



Hydrous pyrolysis of organic sulfur compounds: Species and distribution of secondary derivatives

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ABSTRACT

The species and distributions of secondary compounds generated from eight organic sulfur compounds by way of hydrous pyrolysis were investigated. The results indicate that the formation of the secondary compounds and their structures and distribution depend on their thermal stability and the types of initial model compounds, as well as hydrous pyrolysis temperatures, while a large number and higher abundance of the secondary compounds appear to be formed mainly between 200 and 270 °C. Assignment of these secondary compounds indicates that alkyl thiols and sulfides are the most reactive compounds, producing a large number and relatively high amount of secondary organic thiols, sulfides, disulfides, sulfoxides and sulfones; while the secondary compounds generated from the thiophenic compounds are mainly low abundant methylated isomers of their own. Disulfidization, sulfidization and oxidation are the most significant mechanism(s) associated with the transformation of the initial thiols and sulfides model compounds. Alkyl thiophenes are only found to be formed from the alkyl thiol and sulfides, while it is noticed that thiophene, benzothiophene and dibenzothiophene are not genetically connected as they are not precursors of each other. Methylated thiophenic compounds are quantitatively insignificant but commonly present in the pyrolysates of thiophenes, benzothiophenes and dibenzothiophenes.

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1. Introduction

The reactivity of individual sulfur compounds under elevated pressure with added pure organic agents or pure clay minerals has been previously investigated by a number of authors using aquathermolysis approaches [1–4] and are well documented [5,6]. These experimental studies have provided some fundamental understanding of the aquathermal reactions of individual sulfur compounds and are helpful for studies of organic sulfur transformation in sediments. However, the geochemical implications of these aquathermal and thermolysis of organic sulfur compounds are limited. The reasons are: (i) the geochemical transformations of organic sulfur compounds are significantly different from reactions of pure compounds as they involve a complicated natural organic complex and (ii) most geochemical transformations are mild reactions that mainly cause cleavage of heter-atom bonds such as S–S and S–C bonds, while the temperature applied during aquathermolysis and thermolysis was >330 °C, causing the breakage of C–C bonds as well.

Closed system hydrous pyrolysis has been widely used in simulating sedimentary organic matter (OM) maturation and petroleum

hydrocarbon generation, as well as in studying the structures and geochemical evaluation of organic sulfur compounds in sulfur-rich sediments and kerogen [7–14]. Song et al. [15,16] carried out a series of closed system hydrous pyrolysis experiments on three Australia brown coals and a number of individual sulfur compounds, showing that organic sulfur compounds (OSCs) were eventually degraded to H₂S as temperature increased and that if the generated H₂S was not removed from the reaction system, it would continue to react with organic species to form a secondary sulfur structure or sulfur compounds. This suggests that previous thermal pyrolysis studies on sulfur or sulfur compound transformation did not distinguish the possible newly formed secondary sulfur compounds (or structures) generated from the reaction between the sulfur species in the H₂S/S⁰/H₂S_x system (mainly as H₂S) and organic radicals and the secondary derivatives derived from the initial sulfur compounds. This drawback may cause misinterpretation relating to the application of sulfur structures and compounds in sedimentary OM and fossil fuels.

In this study, we therefore aimed to investigate (i) the species and distribution of the secondary sulfur compounds that are direct derivatives of the initial sulfur compounds and (ii) the genetic connections among these commonly occurring sulfur compounds in sedimentary OM and fossil fuels. Accordingly, we carried out a series of specially designed hydrous pyrolysis experiments in which the newly formed H₂S was removed to give a metal sulfide, thereby

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ensuring that the secondary sulfur compounds were truly direct derivatives of the initial sulfur compounds.

2. Selection of model compounds and experimental procedures

A total of eight OSCs were selected as model compounds (Table 1). They comprise thiol (mercaptan), alkyl- and aryl-sulfide, thiophenes, and condensed thiophenic compounds (aromatic thiophenes). Some of them are commonly found in recent and ancient sedimentary OM and fossil fuels.

The hydrous pyrolysis experiments were designed to cope with the two major considerations of the study. First, they should have a natural organic matrix involved in order to simulate the geochemical reaction medium and to promote reactions that organic sulfur may participate in during the natural maturation of sedimentary OM. Secondly, they should be able to stimulate geochemical reactions in which the H₂S would be effectively removed and the possible reaction between it (or even elemental S) and organic radicals (to form newly formed secondary sulfur compounds) would be prevented. Hence, a virtually no or low sulfur brown coal was used, while a proportion of CdOAc₂ was used to remove possible H₂S and elemental S generated from the decomposition of sulfur compounds and therefore to eliminate the possible reactions between H₂S and organic radicals.



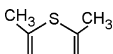

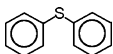
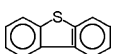
Detailed information about the brown coal chosen (Loy Yang, Australia) is provided by Song et al. [15]. In brief, it has a very low total S (<0.2%) and low ash content (<1.0%). Its use ensured that the sulfur involved in the hydrous pyrolysis reactions was overwhelmingly sourced from the model sulfur compounds.

Water was the liquid phase medium and is widely considered as playing an important role in the evolution of sedimentary OM. Although it is not fully understood or clearly defined both in the natural process and laboratory hydrous pyrolysis, its key role in hydrous pyrolysis as reactant to provide hydrogen and as catalyst to stimulate reactions in hydrous pyrolysis has been demonstrated by a number of studies [5,17,18 and references therein]. In this study, by using same amount of water in all experiments, we aimed to maintain approximately the same pressure in the experiments at the same temperature.

It is well documented that H₂S and elemental sulfur produced from the bacterial reduction of sulfate and from the diagenesis of sedimentary OM will preferentially react with a base metal (or metal ions) to form the corresponding metal sulfide [mainly iron sulfide (pyrite)] [19], whereas if the sediment is depleted in metal ions, the H₂S will react with OM to form OSCs [15,20–22]. So, by introducing a metal compound into the experiments, the H₂S or elemental S produced from the decomposition of OSCs would react with metal ions preferentially to form a metal sulfide, preventing reaction between the H₂S and OM to form secondary OSCs. The initial reason of choosing CdOAc₂ to remove H₂S was because of the distinguishing color of CdS, which is also easier to be converted to other metal sulfides for quantification. However, it must be borne in mind that the metal ions might accelerate the decomposition rate of some types of sulfur compounds in aqueous solution under subcritical temperature conditions [1,23]. There was also the controversial evidence to consider that chromium does not reduce or liberate either organic S or sulfate S [24]. Considering the possible direct or side effect that CdOAc₂ might have on the hydrous pyrolysis reaction of OSCs, it was added to the water and brown coal under all the temperature conditions used. The results [15] suggest that it has little impact on the composition of the pyrolysis products and there was no formation of sulfate. Further support for this assumption was obtained from comparison hydrous pyrolysis experiments with thiophene in the presence of the low sulfur brown coal both with and without CdOAc₂ at 200 °C. The thiophene was virtually unreacted and was fully recovered from both experiments, implying that the CdOAc₂ had little influence on the behavior of this OSC.

The detailed experimental procedure involved transferring an appropriate amount of model sulfur compound containing (ca. 20 mg of elemental S by wt), 0.5 g dried Loy Yang brown coal, CdOAc₂ (in slight excess of the amount required to convert 20 mg elemental S to CdS) and 0.5 ml water to a Pyrex glass tube with a total volume of ca. 2 ml. The contents were mixed well by stirring with a thin steel wire. A small goblet of glass wool was used to clear the steel wire and was packed into the top of the glass tube, with the top section of the tube also cleared to make flame sealing easier. The amount of water was barely enough to saturate the brown coal and there was never a situation whereby the brown coal floated on top of the water. After flame sealing, the tube was placed to a steel bomb (ca. 10 ml) with 2 ml water and 0.5 g of the brown coal; the

Table 1
Percentage of model compounds transformed to the secondary compounds and of unreacted initial compounds.

Sulfur compounds	Structures	Sulfur proportion (%) in secondary compounds and in unreacted initial compounds (in parentheses)			
		200 °C	230 °C	270 °C	330 °C
Nonyl mercaptan	CH ₃ (CH ₂) ₈ -SH	46.1 (tr.)	44.3 (tr.)	31.2 (0)	15.4 (0)
Dodecyl sulfide	CH ₃ (CH ₂) ₁₁ -S-(CH ₂) ₁₁ CH ₃	–	>34 (5.7)	>42.0 (5.1)	22 (4.0)
Thiophene		–	2.3 (88.0)	3.8 (63.0)	10.2 (13.5)
2-Methyl thiophene		1.9 (82.0)	1.6 (64.0)	3.2 (26.8)	9.6 (14.6)
2,5-Dimethylthiophene		16.6 (77.4)	5.9 (69.7)	8.5 (30.0)	9.9 (28.0)
Benzothiophene		–	–	1.9 (83)	<1.0 (80.0)
Phenyl sulfide		–	–	–	<5 (95.0)
Dibenzothiophene		–	–	–	0 (100)

Notes: (1) the numbers or tr. within parentheses indicates the percentages of unreacted initial compounds; (2) tr. for trace.

aim was to equalize the pressure between the inside and outside of the glass tube. The bomb was then cap sealed, placed flat in an oven and heated at the desired temperature of 200, 230, 270 and 330 °C for 66 h.

After heating, the bomb was cooled to room temperature and opened. The unbroken reaction glass tube was recovered and cooled in liquid N₂. When frozen, it was broken and thawed under dichloromethane (DCM). The whole contents were removed using a small volume of MeOH and DCM and filtered. It should be pointed out that the both inside and outside walls of the glass tubes were always clear and in mint condition, and there was never a sign of black carbon (or char) deposited on the inside wall of the tube. The products were extracted using a Soxhlet extractor for 66 h and a DCM/MeOH (1:9). During extraction, Cu turnings were added to remove any elemental S that might have been produced. The extracts were concentrated to a small volume and retained for further analysis.

The extracts were analyzed using a combination of gas chromatography (GC) and GC–mass spectrometry (MS) for quantifying the remaining initial model compounds and identifying newly formed secondary sulfur compounds. The GC instrument was operated in a split less mode using He as carrier gas, a (J&W) DB1 column (50 m × 0.33 mm i.d.) and an injector temperature of 250 °C. The oven temperature program was: 40 °C (4 min) and then heated at 4 °C per minute to 300 °C (held 30 min). GC–MS was performed with a Fisons GC8000 gas chromatograph interfaced to a Fisons MD800 mass spectrometer with a Masslab data acquisition system. The MS operating parameters were: ionization energy 70 eV, source temperature 200 °C, emission current 100 μA, scan rate m/z 35–600 Da in 2 s, with an interface temperature of 250 °C.

3. Secondary sulfur compound species and distribution

The sulfur species and their distributions are direct indication of the thermal reactivity and possible geochemical behavior of the individual model compounds. The sulfur species in the pyrolysates were classified as follows: (i) sulfur mainly as H₂S (in the H₂S/S⁰/H₂S_x system) trapped as CdS, (ii) sulfur incorporated into the coal matrix in the form of macromolecular organic sulfur, (iii) sulfur remaining in the unreacted initial compound, (iv) sulfur in newly formed secondary compounds, (v) sulfur in the gas phase and lost. Details of the measurement of these sulfur species have been described in our earlier studies [15,16]. Briefly, the first three sulfur species were determined by direct measurement using standard methods and GC analysis using an internal standard. The sulfur in the gas phase and lost was experimentally measured as being far less than 5%. Therefore, the sum of the sulfur in the secondary compounds and in the gases and lost were combined and calculated as the difference between the total sulfur in the initial compounds and the sum of first three species. Briefly, the proportion (%) of sulfur in the initial model compounds transformed to the secondary sulfur compounds and the proportion of sulfur in the residual initial compounds (percentages inside the brackets) at four temperatures are tabulated in Table 1.

The OSCs except the initial model compounds remaining in the pyrolysates are defined as the secondary sulfur compounds. Their tentative assignment was mainly from comparison of their mass spectra with those of the initial model compounds. The structures of the latter and the secondary compounds are displayed in Fig. 1, in which the numbers in the round brackets beneath the derivatives represent the major secondary compounds that coincide with the identity peak number marked on the representative mass chromatograms (Figs. 2 and 4), and proportions indicate the relative abundance of the initial sulfur compounds converted to the secondary compound, respectively. For each model compound, the sum of all individual secondary compounds would not

exceed the total proportion of initial compounds transformed to secondary compounds at the corresponding hydrous pyrolysis temperature as listed in Table 1. The proportions were determined from reference of peak areas from the secondary compounds to that of external standard.

The species and distribution of the secondary sulfur compounds generated via the hydrous pyrolysis of the model compounds are described in following three sections, respectively.

3.1. Aliphatic thiol and sulfide

This group includes nonyl mercaptan and didodecyl sulfide; they are the most reactive as the initial model compounds and were almost completely reacted at the lowest temperature of 200 to the highest of 330 °C, with a large quantity of the secondary sulfur compounds formed. The proportions of initial model compounds transformed to the secondary sulfur compounds were 15.4–46.1% (Table 1). A decreasing tendency in the proportion of secondary compounds with increasing temperature is largely due to the secondary compounds formed from the alkyl thiol and sulfides not being thermally stable and themselves being decomposed with the rising temperature.

Nonyl mercaptan is the most unstable as 46–31% of the initial compound was transformed to secondary compounds at 200–270 °C and ca. 15% at 330 °C, respectively. The composition of the secondary compounds was about the same at 200 to 270 °C but significantly reduced at 330 °C (Fig. 2). The major species at 200–270 °C were dinonyl disulfide, dinonyl sulfoxide, dinonyl sulfide, nonyl nonene disulfide and dinonyl sulfone, with dinonyl disulfide and dinonyl sulfoxide dominant. At 330 °C, the secondary disulfides disappeared and only dinonyl sulfide and dinonyl sulfoxide and dinonyl sulfone survived. Fig. 3 shows the assignment of 2-pentylthiophene and 2,5-diheptylthiophene in the pyrolysates at 150–270 °C and 200–270 °C, respectively. As displayed in Fig. 1, these newly formed secondary compounds are clearly direct derivatives of the initial model compound.

Didodecyl sulfide was significantly converted to secondary compounds at 230–330 °C, conversion being 32%, 42% and 22% at 230, 270 and 330 °C, respectively. The secondary compounds were 1-(methyl)-dodecane, dodecyl-dodecene disulfides, didodecyl disulfide and didodecyl sulfone (see Figs. 1 and 4). In addition, 2-octylthiophene and 2,5-didodecylthiophene were also present in trace amounts in the pyrolysates at 230–330 °C (Fig. 5). Obviously, 2,5-didodecylthiophene was via cyclization of dodecyl sulfide, while 2-octylthiophene was formed from cyclization of dodecylthiol formed from the cleavage of dodecyl sulfide.

The significant number and abundance of the secondary compounds formed from nonyl mercaptan and dodecyl sulfide suggest that alkyl thiols and sulfides are important precursors for a number of sulfur compounds in sedimentary OM, while the occurrence of alkyl thiophenes indicates that they are also precursors for simple thiophenic compounds.

The occurrence of alkyl thiophenes and oxidized sulfur compounds in the pyrolysates of thiols and sulfides seems to be different from the results from the thermolysis and aquathermolysis of aliphatic thiols by Siskin et al. [25] and Katritzky et al. [2,26]. For example, Katritzky et al. [26] reacted 1-decanethiol with water and cyclohexane at 250 °C for up to 13.5 days and the major secondary compounds were various isomeric dodecyl sulfides, disulfides and even trisulfides. When the temperature was increased to 300 °C, 33% of starting compound was converted to 1-, 2- and 3-decanethiols, while only a small amount of the initial compound was converted to 2-hexyl pentamethylene sulfide (1%) and dodecylsulfide (2%).

One of the important differences is the formation of thiophenes from the hydrous pyrolysis of nonyl mercaptan and didodecyl

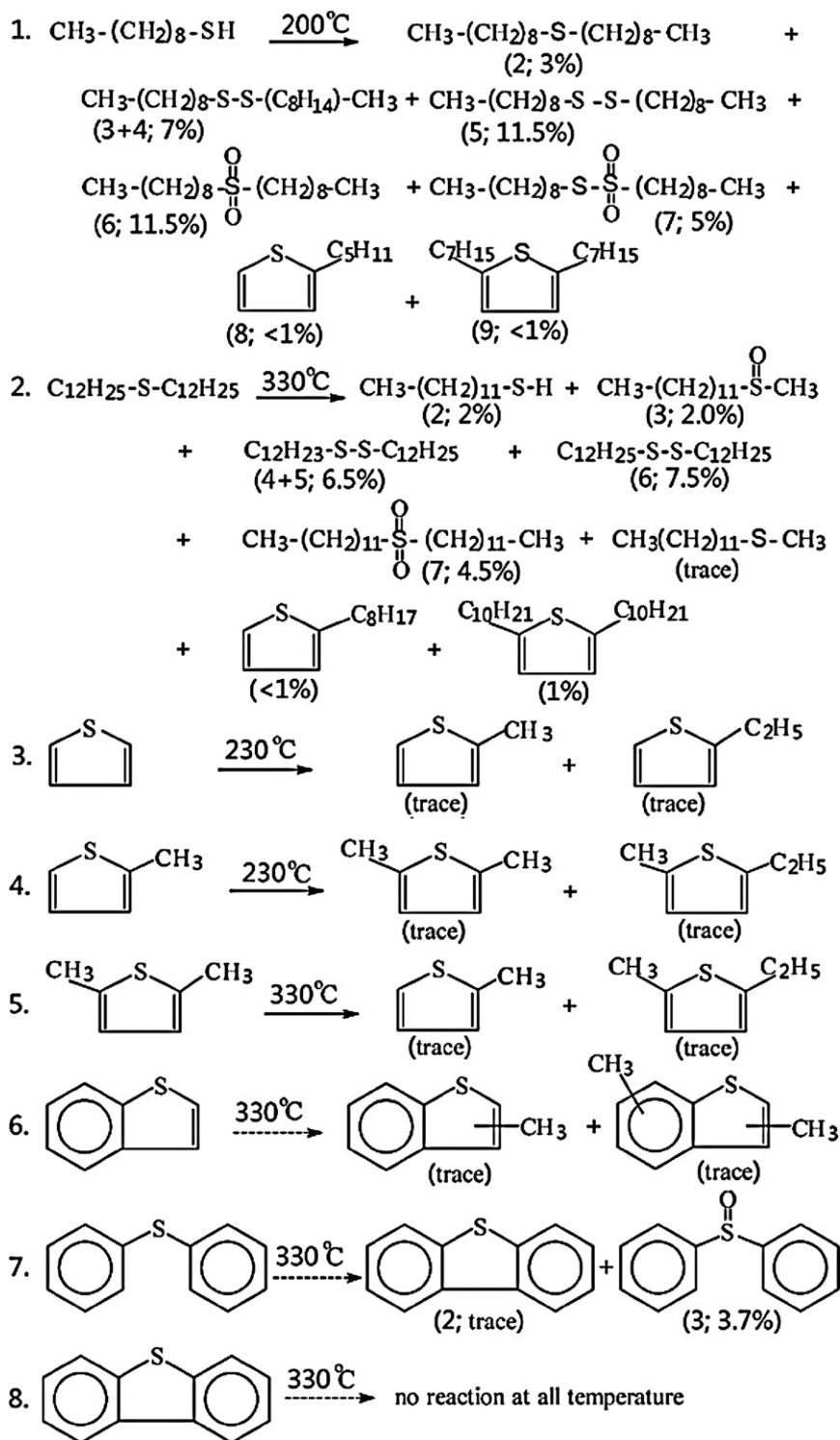


Fig. 1. The model compounds and their derivatives from hydrous pyrolysis (note: the names of derivatives are described in related figures and sections).

sulfide. It is well known that simple thiophenes occur widely in the relative low maturity sedimentary OM and crude oils. The formation of alkyl thiophenes has been suggested as occurring by way of reaction between alkenes or lipids and H_2S [27]. However, because H_2S was removed during the hydrous pyrolysis of the model compounds, the occurrence of thiophenes in the pyrolysates of nonyl mercaptan and dodecyl sulfide suggests that alkyl thiols and sulfides are also likely precursors for thiophene compounds via cyclization. Hence, the formation of thiophenes suggests that

the hydrous pyrolysis conditions employed here provide an additional route simulating the natural process in producing naturally occurring sulfur compounds.

The second difference is the formation of the oxidized sulfur compounds that were not reported among the products of aquathermolysis experiments. It is assumed that there was a lack of oxygen source under the aquathermolysis experiments, while the employment of high oxygen content brown coal in the hydrous pyrolysis of this study would promote a highly oxidic reaction

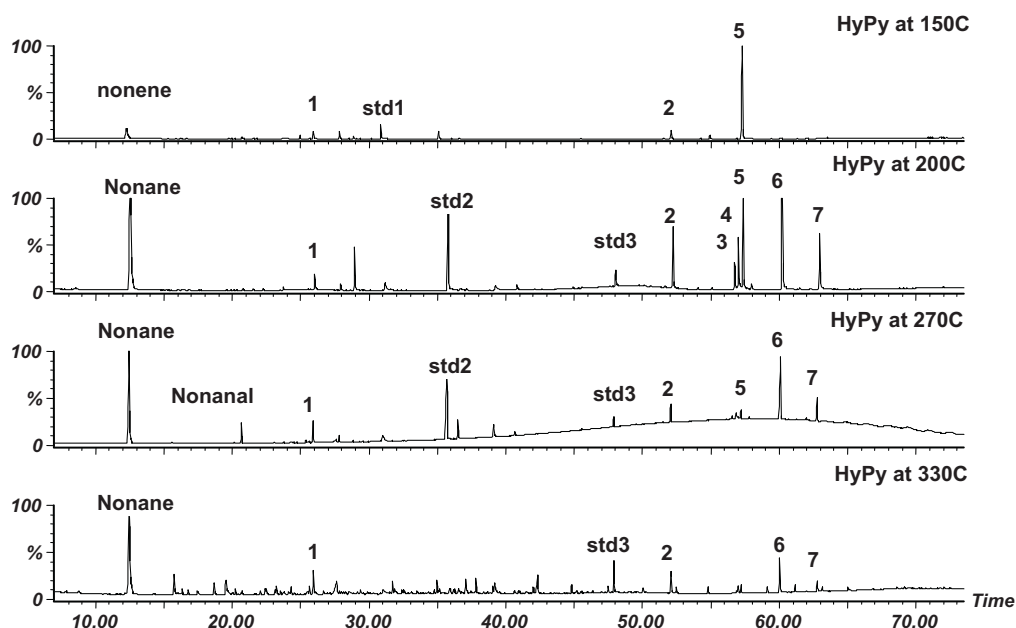


Fig. 2. Total ion chromatograms for identification of derivatives from nonyl mercaptan from hydrous pyrolysis at 150, 200, 270 and 330 °C (1: nonyl mercaptan; 2: dinonylsulfide; 3+4: nonyl nonene disulfide; 5: dinonyldisulfide; 6: dinonylsulfonyl; 7: nonyl-nonylsulfonyl sulfide).

condition and therefore lead to the formation of oxidized sulfur compounds via organic oxidation. A more detailed discussion can be seen in the later section of oxidation.

3.2. Simple thiophenes

The simple thiophenes include thiophene, 2-methylthiophene and 2,5-dimethylthiophene, which are virtually stable below 270 °C, but largely transformed at 330 °C, with a few secondary sulfur compounds formed in small amounts. The secondary

compounds displayed a general increase with temperature increase (Table 1). The maximum proportion of the secondary sulfur compounds formed was <10% of the initial model compounds used at 330 °C. The secondary compounds formed from these simple thiophenes were themselves simple, comprising trace levels of methyl and methyl- and ethyl thiophenes as shown in equations 4, 5 and 6 in Fig. 1.

Katritzky et al. [3] showed that simple thiophenes stay virtually intact under both thermolysis and aquathermolysis up to 350 °C, but reacted significantly with 10% aqueous H₃PO₄ at 350 °C,

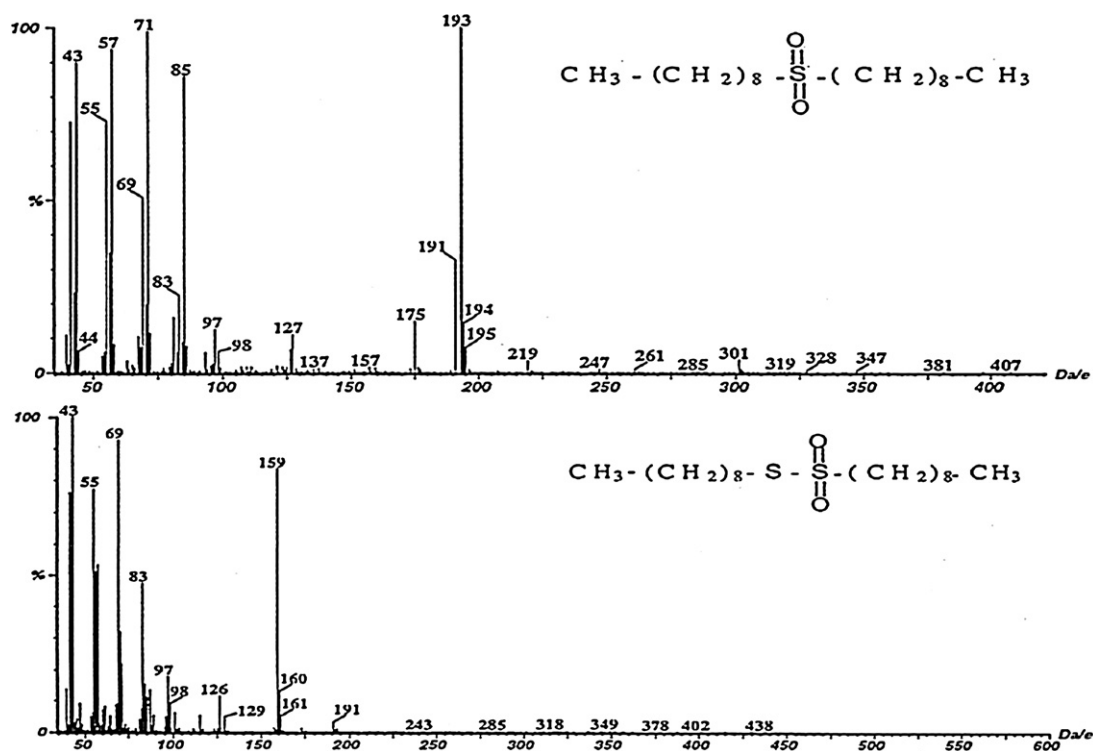


Fig. 3. Mass spectra of oxidized sulfur compounds formed from hydrous pyrolysis of nonyl mercaptan.

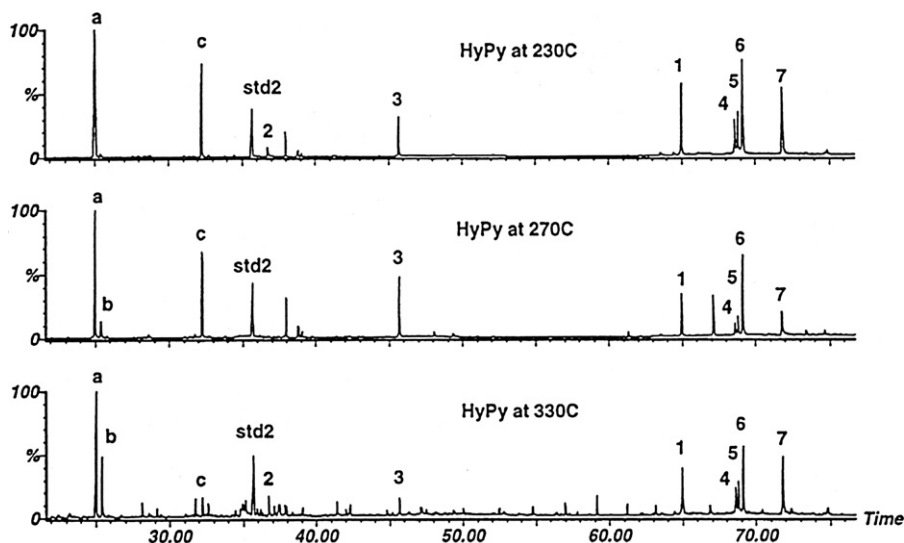


Fig. 4. Total ion chromatograms for identification of derivatives from didodecyl sulfide hydrous-pyrolysed at 230, 270 and 330 °C (a: dodecane; b: dodecene; c: dodecanal; 1: didodecyl sulfide (initial model compound); 2: dodecylthiol; 3: 1-(methylsulfinyl)-dodecane; 4 + 5: dodecyl dodecene disulfides; 6: didodecyl disulfide; 7: didodecylsulfonyl).

generating tetrahydrothiophene and other alkyl thiophenes as major secondary compounds, while 2-methylthiophene mainly produced dimethyl benzothiophenes, alkyl thiophenes and 2-methyltetrahydrothiophene as major secondary compounds. Clark et al. [1] also investigated the thiophene under the catalyzed aquathermolysis condition at 250 °C and found a slight extent of desulphurization and significant polymerization. Obviously, there are significant differences between the thermolysis and aquathermolysis experiments and the hydrous pyrolysis experiments in

this study in terms of the species of secondary sulfur compounds formed. The first difference is that the hydrogenation of thiophene seems to be a significant reaction under aquathermolysis conditions as 23% of the initial thiophene was converted to tetrahydrothiophene [3,6], while no hydrogenation of thiophenes occurred under hydrous pyrolysis conditions as no hydrogenated thiophenes were detected. The second difference is that hydrous pyrolysis of simple thiophenes does not result in the formation benzothiophenes and dibenzothiophenes. Furthermore, the secondary

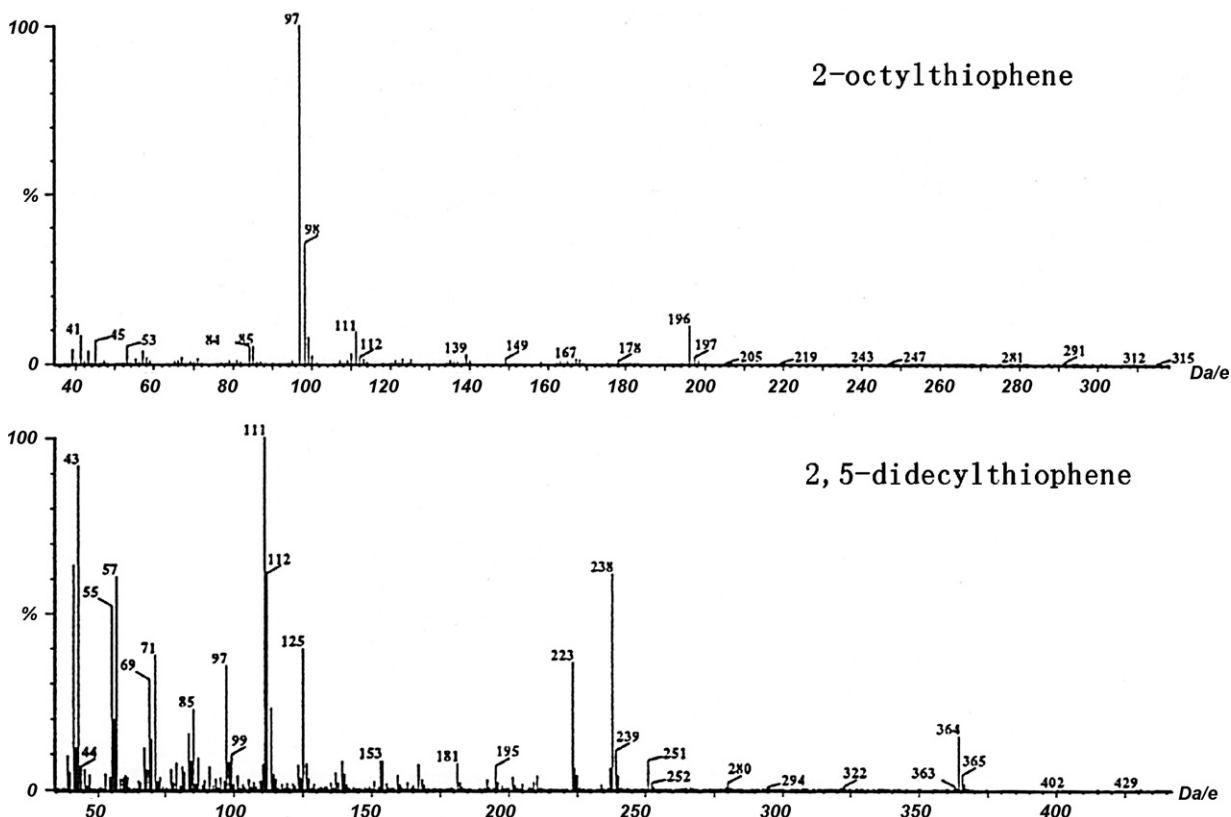


Fig. 5. Mass spectra of alkylthiophenes formed from the hydrous pyrolysis of didodecyl sulfide.

compounds from the hydrous pyrolysis of these simple thiophenes seems to be characterized by the formation of isomers of themselves.

The hydrous pyrolysis of these simple thiophenes does not yield condensed thiophenes indicates that condensed thiophenes could not be formed directly from the simple thiophenes and also suggests that there is no genetic connections between simple thiophenes and condensed thiophenes. This is contradictory to the results of the thermolysis and aquathermolysis which showed that the condensed thiophenes can be formed from thiophenes. However, because the H_2S had not being removed in the thermolysis and aquathermolysis experiments, it could not be excluded that these condensed thiophenes are newly formed through the reactions between sulfur species in the $H_2S/S^0/H_2S_x$ system and organic radicals. Actually, it had been demonstrated that thiophenes included condensed thiophenes could be simply formed by hydrous pyrolysis of non-sulfur brown coal with elemental S [28].

3.3. Aryl sulfide, benzothiophene and dibenzothiophene

This group of model compounds are virtually stable and only phenyl sulfide and benzothiophene showed very small proportion of transformation to secondary compounds at 270 °C and 330 °C, while dibenzothiophene is completely intact at 330 °C. The secondary compounds formed from benzothiophene are traces of methyl- and dimethyl-benzothiophenes and this is similar to that of simple thiophenes. It is worthwhile to point out that the hydrous pyrolysis of benzothiophene did not produce dibenzothiophene and suggests that benzothiophene is not a precursor for dibenzothiophene.

The slightly reacted phenyl sulfide only produced two trace level secondary compounds at 330 °C and they are dibenzothiophene and diphenylsulfoxide. The occurrence of the oxidized OSCs further suggests that sulfides are the major type of sulfur compounds that could be oxidized to produce oxidized OSCs when there is an oxic condition, while the formation of dibenzothiophene implies that aryl sulfides are kinds of precursors for dibenzothiophenes.

It is noticed that these condensed sulfur compounds are generally stable as they were completely intact at temperature of <400 °C under the aquathermolysis condition [4]. The slightly reaction of these condensed sulfur compounds under hydrous pyrolysis therefore suggests that the involvement of natural OM (brown coal) is capable of simulating the geochemical reactions in the sedimentary system, while the pure chemical reaction such as the aquathermolysis has limited application in the understanding of organic sulfur geochemistry.

4. The transformation of organic sulfur compounds

The secondary compounds formed from model compounds are summarized in Fig. 1. As seen in Fig. 1, these secondary compounds are structurally related with the basic structures of the model compounds. Considering the H_2S generated from sulfur compounds was removed by $CdOAc_2$, the reaction between H_2S and OM to form new compounds are effectively prevented [16], the secondary compounds therefore can be regarded as the derivatives of the model compounds.

4.1. Reactions or mechanism(s) for secondary compounds (derivatives) formation

According to the abundance of the derivatives, the following types of the derivatives appear to be formed either in significant amount or widely present in the pyrolysates of the model compounds. These are sulfides, disulfides, sulfoxide (R_1-SO-R_2) and sulfone ($R_1-SO_2-R_2$) compounds, and methylated thiophenic

compounds. Because the molecular structures of these derivatives are closely related the structures of initial model compounds, the reaction mechanism (s) for forming derivatives could be summarized as: (a) disulfidization, (b) sulfidization, (c) oxidation, and (d) methylation. These reaction mechanism(s) are mainly associated with the hydrous pyrolysis of thiol, sulfide and thiophenic compounds.

4.1.1. Disulfidization

As shown in Fig. 1, disulfides are the most significant derivatives among the secondary compounds formed from the hydrous pyrolysis of nonyl mercaptan and didodecyl sulfide. The disulfidization is actually an oxidation process that also occurs in micro-organisms [29]. The exact mechanism(s) for the formation of these disulfides are not clear yet. However, the molecular structures of newly formed disulfides suggest that disulfides are formed from two initial compound molecules or radicals jointed together through S–S bond as in the case of nonyl mercaptan. During hydrous pyrolysis, the model compounds broken to –SH or –S–CH₃ group and two similar sulfur containing group join together to form a disulfide through a –S–S– double bond. Fig. 1 also shows that these disulfides could survive a wide range of temperature from 200 to 330 °C and depends on the length of alkyl chain. So, the disulfidization appear to be an important mechanism(s) for the formation and preservation of sulfur compounds and organic sulfur during the sedimentary maturation process.

4.1.2. Sulfidization

Because sulfides are the second quantitatively important derivatives in the pyrolysates of nonyl mercaptan and dodecyl sulfide (referred to Fig. 1), sulfidization appear to be another important transformation of alkyl thiols and sulfides. Fig. 4 shows that dinonyl sulfide was formed and identified from the pyrolysates of nonyl mercaptan at temperature from 150 to 330 °C, while maximized at 200 °C. As the structures of newly formed sulfides would suggest, the sulfide compounds were likely being formed through the combination of one molecule ion of initial compound with one alkyl group via sulfur bond. On the other hand, secondary disulfides could be also converted to sulfide when –S–S– bond was cleaved to produce new radicals, for example mercaptan-like radicals, while the new radicals quickly react with other alkyl groups to form sulfides.

4.1.3. Oxidation

Significant amounts of sulfoxide and sulfones were identified in the pyrolysates of thiols and sulfides and may account for up to one third quantities of the initial model compounds. This suggests that oxidation of sulfur compounds is an important reaction mechanism for the transformation of sulfur compounds. The oxidized sulfur compounds occur over a wide range of temperatures from 200 to 330 °C. Obviously, the formation of oxidized sulfur compounds in large quantity and at broad temperature range suggests that oxidation of sulfur compounds is a important reaction mechanism(s) for the preservation and transformation of sulfidic compounds in sedimentary sulfur geochemical systems.

Because coals are mainly deposited under relative oxic environments and they are often in high content of oxygen, the oxidized compounds such as sulfoxides and sulfones are often seen in sulfur containing coals and their products [30,31]. The brown coal employed in the hydrous pyrolysis experiments of this study is in high oxygen content of 22.7% and therefore it is reasonable to assume that during the hydrous pyrolysis the highly oxidic oxygen atom released from the brown coal will oxidate S atom in sulfur compounds to sulfinyl and sulfonyl groups and lead to the formation of sulfoxides with a general formula of $R-S(=O)-R'$ and sulfones with a general formula of $R-S(=O)_2-R'$. The species of oxidized sulfur compounds occurred in the pyrolysates are also in

agreement with the results from the oxidation studies of high sulfur coal, which showed that only sulfidic structures were oxidized to sulfones and sulfoxides but the thiophenic components were inactive [32,33].

4.1.4. Methylation of thiophenic compounds

Methylated thiophenic compounds are the only secondary compounds formed from the hydrous pyrolysis of thiophene, 2-methylthiophene, 2,5-dimethylthiophene and benzothiophene. Although in lower or even trace abundance, these methylated compounds are identified in the pyrolysates over a wide range of temperature from 200 to 330 °C. Because methylated thiophenic compounds are widely existed in the sedimentary OM and crude oils, the methylation is a very important alteration for the thiophenic compounds.

4.2. The genetic linkages among thiophenes, benzothiophene and dibenzothiophene

Thiophenes, benzothiophenes and dibenzothiophenes are the three most common types of OSCs identified in sedimentary OM and crude oils. Therefore, the genetic linkages among these thiophenic compounds are important in understanding the evolution of OSCs. It was previously proposed that there is a genetic sequence for the formation of thiophene, benzothiophene and dibenzothiophene [34,35]. Obviously, the evidence in this study clearly suggests that there is no genetic linkages between these thiophenes, benzothiophene and dibenzothiophene, although these compounds may be formed in such an order during the diagenesis process of sedimentary organic matter evolution, which seems to suggest a genetic linkage proposed by other researchers [35]. In other words, thiophenes, benzothiophene and dibenzothiophene are not precursors for each others. Although, benzothiophene and dibenzothiophenes were identified from the aquathermolysis of thiophenes and benzothiophenes, the newly formed thiophenic compounds are generally in very low concentrations and it is not clear whether these thiophenic compounds are transformed from simple thiophenes or generated from the reaction between sulfur species in $H_2S/S^0/H_2S_x$ system and organic radicals.

Finally, although there are no genetic connections among these three thiophenic compounds, the formation of thiophenes, benzothiophenes and dibenzothiophenes are clearly related to the maturation stages of sedimentary OM.

5. Conclusions

According to the identification of the secondary compounds formed from eight OSCs by hydrous pyrolysis, following conclusions or significances could be useful for our better understanding of the mechanism(s) of sedimentary organic sulfur transformation and of OM evolution and petroleum hydrocarbon formation. First, the aliphatic and aryl sulfides and thiols are most likely the intermediate or precursor compounds for many types of OSCs found in sedimentary organic matter; while the formation of large number and quantity of the secondary derivatives from these OSCs also suggests that the large quantity and types of sedimentary sulfur compounds are mainly formed at lower maturation stage of equivalent to the hydrous pyrolysis temperature of below 270 °C. Secondly, high quantity of secondary disulfides, sulfides and oxidized sulfur compounds indicates that disulfidization, sulfidization and oxidation are three most important reactions associated with the hydrous pyrolysis of sulfides and thiols and may play important role in the preservation of sulfur compounds during geochemical maturation, in particular the oxidation reaction. Thirdly, methylated sulfur compounds are

quantitatively insignificant but geochemically important because these compounds are only observed among the thiophenic and benzothiophenic compounds and suggests that the methylation is also an important reaction mechanism(s) for the formation of secondary derivatives. Furthermore, Thiophenes, benzothiophenes and dibenzothiophenes are not genetic connected with each others as they are not precursors for each other.

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References

- [1] P.D. Clark, N.I. Dowling, J.B. Hyne, K.L. Lesage, The chemistry of organosulfur compound types occurring in heavy oils. 4. The high-temperature reaction of thiophene and tetrahydrothiophene with aqueous solutions of aluminium and first-row transition-metal cations, *Fuel* 66 (1987) 1353–1357.
- [2] A.R. Katritzky, R. Muruban, M. Balasubramania, J.V. Greenhill, M. Siskin, G. Brons, Aqueous high-temperature chemistry of carbo-and heterocycles. 16. Model sulfur compounds: a study of hydrous sulfide generation, *Energy Fuels* 5 (1991) 823–834.
- [3] A.R. Katritzky, M. Balasubramania, J.V. Greenhill, M. Siskin, G. Brons, Aqueous high-temperature chemistry of carbo-and heterocycles. 17. Thiophene, tetrahydrothiophene benzo[b]thiophene, and dibenzothiophene, *Energy Fuels* 6 (1992) 431–438.
- [4] O.M. Oguniola, N. Bertowitz, Removal of heterocyclic S and N from oil precursors by supercritical water, *Fuel* 74 (1995) 1485–1490.
- [5] M. Siskin, A.R. Katritzky, Reactivity of organic compounds in superheated water: general background, *Chem. Rev.* 101 (2001) 825–835.
- [6] A.R. Katritzky, D.A. Nichols, M. Siskin, R. Murugan, M. Balasubramania, Reaction in high temperature aqueous media, *Chem. Rev.* 101 (2001) 837–892.
- [7] M.D. Lewan, J.C. Winters, J.H. McDonald, Generation of oil-like pyrolyzates from organic-rich shales, *Science* 203 (1979) 897–899.
- [8] T.C. Hoering, Thermal reactions of kerogen with water heavy water and ore organic substances, *Org. Geochem.* 5 (1984) 267–278.
- [9] P.A. Comet, J. McEvoy, W. Giger, A.G. Douglas, Hydrous and anhydrous pyrolysis of DSDP Leg 75 kerogens—a comparative study using a biological marker approach, *Org. Geochem.* 9 (1986) 171–182.
- [10] J.W. Smith, D. Rigby, B. Luo, Z. Song, Y. Wang, The determination of the petroleum potential of terrestrial source rocks, *Org. Geochem.* 21 (1994) 287–301.
- [11] B.J. Huizinga, E. Tannenbaum, I.R. Kaplan, The role of minerals in the thermal alteration of organic matter. IV. Generation of n-alkanes acyclic isoprenoids, and alkenes in laboratory experiments, *Geochim. Cosmochim. Acta* 51 (1987) 1083–1097.
- [12] T.I. Eglinton, A.G. Douglas, Quantitative study of biomarker hydrocarbon releases from kerogen during hydrous pyrolysis, *Energy Fuels* 2 (1988) 81–88.
- [13] R.N. Leif, B.R.T. Simoneit, K.A. Kvenvolden, Hydrous pyrolysis of n-C₃₂H₆₆ in the presence and absence of inorganic components, in: American Chemical Society Division of Fuel Chemistry 204th Nat. Meet. Preprints, vol. 37, 1992, pp. 1748–1753.
- [14] M.P. Koopmans, F.C. Carson, J.S. Sinninghe Damsté, M.D. Lewan, Biomarker generation from Type II-S kerogens in claystone and limestone during hydrous and anhydrous pyrolysis, *Org. Geochem.* 29 (1998) 1395–1402.
- [15] Z. Song, B.D. Batts, J.W. Smith, Hydrous pyrolysis reactions of sulfur in three Australian Brown Coals, *Org. Geochem.* 29 (1998) 1469–1485.
- [16] Z. Song, M. Wang, B. Batts, X. Xiao, Hydrous pyrolysis transformation of organic sulfur compounds. 1. Their reactivities and chemical changes, *Org. Geochem.* 36 (2005) 1523–1532.
- [17] M.D. Lewan, Sulfur-radical control on petroleum formation rates, *Nature* 391 (1998) 164–166.
- [18] M.D. Lewan, S. Roy, Role of water in hydrocarbon generation from Type-I kerogen in Mahogany oil shale of the Green River Formation, *Org. Geochem.* 42 (2011) 31–41.
- [19] L.W. Orr, J.S. Sinninghe Damsté, Geochemistry of sulfur in petroleum systems, in: W.L. Orr, C.M. White (Eds.), *Geochemistry of Sulfur in Fossil Fuels*, ACS Symposium Series 429, 1990, pp. 2–29.
- [20] B.M. Goldhaber, I.R. Kaplan, in: E.D. Goldberg (Ed.), *The Sea*, Wiley, New York, 1974, pp. 569–655.
- [21] R.A. Berner, Sedimentary pyrite formation: an update, *Geochim. Cosmochim. Acta* 48 (1984) 605–615.
- [22] R.T. Kimblin, A.C. Johnson, Recent localised sulphate reduction and pyrite formation in a fissured Chalk aquifer, *Chem. Geol.* 100 (1992) 119–127.
- [23] J. De Roo, G.W. Hodgson, Geochemical origin of organic sulfur compounds: thiophene derivatives from ethylbenzene and sulfur, *Chem. Geol.* 22 (1978) 71–78.

- [24] D.E. Canfield, R. Raiswell, J.T. Westrich, C.M. Reaves, R.A. Berner, The use of chromium reduction in the analysis of reduced inorganic sulphur in sediments and shales, *Chem. Geol.* 54 (1986) 149–155.
- [25] M. Siskin, G. Brons, A.R. Katritzky, M. Balasubramanian, Aqueous organic chemistry. 1. Aquathermolysis: comparison with thermolysis in the reactivity of aliphatic compounds, *Energy Fuels* 4 (5) (1990) 475–482.
- [26] A.R. Katritzky, A.R. Lapucha, J.V. Greenhill, M. Siskin, Aqueous high-temperature chemistry of carbo- and heterocycles. 13. Sulphides and disulfides, *Energy Fuels* 4 (5) (1990) 562–570.
- [27] M.E.I. Kohnen, J.S. Sinninghe Damste, W.R.C. Rijpstra, J.W. de Leeuw, Alkyl thiophene as sensitive indicators of palaeoenvironmental changes, in: W.L. Orr, C.M. White (Eds.), *Geochemistry of Sulfur in Fossil Fuels*, ACS Symposium Series 429, published by American Chemical Society, Washington, DC, 1990, pp. 444–485.
- [28] Z. Song, *Hydrous Pyrolysis Reaction of Organic Sulfur in Model Compounds and in three Australian Brown Coals*, PhD thesis, Macquarie University, 1999.
- [29] J.W. Anderson, *Sulfur in Biology*, Edward Arnold Limited, London, 1978, 59 pp.
- [30] R.E. Winans, P.H. Neill, Multiple-heteroatom-containing sulfur compounds in a high sulfur coal, in: W.L. Orr, C.M. White (Eds.), *Geochemistry of Sulfur in Fossil Fuels*, ACS Symposium Series 429, 1990, pp. 249–260.
- [31] S.R. Palmer, E.J. Hippo, M.A. Kruger, J.C. Crelling, Characterization of organic sulfur compounds in coals and coal macerals, in: W.L. Orr, C.M. White (Eds.), *Geochemistry of Sulfur in Fossil Fuels*, ACS Symposium Series 429, 1990, pp. 296–315.
- [32] S.R. Kelemen, G.N. George, M.L. Gorbaty, Direct determination and quantification of sulphur forms in heavy petroleum and coals. 1. The X-ray photoelectron spectroscopy (XPS) approach, *Fuel* 69 (1990) 939–944.
- [33] M.L. Gorbaty, S.R. Kelemen, G.N. George, Characterization and chemistry of organically bound sulphur during coal conversion, in: 1991 International Conference on Coal Science Proceedings, The International Energy Agency Coal Research Ltd., Butterworth-Heinemann, Oxford, United Kingdom, 1991, pp. 961–964.
- [34] J.C. Schmid, J. Connan, P. Albrecht, Occurrence and geochemical significance of long-chain dialkylthiacyclopentanes, *Nature* 329 (1987) 54–56.
- [35] J.S. Sinninghe Damste, J.W. de Leeuw, Analysis, structure and geochemical significance of organically-bound sulfur in the geosphere: state of the art and future research. *Advances in Organic Geochemistry, Org. Geochem.* 16 (1989) 1077–1101.