conditions. SCW in this high-temperature, low-density region is a poor medium for ionic chemistry [10].

Also, the properties such as viscosity, density, viscosity, dielectric constant, and K_w in SCW continuously changes over a much larger range in the supercritical state. It makes it easy to adjust the properties of the reaction medium to the optimum values for a given chemical transformation by changing the pressure and temperature.

Because of these characteristics of SCW, SCW is used for oxidation or hydrolysis. Supercritical water oxidation (SCWO) uses SCW to oxidize hazardous waste, eliminating toxic products. Supercritical water hydrolysis is a method of converting biomass polysaccharides as well as the associated lignin into low molecular compounds by reacting them with SCW. The SCW acts as a solvent, a supplier of bond-breaking thermal energy, a heat transfer agent and as a source of hydrogen atoms [10, 39-40].

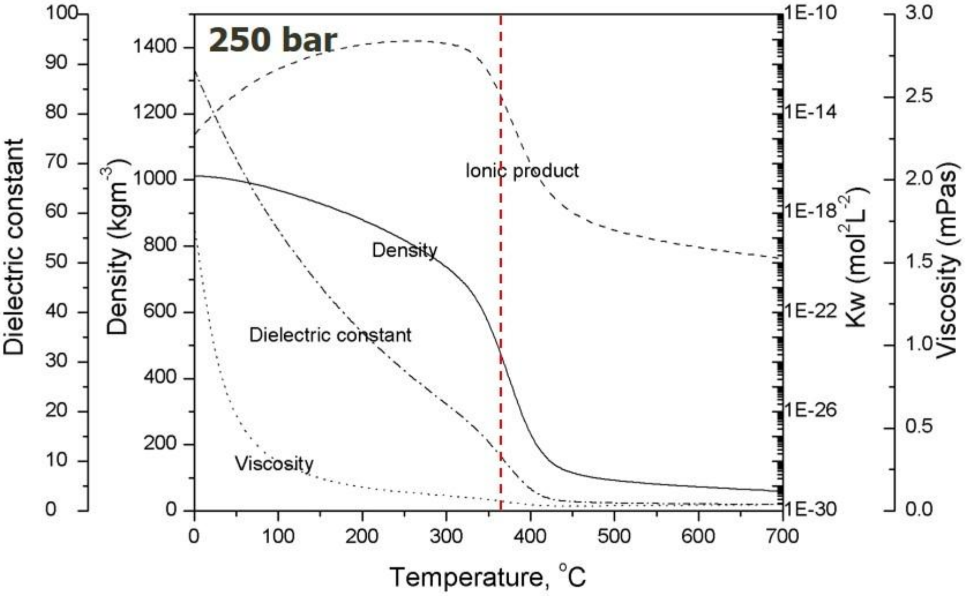


Figure 2.4. The density, viscosity, dielectric constant, and ionic product changes of water with the temperature at the pressure of 250 bar[41].

2.3. Upgrading of heavy oil in supercritical water

Thermal decomposition, which is also referred to as pyrolysis, is one of the conventional heavy oil upgrading methods by which complex heavy hydrocarbon molecules are broken into lighter hydrocarbon molecules by means of heat. The decomposition of heavy hydrocarbons takes place due to the limited thermal stability of chemical bonds of materials, which allows them to be disintegrated by using the heat. It was known that high molecular hydrocarbons are broken into low molecular hydrocarbons with asphaltene cracking at high temperatures above 400 °C under catalyst-free conditions [42]. In addition, it can reduce the viscosity of heavy crude oil with cracking and remove the impurities including sulfur and heavy metals with low cost. It has been the most widely used for heavy crude oil upgrading up to date. However, thermal decomposition has the fatal disadvantage of producing by-products such as coke with the low yield of light oil.

Recently, SCW is attracting the attention as a reaction solvent for upgrading heavy oil because it has been reported that there are two benefits of the upgrading of heavy oil in SCW; decomposition of hydrocarbons and inhibition of coke formation [11-21].

First, supercritical water has an excellent effect on the decomposition of hydrocarbons. Many studies showed that upgrading in SCW increases the light hydrocarbon with a higher H/C ratio and decrease the heavy hydrocarbon such as asphaltene [11-13, 15, 17-18, 22]. High molecular hydrocarbons in SCW are decomposed into low-molecular hydrocarbons through various radical reactions such as β-scission, H-abstraction, and C-C cleavage in Figure 2.5 [13-14]. And SCW, which has been known to stabilize radicals, participates in these radical reactions [11, 13, 19-20].

Second, upgrading in SCW effectively reduces the coke formation when compared with thermal decomposition [12-13, 15, 18, 21]. SCW can dissolve the heavy oil with a pseudo single phase [21]. Since the oil and water form a pseudo single phase, high molecular compounds such as asphaltene are dispersed in SCW as shown in Figure 2.6. Therefore, it is possible to prevent the high molecular compounds from aggregating to form coke.

Thus, it has been well-proven with several mechanisms that SCW is effective in the upgrading of heavy oil. In the SCW process, aggregation of asphaltenes is suppressed with pseudo single-phase structure and coke formation is inhibited. In addition, the decomposition of high molecular compounds including asphaltene are active in SCW in Figure 2.7.

Nowadays, many attempts have been made to upgrade various types of heavy oils using SCW. Furthermore, there are some studies for the kinetics of the upgrading of heavy oil in supercritical fluids to understand the upgrading reactions [23-26]. Nevertheless, the removal mechanism of sulfur, which occupies a high proportion in many heavy oils, have not yet been known. In the refining industry, most sour heavy crude oils have sulfur levels in the range of 1.0–2.0 wt%, but some have sulfur levels >4 wt% [7]. The upgrading mechanism of heavy crude oil with such a high sulfur content in SCW is so complex as to be difficult explain by the conventional upgrading mechanism in SCW without the desulfurization mechanism in SCW.

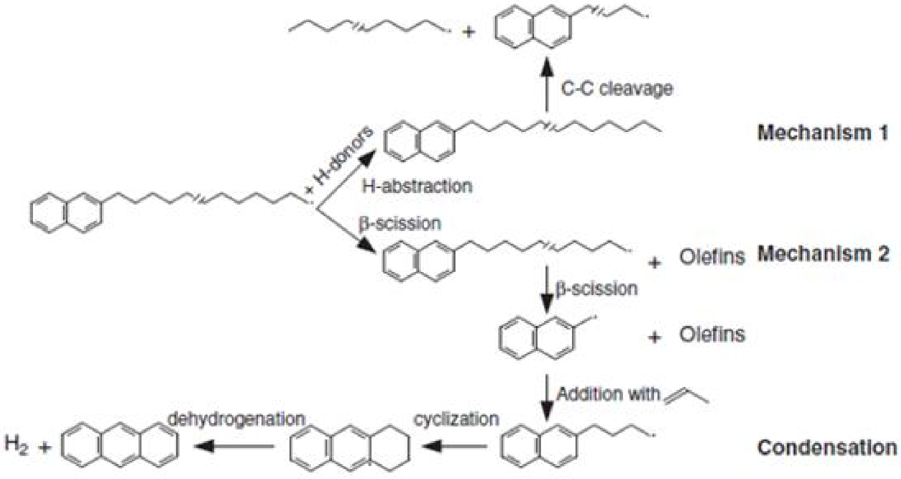


Figure 2.5. Key reactions involved in the upgrading of heavy oil in SCW [13]. SCW has an excellent effect on the decomposition of hydrocarbons.

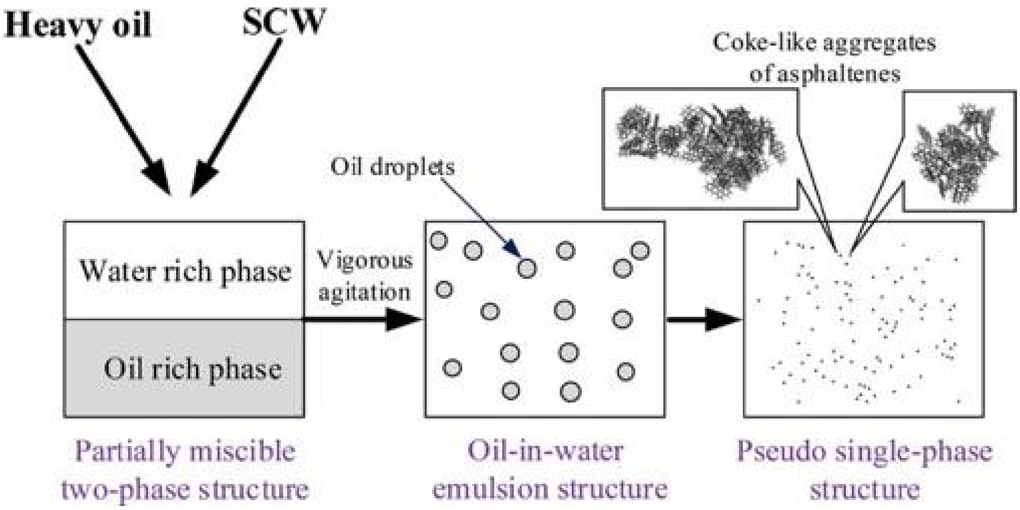


Figure 2.6. The phase diagram of heavy oil upgrading in SCW [21]. In SCW, water phase and oil phase become pseudo single-phase structure.

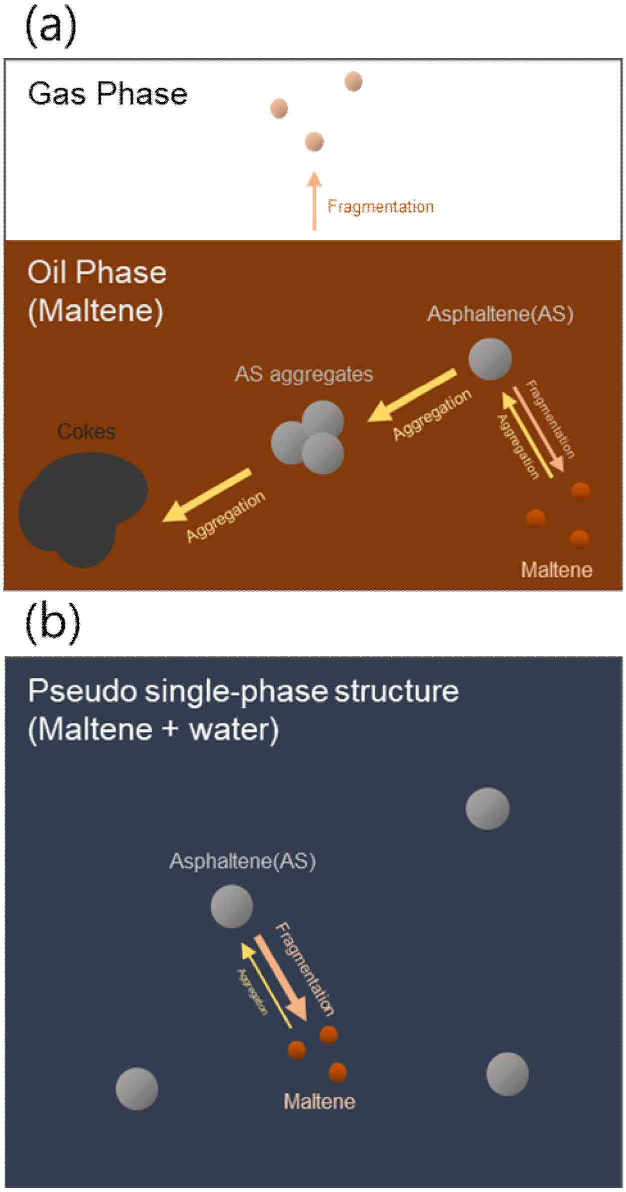


Figure 2.7. Upgrading of heavy oil using (a) thermal decomposition process and (b) SCW process. In the SCW process, aggregation of asphaltenes is suppressed with pseudo single-phase structure and coke formation is inhibited. In addition, the decomposition of high molecular compounds including asphaltene are active in SCW.

2.4. Desulfurization in supercritical water

2.4.1. The desulfurization in supercritical water

It has been reported that sulfur in heavy oil exists as a bridge between core segments such as thiols, sulfides, disulfides and heterocycles, such as thiophene shown in Table 2.2. [27]. Many studies showed that SCW can reduce the sulfur content of heavy oil, but it was also known that the removal of sulfur contents is closely related to the molecular structure of sulfur compounds. Depending on their molecular structure, the different sulfur compounds showed varying reactivity under the SCW environment [12, 14, 16, 43]. The aliphatic sulfur (in thiols, sulfides, and disulfides) cleaves easily in SCW, while the aromatic sulfur (in thiophene) is difficult to be reduced. Sulfur removal in aliphatic sulfur compounds occurs well only with supercritical water, but sulfur removal in thiophene requires a desulfurization catalyst [11, 14, 16]. For example, the dibenzothiophene was effectively desulfurized only when the NiMo/Al_2O_3 catalyst was used [11].

Table 2.2. Typical organosulfur compounds in heavy crude oil

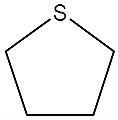
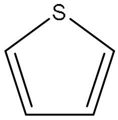
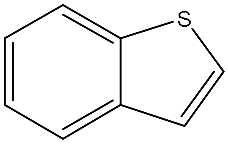
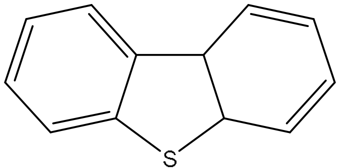
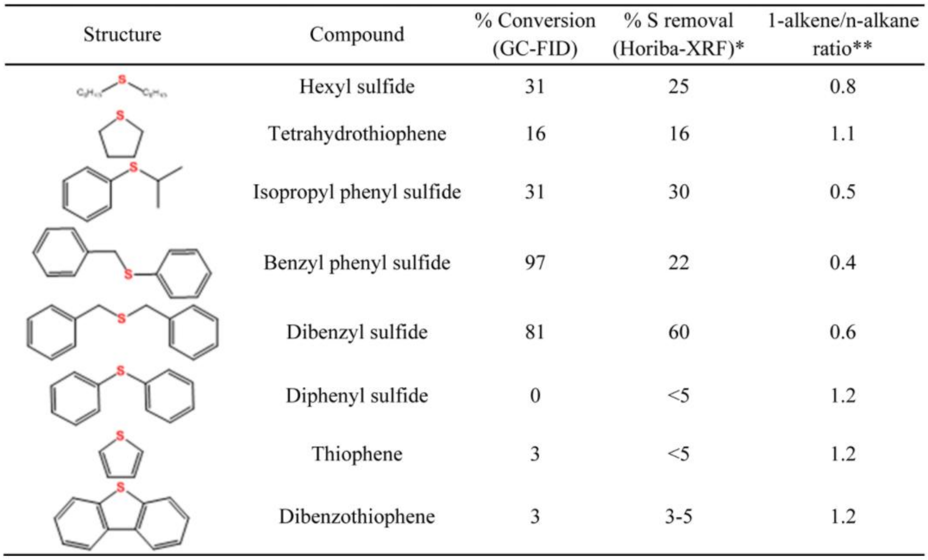
Type of organosulfur compounds	Chemical structure
Thiols	$R—S—H$
Sulfides	$R_1—S—R_2$
Disulfides	$R_1—S—S—R_2$
Thiolane	
Thiophene	
Benzothiophene	
Dibenzothiophene	

Table 2.3. Conversion and Percent S Removal of Various Sulfur Compounds in SCW. Reaction Conditions: 400°C, 235 bar, 1000 rpm, hydrocarbon/water feed ratio at room temperature 1:1 v/v, 31 min [14, 16]



Structure	Compound	% Conversion (GC-FID)	% S removal (Horiba-XRF)*	1-alkene/n-alkane ratio**
	Hexyl sulfide	31	25	0.8
	Tetrahydrothiophene	16	16	1.1
	Isopropyl phenyl sulfide	31	30	0.5
	Benzyl phenyl sulfide	97	22	0.4
	Dibenzyl sulfide	81	60	0.6
	Diphenyl sulfide	0	<5	1.2
	Thiophene	3	<5	1.2
	Dibenzothiophene	3	3-5	1.2

2.4.2. Desulfurization mechanism in supercritical water

Several studies have been conducted to study the desulfurization mechanism in SCW. To explain the formation of alkenes in the decomposition of octyl sulfide, the radical mechanism which does not involve water was proposed [29]. In the other study, it was claimed that the free-radical mechanism is the main mechanism in the reaction of benzyl phenyl sulfide [30]. Nowadays, quantum chemistry calculations have been widely used to predict the various reaction mechanisms at the molecular level. They also have been used to predict the desulfurization reactions in SCW. Both experiments and theory were combined to study the sulfide decomposition in SCW using quantum chemistry calculations and multi-step reaction sequence for hexyl sulfide reacting with SCW in Figure 2.8. was suggested [32]. In the study of isopropylthiobenzene decomposition in SCW, three possible decomposition paths in SCW in Figure 2.9. were suggested using quantum chemistry calculations [31]. Despite these studies of desulfurization in SCW, it is very complex to understand and much of the desulfurization mechanism is still unknown.

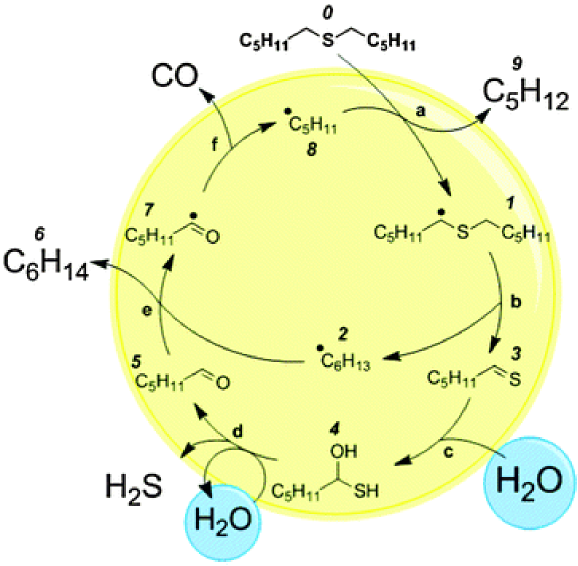


Figure 2.8. Hexyl sulfide decomposition mechanism in SCW [32].

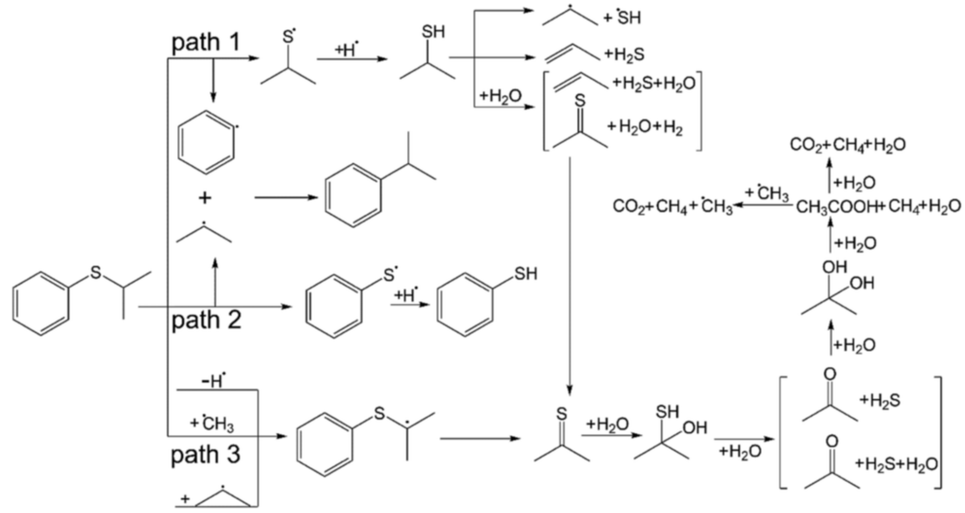


Figure 2.9. Isopropylthiobenzene decomposition pathways [31].

3. Experimental and computational methods

3.1. Raw materials

In this study, alkyl sulfides and thiols decomposition experiments were carried out using hexyl sulfide($[CH_3(CH_2)_5]_2S$) and hexanethiol($CH_3(CH_2)_5SH$). Hexyl sulfide has been one of the common sulfides in research, and hexanethiol is the major intermediate products of hexyl sulfide decomposition [32]. Since hexanethiol is indispensable for the investigation of hexyl sulfide decomposition mechanism, hexanethiol decomposition, as well as hexyl sulfide decomposition were carried out.

Naphthalene was used as an internal standard to determine the amounts of products. Naphthalene is so stable and inert in SCW that the decomposition of naphthalene in SCW even requires the supply of oxygen at the high temperature of 600 °C [44]. Therefore, naphthalene is widely used as an internal standard in decomposition experiments of organic materials in SCW [32, 45-46]. Even if the sample is lost in the experiment, the amounts of products can be determined by analyzing the ratio of naphthalene to products in the remaining sample.

Hexanethiol (>95%) and naphthalene (>99%) was purchased from Sigma-Aldrich Co., German. Hexyl sulfide (>98%) was purchased from Tokyo Chemical Industry Co., Japan. Water was purified by Millipore, Milli-Q Advantage A10.

3.2. Experimental systems

Hexyl sulfide and hexanethiol decomposition were carried out using custom-built batch reactors in the molten salt bath with an electric shaker in Figure 3.1. Batch type reactor was made of 316 type stainless steel, which is superior in corrosion resistance and high-temperature strength. It has a structure in which a large head surrounds the inlet of the reactor to withstand high pressure and tightly seals with a spiral. The internal volume of reactors was 22 ml.

A molten salt bath is to maintain the temperature of batch reactor supplying heat to the batch reactor. It was custom-made in Daepoong Industry. The salt was composed of $NaNO_3/KNO_3/Ca(NO_3)_2$ in a ratio of 46:24:30, and the use of molten salt bath was in the temperature range from 120 to 500 °C. It was controlled by the proportional-integral-derivative (PID) controller with the K-type thermocouple. On the upper part of the molten salt bath, a stirrer for reciprocating right and left was installed, and the stirring speed was set to perform about 47 reciprocating movements per minute during the experiment. The reactor was fixed on a mount and the mount with the reactor was connected to the stirrer to transfer the reciprocating motion of the stirrer to the reactor.

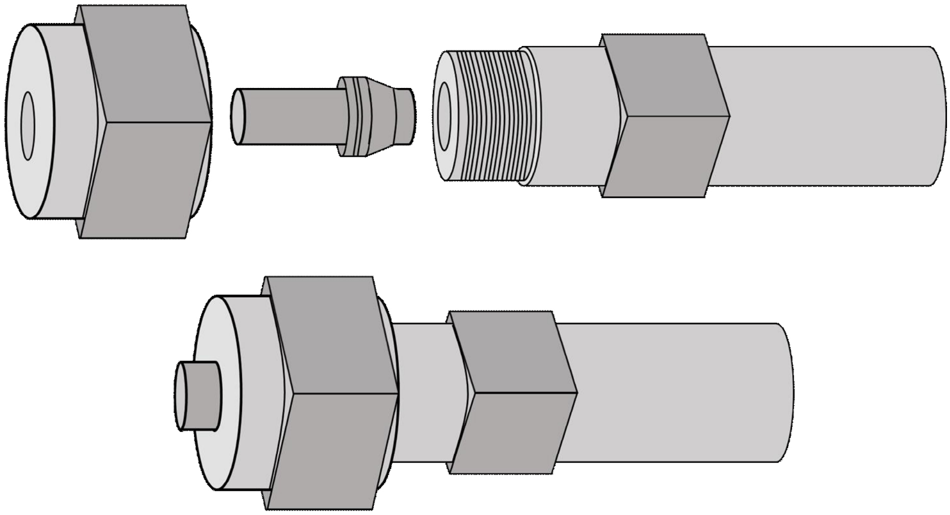


Figure 3.1. Batch type reactor. 22mL, SUS316 steel.

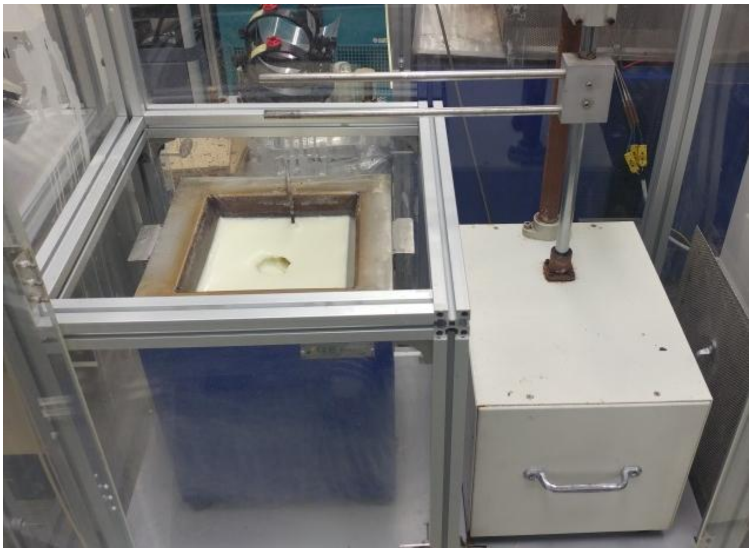


Figure 3.2. Molten salt bath

3.3. Experimental procedure

For the thermal decomposition experiments, the reactor was loaded with 0.90 g hexyl sulfide (or hexanethiol) and 0.10 g naphthalene. For the SCW decomposition experiments, 3.00g water was additionally injected and the reaction pressure was in the range of 24.7–25.6 MPa, which are above the critical point of water. Then, a sealed reactor was placed in a preheated molten salt bath at the set temperature of 673 K for the reaction time while constantly shaking. The heating-up time of reactor to reach the set temperature was almost 2.5 min for both thermal decomposition and SCW decomposition in Figure 3.3., so the reaction time was calculated by excluding 2.5 min of the heating-up time. When the reaction time was over, the reactor was withdrawn from the molten salt bath and quenched to the room temperature in a water bath.

For the hexyl sulfide decomposition, the reaction time was 0, 5, 10, and 30 min. The reason for setting 0 min is that the decomposition of hexyl sulfide can occur during the heating-up time of the reactor. At each reaction time, it experimented twice for reproducibility. For the hexanethiol decomposition, the reaction time was only 5 min.

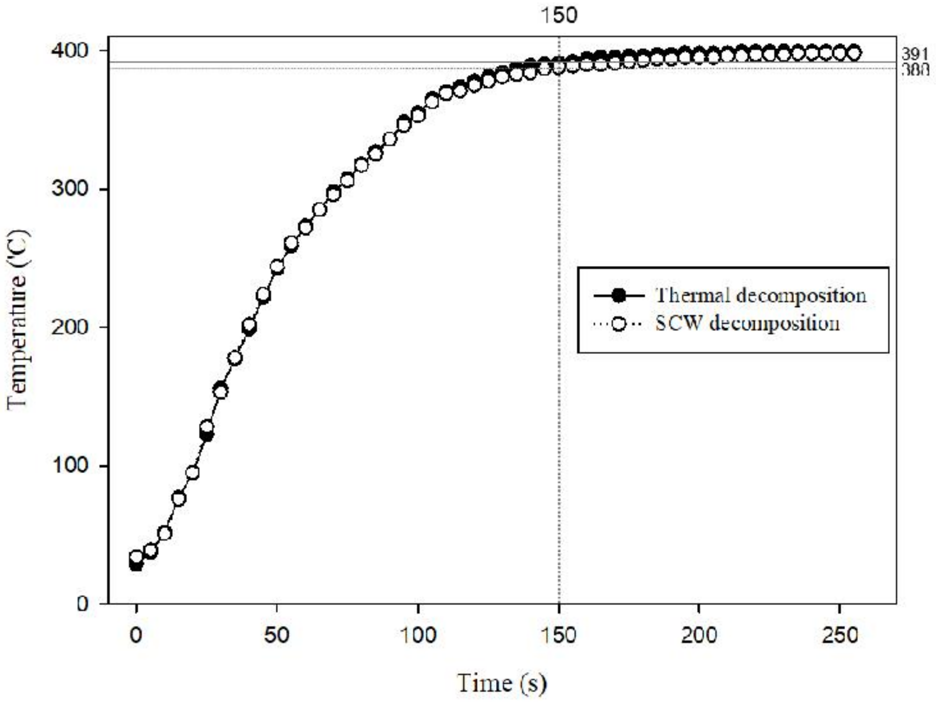


Figure 3.3. Temperature profile of batch type reactor for thermal decomposition and SCW decomposition. 150 s was heating-up time, and the inner temperatures of reactor were 391°C for thermal decomposition and 388°C for SCW decomposition.

3.4. Analytical procedures

The products of hexanethiol and hexyl sulfide decomposition were analyzed by the following procedure. For the thermal decomposition, products are composed of only oil phase and they were analyzed by gas chromatography after the oil phase was recovered from the reactor using 3 g of dichloromethane and shaken thoroughly. For the SCW decomposition, products have oil phase and water phase so that the products should be separated. After the products including oil phase and water phase were recovered using 3 g of dichloromethane, they were fractionated into the water phase and oil phase using centrifuge (Mega 21R, Hanil Scientific Inc.) at 2000 rpm for 10 min. Then, the oil phase of products was recovered and analyzed using gas chromatography.

GC-MS was used for the oil phase of products to characterize the exact compounds after the decomposition of hexyl sulfide and hexanethiol. GC-MS were performed using ISQ LT Thermo Scientific GC-MS equipped with HP-5 column. The products were analyzed by Peak total ion chromatography (TIC) according to retention time and compared with Wiley/NBS library to identify the products.

GC-FID was used to observe the amount changes of major compounds over reaction time. GC-FID was performed using 7890B Agilent GC-FID equipped with HP-5 column. Injection volume was 0.2 μl, the total flow was 38.1 mL/min, and the Septum purge flow was 3 mL/min at the temperature of 320 °C and the pressure of 39.24 psi. The oven temperature condition was initially maintained at 35 °C for 3 minutes, then heated from 120 °C to 280 °C at the rate of 5 °C/min until 120 °C, and then held at 280 °C for 5 minutes. FID was set at 260 °C. Air flow was 400 ml/min, H_2 flow was 30 ml/min, and makeup gas flow (N_2 gas flow) was 25 ml/min. The amount of each component was calculated based on the peak areas and the response factors.

3.5. Computational methods

To investigate the decomposition of hexanethiol and hexyl sulfide in thermal decomposition, the automated reaction mechanism generator (RMG, version 2.4.0) software was used. RMG is an automatic chemical reaction mechanism generator that constructs kinetic models composed of elementary chemical reaction steps using a general understanding of how molecules react. It uses known chemistry knowledge stored in a database along with parameter estimation methods and generates elementary reactions from chemical species using an extensible set of 45 reaction families with the detailed chemical kinetic mechanisms. A hierarchical tree of rate estimation rules associated with each reaction family assigns kinetics between reaction sites according to their closest-matching functional groups [34]. RMG has been successfully used to develop mechanisms for many systems including thermal decomposition [47-50]. RMG can develop the mechanisms for many systems including containing C/H/O, and through the extensions to additional software and improved estimation methods, it also can be used to analyze the mechanisms for sulfur-containing compounds [34]. For example, the automated Reaction Mechanism Generator (RMG) was used to build the reaction networks for the thermal decomposition of di-*tert*-butyl sulfide using rate parameters derived from *ab initio* CCSD(T) calculation[51].

The RMG simulations for the thermal decomposition of neat hexyl sulfide and hexanethiol proceeded as follows. The reaction model was set for a reactor at a temperature of 400 °C and 6 MPa. Instead of setting the goal conversion of the reactants, reaction time was set. Thermochemical parameters for reaction pathways were calculated using the Benson group additivity, which uses the experimentally calculated heat of formation for individual groups of atoms to calculate the entire heat of formation for a molecule under investigation [52]. The reaction rate constants were estimated from the kinetic parameter of rate rules in the RMG database, which contains various rate parameters for organosulfur reactions including hydrogen abstraction, β-scission, homolytic scissions, and unimolecular decomposition. After the simulation, the reaction pathways obtained from the model and the experimental data were compared and modified.

However, RMG is not appropriate for investigating reactions in SCW. SCW participates in various reactions as a reaction medium, solvent, reactant or even catalyst [10]. In the reactions where water directly participates in or catalyzes, water normally forms a ring transition state but RMG has several limitations in suggesting cyclic sulfur compound. Simulation results derived from existing databases in RMG have significant differences from experimental data. Therefore, to investigate the decomposition of hexanethiol and hexyl sulfide in SCW, Density Functional Theory (DFT) calculations were performed using Gaussian 09. DFT is a computational quantum mechanical modeling method used in physics, chemistry, and materials science to investigate the electronic structure of many-body systems, in particular atoms, molecules, and the condensed phases. It finds an increasingly broad application in chemical reactions for the interpretation and prediction of complex system behavior at an atomic scale. [53-55]. Numbers of DFT calculations for water have been reported to elucidate the catalytic role of water molecules, which were regarded as having a pivotal role in many reactions in SCW [56]. For example, the activation barrier of transition state complex in formic acid decomposition decreases with the presence of water, suggesting that the water molecules act as a catalyst for both dehydration and decarboxylation [57]. The activation barrier calculation for the ethanol oxidation into acetaldehyde also showed the catalytic role of water in SCW with the direct participation of water molecules through multi-center transition states [58].

The DFT calculations using Gaussian 09 proceeded as follows. The initial reaction model was set using the final reaction model in thermal decomposition. For each reaction pathway in the reaction model, water molecules were introduced, and the changes in the energy barrier were calculated using Gaussian 09. All the calculations were performed in supercritical conditions by considering zero-point and thermal energy collections at 673 K and 25 MPa. The thermochemical calculation, geometric optimization and the intrinsic reaction coordinate (IRC) were conducted at the B3LYP/6-311 +G(d, p) basis set. The B3LYP method is the most popular functional in DFT and well established in the literature with fast speed and high accuracy. 6-311 basis set was chosen because it is the split-valence triple-zeta basis and deemed to give better results for sulfur compounds. Diffuses function was applied for accuracy because of the molecules with lone pairs. And the spin-unrestricted was used because of the odd number of ions. All the species with even number of electrons were selected as singlet and radical species were selected as a doublet. Transition state was searched with the QST2 or QST3 using the Synchronous Transit-Guided Quasi-Newton (STQN) Method through the imaginary frequency and the intrinsic reaction coordinate (IRC). Also, normal-mode frequency analysis was performed to confirm the optimized structures and transition state.

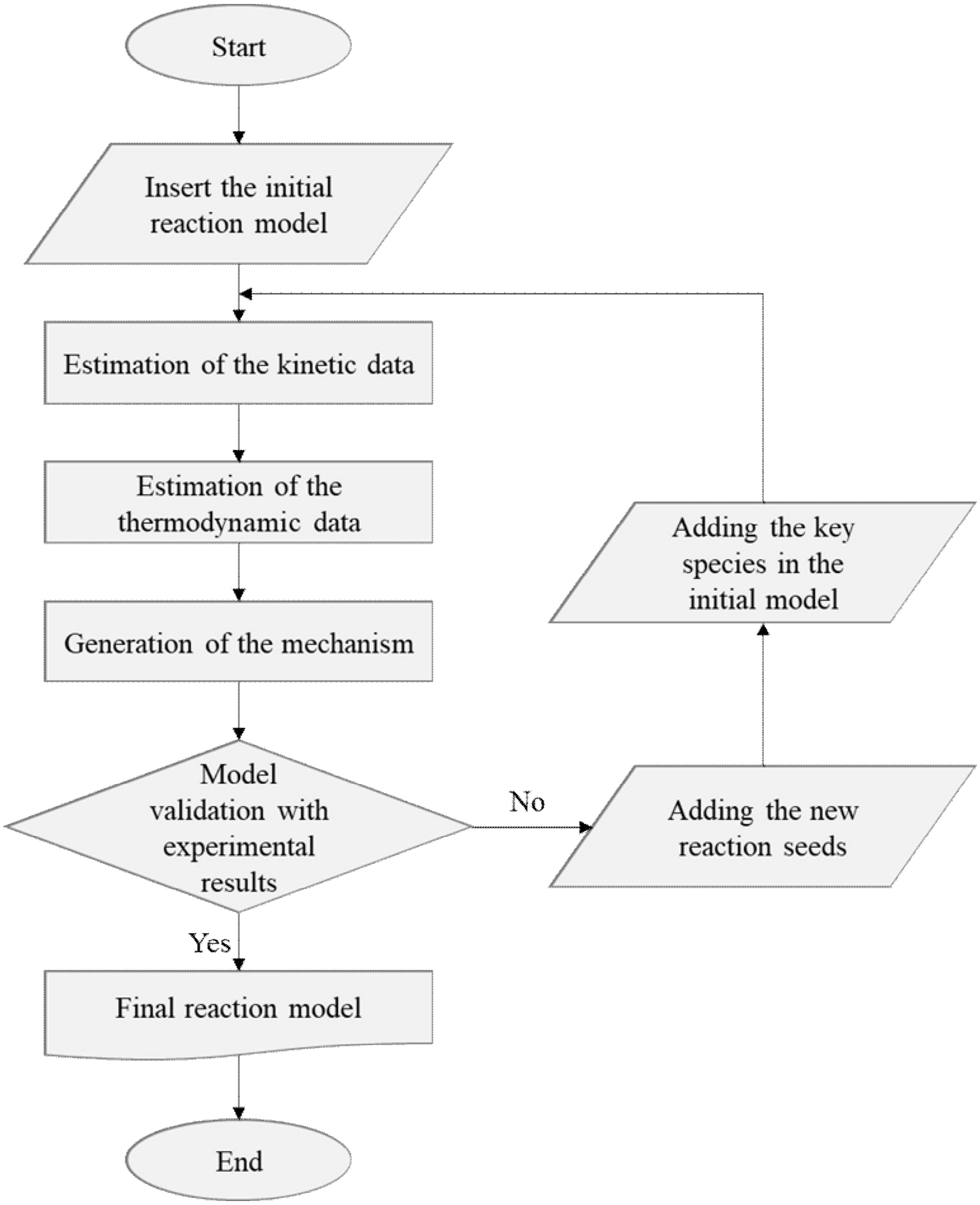


Figure 3.4. Flowchart of reaction mechanism construction algorithm for thermal decomposition using RMG. Reaction model

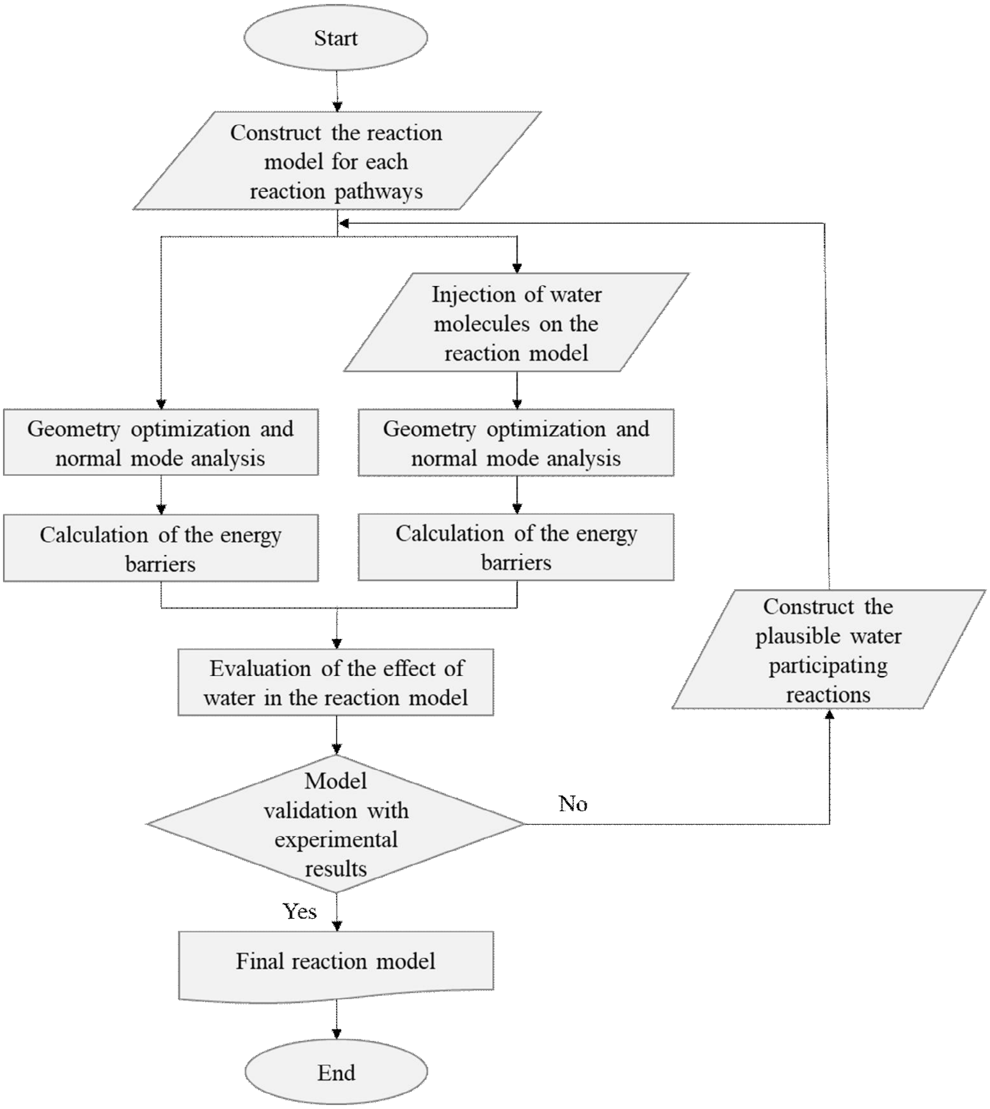


Figure 3.5. Flowchart of reaction mechanism construction algorithm for SCW decomposition using Gaussian 09.

4. Results and discussions

4.1. Hexyl sulfide decomposition

4.1.1. Characterization of the products

To characterize the products of hexyl sulfide decomposition, the products reacted for 5 min in thermal decomposition and SCW decomposition were chosen and analyzed using GC-MS. Each component in products was determined from peak ionization chromatography (TIC) with retention time. The products of hexyl sulfide by thermal decomposition and SCW decomposition are listed in Table 4.1. and the structures of them are shown in Figure 4.1.

The results could be classified into three major groups; hydrocarbons, sulfur compounds, and oxygen compounds. The hydrocarbons including pentane, hexane, hexenes, and cycloalkane were found in both conditions. Hexenes were more abundant in thermal decomposition, whereas hexane and pentane were more abundant in SCW decomposition. The sulfur compounds are classified into thiols, sulfides, disulfides, thiophenes, and alkyl-thiacycloalkane in addition to the reactant hexyl sulfide. Hexanethiol accounted for the largest proportion of newly formed sulfur compounds in both conditions. Thiophenes, alkyl-thiacycloalkanes, and disulfides were produced in higher amounts under thermal decomposition conditions. The oxygen compounds were produced only in SCW decomposition.

Table 4.1. GC/MS analysis of the products of hexyl sulfide decomposition. The products reacted for 5 minutes through thermal decomposition and SCW decomposition were analyzed.

Name of compounds	Retention time (min)	Area (%)	
		Thermal	SCW
Pentane	4.82	0.46	2.58
Hexene	5.38	4.48	1.50
Hexane	5.51	13.62	7.45
2-Hexene	5.62	8.73	0.59
3-Hexene	5.79	2.88	0.28
Methyl cyclopentane	6.09	0.10	0.03
Cyclohexane	6.85	-	0.02
Thiophene	6.97	0.55	0.02
2-Methylthiophene	10.00	0.10	-
2-Hexanone	10.55	-	0.03
2-Hexanol	10.96	-	0.16
2-Hexanethiol	13.23	1.64	0.03
2-Ethylthiophene	13.30	1.69	-
Hexanol	13.34	-	0.08
2,5-Dimethylthiophene	13.47	0.94	-
Trans-2,5-dimethylthiophane	14.02	0.12	-
Cis-2,5-dimethylthiophane	14.13	0.17	-
1-Hexanethiol	15.29	15.42	2.46
2-Methylthiacyclohexane	15.65	0.50	0.07
2-Ethylthiolane	16.41	1.94	0.56
Methyl hexyl sulfide	18.65	0.26	0.16
Ethyl hexyl sulfide	21.11	0.26	0.09
2-Methylcyclopentanethiol	22.23	-	0.04
2-Pentylthiophene	22.50	0.10	-
Naphthalene	23.06	17.95	14.37
Ethyl hexyl disulfide	24.81	0.08	-
2-(Hexylthio)Hexane	25.74	1.50	0.07
2-(3-Methylbutyl)-5-propylthiophene	25.87	0.28	-
2,5-Dibutylthiophene	25.95	0.15	-
2-Ethyl-5-propylthiophene	26.00	0.28	-
Cyclohexyl hexyl sulfide	26.24	0.15	-
Hexyl sulfide	26.34	20.73	67.96
Hexyl disulfide	27.89	1.28	0.04
Undetected matter		3.65	1.43
Total area (%)		100.00	100.00

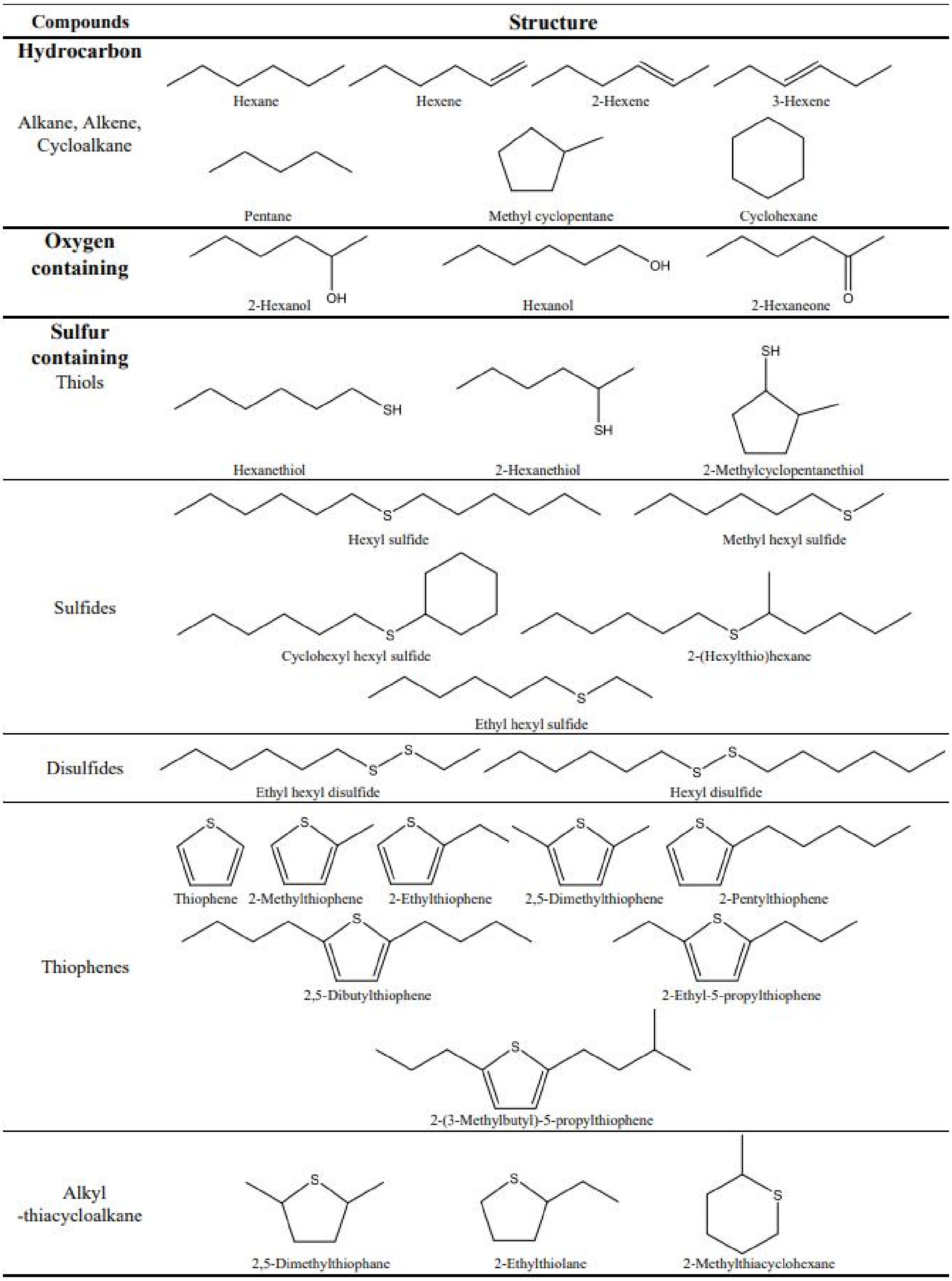


Figure 4.1. The identified compounds in the products of hexyl sulfide decomposition by GC-MS. Hydrocarbon including alkane, alkene, cycloalkane, oxygen containing compounds and Sulfur containing compounds including thiols, sulfides, disulfides, thiophenes, and alkyl-thiacycloalkane were found.

4.1.2. Quantification of the products

From the characterization of products, the major products with reaction times were quantified by GC-FID. The products distribution of hexyl sulfide by thermal decomposition and SCW decomposition with reaction times are shown in Table 4.1. and Table 4.2.

First, the conversion of hexyl sulfide, the reactant of this experiment, was examined in Figure 4.1. The conversion of hexyl sulfide increased with the reaction time in both conditions, and hexyl sulfide was almost completely decomposed in both conditions at the reaction time of 30 min. At the reaction time of 0 min only including the heat-up time, a small amount of hexyl sulfide was decomposed in both conditions, indicating that the decomposition reaction started to happen during the heat-up time. Overall, the conversion rate of hexyl sulfide was much faster in the thermal decomposition than in the SCW decomposition at all reaction times.

Second, the distributions of major products are shown in Figure 4.2. Hexanethiol is the most abundant at 5 min and then decrease with reaction time, so it is presumed to be the main intermediate product of hexyl sulfide. Comparing the final products in thermal decomposition and SCW decomposition, pentane and hexene were mainly observed in SCW decomposition, whereas hexane and hexene were mainly observed in thermal decomposition. Hexene was observed in both conditions, but in SCW decomposition, it occupied up to 10%, whereas in thermal decomposition it occupied up to 20%.

Finally, the distributions of sulfur and oxygen-containing compounds except for hexyl sulfide and hexanethiol were investigated in Figure 4.3. Overall, more sulfur-containing compounds were found in thermal decomposition than in SCW decomposition. Thiophenes including thiophene, 2-ethylthiophene, and 2,5-dimethylthiophene were only produced in thermal decomposition, not in SCW decomposition. It was expected that most of the sulfur-containing compounds in thermal decomposition were converted to thiophenes. It is supported by the previous study which shows that thiophene is a stable substance among the organosulfur and is not easily decomposed [16]. Meanwhile, in SCW decomposition, it was found that most of the sulfur-containing compounds were converted to the alkyl-thiacycloalkanes, not the thiophenes.

Table 4.2. The products distribution of hexyl sulfide using thermal decomposition with reaction time. The mass of each compounds were calculated based on the initial amount of hexyl sulfide.

Name of compounds		Mass (wt%)			
		Reaction time(min)			
		0	5	10	30
	Hexyl sulfide	75.83	13.90	3.14	0.13
Hydrocarbons	Pentane	0.06	0.42	0.18	0.37
	Hexane	5.49	24.61	16.67	11.33
	Hexene	4.93	7.65	8.11	12.13
	2-Hexene	0.62	9.58	7.61	3.90
	3-Hexene	0.29	3.24	2.57	2.48
Thiols	Hexanethiol	4.25	9.83	4.85	1.13
	2-Hexanethiol	0.10	1.33	0.78	0.59
Sulfides	Methyl hexyl sulfide	0.06	0.17	0.12	0.00
	Cyclohexyl hexyl sulfide	0.90	0.27	0.00	0.00
	2-(Hexylthio)hexane	0.62	1.34	0.49	0.00
Thiophenes	Thiophene	0.24	1.14	1.21	1.23
	2-Ethylthiophene	0.46	1.87	1.78	2.24
	2,5-Dimethylthiophene	0.00	0.68	0.77	0.74
Alkyl-thiacycloalkanes	2-Methylthiacycloheaxne	0.22	0.34	0.26	0.15
	2-Ethylthiolane	0.38	1.45	1.34	0.95
Disulfides	Hexyl disulfide	0.87	0.57	0.14	0.05
	Total (%)	95.31	78.37	50.02	37.42

Table 4.3. The major products distribution of hexyl sulfide by SCW decomposition with reaction time. The mass of each compounds were calculated based on the initial amount of hexyl sulfide.

Name of compounds		Mass (wt%)			
		Reaction time(min)			
		0	5	10	30
	Hexyl sulfide	93.46	44.36	18.45	0.19
Hydrocarbons	Pentane	0.37	8.91	16.72	21.40
	Hexane	2.80	15.96	28.77	37.19
	Hexene	1.67	3.32	3.24	1.28
	2-Hexene	0.10	1.87	3.96	6.70
	3-Hexene	0.04	0.77	1.50	2.19
Thiols	Hexanethiol	1.32	4.12	3.96	2.19
Sulfides	Methyl hexyl sulfide	0.03	0.21	0.28	0.13
	Cyclohexyl hexyl sulfide	0.49	0.50	0.27	0.00
Alkyl-thiacycloalkanes	2-Methylthiacycloheaxne	0.10	0.32	0.31	0.20
	2-Ethylthiolane	0.15	0.69	0.92	1.02
Disulfides	Hexyl disulfide	0.19	0.20	0.12	0.12
Oxygen containing	2-Hexanol	1.74	0.95	0.42	0.11
	Total (%)	102.46	82.18	78.92	72.73

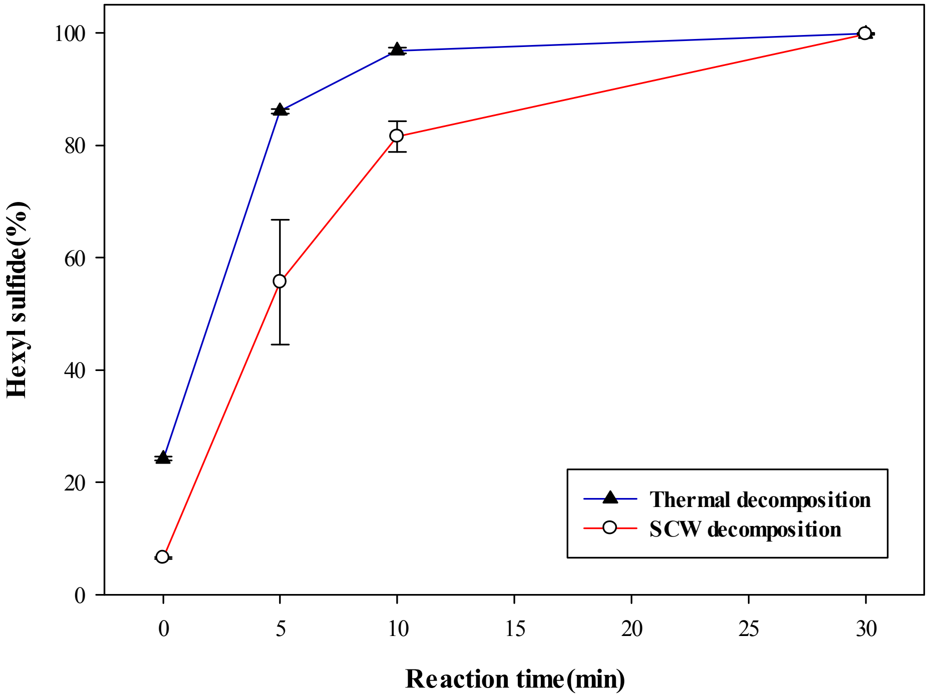
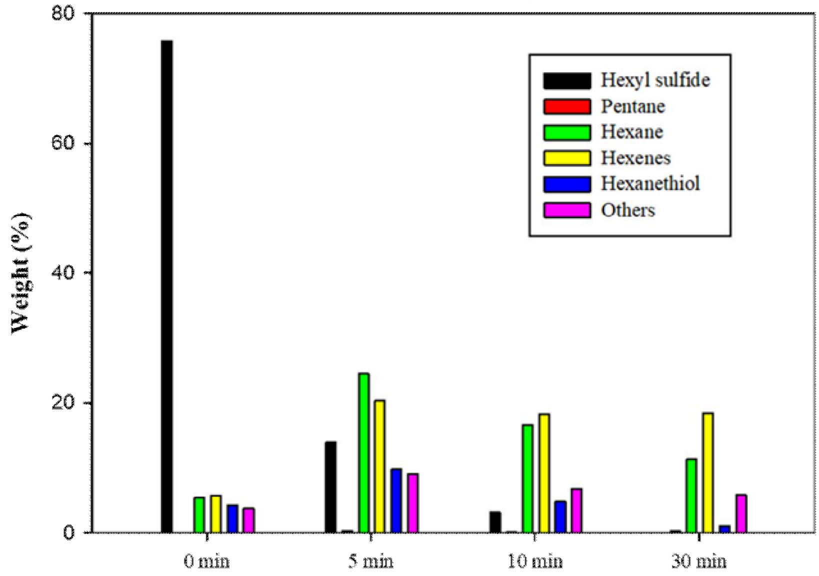


Figure 4.2. The conversion of hexyl sulfide with reaction times. The conversion rate of hexyl sulfide was much faster in the thermal decomposition than in the SCW decomposition at all reaction times.

a) Thermal decomposition



b) SCW decomposition

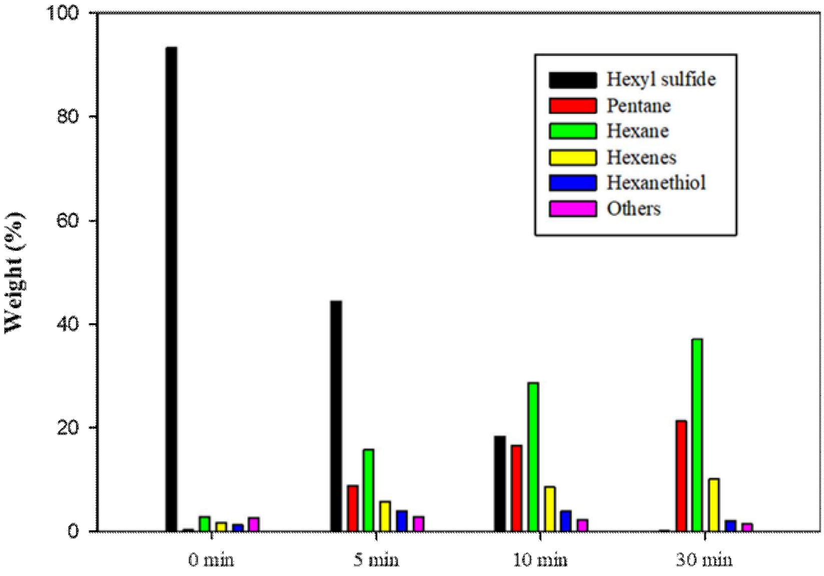


Figure 4.3. The major products distribution of hexyl sulfide in a) thermal decomposition and b) SCW decomposition with reaction times. 'Others' includes sulfur and oxygen compounds. Pentane was one of the major products in SCW decomposition but not in thermal decomposition. Also, the ratio of hexane to hexenes was much higher in SCW decomposition.

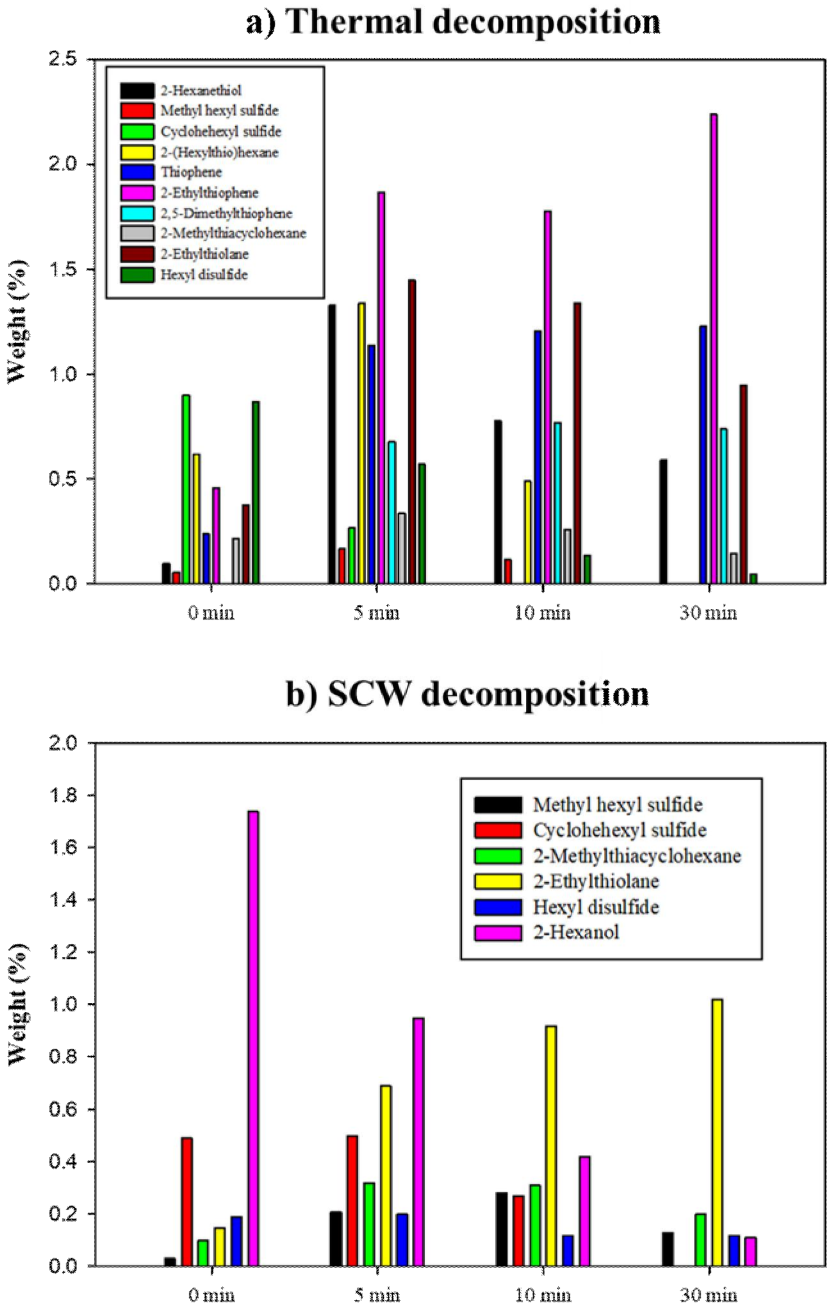


Figure 4.4. The sulfur and oxygen-containing compounds distributions of hexyls sulfide in a) thermal decomposition and b) SCW decomposition with reaction times. Thiophenes including thiophene, 2-ethylthiophene, and 2,5-dimethylthiophene were only found in thermal decomposition.

4.2. Hexanethiol decomposition

As discussed earlier, hexanethiol is one of the important intermediate products in hexyl sulfide decomposition. Therefore, in order to understand the reaction route of hexyl sulfide, it is necessary to understand the decomposition of hexanethiol. The decomposition of hexanethiol was carried out by the same experimental equipment, experimental methods, analytical methods and reaction temperature as the decomposition of hexyl sulfide, and the reaction time was 5 min. The products of hexanethiol decomposition in thermal decomposition and SCW decomposition are listed in Table 4.4. and the structures of them are shown in Figure 4.5. The characterization results of hexanethiol decomposition are very similar to that of hexyl sulfide decomposition.

From the characterization of products, the major products were also quantified by GC-FID. The products distribution of hexanethiol decomposition in thermal decomposition and SCW decomposition are shown in Table 4.5. and compared with each other in Figure 4.6 and Figure 4.7. Pentane was mainly observed in SCW decomposition while it was rarely observed in thermal decomposition. Comparing the ratio of hexane to hexenes, hexane was more than half of hexene in thermal decomposition, but hexane was only one third of hexenes in SCW decomposition. Among the sulfur compounds except for hexanethiol, 2-hexanethiol has the largest proportion. Sulfides, alkyl-thiacycloalkane, and disulfides were observed in both conditions, but thiophenes including thiophene and 2-ethylthiophene were only observed in thermal decomposition.

Table 4.4. GC/MS analysis of the products of hexanethiole decomposition. The products reacted for 5 minutes through thermal decomposition and SCW decomposition were analyzed.

Name of compounds	Retention time (min)	Area (%)	
		Thermal	SCW
Pentane	4.82	0.37	3.15
Hexene	5.38	4.91	4.07
Hexane	5.51	10.24	6.40
2-Hexene	5.62	12.04	5.18
3-Hexene	5.79	4.17	2.54
Methyl cyclopentane	6.09	0.14	0.09
Cyclohexane	6.85	0.10	0.03
Thiophene	6.97	0.58	0.05
1-Butanethiol	8.22	0.04	0.03
2-Methylthiophene	10.01	0.07	0.01
3-Hexanone	10.40	-	0.03
2-Hexanone	10.53	-	0.18
3-Hexanol	10.83	-	0.04
2-Hexanol	10.96	-	0.21
1-Pentanethiol	11.62	-	0.02
2-Hexanethiol	13.24	1.99	0.78
2-Ethylthiophene	13.31	2.04	0.18
2,5-Dimethylthiophene	13.47	0.48	0.02
Trans-2,5-dimethylthiophane	14.02	0.15	0.07
Cis-2,5-dimethylthiophane	14.14	0.17	0.12
3-Methylpentanethiol	14.27	0.08	0.09
2-Methylcyclopentanethiol	14.96	0.04	-
1-Hexanethiol	15.35	33.87	53.32
2-Methylthiacyclohexane	15.68	0.92	0.40
2-Ethylthiolane	16.43	2.66	1.08
2-Isopropylthiophene	16.73	0.02	-
Methyl hexyl sulfide	18.65	0.02	0.03
2-Ethylhexanol	18.89	-	0.02
2-Ethylhexanethiol	20.16	-	0.02
Ethyl hexyl sulfide	21.11	0.21	0.15
1-Octanethiol	21.80	-	0.05
2-Butyltetrahydrothiophene	22.41	-	0.01
2-Pentylthiophene	22.50	0.02	-
Naphthalene	23.08	20.32	19.58
Hexyl ether	24.13	-	0.06
2-(Hexylthio)hexane	25.74	0.37	0.19
2-(3-Methylbutyl)-5-propylthiophene	25.87	0.13	-
2,5-Dibutylthiophene	25.95	0.05	-
2-Ethyl-5-propylthiophene	26.00	0.04	-
Cyclohexyl hexyl sulfide	26.24	0.09	0.01
Hexyl sulfide	26.33	1.24	1.04
Hexyl disulfide	27.89	0.55	0.22
Undetected matter		1.88	0.54
Total area (%)		100.00	100.00

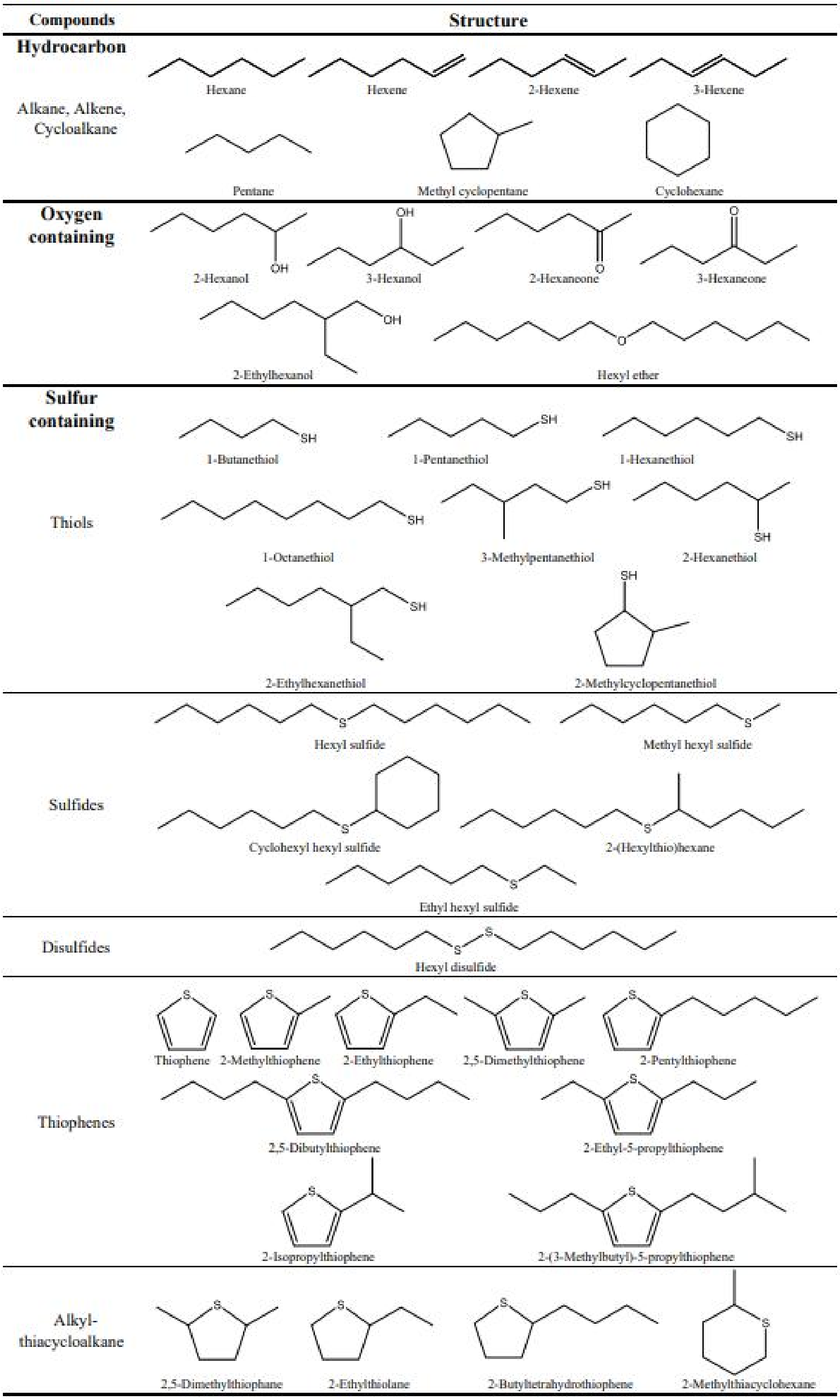


Figure 4.5. The identified compounds in the products of hexanethiol decomposition by GC-MS. Hydrocarbon including alkane, alkene, cycloalkane, oxygen containing compounds and Sulfur containing compounds including thiols, sulfides, disulfides, thiophenes, and alkyl-thiacycloalkane were found.

Table 4.5. The products distribution of hexanethiol in thermal decomposition and SCW decomposition with the reaction time of 5 min. The mass of each compounds were calculated based on the initial amount of hexanethiol.

Name of compounds		Mass (wt%)	
		Thermal	SCW
	Hexanethiol	29.53	56.72
Hydrocarbons	Pentane	0.38	3.65
	Hexane	12.39	6.37
	Hexene	5.06	4.71
	2-Hexene	12.69	8.38
	3-Hexene	4.24	2.89
Thiols	2-Hexanethiol	1.83	0.76
Sulfides	Hexyl sulfide	1.21	0.57
	2-(Hexylthio)Hexane	0.27	0.15
Thiophenes	Thiophene	0.58	0.04
	2-Ethylthiophene	1.28	0.08
Alkyl-thiacycloalkanes	2-Methylthiacyclohexane	0.65	0.31
	2-Ethylthiolane	1.78	0.77
Disulfides	Hexyl disulfide	0.34	0.34
Total area (%)	Total area (%)	72.24	85.75

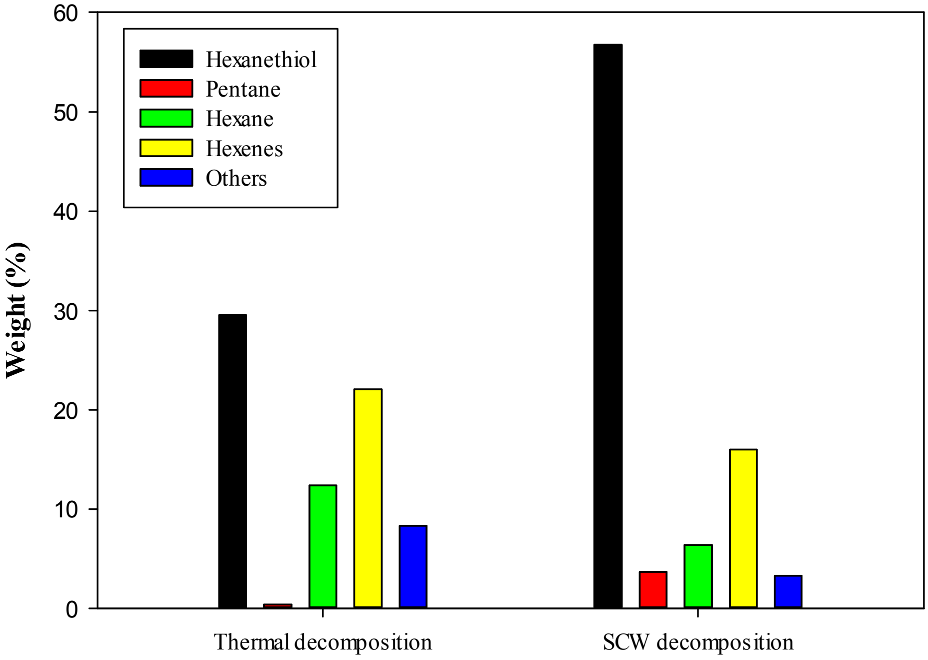


Figure 4.6. The major products distribution of hexanethiol using thermal decomposition and SCW decomposition. Pentane was one of the major products in SCW decomposition but not in thermal decomposition. Also, the ratio of hexane to hexenes was much higher in SCW decomposition.

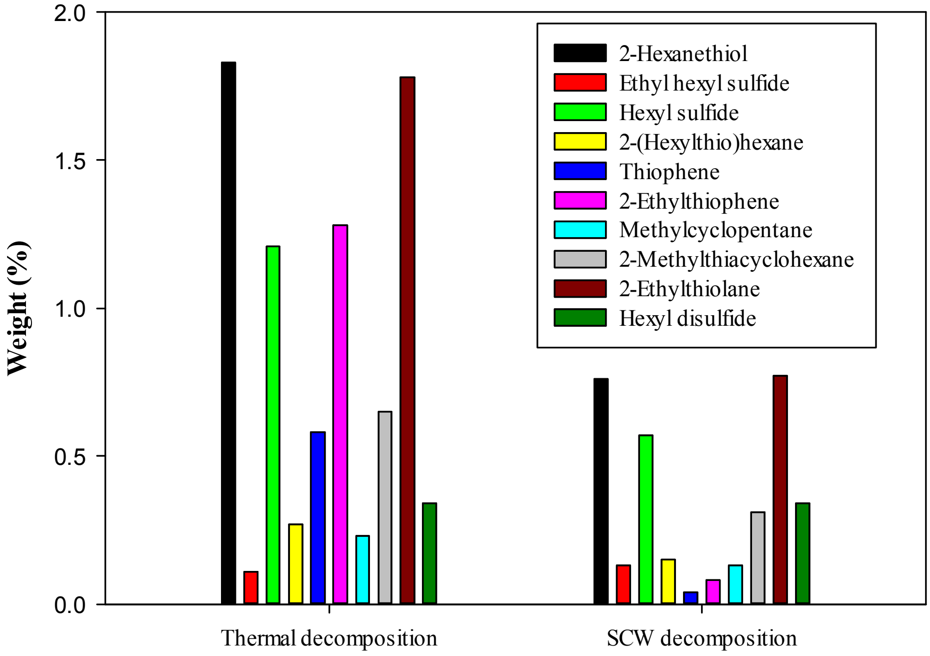


Figure 4.7. The sulfur and oxygen-containing compounds distribution of hexanethiol using thermal decomposition and SCW decomposition. Thiophenes including thiophene, 2-ethylthiophene, and 2,5-dimethylthiophene were only found in thermal decomposition.

4.3. The change of sulfur balances

As shown in the experimental results, thermal decomposition and SCW decomposition of hexanethiol and hexyl sulfide have different reaction paths. In thermal decomposition, various kinds of organosulfur compounds are produced with a large number of aromatic sulfur groups including thiophenes. In SCW decomposition, however, the amount of organosulfur compounds is smaller than thermal decomposition, and aromatic sulfur groups such as thiophene are very small or not formed. The difference in these reaction paths can affect the desulfurization effect with the difference in the amount of sulfur remaining in the product. In this chapter, the desulfurization effects for thermal decomposition and SCW decomposition were examined by comparing the sulfur balance of products.

The amount of sulfur remaining after the decomposition of hexanethiol was investigated. The total residual sulfur contents in the oil product after the decomposition of hexanethiol and hexyl sulfide were investigated from the GC-FID results. After the decomposition of hexanethiol at 400 °C for 5 min, 37.24 wt% of sulfur remained in the thermal decomposition while 59.52 wt% of sulfur remained in SCW decomposition. This is due to the difference of hexanethiol amount that 29.53% hexanethiol remained in thermal decomposition while 56.72% hexanethiol remained in SCW decomposition. Also, the amount of sulfur remaining after the decomposition of hexyl sulfide and effective sulfur reduction for hexyl sulfide was investigated in Figure 4.8. Sulfur balance of products was lower in thermal decomposition until 10 min, but it was lower in SCW at 30 min. It can be explained that sulfur balance depends on the amount of hexyl sulfide and hexyl sulfide decomposition is faster in thermal decomposition than in SCW.

Overall, the decomposition of hexanethiol and hexyl sulfide is faster in thermal decomposition so that thermal decomposition was effective in removing sulfur until 10 mins. However, at 30 mins when most of hexanethiol and hexyl sulfide are decomposed, SCW decomposition was effective in removing sulfur because sulfur compounds including thiophene and alkyl-thiacycloalkane are formed with different reaction pathway in thermal decomposition.

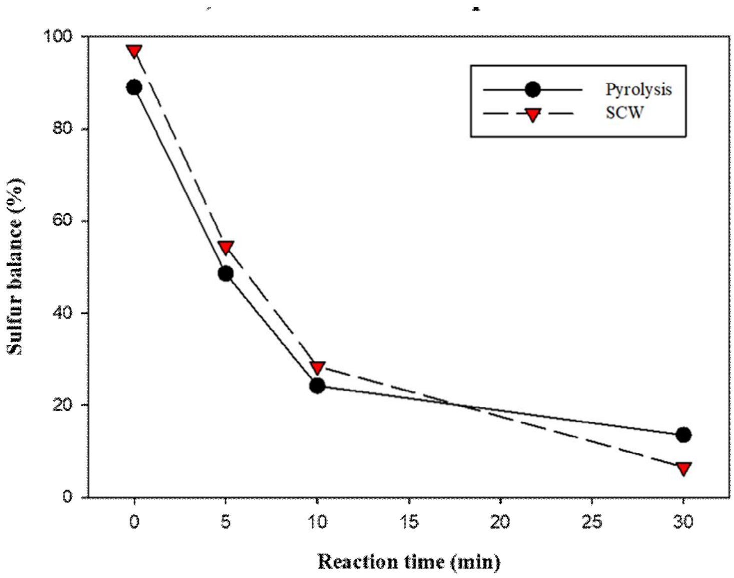


Figure 4.8. The sulfur balance of products in hexyl sulfide decomposition.

4.4. The mechanism construction in thermal decomposition

To understand the hexyl sulfide and hexanethiol decomposition, it is effective to study the mechanism of hexyl sulfide and hexanethiol decomposition. However, as can be seen that a considerable number of compounds are detected in the decomposition reaction of hexyl sulfide and hexanethiol, the decompositions of such sulfur-containing compounds are very complex and difficult to provide an accurate mechanism.

In this study, the mechanisms were constructed by considering entire decomposition mechanisms of reactants (hexyl sulfide and hexanethiol) and adding the cross-reactions between the major products and radicals produced by products. These various types of coupling reactions must be considered in a systematic way, taking into consideration the various kinds of elementary reactions. To investigate the reactions involved in the thermal decomposition of hexyl sulfide and hexanethiol, a detailed kinetic model was automated using automated reaction mechanism generation software, Reaction Mechanism Generator (RMG), various works, and experimental results. The proposed reaction pathways built using RMG were verified through various works of literature and experimental results. Some inappropriate reaction pathways were corrected, and modified reaction pathways presented. For products detected in the experiment but not shown in the reaction model, possible reaction pathways are presented based on existing literature.

4.4.1. The thermal decomposition mechanism of hexanethiol

RMG was used to build the network of hexanethiol decomposition and it generated a mechanism with 26 core species and 16 reactions for the hexanethiol decomposition. The main reactions in the kinetic model include unimolecular decomposition reaction (Reaction pathway (a)), homolytic scissions reaction (Reaction pathway (b)), and hydrogen abstraction (Reaction pathway (c)) in Figure 4.9., and the kinetic parameters of these main reactions are shown in Table 4.6.

The reaction pathway (a) is the unimolecular decomposition reaction that directly forms hexenes and hydrogen sulfide. It is the main sulfur removal route in hexanethiol decomposition. In the decomposition mechanisms of ethanethiol in thermal decomposition, the unimolecular decomposition reaction pathway was suggested as the main reaction pathway [59-62]. In this study, RMG results also show that unimolecular decomposition reaction is the most dominant reaction with the highest rate constants among the reaction pathways in the hexanethiol decomposition.

The reaction pathway (b) is the homolytic scission reaction of the C-S bond. According to the reaction mechanisms proposed in RMG, homolytic scissions including not only C-S bond but also the C-C bond can occur, so the kinetic parameters of the C−S/C-C bonds are compared with each other. From the rate constants derived from rate rules and other parameters estimated *via* group additivity methods in RMG, the homolytic scissions reactions for C-S bond is much faster than any other homolytic scissions reactions for C-C bond with the difference of orders of magnitude so that only homolytic scission reaction of C-S bond was included in the reaction pathway. From this homolytic scission reaction of C-S bond, sulfanyl(HS•) and hexyl radical are formed.

The reaction pathway (c) is the hydrogen abstraction. Among the C-H/S-H bonds in hexanethiol, the strength of S-H bond is much lower than C-H bond, resulting in much higher rate constants for the S-H bonds hydrogen abstraction than that for the C-H bonds hydrogen abstraction so only the hydrogen abstraction reaction at S-H was included in this reaction forming hexyl radical.

After the hexanethiol decomposition, major products including hexenes, hexane, 2-hexanethiol, sulfides, alkyl-thiacycloalkanes, thiophenes, and hexyl disulfide were produced. For these major products, the plausible reactions including the unimolecular and bimolecular initiation, unimolecular and biomolecular isomerization, ipso-additions between the alkyl radicals and H_2S, the decomposition by β-scission, H-transfer, terminations, and the additions of free radicals to alkenes are suggested in Figure 4.10.

Hexenes and hexane can be formed from the hexyl radicals. Hexyl radicals react with stable molecules as a propagation step in the radical chain reaction or react with other radical radicals as a termination step in the radical chain reaction. In the propagation step, they react with stable molecules, producing hexane and new free radicals. In the termination step, radical disproportionation, in which two radicals react to form two different non-radical products, occurs producing hexenes. Because hexyl radicals can change their form into various types of hexyl radicals including 1-hexyl radicals, 2-hexyl radical and 3-hexyl radical through bimolecular initiation (or RRD, reverse radical disproportionation) between H_2S and hexenes, hexenes including 1-hexene, 2-hexene and 3-hexene are formed [63-65]. Also, 1-hexene can be isomerized into other hexenes; the C-C double bond of 1-hexene migrates from the terminal position to an internal position [66]. Therefore, 2-hexene and 3-hexene in addition to 1-hexene are generated in the thermal decomposition of hexanethiol.

2-Hexanethiol is the product of the following two reactions; bimolecular initiations(or RRD, reverse radical disproportionation) between H_2S and hexenes and ipso-additions between H_2S and alkyl radicals. The bimolecular initiations produce hexyl radical, 2-hexyl radical, and 3-hexyl radicals from the hexenes [63-65]. Among them, 2-hexyl radical reacts with the H_2S as an ipso-additions to become a 2-hexanethiol [67]. Sulfides including hexyl sulfide and 2-(hexylthio)hexane are formed by the coupling of thiol radicals and alkyl radicals. Hexyl sulfide is formed by coupling reaction of hexyl thiol radical and hexyl radical, and 2-(hexylthio)hexane is formed by coupling reaction of hexyl thiol radical and 2-hexyl radical.

Alkyl-thiacycloalkanes including 2-methylthiacyclohexane and 2-ethylthiolane are derived from the intramolecular radical cyclization reaction of thiol radicals. Due to the larger bond length of C-S bond compared to C-C, C-O or C-N, the orthogonal overlap of the thiol radical allows for cyclization with the carbon in alkane chains with the intramolecular thiol-*ene* reaction [68]. According to the molecular orbital explanation for the absence of regioselectivity in the intramolecular thiol-*ene* reaction by Baldwin, the rationale for the allowed cyclization reaction at the terminal position is due to the presence of the unoccupied 3d orbitals on the sulfur atom that undergo back bonding interactions with the filled π-orbital of the double bond thereby reducing the geometric constraint usually associated with terminal ring closing reactions [69]. In the intramolecular thiol-*ene* reactions, the ring-closure reaction is determined by the cyclization corresponding to *exo* or *endo*, with 5 or 6 number of atoms in the newly formed ring. In this study, there are two main cyclic 6 carbon-sulfur species, 5 number of atoms in the ring (2-ethylthiolane) and 6 number of atoms in the ring (2-methylthiacyclohexane), which correspond to the cyclization with *exo* and *endo* so the reaction pathways in which 2-methylthiacyclohexane and 2-ethylthiolane were synthesized by thiol radicals in this study.

Thiophenes including thiophene and 2-ethylthiophene are the products from the alkyl-thiacyclopentanes by the dehydrogenation reaction and ipso-addition reaction. For example, in 2-ethylthiolane, the carbon to which the ethyl group and the thiophene group are connected can easily lose hydrogen atom and become a radical in thermal decomposition. The generated radical is very unstable and decompose to alkyl-thiacyclopentenes losing additional hydrogen atom by the β-scission. Then, alkyl-thiacyclopentenes become thiophenes with two double C-C bonds as the two hydrogen atoms are continuously lost through the reaction described above. And among the thiophenes, alkyl-thiophenes are subjected to ipso-reaction in which hydrogen radicals react to remove the alkyl group and become thiophene [67, 70]. For the hexyl disulfide, disulfide is usually derived by the coupling of two thiol groups [71-72]. Hexyl disulfide is also expected to be derived by the coupling of thiol radicals [73]. But this disulfide bond is being about 40% weaker than C−C and C−H bonds and the disulfide bond is the weak link in hexyl disulfide, so it is easier to react to other substances with shorter retention time in thermal decomposition.

Taken together these reactions, the thermal decomposition pathways of hexanethiol were suggested in Figure 4.11. Rounded rectangles are the remaining compounds in the final products. Overall, the thermal decomposition of hexanethiol is a hydrogen-deficient process. Sulfanyl (HS•) requires hydrogen in the process of forming hydrogen sulfide. To make up for the hydrogen, hexanethiol radical reacts to alkyl-thiacycloalkane, followed by the reaction from the alkyl-thiacycloalkane to form thiophene. Also, hexyl radical reacts to hexene producing hydrogen, rather than reacts to hexane consuming hydrogen. Therefore, the production of hexene is much higher than that of hexane with the low ratio of hexane to hexene in thermal decomposition.

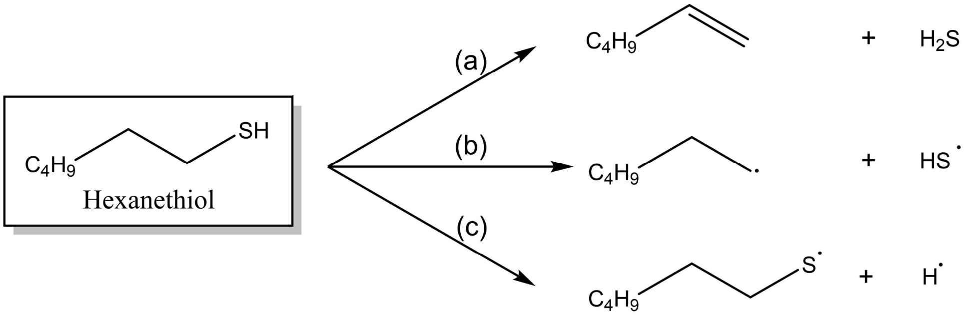


Figure 4.9. The thermal decomposition pathways of hexanethiol; (a) unimolecular decomposition reaction, (b) homolytic scissions reaction, and (c) hydrogen abstraction. The reaction pathway (a) is the main sulfur removal route in hexanethiol decomposition with the lowest activation energy.

Table 4.6. The kinetic parameters for the hexanethiol decomposition pathways in thermal decomposition

Decomposition reactions	$log_{10}A$	n	E_a (kcal/mol)
(a) Unimolecular decomposition	8.22	1.79	60.68
(b) Homolytic scissions	13.82	0.50	74.66
(c) Hydrogen abstraction	12.21	0.60	85.52

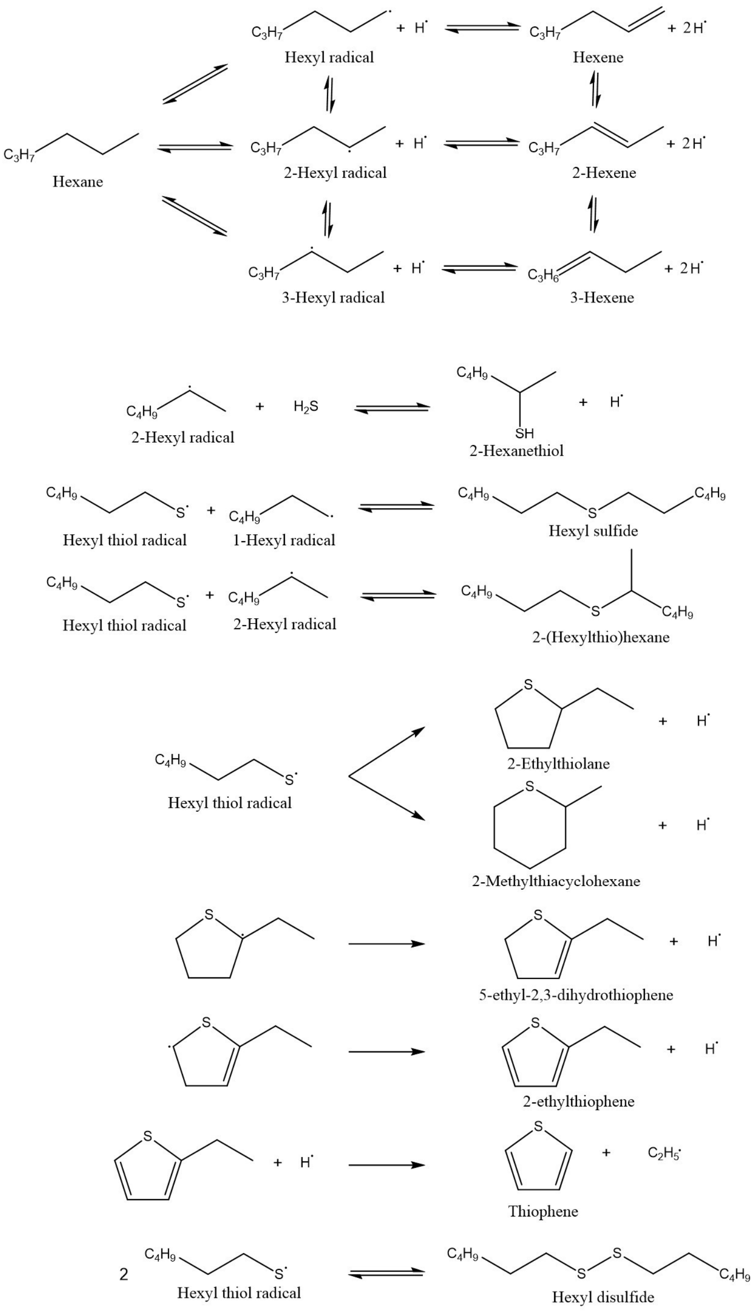


Figure 4.10. The reactions of hexanethiol by thermal decomposition. They include the unimolecular and bimolecular initiation, unimolecular and biomolecular isomerization, ipso-additions, the decomposition by β-scission, H-transfer, terminations, and the additions of free radicals to alkenes.

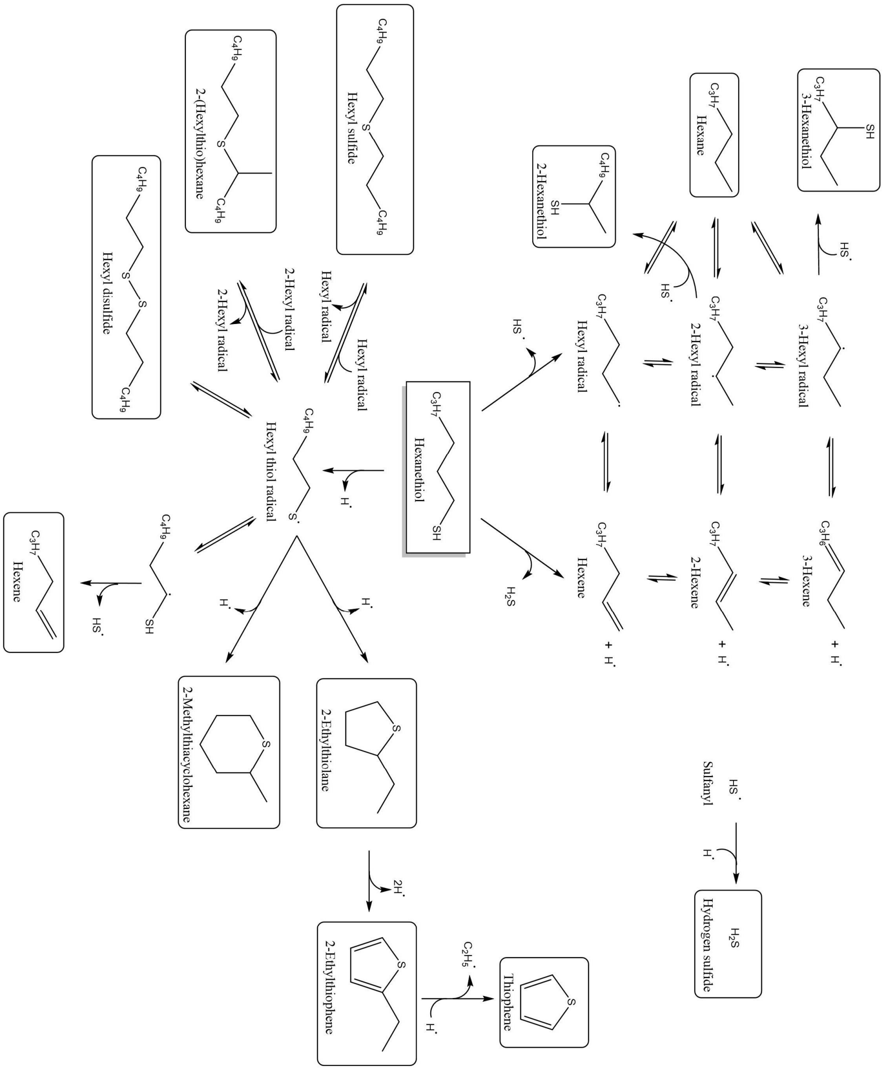


Figure 4.11. The thermal decomposition mechanism of hexanethiol. It is a hydrogen-deficient process in which sulfanyl (HS•) requires hydrogen to remove sulfur in the form of hydrogen sulfide. Therefore, hexanethiol radical reacts to alkyl-thiacycloalkane, followed by the reaction from the alkyl-thiacycloalkane to form thiophene . Also, hexyl radical reacts to hexene producing hydrogen, rather than reacts to hexane consuming hydrogen.

4.4.2. The thermal decomposition mechanism of hexyl sulfide

For the neat system, RMG generated a mechanism with core 23 species and core 15 reactions for the hexyl sulfide decomposition. The main reactions in the kinetic model include unimolecular decomposition reaction (Reaction pathway (a)), homolytic scissions reaction (Reaction pathway (b)), and hydrogen abstraction and β-scission reaction (Reaction pathway (c)) in Figure 4.12. and the kinetic parameters of these main reactions are shown in Table 4.7.

The reaction pathway (a) is the unimolecular decomposition reaction that directly forms hexanethiol and hexene. It was reported in the preceding study that the most dominant reaction pathway of di-*tert*-butyl sulfide decomposition in thermal decomposition is the unimolecular reaction with the transition state in which the β-hydrogen is connected to sulfur [51]. The unimolecular decomposition reaction was also found to be the most dominant reaction in the decomposition of hexyl sulfide in thermal decomposition.

The reaction pathway (b) is the homolytic scission reaction. In hexyl sulfide, homolytic scission reaction can occur in C-C bonds and C-S bonds, but the rate constants derived from rate rules *via* group additivity methods in RMG showed that the homolytic scissions reaction for C-S bond is faster with the difference in the orders of magnitude, so only homolytic scission reaction of C-S bond is included in the reaction pathway. From this homolytic scission reaction of C-S bond, hexanethiol radical and hexyl radical are formed.

The reaction pathway (c) is the hydrogen abstraction and β-scission reaction. This reaction pathway requires hydrogen abstraction from one of the methyl group in hexyl sulfide prior to the β-scission reaction that forms free radicals. Each methyl hexyl sulfide radicals can isomerize into other forms of hexyl sulfide radical and the types of β-scission reaction are different depending on the methyl group of hexyl sulfide radicals which hydrogen abstraction occurred. If the hydrogen abstraction occurred in the methyl group connected to sulfur in (1) in Figure 4.13., it gets β-scission to form thioaldehyde and hexyl radical [31-32]. As thioaldehyde is very unstable, thioaldehyde and hexyl radical successively react to form hexanethiol radical and hexene in thermal decomposition. If the hydrogen abstraction occurred in the other five methyl groups, the resulting radical species get β-scission to form alkene and the radical of alkyl sulfide with C-C bond cleavage. If the hydrogen abstraction occurs in the second methyl group connected to sulfur in (2), pentene and methyl hexyl sulfide radical are formed and if it occurs in the third methyl group connected to sulfur in (3), butene and methyl hexyl sulfide radical are formed. Meanwhile, cyclohexyl hexyl sulfide also can be formed from the hexyl sulfide radicals in which the hydrogen abstraction occurs in the methyl group connected to sulfur in (1). Cyclohexyl hexyl sulfide is formed through the intramolecular radical cyclization reaction of hexyl sulfide radical. Hexyl sulfide radical also has the orthogonal overlap of radical due to the larger length of C-S bond, allowing for terminal ring closing reactions with the regioselectivity in the intramolecular thiol-*ene* reaction [68-69].

After the hexyl sulfide decomposition in thermal decomposition, major products including the main intermediate product hexanethiol, 2-hexanethiol, sulfides, alkyl-thiacycloalkanes, thiophenes, and disulfides were found. Among these, the sulfur-containing compounds except methyl hexyl sulfide and cyclohexyl hexyl sulfide can be explained by the various reaction pathways which were suggested in the previous section about the decomposition of hexanethiol in thermal decomposition. And methyl hexyl sulfide and cyclohexyl sulfide are formed from the methyl hexyl radical in which the hydrogen abstraction occurs in the first methyl group connected to sulfur. The model also involves the same reactions of hexanethiol decomposition including unimolecular and bimolecular initiation, unimolecular and biomolecular isomerization, ipso-additions between the alkyl radicals and H_2S, the decomposition by β-scission, H-transfer, terminations, and the additions of free radicals to alkenes in Figure 4.10.

Taken together these reactions, the reaction pathways of hexyl sulfide in thermal decomposition were suggested in Figure 4.13. Rounded rectangles are the remaining compounds in the final products. The thermal decomposition of hexyl sulfide is a hydrogen-deficient process, which is very similar to the thermal decomposition of hexanethiol.

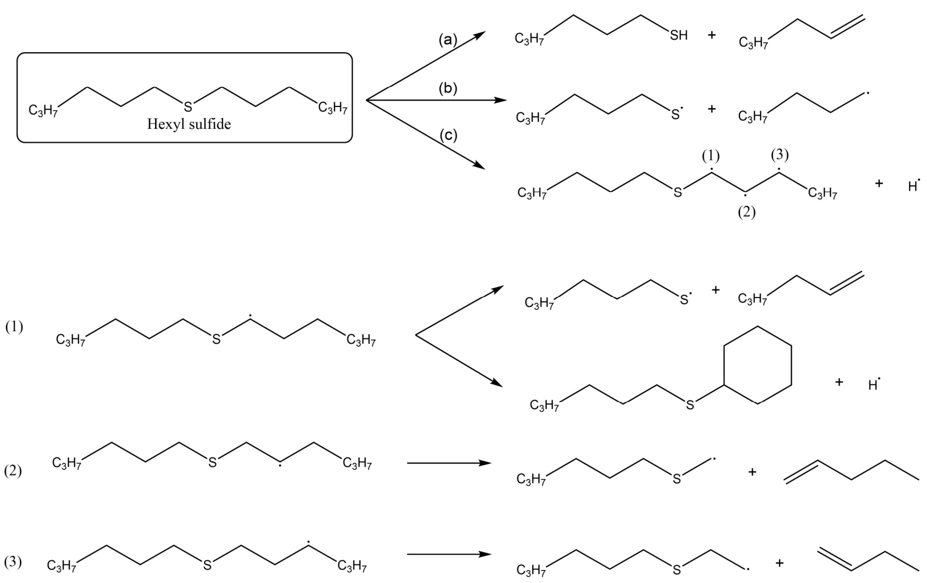


Figure 4.12. The thermal decomposition pathways of hexyl sulfide; (a) unimolecular decomposition reaction, (b) homolytic scissions reaction, and (c) hydrogen abstraction and β-scission. Depending on the carbon hydrogen abstraction occur, the subsequent reaction is different as shown in (1), (2) and (3). The reaction pathway (a) is the main sulfur removal route in hexyl sulfide decomposition with the lowest activation energy.

Table 4.7. The kinetic parameters for the hexyl sulfide decomposition pathways in thermal decomposition.

Decomposition reactions	$log_{10}A$	n	E_a (kcal/mol)
(a) Unimolecular decomposition	7.73	2.04	59.72
(b) Homolytic scissions	16.60	-0.15	70.28
(c) Hydrogen abstraction in (1)	16.81	-0.35	92.83
(c) Hydrogen abstraction in (2), (3)	18.83	-0.96	98.36

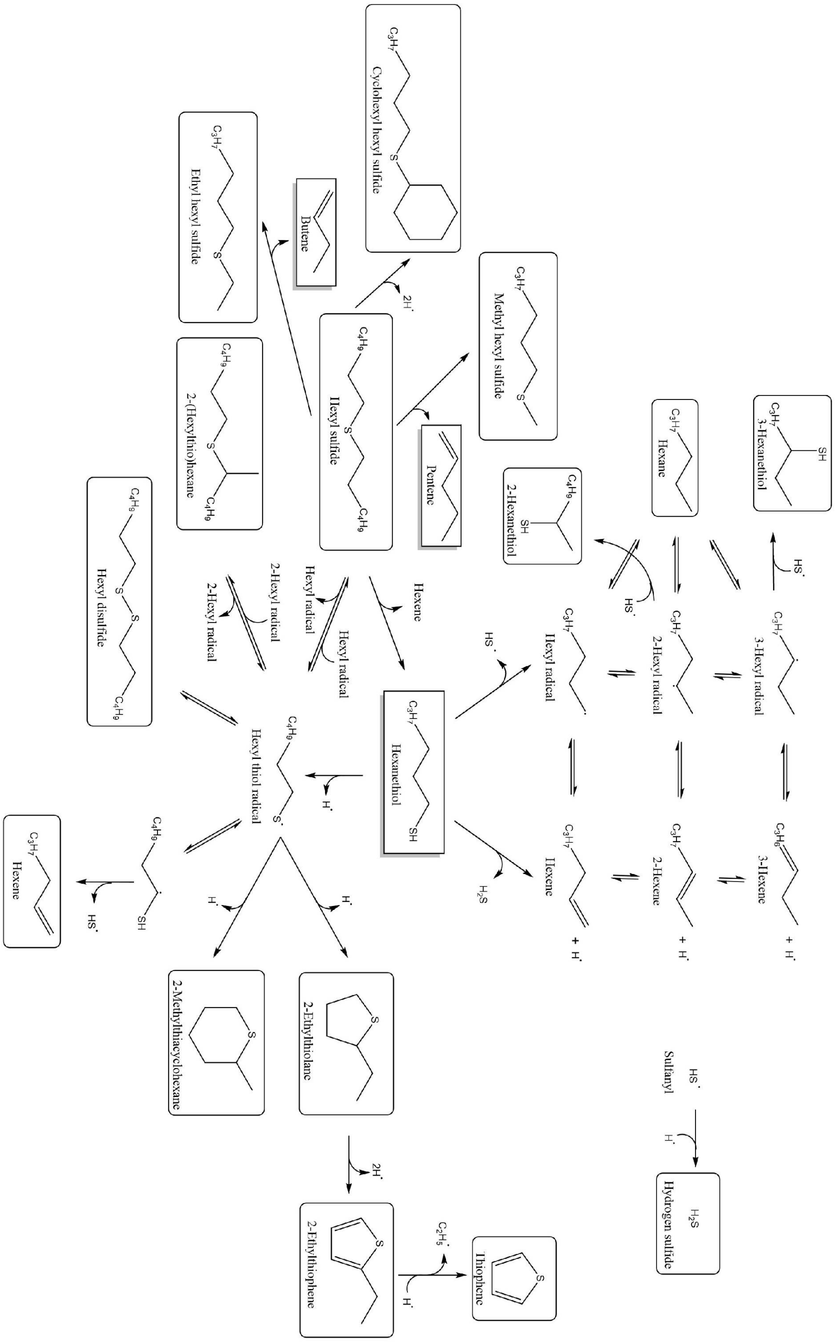


Figure 4.13. The thermal decomposition mechanism of hexyl sulfide. Like the hexanethiol decomposition in 3.3.1, it is a hydrogen-deficient process in which sulfanyl reacts with hydrogen to form hydrogen sulfide. Alkyl-thiacycloalkane and thiophene are produced, and hexene is produced in a large amount.

4.5. The mechanism construction in SCW decomposition

In the previous chapter, the thermal decomposition of hexyl sulfide and hexanethiol was investigated using RMG with the detailed kinetic model. However, it is very difficult to investigate the decomposition of hexyl sulfide and hexanethiol in SCW using existing automated reaction mechanism generation software including RMG. The reactions in SCW has been hindered by a lack of knowledge at the molecular level. The key issue is whether this environment is more like ambient water, a polar organic solvent, a gas phase, reactant or even catalyst, for a given value of the density and temperature [74].

For the development of the decomposition reaction model in SCW, the various possible reaction pathways in SCW were suggested from the DFT calculation using Gaussian 09 based on the reaction model in thermal decomposition. For each reaction pathway in the reaction model, water molecules were introduced, and the reaction barriers with water molecules for reaction pathways were calculated using Gaussian 09 and compared with the reaction barriers without water molecules to clarify the reaction mechanism in SCW. Also, other reaction pathways where water can participate are investigated from the experimental results.

For the calculation of reaction barrier using Gaussian 09, optimization facility was used to locate the transition structures as well as ground state structures because transition structures and ground state correspond to the stationary points on the potential energy surface. Gaussian geometry optimizations start with the molecular structures, and the potential energy surfaces are computed with the energy and the gradient at each point. By comparing the number of imaginary frequencies and the normal mode corresponding to the imaginary frequency, transition state, which is the saddle point, can be obtained.

4.5.1. The SCW decomposition mechanism of hexanethiol

In SCW, the hexanethiol decomposition reaction pathways including unimolecular decomposition reaction (Reaction pathway (a)), homolytic scissions reaction (Reaction pathway (b)), hydrogen abstraction (Reaction pathway (c)) and hydrogen production reaction with hexylthioaldehyde (Reaction pathway (d)) were suggested with the transition complexes with water molecule in Figure 4.14. For these reaction pathways, reaction barriers were calculated without water molecules and with water molecules using Gaussian 09.

The difference in the reaction barriers with the presence of water molecules only appeared in the reaction pathway (a) and (d) with water catalysis mechanism. In the reaction pathway (a), the transition complex including water molecules is significantly stabilized due to the interactions. Transition complex forms ring transition state with water molecules when the water molecules were introduced. In the transition complex, the hydrogen atom of water interacts with sulfur, and at the same time, the oxygen atom of water interacts with the β-hydrogen of hexanethiol to be greatly stabilized. Without water, the calculated activation energy was 62.91 kcal/mol, but with two water molecules, it was 53.79 kcal/mol. The decreased energy barriers mean that water acted as a reaction catalyst in the hexanethiol decomposition. Also, in the reaction pathway (d), transition complex with water molecules is stabilized with ring transition state. The calculated activation energy decreased from 65.78 kcal/mol to 60.16 kcal/mol. On the other hand, in the other reaction pathways (b) and (c), there was no specific energy level difference in the reactant complex, transition complex and product complex. In the absence of water, the reaction barrier of the reaction pathway (b) was 73.3 kcal/mol and the reaction barrier of the reaction pathway (c) was 86.93 kcal/mol. When the water molecules were introduced in these reactions, the change of reaction barrier was little or very small with the 1~2 kcal/mol. The reaction pathway (a), in contrast to other reaction pathways, directly removes sulfur in the form of gas, which means that desulfurization is being performed efficiently with the accelerated progress of the reaction pathway.

Overall, the other plausible reactions of hexanethiol decomposition in SCW are similar to those in thermal decomposition, but there are some reactions in which water directly participates. Hexylthioaldehyde, which are formed from the hydrogen abstraction of hexanethiol radical or hydrogen production pathway in hexanethiol decomposition, is very reactive and usually react rapidly with each other and polymerize in thermal decomposition [75]. However, in the excess of water, it reacts with a water molecule to form 1-mercaptohexan-1-ol, and then decomposes into H_2S and hexanal *via* the water-catalyzed mechanism. And hexanal decomposes into pentane and CO very fast under the radical-rich conditions with the high conversion rate. This is also supported by the observations that when octanal spiked into hexyl sulfide were treated in SCW, octanal was converted into the only heptane with almost 100% selectivity and not into octene or octane [32]. These hexylthioaldehyde reaction mechanisms were suggested in Figure 4.15.

In addition to the hexylthioaldehyde reaction pathways suggested in previous studies, several other water participating reactions were predicted in Figure 16. 2-hexanol and 3-hexanol are predicted to be formed by the reaction between the 2-hexyl radicals and 3-hexyl radicals with water participation, and 2-hexanone is predicted to be formed by the reaction between 2-hexanethiol and water through the intermediate compound, 2-hexylthioaldehyde. Indeed, 2-hexanol, 3-hexanol, 2-hexaneone, and 3-hexaneone are the compounds observed in the experimental results of this study, demonstrating that the above reactions proceed. In these reactions, water not only participates in the reaction removing sulfur from the various intermediates, but it also catalyzes several reactions with stabilized transition complex.

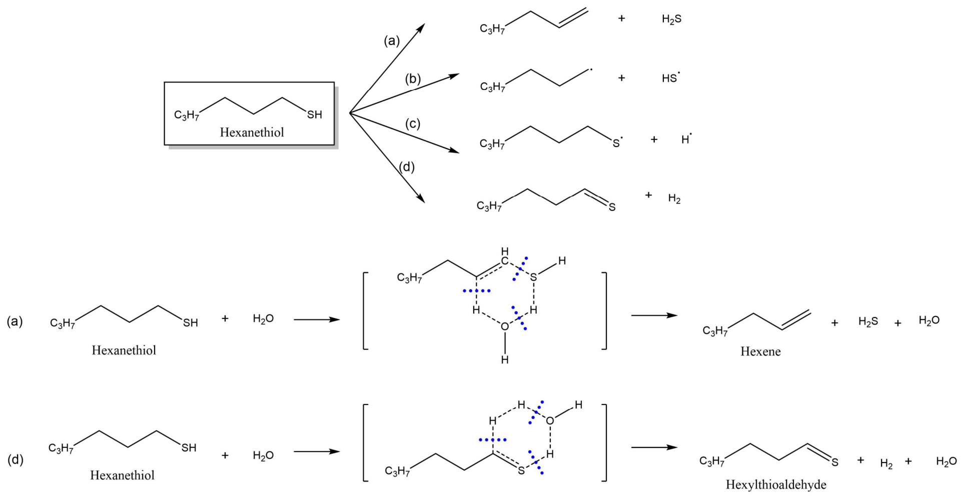


Figure 4.14. The SCW decomposition pathways of hexanethiol; (a) unimolecular decomposition reaction, (b) homolytic scissions reaction, (c) hydrogen abstraction, and (d) hydrogen production. The hexanethiol decomposition transition complexes with water molecules in the reaction pathway (a) and (d) were also suggested as water-catalyzed mechanisms.

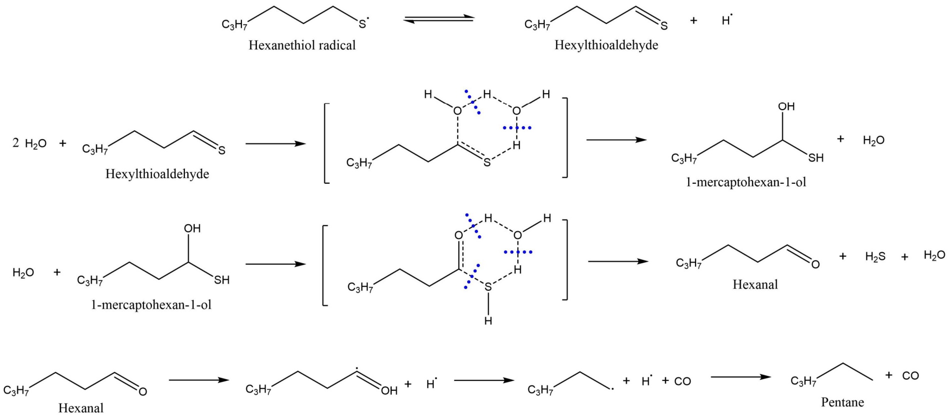


Figure 4.15. The reactions of hexylthioaldehyde with water molecules in the SCW decomposition of hexanethiol. Water directly participates in the reactions of hexylthioaldehyde, and also water forms a 6-ring transition complexes with water catalysis mechanism.

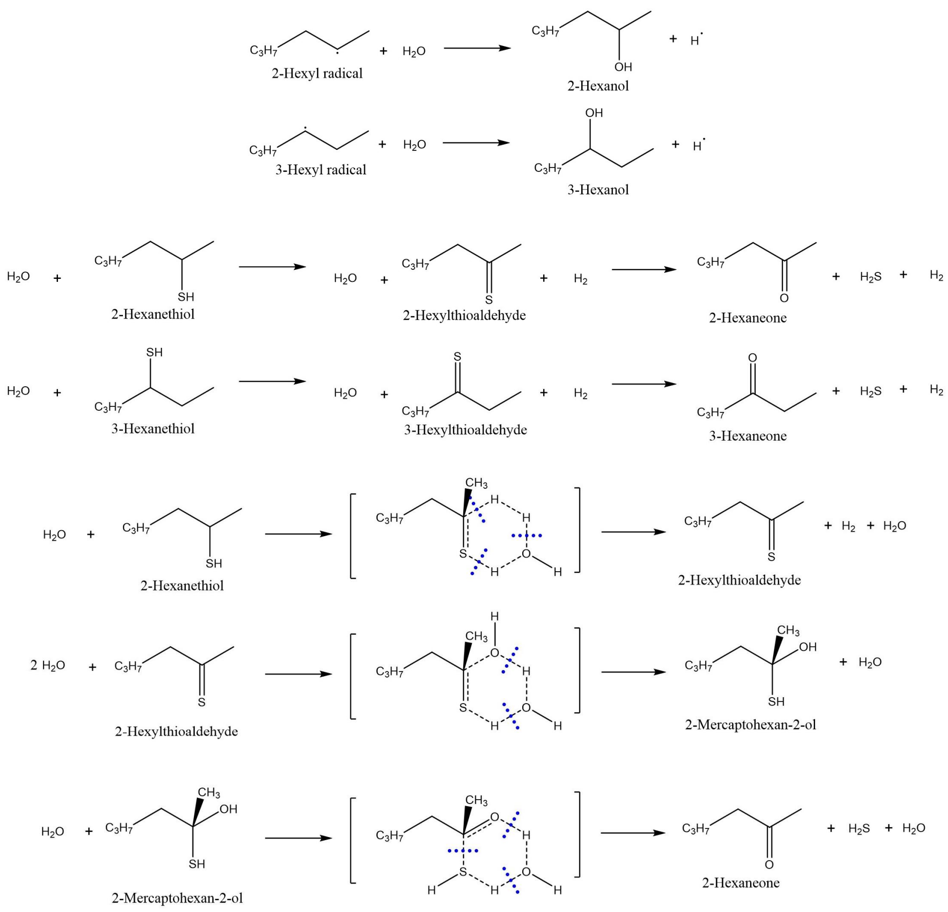


Figure 4.16. Other water participating reactions of the hexanethiol decomposition mechanism in SCW. Water not only participates in these reactions, but it also catalyzes several reactions with stabilized transition complex.

4.5.2. The SCW decomposition mechanism of hexyl sulfide

The decomposition of hexyl sulfide in SCW has been studied in detail in the previous papers [32-33]. They have commonly shown the decomposition of hexyl sulfide through thioaldehyde in SCW; when the hydrogen abstraction occurred in the methyl group connected to sulfur, hexyl sulfide gets β-scission to form thioaldehyde and hexyl radical, and hexylthioaldehyde reacts with a water molecule to form 1-mercaptohexan-1-ol and decompose into H_2S and hexanal *via* the water-catalyzed mechanism. Hexanal quickly decomposes into pentane and CO very fast. In addition to the thioaldehyde reaction pathways involving water, various reaction pathways involving water for the decomposition of hexanethiol in Figure 4.16. were also predicted to react in the hexyl sulfide decomposition in SCW as hexanethiol is the major intermediate product of hexyl sulfide.

As discussed above, water acts as a catalyst and reactants in the SCW decomposition of hexanethiol and hexyl sulfide. Water not only catalyze the thiol decomposition but also participates in the decomposition of various sulfur containing intermediates as a reactant and catalyst. As a results, water helps in removing sulfur in the hexyl sulfide and hexanethiol with donating hydrogen.

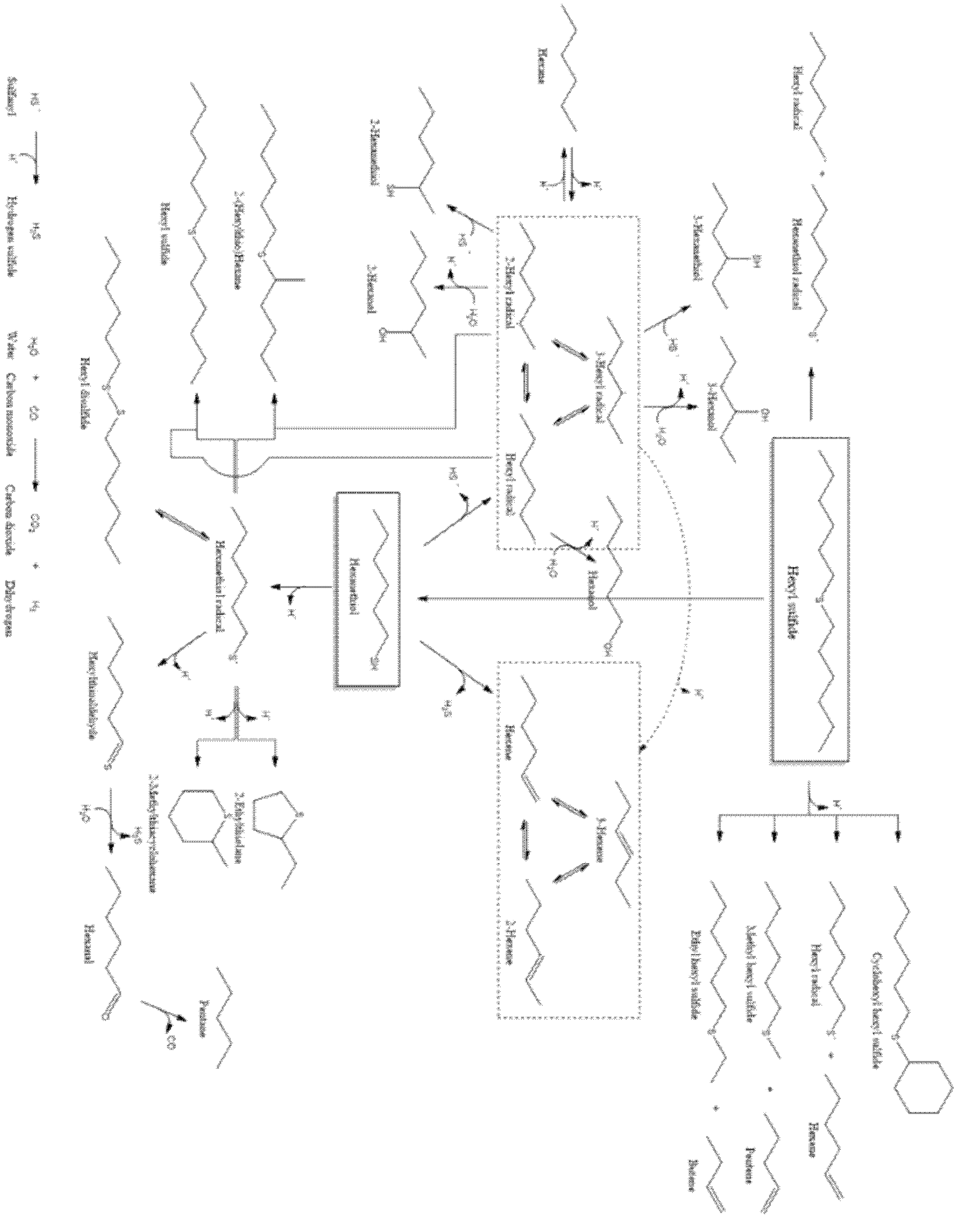


Figure 4.18. The SCW decomposition mechanism of hexyl sulfide.

5. Conclusions

Desulfurization mechanism of hexyl sulfide and hexanethiol in supercritical water were studied by combining experimental and computational methods. Hexyl sulfide and hexanethiol were decomposed at 400 °C by thermal decomposition and SCW decomposition, and the products were analyzed using gas chromatography. Based on the experimental results, thermal decomposition pathways were built using the automated Reaction Mechanism Generator (RMG), which constructs kinetic models using chemistry database. For the SCW decomposition, the quantum chemistry calculations with density functional theory using Gaussian 09 were performed as the reaction mechanisms in SCW decomposition were largely different from those in the reaction model through RMG.

In the experimental results, thermal decomposition and SCW decomposition showed considerable differences in the products composition. C6-hydrocarbons (hexane, hexene) were mainly detected as final products in the thermal decomposition of hexyl sulfide and hexanethiol, whereas C5-hydrocarbon (pentane) as well as C6-hydrocarbons (hexane, hexene) were detected in SCW decomposition. C5-hydrocarbon (pentane) was only detected in SCW decomposition. Also, in the thermal decomposition, a large amount of sulfurs remained in the product such as aromatic sulfur compounds including thiophenes and alkyl-thiacycloalkanes, but in the SCW decomposition, most of sulfurs were removed as low molecular compounds; thiophenes were not detected and alkyl-thiacycloalkanes were detected in a relatively small amount.

Based on these experimental results, the reaction pathways in thermal decomposition were investigated using Reaction Mechanism Generator software (RMG), which constructs kinetic models using chemistry database, and corrected through various works of literature and experimental results. The thermal decomposition of hexyl sulfide and hexanethiol is a hydrogen-deficient process with the formation of thiophene formation and the low ratio of hexane to hexene. The reactions pathways in SCW decomposition were investigated by the quantum chemistry calculations with density functional theory using Gaussian 09 to study the role of water in SCW decomposition. In SCW decomposition, water played the major roles: H-transfer catalyst in the unimolecular decomposition of hexanethiol, reactants in the decomposition of hexylthioaldehyde, and even catalyst in the decomposition of hexylthioaldehyde. These computational results support the experimental results that SCW decomposition effectively removes sulfur in hexyl sulfide and hexanethiol as low molecular sulfur compounds while thermal decomposition produces high molecular sulfur compounds such as thiophenes and alkyl-thiacycloalkanes with hydrogen deficient process

These results suggest that the removal of sulfur in SCW decomposition is more efficient than thermal decomposition in the decomposition of alkyl sulfides and alkyl thiol. In SCW, water can act as a H-transfer catalyst in the unimolecular decomposition of alkyl thiol to eliminate sulfur as a H_2S gas, and it also acts as reactants in the decomposition of alkyl thioaldehyde, the major intermediate compound of alkyl sulfide and alkyl thiol, to eliminate sulfur as a H_2S, CO, CO_2 gas by providing H source and O source as well as acts as catalyst. In contrast, aromatic sulfur compounds such as thiophenes are produced due to the hydrogen deficiency in thermal decomposition. These experimental and computational studies would present a reliable guide to the various mechanisms of organosulfur compounds in thermal decomposition and SCW decomposition with a deeper understanding of the role of water. It can give great help in the upgrading of heavy oil which contains a large amount of sulfur with the optimization of process design for the SCW upgrading.

Appendix. Input for Reaction Mechanism Generator (RMG)

1. RMG input for hexyl sulfide desulfurization using thermal decomposition

```
# Data sources
database(
    thermoLibraries = ['primaryThermoLibrary'],
    reactionLibraries = [],
    seedMechanisms = [],
    kineticsDepositories = 'default',
    kineticsFamilies = 'default',
    kineticsEstimator = 'rate rules',
)

# List of species
species(
    label='hexylsulfide',
    reactive=True,
    structure=adjacencyList(
                """
1   C u0 p0 c0 {2,S} {14,S} {15,S} {16,S}
2   C u0 p0 c0 {1,S} {3,S} {17,S} {18,S}
3   C u0 p0 c0 {2,S} {4,S} {19,S} {20,S}
4   C u0 p0 c0 {3,S} {5,S} {21,S} {22,S}
5   C u0 p0 c0 {4,S} {6,S} {23,S} {24,S}
6   C u0 p0 c0 {5,S} {7,S} {25,S} {26,S}
7   S u0 p2 c0 {6,S} {8,S}
8   C u0 p0 c0 {7,S} {9,S} {27,S} {28,S}
9   C u0 p0 c0 {8,S} {10,S} {29,S} {30,S}
10 C u0 p0 c0 {9,S} {11,S} {31,S} {32,S}
```

```
11 C u0 p0 c0 {10,S} {12,S} {33,S} {34,S}
12 C u0 p0 c0 {11,S} {13,S} {35,S} {36,S}
13 C u0 p0 c0 {12,S} {37,S} {38,S} {39,S}
14 H u0 p0 c0 {1,S}
15 H u0 p0 c0 {1,S}
16 H u0 p0 c0 {1,S}
17 H u0 p0 c0 {2,S}
18 H u0 p0 c0 {2,S}
19 H u0 p0 c0 {3,S}
20 H u0 p0 c0 {3,S}
21 H u0 p0 c0 {4,S}
22 H u0 p0 c0 {4,S}
23 H u0 p0 c0 {5,S}
24 H u0 p0 c0 {5,S}
25 H u0 p0 c0 {6,S}
26 H u0 p0 c0 {6,S}
27 H u0 p0 c0 {8,S}
28 H u0 p0 c0 {8,S}
29 H u0 p0 c0 {9,S}
30 H u0 p0 c0 {9,S}
31 H u0 p0 c0 {10,S}
32 H u0 p0 c0 {10,S}
33 H u0 p0 c0 {11,S}
34 H u0 p0 c0 {11,S}
35 H u0 p0 c0 {12,S}
36 H u0 p0 c0 {12,S}
37 H u0 p0 c0 {13,S}
38 H u0 p0 c0 {13,S}
39 H u0 p0 c0 {13,S}
                """),
)
simpleReactor(
    # specifies reaction temperature with units
    temperature=(673, 'K'),
```

```
    # specifies reaction pressure with units
    pressure=(60.0, 'bar'),
    # list initial mole fractions of compounds using the label from the 'species' label.
    # RMG will normalize if sum/=1
    initialMoleFractions={          "hexylsulfide": 1,
    },
    # the following two values specify when to determine the final output model
    # only one must be specified
    # the first condition to be satisfied will terminate the process
    terminationTime=(1800, 's'),
    # the next two optional values specify how RMG computes sensitivities of
    # rate coefficients with respect to species concentrations.
    # sensitivity contains a list of species' labels to conduct sensitivity analysis on.
    # sensitvityThreshold is the required sensitiviy to be recorded in the csv output file
    # sensitivity=['CH4'],
    # sensitivityThreshold=0.0001,
)
model(
    toleranceKeepInEdge=0.0,
    toleranceMoveToCore=0.1,
    toleranceInterruptSimulation=0.1,
    maximumEdgeSpecies=100000,
)

options(
    units='si',
    saveRestartPeriod=None,
    generateOutputHTML=True,
    generatePlots=True,
    saveEdgeSpecies=True,
    saveSimulationProfiles=True,
)
```

2. RMG input for hexanethiol desulfurization using thermal decomposition

```
# Data sources
database(
    thermoLibraries = ['primaryThermoLibrary'],
    reactionLibraries = [],
    seedMechanisms = [],
    kineticsDepositories = 'default',
    kineticsFamilies = 'default',
    kineticsEstimator = 'rate rules',
)

# List of species
species(
    label='hexanethiol',
    reactive=True,
    structure=adjacencyList(
            """
1   C u0 p0 c0 {2,S} {8,S} {9,S} {10,S}
2   C u0 p0 c0 {1,S} {3,S} {11,S} {12,S}
3   C u0 p0 c0 {2,S} {4,S} {13,S} {14,S}
4   C u0 p0 c0 {3,S} {5,S} {15,S} {16,S}
5   C u0 p0 c0 {4,S} {6,S} {17,S} {18,S}
6   C u0 p0 c0 {5,S} {7,S} {19,S} {20,S}
7   S u0 p2 c0 {6,S} {21,S}
8   H u0 p0 c0 {1,S}
9   H u0 p0 c0 {1,S}
10 H u0 p0 c0 {1,S}
11 H u0 p0 c0 {2,S}
12 H u0 p0 c0 {2,S}
13 H u0 p0 c0 {3,S}
14 H u0 p0 c0 {3,S}
```

```
15 H u0 p0 c0 {4,S}
16 H u0 p0 c0 {4,S}
17 H u0 p0 c0 {5,S}
18 H u0 p0 c0 {5,S}
19 H u0 p0 c0 {6,S}
20 H u0 p0 c0 {6,S}
21 H u0 p0 c0 {7,S}
                    """),
)
simpleReactor(
    # specifies reaction temperature with units
    temperature=(673, 'K'),
    # specifies reaction pressure with units
    pressure=(60.0, 'bar'),
    # list initial mole fractions of compounds using the label from the 'species' label.
    # RMG will normalize if sum/=1
    initialMoleFractions={          "hexylsulfide": 1,
    },
    # the following two values specify when to determine the final output model
    # only one must be specified
    # the first condition to be satisfied will terminate the process
    terminationTime=(1800, 's'),
    # the next two optional values specify how RMG computes sensitivities of
    # rate coefficients with respect to species concentrations.
    # sensitivity contains a list of species' labels to conduct sensitivity analysis on.
    # sensitvityThreshold is the required sensitiviy to be recorded in the csv output file
    # sensitivity=['CH4'],
    # sensitivityThreshold=0.0001,
)
model(
    toleranceKeepInEdge=0.0,
    toleranceMoveToCore=0.1,
    toleranceInterruptSimulation=0.1,
    maximumEdgeSpecies=100000,
```

```
)

options(
    units='si',
    saveRestartPeriod=None,
    generateOutputHTML=True,
    generatePlots=True,
    saveEdgeSpecies=True,
    saveSimulationProfiles=True,
```

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국문 초록

초임계수에서 헥실 설파이드와 헥산사이올의 탈황 반응 메커니즘

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오늘날 전세계적으로 에너지에 대한 수요가 지속적으로 증가하면서 석유 자원에 대한 수요 역시 증가하고 있으나 고갈되어가는 기존의 경질 원유만으로는 이러한 수요를 따라가기 어렵다. 이에 따라 매장량이 많을 뿐만 아니라 기술 개발로 인해 생산 비용이 크게 감소하여 가격 경쟁력을 가진 중질 원유가 대안으로 각광받고 있다. 하지만 중질 원유를 활용하는 것은 쉽지 않다. 중질 원유는 점도가 높고 밀도가 높으며 많은 양의 황(2~5 wt%)과 V, Ni, Fe, Na, Ca 등의 중금속이 함유되어 있다. 기존의 정유 공정에서 중질 원유를 전처리 없이 사용할 경우 관이나 파이프가 막히거나 부식될 뿐만 아니라 촉매 비활성화를 일으키고, 디솔터에서 물-오일의 유화액이 형성되는 등의 여러가지 심각한 문제를 야기할 수 있다. 또한 높은 황 함량으로 인해 연소 과정에서 다량의 이산화황을 생성할 수 있어서 산성비를 일으키고 토양 및 담수 체의 pH를 낮추는 등의 심각한 환경 영향을 줄 수 있다. 중질 원유를 활용하기 위해서는 황 및 중금속과 같은 불순물을 제거하는 중질 원유 개질 공정이 필수적이다.

초임계수(SCW, $T_c = 647.5$ k, $P_c = 22.05$ MPa)는 중질 원유를 개질하는 유망한 기술이다. 초임계수는 뛰어난 열 및 물질전달 특성을 가지고 있을 뿐만 아니라 높은 해리 상수(K_w)을 가지고 있어 H+를 고농도로 생성하고,

유전 상수가 낮아서 극성이 낮아 유기 화합물을 용해시킬 수 있다. 초임계수는 중질 원유 내의 탄화수소의 분해, 코크스 형성의 억제 및 황의 제거에 매우 효과적인 것으로 알려져 있다. 그러나 아직까지 초임계수에서의 탈황 메커니즘은 불분명하다.

이 연구에서는 열분해 및 초임계수 분해에서 헥실 설파이드와 헥산사이올의 탈황 메커니즘을 알아보았다. 헥실 설파이드와 헥산사이올을 400℃에서 0-30 분 동안 열분해와 초임계수 분해(24.7-25.6MPa)로 탈황 반응을 진행하고 가스 크로마토그래피를 이용하여 분석하였다. 또한 화학반응 데이터베이스를 기반으로 반응 경로를 예측하는 Automatic Reaction Mechanism Generator(RMG) 프로그램 및 밀도 함수 이론을 기반으로 하는 양자 화학 계산 프로그램인 Gaussian 09 프로그램을 이용하여 탈황 반응의 메커니즘을 연구하였다.

실험 결과, 열분해와 초임계수 분해는 생성물의 조성에서 상당한 차이가 있었다. 헥실 설파이드와 헥산사이올의 열분해에서 최종 생성물로 C6 탄화수소(헥산, 헥센)이 주로 검출되었으나, 초임계수 분해에서는 C6-탄화수소뿐만 아니라 C5-탄화수소인 펜탄이 최대 21.4wt%를 차지하는 주요 생성물로 검출되었다. 또한 헥실 설파이드와 헥산사이올의 열분해를 거쳐 사이오펜, 알킬 시아사이클로알칸을 비롯한 방향족 황 화합물 형태의 생성물이 5wt% 이상 검출된 반면에, 초임계수 분해 생성물에서는 1wt% 미만의 소량만이 검출되었다.

열분해에서의 반응 경로는 먼저 RMG를 통해 반응 모델을 세우고 다양한 문헌 및 실험 결과를 통해 보정하였다. 헥실 설파이드 및 헥산사이올의 열분해는 수소 결핍 공정(hydrogen deficient process)으로, 사이오펜이 형성될 뿐만 아니라 헥산 대 헥센의 낮은 비를 가지는 것을 알 수 있었다. 초임계수 분해에서 반응 경로는 Gaussian 09를 사용하여 밀도 함수 이론을 통해 알아보았다. 초임계수 분해에서 물은 수소 전달 촉매, 반응물, 및 촉매로 작용했다. 이는 초임계수 분해는 헥실 설파이드 및 헥산티올의 황을 저분자의 형태로 효과적으로 제거하였으나 열 분해는 수소 결핍 공정으로 인해 사이오펜 및 고리형 황 화합물 등을 생성하였던 실

험 결과를 잘 설명해줄 수 있었다.

이러한 결과는 일반적인 알킬 설파이드 및 알킬 사이올의 분해에서 초임계수 분해를 통한 황의 제거가 열분해보다 더 효율적임을 시사한다. 초임계수에서 물은 알킬 사이올의 수소 전달 촉매로서 작용하여 황을 황화수소 가스 형태로 제거할 뿐만 아니라 알킬 설파이드 및 알킬 티올의 주요 중간 화합물들을 분해하는 반응에서 반응물이자 촉매로 참여하여 수소 및 산소를 공급하여 황화수소, 일산화탄소 및 이산화탄소 등으로 황을 제거한다. 대조적으로, 열분해에서는 수소 결핍으로 인해 사이오펜과 같은 방향족 황 화합물은 생성된다.

이 연구는 황 화합물의 초임계수 분해 메커니즘 및 초임계수 분해에서 물의 역할에 대해서 알아보았으며, 앞으로 초임계수에서 다양한 탈황 반응 연구에 도움이 될 것을 기대한다. 또한 차후 다량의 황을 포함하는 중질유의 업그레이딩에 공정 개발에 큰 도움을 줄 수 있을 것이라 기대한다.