Impacts of sonication and post-desulfurization on organic sulfur species by reductive pyrolysis
Peer-reviewed author version

Full Length Article

Impacts of sonication and post-desulfurization on organic sulfur species by reductive pyrolysis

Sh. Mesroghli[a]

J. Yperman[b, *]

jan.yperman@uhasselt.be

G. Reggers[b]

E. Jorjani[a]

R. Carleer[b]

[a]Department of Mining Engineering, Science and Research Branch, Islamic Azad University, Tehran, Iran

[b]Research Group of Applied and Analytical Chemistry, CMK, Hasselt University, Agoralaan – gebouw D, B-3590 Diepenbeek, Belgium

*Corresponding author.

Abstract

A comparative research on the effect of the ultrasound irradiation and peroxyacetic acid (PAA) desulfurization on sulfur forms in high sulfur coal samples (gathered from Tabas mine in Iran) was studied by reductive pyrolysis method. The total sulfur reduction after chemical desulfurization by PAA for sonicated samples is achieved in a range of 49–58%. Moreover, the studied sonicated-desulfurized samples showed that the pyritic and sulfate sulfur were mainly attacked by PAA. The maximum organic sulfur reduction was obtained for longer sonication treatment times (15 and 20 min) being around 42–44%. For the first time the role of advanced oxidation process (AOP) in the sonication treatment of coal samples has been considered. The profiles of m/z 48 (SO^+) and 64 ($SO_2{}^{-+}$) obtained by Atmospheric Pressure-Temperature Program Reduction on-line coupled with MS (AP-TPR/MS) experiments for sonicated and sonicated-desulfurized samples exhibited identical trends over the whole temperature range. This achievement demonstrated the presence of high amounts of oxidized sulfur functionalities as a function of sonication treatment and post-chemical PAA desulfurization. Furthermore, AP-TPR "off-line" coupled with TD-GC/MS showed quantitative changes in the refractory sulfur forms as a result of sonication settings before and after desulfurization.

1 Introduction

Sonication is a process in which sound waves are used to agitate particles in solution. Ultrasound is a cyclic sound pressure with a frequency greater than the upper limit of human level of hearing starting from the frequency of 20 kHz. Ultrasound behaves differently in liquid and liquid–solid media compared to gas medium [1].

Ultrasound in aqueous medium produces highly reactive species such as OH radicals, H_2O_2 and ozone that are also strong oxidizing agents. These radicals are capable of initiating and enhancing oxidation and reduction reactions. By using ultrasound in aqueous medium, an oxidation phenomenon called: "advanced oxidation process" (AOP), occurred. Sonication enhances mass transfer and chemical reactions and is expected to reduce or eliminate the use of chemicals, resulting in minimum disposal problems [1].

Several methods have been considered for removal of total sulfur and different forms of sulfur from coal prior to combustion. These approaches can be subdivided into physical and chemical methods. Many chemical desulfurization methods have been accomplished in recent years [2–22].

Some researchers have focused on ultrasonic coal desulfurization; existing literature fails to explain the mechanisms involved in the ultrasonic-assisted coal desulfurization and conclusions drawn by these researchers are very general in nature. The ultrasonic desulfurization methods studied are either aqueous or chemical based. The main advantage of ultrasonic method is the simultaneously removal of ash and sulfur.

Zaidi [23] investigated ultrasound-promoted desulfurization of low rank coals with diluted solutions of sodium hydroxide (0.025 to 0.2 M) at 30 and 70 °C. The range of sulfur removal was higher for samples sonicated at a lower temperature. However, the mechanism involved in the interaction between sonication and dilute sodium hydroxide is not explained. Ze et al. [24] investigated the enhancement of desulfurization and de-ashing of coal using sonication and then flotation. Zibo coal and a water mixture were sonicated for 10 min using 20 kHz frequency and 200 W power. Results revealed that ultrasonic conditioning can drive physical separation of pyrite and thus enhance the performance of coal flotation methods used for desulfurization.

The hydrogenation of cyclohexene, biphenyl and quinoline, as the hydro-desulfurization of benzothiophene in the presence of formic acid (a hydrogen precursor) and a Pd/C catalyst by ultrasound irradiation was studied and found to be effective at ambient temperature and pressure [25]. Several carbon-based sorbents assisted by ultrasound for desulfurization of a model jet fuel were used by Wang et al. [26]. The results showed that the selective adsorption ability of $PdCl_2$ was higher than those of Cu(I)Cl and metallic Pd. The oxidative process for sulfur removal from petroleum products feedstock has been investigated by Mello et al. [27]. Dibenzothiophene is used as a model sulfur compound. The effect of sonication time, volume of oxidizing reagents, kind of solvent for the extraction step and kind of organic acid as hydrogen precursor were investigated. Higher efficiency of sulfur removal was achieved using sonication in comparison to experiments performed without its application under the same reaction conditions.

Recently, a study combining microwave irradiation and sonication as a pre-treatment method to produce ultra clean coal in a leaching process using HF followed by HNO_3 shows that the sulfur content (1.89 wt%) of non-pretreated sample decreased down to 1.26 wt%, whereas this reduction for microwave-ultrasonic pretreated sample was more noticeable and decreased down to 0.8 wt% [28].

In the present research, the impact of pre-sonication at different times of irradiation on high sulfur Tabas coal sample followed by an optimized chemical desulfurization using peroxyacetic acid (PAA) has been studied. The main purpose is to define the differences in the effects of different sonication time settings on the organic sulfur forms and especially in the production of oxidized organic sulfur compounds. The same investigation is done for the desulfurized sonicated samples. To analyze the mentioned changes, an analytical method called "AP-TPR/MS" and "AP-TPR TD-GC/MS" is used.

2 Experimental

2.1 Coal sample characteristics

A 40 kg coal sample from active stopes in C_1 seam of Tabas coal mine with high sulfur content was collected. Sampling techniques similar to those of Jones riffles, conning and quartering methods were adapted and representative samples were prepared for further studies. High sulfur Tabas coal is subjected to a sonication process and to a post chemical treatment by PAA. The results of proximate and ultimate analysis have been illustrated for all sonicated and sonicated-desulfurized coal samples in the Tables 1 and 2 respectively.

Table 1 Proximate and ultimate analysis of initial and sonicated samples.

No.	Sample	Proximate analysis (%) (as received)				Ultimate analysis (%) (daf)				
		M	A	Vol.	FC[a]	C	H	N	S	O[a]
1	Initial	1.11	18.77	24.30	55.82	82.30	5.01	3.21	3.37	6.11
2	7510	1.09	19.23	24.27	55.41	83.15	5.11	2.37	3.30	6.07
3	7515	1.10	20.05	24.38	54.47	83.21	5.09	2.27	3.25	6.18
4	7520	1.08	20.23	24.47	54.22	83.26	5.14	2.11	3.29	6.20
5	7525	1.09	19.84	24.31	54.76	83.19	5.16	2.15	3.26	6.24

[a] By difference.

Table 2 Proximate and ultimate analysis of initial and desulfurized initial and desulfurized sonicated samples.

No.	Sample	Proximate analysis (%) (dry basis)			Ultimate analysis (%) (daf)			Calorific value (MJ kg^{-1})

		M	A	Vol.	FC[a]	C	H	N	S	O[a]	
1	Initial	1.11	18.77	24.30	55.82	82.30	5.01	3.21	3.37	6.11	34.64
2	Initial[DS]	1.10	17.40	24.16	57.34	84.35	3.71	2.37	1.95	7.62	33.19
3	7510[DS]	1.09	14.41	23.60	60.90	83.55	4.21	2.27	1.76	8.21	33.40
4	7515[DS]	1.09	13.20	23.36	62.35	83.41	4.49	2.17	1.59	8.34	32.21
5	7520[DS]	1.10	10.49	23.16	65.25	83.11	4.61	2.23	1.51	8.54	33.46
6	7525[DS]	1.09	10.22	23.32	65.37	83.19	4.64	2.14	1.45	8.58	33.52

[a] By difference. DS: Desulfurized

The ultrasound treated samples are labeled in the following way, for example: "7510" is related to the sample fraction size under 75 μm and sonicated for 10 min.

2.2 Sonication process

Ultrasound as a sonication pretreatment is used in desulfurization process. Ultrasonic is a series of vertical waves that are alternating unevenly. There are two effects of cavitations formed by ultrasound near the extended liquid-solid interfaces in the liquid-solid systems: micro jet impact and shock wave damage [29]. Each cavitated bubble reaches a temperature of nearly 5000 K and a pressure of more than 50 MPa [30]. The temperature at the interface between the water and the bubble can be as high as 2000 K. The rate of heating and cooling can be faster than 10^9 K/s. As a result, ultrasonic treatment can change the pulp nature [31].

In this study, a Q280 multifunction ultrasonic transmitter has been used for coal sample pretreatment. The frequency of its ultrasonic head was 43 kHz and the power of its ultrasonic transmitter was 225 W. Around 10 g of coal (less than 75 μm) was mixed with 150 ml of distilled water into a beaker. The prepared pulp with the beaker as its container was fixed and soaked into the water media in the ultrasound transmitter to start sonication process. The sonicated samples were filtered and subsequently dried in an oven at 100 ± 5 °C for 1 h. To evaluate the effects of irradiation time on sulfur functionalities, the coal samples were irradiated for 10, 15, 20 and 25 min. The dried sonicated samples were cooled in a desiccator, weighed and its sulfur forms were determined.

2.3 Chemical desulfurization

After sonication at different times, the samples were chemically desulfurized with PAA. The procedure involved dispersing 8 g of sonicated coal in 240 ml of glacial acetic acid and warming up to the desired temperature of 55 °C and then adding 80 ml of H_2O_2 solution (30% v/v) holding temperature at 55 °C [32]. The experiments were performed in a 500 ml Pyrex reactor isolated with glass wool equipped with a thermometric probe and stirrer. Based on a previous study [19], identical optimized parameters for desulfurization of Tabas coal by PAA were applied: desulfurization time of 90 min and temperature adjusted to 55 °C. After 90 min of reaction, the reactor was cooled down and the residual solution was filtered. The desulfurized coal was washed with hot distilled water and dried in an oven at 100 °C for 1 h and analyzed for sulfate, pyritic and total sulfur content. All chemical reagents were obtained from Merck manufacturer. The results of sulfur content before and after desulfurization are shown in Table 3. The measurements have been done at least twice for each sample.

Table 3 Comparison of the sulfur content before and after desulfurization of initial and sonicated samples.

No.	Sample	Sulfur content (db) (before desulfurization) %				Sulfur content (db) (after desulfurization) %				Coal yield %
		S_{Total}	S_{Pyrite}	$S_{Sulfate}$	$S_{Organic}$	S_{Total}	S_{Pyrite}	$S_{Sulfate}$	$S_{Organic}$	
1	Initial	3.17 ± 0.07	1.16 ± 0.07	0.15 ± 0.04	1.86 ± 0.09	1.88 ± 0.07	0.45 ± 0.07	–	1.43 ± 0.07	96
2	7510	3.14 ± 0.06	1.21 ± 0.07	0.10 ± 0.03	1.83 ± 0.07	1.60 ± 0.08	0.47 ± 0.07	–	1.13 ± 0.08	95
3	7515	3.12 ± 0.07	1.20 ± 0.09	0.10 ± 0.04	1.82 ± 0.08	1.47 ± 0.07	0.41 ± 0.07	–	1.06 ± 0.08	97
4	7520	3.15 ± 0.08	1.19 ± 0.07	0.18 ± 0.04	1.78 ± 0.08	1.35 ± 0.06	0.35 ± 0.08	–	1.00 ± 0.09	94
5	7525	3.13 ± 0.09	1.18 ± 0.07	0.16 ± 0.05	1.79 ± 0.07	1.31 ± 0.09	0.26 ± 0.09	–	1.05 ± 0.08	96

A broader study regarding the impact of different particle sizes on the total and organic sulfur reduction % in above mentioned conditions showed that by the reduction of particle size from 1000 µm to under 75 µm, the total and organic sulfur reduction (%) increased from 10 up to 43% and from 4 up to 26%, respectively for non-sonicated sample. For sonicated sample a further total and organic sulfur reduction is noticed from 12 up to 58% and from 7 up to 41%, respectively (Fig. 1).
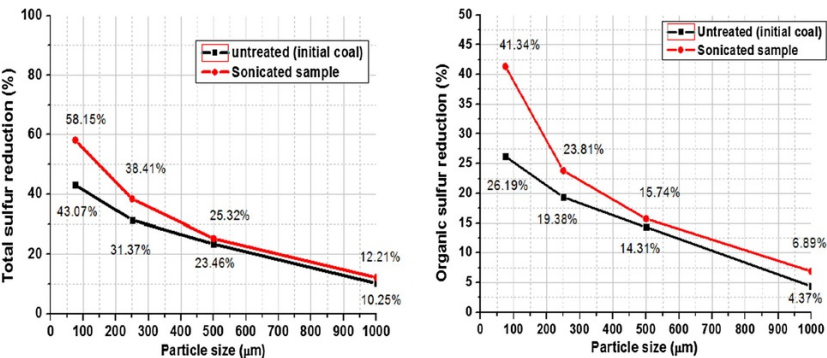

Fig. 1 Relationship between particle size and total and organic sulfur reduction by PAA.

2.4 Atmospheric Pressure-Temperature Programmed Reduction technique

2.4.1 AP-TPR "on-line" MS analysis

AP-TPR coupled "on-line" with mass spectrometry (AP-TPR/MS) under hydrogen gas flow is used to specify organic sulfur functionalities in initial, sonicated, desulfurized initial and desulfurized sonicated coals and to assess the sulfur forms changes as a result of different treatments. The analyses are performed in the AP-TPR set-up described previously [33]. Briefly, 40 mg of coal sample and 25 mg of fumed silica are placed in the reactor under a 100 ml min^{-1} flow of pure hydrogen. A linear temperature program of 5 °C min^{-1} from ambient temperature up to 1025 °C is applied. AP-TPR reactor is coupled "on-line" with a mass spectrometer (FISONS-VG Thermolab MS) equipped with a quadrupole analyzer set at an ionizing voltage of 70 eV. The MS signals of ions with m/z 10–250 are "on-line" monitored.

2.4.2 AP-TPR "off-line" TD-GC/MS analysis

The above mentioned system, can also be used in the adsorption/desorption mode in order to study volatile sulfur compounds other than produced H_2S, which were neither hydrogenated/reduced in the AP-TPR condition nor captured in the tar/char fraction. In previous studies, the volatiles were trapped by Tenax tubes [34–38] in order to improve qualitative and quantitative interpretation of volatile sulfur compounds released during pyrolysis experiment, Tenax tubes were replaced by tubes filled with a set of different sorbents: i.e. a set of metal adsorption tubes, with SilcoSteel coating, filled with Tenax/Carbpack B/Carbosieve SIII (Markes), were used and ice-cooled during the AP-TPR experiment. The volatile sulfur compounds are trapped in the temperature range from 25 °C (ambient temperature) up to 700 °C, in temperature intervals of 100 °C. H_2S is not adsorbed at all; neither in the Tenax tubes, nor in the SilcoSteel coated tubes. This makes these adsorbents optimal for all other volatile sulfur compounds to be maximal adsorbed (no problem of saturation, nor competition with a volatile sulfur compound present in high amounts). The adsorption tubes were then thermally desorbed systematically in a He atmosphere (Markes Unity) and analyzed by TD-GC/MS (Interscience DSQ quadrupole mass spectrometer).

3 Results and discussion

The different kinds of sulfur forms after chemical desulfurization are determined and the sulfur reduction results are shown in Table 4 with $\Delta S_i = S_{initial} - S_{DS}$ (i = total, pyrite or organic sulfur).

Table 4 Sulfur forms reduction of initial-desulfurised and sonicated-desulfurised samples, in % (dry basis) and effects on sulfur form amount content for sonicated desulfurized samples in %.

No	Sample	Sulfur reduction (%) (db)				$\Delta S/S_{initial}$ (%) (db)		
		S_{Total}	S_{Pyrite}	$S_{Organic}$	$S_{Sulfate}$	S_{Total}	S_{Pyrite}	$S_{Organic}$
1	Initial^{DS}	40.70	61.21	23.12	100	–	–	–

No.	Sample name							
2	7510^{DS}	49.04	61.16	38.25	100	20.49	0.08	65.44
3	7515^{DS}	52.88	65.83	41.76	100	29.93	7.55	80.62
4	7520^{DS}	57.14	70.59	43.82	100	40.39	15.32	89.53
5	7525^{DS}	58.15	77.97	41.34	100	42.87	27.38	78.81

DS:Desulfurized

Executing the ultrasound irradiation at a constant power (225 W) followed by a chemical desulfurization by PAA resulted in an overall total sulfur reduction, with a maximum for the 25 min sonication of about 58% (from 3.13% down to 1.31%). Pyritic sulfur reduction increased also and reached a maximum at 25 min of about 78% (from 1.18% down to 0.26%). For the organic sulfur a reduction increase is also found, but reached now a maximum at 20 min of about 44% (from 1.79% down to 1.05%). In global, for organic sulfur reduction not that much difference is found between the 15 and 25 min treatment and the one at 20 min. Economical speaking, considering energy cost aspects and taking additionally into account that $S_{Organic}$ is more difficult to remove than S_{Pyrite}, 20 min sonication time is more interesting and even more beneficial. It can be noticed from Table 4 that the pyrite reduction is less pronounced compared to the organic sulfur reduction for all pre-sonication times. On the other hand according to Table 4, there is no significant difference in total sulfur reduction between 20 and 25 min sonication. Twenty min sonication treatment can be proposed as an optimum, soft and simple approach for enhanced organic sulfur removal. Sulfate sulfur was completely removed after chemical desulfurization by PAA. As can be noticed in Table 2 the applied chemical desulfurization decreased the heating value of the samples by only 1 up to 2.40 MJ/kg, calculated according to the formula of Channiwala [39]. In view of practical application, this desulfurization approach is important, interesting and beneficial.

3.1 AP-TPR experiments coupled "on-line" with MS detection

The kinetograms of AP-TPR/MS of initial sample before and after desulfurization are visualized in Fig. 2A and B and detailed discussed in previous papers [40,41]. The peak in the lower temperature region can be assigned to the presence of di-alkyl sulfides, alkyl-aryl sulfides, more-reactive di-aryl sulfides and pyrite. The second peak refers to less-reactive di-aryl sulfides and simple thiophenic structures [42].
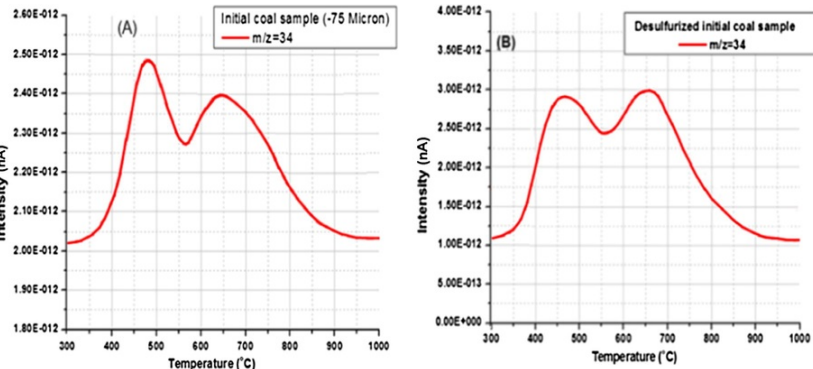

Fig. 2 AP-TPR/MS (H$_2$), $m/z = 34$ kinetograms of initial and desulfurized sample.

In order to compare different AP-TPR/MS experiments, profiles are normalized. The area under each dominant H$_2$S peak is determined by a deconvolution strategy of the H$_2$S profiles using multiple Gaussian functions (using Origin software (version 8)). Percent of peak area is calculated for each AP-TPR/MS experiment according to: (Area P$_i$/Area P$_{tot}$) × 100. The calculated areas and the relevant peak temperatures for initial and sonicated coal samples and for desulfurized initial and desulfurized sonicated coal samples are illustrated in Tables 5 and 6, respectively. The results are achieved based on at least two experiments.

Table 5 H$_2$S peak areas and relevant peak temperatures for initial and sonicated samples.

No.	Sample name	Peak area $m/z = 34$		Peak area normalization (%)		Peak temperature (°C)	
		Peak (I)	Peak (II)	Peak (I)	Peak (II)	Peak (I)	Peak (II)
1	Initial coal	3.15 ± 0.08e−11	5.71 ± 0.07e−11	35.6 ± 0.4	64.4 ± 0.5	475 ± 2	649 ± 2

| No.	Sample name	Peak area m/z = 34		Peak area normalization (%)		Peak temperature (°C)	
		Peak (I)	Peak (II)	Peak (I)	Peak (II)	Peak (I)	Peak (II)
2	7510	4.51 ± 0.06e−11	7.36 ± 0.07e−11	37.9 ± 0.5	62.1 ± 0.5	488 ± 8	659 ± 8
3	7515	5.49 ± 0.08e−11	7.61 ± 0.07e−11	41.9 ± 0.4	58.1 ± 0.4	486 ± 8	663 ± 8
4	7520	6.15 ± 0.05e−11	7.45 ± 0.07e−11	45.2 ± 0.5	54.8 ± 0.5	491 ± 8	661 ± 8
5	7525	5.98 ± 0.08e−11	7.92 ± 0.06e−11	43.0 ± 0.4	57.0 ± 0.5	492 ± 8	662 ± 8

Table 6 H_2S peak areas and relevant peak temperatures for desulfurized initial and desulfurized sonicated samples.

No.	Sample name	Peak area m/z = 34		Peak area normalization (%)		Peak temperature (°C)	
		Peak (I)	Peak (II)	Peak (I)	Peak (II)	Peak (I)	Peak (II)
1	Initial Coal[DS]	8.78 ± 0.07e−11	1.08 ± 0.08e−10	45.1 ± 0.4	54.9 ± 0.5	489 ± 7	650 ± 6
2	7510[DS]	7.15 ± 0.06e−11	9.48 ± 0.07e−11	42.9 ± 0.5	57.1 ± 0.5	488 ± 8	659 ± 8
3	7515[DS]	5.45 ± 0.08e−11	7.84 ± 0.07e−11	41.0 ± 0.5	59.0 ± 0.5	486 ± 8	663 ± 8
4	7520[DS]	6.23 ± 0.05e−11	1.06 ± 0.07e−10	37.0 ± 0.5	63.0 ± 0.5	491 ± 8	661 ± 8
5	7525[DS]	5.63 ± 0.08e−11	9.93 ± 0.06e−11	36.2 ± 0.5	63.8 ± 0.5	492 ± 8	662 ± 8

DS:Desulfurized

For initial and desulfurized initial coal sample the first and second peak appeared around 490 °C and 650 °C, respectively. For initial coal sample the area under the first peak is 36% and the area under the second peak is 64%. For the desulfurized initial coal the area under the first and second peak is 45% and 55%, respectively. According to Fig. 2A for the initial sample, the sharp first peak changed and became broader after chemical desulfurization by PAA (Fig. 2B). Not only because of an absolute decrease in its pyritic sulfur form amount (37% down to 24% of total sulfur [40]) (Tables 3 and 4), but also because of its higher pyrite sulfur %-removal compared to the organic sulfur %-removal. This results in higher organic sulfur forms presence (59% up to 76% of total sulfur) compared to pyritic sulfur, thus leading to a less sharp first H_2S signal [34].

Moreover, PAA not only removes sulfur compounds, but can also oxidize them into SO_n-functionalities as a result of a specific reaction mechanism that in its end state should result in a removable oxidized sulfur compound. However, if the end state is not reached, it is left in a sulfur form excluding the formation of H_2S during an AP-TPR/MS experiment or at least to a much lesser extend [43–45]. Therefore, these sulfur forms will be present in an oxidized state as organic sulfoxide, sulfone or sulfonic acid compounds [46]. During an AP-TPR/MS experiment this will lead rather to the formation of sulfur dioxides detectable by MS as vom/z 64 (SO_2^+) and 48 (SO^+). By the off-line setup, SO_2 as target for volatile oxidized sulfur compounds can also be captured by the absorbents in the SilcoSteel coated tubes together with other volatile sulfur compounds and (semi-) quantitatively determined. For the desulfurized initial sample (in the on-line detection system) m/z 48 and 64 profiles are visualized in Fig. 3.
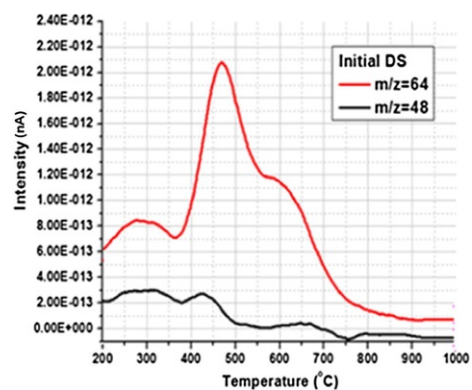
Fig. 3 AP-TPR-MS (H$_2$), $m/z = 48$ (SO$^+$) and $m/z = 64$ (SO$_2$$^+$) kinetograms of the desulfurized initial coal sample.

Only when m/z 48 and 64 exhibit the same profile absolute confirmation of formed SO$_n$-functionalities can be proved. Based on a similar study on the initial coal, it was clear that no specific peaks or profiles could be seen for these m/z 48 and 64 fragments. This means that no oxidized sulfur compounds were present. On the other hand for desulfurized initial sample by PAA (Fig. 3), a distinct signal for m/z 48 and 64 is noticed and also some weak partially similarities over the whole temperature region, indicating the presence of small amounts of SO$_n$-functionalities. The first weak peak around 300 °C for both m/z profiles refers to the presence of organic sulfonic acids [46]. For m/z 48, second peak around 425 °C, as well as the third peak around 650 °C, could to some extend be correlated with the m/z 64 s peak signal and its shoulder at higher temperature, respectively. Therefore, this could be attributed to the presence of minor amounts of organic sulfones and sulfoxides, respectively. It should be noted that both m/z 48 and 64 are not unique fragments referring only to SO$^+$ and SO$_2$$^+$ and therefore cannot be correlated with the presence of SO$_n$-functionalities alone.

For sonicated samples in the on-line detection also m/z 48 and 64 are visualized in Fig. 4.
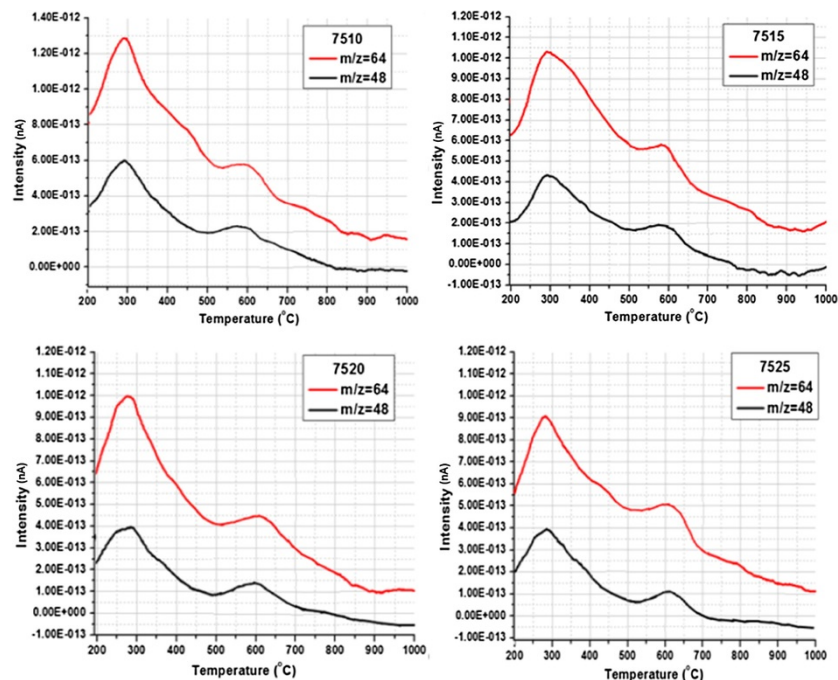
Fig. 4 AP-TPR-MS (H$_2$), $m/z = 48$ (SO$^+$) and $m/z = 64$ (SO$_2$$^+$) kinetograms of sonicated coal samples.

For all sonicated coal samples, m/z 48 and m/z 64 now exhibit clearly a similar profile. Two relevant peaks at around 300 °C and 600 °C for both m/z 48 and 64 are noticed. This means that the sonication process has a direct impact on the increased oxidation degree in terms of the formation of SO$_n$-functionalities as a function of the sonication time. A clear increase in the first peak of both m/z profiles is noticed referring to an enhancement of organic sulfonic acids [46] compared to Fig. 3 profiles. The mentioned process is related to the ultrasound behavior in the liquid and liquid-solid interfaces (AOP). As already mentioned, ultrasound in aqueous medium produces highly reactive species such as OH radicals, H$_2$O$_2$ and ozone that are strong oxidizing reagents with high oxidation potential. These oxidation agents are capable of initiating and enhancing oxidation reactions [47–57]. Using PAA, m/z 48 and m/z 64 profiles are even more pronounced and exhibit systematically simultaneously changes over the whole temperature range as demonstrated in Fig. 5 for the desulfurized sonicated samples (in the on-line detection mode).
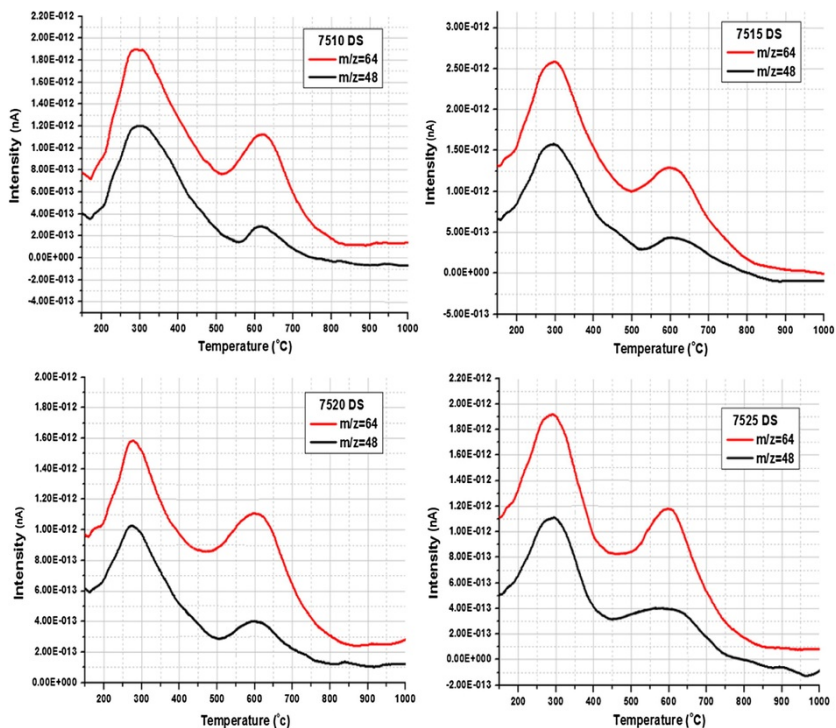
Fig. 5 AP-TPR-MS (H_2), $m/z = 48$ (SO^+) and $m/z = 64$ (SO_2^+) kinetograms of desulfurized sonicated coal samples.

Two dominant peaks in the m/z 64 profiles with more pronounced intensities (specifically the second peak around 600 °C) are found, compared to the corresponding profiles in Fig. 4. This could be related to the increased "catalytic" oxidizing impact on the coal samples in using PAA after sonication. Figs. 4 and 5 will be discussed in more details in chapter 3.3.

## 3.2 Effect of sonication time on sulfur removal by PAA

3.2.1 Qualitative approach

A comparison between the AP-TPR/MS profiles for the sonicated (Fig. 6) and desulfurized sonicated coal samples (Fig. 7) revealed that for the m/z 34 signal a reliable decrease in the intensity of the first peak compared to the second peak can be observed.
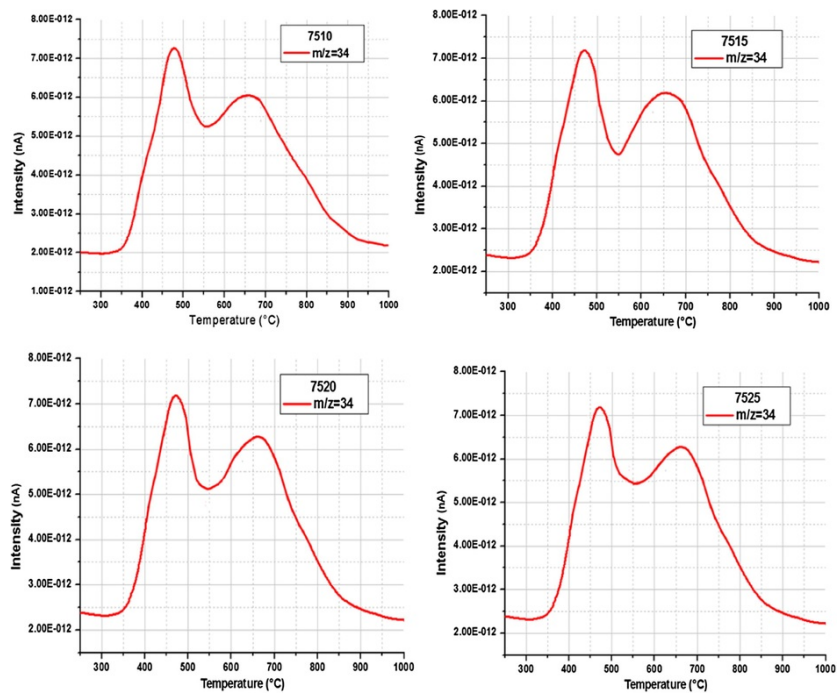
Fig. 6 AP-TPR/MS (H$_2$), m/z = 34 kinetograms of sonicated samples.
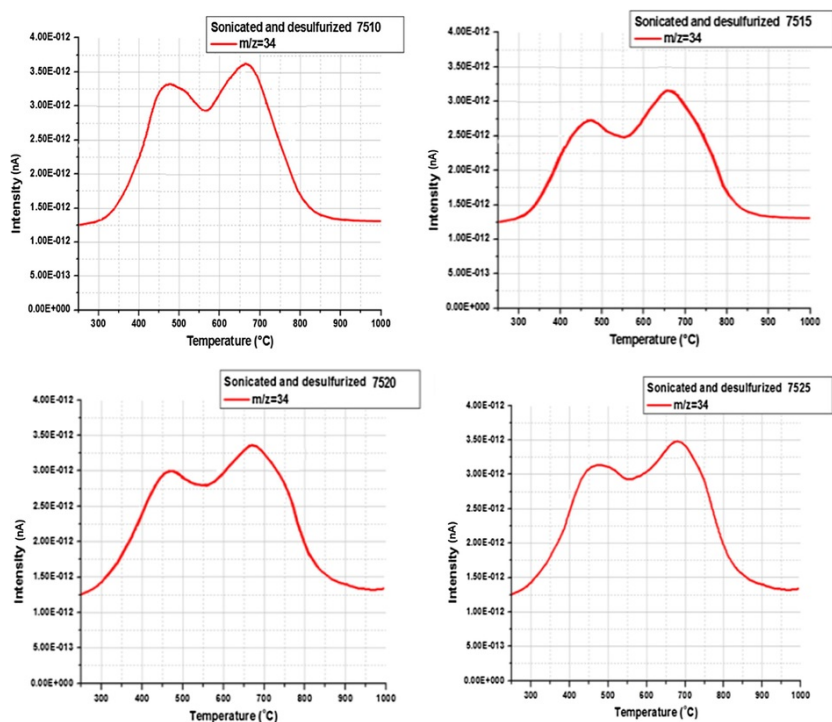
Fig. 7 AP-TPR/MS (H_2), $m/z = 34$ kinetograms of desulfurized sonicated samples.

From Fig. 6, for all applied time settings of sonication experiments, it can be deduced that for both peak temperatures no specific temperature shifting in the H_2S signal occurred. The normalized second H_2S peak area % decreased slightly to 55%–57% as a function of sonication time, compared to the peak % area of the initial coal sample, being 64% (Table 5). The first peak area % increased accordingly up to 45%–43% compared to the initial one, being 36%. According to the Table 6, the reversed is found for the desulfurized sonicated samples, as already suggested in Fig. 7. This means that the sonication process has a definite impact on the chemical post-desulfurization process by PAA.

Based on Tables 3 and 4, the total sulfur reduction is flattening for sonication times up to 20–25 min with a maximum reduction value of 57–58%. On the other hand, the organic sulfur reduction showed rather a maximum percentage around 44% at 20 min of sonication. From Table 5 it can be concluded that due to 20 min of sonication, somewhat more-reactive di-aryl sulfur compounds were formed (increase of the first peak percentage up to 45% and consequently decrease of second H_2S peak area % down to 55%). It is believed that the more-reactive di-aryl sulfur compounds are also more PAA sensitive and thus resulted in a higher sulfur removal degree. In accordance with Table 5, for 25 min of sonication, more less-reactive di-aryl sulfur compounds were formed and a consequently decrease of the first peak area % is noticed (43%). For this reason organic sulfur reduction % showed a decreasing tendency reaching only 41% at 25 min of sonication, but reaching almost 44% sulfur reduction at 20 min of sonication. Based on Table 5, with increasing the sonication time from 10 to 20 min, the less-reactive di-aryl sulfur compound showed decreasing amount tendency, coinciding with an increase of more-reactive di-aryl sulfur compounds, in contrast to initial coal. Consequently, the organic sulfur reduction % by PAA showed an increasing tendency as a function of sonication time (Table 4). According to Table 6 a systematic increase in the second H_2S peak area % is noticed, supporting the idea that PAA indeed removed the first H_2S peak sulfur compounds more easily and left less-reactive di-aryl sulfur compounds and thiophenic structures unchanged.

3.2.2 Quantitative approach

The amount of sulfur in the tar and the residual char in the reactor after the AP-TPR/MS experiment was determined as well. In this way, all sulfur forms which reacted with hydrogen during the AP-TPR/MS experiment forming H_2S can be quantitatively calculated and can thus be quantitatively related to the peak % area under the H_2S profiles. The amount of sulfur in tar and char (S_{T+C}) and sulfur which reacted with hydrogen (S_{AP-TPR}) are given in Table 7.

Table 7 Measured sulfur amount in desulfurized initial and desulfurized sonicated samples before and after AP-TPR/MS (H$_2$) measurements.

No.	Sample	S$_{total}$ (%)	S$_{(T+C)}$ (%)	S$_{AP-TPR}$ (%)	AP-TPR recovery (%)	Sulfur 1st peak (mg S/g)	Sulfur 2nd peak (mg S/g)
1	Initial DS (should be a superscript as in table 4)	1.88	0.66	1.22	65	5.50	6.70
2	7510 DS (should be a superscript as in table 4)	1.60	0.33	1.27	79	5.46	7.24
3	7515 DS (should be a superscript as in table 4)	1.47	0.22	1.25	85	5.13	7.38
4	7520 DS (should be a superscript as in table 4)	1.35	0.23	1.12	83	4.14	7.06
5	7525 DS (should be a superscript as in table 4)	1.31	0.21	1.10	84	3.96	7.04

DS:Desulfurized

Except for the non-sonicated sample (only 65%), the AP-TPR/MS recoveries are relatively high (between 79% and 84%). Probably, the sonication process makes the hydrogenation of sulfur compounds also more accessible as found in the case of the microwave treatment [58], resulting in a higher AP-TPR/MS H$_2$S recovery after PAA treatment. Looking in more detail to Table 7, for all desulfurized sonicated samples by PAA, the second H$_2$S peak amount is always more intense than the one for the desulfurized initial sample. Further on, the first H$_2$S peak amount showed a rather clear decreasing tendency as a function of sonication time from 5.46 down to 3.96 mg S/g$_{coal}$. This means that due to the sonicating process, the ability of PAA to remove different sulfur group is much higher towards the pure aliphatic, the mixed aliphatic-aryl and the more-reactive di-aryl sulfur compounds (which are identified by the first peak in the AP-TPR/MS H$_2$S profile). For the second peak, a rather constant sulfur amount is noticed, even slightly comparable with the initial coal sample. This explains a constant total presence of less-reactive di-aryl sulfur compounds and simple thiophenic structures. One can conclude that sonication and PAA treatment have no removal impact on the mentioned latter sulfur compounds.

3.3 Oxidized sulfur compound formation

3.3.1 Oxidized sulfur compound formation in sonicated samples

It is known that in AP-TPR/MS experiments, oxidized sulfur forms present in the sample are only partly reduced into H$_2$S [58,59]. As a result of thermal decomposition during pyrolysis, the oxidized sulfur species can form SO and SO$_2$. Depending on the temperature region in which they are released (if they exhibit the same m/z 48 and 64 evolution profiles), the sulfur distribution of oxidized sulfur forms in coal can be revealed. Based on Fig. 4, a huge peak at a lower temperature maximizes around 300 °C for m/z 48 and for m/z 64, which refers to the presence of organic sulfonic acids [46,58]. Its weak shoulder at the right side refers towards sulfones presence (aliphatic, mixed aliphatic-aryl and more-reactive di-aryl). At the higher temperature range (more than 500 °C), m/z 48 and 64 profiles keep demonstrating the same trend. At around 600 °C, a second peak is visible for all sonicated samples which can be assigned to both organic sulfones and to sulfoxides (rather less-reactive di-aryl ones). The above peak assignments, as for Figs. 6 and 7 are based on previous studies and on the typical CH-fragments profiles referring to aliphatic and aromatic compounds as given in Fig. S1 (see supplementary material).

It is obvious that m/z profiles of Figs. 4 and 5 give us ground to suppose that m/z 48 and 64 are referring to SO$^+$ and SO$_2^+$, but as its ratio is not constant, these m/z values also refer to other CH-fragments. Despites this, it makes sense to quantize both peaks. The normalized % peak areas have been calculated and are summarized in Tables 8 and 9.

Table 8 Normalized (%) peak areas and relevant peak temperatures of m/z 48 (SO$^+$) for sonicated samples.

No.	Sample name	Peak area		Peak area normalization (%)		Peak temperature (°C)	
		m/z = 48					
		Peak (I)	Peak (II)	Peak (I)	Peak (II)	Peak (I)	Peak (II)
1	7510	2.48 ± 0.07e−11	6.9 ± 0.07e−12	78.2 ± 0.5	21.8 ± 0.5	296 ± 7	603 ± 6
2	7515	1.70 ± 0.06e−11	5.7 ± 0.07e−12	74.9 ± 0.4	25.1 ± 0.5	297 ± 7	600 ± 6
3	7520	1.73 ± 0.08e−11	6.1 ± 0.07e−12	73.9 ± 0.6	26.1 ± 0.5	297 ± 7	602 ± 6

| 4 | 7525 | 1.64 ± 0.07e−11 | 7.0 ± 0.06e−12 | 70.1 ± 0.5 | 29.9 ± 0.6 | 298 ± 7 | 601 ± 6 |

Table 9 Normalized (%) peak areas and relevant peak temperatures of m/z 64 (SO_2^+) for sonicated samples.

No.	Sample name	Peak area		Peak area normalization (%)		Peak temperature (°C)	
		$m/z = 64$					
		Peak (I)	Peak (II)	Peak (I)	Peak (II)	Peak (I)	Peak (II)
1	7510	2.88 ± 0.07e−11	7.56 ± 0.08e−12	79.1 ± 0.5	20.9 ± 0.4	297 ± 7	601 ± 6
2	7515	2.36 ± 0.08e−11	7.32 ± 0.08e−12	76.1 ± 0.4	23.9 ± 0.4	298 ± 7	598 ± 6
3	7520	2.45 ± 0.06e−11	8.22 ± 0.07e−12	74.9 ± 0.6	25.1 ± 0.5	296 ± 7	601 ± 6
4	7525	2.31 ± 0.07e−11	8.36 ± 0.07e−12	73.3 ± 0.5	26.7 ± 0.4	297 ± 7	602 ± 6

We expected that changes in organic sulfonic acids, sulfone and sulfoxide groups occurred due to oxidation mechanisms during sonication process as a function of sonication time. Normalized first peak area % for both m/z 48 and 64 (Tables 8 and 9) decreases with increasing time of sonication, demonstrating a decreased presence of organic sulfonic acids (for m/z 48, from 78% down to 70%, for m/z 64, from 79% down to 73%). On the other hand, for the second peak, which is rather related to aliphatic, mixed aliphatic-aryl and di-aryl sulfones than to sulfoxides (for both sulfur oxide it is the representative fragment ion), an increasing tendency is found (for m/z 48, from 22% to 30%, for m/z 64, from 21% to 27%) (see further off-line experiments, Tables 12 and 13).

3.3.2 Oxidized sulfur compound formation in the desulfurized sonicated samples

The profiles of both m/z 48 (SO^+) and 64 (SO_2^+), for desulfurized initial and desulfurized sonicated coal samples, have been visualized in Figs. 3 and 5 respectively. A simple comparison between Figs. 3 and 5 shows that for desulfurized initial coal the second peak around 475 °C for m/z 64 and around 425 °C for m/z 48, which refers to aliphatic, mixed aliphatic-aryl and di-aryl sulfones, almost disappeared for all desulfurized sonicated samples and is only visible as a very weak shoulder on the first peak. Additionally a new peak appears in the higher temperature region around 600 °C. The above peak assignments, as for Figs. 3 and 5, are based on previous studies and on the typical CH-fragments profiles referring to aliphatic and aromatic compounds given in Fig. S2 (see supplementary material).

The huge first peak at around 300 °C (Fig. 5) refers to a further oxidation of the above mentioned sulfones into organic sulfonic acids [46]. As no aliphatic fragments were detected in this temperature range, the decomposition of the SO_n-functional group from CH-skeleton occurred only as SO_2.

An even complete removal of SO_n-functionalities combined with an additional oxidation of other organic sulfur compounds in its sulfoxide and sulfone form can occur.

Further on, the sonication process also seems to affect the amount of formed oxidized sulfur compounds by PAA treatment. Based on Fig. 5, the first and second peak in the lower (300 °C) and higher temperature region (600 °C) showed higher intensities compared to the profiles of only sonicated samples (Fig. 4). Therefore these profiles give us ground to suppose an enhanced oxidative impact of PAA. Both peaks have been quantified. Normalized % peak area for m/z 48 and 64 are given in Tables 10 and 11, respectively.

Table 10 Normalized (%) peak areas and relevant peak temperatures of m/z 48 (SO^+) for desulfurized sonicated samples.

No.	Sample name	Peak area		Peak area normalization (%)		Peak temperature (°C)	
		$m/z = 48$					
		Peak (I)	Peak (II)	Peak (I)	Peak (II)	Peak (I)	Peak (II)
1	7510[DS]	8.91 ± 0.07e−11	1.43 ± 0.07e−11	86.2 ± 0.5	13.8 ± 0.5	300 ± 8	612 ± 8
2	7515[DS]	8.62 ± 0.06e−11	1.91 ± 0.07e−11	81.9 ± 0.5	18.1 ± 0.5	299 ± 7	602 ± 9
3	7520[DS]	7.63 ± 0.08e−11	1.84 ± 0.07e−11	80.6 ± 0.6	19.4 ± 0.6	298 ± 8	602 ± 6

No.	Sample name						
4	7525DS	7.89 ± 0.07e−11	2.21 ± 0.06e−11	78.1 ± 0.5	21.9 ± 0.5	300 ± 7	602 ± 8

DS: desulfurized.

Table 11 Normalized (%) peak areas and relevant peak temperatures of m/z 64 (SO_2^+) for desulfurised sonicated samples.

No.	Sample name	Peak area		Peak area normalization (%)		Peak temperature (°C)	
				$m/z = 64$			
		Peak (I)	Peak (II)	Peak (I)	Peak (II)	Peak (I)	Peak (II)
1	7510DS	9.47 ± 0.07e−11	2.21 ± 0.08e−11	81.1 ± 0.5	18.9 ± 0.6	298 ± 7	610 ± 9
2	7515DS	1.11 ± 0.08e−10	4.25 ± 0.08e−11	72.1 ± 0.5	27.9 ± 0.5	300 ± 6	601 ± 8
3	7520DS	1.02 ± 0.06e−10	4.34 ± 0.07e−11	70.2 ± 0.6	29.8 ± 0.5	295 ± 8	603 ± 8
4	7525DS	1.21 ± 0.07e−10	5.55 ± 0.07e−11	68.4 ± 0.6	31.6 ± 0.5	299 ± 7	601 ± 7

DS: desulfurized.

Based on these tables, the first peak area % (referring to organic ~~sulphonic~~ sulfonic acids) for both m/z 48 and 64 showed a decreasing trend by increasing sonication time (for m/z 48, from 86% to 78%, for m/z 64, from 81% to 68%). For the second % peak area (referring to sulfones and to some extend to sulfoxides) for both m/z 48 and 64 an increasing tendency could be noticed (for m/z 48, from 14% to 22%, for m/z 64, from 19% to 32%)- (see further discussion in off-line experiments, Tables 12 and 13).

Table 12 Organic sulfur compounds determined by AP-TPR/GC−MS in initial and sonicated samples <u>before</u> desulfurization, in μg S/g.

Sulfur compounds	Samples		
	Initial	7510	7525
SO_2	–	7.4 ± 0.08	5.6 ± 0.08
Dimethyl sulfone	–	1.2 ± 0.07	4.3 ± 0.08
Dimethyl sulfoxide	–	0.2 ± 0.06	0.6 ± 0.09
Thiophene (Th)	1.5 ± 0.08	1.7 ± 0.07	1.4 ± 0.08
Methyl thiophene (Me-Th)	4.3 ± 0.07	4.7 ± 0.07	4.3 ± 0.08
Dimethyl thiophene (Di-Me-Th)	7.5 ± 0.08	7.7 ± 0.08	7.4 ± 0.09
Benzothiophene (Be-Th)	4.4 ± 0.08	4.6 ± 0.07	4.2 ± 0.08
Methyl Benzothiophene (Me-Be-Th)	1.8 ± 0.07	1.7 ± 0.06	1.9 ± 0.07
Dimethyl Benzothiophene (Di-Me-Be-Th)	1.2 ± 0.08	1.1 ± 0.07	1.4 ± 0.07
Dibenzothiophene (Di-Be-Th)	3.3 ± 0.07	3.4 ± 0.08	3.6 ± 0.08

Table 13 Organic sulfur compounds determined by AP-TPR/GC−MS in initial and sonicated samples <u>after</u> desulfurization, in μg S/g.

Sulfur compounds	Samples

	Initial[DS]	7510[DS]	7525[DS]
SO$_2$	3.2 ± 0.08	13.5 ± 0.09	8.8 ± 0.08
Dimethyl sulfone	1.2 ± 0.08	3.4 ± 0.08	10.4 ± 0.08
Dimethyl sulfoxide	–	0.3 ± 0.07	1.1 ± 0.07
Thiophene (Th)	1.0 ± 0.07	2.2 ± 0.07	2.5 ± 0.08
Methyl thiophene (Me-Th)	2.7 ± 0.08	2.1 ± 0.07	3.2 ± 0.08
Dimethyl thiophene (Di-Me-Th)	6.8 ± 0.09	5.8 ± 0.08	6.1 ± 0.09
Benzothiophene (Be-Th)	3.2 ± 0.09	3.1 ± 0.09	3.9 ± 0.08
Methyl Benzothiophene (Me-Be-Th)	1.7 ± 0.08	1.7 ± 0.08	2.1 ± 0.09
Dimethyl Benzothiophene (Di-Me-Be-Th)	1.2 ± 0.06	1.0 ± 0.07	0.9 ± 0.09
Dibenzothiophene (Di-Be-Th)	3.2 ± 0.07	3.1 ± 0.08	3.1 ± 0.09

DS: desulfurized.

3.3.3 AP-TPR "off-line" TD-GC/MS experiments

AP-TPR experiments "off-line" coupled with TD-GC/MS are also applied to get information of volatile sulfur containing organic compounds, neither reduced in AP-TPR experimental conditions (into H$_2$S) nor captured into its char/tar fractions. These volatile organic sulfur compounds released during pyrolysis are quantitatively determined by AP-TPR "off-line" experiments in hydrogen atmosphere applying single ion monitoring (SIM):

- m/z = 87 + 14n, where n is the number of alkyl groups for thiophenes (Th): Th, methyl-Th and di-methyl-Th.

- m/z = 134 + 14n, for the benzothiophenes (BeTh): BeTh, methyl-BeTh and dimethyl- BeTh.

TD-GC/MS profiles are quantitatively interpreted by spiking with 0.5 µg d$_6$-benzene. The "off-line" experiments have only been performed in both extreme times of sonication: 10 and 25 min. The higher homologues, like three/tetra/penta substituted thiophenes and three substituted benzothiophenes were not detected in the studied temperature intervals (from ambient temperature up to 700 °C with 100 °C intervals). Based on TD-GC/MS quantifications, the total content of sulfur compounds under consideration is expressed in µg S/g coal: Tables 12 and 13.

Besides SO$_2$, also alkyl substituted sulfones and sulfoxides are recorded, demonstrating the presence of SO$_n$-functionalities (see further Tables 16–18). Therefore the amount of SO$_2$, dimethyl sulfone and dimethyl sulfoxide products recorded by "off-line" experiments in different temperature intervals have also been expressed in µg S/g coal per temperature interval in Table 14.

Table 14 Amount of SO$_2$, dimethyl-sulfone and dimethyl sulfoxide compounds determined by AP TPR/GC−MS in µg S/g, in different temperature intervals for desulfurized initial and desulfurized sonicated samples.

No	Sample		Oxidized sulfur compounds (µg S/g)						Total
			25–200 °C	200–300 °C	300–400 °C	400–500 °C	500–600 °C	600–700 °C	
1	Initial DS	SO$_2$	0.4 ± 0.04	1.7 ± 0.05	0.7 ± 0.05	0.2 ± 0.04	0.2 ± 0.04	–	3.2
		Dimethyl Sulfone	–	0.2 ± 0.03	0.2 ± 0.04	0.7 ± 0.05	0.1 ± 0.05	–	1.2
		Dimethyl sulfoxide	–	–	–	–	–	–	–
2	7510 DS	SO$_2$	1.3 ± 0.08	7.9 ± 0.05	2.5 ± 0.05	0.8 ± 0.05	0.6 ± 0.06	0.4 ± 0.05	13.5
		Dimethyl Sulfone	–	–	0.3 ± 0.04	2.2 ± 0.04	0.6 ± 0.05	0.4 ± 0.04	3.4

		Dimethyl sulfoxide	–	–	–	0.1 ± 0.03	0.2 ± 0.04	–	0.3
3	7525 DS	SO$_2$	1.4 ± 0.08	5.1 ± 0.08	1.2 ± 0.05	0.7 ± 0.05	0.4 ± 0.04	–	8.8
		Dimethyl Sulfone	0.3 ± 0.07	0.8 ± 0.07	1.5 ± 0.07	5.7 ± 0.06	1.9 ± 0.06	0.2 ± 0.04	10.4
		Dimethyl sulfoxide	–	–	–	0.1 ± 0.04	0.8 ± 0.05	0.2 ± 0.04	1.1

DS: Desulfurized.

The quantitatively recorded amounts of the oxidized sulfur compounds in different temperature intervals (off-line experiments) (Table 14), showed that the amount of sulfur dioxide maximized in the range of 200–300 °C in all studied samples. This confirmed Tables 10 and 11 findings concerning the first huge evolved peak in the lower temperature region for desulfurized initial and desulfurized sonicated samples. The amount of dimethyl sulfone however maximized in the range of 400–500 °C and the amount of dimethyl sulfoxides maximized at the higher temperature range of 500–600 °C. This confirms early findings using model compound approach [44] and the given interpretation of these on-line results. Looking at the sonication treatment time, for SO$_2$ its highest amount is found in the temperature interval of 25–200 °C for the 25 min treatment. For all other intervals the 10 min sonication treatment resulted in the highest SO$_2$ releases. Looking at the dimethyl sulfone and the dimethyl sulfoxides species, the highest values are always found for the 25 min sonication treatment. This gives us ground to state that for a longer sonication treatment, PAA is indeed able to oxidized organic sulfur compounds to a higher extend.

These results confirm also the findings of the AP-TPR/MS on-line data for *m*/*z* profiles 64 and 48 from deduced tables (Tables 10 and 11).

Total sulfur dioxide amounts for the 10 min desulfurized sonication experiment showed an increasing tendency compared to the desulfurized initial sample from 3.2–13.5 µg S/g. On the other hand, in the case of 25 min desulfurized sonication experiment, the maximal total sulfur dioxide is lower and reached only 8.8 µg S/g.

Based on the data from AP-TPR "off-line" TD-GC/MS (Table 12), the amounts of all other kinds of volatile organic sulfur compounds did not change that much (or rather fluctuated randomly), demonstrating that sonication promotes only the oxidation of organic sulfur functionalities.

The results from the "off-line" TD-GC/MS for desulfurized sonicated samples in Table 13, showed the same tendencies for all other volatile organic sulfur compounds. The fragments which are related to dimethyl sulfone (*m*/*z* 94 and *m*/*z* 79 (= minus one methyl group)) and dimethyl sulfoxides (*m*/*z* 78 and *m*/*z* 63 (= minus one methyl group)) have been illustrated in Fig. 8. As can be seen, these profiles show all two peaks, one in the lower (around 350 °C) and one in the higher (550 °C) temperature region.
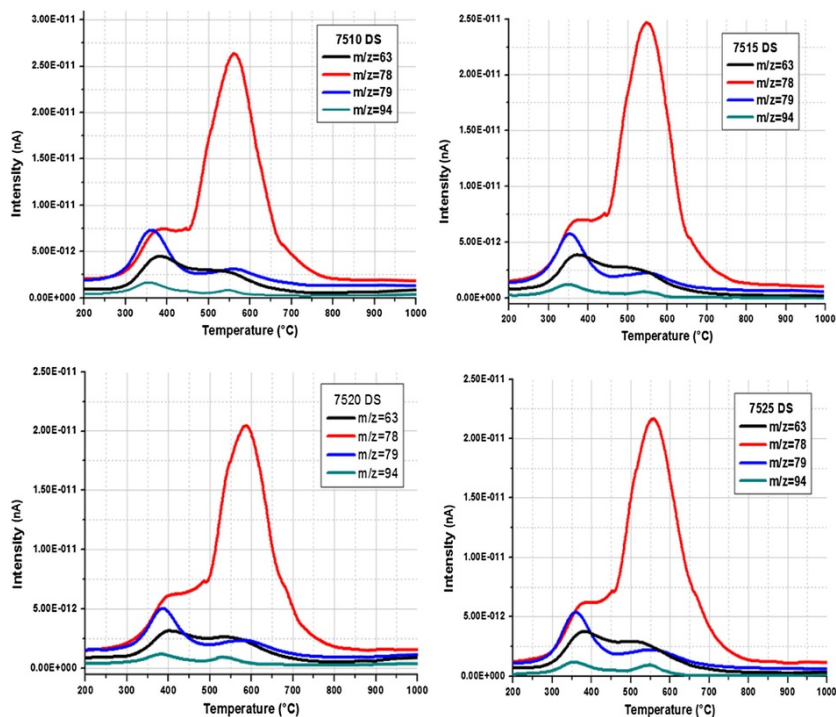
Fig. 8 AP-TPR/MS (H$_2$) evolution profiles of desulfurized sonicated samples, for m/z = 63, 78, 79 and 94.

As should be expected, the signals for m/z 94 and 78 should be more intense than the ones for m/z 79 and 63. m/z 94 and 79 signals exhibit the same trend, but the intensity of the m/z 94 is similar to the m/z 79 signal. This indicates that m/z 79 is a fragment ion coming from another species too. For the combination of m/z 78 and 63 interferences from other compounds can be noticed. For m/z 78, certainly the second peak is completely in disharmony with m/z 63. This means that m/z 78 also refers to other CH-fragments. Nevertheless, the normalized area percentages of m/z = 63, 78, 79 and 94 are calculated and reported in Tables 15–18.

Table 15 Normalized (%) peak areas and relevant peak temperatures of m/z 63 (minus one methyl group for dimethyl-sulfoxide fragment) for desulfurized sonicated samples.

No.	Sample name	Peak area		Peak area normalization (%)	
		m/z = 63			
		Peak (I)	Peak (II)	Peak (I)	Peak (II)
1	7510[DS]	1.88 ± 0.06e−10	5.34 ± 0.08e−11	78.3 ± 0.5	21.7.±0.5
2	7515[DS]	1.43 ± 0.08e−10	5.08 ± 0.06e−11	73.7 ± 0.7	26.3 ± 0.6
3	7520[DS]	1.08 ± 0.07e−10	5.65 ± 0.08e−11	65.5 ± 0.5	34.5 ± 0.7
4	7525[DS]	1.31 ± 0.08e−10	7.20 ± 0.08e−11	64.0 ± 0.6	36.0 ± 0.6

DS:Desulfurized

Table 16 Normalized (%) peak areas and relevant peak temperatures of m/z 79 (minus one methyl group for dimethyl-sulfone fragment) for desulfurized sonicated samples.

No.	Sample name	Peak area	Peak area normalization (%)

		m/z = 79			
		Peak (I)	Peak (II)	Peak (I)	Peak (II)
1	7510DS	4.10 ± 0.07e−10	8.85 ± 0.07e−11	82.2 ± 0.6	17.8 ± 0.6
2	7515DS	3.45 ± 0.06e−10	7.71 ± 0.07e−11	81.8 ± 0.5	18.2 ± 0.5
3	7520DS	2.64 ± 0.08e−10	7.80 ± 0.07e−11	77.2 ± 0.6	22.8 ± 0.6
4	7525DS	2.71 ± 0.07e−10	7.20 ± 0.06e−11	76.3 ± 0.5	23.7 ± 0.5

DS: Desulfurized.

Table 17 Normalized (%) peak areas and relevant peak temperatures of m/z 78 (dimethyl-sulfoxide fragment) for desulfurized sonicated samples.

No.	Sample name	Peak area		Peak area normalization (%)	
		m/z = 78			
		Peak (I)	Peak (II)	Peak (I)	Peak (II)
1	7510DS	2.70 ± 0.06e−10	2.44 ± 0.08e−9	9.9 ± 0.5	90.1 ± 0.5
2	7515DS	1.50 ± 0.08e−10	2.17 ± 0.06e−9	6.5 ± 0.7	93.5 ± 0.6
3	7520DS	7.50 ± 0.07e−11	1.72 ± 0.08e−9	4.2 ± 0.5	95.8 ± 0.7
4	7525DS	8.21 ± 0.08e−11	2.31 ± 0.08e−9	3.4 ± 0.6	96.6 ± 0.6

DS: Desulfurized.

Table 18 Normalized (%) peak areas and relevant peak temperatures of m/z 94 (dimethyl-sulfone fragment) for desulfurized sonicated samples.

No.	Sample name	Peak area		Peak area normalization (%)	
		m/z = 94			
		Peak (I)	Peak (II)	Peak (I)	Peak (II)
1	7510DS	6.74 ± 0.06e−11	7.31 ± 0.08e−12	90.2 ± 0.5	9.8 ± 0.6
2	7515DS	5.81 ± 0.06e−11	8.10 ± 0.06e−12	87.8 ± 0.6	12.2 ± 0.6
3	7520DS	4.53 ± 0.08e−11	8.23 ± 0.08e−12	84.7 ± 0.5	15.3 ± 0.5
4	7525DS	3.71 ± 0.07e−11	8.55 ± 0.07e−12	81.23 ± 0.7	18.8 ± 0.6

DS: Desulfurized.

It can be noticed that, the normalized % area for all first peak fragments showed decreasing tendency as a function of time of sonication from 10 to 25 min and consequently, the second peak for all fragments at higher temperature region increased. In the case of m/z 94% peak areas in the lower and higher temperature region showed an identical tendency and similar peak surface values with m/z 79. This confirmed that the studied fragments could be related to the sulfones degradation rather than to other CH-fragments. In the case of m/z 78 and 63, the tendency in the decrease of the first peak area % and an increase in their second peak area % is identical, but their peak surface values are inverse comparable. This confirmed that the selected fragment ions could not only be related to dimethyl sulfoxides alone but also to other CH-fragments, certainly m/z 78.

4 Conclusion

In this study the total sulfur reduction after chemical desulfurization by PAA for sonicated samples are achieved in the range of 49–58%. The results showed that the sulfate and pyritic sulfur were mainly attacked by PAA after sonication, resulting in a 100% removal of sulfate sulfur and 61–78% pyritic sulfur removal depending on the sonication time. The results showed that the maximum organic sulfur reduction was obtained for a longer sonication time of 15 up to 20 min being around 42–44%. The profiles obtained by AP-TPR/MS (on-line) experiments for m/z 48 and 64 for sonicated and desulfurized sonicated samples exhibited the same trend over the whole temperature range, demonstrating the presence of high amounts of different oxidized sulfur functionalities. For the first time organic sulfur changes by AP-TPR/MS as a result of a sonication process followed by PAA desulfurization have been studied. The information obtained by AP-TPR "off-line" (TD-GC/MS) showed some quantitatively changes in the refractory sulfur forms as a result of sonication time settings before and after desulfurization. Based on the results from "off-line" experiments the amounts of all kinds of volatiles organic sulfur compounds did not show any significant changes (only random fluctuation have been seen), whereas, the amount and the patterns of the variation of the oxidized sulfur functionalities, gave strong evidence of the role of sonication process on the oxidation of organic sulfur compounds. Nevertheless, the aforementioned findings gives a better understanding of the advanced oxidation process and its mechanisms towards oxidized sulfur form formations, some additional research is needed to investigate these findings more detailed with advanced instrumental analyses and chemical thermodynamic approaches.

Acknowledgment

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.fuel.2016.06.037.

References

[1] K.S. Suslick, The chemical effects of ultrasound, *Sci Am* 1989, 62–68.

[2] M. Steinberg, R.T. Yang, T.K. Horn and A.L. Berlad, Desulfurization of coal with ozone: an attempt, *Fuel* **56**, 1977, 227–228.

[3] P.E. Araya, R.B. Ohlbaum and S.E. Droguett, Study of the treatment of sub bituminous coals by NaOH solutions, *Fuel* **60**, 1981, 1127–1130.

[4] D. Chandra, J.N. Chakrabarti and Y.V. Swamy, Auto-desulfurization of coal, *Fuel* **61**, 1982, 204–205.

[5] L.L. Krzymien, Complete removal of sulfur from coal using solutions containing cupric ions, *Fuel* **61**, 1982, 871–873.

[6] K.C. Chaung, R. Markuszewesky and T.D. Wheelock, Desulfurization of coal by oxidation in alkaline solutions, *Fuel Process Technol* **7**, 1983, 43–57.

[7] R.T. Yang, S.K. Das and B.M.C. Tsai, Coal demineralization using sodium hydroxide and acid solutions, *Fuel* **65**, 1985, 735–742.

[8] H. Kara and R. Ceylan, Removal of sulfur from four Central Anatolian lignite's by NaOH, *Fuel* **67**, 1988, 170–172.

[9] E. Ahnonkitpanit and P. Prasassarakich, Coal desulfurization in aqueous hydrogen peroxide, *Fuel* **68**, 1989, 819–824.

[10] M. Ozdemmir, S. Bayrakceken, A. Gurses and S. Gulaboglu, Desulfurization of two Turkish lignites by chlorinolysis, *Fuel Process Technol* **26**, 1990, 15–23.

[11] A. Ali, S.K. Srivatsava and R. Haque, Chemical desulfurization of high sulfur coals, *Fuel* **71**, 1992, 835–839.

[12] P. Prasassarakich and T. Thaweesri, Kinetics of coal desulfurization with sodium benzoxide, *Fuel* **75**, 1996, 816–820.

[13] R.A. Rodriguez, C.C. Jul and D.G. Limon, The influence of process parameters on coal desulfurization by nitric leaching, *Fuel* **75**, 1996, 606–612.

[14] C. Hamamci, F. Kahraman and M.Z. Diiz, Desulfurization of southeastern anatolianasphaltites by the Meyers method, *Fuel Process Technol* **50**, 1997, 171–177.

[15] C. Aacharya, R.N. Kar and L.B. Sukla, Bacterial removal of sulfur from three different coals, *Fuel* **80**, 2001, 2207–2216.

[16] S. Mukherjee and P.C. Borthakur, Chemical demineralization/desulfurization of high sulfur coal using sodium hydroxide and acid solutions, *Fuel* **80**, 2001, 2037–2040.

[17] S. Ratanakandilok, S. Ngamprasertsith and P. Prasassarakich, Coal desulfurization with methanol/water and methanol/KOH, *Fuel* **80**, 2001, 1937–1942.

[18] O. Sonmez and E.S. Giray, The influence of process parameters on desulfurization of two Turkish lignite's by selective oxidation, *Fuel Process Technol* **70**, 2001, 159–169.

[19] E. Jorjani, B. Rezai, M. Vossoughic and M. Osanloo, Desulfurization of Tabas coal with microwave irradiation/peroxyacetic acid washing at 25, 55 and 85 °C, *Fuel* **83**, 2004, 943–949.

[20] C. Aacharya, L.B. Sukla and V.N. Misra, Biological elimination of sulfur from high sulfur coal by aspergillus-like fungi, *Fuel* **84**, 2005, 1597–1600.

[21] B.P. Baruah, B.K. Saikia, P. Kotoky and P.G. Rao, Aqueous leaching on high sulfur subbituminous coals, in Assam, India, *Energy Fuels* **20**, 2006, 1550–1555.

[22] K. Liu, J.J. Yang and Y. Wang, Desulfurization of coal via low temperature atmospheric alkaline oxidation, *Chemosphere* **71**, 2008, 183–188.

[23] S.A.H. Zaidi, Ultrasonically enhanced coal desulfurization, *Fuel Process Technol* **33**, 1993, 95–100.

[24] K.W. Ze, X.H. Xin and C.J. Tao, Study of enhanced fine coal desulfurization and de-ashing by ultrasonic floatation, *J Chin Univ Min Technol* **17**, 2007, 358–362.

[25] J. Grobas, C. Bolivar and C.E. Scott, Hydro-desulfurization of benzothiophene and hydrogenation of cyclohexene, biphenyl, and quinoline, assisted by ultrasound, using formic acid as hydrogen precursor, *Energy Fuels* **21**, 2007, 19–22.

[26] Y. Wang and R.T. Yang, Desulfurization of liquid fuels by adsorption on carbon-based sorbents and ultrasound-assisted sorbent regeneration, *Langmuir* **23**, 2007, 3825–3831.

[27] P.A. Mello, F.A. Duarte, M.A.G. Nunes, M.S. Alencar, E.M. Moreira, M. Korn, et al., Ultrasound-assisted oxidative process for sulfur removal from petroleum product feedstock, *Ultrason Sonochem* **16**, 2009, 732–736.

[28] M.M. Royaei, E. Jorjani and S. Chehreh Chelgani, Combination of microwave and ultrasounic irradiation as a pretreatment method to produce ultra clean coal, *Int J Coal Prepar Utiliz* **32** (3), 2012, 143–155.

[29] M.A. Vieira, B. Welz and A.J. Curtius, Determination of arsenic in sediments, coal and fly ash slurries after ultrasonic treatment by hydride generation atomic absorption spectrometry and trapping in an iridium-treated graphite tube, *Spectrochim Acta B* **57**, 2002, 2057–2067.

[30] K.S. Suslick, Sonochemistry, *Science* **247** (49), 1990, 1439–1445.

[31] K. Wen-ze, X. Hai-xin, K. Xiao-hong and L. Ming-ming, Effects from changes in pulp nature after ultrasonic conditioning on high-sulfur coal flotation, *Min Sci Technol* **19**, 2009, 498–502.

[32] S.R. Palmer, E.J. Hippo and A. Dorai, Selective oxidation pretreatment for enhanced desulfurization of coal, *Fuel* **74** (2), 1995, 193–200.

[33] J. Yperman, I.I. Maes, H. Van den Rul, S. Mullens, J. Van Aelst, D.V. Franco, et al., Sulfur group analysis in solid matrices by atmospheric pressure–temperature programmed reduction, *Anal Chin Acta* **395**, 1999, 143–155.

[34] S. Mullens, J. Yperman, R. Carleer, T. Bozdemir, T. Durusoy and Y. Yürüm, Sulfur analysis of Bolu-Mengen lignite before and after microbiological treatment using reductive pyrolysis and gas chromatography/mass spectrometry, *Energy Fuels* **19**, 2005, 1029–1036.

[35] M. Stefanova, S.P. Marinov, J. Yperman and R. Carleer, Reductive pyrolysis of Miocene-aged lignite lithotypes using MS and GC/MS detection system for analysis of organic sulfur groups, *Fuel* **84**, 2005, 71–79.

[36] S.P. Marinov, M. Stefanova, V. Stamenova, R. Carleer and J. Yperman, Sulfur functionality study of steam pyrolyzed "Mequinenza" lignite using reductive pyrolysis technique coupled with MS and GC/MS detection systems, *Fuel Process Technol* **86**, 2005, 523–534.

[37] S.P. Marinov, M. Stefanova, V. Stamenova, L. Gonsalvesh, R. Carleer and J. Yperman, Sulphur analysis of household briquettes using MS and GC/MS detection systems after reductive pyrolysis, *J Fuel Chem Technol* **34** (3), 2006, 257–264.

[38] L. Gonsalvesh, S.P. Marinov, M. Stefanova, Y. Yürüm, A.G. Dumanli, G. Dinler-Doganay, et al., Biodesulphurized subbituminous coal by different fungi and bacteria studied by reductive pyrolysis. Part 1: Initial coal, *Fuel* **87**, 2008, 2533–2543.

[39] S.A. Channiwala and P.P. Parikh, A unified correlation for estimating HHV of solid, liquid and gaseous fuels, *Fuel* **81** (8), 2002, 1051–1063.

[40] Sh. Mesroghli, J. Yperman, E. Jorjani, J. Vandewijngaarden, G. Reggers, R. Carleer, et al., Changes and removal of different sulfur forms after chemical desulfurization by peroxyacetic acid on microwave treated coals, *Fuel* **154**, 2015, 59–70.

[41] Sh. Mesroghli, J. Yperman, E. Jorjani, R. Carleer and M. Noaparast, Evaluation of microwave treatment on coal structure and sulfur species by reductive pyrolysis-mass spectrometry method, *Fuel Process Technol* **131**, 2015, 193–202.

[42] L. Gonsalvesh, S.P. Marinov, M. Stefanova, R. Carleer and J. Yperman, Biodesulfurized low-rank coal: Maritza east lignite and its "humus-like" by product, *Fuel* **103**, 2013, 1039–1050.

[43] J. Van Aelst, J. Yperman, D.V. Franco, J. Mullens, L.C. Van Poucke and S.R. Palmer, Sulfur distribution in Illinois No. 6 coal subjected to different oxidation pre-treatments, *Fuel* **76** (14/15), 1997, 1377–1381.

[44] J. Van Aelst, J. Yperman, D.V. Franco, L.C. Van Poucke, A.C. Buchanan and P.F. Britt, Study of silica-immobilized sulfur model compounds as a calibrants for the AP-TPR study of oxidized coal samples, *Energy Fuels* **14** (5), 2000, 1002–1008.

[45] S. Mullens, J. Yperman, G. Reggers, R. Carleer, A.C. Buchanan, III and P.F. Britt, A study of the reductive pyrolysis behavior of sulfur model compounds, *J Anal Appl Pyrol* **70** (20), 2003, 469–491.

[46] A.P. Terzyk, *J Colloid Interface Sci* **268**, 2003, 301–329.

[47] O. Lindstrom and O. Lamm, The chemical effects produced by ultrasonic waves, *J Phys Chem* **55**, 1951, 1139–1146.

[48] E. Webster, Cavitation, *Ultrasonics* **1**, 1963, 39–48.

[49] K. Makino, M.M. Mossoba and P. Riesz, Chemical effects of ultrasound on aqueous solutions evidence for OH− and H+ by spin trapping, *J Am Chem Soc* **104**, 1982, 3537–3539.

[50] P. Riesz, D. Berdahl and C.L. Christman, Free radical generation by ultrasound in aqueous and non-aqueous solutions, *Environ Health Perspect* **64**, 1985, 233–252.

[51] C.L. Christman, A.J. Carmichael, M.M. Mossoba and P. Riesz, Evidence for free radicals produced in aqueous solutions by diagnostic ultrasound, *Ultrasonics* **25**, 1987, 31–34.

[52] V. Misik and P. Riesz, Free radicals formation by ultrasound in organic liquids: a spin trap and EPR study, *J Phys Chem* **98**, 1994, 1634–1640.

[53] V. Misik and P. Riesz, Peroxyl radical formation in aqueous solutions of n-dimethyl formamide, n-methylformamide, and dimethylsulfoxide by ultrasound, *Free Radical Biol Med* **20**, 1996, 129–138.

[54] M.H. Entezari and P. Krus, Effect of frequency on sono chemical reaction, *Ultrason Sonochem* **1**, 1994, 75–79.

[55] J.L. Luche, Effect of ultrasound on heterogeneous system, *Ultrason Sonochem* **1**, 1994, 111–118.

[56] A. Henglein, Chemical effects of continuous and pulsed ultrasound in aqueous solutions, *Ultrason Sonochem* **2**, 1995, 115–121.

[57] M.R. Hoffmann, I. Hua and R. Hochemer, Application of ultrasonic irradiation for the degradation of chemical contaminants in water, *Ultrason Sonochem* **3**, 1996, 163–172.

[58] S. Mullens, J. Yperman, G. Reggers, R. Carleer, A.C. Buchanan, III and P.F. Britt, A study of the reductive pyrolysis behavior of sulfur model compounds, *J Anal Appl Pyrol* **70** (20), 2003, 469–491.

[59] P. Rutkowski, S. Mullens, J. Yperman and G. Gryglewicz, AP-TPR investigation of the effect of pyrite removal on the sulfur characterization of different rank coals, *Fuel Process Technol* **76**, 2002, 121–138.

Appendix A. Supplementary material

Multimedia Component 1

Supplementary data 1

Graphical abstract
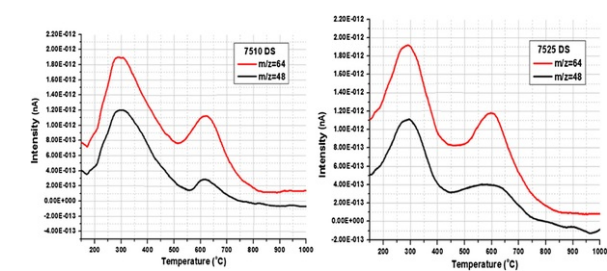
Highlights

- Desulphurised sonicated coal using PAA result in complex sulfur form changes.

- Role of AOP on coal oxidation as a function of different sonication times was investigated.

- High amounts of oxidized sulfur compounds are present in desulphurised sonicated coal.

- Quantitative organic sulfur form changes were determined.

- Sonication for 20 min resulted in the highest organic sulfur reduction.

Queries and Answers

Query: Your article is registered as a regular item and is being processed for inclusion in a regular issue of the journal. If this is NOT correct and your article belongs to a Special Issue/Collection please contact aravind.kumar@elsevier.com immediately prior to returning your corrections.

Answer: this is correct

Query: The author names have been tagged as given names and surnames (surnames are highlighted in teal color). Please confirm if they have been identified correctly.

Answer: names are correct