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Evaluation of irradiation effects on coal sulfur forms and chemical desulfurization using AP-TPR method

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List of abbreviations

BTU/lb: British thermal unit per pound

ASTM: American society for testing and materials

CCT: Clean coal technology

FGD: Flue gas desulfurization

IGCC: Integrated gasification combusted cycle

TOC: Total organic carbon

GC/MS: Gas chromatograph/mass spectrometer

AMD: Acid mine drainage

ARD: Acid rain drainage

AP-TPR: Atmospheric pressure temperature programmed reduction

HP-TPR: High pressure temperature programmed reduction

PAA: Peroxyacetic acid

DS: Desulfurized coal sample

daf: Dry ash free

db: Dry basis

Th: Thiophene

Me-Th: Methyl thiophene

Di-Me-Th: Di methyl thiophene

Be-Th: Benzo thiophene

Me-Be-Th: Methyl benzo thiophene

Di-Me-Be-Th: Di methyl benzo thiophene

Di-Be-Th: Di benzo thiophene

M: Moisture

A: Ash

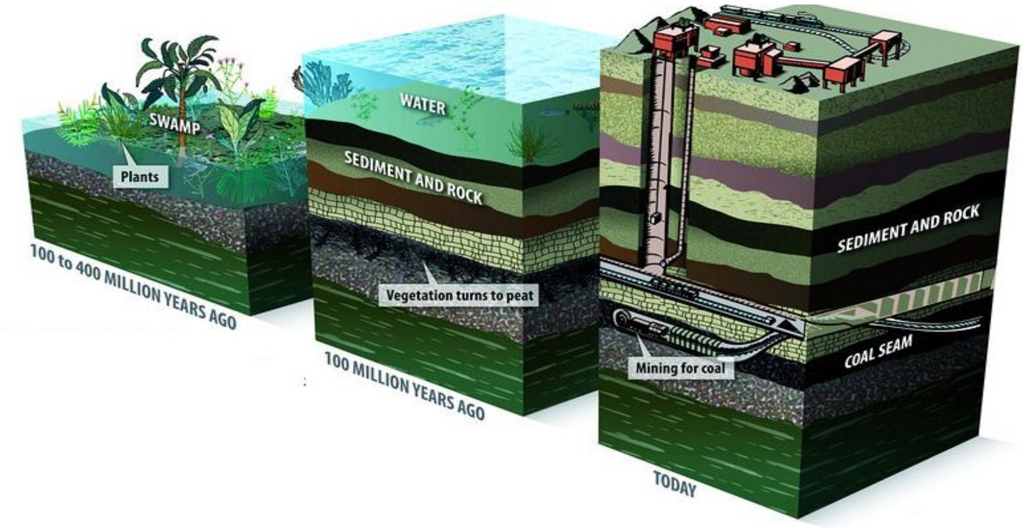
Vol: Volatile matter

FC: Fixed carbon

Chapter One: Introduction

1.1. Origin of coal

The standard, uniformitarian process of coal formation begins in a swamp (Fig 1.1). In this water-saturated environment, dead mosses, leaves, twigs, and other parts of trees do not decompose completely. Instead, this plant matter becomes a layer of peat. At various intervals, the swamp may be covered by sand and mud when a river floods or when ocean levels rise. Under the weight of these sediments, the peat may lose some of its water and gases, eventually turning into a soft brown coal called lignite. With increasing pressures or temperatures, more water and gases are driven out, forming the common bituminous family of coals. Finally, high temperatures and pressures may cause bituminous coal to turn into a hard black coal called anthracite. An increase in rank represents an increase in the proportion of carbon within the coal [1].



Fig(1.1) . The process how coal was formed [1]

The type or rank of coal is thought to depend more on depth of burial than time. For example, it is possible to find lignite and bituminous coals that seem to have formed at the same time, but in different places. In other words, rank is not a good predictor of age [1].

1.1.1. Coal formation

If coal has formed from the gradual build-up and burial of organic matter in a swamp, we would expect to find some gradation in rank from the top of a coal deposit to the bottom. Theoretically, material in the lower sections has had more time to change, and has been under greater heat and pressure, than the material at the top.

In a vertical sequence, at any one locality in a coalfield, the rank of the coal seams rises with increasing depth. For example, in the Pie Rough borehole, which penetrated forty-two coals in 3,500 feet of strata, researchers found increases in carbon content and calorific (heating) value, and decreases in moisture and volatile content [2]. These four trends are consistent with an increase of rank with depth. Yet the change over this great distance spans only two adjacent subgroups from low volatile bituminous coal at the top to semi-anthracite coal at the bottom. Greater variations may occur laterally in a coalfield, with ranks changing gradually over several miles. The presumed cause of such variation is regional tectonic activity, such as faulting, folding, volcanism, and intrusions. These large-scale disturbances may bring extra heat or depth to one part of the coalfield, and cause an increase in rank in the affected area. However, nowhere do we find a swamp in which peat is changing into coal. In some cases, peat swamps lie over rocks containing sub-bituminous coal seams, but there is no subtle gradation between the two. By uniformitarian estimates, the coal preceded the peat by fifty million years [3], and the two deposits are related by nothing more than geography.

The making of coal, it appears, is a threshold process. That is, all the right conditions have to be in place before organic matter is turned into coal. Limited variations do exist, but they are within the system of coal ranks. Coal deposits appear in geological strata already formed, and do not show evidence of the presumed evolutionary pathway leading from a peat swamp. Certainly, a transformation from plant material to coal has occurred, but not in the way suggested by the uniformitarian swamp model.

1.1.2. Coal composition

As it has been discussed in coal formation part the coal is composed of complex mixtures of organic and inorganic compounds. The organic compounds, inherited from the plants that live and die in the mires, number in the millions. The more than 100 inorganic compounds in coal either were introduced into the mire from water-borne or wind-borne sediment or were derived from elements in the original vegetation; for instance, inorganic compounds containing such elements as iron and zinc are needed by plants for healthy growth. After the plants decompose, the inorganic compounds remain in the resulting peat. Some of those elements combine to form discrete minerals, such as pyrite. Other sources of inorganic compounds used by the plants may be the mud that coats the bottom of the mire, sediments introduced by drainage runoff, dissolved elements in the mire water, and wind-borne sand, dust, or ash [4].

Coals may contain as many as 76 of the 90 naturally occurring elements of the periodic table (Fig 1.2); however, most of those elements usually are present in only trace amounts (on the order of parts per million).

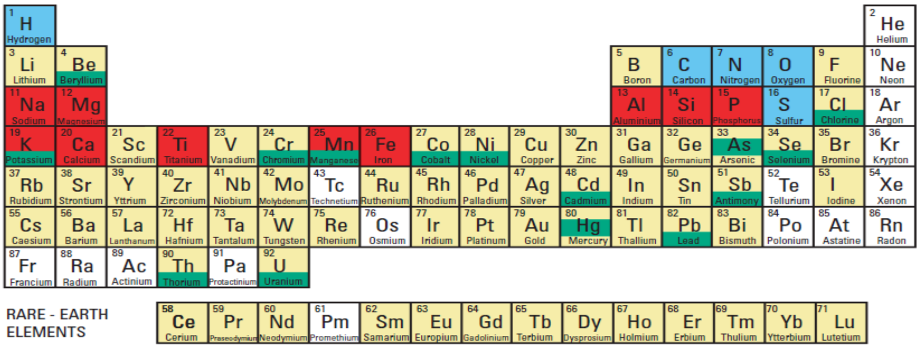
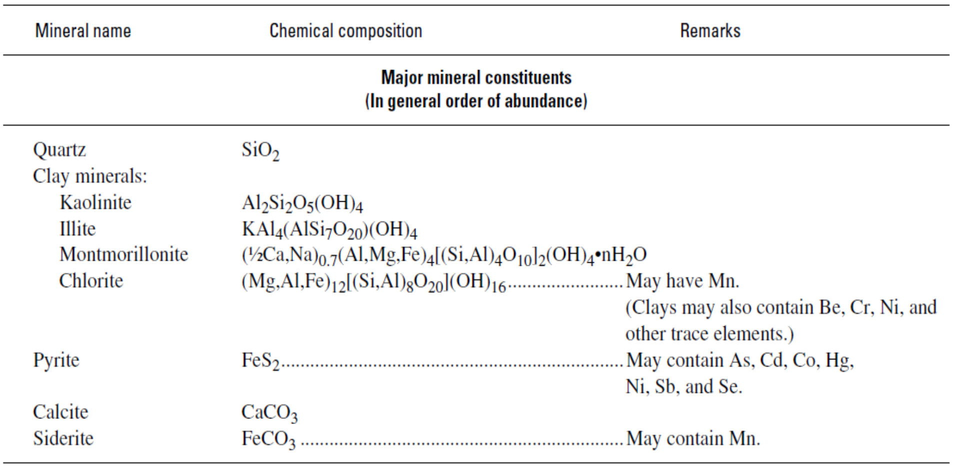


Fig (1.2). Periodic table of the elements showing all known naturally occurring elements on Earth. The 76 elements found in coal are highlighted by colors with regard to their general abundance in coal, as follows: blue, major elements (generally greater than 1.0 percent in abundance); red, minor elements (generally greater than or equal to 0.01 percent); and yellow, trace elements (generally less than 0.001 percent) the green bars in their boxes indicates 15 elements are cause human health problem and have potential as ground water pollutant that flows through fly-ash and coal mine spoil piles [6].

Occasionally, some trace elements may be concentrated in a specific coal bed, which may make that bed a valuable resource for those elements (such as silver, zinc, or germanium) [5]. Some elements, however, have the potential to be hazardous (for example, cadmium or selenium), particularly if they are concentrated in more than trace amounts. Although as many as 120 different minerals have been identified in coal, only about 33 of them commonly are found in coal, and, of these, only about eight are abundant enough to be considered as major constituents (Table 1.1).

Table(1.1). Common minerals found in coal and their elemental compositions [6]



Mineral name	Chemical composition	Remarks
Major mineral constituents (In general order of abundance)		
Quartz	SiO_2	
Clay minerals:		
Kaolinite	$Al_2Si_2O_5(OH)_4$	
Illite	$KAl_4(AlSi_7O_{20})(OH)_4$	
Montmorillonite	$(\frac{1}{2}Ca,Na)_{0.7}(Al,Mg,Fe)_4[(Si,Al)_4O_{10}]_2(OH)_4 \bullet nH_2O$	
Chlorite	$(Mg,Al,Fe)_{12}[(Si,Al)_8O_{20}](OH)_{16}$	May have Mn. (Clays may also contain Be, Cr, Ni, and other trace elements.)
Pyrite	FeS_2	May contain As, Cd, Co, Hg, Ni, Sb, and Se.
Calcite	$CaCO_3$	
Siderite	$FeCO_3$	May contain Mn.

The organic compounds in coal are composed of the elements carbon, hydrogen, oxygen, nitrogen, sulfur, and trace amounts of a variety of other elements. Although only a few elements compose the organic compounds found in coal, these compounds are extremely complex and, as a result, they are not well understood; however, research is being conducted into understanding organic structures in coal. The organic compounds in coal produce heat when coal is burned; they also may be converted to synthetic fuels or may be used to produce the organic chemicals [5].

The affinities of trace elements for either the organic compounds or the minerals in coal affect the quality of the coal. If trace elements are organically bound, then it is difficult to remove them from the coal by cleaning processes such as crushing and washing, which remove mineral matter from coal before it is burned. Organically bound trace elements may be released only by burning, or by deep chemical leaching, which is both very difficult and uneconomical. In contrast, trace elements associated with clays or pyrite may be removed largely from the coal by cleaning processes [5,6].

1.1.3. Coal Rank

A major factor in determining coal quality is coal rank. Rank refers to steps in a slow, natural process called "coalification" during which buried plant matter changes into an ever denser, drier, more carbon rich, and harder material. The major coal ranks, from lowest to highest, are lignite (also called "brown coal" in some parts of the world), subbituminous coal, bituminous coal, and anthracite. Each rank may be further subdivided, as shown in Fig (1.3).

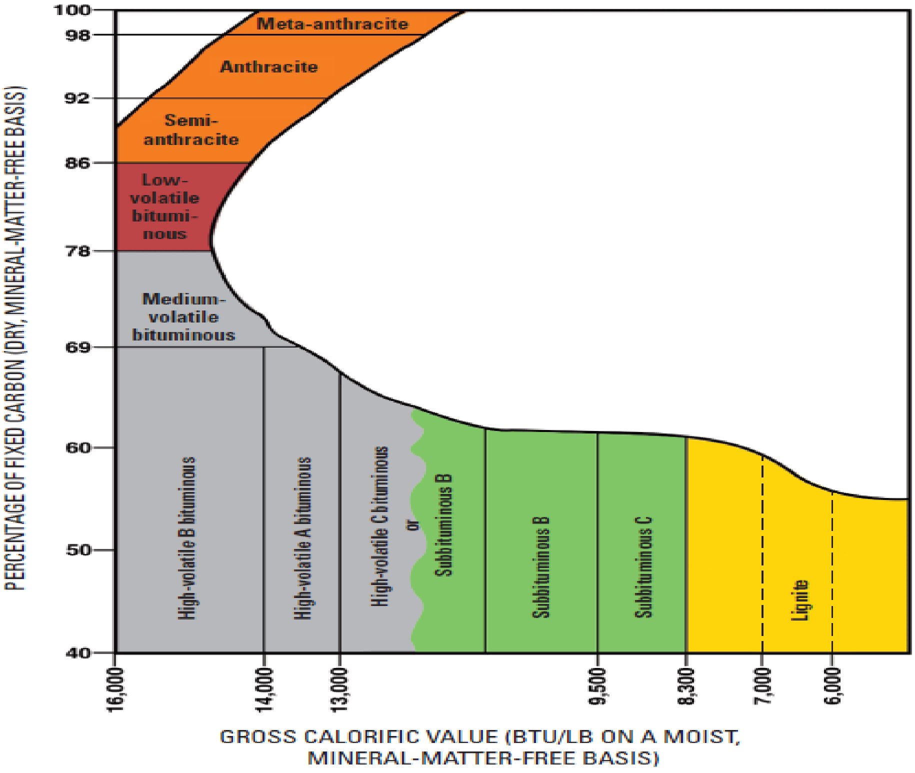


Fig (1.3). Diagram showing classification of coals ranks [6]

The rank of coal is determined by the percentage of fixed carbon, moisture (inherent water), volatile matter, and calorific value in British thermal units per pound (Btu/lb) after the content of mineral matter and sulfur have been subtracted from the total. Fixed carbon is solid, combustible matter left in coal after the lighter, volatile, hydrogen-rich compounds are driven off during coalification. Volatile matter is slowly removed from coal during coalification but may be rapidly removed during destructive distillation. The volatile matter contains the raw materials from which the organic chemicals are obtained. It should be mentioned that in the United States, the tests to determine the amounts of the above-mentioned substances and the rank of the coal are performed using standards published by the American Society for Testing and Materials (1999) (ASTM) [7].

The geochemical process consisting of the alteration of plant debris into coal which is happened in coalification process is structured as follows [8]:

Peat → Lignite → Sub-bituminous Coal → Bituminous Coal → Anthracite

In general, the higher the rank of a coal, the more deeply it was buried, and, therefore, the higher the temperature it was subjected to during and after burial. Older coals tend to be of higher rank because they are more likely to have been buried more deeply for longer periods of time than younger coals. To give a sense of the effects of increasing rank, the following example may be used: lignite is soft, dusty, and can ignite spontaneously under the appropriate conditions, whereas anthracite is quite hard, clean to the touch, and must reach a temperature of about 496°C before it will ignite. Furthermore, anthracite contains about twice the calorific value of lignite (about 15000 Btu/lb, 3780 cal/g, 15.8 kJ/g and 7000 Btu/lb, 1764 cal/g, 7.4 kJ/g, respectively) because lignite contains more moisture and oxygen and less fixed carbon than anthracite. Subbituminous and high-volatile bituminous coals have oxygen and moisture contents and calorific values that range between those of lignite and anthracite. Bituminous coals of higher rank than high-volatile A (Fig 3) have calorific values that may exceed those of anthracite [9].

1.1.4. Why is coal so complex?

Coal is complex because of the wide variety of factors that determine the quality of coal. These factors include (1) the plants, plant remains, and other organisms (such as bacteria) in the peat mire, (2) biological and chemical processes and the degree of preservation of the plant matter, (3) the geometry and location of the mire, (4) the mineral matter that accumulated with the plant material or that was introduced at some later stage, and (5) coalification. Geologic age and history will be a recurring theme throughout this discussion. Because of above mentioned reasons pre-treatment of coal is necessary and a complicated procedure for upstream processes to beneficiation and to make an environmental friendly product [1].

1.1.5. Importance of coal and associated environmental problems

About eighty percent of world coal production is used to generate power and for other industrial purposes depending on its characteristics and heat value. Coal is also a raw material used for oil, petrol, tar and other chemicals' manufacturing. It further contributes to the formation of sulfuric acid, amino acids and proteins [10,11]. Despite the economic value of coal, it has environmental problems associated to its mining process and use. Coal is well known as a precursor of the green-house gas and acid rain that contribute to brown haze, global warming besides other environmental problems [11-13]. The increasing use of coal has to be balanced by the advanced clean coal technology (CCT) so as to avoid global warming and reduce or eliminate its negative effects on the ecosystem [14]. Since the Industrial Revolution and the oil crisis, research has been done and has shown how coal causes major damages to the ecosystem through atmospheric pollution, danger to public health, harm to flora and fauna, as well as alteration of nature and manmade structures [14-15]. Generally, there is no detectable environmental concern with natural coal. It becomes a danger to the ecosystem when it is mined, processed and used for various purposes. Some of the harmful outcomes include air pollution, water pollution, accumulation of solid waste, not to mention the land degradation and human illness. The major pollutants from coal processing are carbon dioxide, nitrogen dioxide, sulfur dioxide, methyl mercaptan, dimethyl sulfide, dimethyl disulfide, mercury, lead, arsenic, and particulates matter [11,16]. The exposure of coal or its solid waste to rain can cause environmental concerns such as acid mine drainage [17]. Flue Gas De-sulfurization (FGD) is one of the techniques used for removing sulfur dioxide from exhaust stacks in plants by scrubbing the gaseous compounds resulting from coal processing. Other methods for coal processing require a good knowledge of different organic sulfur compounds present in coal in order to improve the scrubbing gas procedure [18,19].

Volatile organic compounds in coal are more reactive, thus they combine with the atmospheric compounds when released to form new compounds with great consequences on the composition of the atmosphere and the entire ecosystem [20,21].

1.2. Coal technology used to reduce pollution

The technological processes adapted to date in various industries are dependent on coal chemistry. Further investigations on coal could suggest ease and economically profitable ways for coal processing. The pre-combustion desulfurization processes such as coal washing, liquefaction and gasification as well as the post-combustion desulfurization processes such as scrubbing flue gas with various solutions are beyond the present scope of discussion [22,23]. Integrated gasification combined cycle (IGCC), Flue gas desulfurization (FGD) and high exhaust stacks (more than 150 meters) are the actual technologies to reduce sulfur emission during coal processing. Many types of FGD systems have been developed. These can be classified in two major groups, wet and dry processes, which include several types depending on the specific chemical reactions taking place and the flow conditions employed. Among them, the wet limestone FGD process is by far the most widely used because of its high de-sulfurization performance, reliability and low utility consumption [24]. In this system SO_2 is removed from the flue gas by absorption into limestone slurry as sulfate which in turn is extracted from the absorber as gypsum slurry and finally dewatered. The chemical reaction occurring in a wet limestone FGD process [25] can be summarized as in Equation (1-1).

$$\mathbf{CaCO_3\ (s)+SO_2\ (g)+\tfrac{1}{2}\ O_2\ (g)+2\ H_2O\ (l)\rightarrow CaSO_4.2H_2O\ (s)+CO_2\ (g)} \quad \textbf{Eq. (1-1)}$$

However the above-mentioned strategies prove costly to be used in most plants [26,27]. Whether scrubbers systems are eventually installed on many number of coal power plants they might depend on the continued viability of fuel switching (which is in turn sensitive to relative fuel costs). Ongoing concerns about acid deposition, combined with new imperatives to address fine particulate pollution and regional haze, lead to a further tightening of the sulfur dioxide cap [28]. Researchers always carry out explorations on coal and its products during and after processing. Waste coming from any coal usage should be reprocessed to remove toxic elements or any form of compounds which could contribute to negative consequences on the environment.

For that purpose, research on coal is still the main key to facilitate the reuse of its waste, or else the waste generated has to be discarded regardless of any consequence it may yield to the environment. The discarded coal waste is generally one of the major sources of environmental concerns beside other gases and particulate matter occurring during a process.

Research should therefore aim to reprocess coal waste with minimal damage to the environment. Fig (1.4) shows a summarized interdependence between research, coal material, its processing and products [7].

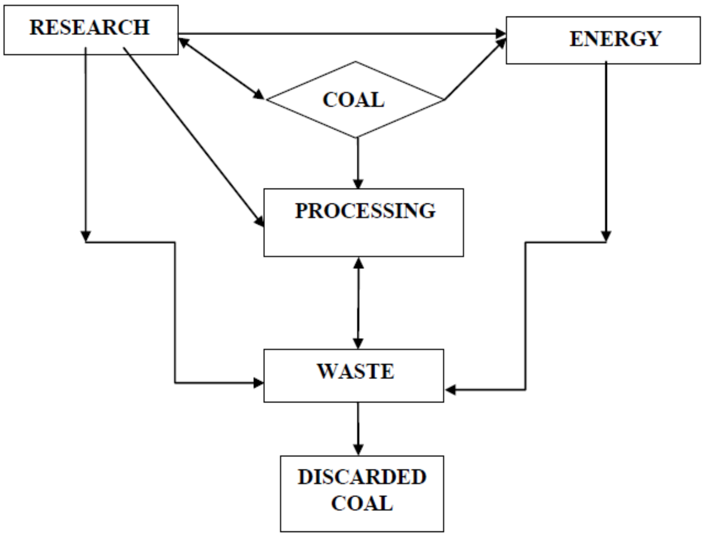


Fig (1.4). An illustration of interdependence of coal processing, usage and its waste on research [7].

According to the Fig (1.4) it is obvious that the research around coal and its relevant branches can be accomplished. As illustrated in Fig (1.4), energy, processing (producing clean coal for upstream processes) and waste (waste management studies) are the main concepts that are studied and need to be researched.

1.2.1. Organic carbon in coal

The organic carbon is determined as total organic carbon (TOC) and allows understanding the organic material in coal which originally came from decaying vegetation, bacterial growth, and metabolic activities of living organisms or chemicals. The standard wet chemistry technique for TOC determination extraction involves the rapid dichromate oxidation of organic matter. Perhaps the best known of the rapid dichromate oxidation methods is the Walkley-Black procedure which has been the "reference" method for comparison to other methods in numerous studies [29]. The chemistry of this extraction is based upon the Walkley-Black reaction shown in Equation (1-2) below.

$$2\ Cr2O7^{2-} + 3\ C^0 + 16\ H^+ \leftrightarrow 4\ Cr^{3+} + 3\ CO2 + 8\ H_2O \qquad \text{Eq.(1-2)}$$

The Walkley-Black procedure is widely used because it is simple, rapid, and has minimal equipment needs [30]. The sample and extraction solutions are gently boiled at 150 °C for 30 minutes, allowed to cool, and then water is added to halt the reaction. The addition of heat to the system leads to a complete digestion of the organic carbon in the sample; therefore**,** no correction factor is needed [31]. The characterization of sulfur in coals in relation with its organic and inorganic content are much determined and considered. However, coal characterization is still an interesting area as its utilization remains challenging. Enhancing knowledge on coal, its processing and waste could lead to other interesting hints on coal science.

1.2.2. Origin of sulfur in coal

The presence of sulfur in coal is generally originated from parent plant composition. Proteins are the main precursors of sulfur. On the other hand, rocks, inorganic compounds in soil which accompany coal in its formation contribute to sulfur presence in coal. The decomposition of sulfur compounds into others (minerals into mercaptans, into sulfides and thiophenes) plays an interesting role in the diversification of sulfur forms in coal. The sulfur cycle as shown in Fig (1.5) below explains how sulfur is transformed by weathering, microbial processes and industrial activities into various species.

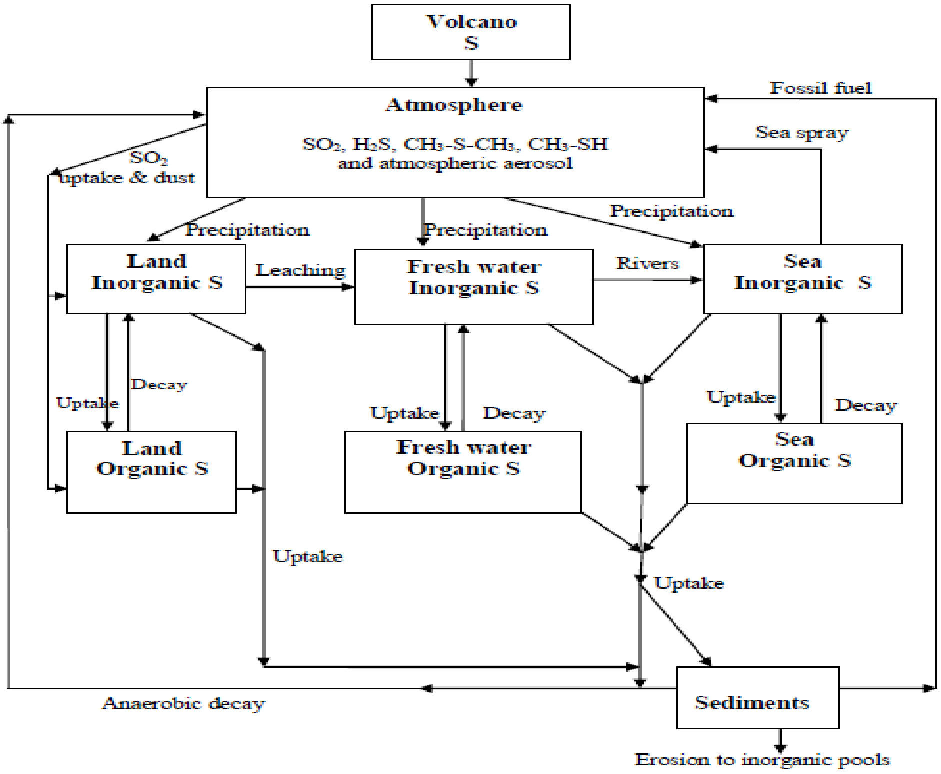


Fig (1.5). Sulfur cycle in nature [7].

When sulfur dioxide enters the atmosphere it will react with oxygen to produce sulfur trioxide gas (SO_3) or with other chemicals in the atmosphere, to produce sulfur salts. Sulfur trioxide may also react with water to produce sulfuric acid (H_2SO_4). Sulfur acid may also be produced from organic compounds such as dimethyl sulfide, which is emitted to the atmosphere by plankton species. All particles made of sulfur will settle back onto earth or react with rain and fall back onto earth as acid deposition. The particles will then be absorbed by plants again and are released back into the atmosphere, so that the sulfur cycle will start over again. Sulfur is absorbed by plants via the roots from soil as sulfate ion and reduced to sulfide before it is incorporated into cysteine and other organic sulfur compounds. Sulfur is regarded as a secondary nutrient although plant requirements for sulfur are equal to and sometimes exceed those for phosphorus. However sulfur is recognized as one of the major nutrients essential for growth, root nodule formation of legumes and plants protection mechanisms. Like nitrogen, carbon and phosphorus, sulfur passes through the gaseous, liquid, and solid parts of the planet in a series of continuous reactions known as the sulfur cycle. When plants and animals die, sulfur is returned to the soil where it is converted by microorganisms into hydrogen sulfide. Hydrogen sulfide gas is then emitted to the atmosphere where it is oxidized to sulfuric acid [1-7].

1.3. Forms of sulfur in coal

1.3.1. Total sulfur

The total sulfur is the sum of all forms of sulfur encountered in coal. They are influenced by many factors such as parent plant which generated coal, the rocks and minerals involved in coal formation and coal basin. There are several methods for determination of the total sulfur in coal; the main method has been explained in the next chapter. The determination of the forms of sulfur allows the verification of the total sulfur in all coal samples and provides information on sulfur species. The amount of the total sulfur should be consistent with the sum of sulfur in various forms investigated. Total sulfur content in coal varies from 0.3 up to 15% by weight according to the rank and the genesis of coal. For instance, the average sulfur content of South African coal is generally less than or equal to 1% by weight. Many researches have reported that the total sulfur in coal ranges from 0.59-9.45%. In some other cases the different contents of total sulfur reported in a range of 5.4-15.1 %. The average amount of total sulfur in Tabas coal resource in Iran which has been reported by Jorjani et al. and other researchers is about 1-4.3 % [32-44].

1.3.2. Elemental sulfur

Sulfur as an element is more reactive than oxygen. It can react with itself to form -S-S-bonds and it is photosensitive. Elemental sulfur contains a variety of allotropic forms of sulfur as elements. Many allotropic forms can be attributed to sulfur but the most important are rhombic and monoclinic.

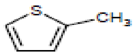
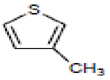
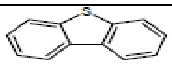
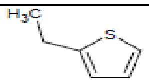
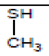
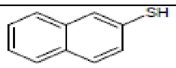
Natural sources of elemental sulfur are mainly volcanic eruptions, evaporation from water, bacterial processes and decaying. In coal, elemental sulfur is mainly due to decaying organisms and bacterial process.

Gryglewicz et al. have quantified the elemental sulfur in coal samples after extraction using cyclohexane on Soxhlet apparatus and subsequent quantitative analysis on Gas chromatograph-Mass spectrometer (GC/MS), 0.111 % of elemental sulfur was obtained [33].

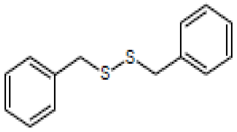
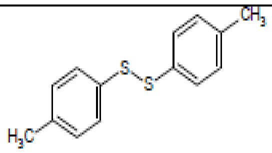
1.3.3. Organic sulfur

Organic sulfur species present in coal depend upon the degree of biochemical change of peat (accumulation of partially decayed vegetation matter), the temperature, pressure and the mineral forms involved in the coal formation [34,35]. Organic sulfur compounds are generally grouped into thiophenes, mercaptans and sulfides. Table (1.2) shows the major organic sulfur compounds encountered in coal. Thiophene forms are almost well known than other forms [34,36,37]. Some organic sulfur compounds are also formed during condensation, rearranging and concerted reactions during coalification. Others are also formed as a result of biochemical reactions in living systems and the conversion between organic sulfur forms is mainly due to microorganisms [38, 39]. Beside those occurrences, some complex sulfur compounds are formed at the surface of metals when coal is leached. These sulfur compounds form the layers called self-assembled compounds which can be mono or multi-layers [19,40]. Microbes in coal can degrade some organic sulfur compounds such as di-benzothiophene to sulfate. An example of this is Thiobacillus, Sulfolobus, Acinobacter and Pseudomonas CB1 that can remove about 25 % of both inorganic and organic sulfur compounds [11]. These kinds of microbes can be used to remediate coal as part of biotechnology now seen as clean environmental technology. The sulfur compounds in coal are generally transformed from one form to the other during coal processing. Such conversions results in the production of sulfur dioxide responsible for acid rain and global warming. The number and abundance of cyclic organic sulfur compounds increases with the maturity level of coal while the aliphatic sulfide and mercaptan forms decrease [34]. All types of organic sulfur compounds can be identified in coals but their abundance differs from one coal to another. For example, the percentage composition of the organic sulfur in USA coal have respectively determined from 0.46-4.3 % and 2.7- 12.2 % [41].

Table (1.2). Main organic sulfur forms in coal [34]

Organic Sulfur form	**Sulphur compound**	**Structure**	**Physical properties (°C)**		**Bond dissociation energies (kJmol^{-1})**	
			MP	**BP**	**C-S**	**S-S**
Thiophene	2-Methyl thiophene		-63	113		
	3-Methyl thiophene		-69	114		
	Dibenzothiophene		97	332	309	
	2-Ethyl thiophene			133		
Sulfide	Dibenzyl sulfide		49		258.2	
Mercaptan	Methylthiol	 $\begin{array}{c} SH \\ \vert \\ CH_3 \end{array}$	-123	5.95		
	2-Naphthalene thiol		80-81	92-94	297.7	

Table(1.2). **Main organic sulfur forms in coal (continued)[34]**

Organic Sulfur form	Sulphur compound	Structure	Physical properties (°C)		Bond dissociation energies ($kJmol^{-1}$)	
			MP	BP	C-S	S-S
Disulfide	Dibenzyl disulfide		70	270	266.8	277.9
	p-tolyl disulfide		45	350	311.8	275.8

1.3.4. Inorganic sulfur

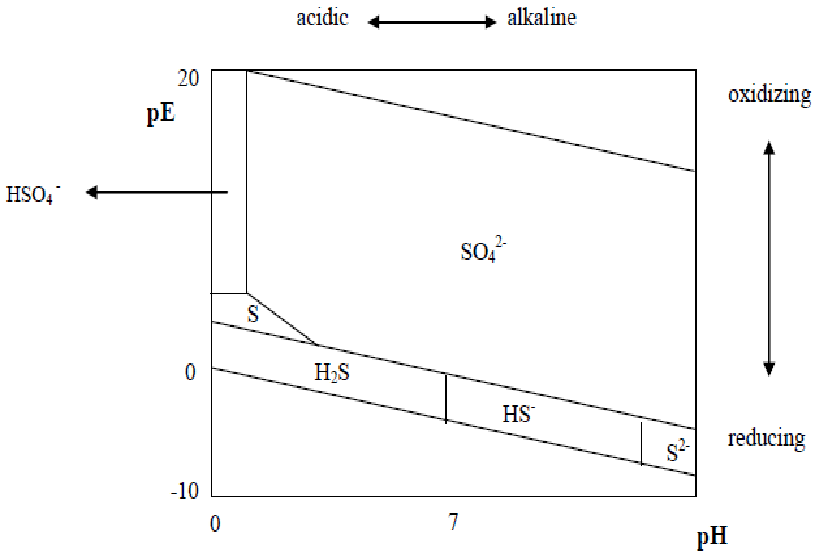
Inorganic compounds constitute the major ash content in coal. They are intimately mixed with organic compounds in their matrix. They are also the sources of carbon dioxide and sulfur dioxide emitted during coal processing and usage. Pyritic, sulfate and silicate forms are the main inorganic sulfur forms encountered in coal. They are almost well defined compared to organic forms [34]. In any studies of organic sulfur compounds in coal, inorganic forms are also determined [35,42,43].

This is because of the inter relationships between various sulfur forms and to set a complete picture. Inorganic sulfur forms are mainly determined in coals as sulfate and pyritic forms. Sulfate form can be more abundant than pyrite or vice versa according to coal genesis and properties. A study of organic sulfur compounds in coals[41] found 1.5 % of sulfate sulfur and 3.9 % of pyritic sulfur [41]. In Iran the contents of sulfate sulfur in non –oxidized coals is negligible.

In addition of all mentioned above, it can be noticed that some coal seams may contain small quantities of Sphalerite (ZnS), Galena (PbS) and Chalcopyrite ($FeCuS_2$) in particular if hydrothermal vein are close to the coal seam. Bacterial activity has a vital role to play in peats and organic muds by reducing sulfates to sulfur, making the formation of pyrite and marcasite possible. It has been shown that FeS_2 can only be formed in peats from bacterial activity since from basic reaction kinetics, it has been shown that there is insufficient energy available for a purely chemical reduction of sulfates to disulfides, providing, of course that there is a sufficient supply of sulfur and iron [42]. The variation in sulfur content depends largely on geological conditions, with the sulfur available during plant growth, which is the principle source of sulfur in low-sulfur coals (<1 %). In contrast in medium (1-3% total sulfur) and high sulfur (>3% total sulfur) coal overlain by a marine environment, most of the sulfur is derived from seawater sulfate [44,45].

1.4. Environmental effects of sulfur compounds in coal

The information of abundance, distribution and origin of sulfur in coal is important in coal combustion due to the adverse effect of sulfur oxide emission on human health and of course for the environment. Coal burnt by industry and power plants generates sulfur dioxide (SO_2) which reacts with atmospheric water and oxygen to produce sulfuric acid (H_2SO_4). Sulfuric acid is a component of acid rain, which lowers the pH of soil and freshwater bodies, sometimes resulting in substantial damage to the environment and chemical weathering of statues and structures. The oxidation of pyrite and other reduced-sulfur minerals that occur in coal and metal mines and their wastes can cause the acidification of surface water or groundwater. Therefore metals can be liberated from their ores and be more available. This increases their toxicity which enhances the possibility of metals entering the food chain. Lime addition can allow the control of pH (by neutralization for example) [46]. Equations (1-3 to 1-6) show the generation of Acid Mine Drainage (AMD). More protons (H^+) are created and induce the acidification of water enabling the leaching of metals. The speciation of sulfur in the whole sulfur content system is dependent upon many parameters. To ease the understanding of sulfur species occurrence, the Pourbaix diagram of sulfur species in water is used. This gives boundaries between species according to the environmental conditions. The Pourbaix diagram (Fig (1.6)) shows the dominating species at equilibrium in different redox potential and acidity. Whereas the pH (x-axis) measures the relative acidity (or hydrogen ion concentration [H^+]) of a solution, the redox potential (E in volt; y-axis) is a measure of the tendency to accept or release electrons.



Fig(1.6). Pourbaix diagram of sulfur species in water [47].

An increase in oxygen pressure means higher oxidizing ability (or higher redox potential) of the system [47]. At very reducing conditions or in the absence of oxygen, the elemental sulfur is the most stable sulfur form. It will therefore be the most predominant, but if iron ions are present, they will form pyrite which might coexist with elemental sulfur. At very aerated condition, toward the surface of water, sulfur does exist in its oxidized forms and compounds in which sulfur has its highest oxidation stage. These forms are more stable and therefore likely to occur in that region.

On the other hand, the more protonated the sulfur ion is, the more acidic is the compound. Thus it is most stable and likely to occur at lower pH. This is justified by the occurrence of H_2S, HS^- and S^{2-} in various regions on the diagram shown in Fig (1.6). Organic sulfur compounds might also be stable in some of the conditions above depending on the oxidation state of sulfur they contain. However, their acidity is relatively low because of the weak or absence of H-S bond apart from mercaptans. Equations responsible for AMD generation are summarized below.

$$2FeS_2+7O_2+2H_2O\rightarrow 2Fe^{2+}+4SO_4^{2-}+4H^+ \quad \text{Eq (1-3)}$$

$$4Fe^{2+}+O_2+4H^+\rightarrow 4Fe^{3+}+2H_2O \quad \text{Eq.(1-4)}$$

$$4Fe^{3+}+12H_2O\rightarrow 4Fe(OH)_3+12H^+ \quad \text{Eq.(1-5)}$$

$$FeS_2+14Fe^{3+}+8H_2O\rightarrow 15Fe^{2+}+2SO4^{2-}+16H^+ \quad \text{Eq.(1-6)}$$

The release of protons in AMD creates massive leaching of metals which will then affect the environment. Sulfuric acid generated due to oxidation of FeS2 results into Acid Rain Drainage (ARD). The acidic environment results into possible mobilization of metals. In the stratosphere, photochemical oxidation mostly produces sulfur dioxide as do volcanic activity, and ultimately sulfate anion, which is an important component of the stratospheric aerosol. Sulfur compounds in the stratosphere take part in other chemical processes having various environmental consequences [48].

1.5. Study about the sulfur forms in coal in recent years

Coal is the most important non-renewable energy source of fossil origin. It is also the most common fuel in thermal power plants. In recent years, with the rising prices of crude oil and natural gas and shortage of oil and gas resources, worldwide energy industries have been focusing on accelerating the development of coal industry. The coal industry can make a significant contribution in the sustainable development of some countries energy resources in the next twenty years, and will thereby take extra efforts to reduce environmental pollution caused by coal burning. It will also reduce dependency on oil and gas as energy sources [49].

Coal usually contains significant quantities (normally more than 10%) of different impurities such as sulfur, silicates, carbonates, sulfates, (heavy) metal ions, etc. Focusing on sulfur, harmful effects on agricultural products, corrosion of metal structures and respiratory problems of humans and animals are undesirable effects of sulfur and its compounds in coal. Therefore, it is essential to reduce sulfur and mineral matter (ash: f.i. pyrite, sulfates,..) from coal prior to usage in many applications. The main reason is that during coal incineration in power plants, high sulfur content of coal poses serious environmental problems owing to sulfur dioxide emission. Combustion of fossil fuels such as coal in thermal power plants releases SO_2, which is formed by oxidation of sulfur present in coal. Oxides of sulfur undergo photochemical oxidation in the atmosphere, to be eventually converted into sulfuric acid. The acids when washed by rain make the rainwater acidic. Total worldwide SO_2 emissions from coal utilization are 90 million ton/year [49].

Combustion of coal produces pollutants (SO_x and NO_x) in addition to particulate matter. It causes acid rain which has harmful effects on buildings, lakes and vegetation, and cause corrosion. ''S'' reduces heating value of coal. Sulfur is removed to sell coal to customers whether they have installed pollution control measures or not, to reduce transportation and combustion cost, and also to reduce load on flue gas scrubber [49].

Methods to control SO_2 emissions may be classified as [49]:

- Desulfurization of coal prior to combustion (Physical, Chemical, Microbial).
- The removal of sulfur oxides during combustion.
- The removal of sulfur oxides after combustion.
- Conversion of coal to a clean fuel by gasification and liquefaction.

Demineralization and desulfurization of coal may be achieved by both physical and chemical methods. Physical processes are cost effective methods but not effective in separation of the finely dispersed minerals and those bound to the coal structure. However, chemical method is known as being the solution for obtaining clean demineralized and desulfurized coal, which involves solubilization of inorganic constituents in various solvents. As it has been stated, the sulfur present in coal appears in pyritic, organic and sulfate forms. The organic and pyritic sulfur contents are almost equally partitioned in many coals and the sulfate form is usually very small. Organic sulfur is fixed in the chemical structure of coal and often much more difficult to remove than inorganic sulfur. Organic sulfur is partially removed by breaking its chemical bonds using chemical and biochemical methods. Coal desulfurization prior to usage is a preprocessing in order to achieve clean fuel and reduce environmental impacts such as acid rain [49]. The structural model of hard coal illustrated in Fig (1.7).

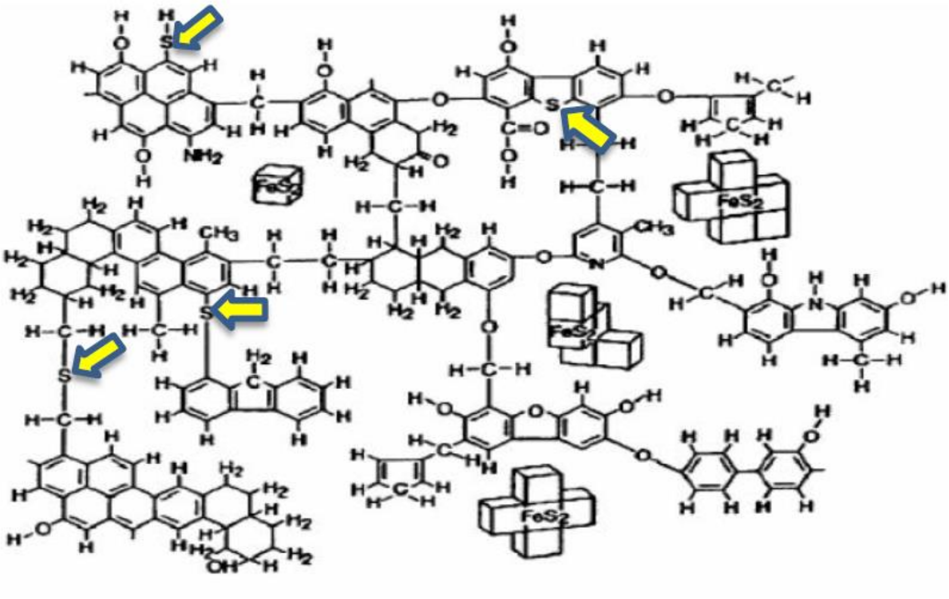


Fig (1.7). Chemical structure of hard coal [49]

Coal is the mineral rock of organic origin characterized by highly complex structure [49], which has been a subject of interest of many authors.

Studies of the coal structure have been performed with many different methods including the classical chemical ones, physical and physico-chemical ones. One of the most often used methods is based on the reaction of coal oxidation. The coal ability to react with oxygen is also of great practical importance as the process of oxidation significantly changes certain technological characteristics of coal reducing its worth as heat producing material and industrial product. The reaction of coal oxidation can be conducted either in the dry phase [50-52] or in aqueous media [53,54]. From the point of view of structural investigation, the oxidation should be performed in mild conditions. In recent years much attention has been given to the sulfur compounds contained in coals. Their identification and determination of their transformations in different processes is of great importance from the point of view of the natural environment protection [55]. Quantitative and qualitative analysis of inorganic sulfur is not too difficult and there are normalized conventional methods for its determination. Unfortunately, analysis of organic sulfur species is much more complex. Many methods have been proposed for this purpose, and the majority of them are discussed in the review works by Davidson [56], Calkins [57], Stock et al.[58], and in some recent papers. The most often used are: X-ray absorption near-edge structure [59,60], X-ray photoelectron spectroscopy [61,62], temperature-programmed oxidation [63,64], temperature-programmed pyrolysis [65], flash pyrolysis [66], temperature-programmed reduction (TPR)[67], its atmospheric-pressure (AP–TPR)[68] and high-pressure variants (HP-TPR)[69]. The more conventional methods include: stepwise oxidation of sulfur groups with $HClO_4$ [70,71] and reaction of coal with HI [72] (quantitative thiol determination). The effect of oxidation on sulfur groups has also been studied by IR spectroscopy [73]. Comprehensive analysis of the above literature data proves that the methods proposed are not perfect and at present there is no method, which would permit true and verifiable quantitative determination of particular species of organic sulfur.

Kozłowski et al. have studied two types of high-sulfur coals Mequinenza and Illinois No. 6, in their initial form and subjected to potassium/liquid ammonia reduction. They were further analyzed by atmospheric pressure–temperature programmed reduction (AP–TPR) method. This research showed that preliminary demineralization was beneficial for AP–TPR measurements because of the removal of calcium compounds. Furthermore, it has been shown that the coal reduction in the potassium/liquid ammonia system apart from transformations of non-thiophene sulfur groups also leads to breaking up of the C–S bonds in some thiophene systems [74].

AP-TPR and its analogous in oxidative atmosphere coupled “on-line“ with a mass spectrometer (MS) were used to study the behavior of organic sulfur forms of Mequinenza lignite during their mild steam pyrolysis by Marinov et al. [75]. Lastly the obtained data were confirmed and completed by the AP-TPR-GC/MS “off-line” analysis. The experiment performed at 500 °C in water vapor flow proved that the C–S bond splitting in di-benzothiophene results in biphenyl formation. Reductive pyrolysis of sulfur compounds in different Tabas coal samples have been investigated by Jorjani et al. [76]. In that study the presence of CH fragments on gases emitted during AP-TPR investigation of demineralized and demineralized pyrite-free samples, shows evidence for the formation of shorter CH chains and of poly-aromatic compounds, and lower molecular weight material in the demineralization and pyritic sulfur removal stages.

Reductive pyrolysis of Miocene-aged lignite lithotypes using MS and GC/MS detection systems just for the detection of organic sulfur groups have been researched and investigated by Stefanova et al.[77].

The effects of temperature and atmospheres on sulfur transformation during pyrolysis of Zunyi (ZY) raw coal and chars by AP-TPR-MS combined with chemical analysis have been considered by Fenrong Liu et al. [78]. The results show that stable organic sulfur is the main sulfur form in ZY coal. Pyrite can be removed under all the atmospheres in the tests, except for nitrogen at 500ºC. 1% O_2-N_2 atmosphere has strong ability to remove the stable organic sulfur in ZY coal, especially at 700 ºC. Under 1% O_2-N_2 atmosphere, not only a part of stable organic sulfurs can be decomposed, but also more stable organic sulfur-containing structure can be broken down into less stable one.

Reviewing and investigating about sulfate transformation during pyrolysis of Australian lignite have been performed by Yani and Zhang [79]. The transformation of sulfate minerals during pyrolysis of Australian lignite has been studied using pure sulfates ($CaSO_4$, $FeSO_4$ and $Fe_2(SO_4)_3$), a high mineral (HM) lignite sample and a low mineral (LM) lignite sample collected from different locations of the same deposit, and samples of acid-washed LM doped with sulfates. In this research the "TGA" experiments showed that $CaSO_4$ decomposes between 1400 and 1700 K in nitrogen and a 50/50 N_2/CO_2 mixture, while in air $CaSO_4$ decomposes between 1500 and 1700 K. Using a "TGA–MS" it was found that only a small fraction of CaSO4 in $CaSO_4$+LM decomposed at 653 K, releasing SO_2. $CaSO_4$ was still observed in the char recovered at 1073 K as confirmed by the FTIR and XRD analysis. $FeSO_4 \cdot 7H_2O$ released the bound water below 543 K and the remaining $FeSO_4$ decomposed between 813 and 953 K. $FeSO_4$ in $FeSO_4$+LM decomposed at 500 K to release SO_2. Lastly, the investigation showed that $FeSO_4$+LM produced more volatile sulfur than $CaSO_4$+LM during pyrolysis.

Combustion behavior of some bio-desulfurized coal assessed by thermo-gravimetry and differential thermal analyses has been considered by Marinov et al [80]. The results of this experiment for one lignite and two subbituminous coal samples from different region of "Bulgaria" showed that the differences in burning profiles can be related to structural changes resulted from biological treatments. Also well determined decrease of self-heating temperature after bio-treatments evolves high risk of spontaneous unmanageable coal combustion.

1.6. Recent studies about desulfurization assisted by irradiation on coal

Some ash minerals within coal readily heat within an applied electric field, (pyrite has an average heating rate of 1.0 ° C/s when exposed to a microwave field at a power of 650W and frequency of 2.45GHz) whilst others appear transparent to the radiation (quartz has an average heating rate of 0.08 ° C/s when exposed to a microwave field at a power of 650W and frequency of 2.45GHz) [81]. Whilst the organic components of coals are relatively poor absorbers of microwave energy, [82] coals naturally contain water in varying degrees depending upon rank, microstructure and geological location. Water is considered as a good absorber of microwave energy, at a frequency of 2.45GHz, and at an applied power of 650W coal's average heating rate has been calculated at 0.52 ° C/s. Water molecules are polar, when exposed to an alternating electric field; the molecules position themselves in the direction and at the same frequency to that of the applied field [83] (Fig.(1.8)).

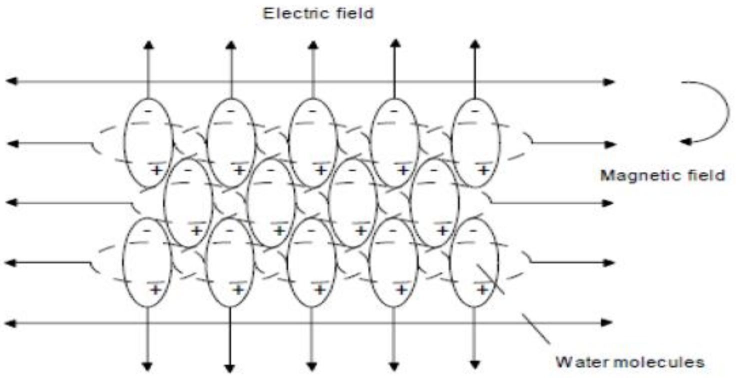


Fig (1.8). Realignment of polar molecules in an electric field giving rapid heating [79]

This movement produces frictional heating. When a coal is exposed to microwave energy; water will heat, change phase and expand creating internal pressures within the coal matrix. Further embrittlement would be expected due to the differential expansion rates of gangue minerals found in coals [84]. The extent to what this happens depends on the minerals dielectric constant, the quantity of mineral, and the position within the coals structure. Scanning electron micrograph images of irradiated Kiverton coal show that fractures occur (Fig.(1.9)). Similar fractures could not be found on untreated samples within this study.

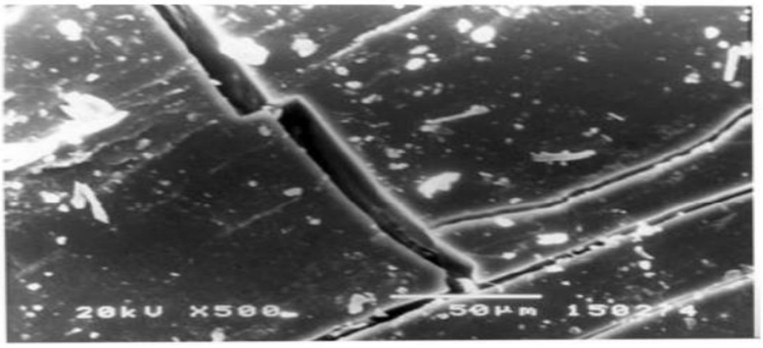


Fig (1.9). SEM micrograph image of irradiated Kiverton coal and its fractures [81]

Sound waves having frequencies higher than those to which the human ear can respond (about 16 kHz) are called ultrasound. Ultrasound in the range of 20 to 100 kHz produces high energy waves sometimes referred to as power ultrasound. Power ultrasound is used for a variety of purposes including: cleaning, welding, rupturing cell walls in biochemistry studies, and dispersing solids in liquids. Power ultrasound produces effects via cavitation bubbles. When power ultrasound is applied to a liquid in sufficient intensity, the liquid is alternately compressed and expanded forming bubbles. When power ultrasound is applied to a mixture of particles and liquid and the bubbles collapse near a solid surface, a high-speed jet of liquid is driven into the particles and this jet can deposit enormous energy densities at the site of impact. Cavitation tends to occur preferentially along gas-filled crevices in particles, creating the conditions necessary for a violent cavitation event termed "transient cavitation". The interfaces that exist where mineral matter is attached to coal are potential sites for transient cavitation and this focused application of energy can selectively break the bonds between the mineral matter and the coal. In addition, cavitation on the surface of the coal particles removes clay, water gel, and any products of oxidation [85].

The feasibility of using ultrasound to enhance the performance of de-sulfurization and de-ashing during slime flotation have been studied by Kang Wen-ze et al.[86]. The results showed that after ultrasonic conditioning the hydrophobicity of coal and hydrophilicity of pyrite increased. This research indicated that the ultrasonic conditioning can enhance the performance of de-sulfurization and de-ashing of coal flotation methods.

The mechanisms of ultrasound irradiation effects on coal flotation have been investigated by Ozkan and Kuyumcu [87]. The experiments were carried out in ultrasonically assisted flotation cells. The results showed that ultrasonic coal flotation yields more combustible recovery and lower ash values in concentrates than conventional flotation by using similar reagent dosages.

The effects of High-Power ultrasonic treatment on slurry-ability of coals have been investigated by Guang-Wen et al.[88]. Ultrasonic treatment can decrease the adsorbed water of complex coal granules, so free water is increased, which makes the apparent viscosity increase and, hence, slurry-ability improves.

Ambedkar et al. [89], have performed a research under title “Ultrasonic coal-wash for desulfurization”. The results showed that ultrasound in aqueous medium produces OH, H_2O_2, HO_2, O_2, and ozone, which are strong oxidizing agents. The oxidation occurring in presence of ultrasound is called “advanced oxidation process”, and this converts the sulfur present in the coal to water-soluble sulfates. In almost all cases, sulfate-sulfur removal is more than 90%, as observed in aqueous-based ultrasonic desulfurization. Furthermore in this study researchers found that, solvent-based ultrasonic desulfurization results in highest removal within a short period of treatment time, at low solvent concentration and with less solvent consumption compared to conventional methods. Also sonication accelerates the solvent-based reaction; this has been confirmed by increased removal of sulfur and significant temperature rise in the reaction mixture within a short span of time. Meanwhile, it should be noted that in an ultrasonic field, the reaction between H_2O_2 and sulfur is very fast, and the temperature rise in the reaction mixture within 4 minutes of treatment is 90 °C. Due to fast reaction and high sulfur removal, low solvent concentration and lack of by-products, hydrogen peroxide seems to be the most suitable solvent for ultrasonic desulfurization.

A novel method for chemical desulfurization of coal in relatively moderate conditions and short times has been proposed by M.Andres et al. [90]. In this method, a concentrated hydro-iodic acid has been used as a desulfurizing agent and microwaves as the energy source. The results showed that different microwave power did not show any singular effect of the microwave irradiation on the removal of sulfur.

The chemical desulfurization process in combination with HI as reagent for leaching and microwave irradiation, have been considered by Elsamak et al.[91]. The purpose of this research was to investigate the effect of the concentration of HI and reaction time in the chemical desulfurization of Cayirhan lignite in a microwave energy set up and to compare the results with those obtained in a thermal heating system.They also considered the rapidity of desulfurization reactions with microwave heating in concentrated HI which was probably due to localized superheating which made HI more effective in reactions such as with thioethers and thiols that normally resisted to cleavage by HI under heating conditions.

Semra has studied the desulfurization of a Turkish lignite at various gas atmosphere by pyrolysis. This investigation followed the removal of pyritic and organic sulfur by pyrolysis at ambient pressure of a Turkish lignite under nitrogen and carbon dioxide atmospheres and the effect of mineral matter on the sulfur removal in pyrolysis of HCl and HCl/HF-treated coal under carbon dioxide atmosphere. Results obtained, indicated that both pyritic and organic sulfur removal increased with increasing pyrolysis temperature [92].

The effects of different Ca-based additives on sulfur removal of coal during pyrolysis up to 900°C in the fixed-bed reactor have been considered by Guan et al. [93]. It was found that $Ca(OH)_2$ and CaO were quite effective to capture the sulfur-containing gases, 95% of the sulfur evolved from untreated coal was retained in the char by the use of additives. Furthermore, there is remarkable sulfur retention effect with $Ca(OH)_2$ prepared by impregnation and ultrasonic treatment due to the higher dispersion in coal particles than by simple mechanical mixing. The results of that study showed that ultrasonic treatment is the best method with regard to the lowest SO_2 release during the char combustion.

Krittika Charutawai et al. [94] researched: "supercritical desulfurization of low rank coal with ethanol/KOH". Desulfurization of samples was studied with mentioned reagents in semi-continuous reactor. The variables investigated in this work were temperature, pressure, time and potassium hydroxide concentration. The analysis of the results from the design showed that two variables, temperature and KOH concentration, can be considered to have a significant effect on the pyritic sulfur and total sulfur reduction.

The role of oxidation pre-treatment for enhancing desulfurization of coal with sodium butoxide have been studied by Jorjani et al. [95]. The results show that peroxy-acetic acid +air oxidation pre-treatment can be used as an effective method for enhancing the removal of organic and inorganic sulfur without severe dissolution of the coal organic matrix.

The role of microwave irradiation along with peroxyacetic acid washing at three different temperatures for Tabas coal have been investigated by Jorjani et al.[96]. The results prove that this method can use as secure process on removal of inorganic and organic sulfur without destruction of coal organic matrix.

The study on desulfurization of Mezino coal using combination of flotation and leaching with potassium hydroxide/Methanol have been proposed by Abdollahy et al. [97]. Using the combination of the two mentioned methods, the total sulfur and ash contents of coal were reduced by 82.50 and 82.34%, respectively. It is an unprecedented and welcome result compared to the previous work.

The research of coal pyrolysis under synthesis gas, hydrogen and nitrogen have been considered by Ariunaa et al. [98]. The results showed the possibility of using synthesis gas instead of pure hydrogen as the reactive gas for coal hydro-pyrolysis. On the other hand, results showed that the pyrite "S" can be easily removed and partially converted to organic "S" under various gaseous atmospheres.

The influence of process parameters on desulfurization of Mezino coal by HNO_3/HCL leaching have been investigated by Alam et al. [99]. Results of this research showed that nitric acid is much more effective than HCl and the effects of reaction time, acid concentration and temperatures as well as stirring speed were studied as major parameters in the nitric leaching process. The findings indicated that acid concentration, with a high contribution, had the most dominant effect on desulfurization performance, followed by temperature, stirring speed and time.

An extremely rapid, convenient and mild coal new desulfurization process which is called sodium boro-hydride reduction and have been proposed by Zhiling et al. [100]. The results of this research showed that the total sulfur removal improved with the increase in the concentration of $NaBH_4$. Moreover, the increase in the calorific values by 3.4–6.9% and the decrease in the ignition temperatures by 2–21 °C for the coal samples were reported. The desulfurization method that was described is extremely rapid, convenient, inexpensive and mild, and therefore, has considerable technological interest.

1.7. Coal in Iran

The coal resources in Iran have been distributed in 100 kilometers square in three zones which are called Kerman, Alborz and Tabas. The probabilistic and exact resource amounts for these three zones are 314, 944 and 713 million tons respectively.

Most of the Iran’s coal has low to average percentage of sulfur. However, the Tabas coal in all layers has a relatively high percentage of sulfur amounts. According to the designed coal washing plant of Tabas, the output coal from the mine, after cleaning with heavy media and flotation, has 9% moisture, 10.5% ash, 30% volatile matter, 1.7% sulfur and 0.03% phosphorus. The studies also showed that the amount of sulfur in concentrate is more than tailing and feed of plant. This causes the distribution of sulfur in coal’s macerals and being syn-genetic pyrite in coal. The flow sheet of Tabas cleaning coal plant is shown below in Fig (1.10).

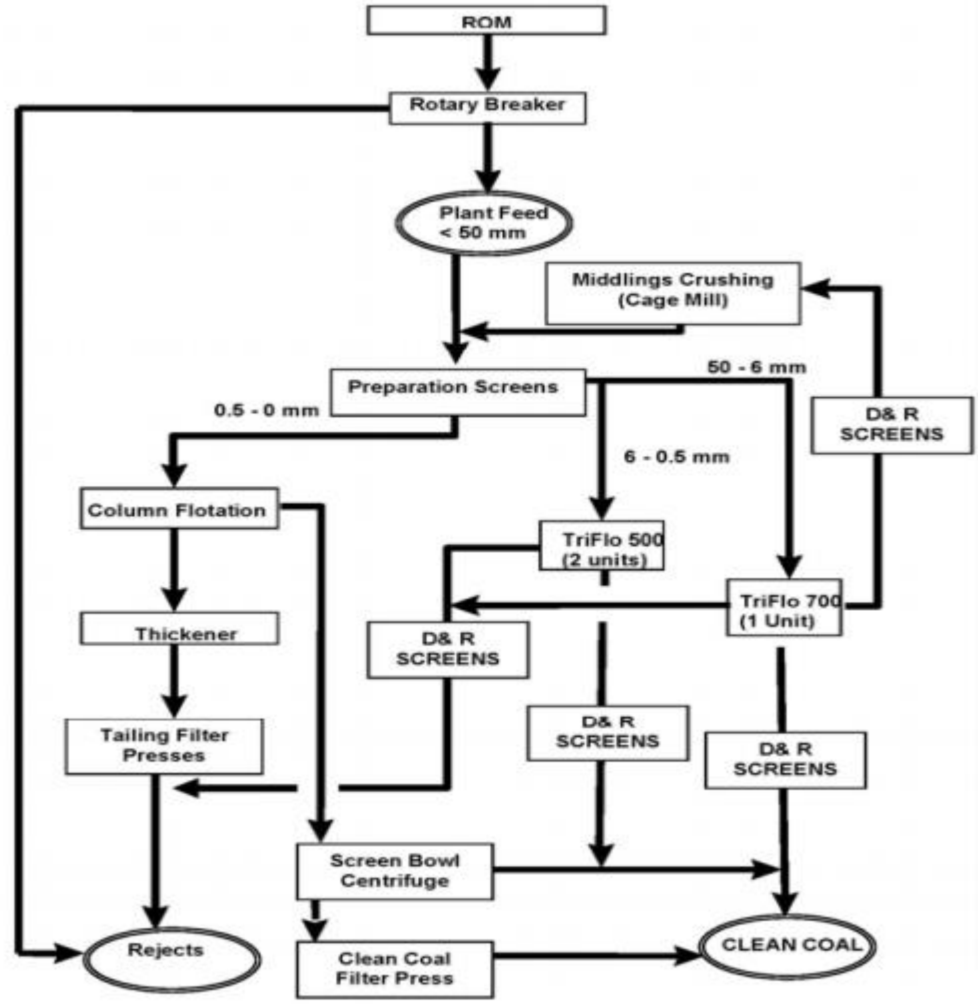


Fig (1.10). Tabas coal preparation plant schematic diagram.

It is obvious that high sulfur coal induces a number of unpleasant and also serious impediments which are related with environmental pollution and technological problems.

Some disadvantages of sulfur in coal can be classified as follows:

- Sulfur deposition in iron furnace and this cause brittleness and fragility of steel.
- Fake increase of coal plastometry.
- Decrease the calorific value of coal.

- Cause environmental pollution during the process of making coke or burning coal.
- Cause the fake increase of the weight and thereafter increasing the transportation cost.
- Sulfur limit use for steel plant is less than 1 per cent, so the concentrate of Tabas cleaning coal plant should be blend with other low sulfur resources and this procedure is not economical. So the cost and value of coal is reduced.

1.8. Summarizing the state of the art

Based on the studies regarding the qualitative and quantitative determination of sulfur in samples which were prepared from Tabas coals, indicated that pyrite as discrete particles, placed into the fractures as a filler (in a regular and irregular forms), which are generally between 1 to 30 microns in size and it is concentrated in macerals and lithotypes of coal. These studies showed that, removal of fine pyrite sulfur and organic sulfur (resistant sulfur such as thiophene) is impossible with conventional desulphurization methods. Therefore the use of non-conventional methods as chemical and microbial sulfur removing is suggested.

The present review on coal irradiation and its effects on coal matrix and also coal sulfur functionalities (qualitatively and quantitatively) indicates that the research in this field is rather limited and more investigation is needed. In the case of coal irradiation some cases are regarding to grinding and drying of coal and the effects of irradiation on those processes are studied. On the other hand, the other investigations are limited to optimization of irradiation conditions in order to increase the effect of pretreatment on desulfurization process and its quantification.

Of course, studies on the organic sulfur transformation after irradiation in different conditions are not available as well. In addition, there are no comprehensive data of probable effects of irradiation on coal matrix and sulfur functionalities.

All above mentioned are partly related to the limitation of the analytical techniques used for coal organic matter characterization and especially for coal organic sulfur forms investigations.

It is believed that by upgrading the available analytical techniques for coal characteristics for determination of sulfur forms (organic and inorganic) an important achievement in this area could be reached. On the other hand, it is believed that more deep knowledge in organic sulfur transformation and the coal matrix after irradiation can give better understanding for upstream chemical desulfurization of Tabas coal. It will bring greater success in desulfurization after irradiation.

1.9. The aims of the work

The main goal of the present study is tracing the probable changes which happened by means of irradiation (microwave and ultrasound) on coal matrix and organic sulfur species, (qualitatively and quantitatively) and their impacts on chemical desulfurization by peroxyacetic acid in optimum conditions. To achieve this purpose the following tasks are specified using AP-TPR method and can be categorized as the present work's novelties:

a- Evaluation of effects of microwave treatment on high sulfur Tabas coal and its probable changes occurred during irradiation on sulfur functionalities, and coal matrix, qualitatively and quantitatively.

b- Investigation of positive or negative effects of microwave irradiation on chemical sulfur removal followed by irradiation with peroxyacetic acid (PAA).

c- Assessment of probable influences of sonication at different times settings on high sulfur Tabas coal structure and sulfur functionalities, qualitatively and quantitatively.

d- Evaluation of positive/negative effects of ultrasound irradiation on sulfur removal followed by irradiation with peroxyacetic acid (PAA).

1.8 References

[1] Trevor major, Genesis and the origin of coal and oil, second edition, 1996.

[2] Williamson, Iain A. *Coal Mining Geology* (London: Oxford University Press), 1967.

[3] Schofield, J.C., The Late Mobile Phase: Tertiary; Stratigraphy: Auckland, South Auckland, & Coromandel Range, *The Geology of New Zealand*, ed. by R.P. Suggate (Wellington, New Zealand: E.C. Keating), 1978, 2:p.449-456.

[4] P. Schweinfurth, an introduction of coal quality, Chapter C of The National Coal Resource assessment overview edited by Brenda S. Pierce and Kristin O. Dennen,2009.

[5] Finkelman, R.B., and Brown, R.D., 1991, Coal as a host and as an indicator of mineral resources, *in* Peters, C.C., ed., Geology in coal resource utilization: Fairfax, Va., Tech Books, p. 471–481.

[6] National Mining Association, 1999, Facts about coal 1997–98: Washington, D.C., National Mining Association, 84 p.

[7] American Society for Testing and Materials, 1999, Coal and coke, *in* Annual book of ASTM standards, section 5, Petroleum products, lubricants, and fossil fuels, v. 05.05, Gaseous fuels; Coal and coke: Philadelphia, Pa., American Society for Testing and Materials, p. 155–584.

[8] Kroschwitz, J.I. and Grant, M.H. (1993). Encyclopaedia of Chemical Technology, 4th ed, Separation Science. Chlorocarbons to Combustion Technology. John Wiley and Sons, inc, USA, p.423-539.

[9] Kalyoncu, Rustu, 1999, Coal combustion products: U.S. Geological Survey Mineral Industry Surveys, 1998 Annual Review, 19 p.

[10] Selsbo, P. Almen, P. and Ericsson, I. (1996). Quantitative analysis of sulfur in coal by pyrolysis-gas chromatography and multivariate data analysis, Energy& Fuels 10, p. 751-756.

[11] Baird, C. (1995). Environmental chemistry, W.H. Freeman and company, p.91-95.

[12] Bartok, W. and Sarofim, A.F. (1991). Fossil fuel Combustion, John Wiley Sons, inc. USA, p.693-710.

[13] Glassman, I., (1987). Combustion, Academic Press, inc, 2nd ed., p.355-357.

[14] South African Mining and Metallurgy (2000). Coal the future, 12th international conference on coal research, symposium series S26, Sept, Sandton, RSA, p.171-176, 203-244.

[15] Asamoah, J. K. (2006). Requirements for a sustainable growth of the natural gas industry in South Africa, Doctor of philosophy in Engineering, University of Witwatersrand, Johannesburg, p. 217.

[16] Valkovic, V. (1983). Trace elements in coal, Vol II, CRC Press, Inc. USA, p. 27-74,103-120,181,203.

[17] Ohki, A. Nakajima, T. Yamashita, H. Iwashita, A. and Takanashi, H. (2004). Leaching of various metals from coal into aqueous solutions containing an acid or a chelating agent. Fuel Processing Technology 85, p.1089–1102.

[18] Hirinchs, R.A. and Merlin, K. (2012), Energy. Its use and the environment, 5th Ed. Thompson Learning, inc, USA, p. 200, 220-255.

[19] Wilson, I.D. Adlard E.R. Cooke M and Poole C.F. (2000). Encyclopaedia of Separation Science, Vol 9. III Pro-Zon, Academic Press, Canada, p. 4414- 4476.

[20] Kgaugelo, E.C. (2004). Volatile organic compounds analysis from Cape Town brown haze II study, Master of Science Dissertation, University of Witwatersrand, Johannesburg, South Africa, p.9, 18-20.

[21] Sipone, J.D. (2005). Spontaneous combustion of coal: Mobilisation of chemical elements and condensation by-product, Master of Science Dissertation, University of Witwatersrand, Johannesburg, South Africa, p. 19- 30, 38-45, 74-77.

[22] Batyko, R. J. Nolan, P.S. Telesz, R.W. (1991). Available technologies for SO2 control furnace to stack. American Society of Mechanical Engineers (Paper) New York, USA, p. 1–5.

[23] Nelson, S.J. and Zhang, C. (1996). Low-capital-cost technology for SO2 control. Proceedings of the air and waste management association’s annual meeting and exhibition, Pittsburgh, PA, USA, Vol. 11, p. RA105A.05.

[24] Kikkawa, H. Nakamoto, T. Morishita, M. and Yamada, K. (2002). New wet FGD process using granular limestone. *Ind. Eng. Chem. Res.* 41*,* p.3028– 3036.

[25] Ayuso, E. A. Querol X. and Tomas A. (2006). Environmental impact of a coal combustion-desulfurization plant: Abatement capacity of desulfurization process and environmental characterisation of combustion by-products. Chemosphere 65, p. 2009–2017.

[26] Wilfrid, F (1961). Coal its formation and composition, 2nd Ed, Edward Arnold Publishers LTD, London, p. 451-459, 744-750.

[27] Hirinchs, R.A. and Merlin, K. (1941), Energy Its use and the environment. 3rd Ed. Thompson Learning, inc, USA, p. 200, 220-255.

[28] Tatsutani, M. And Amar P. (2000). Environmental Regulation and Technology Innovation, Northeast States for Coordinated Air Use Management (NESCAUM), USA. p. IV-1 to IV-31.

[29] Tiessen, H. and Moir, J.O. (1993). Total and organic carbon. In: Soil Sampling and Methods of Analysis, M.E. Carter, Ed. Lewis Publishers, Ann Arbor, MI. p. 187-211.

[30] Nelson, S.J. and Zhang, C. (1996). Low-capital-cost technology for SO2 control. Proceedings of the air and waste management association’s annual meeting and exhibition, Pittsburgh, PA, USA, Vol. 11, p. RA105A.05.

[31] Charles, M.J. and Simmons, M.S. (1986). Methods for the determination of carbon in soils and sediments. Analyst 111, p. 385-390.

[32] E. Jorjani, B. Rezai, M. Vossoughi, M. Osanloo, M. Abdollahi, (2004) Oxidation pretreatment for enhancing desulfurization of coal with sodium butoxide, Minerals Engineering 17, p.545–552.

[33] Gryglewicz, G. and Gryglewicz, S. (2001). Determination of elemental sulfur in coal by gas chromatography – mass spectrometry Fresenius. J Anal Chem 370, p. 60–63.

[34] Meyers, R.A. (1982). Coal structure, Academic press, inc, USA, p. 132-133; 170-193.

[35] [Selsbo, P. (1996). Analytical pyrolysis-studies of sulfur in coal and pulp, Doctoral dissertation, Lund University, Sweden, p. 11-12; 16-19; 30-37.

[36] Xu, X. McDonald, L. M. McGowan C.W. and Glinski, R.J. (1995). Examination of sulfur forms in coal by direct pyrolysis and chemiluminescence detection. Fuel 74 p. 1499-1504.

[37] Harker, J.H. and Backhurst, J.R. (1981). Fuel and Energy, Academic press, inc, London, p. 27-42.

[38] Kroschwitz, J.I. and Grant, M.H. (1993). Encyclopaedia of Chemical Technology, 4th ed, Separation Science. Chlorocarbons to Combustion Technology. John Wiley and Sons, inc, USA, p. 423-539.

[39] Gonenc Z.S., Gibbins J.R. and Katheklakis I.E. (1990). Comparison of coal pyrolysis product distributions from 3 captive sample techniques, Fuel 69, p. 383-390.

[40] Kroschwitz, J.I. and and Szwedo, J. (2009). Examination of the Baltic amber inclusion surface using SEM techniques and X-ray microanalysis. Paleogeography, Paleoclimatology, Paleoecology 271, p. 287–291.

[41] Hsieh K. C. and Wert C. A., (1985). Direct measurement of organic sulfur in coal. Fuel 64, p. 255-262.

[42] Stach E, Coal petrology, Gebruder Brntreager, Berlin (1975).

[43] Laban, K. L. and Atkin, B. P. (2000). The direct determination of the forms of sulfur in coal using microwave digestion and ICP-AES analysis, Fuel 79, I, p. 173-180.

[44] Dai S, Deyi R, Yuegang T, Longyi S, Shengsheng L, (2002). Distribution, isotopic variation and origin of sulfur in coals in the Wuda coalfield, Inner Mongolia, China International Journal of Coal Geology, Volume 51, Issue 4, September 2002, P. 237-250.

[45] Chou, C.L., 1990. Geochemistry of sulfur in coal. In: Orr, W.L., White, C.M. (Eds.), Geochemistry of Sulfur in Fossil Fuels. ACS Symposium Series, 429. American Chemical Society, Washington, D.C., p. 30–52. Chapter 2.

[46] Akcil A. and Koldas S. (2006). Acid Mine Drainage (AMD): causes, treatment and case studies. Journal of Cleaner Production 14, pp. 1139-1145.

[47] Stumm, W. and Morgan, J. J. (1996). Aquatic Chemistry, Chemical Equilibria and Rates in Natural Waters, Wiley-Interscience, 3rd ed., New York. p. 464- 498.

[48] VanLoon, G.W. and Duffy, S (2005). Environmental Chemistry, A global perspective 2nd Ed Oxford university press, p.108-123,227-231,361-364.

[49] M. Kozłowskia,, R. Pietrzak, H. Wachowska, J. Yperman, AP–TPR study of sulphur in coals subjected to mild oxidation. Part 1. Demineralised coals, Fuel 81 (2002) p.2397–2405.

[50] Kister J, Guiliano M, Mille G, Dou H. Fuel 1988; 67:1076.

[51] Tognotti L, Petarca L, D'Alessio A, Benedetti E. Fuel 1991; 70:1059.

[52] Yurum Y, Altuntas¸ N. Fuel 1998; 77:1809.

[53] Hayashi J, Matsuo Y, Kusakabe K, Morooka S. Energy Fuels 1997; 11: 227.

[54] Hayashi J, Aizawa S, Kumagai H, Chiba T, Yoshida T, Morooka S. Energy Fuels 1999; 13:69.

[55] Chadwick MJ, Highton NH, Lindman N, editors. Environmental impacts of coal mining and utilization. Oxford: Pergamon Press; 1987.

[56] Davidson RM. Fuel 1994; 73: 988.

[57] Calkins WH. Fuel 1994; 73: 475.

[58] Stock LM, Wolny R, Bal B. Energy Fuels 1989; 3: 651.

[59] Brown JR, Kasrai M, Bancroft GM, Tan KH, Chen JM. Fuel 1992; 71: 649.

[60] Huffman GP, Mitra S, Huggins FE, Shah N, Vaidya S, Lu F. Energy Fuels 1991;5:574.

[61] Kelemen SR, George GN, Gorbaty ML. Fuel 1990; 69:939.

[62] Gorbaty ML, Kelemen SR, George GN, Kwiatek PJ. Fuel 1992; 71: 1255.

[63] Boudou JP, Boule`gue J, Male´chaux L, Nip M, de Leeuw JW, Boon JJ. Fuel 1987;66:1558.

[64] LaCount RB, Anderson RR, Friedman S, Blaustein BD. Fuel 1987; 66: 909.

[65] Chou C-L, Hackley KC, Cao J. In: Parekh BK, Groppo JG, editors. Processing and utilization of high-sulfur coals V. London: Elsevier; 1993. p.15.

[66] Calkins WH. Energy Fuels 1987;1:59.

[67] Attar A. In: Karr C Jr., editor. Analytical methods for coal and coal products, vol. III. New York: Academic Press; 1979. p.585.

[68] Yperman J, Maes II, Van den Rul H, Mullens S, Van Aelst J, Franco DV, Mullens J, Van Poucke LC. Anal Chim Acta 1999;395:143.

[69] Mitchell SC, Snape CE, Garcia R, Ismail K, Bartle K. Fuel 1994;73: 1159.

[70] Mc Gowan CW, Markuszewski R. Fuel 1988;67:1091.

[71] Zhou X, Chriswell C. Fuel Process Technol 1996;46:41.

[72] Angelova G, Kovaceva V. Khim Tverd Topl 1969;5:22.

[73] Borah D, Baruah MK, Haque I. Fuel 2001;80:501.

[74] M.kozlowski and et al,(2003), Transformations of sulphur compounds in high sulphur coals during reduction in the potassium/liquid ammonia system, Fuel 82 (2003) 1149–1153.

[75] S.P. Marinov, M. Stefanova, V. Stamenova, R. Carleer, J. Yperman, Sulphur functionality study of steam pyrolyzed ‘’Mequinenza’’ lignite using reductive pyrolysis technique coupled with MS and GC/MS detection systems, Fuel Processing Technology 86 (2005) p.523– 534.

[76] E. Jorjani, J. Yperman, R. Carleer, B. Rezai, Reductive pyrolysis study of sulfur compounds in different Tabas coal samples (Iran), Fuel 85 (2006) p.114–120.

[77] Maya Stefanova, Stefan Marinov, Jan Yperman, Robert Carleer, Reductive pyrolysis of Miocene-aged lignite lithotypes using MS and GC/MS detection systems for analysis of organic sulphur groups, Fuel 84 (2005), p. 71–79.

[78] Fenrong LIU, Wen LI, Bao-qing LI, Zong-qing BAI,(2008), Sulfur transformation during pyrolysis of Zunyi coal by atmosphere pressure-

temperature programmed reduction-mass spectrum, Journal of fuel chemistry and technology ,vol.36,p.6-9.

[79] Setyawati Yani, Dongke Zhang, (2009), An experimental study of sulfate transformation during pyrolysis of an Australian lignite, Fuel processing technology,vol.22, p.2083-2092.

[80] S.P. Marinov, L. Gonsalvesh, M. Stefanova, J. Yperman, R. Carleer, G. Reggers, Y. Yürümc, V. Groudeva, P. Gadjanov, (2010) Combustion behaviour of some biodesulphurized coals assessed by TGA/DTA, Thermochimica Acta 497 p.46–51.

[81] S.Marland, B.Han, N.A.Rowson, A.J.Merchant, Microwave embrittlement and desulphurisation of coal, Acta Montanistica Slovaca, (1998), **3**, p.351-355.

[82] Walkiewicz, J. W., Kazonich, G., McGill S. L.,(1988) Microwave heating characteristics of selected minerals and components, Minerals and Metallurgical Processing. p. 39-42.

[83] T.T.Chen;J. E. Dutrizac;K. E. Haque;W. Wyslouzil;S. Kashyap, (1984) The relative transparency of minerals to microwaves, Canadian Metallurgical Quarterly, Vol. 23, No3, p.349-351.

(1988) The effect of power levels on the microwave heating of selected chemicals and minerals, Materials Research Society proceedings. Vol.124, p.247-252.

[85] C. D. Harrison and C. E. Raleigh, Jr.CQ Inc., THE USE OF ULTRASOUND FOR CLEANING COAL.

[86] Kang W., XUN H. and Chen J., Study of enhanced fine coal de-sulfurization and de-ashing by ultrasonic flotation. Journal of China University of Mining & Technology, 2007, 17, p.358-362.

[87] Özkan G. Halit Z., Kuyumcu Z., Investigation of mechanism of ultrasound on coal flotation. International Juornal Mineral Processing, 2006, 81, P.201-203.

[88] CUI Guang-wen, ZHU Shu-quan, ZOU Li-zhuang, XIE Wei-wei, Effects of High-Power Ultrasonic Treatment on the Slurryability of Coals, J China Univ Mining & Technol 2007, 17(4): p.0562 – 0565.

[89] Ramamurthy Nagarajan, B. Ambedkar, R. Nagarajan, S. Jayanti,(2010), Ultrasonic Coal-Wash for De-Sulfurization, Ultrasonics Sonochemistry, Article in press.

[90] Ferrando, A.C Andre´s, Membrado, L., (1996). Chemical desulfurization of coal with hydroiodic acid. Energy & Fuels Vol 10(2), p.425–430.

[91] Gülhan Güllü Elsamak, Nurşen Altuntaş Öztaş, Yuda Yürüm, (2003), Chemical desulfurization of Turkish Cayirhan lignite with HI using microwave and thermal energy, Fuel, vol.82 p. 531–537.

[92] Semra Karaca,(2003), Desulfurization of a Turkish lignite at various gas atmospheres by pyrolysis. Effect of mineral matter, Fuel , vol.82 p.1509–1516.

[93] Rengui Guan and et a,. (2003), Effects of Ca-based additives on desulfurization during coal pyrolysis, Fuel, vol. 82 p.1961–1966.

[94] Charutawai K, Ngamprasertsisith S, Prasassarakich P,(2003), Supercritical desulfurization of low rank coal with ethanol/KOH, Fuel Processing Technology ,vol. 84, p.207– 216.

[95] Jorjani, E.; Rezai, B.; Vossoughi, M.; Osanloo, M.; Abdollahi, (2004), Oxidation pretreatment for enhancing desulfurization of coal with sodium butoxide, Minerals Engineering , vol.17 p.545–552.

[96] E.Jorjani, B.rezai, M.Vossoughi, M.Osanlo,(2004). Desulfurization of Tabas coal with microwave irradiation/peroxyacetic acid washing at 25, 55 and 85 C.Fuel Vol 83, p.943-949.

[97] Abdollahy, M.; Moghaddam, A.Z.; Rami, K. (2006), Desulfurization of Mezino coal using combination of ‘flotation’ and ‘leaching with potassium hydroxide/methanol, Fuel vol. 85 p.1117–1124.

[98] ARIUNAA A, LI Bao-qing, LI Wen, PUREVSUREN, MUNKHJARGAL Sh, LIU Fen-rong,BAI Zong-qing1, WANG Gang, (2007), Coal pyrolysis under synthesis gas, hydrogen and nitrogen, J Fuel Chem Technol, , 35(1), p.1−4.

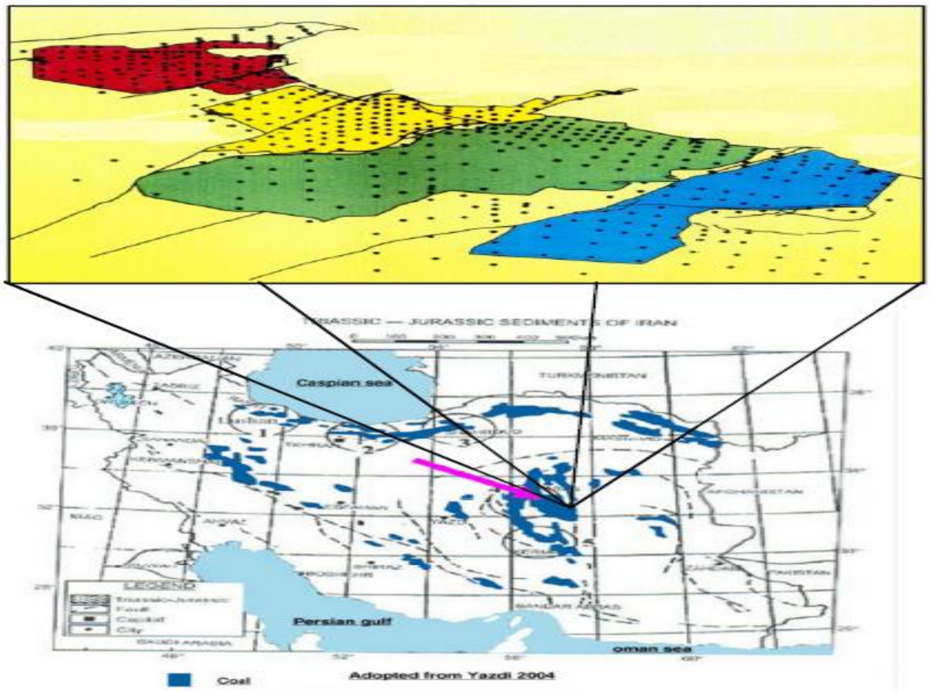
[99] H.G. Alam , H., Ghadrdan, M., , H.G., Moghaddam, A.Z., Omidkhah, M.R. (2009), The influence of process parameters on desulfurization of Mezino coal by HNO_3/HCl leaching, Fuel processing technology, vol.9 0, p.1 – 7.

[100] Zhiling Li Tonghua Sun Jinping Jia , (2010), An extremely rapid, convenient and mild coal desulfurization new process: Sodium borohydride reduction, Fuel processing technology ,vol.91 ,p.1162–1167.

Chapter Two: Materials and Methods

2.1. Coal sample

Coal is one of Iran’s most abundant but least developed mineral resources. Proven reserves are estimated at some 1,075 Mt, mainly coking and bituminous coal. Development of the Tabas Coalfield is the major coal-sector investment aiming to produce 1.5 Mt/y of coking coal from a new long wall operation. The sampling and investigation for this study has been done from the Late Triassic of coal deposits from Parvade coalfield in south of Tabas town. It is located geologically in central zone of Iran. Main coal seam in Parvade coal is named C1. Parvade area is one of coalfield Tabas region which located the longitude in the 75 Km south of Tabas between the longitudes of 56 46 30 56 51 10 East and latitudes 32 59 48 to 38 2 15 North (Fig (2.1)). Average height region is 730 to 1050 m from sea level and average height of 850 meters [1].



Adopted from Yazdi 2004

Fig (2.1). Teriassic Jurassic sediments of Iran, Parvade coalfield indicated, Parvade I,II (red), Parvade III (yellow),Parvade IV (green) and Parvade V (blue) [1]

Proximate, ultimate and sulfur species analysis of initial sample are presented in Table (2-1).

Table (2.1) Proximate, ultimate and sulfur forms analysis for studied initial sample.

Analysis	Initial sample
Proximate (wt.%) as received	
Moisture	1.11
Ash	18.77
Volatile matter	24.30
Fixed carbon (by difference)	55.82
Ultimate analysis (wt.%) dry ash free	
Carbon	82.30
Hydrogen	5.01
Nitrogen	3.21
Sulfur	3.37
Oxygen (by difference)	6.11
Sulfur Species (wt.%) dry basis	
S_{total}	3.17
$S_{sulfate}$	0.15
S_{pyrite}	1.16
$S_{organic}$	1.86

2.2. Irradiation

2.2.1. Microwave irradiation

Microwave power was first used as a means of volumetric heating up to fifty years ago and has since become readily accepted in the food industry for operations including drying, pasteurization and sterilization and also as a means of processing both rubber and plastics [2,3]. Industry as a whole, is continually seeking to reduce manufacturing and processing costs whilst at the same time improving the quality of the product [4,5]. Electricity is a high grade energy source which offers a number of advantages and possibilities in this respect. There are many different ways in which electricity can be used in heating, such as resistance heating, infrared heating, ultraviolet curing, dielectric heating, induction heating, plasma and laser heating [6-9]. Conventional radiant heating can cause problems, particularly where non-conducting or insulating materials have to be heated. This is due to the fact that heat is applied externally and allowed to "soak" into the material by conduction. This can be a slow energy consuming process with materials of poor thermal conductivity. Another disadvantage of conventional heating is that overheating may occur at the surface of the heated product before the center has reached the required temperature, particularly if attempts are made to accelerate the heating rate. Large temperature variations within a material can be overcome (or even exploited) using electromagnetic heating. Electromagnetic heating energy is delivered instantaneously throughout the mass of the material, achieving controlled heating rates and accurate process temperatures become easier. Microwave heating applications usually make use of the 0.915 and 2.45GHz frequencies in order to minimize interference with communication band microwaves.

Microwaves form part of a continuous electromagnetic spectrum that extends from low frequency alternating currents to cosmic rays. Electromagnetic waves are produced as a consequence of two effects:

- A changing magnetic field produces an electric field.
- A changing electric field produces a magnetic field.

In a heterogeneous dielectric material where a highly conductive phase is present and interspersed in a phase of low conductivity, charge builds up at the boundary of the two phases in line with the applied field. This mechanism is active over a broad range of the electromagnetic spectrum including the microwave region [9]. An example would be a dispersion of metallic particles in sulfur. Sulfur is microwave transparent and metals reflect microwaves. However, this combination forms a composite which is an extremely good microwave absorbing material. Interfacial polarization is a complex effect which is difficult to treat in a simple manner and is viewed as a combination of conduction and dipolar polarization effects. If a material has a low electrical resistance, most of the microwave energy will not penetrate the surface of the material, but will be reflected from it [9,10]. The variables in microwave treating have been illustrated in Fig (2-2).

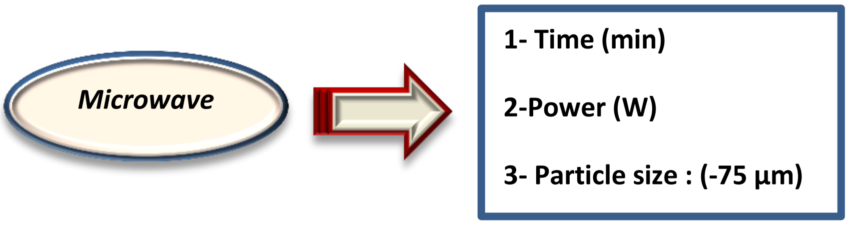


Fig (2-2). Studied variables for microwave irradiation

In the present study, for the pretreatment by microwave irradiation, coal samples (minus 75µm) were spread on the Pyrex glass container (8 g). The irradiation was performed by a Samsung microwave oven with 2.45 GHz frequency and 0-1250 Watt power, with different irradiation times (2,4,6 and 8 minutes) and at different irradiation powers (300,600 and 900 watt). The microwaved samples were cooled in the desiccator, weighed, and used for post chemical desulfurization by PAA. The microwave treated samples are labeled in the following way, for example: “753002” is related to the sample fraction size under 75µm, treated with microwave power of 300 W and for 2 minutes.

2.2.2. Ultrasound irradiation

Sonication is a process in which sound waves are used to agitate particles in solution. Such disruptions can be used to mix solutions, speed the dissolution of a solid into a liquid (like sugar into water), and remove dissolved gas from liquids. Sound is a wave made up of alternating regions of high and low pressure. The frequency of a sound wave is a measure of how often the particles of a substance vibrate. The sound waves used in sonication are usually ultrasound waves with frequencies above what you can hear (above 20 kHz that is 20,000 cycles per second) and as frequency increases the strength of the agitation increases. In solution, the particles vibrate because as they experience cycles of pressure, microscopic vacuum bubbles form and then collapse into solution, a process called cavitation. These vibrations can disrupt molecular interactions (e.g. between molecules of water), break clumps of particles apart, and lead to mixing. In the case of dissolved gas, these vibrations can allow the gas bubbles to come together and more easily leave the solution. Sonicators either produce sound waves into a water bath, where samples are placed, or can be probes that are put directly into the sample to be sonicated [11].

Ultrasound behaves differently in liquid and liquid-solid media compared to gas medium. Ultrasound in aqueous medium produces highly reactive species such as OH radicals, H_2O_2 and ozone that are strong oxidizer agents of high oxidation potential (2.8, 1.8 and 2.1 V respectively). These radicals are capable of initiating and enhancing oxidation and reduction reactions. Oxidation occurring due to ultrasound is called "advanced oxidation process" (AOP). Sonication enhances mass transfer and chemical reaction and is expected to reduce or eliminate chemical usage, resulting in minimum disposal problems [11]. Lindstorm and Lamm [12] first suggested that the mechanism for this reaction, followed by many researchers who proved in it different manners by experiments. Webster [13] explained the cavitation mechanism as follows: Two classes of chemical effect are induced by ultrasonic cavitation. The first is the acceleration of reactions, and the second class of effect is the initiation of reactions that would not action of cavitation, water decomposes into free radicals as below:

$$H_2O \rightarrow H^* + OH^* \qquad \textbf{Eq(2-1)}$$

The predominant back reactions attendant on this process are:

$$OH^* + OH^* \rightarrow H_2O_2 \quad ; \quad H^* + H^* \rightarrow H_2 \qquad \textbf{Eq(2-2)}$$

The products of these reactions are then responsible for secondary reactions involving dissolved substances. The reacting ions or molecules will be selectively subjected to reduction or oxidation according to their properties and structure.

The oxidation of dissolved substances is detectable in the absence of dissolved oxygen. In its presence, the rate of formation of hydrogen peroxide is increased, with a consequent increase in the rate of oxidation; this effect has been attributed the occurrence of the reaction.

$H + O_2 \rightarrow HO_2$ followed by $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$ **Eq (2-3)**

Makino et al. [14] reported that intense ultrasound causes chemical damage through the phenomenon called cavitation. Cavitation produces high local instantaneous temperatures and pressure. In sonolysis studies of aqueous solutions, it is proposed that hydroxyl radicals ($OH^{\bullet}$) and hydrogen atoms (H) are produced by ultrasound. Riesz et al. [15] were able to observe by spin traps the highly-reactive radicals produced during cavitation. Christman et al. [16] found experimental evidence for free radicals produced in aqueous solutions by using electron spin resonance method (ESR). Misik and Riesz [17,18] conducted spin trap and electron spin resonance studies to investigate free-radical formation and sono-chemical reactions in organic liquid using 50 kHz frequency of ultrasound. Entezari and Krus [19] conducted an experiment to explain the effect of frequency on sono-chemical reactions. Luche [20] investigated sono-chemical reactions occurring in heterogeneous systems. Henglein [21] stated that free radicals produced by the cavitation effect are responsible for reaction. The OH radicals produced by the ultrasound are strong oxidation agents and lead to H_2O_2 formation. Hoffmann et al. [22] investigated sono-chemical degradation of organic compounds present in water. Three distinct pathways of sono-chemical of organic compounds by acoustic cavitation have been proposed:

- Oxidation by hydroxyl radicals.
- Pyrolytic decomposition.
- Supercritical water oxidation.

In this study, a Q280 multifunction ultrasonic transmitter was 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 grams of coal (under 75 μm) was mixed with 150 ml of distilled water into the 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 are filtered and dried in an oven at 100±10 °C for 3 hours. To evaluate the effects of irradiation time on organic sulfur functionalities, the subjected coal samples irradiated for 10, 15, 20 and 25 minutes. The ultrasound treated samples are labeled in the following way, for example: "7510" is related to the sample fraction size under 75 μm for 10 minutes. The dried sonicated samples were weighed and sulfur forms determined and used for the post chemical desulfurization by PAA.

2.3. Analysis of treated samples

2.3.1. Proximate analysis

The proximate analysis of coal is an assay of the moisture, ash, volatile matter, and fixed carbon as determined by series of prescribed or standard test methods. It was developed as a simple means of determining the distribution of products obtained when the coal sample is heated under specified conditions. By definition, the proximate analysis of coal separates the products into four groups: (1) moisture; (2) volatile matter, consisting of gases and vapors driven off during pyrolysis; (3) fixed carbon, the nonvolatile fraction of coal; and (4) ash, the inorganic residue remaining after combustion[23].

The proximate analysis of coal is presented as a group of test methods (ASTM D-3172; ASTM D-3173; ASTM D-3174; ASTM D-3175; ASTM D-5142; ISO 1171) that has been used widely as the basis for coal characterization in connection with coal utilization. These analyses are in contrast to the ultimate analysis of coal, which provides information about the elemental composition. Moisture, volatile matter, and ash are all determined by subjecting the coal to prescribed temperature levels for prescribed time intervals. The losses of weight are, by stipulation, due to loss of moisture and, at the higher temperature, loss of volatile matter. The residue remaining after ignition at the final temperature is called *ash*. Fixed carbon is the difference of these three values summed and subtracted from 100. In low-volatile materials such as coke and anthracite coal, the fixed-carbon value equates approximately to the elemental carbon content of the sample [24-30].

2.3.1.1. Moisture

There are several sources of the water found in coal. The vegetation from which coal was formed had a high percentage of water that was both physically and chemically bound, and varying amounts of this water were still present at various stages of the coalification process. Water is present in most mines and circulates through most coal seams. After mining, many coals are washed with water during preparation for market and are then subject to rain and snow during transportation and storage. All of these sources contribute to the moisture in coal and to the problems associated with measurement of this moisture. The total moisture in coal is the determination of the moisture (in all forms except water of crystallization of the mineral matter) that resides within the coal matrix. In fact, moisture (or water) is the most elusive constituent of coal to be measured in the laboratory. The moisture in coal ranges from 2 to 15% by weight in bituminous coal to nearly 45% by weight in lignite.

Generally, the moisture content of coal is determined by measuring the weight loss of a sample (expressed as a percentage of the sample) that has been comminuted to pass through a 250μm (60#) sieve (ASTM D-3173; ISO 331; ISO 687). The sample (about 1 g) is maintained under controlled conditions (107 ± 3°C) in an inert atmosphere for 1 hour [25,31,32].

2.3.1.2. Ash

Ash is the residue remaining after the combustion of coal under specified conditions (ASTM D-3174; ISO 1171) and is composed primarily of oxides and sulfates [26,33]. It should not be confused with mineral matter, which is composed of the unaltered inorganic minerals in coal [34-36]. The quantity of ash can be more than, equal to, or less than the quantity of mineral matter in coal, depending on the nature of the mineral matter and the chemical changes that take place in ashing.

The determination of mineral ash in coal is usually by heating (burning) an accurately weighed sample of the coal in an adequately ventilated muffle furnace at temperatures in the range 700 to 750°C for 4 hours (ASTM D-3174) [26]. It should be noted that variations in the amount of ash arise from the retention of sulfur that originates from the pyrite.

2.3.1.3. Volatile matter

Volatile matter, as determined by the standard test methods (i.e., ASTM D-3175; ISO 562), is the percentage of volatile products, exclusive of moisture vapor, released during the heating of coal or coke under rigidly controlled conditions. The measured weight loss of the sample corrected for moisture establishes the amount of material (volatile matter) evolved from the coal under the conditions of the test.

The type of heating equipment and the size and shape of the sample holders as well as the material from which they are made (platinum crucibles specified) all have some influence on the rate of heating of the sample and the range of temperatures to which it is exposed. The crucibles used are 10 to 20 mL in capacity, of specified size, with deep-fitting lids, and there are two procedures for determination of volatile matter. The methods for determining volatile matter content are based on the same principle and consist of heating a weighed sample of coal (usually about 1 g) in a covered crucible to a predetermined temperature; the loss in weight (excluding losses due to water) is the volatile matter content (expressed as a weight percent) [27,37].

In the test method (ASTM D-3175), 1 g of coal is weighed and placed in a pre-weighed platinum crucible (10 to 20 mL in capacity, 25 to 35 mm in diameter, and 30 to 35 mm in height) with a close-fitting cover. The crucible is then suspended at a specified height in the furnace chamber. The temperature of the region in the furnace where the crucible is suspended must be maintained at 950 ±20°C. After the more rapid discharge of volatile matter, as evidenced by the disappearance of the luminous flame, the cover of the crucible should be tapped to ensure that the lid is still properly seated to guard against the admission of air. After heating for exactly 7 minutes, the crucible is removed from the furnace and cooled. The crucible should be weighed as soon as it is cold. The percentage loss of weight minus the percentage moisture equals the volatile matter [27].

2.3.1.4. Fixed carbon

Fixed carbon is the material remaining after the determination of moisture, volatile matter, and ash. It is, in fact, a measure of the solid combustible material in coal after the expulsion of volatile matter, and like determination of the carbon residue of petroleum and petroleum products represents the approximate yield of thermal coke from coal [38-40]. The fixed-carbon value is one of the values used in determining the efficiency of coal-burning equipment. It is a measure of the solid combustible material that remains after the volatile matter in coal has been removed. For this reason, it is also used as an indication of the yield of coke in a coking process. Fixed carbon plus ash essentially represents the yield of coke. Fixed-carbon values, corrected to a dry, mineral-matter-free basis, are used as parameters in the coal classification system (ASTM D-388)[41].

2.3.2. Ultimate analysis

The ultimate analysis of coal involves determination of the weight percent carbon and hydrogen, as well as sulfur, nitrogen, and oxygen (the last usually estimated by difference). Trace elements that occur in coal are often included as a part of the ultimate analysis. The carbon determination includes carbon present as organic carbon occurring in the coal substance and any carbon present as mineral carbonate. The hydrogen determination includes hydrogen present in the organic materials as well as hydrogen in all of the water associated with the coal. In the absence of evidence to the contrary, all of the nitrogen is assumed to occur within the organic matrix of coal. On the other hand, sulfur occurs in three forms in coal:

- As organic sulfur compounds (and elemental sulfur, not present in this coal)
- As inorganic sulfides that are, for the most part, primarily the iron sulfides pyrite and marcasite (FeS_2).
- As inorganic sulfates (e.g., Na_2SO_4, $CaSO_4$).

The sulfur value presented for ultimate analysis may include, depending on the coal and any prior methods of coal cleaning, inorganic sulfur and organic sulfur. Moisture and ash are not determined as a part of the data presented for ultimate analysis but must be determined so that the analytical values obtained can be converted to comparable bases other than that of the analysis sample. In other words, analytical values may need to be converted to an as received basis, a dry basis, or a dry, ash-free basis. When suitable corrections are made for any carbon, hydrogen, and sulfur derived from the inorganic material, and for conversion of ash to mineral matter, the ultimate analysis represents the elemental composition of the organic material in coal in terms of carbon, hydrogen, nitrogen, sulfur, and oxygen [42-54].

2.3.3. Sulfur forms determination standards

For determining of all sulfur forms, this international standard has been used.

The ISO-334 is used for total sulfur (ESCHKA METHOD) and ISO-157 is used for sulfate and pyritic sulfur determination.

A test portion is ignited in intimate contact with Eschka mixture in an oxidizing atmosphere, to remove combustible matter and to convert the sulfur to sulfate. This is then extracted with hydrochloric acid solution and determined gravimetrically by precipitation with barium chloride [48,55,56].

2.3.3.1- Eschka mixture

Mix two parts by mass of light, calcinated magnesium oxide (MgO) with one part by mass of anhydrous sodium (or potassium) carbonate ($Na_2CO_3.nH_2O$). The mixture shall entirely pass a test sieve of 212μm nominal size of openings.

2.3.3.2- Hydrochloric acid

Concentrated, ρ approximately 1.18g/ml, approximately 36% (m/m) [48,55,56].

2.3.3.3- Potassium sulfate *(solution)*

Weight, to the nearest 0.1 mg, about 2 g of potassium sulfate, previously dried at a temperature of 105°C to 110°C. Dissolve in water and dilute to 1 liter [48,55,56].

2.3.3.4- Barium Chloride *(Approximately 85 g/l solution)*

Dissolve 100 g of barium chloride dehydrate in water and dilute to 1 liter. Filter before use through a close-textured, doubly acid-washed filter paper or filter paper pad [48,55,56].

For charging the crucible, the bottom of crucible should be covered uniformly with 0.5 g of Eschka mixture, weight to nearest 0.1 mg. Mixed of test portion (1.0 g) intimately with 2.5 g of Eschka mixture, weighted to the nearest 0.1 mg, in suitable vessel. Transfer the mixture to the 25 ml crucible. Level the contents by tapping the crucible gently on the bench and cover the contents uniformly with 1.0 g of Eschka mixture, weighted to the nearest 0.1 mg. The entire 4 g of the Eschka mixture should be weighted out and also the 0.5 g and 1 g proportions, required for the bottom and top layers. For this purpose, it is convenient to calibrate a small glass tube for each bath of Eschka mixture, to deliver 0.5 g and 1 g without weighing. For ignition part, the charged crucible should be placed in the cold muffle furnace and raise the temperature to 850±25°C in about 1 hour and forty five minutes. Withdraw the crucible (or crucibles) and allow to cooling it down. For recovering the residue, all the ignited mixture should be transferred from crucible to a 400 ml beaker containing 25 ml to 30 ml of water. If un-burnt particles are present, the determination shall be stopped and the test repeated. Wash the crucible thoroughly with about 50 ml of hot water, and add the washings to the contents of beaker [48,55,56].

Place a watch-glass on the beaker and then, while titling the watch-glass, carefully add enough hydrochloric acid to dissolve the solid matter (17 ml normally be required), warming the contents of the beaker to effect solution. Boil for the 5 minutes to expel carbon dioxide and filter, collecting the filtrate in a 400 ml conical beaker [48,55,56].

To prepare the filter-paper pad, shake doubly acid washed filter paper clippings, in pieces with areas of approximately 1 cm^2, with water in a bottle until the paper is thoroughly disintegrated. Place a porcelain filter cone of 25 mm in a 75 mm funnel, close the stem of the funnel with finger and add water until the cone is immersed and the funnel stem is full. Shake, onto the cone, sufficient paper pulp to form a pad of 5 mm thick, and level it with a flat-ended glass rod. Allow the excess water to drain away by removing the finger from the stem and as drainage ceases, lightly tamp the pad edges with the glass rod. A final wash with water renders the filter ready to use. Wash the filter with five 20 ml portions of hot water. Add 2 or 3 drops of the methyl red indicator solution to the combined filtrate and washings, and then cautiously add the ammonia solution until the color of the indicator changes and a trace of precipitate is formed. Add enough hydrochloric acid to just re-dissolve the precipitate and then add 1 ml in excess. For the precipitation of the barium sulfate, after extraction, dilute the solution, if necessary, to approximately 200 ml and cover the beaker containing the solution with a watch-glass. Heating the covered beaker until the solution boils and then reduced the heating slightly until ebullition of the solution ceases. Then add 10 ml of the cold barium chloride solution into the center of the hot solution, while it is being agitated. Keep the solution just below boiling point for 30 minutes. Filter the solution by gravity through a filter-paper pad prepared from ash-less doubly acid washed filter paper. After transferring the filter paper pad to the crucible, wipe the funnel successively with two halves of the ash-less filter paper and place this paper in the crucible with the pad. Insert the crucible slowly into the muffle furnace at a temperature of 800°C±10°C, and then heat for 15 minutes. Cool in a desiccator and reweigh, to the nearest 0.1 mg [48,55,56].

Blank test carried out using the same procedure as for the determination, but omitting the test portion. Using a one-mark pipet, add 25.0 ml of the potassium sulfate solution. Filtrate before adding the methyl red indicator solution. The precipitation of barium sulfate was gathered and was in this study 0.0751 g. The total sulfur for each sample can be calculating by means of (Eq (2.4)) [48,55,56].

$$S_{total} = [13.74\ (M_2 - M_3 + 0.03348\ \rho(K_2SO_4))] / M_1 \qquad \textbf{Eq(2.4)}$$

In above equation M_1, M_2, M_3 and $\rho(K_2SO_4)$ are mass of sample (1 gr for each test), the mass of barium sulfate found in the determination, the mass of barium sulfate found in blank test and the mass concentration expressed in grams per liter of potassium sulfate solution ($\rho K_2SO = 2$) respectively.

The procedure described here in international standard methods, utilizes the difference in solubility of sulfates and pyrites in dilute hydrochloric and nitric acids under reflux conditions, such that each can be taken in solution successively and determined directly. A general schematic representation of the procedure is given in Fig (2.2) [56].

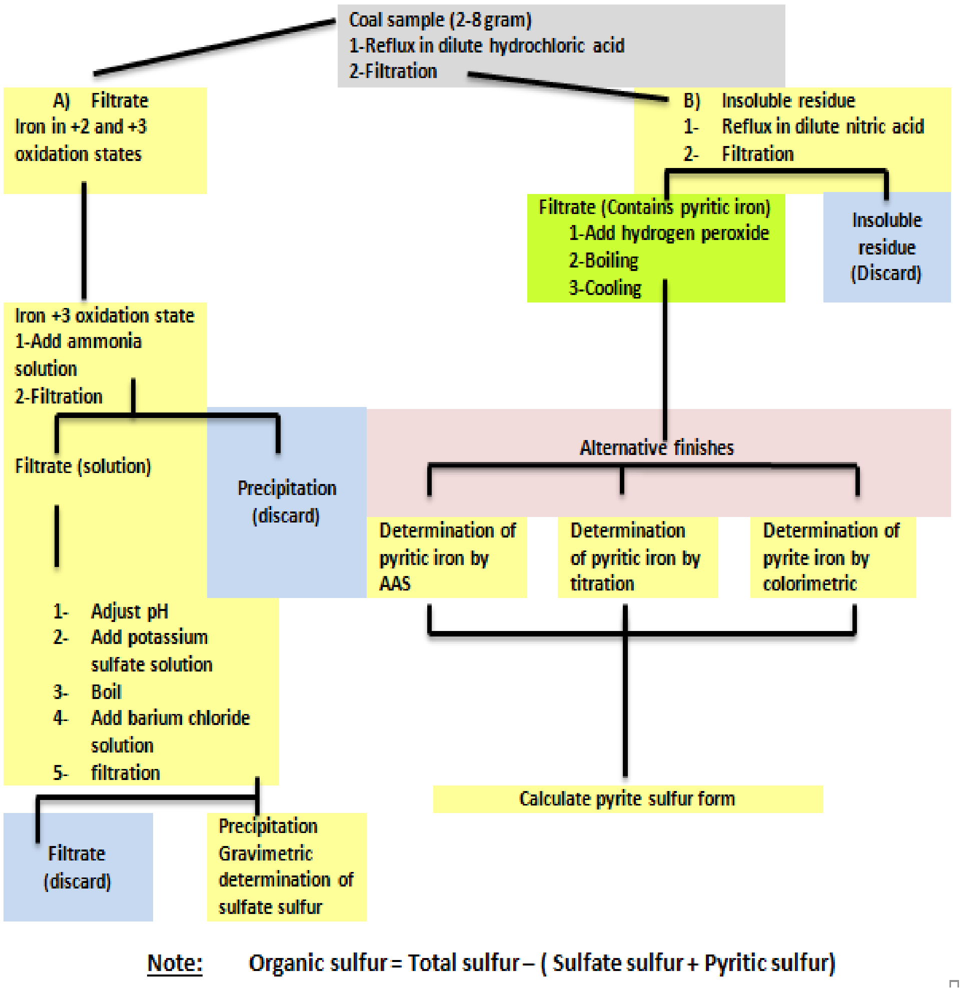


Fig (2.2). General Schematic representation of the procedure [56]

The sulfate sulfur extracted by dilute hydrochloric acid from the test portion is determined gravimetrically by precipitation with barium chloride [48,55].

During the analysis, unless otherwise stated, use only reagents of recognized analytical reagent grade and only distilled water or water equivalent purity. The used reagents are as follows:

Hydrogen peroxide, solution approximately 30% (m/m), Methyl red as indicator solution (dissolve 1g of 2-(4-dimethylaminophenylazo)benzoic acid, sodium salt (methyl red) in one liter water), Ammonia,(concentrated solution not less than 25%), Hydrochloric acid, concentrated approximately 36% (m/m), Potassium sulfate, approximately 2g/l solution (dissolve approximately 2 g of potassium sulfate in water and dilute to 1 liter), Barium chloride, approximately 85 g/l solution,(Dissolve 100 g of barium chloride dehydrate in water and dilute to 1 liter. Filter before use through a close-textured, doubly acid –washed filter-paper or filter-pad.

To the filtrate from the hydrochloric acid extraction add 5 ml of the hydrogen peroxide solution and boil for 5 minutes to convert all the soluble iron to +3 oxidation state. While still hot, add 2 or 3 drops of methyl red indicator solution followed by the ammonia solution, drop by drop, until the solution is just alkaline (becomes yellow color) and then add a further 5 drops in excess. Filter the resultant precipitate on a toughened fast filter paper into a 250 ml beaker. Wash thoroughly with hot water, discharging the precipitate. Cautiously add the concentrated hydrochloric acid to the filtrate drop by drop, until the color of solution changes to pink and then add a further 1 ml in excess. The volume of the solution shall be between 150 and 250 ml. Afterwards 25 ml of the potassium sulfate solution would be added from a one-mark pipet. Cover the beaker with watch glass, heat the cover beaker until the solution boils and then reduce the heating slightly until ebullition ceases. Add 10 ml of the cold barium chloride solution from a pipette with a delivery time of approximately 20 seconds, held so that the barium chloride falls into the center of the solution, whilst this is being agitated. Keep the solution just below boiling point, without agitation for 30 minutes. Filter the solution by gravity through a filter-paper pad prepared from ash-less, doubly acid washed filter paper. To prepare the filter paper pad shake doubly acid washed filter paper pad, shake doubly acid-washed filter paper clippings, in pieces of area approximately 1 cm^2, with water in a bottle until the paper is thoroughly disintegrated. Place a filter cone in a filter funnel of diameter 75 mm, close the stem of the funnel with a finger and add water until the cone is immersed and the funnel stem is full. Shake sufficient paper pulp onto the cone to form a pad 5 mm thick and level it with a flat-ended glass rod as drainage ceases. A final wash with water renders the filter ready for use. After transferring the filter-paper pad to the crucible, wipe out the funnel successively with two halves of an ash-less filter paper which are then incinerated with the pad. Place the wet filter paper or pad in the previously ignited and weighed crucible on the cold, flat plate and insert it into the muffle furnace for 15 minutes at a temperature of 800°C±25°C. Cool in the desiccator and reweight.

For the blank test the same procedure is used but omitting the test portion. Using a pipette, add 25 ml of the potassium sulfate solution to the filtrate before adding the methyl red indicator solution has been done and the precipitated barium sulfate for blank test is 0.126 g.

The sulfate sulfur content of sample expressed as a percentage by mass, is given by the equation (2-5).

$$S_{sulfate} = 13.74\ [(M_2 - M_3)/M_1] \qquad \textbf{Eq (2-5)}$$

In above equation, M_2, M_3 and M_1 are the mass of barium sulfate found in determination, the mass of barium sulfate found in blank test and the mass of test portion taken for hydrochloric acid extraction respectively [48,55].

For pyrite sulfur, the insoluble residue from the hydrochloric acid digestion (sulfate sulfur determination procedure) is further extracted with dilute nitric acid to bring the pyritic iron into solution. The amount of iron present is then determined by titrimetric, colorimetric or atomic absorption spectrometric techniques. It should be noted that in the present work colorimetric method has been utilized [48,55].

For colorimetric method, the standard stock solution has been prepared. For the preparation of a standard solution, dissolve 0.100 g of pure iron wire in 2.5 ml of concentrated nitric acid (approximately 70 % (m/m)) and 7.5 ml of water. Boil to expel oxides of nitrogen, cool and dilute with water to 100 ml in a volumetric flask. 1 ml of this stock solution contains 1 mg of Fe. Some reagents for this method are needed and they are listed below:

Dissolve 10 g of hydroxyl ammonium chloride in water and dilute to 100 ml. Congo red as indicator and Sodium acetate (328 g/l solution for titration), phenanthroline as indicator solution (dissolve 0.625 g of 1,10-phenanthroline hydrate or hydrochloride in water and dilute to 250 ml, it should be store in a dark glass bottle and discard the solution if a brown color developed).

For preparation of the set of calibration solutions an one-mark pipette is used, pipette 20 ml of iron standard stock solution and transferred to a 500 ml volumetric flask, dilute to the mark with water and mix thoroughly. Transfer 1 ml, 2 ml, 3 ml,… 10 ml aliquots of this solution (using one-mark pipettes) into separate 50 ml volumetric flasks. Dilute each aliquot to 25 ml with water, add 5 ml of hydroxyl ammonium chloride solution and small square of the Congo red indicator paper. Titrate the mixture with the sodium acetate solution until the indicator turns red. Add 4 ml of the phenanthroline indicator solution and dilute to 20 ml with water. Mix thoroughly and leave to stand for 1 hour.

Dilute the prepared test solution with water in volumetric flask and make up to 250 ml. Pipette 1 ml (if total sulfur is more than 0.7%) from this flask into a 50 ml volumetric flask and add 20 ml of water, 5 ml of the hydroxyl ammonium chloride solution and a small square of the Congo red indicator paper. Titrate the mixture with the sodium acetate solution until the indicator paper turns red. Add 4 ml of the phenanthroline indicator solution and dilute to 50 ml with water. Mix thoroughly and leave to stand for 1 hour [48,55].

Measure the absorbance of the calibration solution and the solution prepared in this sub-clause with the UV/visible spectrometer, at a wavelength of 510 nm using a cell of suitable path length, against water. Convert the absorbance volume of the diluted test solution to mass of iron, in micrograms, by reference to the calibration curve. The calibration curve is prepared by plotting the absorbance measured by the UV/visible spectrometer (Model: Cary 100) against the iron content, in micrograms of the calibration solutions.

Based on above procedure, the colorimetric method has been used and the standard curve has been prepared. The colorimetric curve is illustrated in Fig(2-3) and the related equation is shown in equation (2-6) [48,55].

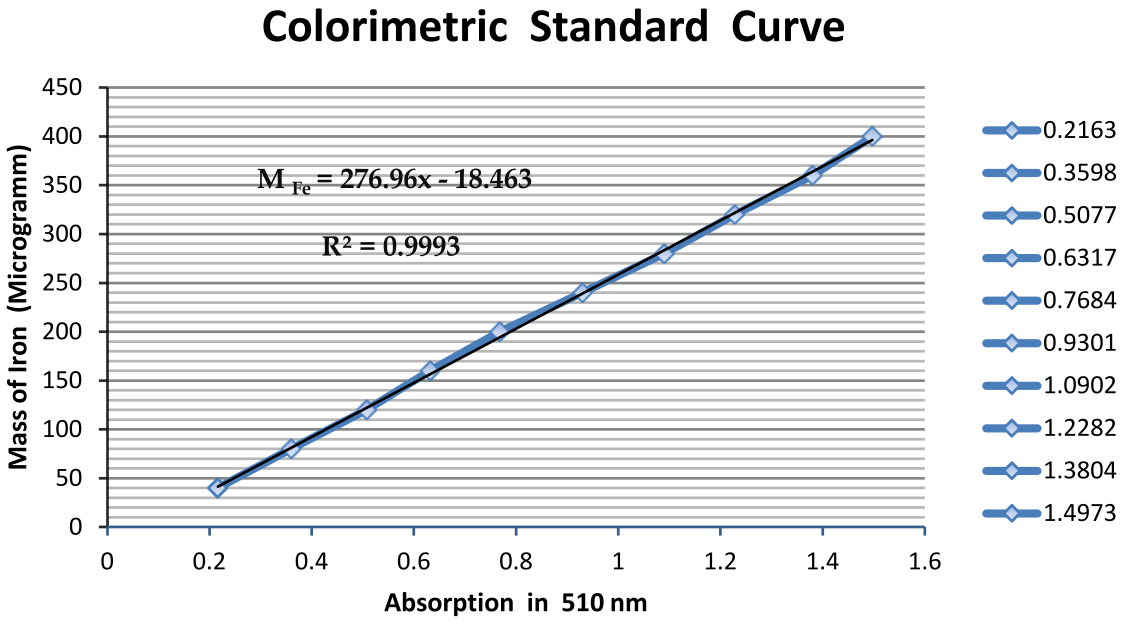


Fig (2-3). Colorimetric standard curve based on standard diluted solutions.

$M_{Fe} = 276.96\ X - 18.463$ **Eq(2-6)**

In above equation, M_{Fe} and X are mass of iron content in the diluted test solution and absorption % measured by the UV spectro-photometer respectively [48,55].

$S_{Pyrite} = 0.0287\ [(M_{Fe}-M_2)/(V_3.M_1)]$ **Eq(2-7)**

Where, M_{Fe}, M_2, V_3 and M_1 are the mass in micrograms of iron in the diluted test solution, the mass of the original test portion taken for hydrochloric acid extraction and the volume in milliliters of the aliquot taken from the diluted test solution and the mass of test portion respectively [48,55].

2.3.4. Energy content – HHV determination

The calorific value is the heat produced by the combustion of a unit quantity of coal in a bomb calorimeter with oxygen and under a specified set of conditions (ASTM D-121; ASTM D-2015; ASTM D-3286; ISO 1928). For the analysis of coal, the calorific value is determined in a bomb calorimeter either by a static (isothermal) method or by an adiabatic method, with a correction made if net calorific value is of interest. The unit is calories per gram, which may be converted to the alternate units (1.0 kcal/kg = 1.8 Btu/lb = 4.187 kJ/kg) [57-60].

The calorific value is a direct indication of the heat content (energy value) of the coal and represents the combined heats of combustion of the carbon, hydrogen, nitrogen, and sulfur in the organic matter and of the sulfur in pyrite and is the gross calorific value with a correction applied if the net calorific value is of interest. The calorific value is usually expressed as the gross calorific value (GCV) or the higher heating value (HHV) and the net calorific value (NCV) or lower calorific value (LHV). The difference between the GCV and the NCV is the latent heat of condensation of the water vapor produced during the combustion process. The GCV assumes that all of vapor produced during the combustion process is fully condensed. The NCV assumes that the water is removed with the combustion products without being fully condensed [57-60].

In this study HHV calculated by the formula of Channiwala [61]. The Flash 2000 CHNS/O analyzer has been used.

$$HHV^{db}(MJ/kg)=0.3491\times\mathbf{C}+1.1783\times\mathbf{H}+0.1005\times\mathbf{S}-0.1034\mathbf{O}-0.0151\times\mathbf{N}-0.0211\times\mathbf{Ash} \qquad \textbf{Eq (2-8)}$$

2.3.5. AP-TPR analysis

The identification of volatile species released during the reductive pyrolysis of the samples under study was done by AP-TPR experiments. This method is developed as a new technique for sulfur compounds determination in coals, upon the knowledge of their chemical compositions. A fundamental requirement of any research into desulfurization is an accurate method for assessment the various forms and species of sulfur in coal. Temperature programmed reduction at atmospheric pressure (AP-TPR) and its different detection modes has been successfully used for the specification of sulfur functionalities in coal [62-85].

Sulfur distribution revealed by AP-TPR is based on the fact that each type of the sulfur group under constant heating rate in a reduction (H_2) gas flow rate has a characteristic temperature region in which it is maximal reduced / hydrogenated into H_2S. The assignment of the temperature region, in which a certain sulfur functional group is reduced / hydrogenated, is based on the pyrolysis of model compounds [31,33,48,50]. The distribution of sulfur functional groups in coal can be deduced by H_2S evolution as a function of the temperature. Despite of the high reduction / hydrogenation efficiency of total sulfur into H_2S achieved for the most studied coals (70-100%) by AP-TPR [62,63,65,67,73,74] in some cases reduction / hydrogenation efficiency of sulfur into H_2S can be rather low. This is especially in the cases:

- Coal samples that contain certain minerals (mainly calcium compounds) as calcium minerals capture in gaseous H_2S, formed under AP-TPR conditions and produce CaS [65,68,73].
- Coals that have been subjected to different oxidizing treatments as this can result in formation of oxidized sulfur functionalities, which are not entirely reduced into H_2S but rather evolved as SO/SO_2 [63,65,68,86,87].

Other explanations for the incomplete reduction of sulfur functionalities might be the original presence or the formation of hydrogenation resistant sulfur containing aromatic species which remain in the tar and char fractions [63,64,71,75,83]. In order to obtain more detailed information on total sulfur distribution during TPR pyrolysis and hence more reliable information on sulfur functionalities in coal, the TPR technique is further developed. AP-TPR "on-line" interfaced to mass spectrometer (AP-TPR-MS) enables the monitoring not only of H_2S but also SO/SO_2 (partly) (released during thermal decomposition of oxidized sulfur functionalities) and volatile organic sulfur compounds, neither reduced in AP-TPR experimental condition into H_2S nor captured into the tar and char fractions, can be qualitatively and quantitatively assessed by AP-TPR "off-line" coupled with TD-GC/MS (AP-TPR-TD-GC/MS).

Quantitative evaluation of the sulfur incorporated into tar and char residue can be achieved by elemental analyzer (FleshEA 1112, Thermo Electron Corporation). After each experiment the residue (tar and char) left in the reactor is quantitatively collected by rinsing the reactor with dichloromethane. The obtained mixture is dried at 70°C for 24 hour and analyzed for its total sulfur content by elemental analyzer. The difference between measured sulfur contents before and after pyrolysis is calculated and can be assigned for all non-treated and treated samples as the sulfur amount detected by MS as H_2S. In this way, the efficiency and yield of the reduction/hydrogenation of all sulfur compounds into H_2S during the AP-TPR experiment can be calculated and correlated with the area under the total H_2S signal and thus under each H_2S peak, making an almost quantitative sulfur compound assignment possible (mentioned method will be discussed in the next chapter). It is proven by AP-TPR "off-line" that for all coals studied up till now, the amount of organic volatile sulfur compounds as SO_2 and SO is only around 1% of the total amount of sulfur present in the coal. Therefore the above formulated statements are rather acceptable.

2.3.5.1. AP-TPR "online" with Mass Spectroscopy

AP-TPR coupled "on-line" with mass spectrometry (AP-TPR-MS) in different gas flow (H_2 or He) can be used to specify organic sulfur functionalities in coal and to assess the changes after microwave or ultrasound treatment. The mentioned analyses are performed in the AP-TPR setup described in Fig (2-3) [88].

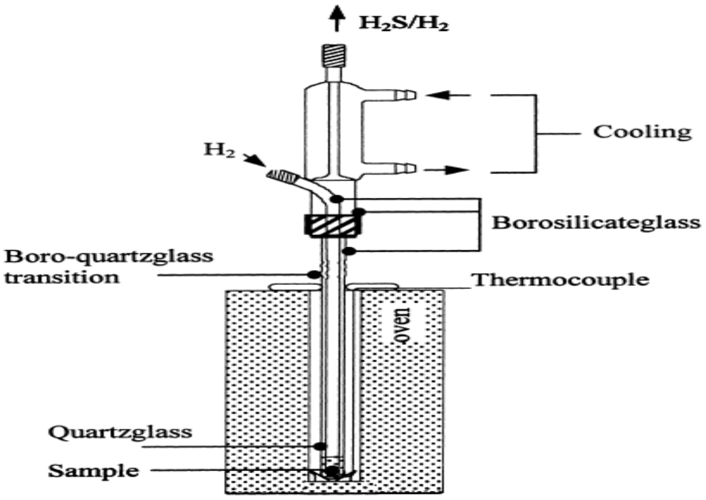


Fig (2-3). AP-TPR reactor setup [88].

The TPR reactor is coupled “on-line” with mass spectrometer (FISONS-VG Thermolab MS) through a capillary heated at 135 °C. The mass spectrometer equipped with a quadrupole analyzer set an ionizing voltage of 70 eV. The MS signals of ions with m/z 10 to 250 are online monitored. The opening around the reactor in the oven is plugged with glass wool for isolation. A linear program of 5°C/min from room temperature up to 1025 °C is followed. During analysis, H_2S is formed and swept out of the reactor by the 100 cm^3/min flow of pure hydrogen. The data are automatically saved on the hard disk during analysis [88].

2.3.5.2. AP-TPR “off-line” with Gas chromatography

The mentioned procedure of AP-TPR system can also be used in adsorption/desorption mode in order to study of volatile sulfur, neither reduced in the AP-TPR condition nor captured in the tar and char fraction. The outlet of the AP-TPR reactor is connected to a set of ice cooled tubes containing Tenax (Sigma-Aldrich), a porous polymer of 2,6-diphenyl-p-phenylene oxide as adsorbent. The volatiles are collected in a temperature range from 200 °C up to 700 °C (temperature range is determined by the results of the AP-TPR-MS experiments) in discrete temperature intervals (in this study 100 °C). The Tenax tubes are desorbed systematically and analyzed by a Perkin Elmer GC/MS apparatus using He as a carrier gas at 48 kPa at following conditions:

- Thermal desorber ATD 400: desorption temperature and time, respectively, 275 °C and 5 min, outlet split: 14 mL/min.
- GC Auto system XL with capillary column ZB1 15 m × 0.32 mm and film thickness of 3 μm: initial at 260 °C during 3 min.
- MS TurboMass Ver. 4.1.1: m/z 25 => 300 in 0.5s. Each Tenax tube is spiked with 0.5 μg d_6–benzene in methanol solution to quantify results of the target sulfur species.

In order to improve qualitative /quantitative interpretation of volatile sulfur released during pyrolysis experiment, the AP-TPR-TD-GC/MS technique is upgraded by replacing the Tenax tubes filled with sulfur compounds selective sorbents, and by the use of deuterated sulfur containing organic compound as internal standard. In this case, the outlet of AP-TPR reactor is connected to ice-cooled metal adsorption tubes with SilcoSteel Coating, filled with Tenax/Carbopack B/Carbosieve SIII (Markes) as adsorbents. The volatiles are trapped in the temperature range from 200 °C up to 950 °C in temperature intervals of 75 °C. the adsorption tubes are desorbed systematically and analyzed by a TD-GC/MS. TD-GC/MS apparatus is used with He as career gas at 85 kPa at the following conditions:

- Unity thermal desorber (Marks): primary desorption 20 min at 320 °C; Cold trap at -8 °C, heated at maximum heating rate up to 320 °C, hold time 15 min; flow path temperature 200°C.
- Trace GC Ultra-Gas chromatography (Thermo Instruments): capillary column 30 meters ZB 5-MS 0.25 mm × 0.25 µ Phenomenex; temperature program – 3 min at 30 °C, heated 8°C/min to 100 °C, heated 12°C/min to 310°C, hold time 5 min,
- DSQ-Mass spectrometer (Thermo instruments): EI spectra; Ionization energy – 70 eV; Scan range – m/z 33-480 in 0.4s. Each tubes is spiked with 3 µg d_4-thiophene to quantify results of the target sulfur species. NIST library spectra are used for peak identification with special interest to the different sulfur species, liberated or in situ formed during the AP-TPR pyrolysis. The formed H_2S gas is not adsorbed by the Tenax tubes, nor by the sulfur selective adsorption tubes.

2.4. References

[1] Hashemi S. M., Structural analysis of coal mines Parvade Tabas, Undergraduate thesis of geology, Ferdowsi University of Mashhad., 1993.

[2] Nott K.P, Hall L.D, (1999). Advances in temperature validation of foods Trends in Food Science & Technology, Volume 10, Issue 11, November 1999, p. 366-374.

[3] Swain M.J, James S.J, Swain M.V.L, (2008). Effect of power output reduction of domestic microwave ovens after continuous (intermittent) use on food temperature after reheating Journal of Food Engineering, Volume 87, Issue 1, July 2008, p. 11-15.

[4] Menezes R R., Souto P. M, Kiminami R, (2007). Microwave hybrid fast sintering of porcelain bodies Journal of Materials Processing Technology, Volume 190, Issues 1-3, 23 July 2007, p. 223-229.

[5] Ostwald P.A, Munoz S (1996). Effects of ore mineralogy on the microbial leaching of low grade complex sulphide ores Hydrometallurgy, Volume 86, Issues 1-2, April 2007, p. 96-104.

[6] De Alwis A. A. P, Fryer P.J, (1990). The use of direct resistance heating in the food industry Journal of Food Engineering, Volume 11, Issue 1, 1990, p. 3-2.7

[7] Ming C, Hower J.C, (2004). Impact of coal properties on coal combustion by-product quality: examples from a Kentucky power plant International Journal of Coal Geology, Volume 59, Issues 3-4, 10 August 2004, p. 153-169.

[8] Maxwell E, Kelland D.R, Jacobs I.S, Levinson L.M, (1982). Magnetic separation and thermo-magneto-chemical properties of coal liquefaction mineral participates Original Research Article Fuel, Volume 61, Issue 4, April 1982, p.369-376.

[9] Meredith R.J., (1998). Engineers` Handbook of Industrial Microwave Heating. The Institution of Electrical Engineers, London.

[10] Whittacker G.. (1997). A basic Introduction to Microwave Chemistry Oxford, Oxford University Press.

[11] http://www.sonicator.com/pdf/Howdoesitwork.pdf

[12] Lindstrom O, Lamm O (1951) The chemical effects produced by ultrasonic waves. J Phys Chem 55,p.1139–1146

[13] Webster E (1963) Cavitation. Ultrasonics 1,p.39–48.

[14] Makino K, Mossoba MM, Riesz P (1982) Chemical effects of ultrasound on aqueous solutions evidence for OH- and H+ by spin trapping. J Am Chem Soc 104,p.3537–3539.

[15] Riesz P, Berdahl D, Christman CL (1985) Free radical generation by ultrasound in aqueous and non-aqueous solutions. Environ Health Perspect 64,p.233–252.

[16] Christman CL, Carmichael AJ, Mossoba MM, Riesz P (1987) Evidence for free radicals produced in aqueous solutions by diagnostic ultrasound. Ultrasonics 25,p.31–34.

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

[18] Misik V, Riesz P (1996) Peroxyl radical formation in aqueous solutions of ndimethylformamide,n-methylformamide, and dimethylsulfoxide by ultrasound. Free Radical Biol Med 20,p.129–138.

[19] Entezari MH, Krus P (1994) Effect of frequency on sono chemical reaction. Ultrason Sonochem 1,p.75–79.

[20] Luche JL (1994) Effect of ultrasound on heterogeneous system. Ultrason Sonochem 1,p.111–118.

[21] Henglein A (1995) Chemical effects of continuous and pulsed ultrasound in aqueous solutions. Ultrason Sonochem 2, p.115–121.

[22] Hoffmann MR, Hua I, Hochemer R (1996) Application of ultrasonic irradiation for the degradation of chemical contaminants in water. Ultrasonic Sonochemistry 3, p.163–172.

[23] Allardice, D. J., and Evans, D. G. 1978. In Analytical Methods for Coal and Coal Products, Vol. I, C. Karr, Jr. (Editor). Academic Press, San Diego, CA, Chap.7.

[24] ASTM D-3172. Standard Practice for Proximate Analysis of Coal and Coke.

[25] ASTM D-3173. Standard Test Method for Moisture in the Analysis Sample of Coal and Coke.

[26] ASTM D-3174. Standard Test Method for Ash in the Analysis Sample of Coal and Coke from Coal.

[27] ASTM D-3175. Standard Test Method for Volatile Matter in the Analysis Sample of Coal and Coke.

[28] ASTM D-5142. Standard Test Methods for Proximate Analysis of the Analysis Sample of Coal and Coke by Instrumental Procedures.

[29] ISO 1171. Determination of Ash.

[30] Russell, S. J., and Rimmer, S. M. 1979. In Analytical Methods for Coal and Coal Products, Vol. 3, C. Karr, Jr. (Editor). Academic Press, San Diego, CA, Chap. 42.

[31] ISO 331. Determination of Moisture in the Analysis of Coal.

[32] ISO 687. Determination of Moisture in the Analysis Sample of Coke.

[33] ISO 1171. Determination of Ash.

[34] Given, P. H., and Yarzab, R. F. 1978. In Analytical Methods for Coal and Coal Products, Vol. 2, C. Karr, Jr. (Editor). Academic Press, San Diego, CA, Chap. 20.

[35] Elliott, M. A. (Editor). 1981. Chemistry of Coal Utilization. Wiley, Hoboken, NJ.

[36] Speight, J. G. 1994. The Chemistry and Technology of Coal, 2nd ed. Marcel Dekker, New York.

[37] ISO 562. Determination of Volatile Matter in Hard Coal and Coke.

[38] Speight, J. G. 1991. Handbook of Petroleum Analysis. Wiley, Hoboken, NJ.

[39] Speight, J. G. 2001. Handbook of Petroleum Analysis. Wiley, Hoboken, NJ.

[40] Zimmerman, R. E. 1979 *Evaluating and Testing the Coking Properties of Coal*. Miller Freeman, San Francisco, CA.

[41] ASTM D-388. Standard Classification of Coals by Rank.

[42] Volborth, A. 1979a. In *Analytical Methods for Coal and Coal Products*, Vol. 3, C. Karr, Jr. (Editor). Academic Press, San Diego, CA, Chap. 47.

[43] ASTM D-3176. Standard Practice for Ultimate Analysis of Coal and Coke.

[44] ASTM D-3178. Standard Test Methods for Carbon and Hydrogen in the Analysis Sample of Coal and Coke.

[45] ASTM D-3179. Standard Test Methods for Nitrogen in the Analysis Sample of Coal and Coke.

[46] ASTM D-4239. Standard Test Methods for Sulfur in the Analysis Sample of Coal and Coke Using High Temperature Tube Furnace Combustion Methods.

[47] ASTM D-3177. Standard Test Methods for Total Sulfur in the Analysis Sample of Coal and Coke.

[48] ISO 334. Determination of Total Sulfur: Eschka Method.

[49] ISO 351. Determination of Total Sulfur: High Temperature Combustion Method.

[50] ISO 609. Determination of Carbon and Hydrogen: High Temperature Combustion Method.

[51] ISO 625. 2003. Determination of Carbon and Hydrogen: Liebig Method.

[52] ISO 333. Determination of Nitrogen: Semi-micro Kjeldahl Method.

[53] ASTM D-3179. Standard Test Methods for Nitrogen in the Analysis Sample of Coal and Coke.

[54] Chakrabarti, J. N. 1982. In Coal and Coal Products: Analytical Characterization Tech-vniques, E. L. Fuller Jr. (Editor). Symposium Series 205. American Chemical Society, Washington, DC, Chap. 8.

[55] ISO 157. Determination of Forms of Sulfur.

[56] Volborth, A., Dahy, J. P., and Miller, G. E. 1987. In Coal Science and Chemistry, A. Volborth (Editor). Elsevier, Amsterdam, p. 417.

[57] ASTM D-121. Terminology of Coal and Coke.

[58] ASTM D-2015. Test Method for Gross Calorific Value of Coal and Coke by the Adiabatic Bomb Calorimeter.

[59] ASTM D-3286. Test Method for Gross Calorific Value of Coal and Coke by the Isoperibol Bomb Calorimeter.

[60] ISO 1928. Determination of Gross Calorific Value and Calculation of Net Calorific Value.

[61] Channiwala SA, Parikh PP. ,A unified correlation for estimating HHV of solid liquid and gaseous fuels, Fuel 2002, 81, (8), p.1051-63.

[62] Jorjani E, Yperman J, Carleer R, Rezaei B (2006). Reductive pyrolysis study of sulfur compounds in different Tabas coal samples (Iran). Fuel; 85, p.114-120.

[63] Rutkowski P, Mullens S, Yperman J, Gryglewicz G. AP-TPR investigation of the effect of pyrite removal on the sulfur characterization of different rank coals. Fuel processing technology 2002;76, p.121-138.

[64] Marinov S, Stefanova M, Stamenova V, Carleer R, Yperman J. (2005) Sulfur functionality study of steam pyrolyzed “Maquinenza” lignite using reductive pyrolysis technique coupled with MS and GC/MS detection systems. Fuel processing technology;85, p.523-34.

[65] Van Aelst J, Yperman J, Franco DV, Mullens J, Van poucke LC Palmer SR. Sulfur distribution in Illinios no.6 coal subjected to different oxidation pre-treatments. Fuel 1997;76 (14-15),p.1377-81.

[66] Marinov SP, Stefanova M, Kostova I, Stamenova V, Carleer R, Yperman J. Peculiarities of sulfur functionalities in the Thracian coal province, Bulgaria. Bulletin of Geosciences 2005; 80(1),p.33-8.

[67] Yperman J, Maes I, Van de Rul H, Mullens S, Van Aelst J, Franco D, Sulfur group analysis in solid matrices by atmospheric pressure-temperature programmed reduction. Analytica Chimica Acta 1999;395, p.143-55.

[68] Van Aelst J, Alvarez Rodriguez R, Yperman J, Clemente Jul C, Franco D, Mullens J. AP-TPR investigation of the effect of nitric acid leaching on the sulfur distribution in coal Fuel 2000;79, p.537-44.

[69] Mullens S, Yperman J, Reggers G, Carleer R, Buchanan Iii AC, Britt PF. A study of the reductive pyrolysis behavior of sulfur model compounds. Journal of analytical and applied pyrolysis 2003;70(2),p.469-491.

[70] Kozlowski M, Wachowska H, Yperman J. Reductive and non-reductive methylation of high-sulfur coals studied by atmospheric pressure-temperature programmed reduction technique. Fuel 3002;82 (9),p.1041-1047.

[71] Marinov SP, Tyuliev G, Stefanova M, Carleer R, Yperman J. (2004) Low rank coals sulfur functionality study by XPS. Fuel Processing Technology 85 (4) p.267-277.

[72] Yperman J, Franco D, Mullens J, Van Pouke LC, Gryglewicz G, Jasienko S. Determination of sulfur groups in Pyrolysed low-rank coalby atmospheric pressure TPR. Fuel 1995;74 (9),p. 1261-1266.

[73] Maes II, Gryglewicz G, Machnikowska H, Yperman J, Franco DV, Mullens J. Rank dependence of organic sulfur functionalities in coal. Fuel 1997;76 (5),p.391-396.

[74] Maes II, Gryglewicz G, Machnikowska H, Yperman J, Franco DV, Mullens J, Van Poucke LC. Effect of calcium and minerals in coal on its thermal analysis. Fuel 1997; 76 (2) ,p.143-147.

[75] Stefanova M, Marinov S, Yperman J, Carleer R. Reductive pyrolysis of Miocene-aged lignite lithotypes using MS and GC/MS detection systems for analysis of organic sulfur groups. Fuel 2005; 85 (1),p.71-79.

[76] Kozlowski M, Maes II, Wachowska H, Franco DV, Mullens J, Van Poucke LC. Reduction of high-sulfur coal in the potassium-liquid ammonia system. Fuel 1999;78 (7),p.769-74.

[77] Liu F, Li B, Li W, Bai Z, Yperman J. Py-Ms study of sulfur behavior during pyrolysis of high-sulfur coals under different atmospheres. Fuel processing Technology 2010; 91 (11), p.1486-90.

[78] Maes II, Mitchell SC, Yperman J, Franco DV, Marinov SP, Mullens J. Sulfur functionalities and physical characteristics of the Maritza Iztok Basin lignite. Fuel 1996;75 (11),p.1286-93.

[79] Kozlowski M, Pietrezak R, Wachowska H, Yperman J. AP-TPR study of sulfur in coals subjected to mild oxidation. Part 1. Demineralized coals. Fuel 2002;81 (18),p.2397-405.

[80] Maes II, Gryglewicz G, Yperman J, Franco DV, D'Haes J, D'Olieslaeger M. Effect of siderite in coal on reductive pyrolytic analyses. Fuel 2000;79 (15),p.1873-81.

[81] Kozlowski M, Wachowska H, Yperman J. Transformations of sulfur compounds in high-sulfur coals during reduction in the potassium/liquid ammonia system. Fuel 2003; 82 (9),p.1149-53.

[82] Gryglewicz G, Wilk P, Yperman J, Franco DV, Maes II, Mullens J,. Interaction of the organic matrix with pyrite during pyrolysis of high sulfur bituminous coal. Fuel, 1996, 75 (13),p.1499-504.

[83] Mullens S, Yperman J, Carleer R, Bozdemir T, Durusoy T, Yurum Y. Sulfur analysis of Bolu-Mengen lignite before and after Microbiological treatment using reductive pyrolysis and Gas Chromatography/Mass Spectrometry. Energy & Fuels 2005, 19 (3),p.1029-36.

[84] Van Aelst J, Yperman J, Franco DV, Van Poucke LC, Buchanan AC, Britt PF Study of Silica-Immobilized sulfur Model compounds as Calibrants for the AP-TPR study of oxidized coal samples. Energy & Fuels 2000, 14 (5), p.1002-8.

[85] Yperman J, Franco D, Mullens J, Van Poucke LC, Snape CE, Mitchell SC. A study of the organic sulfur distribution in solid fuels by means of atmospheric pressure temperature programmed reduction (AP-TPR). In:pajares JA, Tascon JMD (Eds) Coal Science and technology. Elsevier, 1995,p.1673-6.

[86] Ismail K, Mitchell SC, Brown DC, Snap CE, Buchanan III AC, Britt PF. Silica-immobilized sulfur compounds as solid calibrants for temperature programmed reduction and probes for thermal behavior of organic sulfur forms in fossil fuels. Energy Fuels 1995; 9 (4),p.707-16.

[87] Kozlowski M, Pietrzak R, Wachowska H, Yperman J. AP-TPR study of sulfur in coals subjected to mild oxidation. Part 1. Demineralised coals. Fuel 2002;81 (18),p.2397-405.

[88] Yperman J, Maes II, Heidi VD, Mullens S, Aelst VJ, Franco VD, Mullens J, Van Poucke LC. Sulfur group analysis in solid matrices by atmospheric pressure temperature programmed reduction, Analytica Chimica acta,395 (1999),p.143-155.

Chapter 3

Assessment of microwave treatment on coal structure and sulfur forms by AP-TPR method

The results discussed in this chapter have been published in the Journal under title of fuel processing technology: Sh. Mesroghli, J. Yperman, E. Jorjani, R. Carleer, M. Noaparast, Evaluation of microwave treatment on coal structure and sulfur species by reductive pyrolysis- mass spectrometry method.

3.1 Introduction

Coal is one of the world’s most abundant fossil fuel resources. The usefulness of coal as a heat source and the myriad byproducts that can be produced from coal are well understood. The continued and increasingly large-scale use of coal in the world and in many industrialized and developing nations has resulted in increases in known hazards and has raised speculation about other possible hazards to environmental quality and human health. As a result, there is still much to be learned about the harmful and even the beneficial attributes of coal and how they may be removed, modified, avoided, or exploited to make coal use less harmful to humans and nature and (or) more useful for the general welfare [1].

The forms of sulfur in coal can be categorized in two major groups, which are inorganic (disulfides such as pyrite which occurs in mineral matter, marcasite and sulfates) and organic sulfurs which is presented as an integral part of coal matrix (thiols, sulfides, disulfides, thiophenes and cyclic sulfides) [2].

Microwave energy is nonionizing electromagnetic radiation with frequencies that range from 300 MHz to 300 GHz or wavelength that range from 1 to 300 mm. Microwaves can be transmitted, absorbed or reflected. Insulators are transparent to the microwaves and, thus, do not store any of energy in the form of heat. The advantages of microwave heating are rapid and selective heating, uniform heat distribution, flexible modular design, environmentally friendly application, fast switch-on and switch-off and high efficiency [3-5]. In recent years there has been a growing interest of microwave heating in mineral

treatment and for this reason the number of applications has been investigated. Microwave ovens basically operate at a frequency of 2.45 GHz corresponding to a wavelength of 12.2 cm and energy of 1.02 × 1025 eV for domestic and industrial applications [6]. Materials have different responses against microwave irradiation, some of them absorb these waves (dielectric) whilst the others reflect or are transparent to microwaves. The materials that absorb the microwave contain dipoles. When microwaves are applied to the material, the dipoles align and flip around, as the applied field is alternating. Materials are heated when the stored internal energy is lost to friction [7-10]. Some minerals which are present in ash readily heated within an applied electric field, (pyrite has an average heating rate of 1.0 ^{o}C/s when exposed to a microwave field at a power of 650W and frequency of 2.45GHz) whilst others appear transparent to the radiation (quartz has an average heating rate of 0.08 ^{o}C/s when exposed to a microwave field at a power of 650W and frequency of 2.45GHz) [11-13]. It has been proven that by exposing coal to microwave irradiation, localized heating occurs at pyrite sources and pyrite decomposed and produced iron sulfide or iron sulfate (the mentioned reaction progresses by increasing the time of irradiation) [14].
Based on the in-situ reactions between sulfur and other elements in coal [15], in response to the effects of the microwave irradiation, the bonds of sulfur–iron in pyrite and sulfur–carbon in organic sulfur compounds are broken and some of the sulfur is released in gaseous form.

It should be noted that the organic parts of coals are relatively poor absorbers of microwave energy [16]. To determine the suitability of any special coal desulfurization method, knowledge of the distribution of different forms of sulfur within the coal is very important. For this reason the total sulfur content determined with standard methods will not provide sufficient information to assess the application and sustainability of a specific method. Quantitative and qualitative assessment of coal sulfur forms is obligatory. There are several techniques to reach these aims such as X-ray techniques and thermal degradation of coal sample [17-19]. Positive influences of microwave irradiation has been reported [20] in view of the optimization of sulfur leaching process by an in advance different irradiation treatments.

The results of a study about the effects of microwave irradiation treatment on coal composition with considering the physic-chemical aspects showed that microwave irradiation treatment significantly reduced the coal moisture and increased the calorific value and fixed carbon content. The study also proved that the combustion processes of treated coals were delayed toward higher temperature region and some changes in chemical characteristics of treated coal have been noticed [21]. Moreover, the microwave influences as a convenient drying method for low-rank sub-bituminous coal has been investigated. The achieved results demonstrated that microwave drying had several advantages over conventional methods [22]. In another study, it was shown that the floatability of oxidized coals was improved by microwave irradiation. The results of this research revealed the increment of combustible recovery with microwave treatment time by decreasing the moisture content of oxidized coal [23]. Drying characteristics of low rank coals in a local microwave oven were investigated [24], like some variables such as particle size, microwave power level and coal sample size were mentioned. It was found that the drying rate was increased with increasing coal particle size and showed different trends compared with conventional drying methods. The investigation on the coal desulfurization by means of magnetic separation followed by microwave heating for enhanced magnetic removal of pyrite has been accomplished too and many positive effects of microwave irradiation to remove the pyrite have been noticed [25].

To investigate the changes and presence of different organic sulfur functionalities in coal in more detail Atmospheric Pressure-Temperature Programmed-Reduction (AP-TPR) method is applied [26-28].

In this first paper of two, the influences of microwave irradiation on the coal matrix changes has been investigated in view of a subsequent and more effective desulfurization treatment with peroxyacetic acid. Indeed, in literature a positive effect of the microwave irradiation was reported on coal desulfurization [20]. We also tried to find out why by answering the question: “whether microwave irradiation can cause changes in sulfur functionalities into more simple forms with lower bonding energy?”

In this study, relatively high sulfur coal (Tabas coal from C1 seam) is studied by the AP-TPR method in a qualitative but also for the first time in a more quantitative way, applying a new approach. Besides the determination of changes in sulfur compounds of microwave treated coal also coal matrix changes are studied.

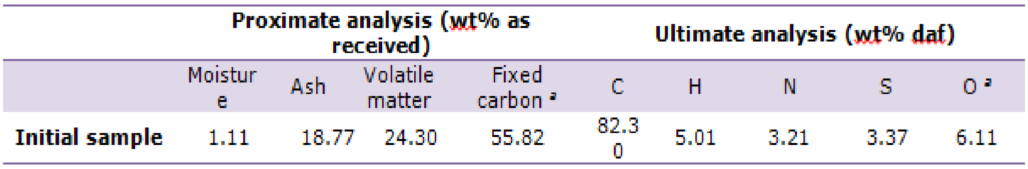
The objective of this work is to assess the effect of power and time of microwave irradiation on organic sulfur forms and on coal matrix changes using the AP-TPR-MS analytical method. It is believed that a deeper knowledge in the kind of organic sulfur functionalities and the organic sulfur transformation in the coal by irradiation will give a better indication which desulfurization method should be best applied.

3.2. Experimental

3.2.1. Coal sample

40 Kg of coal sample from active stops in C1 seam of Tabas coal mine with high sulfur content was collected. The sampling techniques similar to those of Jones riffles, conning and quartering methods were adapted and representative samples were prepared for further studies. Proximate and ultimate analysis of the representative sample has been accomplished according to standard methods (Table (3.1)). Total, pyritic and sulfate sulfur have been determined in all samples by ISO methods 334 and 157 in duplication [29, 31]. In this method, sulfate and pyritic sulfur are determined in separated procedures. The test portion is extracted with dilute hydrochloric acid (15% (*m/m*)) to bring both the sulfate and non-pyritic iron into solution. The pyritic iron and sulfur remain in the residue which is separated by filtration. The sulfate sulfur extracted by dilute hydrochloric acid from the test portion is determined gravimetrically by precipitation with barium chloride. The insoluble residue from the hydrochloric acid digestion is further extracted with dilute nitric acid (9% (*m/m*)) to bring the pyritic iron into solution.

Table (3.1). Proximate and ultimate analysis of initial coal sample



	Proximate analysis (wt% as received)				Ultimate analysis (wt% daf)				
	Moisture	Ash	Volatile matter	Fixed carbon ^{a}	C	H	N	S	O ^{a}
Initial sample	1.11	18.77	24.30	55.82	82.30	5.01	3.21	3.37	6.11

a:by difference

The amount of iron present is then determined by colorimetric technique. [29] The results of total sulfur distribution in different fraction size for the representative coal sample are shown in Table (3.2).

Table (3.2). Distribution of Total sulfur amounts in studied coal sample (Dry basis)

Size fraction (mm)	Remain on Sieve (gr)	Total Sulfur (%)
+ 4.00	19.52	3.283
-4.00 to +3.35	10.69	3.956
- 3.35 to +2.00	28.35	3.566
- 2.00 to +1.70	8.72	3.350
- 1.70 to +1.00	30.44	3.257
- 1.00 to +0.710	19.09	3.983
- 0.710 to +0.500	13.75	3.309
- 0.500 to +0.355	7.83	3.379
- 0.355 to +0.250	19.84	3.127
- 0.250 to +0.150	14.65	3.539
- 0.150 to +0.125	3.90	3.357
- 0.125 to +0.075	9.39	3.470
- 0.075	13.84	3.174
	Summation : 200	Average : 3.13±0.26%

It can be stated from these results that, the distribution of total sulfur amount in the whole fraction sizes are approximately the same. According to the Table (3.2) it can be seen that the sulfur is well distributed in selected sample and that no significant differences between total sulfur content in various fraction sizes is noticed.

3.2.2. Microwave irradiation

About 40 g of coal was ground to below 75 μm and was spread on Pyrex container with less than 0.4 cm thickness for microwave treatment (This mass is divided into 8 g for each set of irradiation process). Microwave irradiation was accomplished in a Samsung microwave oven with 2.45 GHz frequency and 0-1250 Watt power.

The internal capacity of the oven was around 48 dm^3 and equipped with an air circulation system. Irradiation times of 2, 4, 6 and 8 minutes have been used at different powers of 300, 600 and 900 W. The irradiated samples were cooled and dried in a desiccator, weighted and analyzed for total, sulfate, pyritic and organic sulfur. The sulfur species content on dry basis of non-treated and microwave treated samples are summarized in Table (3.3). The influence of irradiation power and time will be discussed later.

Table (3.3). Characteristics of the microwave treated coal samples.

No.	**Sample**	**Total sulfur (%)** ***(dry basis)***	**Pyrite sulfur (%)** ***(dry basis)***	**Sulfate sulfur (%)** ***(dry basis)***	**Oraganic sulfur ^{a}* (%)** ***(dry basis)***
1	**Initial coal**	3.17	1.16	0.15	1.86
2	**753002**	3.09	1.10	0.01	1.98
3	**753004**	3.12	1.18	0.01	1.93
4	**753006**	3.08	1.05	0.03	2.00
5	**753008**	3.06	1.22	0.02	1.82
6	**756002**	3.09	1.17	0.07	1.85
7	**756004**	2.84	0.90	0.03	1.91
8	**756006**	2.87	0.89	0.01	1.97
9	**756008**	3.04	1.05	0.04	1.95
10	**759002**	2.91	1.15	0.01	1.75
11	**759004**	2.85	1.05	0.01	1.79
12	**759006**	2.97	1.15	0.02	1.80
13	**759008**	3.10	1.08	0.03	1.99

**a : by difference*

Twelve samples were qualitatively and quantitatively studied by different microwave treatments to prove direct effects on coal matrix and organic sulfur forms.

In the present paper the microwave treated samples are labeled in the following way, for example: “753002” is related to the sample fraction size under 75 µm, treated with microwave power of 300 W and for 2 minutes.

3.2.3. Sample preparation for AP-TPR experiments

For each experiment, an amount of 40 mg of coal sample (<75µm) was weighed and mixed with 25 mg of fumed silica and put into a quartz reactor and stirred to achieve homogenization. The reactor was placed inside the oven and H_2 gas atmosphere was applied as swept and reacting medium. The released gases evolved during linear heating at 5°C/min were continuously monitored by a quadrupole mass spectrometric detection system.

3.2.4. AP-TPR analyses

The development of new methods for sulfur compound removal from coals depends, in part, upon the knowledge of their chemical forms. The sulfur distribution revealed by AP-TPR is based on the fact that each type of sulfur form under a constant heating rate and in a reducing (H_2) gas flow has a characteristic temperature region in which it is maximal reduced/hydrogenated into H_2S. The distribution of sulfur functional groups in coal can be deduced from these H_2S evolution profiles as a function of the temperature. In order to obtain more detailed information on total sulfur distribution during AP-TPR pyrolysis and hence more reliable information on sulfur functionalities in coal, the AP-TPR technique has been further developed [31-37].

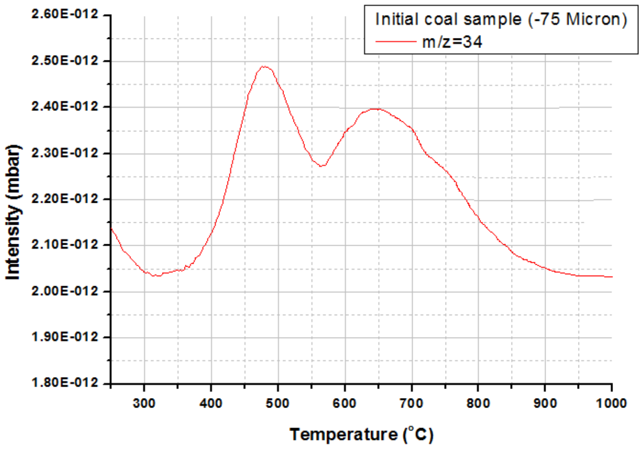
3.2.4.1. AP-TPR/MS measurements

AP-TPR/MS enables the monitoring not only of H_2S but also of SO/SO_2 (released during thermal decomposition of or not completely reduced oxidized sulfur functionalities) and all volatile organic fragments such as hydrocarbons and aromatic compounds. AP-TPR reactor is coupled “on-line” with a mass spectrometer (FISONS-VG Thermo-lab MS) through a fused silica capillary heated at 135°C. The mass spectrometer is equipped with a quadrupole analyzer and set at an ionizing voltage of 70 eV. The MS signals of ions with m/z: 10 - 250 are “on-line” monitored as a function of time. In this way qualitative information is gathered for all detected compounds. To get also more quantitative information from the MS signals related to sulfur species, the residue (tar and char) left in the reactor after the AP-TPR experiment is quantitatively collected by rinsing the reactor with dichloromethane. The obtained mixture is dried at 70°C for 24 hour and analyzed for its total sulfur content by means of an elemental analyzer (FleshEA 1112, Thermo Electron Corporation). The difference between measured sulfur content before and after pyrolysis is calculated and can be assigned as the sulfur amount detected by MS as H_2S. In this way, the efficiency and yield of the reduction/hydrogenation of all sulfur compounds into H_2S during the AP-TPR experiment can be calculated and correlated with the area under the total H_2S signal and thus under each H_2S peak, making an almost quantitative sulfur compound assignment possible. It is found that the amount of other volatile sulfur compounds than H_2S detected by the MS or by the GC/MS "off-line" variant only account for 1 up to 2% of the total volatile sulfur compounds released during an AP-TPR experiment [26], supporting the above formulated quantitative sulfur amount assignments. The sulfur left in the residue is to be considered as complex thiophenic sulfur structures (original present or formed (minor amounts)) and not hydrogenated under these AP-TPR conditions. AP-TPR/MS measurements for each sample are performed at least twice, till reliable and almost identical profiles are obtained. Proper evaluation on mean profile has been performed.

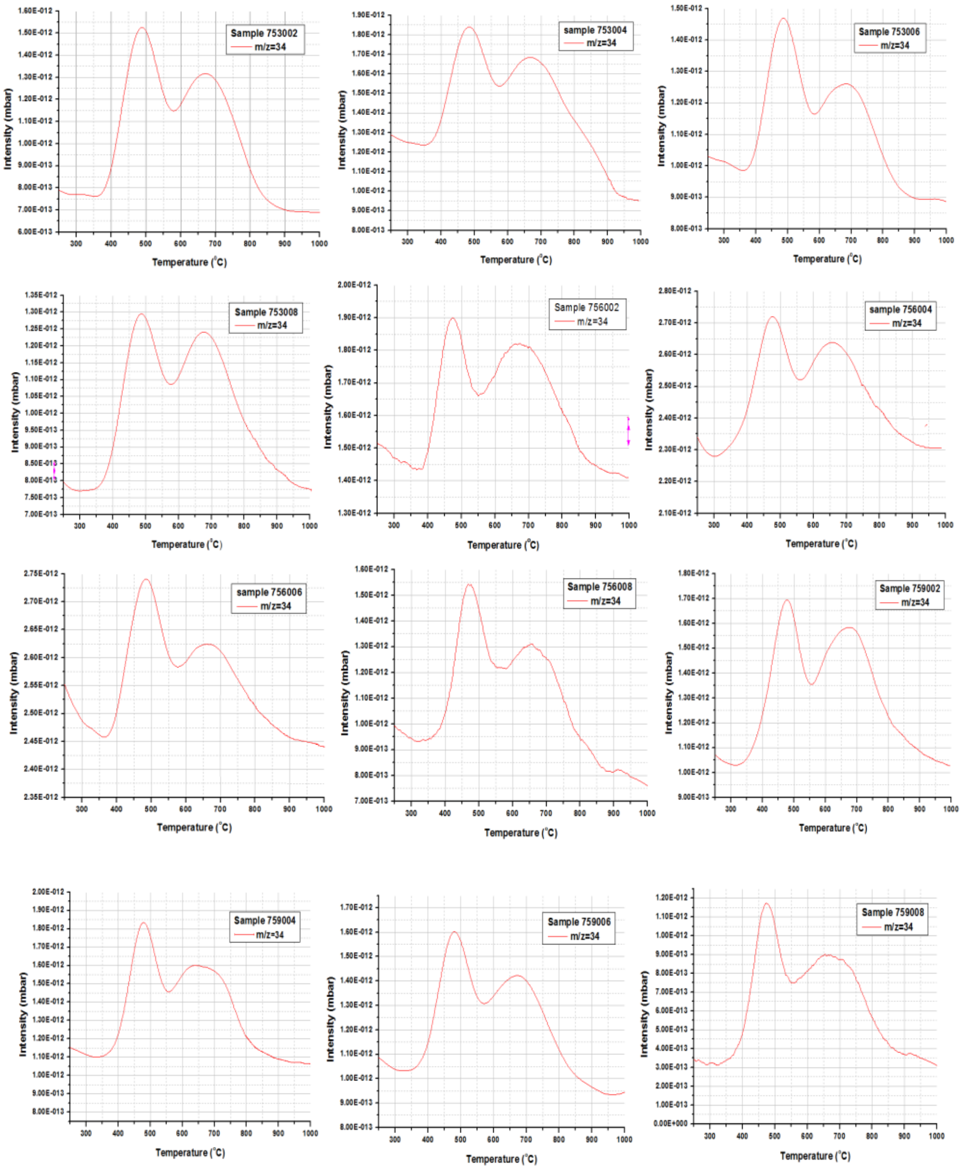
3.3 Results and discussion

3.3.1. AP-TPR experiments coupled "on-line" with MS detection in hydrogen atmosphere

The H_2S kinetograms of AP-TPR/MS of initial and microwave treated samples are shown in Fig (3.1) and Fig (3.2) respectively. The goodness of fits (Coefficient of determination (R^2)) for all fitted curves is around 97-98%.



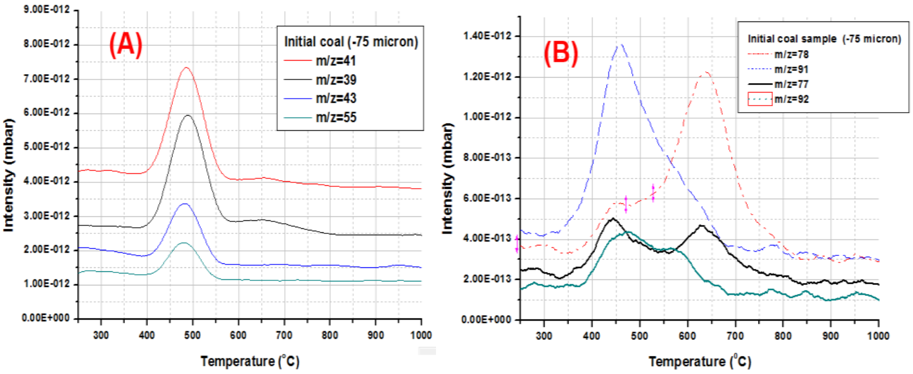
Fig(3.1). AP-TPR/MS (H_2), m/z=34 kinetograms of Tabas coal samples (initial coal)



Fig(3.2). AP-TPR/MS (H_2), m/z=34 kinetograms of Tabas coal samples (Microwave treated samples)(continue)

Because of m/z=34 (H_2S^+) and m/z =33 (HS^+) exhibit the same evolution, only m/z=34 ion profiles are used as they are more intense and more resolved. For all samples always two dominant peaks with T_{max} around 450°C and around 650-700°C are found in the AP-TPR/MS (H_2) H_2S^+ profiles. The first peak from 400-600°C can be assigned to be presence of di-alkyl, alkyl-aryl, reactive di-aryl sulfides and mostly (certainly in this coal samples) to pyrite hydrogenation (Table 2 shows its considerable presence in all samples). There is no indication for the presence of thiols or disulfides, neither in initial nor in microwave treated coals.

This above conclusion are based on model compound studies [26] and also on AP-TPR/MS profiles of typical aliphatic and aromatic CH-fragments, as is shown in Fig (3.3A and B) for the initial coal. Indeed, also the CH-fragments for the microwave irradiated samples did show the same temperature sequence and domain, but different in shape and in ratio, as will be discussed later.



Fig(3.3). AP-TPR/MS (H_2) evolution profiles of initial coal: *A.* for saturated and unsaturated CH-chains (alkenes and alkanes), *B.* for aromatic compounds.

The typical aliphatic target fragments, i.e. unsaturated/saturated CH-fragments (alkenes/alkanes), comprise m/z = 39($C_3H_3^+$), 41 ($C_3H_5^+$), 43 ($C_3H_7^+$), and 55($C_4H_7^+$).

The second peak in the H_2S^+ profile Fig (3.1) from 600-900°C refers to the presence of less reactive di-aryl sulfides, thiophenic compounds and the hydrogenation of in situ formed troilite (certainly in this coal samples). This is again based on model compound studies and on the evolution of typical aromatic CH-fragment ions in that temperature region. Fig (3.3B) shows for initial coal typical target ion fragments referring to aromatic compounds: benzene m/z = 77 ($C_6H_5^+$), m/z = 78 ($C_6H_6^+$), toluene m/z = 92 ($C_7H_8^+$), m/z = 91($C_7H_7^+$) and xylene m/z = 91 ($C_7H_7^+$).

3.3.1.1. Initial coal

(Fig 3.1) shows the evolution of H_2S during an AP-TPR experiment for initial coal sample (which represent the untreated coal sample or "time=zero"). Absolute MS intensity of obtained signals cannot be compared with each other between different AP-TPR experiments, since MS detection system is only a qualitative method as its total recorded intensity changes for each AP-TPR experiment. For this reason it is necessary to normalize the profiles for comparisons of selected fragments between different samples. Further on, the area under each dominant H_2S peak is determined by a deconvolution strategy of the H_2S profiles using multiple Gaussian functions (using Origin software (version 8)). Percent of peak area is calculated for each AP-TPR experiment according to: (Area P_i/Area P_{tot})×100. These % data are compared with each other to formulate some additional interpretations.

For the initial coal sample the first and second peak appeared at 475°C and 650°C, respectively.

The area under the first peak is 36% and under the second peak is 64% of total H_2S peak area/profile (Table (3.4)). The sharp peak in the lower temperature region is dominated by the reduction of pyrite sulfur into troilite with the formation of H_2S. Because the pyrite content is very high in the sample, accounting almost 47% of the total sulfur amount (Table (3.3)).

Table (3.3). Characteristics of the microwave treated coal samples.

No.	Sample	Total sulfur (%) *(dry basis)*	Pyrite sulfur (%) *(dry basis)*	Sulfate sulfur (%) *(dry basis)*	Oraganic sulfur ^{a*} (%) *(dry basis)*
1	**Initial coal**	3.17	1.16	0.15	1.86
2	**753002**	3.09	1.10	0.01	1.98
3	**753004**	3.12	1.18	0.01	1.93
4	**753006**	3.08	1.05	0.03	2.00
5	**753008**	3.06	1.22	0.02	1.82
6	**756002**	3.09	1.17	0.07	1.85
7	**756004**	2.84	0.90	0.03	1.91
8	**756006**	2.87	0.89	0.01	1.97
9	**756008**	3.04	1.05	0.04	1.95
10	**759002**	2.91	1.15	0.01	1.75
11	**759004**	2.85	1.05	0.01	1.79
12	**759006**	2.97	1.15	0.02	1.80
13	**759008**	3.10	1.08	0.03	1.99

But also the hydrogenation of some aliphatic, mixed aliphatic-aryl as reactive di-aryl sulfides are to be considered. The broad second peak can be attributed to di-aryl sulfides and thiophenic structures, as the hydrogenation/reduction of troilite to form Fe and H_2S. For the initial coal sample no clear SO_2^+ and SO^+ signals were found, demonstrating the almost absence of oxidized sulfur compounds.

3.3.1.2. Irradiated coal samples

According to the AP-TPR profiles (Fig. (3.2)) for treated samples, some shift to an higher temperature of the second peak compared with the initial state (time=zero) is noticed. The H_2S peak temperatures and the normalized peak areas are shown in Table (3.4). (The peak areas are expressed in: (°C.mbar)).

Table (3.4). Sulfur peak areas and relevant peak temperatures for treated and non-treated coal sample

No	Sample name	Peak area		Peak Normalization (%)		Peak Temperature (˚C)	
		1st Peak	**2nd Peak**	***1st Peak***	**2nd Peak**	***1st Peak***	**2nd Peak**
1	**Initial coal**	3.15 ± 0.08e-11	5.71 ± 0.07e-11	36	64	475 ± 2	649 ± 2
2	**753002**	1.14 ± 0.01e-10	1.39 ± 0.06e-10	45	55	474 ± 2	668 ± 2
3	**753004**	8.50 ± 0.08e-11	1.65 ± 0.07e-10	34	66	475 ± 2	665 ± 2
4	**753006**	9.72 ± 0.08e-11	1.97 ± 0.08e-10	33	67	476 ± 2	681 ± 2
5	**753008**	3.24 ± 0.05e-11	7.21 ± 0.07e-11	31	69	476 ± 2	678 ± 2
6	**756002**	2.99 ± 0.01e-11	6.97 ± 0.09e-11	30	70	475 ± 2	663 ± 2
7	**756004**	5.16 ± 0.08e-11	7.12 ± 0.09e-11	42	58	475 ± 2	661 ± 2
8	**756006**	3.09 ± 0.10e-11	4.64 ± 0.10e-11	40	60	477 ± 2	672 ± 2
9	**756008**	7.99 ± 0.09e-11	1.30 ± 0.09e-10	38	62	476 ± 2	661 ± 2
10	**759002**	6.05 ± 0.09e-11	8.35 ± 0.08e-11	42	58	474 ± 2	678 ± 2
11	**759004**	7.44 ± 0.08e-11	9.87 ± 0.07e-11	43	57	475 ± 2	662 ± 2
12	**759006**	7.11 ± 0.08e-11	9.06 ± 0.07e-11	44	56	476 ± 2	677 ± 2
13	**759008**	9.22 ± 0.08e-11	1.44 ± 0.01e-10	39	61	476 ± 2	668 ± 2

According to Table (3.4), for the 300, 600 and 900 W irradiation experiments, the temperature for the dominant first peak in all treated samples shows no specific shifting. On the other hand, the temperature shift for the second main peak compared with the initial coal sample is around 20 °C and peak % areas changed apparent randomly between 55 and 70%.

This means that the microwave irradiation has direct influences on the organic sulfur functionalities. It will be proved that changes in organic sulfur forms has to be attributed mainly to changes in amounts of reactive and less-reactive di-aryl sulfides. Microwave irradiation has simultaneously direct influence on the coal matrix as well, as will be discussed later. The impact is pronounced for all treated samples.

In the Fig (3.4), which is deduced from Table (3.4), a comparison of the calculated areas under the two dominant peaks for all treated and non-treated samples in H_2S profiles (m/z = 34) is visualized.

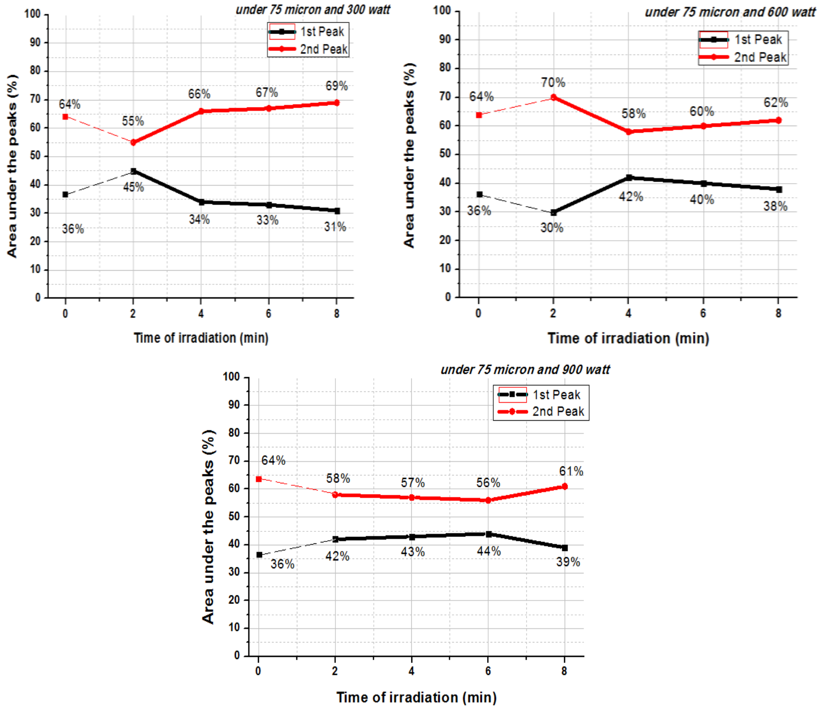


Fig (3.4). Area under two dominant peaks appeared in H_2S profiles for all microwave treated samples (for the time equal zero the percentage of 1st and 2nd peak is 36 and 64% respectively).

Based on the Fig (3.4), it can be seen that microwave irradiation at different power results in a different change in sulfur amounts form as a function of irradiation time and will be discussed later.

As the first H_2S peak temperature is rather not influenced by the irradiation treatment, but the second clearly is, the impact of the irradiation is rather limited to a change within aromatic/thiophenic sulfur compounds. Therefore the discussion of irradiation effects is focused on the changes for the second sulfur peak. But as sulfur peak areas are related with each other, the first peak area will have a comparable % change, but into the opposite direction.

In the case of the 300 W treatment, the area under the second peak shows some specific tendency. In the first 2 minutes of the microwave treatment, the area of the second peak decreased compared with the initial state from 64 to 55%. By increasing the irradiation from 4 to 8 minutes, compared to the initial state, the area of second peak tends to increase again from 55 up to 69%. It has to be concluded that for the 2 minutes irradiation, less-reactive aromatic sulfur compounds becomes more-reactive aromatic sulfur compounds, resulting a peak area % change accordingly. Additionally resulting in a second peak temperature shift towards higher temperature.

According to Table (3.5), in the case of 300 W and 2 minutes treatment, a significant increase in half width of 1^{st} H_2S evolution profile peak compared to the initial state appeared, confirming the above mentioned conversion of less-reactive into more-reactive aromatic sulfur compound forms.

Table (3.5). Half width of first peak in H_2S evolution profile

No	Sample	Half width of 1st peak in H_2S evolution (°C)
1	**Initial**	29.0 ± 0.9
2	**753002**	55.4 ± 0.9
3	**753004**	26.2 ± 0.9
4	**753006**	23.2 ± 0.8
5	**753008**	24.0 ± 1.0
6	**756002**	17.4 ± 0.9
7	**756004**	38.0 ± 0.9
8	**756006**	31.0 ± 1.0
9	**756008**	29.5 ± 0.9
10	**759002**	38.2 ± 0.9
11	**759004**	36.2 ± 0.9
12	**759006**	37.0 ± 1.0
13	**759008**	29.4 ± 0.9

Longer irradiation times at 300 W results in a small increase of less-reactive aromatic sulfur compounds compared to the initial coal sample, resulting in a systematic increase of the second peak area% from 64 to 66 up to 69%. Half width of the first H_2S evolution profile peak, compared to the initial state, accordingly decreases.

For 600 W, the area under the second H_2S peak shows a different tendency compared with the 300 W treatment. A clear increase of the second peak area % for the first 2 minutes of irradiation is noticed, indicating that more less-reactive aromatic sulfur compounds are formed probably at the cost of more-reactive aromatic sulfur compounds. Indeed, a clear decrease in half width is noticed for the first sulfur peak compared to the initial state. For 4, 6 and 8 minutes irradiation a continuously increase in the second peak area % is noticed from 58 up to 62%, but not reaching the initial 64% first peak area value. Meaning that as a function of increasing irradiation time, from 4 minutes, more-reactive aromatic sulfur compounds becomes again less-reactive ones. Confirmed by a decrease in half width value of the first sulfur peak, almost reaching its original value. The first 2 minutes treatment has the most important effect, as in the case of the 300 W, but now into the opposite direction. The used higher power has thus a different global effect.

For 900 W, again a different trend occurred, the area % under the second peak first decreased continuously (64 to 58 down to 56%) but during 8 minutes of irradiation its area % increase again (61%) but is still lower than for the initial sample, as is also noticed for the 600 W treatment. Power and time of irradiation have thus a systematic but different global effect on coal matrix structure and on the organic part related with more-reactive and less-reactive aromatic sulfur compounds, resulting in a different outcome. In this case, the 2 minutes treatment does not induced a drastic changes in aromatic sulfur compound amounts as found for the 300 and 600 W treatment.

As is noticed in Table (3.4), the second peak temperature shifted always to a higher value for all irradiation times compared to the initial state. Some analogue trends are found, in the irradiation time set 0-2-4 and 0-6-8 minutes: first we get a clear shift towards a maximum peak temperature and then a lower temperature is noticed by a further increase of the irradiation time, but still higher than that of the untreated sample. This could point to a different impact of irradiation time, related to a greater or smaller change in less-reactive and more-reactive aromatic sulfur compounds in competition with more or less structural changes in the coal matrix.

Nevertheless, according to Fig (3.4), it can be concluded that for the 300 and 600 W experiments more drastic changes in aromatic sulfur compound amounts occurred within the short irradiation time set of 0-2-4 minutes. Longer irradiation times than 2 minutes (irradiation time set 0-4-6-8 minutes) with these power settings, when compared to the initial state, results in rather smooth changes in aromatic sulfur compound amounts. For the 900 W treatments, these smooth changes in aromatic sulfur compound amounts occurred for all applied irradiation times.

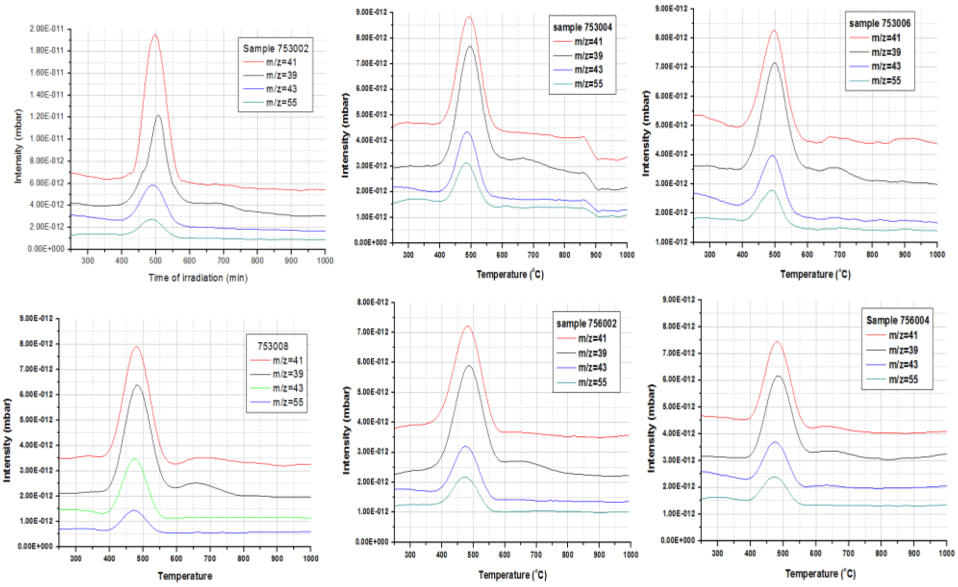
The different impact of power setting and irradiation time seems to have also an influence on the post chemical desulfurization treatment efficiency by peroxyacetic acid (PAA) where the organic sulfur reduction differently increases compared to the initial state, as will be discussed in the next chapter.

3.3.2. Profiles of AP-TPR/MS (H_2) evolution for CH-fragments

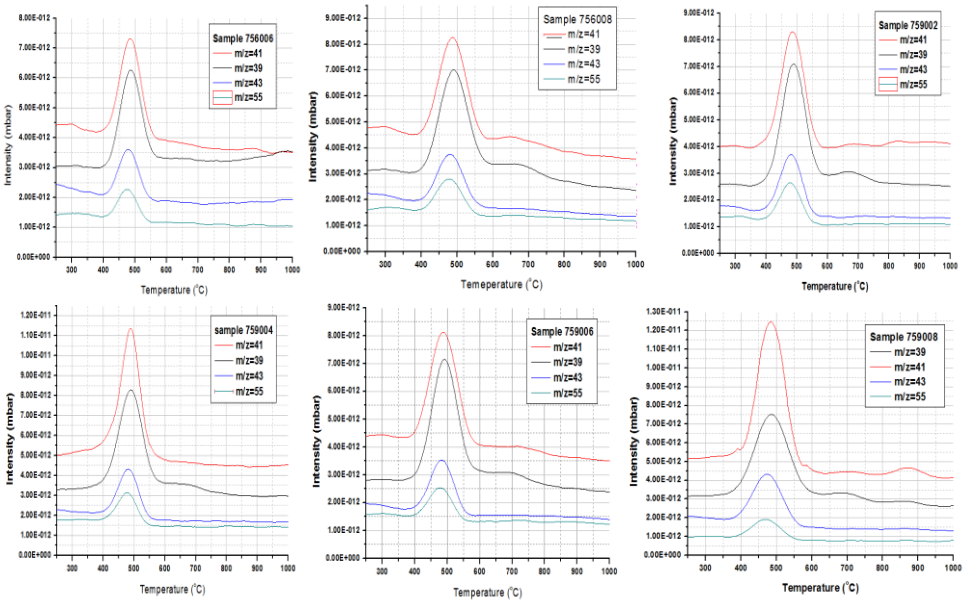
3.3.2.1. Saturated and unsaturated CH-chains

All CH-fragment profiles of all microwave treated samples have also been studied did shown different patterns. Some typical unsaturated and saturated ((m/z =39 ($C_3H_3^+$), 41 ($C_3H_5^+$), 43 ($C_3H_7^+$), and 55 ($C_4H_7^+$)) aliphatic fragments of treated samples are shown in Fig (3.5) and will be discussed in more detail.

To achieve some idea about the impact of microwave irradiation not only on sulfur compounds but also on the coal matrix, the area under the peak of each normalized fragment compared with initial sample is discussed.



Fig(3.5). The effect of microwave irradiation on saturated and unsaturated CH-chains (alkenes and alkanes) (m/z =39($C_3H_3^+$), 41 ($C_3H_5^+$), 43 ($C_3H_7^+$), and 55($C_4H_7^+$)).



Fig(3.5). The effect of microwave irradiation on saturated and unsaturated CH-chains (alkenes and alkanes) (m/z =39($C_3H_3^+$), 41 ($C_3H_5^+$), 43 ($C_3H_7^+$), and 55($C_4H_7^+$)).

As in the case of the H_2S profiles, the area under each target aliphatic fragment in the initial and treated coal sample have been calculated by de-convolution of fragment's profile using multiple Gaussian functions. In order to have more reliable discussion, the area % differences between treated and initial sample are calculated as follows:

Area differences (%)=$(At - Ai)$ **(Eq.3.1)**

Where, At and Ai, are the area % under the peak of the studied fragment in the microwave treated samples and the area % under the peak for the same fragment in the initial sample, respectively.

In Table (3.6) all calculated area % differences of typical selected aliphatic fragment profiles from Fig (3.5) are given.

Table(3.6). The area % differences of fragment peaks regarding to the initial coal

No.	Sample name	The normalized area differences (%)			
		m/z=39 $(C_3H_3)^+$	m/z=41 $(C_3H_5)^+$	m/z=43 $(C_3H_7)^+$	m/z=55 $(C_4H_7)^+$
1	**753002**	-6.98	+14.03	-2.74	-4.30
2	**753004**	+0.68	-1.44	+0.26	+0.51
3	**753006**	+0.86	-0.67	+0.32	-0.50
4	**753008**	-0.39	+2.97	+0.47	-3.04
5	**756002**	-0.26	-0.52	-1.05	-0.39
6	**756004**	+1.20	+0.94	-0.37	+0.05
7	**756006**	-0.13	-0.39	-0.95	+0.48
8	**756008**	+0.14	-0.12	-0.12	+0.82
9	**759002**	-0.01	-0.19	-0.34	+0.55
10	**759004**	+6.80	-2.22	-2.99	-1.55
11	**759006**	+2.67	+0.74	-1.90	-1.50
12	**759008**	-5.05	+10.25	-1.02	-4.17

- *The normalized area percentages of studied fragments for initial sample for m/z=39, 41, 43 and 55 are: 35.9, 36.2, 17.4 and 10.5, respectively.*

According to Table (3.6), the microwave treatment has also an impact on the coal matrix as is already suggested [21]. The trends of different treatment conditions in view of the impact of time and power of irradiation on different fragments are also visualized in Fig (3.6, A-D).

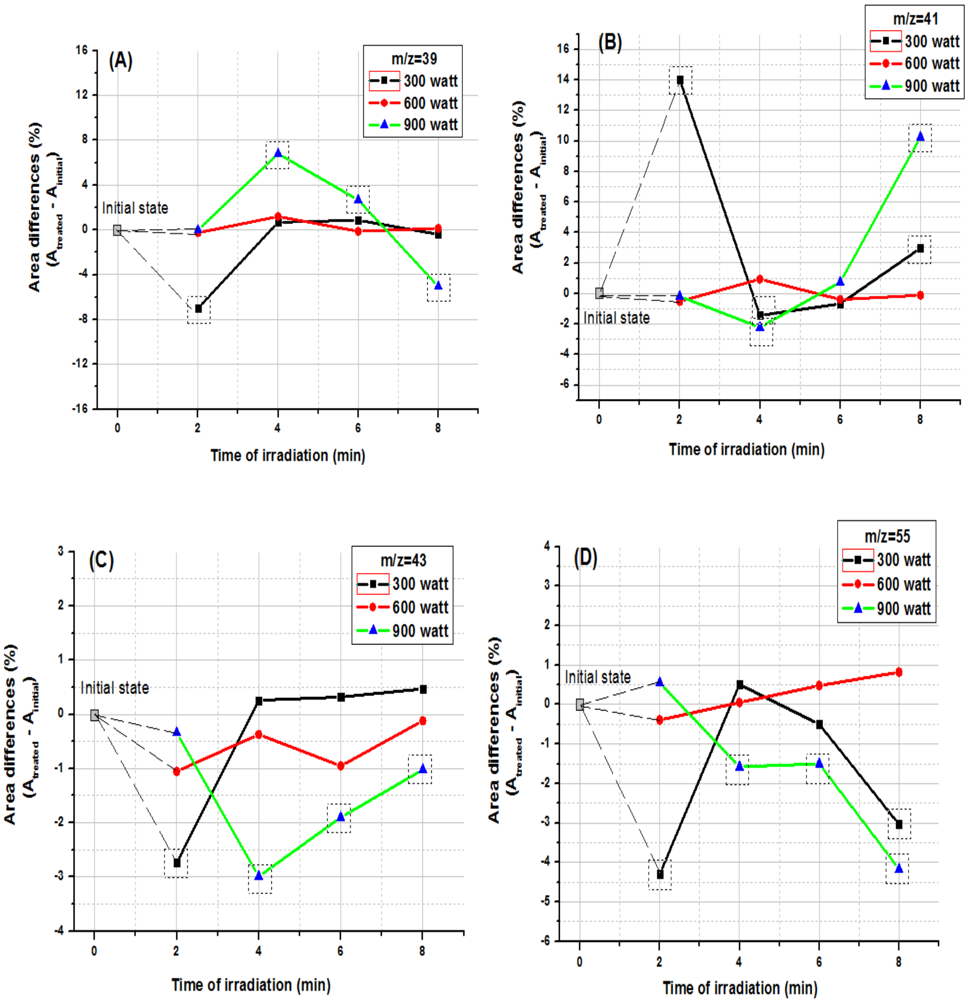


Fig (3.6). Influences in area % differences of time and power of irradiation on the m/z= 39, 41, 43 and 55. (the values greater than 1 % are highlighted by squares)

Based on Fig (3.6) and Table (3.6), the main impact on the studied aliphatic fragments occurred in the first 2 minutes of irradiation at 300 W for all fragments. The same impact is found for the H_2S peak area changes within this time and power. At irradiation time of 4 minutes and 300W for m/z 41 and 55 fragments, compared with the initial state, also significant changes occurred. The 600 W treatment has less impact for all fragments, but nevertheless a divers pattern is noticed as a function of irradiation time, not comparable with its H_2S peak area % changes. For the 900 W treatment, the impact on the coal matrix is overall greater and more divers compared with the 300 and 600 W treatments as is demonstrated by its complete different trend in area % differences of the divers fragments. The first 2 minutes irradiation at 900 W causes the smallest changes as is approximately found for its H_2S peak area % changes. For longer irradiation times, the pattern clearly depends on the different fragments and are more striking for all fragments. This makes the discussion on the effect of irradiation on coal matrix and sulfur functionalities not easy. For a better understanding, changes in the aromatic fragments profiles of the treated coal samples are therefore also studied.

3.3.2.2 AP-TPR/MS (H_2) evolution profiles for aromatic fragments

The profiles of aromatic fragments (benzene m/z=77 ($C_6H_5^+$), m/z=78 ($C_6H_6^+$), toluene m/z=92 ($C_7H_8^+$), m/z=91 ($C_7H_7^+$) and xylene m/z=91 ($C_7H_7^+$)) are shown in Fig (3.7). The different scales for Y-axis in Figs (7) are used to maximize the visualization of their profile changes.

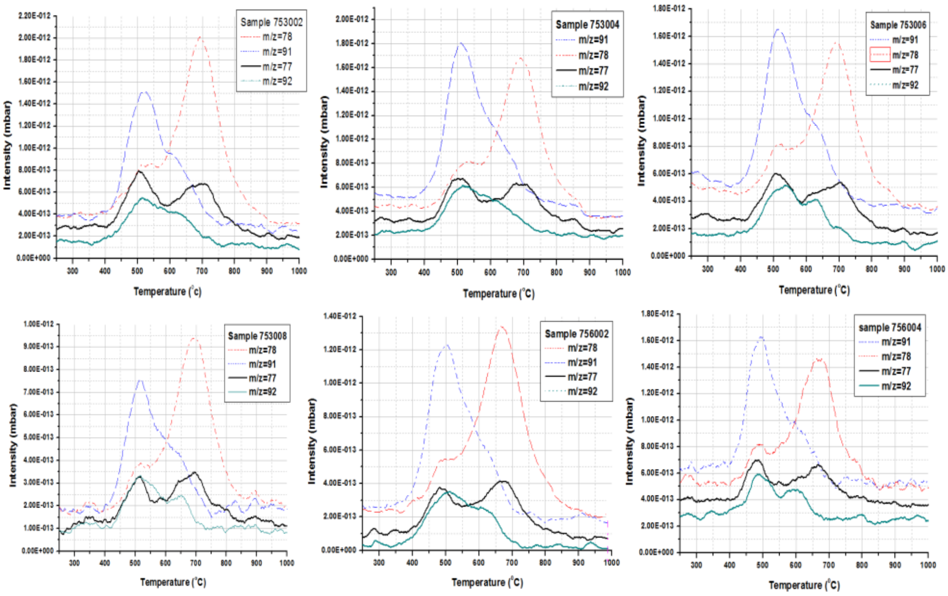


Fig (3.7). **The effect of microwave irradiation in different condition on aromatic compounds (benzene m/z=77 ($C_6H_5^+$), m/z=78 ($C_6H_6^+$), Toluene m/z=92 ($C_7H_8^+$), m/z=91($C_7H_7^+$) and xylene m/z=91 ($C_7H_7^+$))**

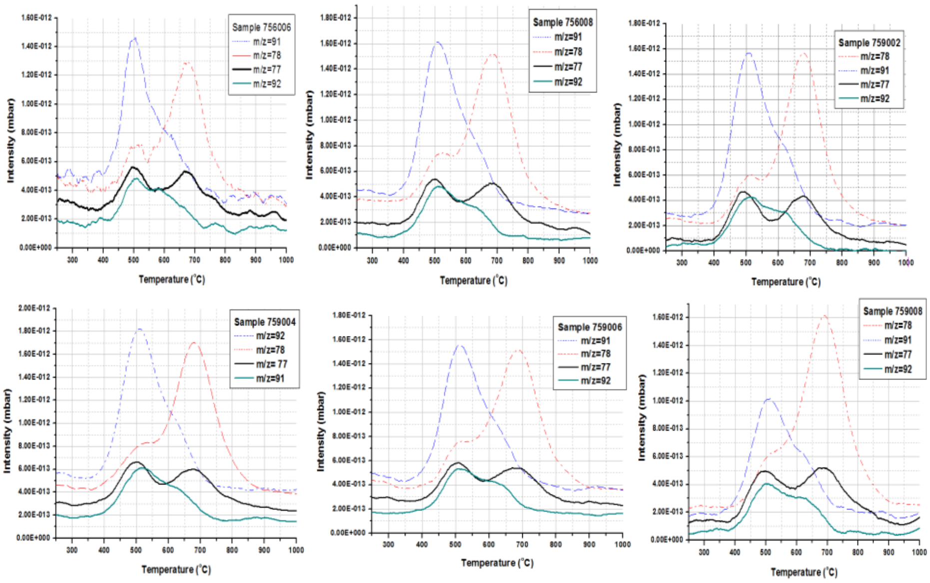
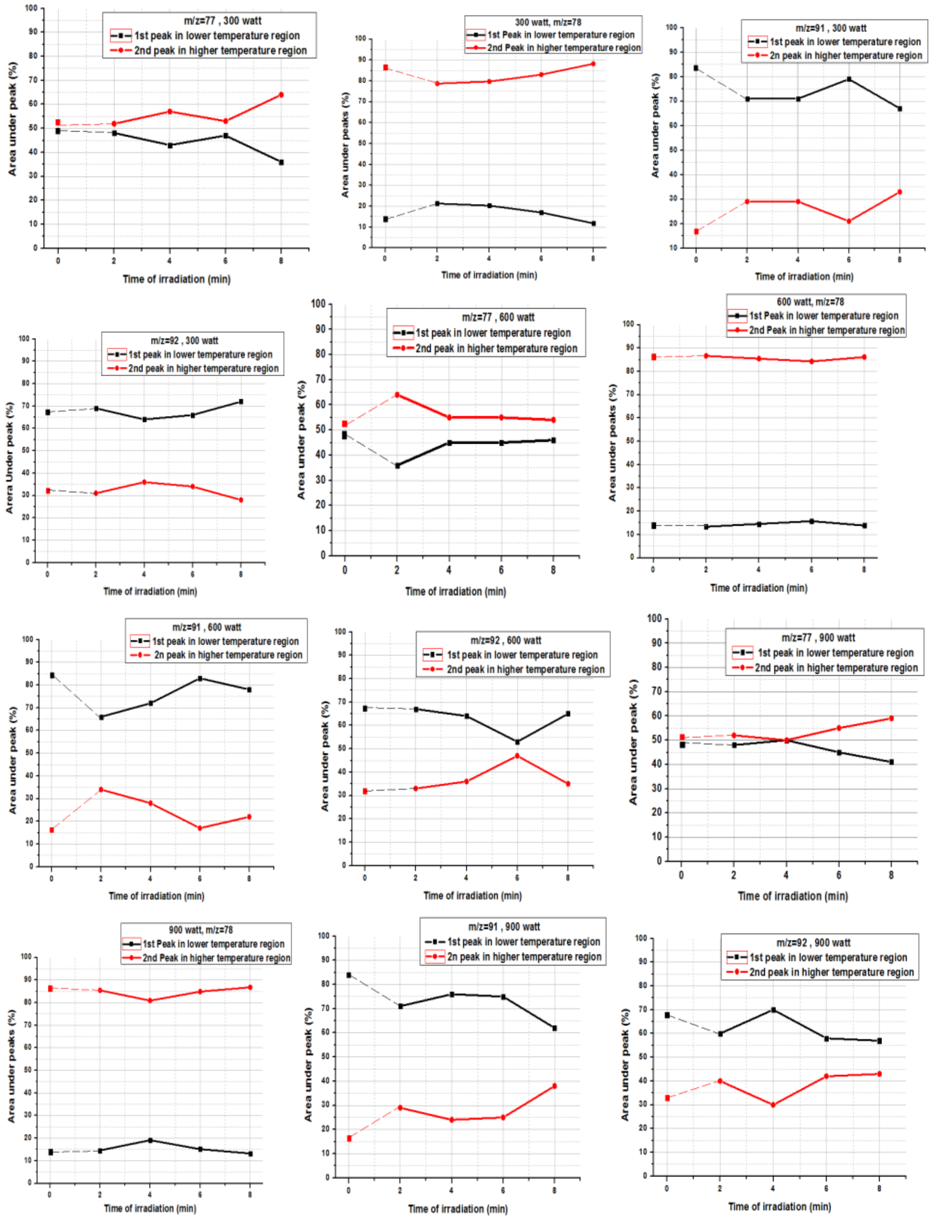


Fig (3.7). The effect of microwave irradiation in different condition on aromatic compounds (benzene m/z=77 ($C_6H_5^+$), m/z=78 ($C_6H_6^+$), Toluene m/z=92 ($C_7H_8^+$), m/z=91($C_7H_7^+$) and xylene m/z=91 ($C_7H_7^+$)) (continue)

Additionally, intensities cannot be compared with each other, therefore in Fig (3.8) peak area % changes for the first and second peak are given for different powers as a function of irradiation time. As already mentioned, a significant shift to higher temperature region in all treated samples occurred due to the polycyclic aromatic ring formation/changes as a result of the microwave treatment compared with corresponding profiles of the initial sample (see Fig (3.3B)).



m/z=77 , 300 watt

300 watt, m/z=78

m/z=91 , 300 watt

m/z=92 , 300 watt

m/z=77 , 600 watt

600 watt, m/z=78

m/z=91 , 600 watt

m/z=92 , 600 watt

m/z=77 , 900 watt

900 watt, m/z=78

m/z=91 , 900 watt

m/z=92 , 900 watt

Fig (3.8). Effect of power of irradiation on studied aromatic fragments (benzene m/z=77 ($C_6H_5^+$), m/z=78 ($C_6H_6^+$), Toluene m/z=92 ($C_7H_8^+$), m/z=91($C_7H_7^+$) and xylene m/z=91 ($C_7H_7^+$))

The values of temperature shifts compared to the initial state are given in Table (3.7). The irradiation treatment of the coal samples, not only caused coal matrix changes but also results in simultaneous degradation of the organic matrix. As a result, lower molecular weight aromatic matrial is formed out of higher molecular weight aromatic material. This is clearly demonstrated in Fig (3.7) compared with Fig (3.3B). Indeed, the mass kinetograms for m/z=91,92 show a main peak in the lower temperature region for the initial sample (time of irradiation is zero) around 454 °C, while for all treated samples these fragments peak apeared at around 510 °C. On the other hand, for the m/z=77, the peak maximum of non-treated sample appeared at 640 °C and in all treated samples this peak maximum clearly shifted to arround 700 °C. The changes in the coal matrix can also originate from the formation of reactive species which can further react to form refractory structures (producing poly cyclic aromatic compounds by carbonization process).

Table(3.7). The temperature differences of fragments peaks regarding to the same fragment in the initial coal

		Peak temperature differences (°C)							
No	**Sample**	**m/z=77**		**m/z=78**		**m/z=91**		**m/z=92**	
		1st Peak	***2nd Peak***	***1st Peak***	***2nd Peak***	***1st Peak***	***2nd Peak***	***1st Peak***	***2nd Peak***
1	**753002**	58	58	94	51	81	12	51	60
2	**753004**	52	58	92	51	56	15	59	44
3	**753006**	54	60	75	50	57	15	75	69
4	**753008**	63	58	62	53	57	21	40	79
5	**756002**	40	41	37	16	48	none	38	39
6	**756004**	39	31	43	21	44	none	15	29
7	**756006**	54	29	78	24	48	3	30	16
8	**756008**	52	51	83	22	49	3	31	12
9	**759002**	48	41	57	27	56	4	56	54
10	**759004**	52	42	91	25	55	none	55	54
11	**759006**	53	49	68	34	54	none	35	36
12	**759008**	*52*	*54*	*58*	47	56	*21*	*30*	*62*

Based on Fig (3.7), the areas under the main peak and its shoulder for all aromatic fragments have been calculated according a previous described procedure and their tendency changes as a result of different microwave treatment parameters (time and power) are illustrated in Fig (3.8).

According to Fig (3.8) for m/z=77 ($C_6H_5^+$), the area under the first peak decreased by increasing the time of irradiation at 300 W, and consequently the area % under the second peak increased. This is a confirmation that more complex aromatic compounds are formed. The tendency for m/z=77 with a power of 600 W is somewhat different, only a clear decrease in peak area % after 2 minutes for the first peak is noticed, but for longer irradiation times no great coal matrix changes are further induced. As already noticed, the impact of irradiation power setting is clearly not uniform. For the 900W, the pattern resembles more or less the 300 W tendencies for this fragment. No great changes are induced in the case of the 600 W treatments for 4 minutes irradiation, but for 900 W the changes are more pronounced. For 600 W significant changes are only noticed for 6 to 8 minutes of irradiation. It is clear that this distinctive trends for m/z=77 demonstrates the variable effects of microwave treatment in power and time settings on the coal matrix.

For m/z=78 ($C_6H_6^+$), the area % changes in view of power and irradiation time under the main peak and its shoulder are less pronounced as found for the m/z=77 fragment. Additionally for the 600 W experiment even after two minutes of irradiation no great changes are observed in contrast with the m/z=77 fragment. This demonstrates again the different impact of irradiation power and time setting on the coal matrix.

For aromatic fragment m/z=91 ($C_7H_7^+$) in the 2, 4 and 8 minutes irradiation the greatest change in peak area % is induced at a 300 W power application, and consequently for its lower temperature shoulder. This is also noticed for the 600 W treatment but only for the 2 and 4 minutes irradiation time. For the 900 W treatments rather at 2 and 8 minutes of irradiation the greatest changes in peak area % is noticed. Although the changes in peak area % are more pronounced than for m/z 78 by power and irradiation time, it demonstrates its different impact on the coal matrix or the different coal structure reactions by microwave irradiation settings.

For fragment m/z=92 ($C_7H_8^+$) again a different trend in peak area % as a function of power and time of irradiation is noticed. The area % under the shoulder for 300 W treatment and consequently for its peak area %, does not change spectacularly. For the 600 W treatments more severe changes are seen for shoulder and peak areas % for the 6 minutes irradiation treatment. For the 900 W application, again a different tendency, and severe changes after 2, 6 and 8 minutes compared with the initial coal sample are noticed. Comparing 6 and 8 minutes results reveals that longer irradiation induced no further changes. For 300 and 600W this is clearly different.

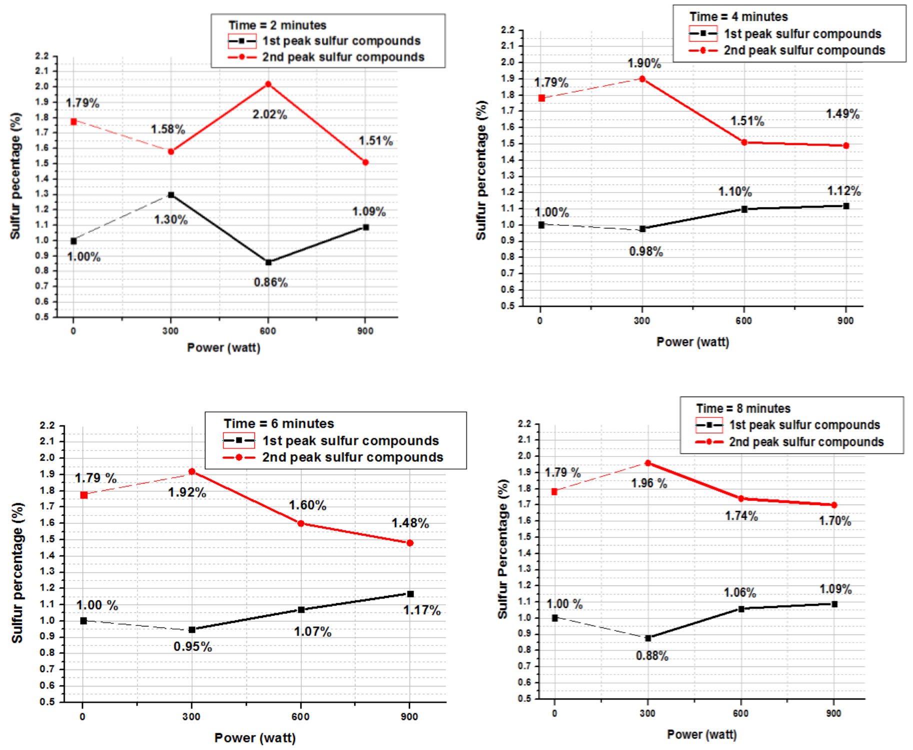
3.3.3. Influence of time and power of microwave irradiation on first and second peak sulfur compounds in AP-TPR/MS profiles

The total sulfur percentage forms for all treated and non-treated samples have been summarized in Table (3.3). The amount of sulfur in tar and char, which are remaining in the reactor after coal hydrogenation process, is determined as well. In this way, all sulfur which reacted with hydrogen forming H_2S can be calculated and is related to the area under the H_2S profiles. The amount of sulfur in tar and char (S_{T+C}) and sulfur which reacted with hydrogen ($S_{AP\text{-}TPR}$) are shown in Table (3.8).

Table (3.8). Measured sulfur amount in AP-TPR/MS (H_2) process

No	**Sample**	**S_{total} (%)**	**$S_{(T+C)}$ (%)**	**$S_{(APTPR)}$ (%)**	**Sulfur recovery (%)**	**Sulfur (1st Peak) (%)**	**Sulfur (2nd Peak) (%)**
1	**Initial coal**	3.17	0.38	2.79	88.01	1.00 ± 0.03	1.79 ± 0.04
2	**753002**	3.09	0.21	2.88	93.20	1.30 ± 0.04	1.58 ± 0.04
3	**753004**	3.12	0.24	2.88	92.31	0.98 ± 0.03	1.90 ± 0.04
4	**753006**	3.08	0.21	2.87	93.18	0.95 ± 0.04	1.92 ± 0.03
5	**753008**	3.06	0.22	2.84	92.81	0.88 ± 0.03	1.96 ± 0.04
6	**756002**	3.09	0.21	2.88	93.20	0.86 ± 0.03	2.02 ± 0.04
7	**756004**	2.84	0.23	2.61	91.90	1.10 ± 0.03	1.51 ± 0.04
8	**756006**	2.87	0.20	2.67	93.03	1.07 ± 0.04	1.60 ± 0.05
9	**756008**	3.04	0.24	2.80	92.11	1.06 ± 0.05	1.74 ± 0.04
10	**759002**	2.91	0.31	2.60	89.34	1.09 ± 0.03	1.51 ± 0.04
11	**759004**	2.85	0.24	2.61	91.58	1.12 ± 0.04	1.49 ± 0.03
12	**759006**	2.97	0.31	2.66	89.56	1.17 ± 0.04	1.48 ± 0.03
13	**759008**	3.10	0.31	2.79	90.00	1.09 ± 0.04	1.70 ± 0.03

According to the Fig (3.5-3.8), it is concluded that microwave irradiation shown significant effects on the coal matrix too. In Fig (3.9) a comparison is made of the quantitative changes expressed as H_2S of first peak sulfur compounds and second peak sulfur compounds as a function of irradiation time and power setting. The sulfur recovery measured by the AP-TPR-MS set-up for all samples studied reaches more than 90%, demonstrating the high reaction efficiency of this technique towards the conversion of the different sulfur functionalities present in the coal into H_2S. As additional other formed volatile sulfur compounds are around 1-2%, makes a more quantitative interpretation of the obtained H_2S profiles possible. Further on, it is found that only 1 up to 5% difference in % sulfur recovery as H_2S is found for all samples among the different AP-TPR-MS experiments, making a quantitative comparison of the H_2S profiles more straightforward.



Fig(3.9). Influence of time of irradiation in different powers on first and second peak's sulfur amounts in AP-TPR/MS (H_2)

Based on Fig (3.9), for the 2 minutes irradiation experiments at different power settings, a decrease of second peak sulfur compounds is noticed, compared with the initial state, when a power of 300 and 900 W is applied. This is in contrast with the 600 W application where an increase in the second peak sulfur compounds amount is found compared with the initial state. Consequently, for the first peak sulfur compounds amount the reverse tendency is obtained. As stated at the beginning, due to the irradiation the greatest changes in sulfur forms could be associated with aromatic sulfur compounds and aromatic matrix effects. The alteration of less-reactive and more-reactive aromatic sulfur compounds is the key parameters for the changes observed. As discussed already, these changes were not linear as a function of irradiation time and power. As further on stated, the impact of the different irradiation treatments on the coal matrix complexity and its degradation will also affect the possible hydrogenation/reduction mechanism of each sulfur functionality group resulting in an alternating reaction behavior. For the 4 minutes treatment at 300 W, only some small changes in sulfur peak amounts are noticed compared to the initial state. The second peak sulfur compounds increased in amount at the cost of the first peak sulfur compounds, just the opposite trend as found in the 2 minutes and 300 W treatment. For 600 and 900 W, this change in second and first peak sulfur amounts are greater compared with initial state values. For the 4 minutes treatment at 600 W compared to the 2 minutes treatment, a decrease in second peak sulfur compounds is found instead of an increase. The 4 minutes 900 W treatment is analogue to the 2 minutes 900 W irradiation, a decrease in second peak sulfur compounds compared to the initial state and consequently an increase in first peak sulfur compounds. For the 6 and 8 minutes irradiation treatment we get quiet an analogue trend as described for the 4 minutes irradiation. Thus as formulated, the 2 minutes microwave treatment results in the biggest alternating changes as a function of the applied power.

3.4- Conclusion

AP-TPR device coupled with MS detection system (AP-TPR/MS) demonstrates the opportunity to elucidate organic matrix and organic sulfur species alteration in the microwave treated high sulfur coal samples (Tabas, Iran). For the first time, organic sulfur alterations are investigated qualitatively and quantitatively. According to the present state and the obtained profiles using AP-TPR method, the 2 minutes irradiation time has the most significant impact for all used power settings. Changes in H_2S peak profiles due to microwave treatment can be mainly explained by conversion of less-reactive and more-reactive aromatic sulfur compounds into each other and by coal matrix effects. Peak maximum of all aromatic carbon fragments shifted towards higher temperature region, due to the poly cyclic aromatic ring formation as a result of microwave treatment. The irradiation treatment used on the coal samples, resulted in coal matrix degradation and also changes in terms of physical characteristics and causing a simultaneous degradation of the organic matrix. Microwave irradiation of coal can cause phase changes and also expansion which is creating internal pressures within the coal matrix and possibly weakening the structure can creating fracture [38], therefore the positive effects reported for microwave irradiation on the post desulfurization probably related to this mentioned phenomena and easy access of leaching reagent to sulfur targets. Based on above mentioned physico-chemical phenomena and the effects of irradiation treatment on coal matrix, this will influence the effect and efficiency of further desulphurization of organic sulfur compounds as will be proved in the next paper.

3.5- References

[1] Stanley P. Schweinfurth, an introduction of coal quality, chapter C, U.S. Geological Survey Professional Paper, Reston,Virginia, 2009.

[2] Calkins WH. Fuel 1994;73:475.

[3] D.K. Xia, C.A. Pickles, CIM Bulletin 90 (1997) 99.

[4] S.A. Matthes, R.F. Farrell, A.J. Mackie, US Bureau of Mines Report of Technical Progress 120 (1999) 9.

[5] N.P. Vasilakos, F. Magalhaes, Journal of Microwave Power 19 (1984) 135.

[6] Jones DA, Lelyveld TP, Mavrofidis SD, Kingman SW, Miles NJ. Microwave heating applications in environmental engineering—a review. Resour Conserv Recycling 2002;34,p.75–90.

[7] Church RH, et al. Dielectric properties of low loss materials. US Bureau of mines Report of Investigations 9194. Washington, US; 1993.

[8] R.M. Kelly, N.A. Rowson, Minerals Engineering 18 (1995) 1427.

[9] S.W. Kingman, G.M. Corfield, N.A. Rowson, Magnetic and Electrical Separation 9 (1999) 131.

[10] K.E. Haque, International Journal of Mineral Processing 57 (1999) 1.

[11] Walkiewicz J.W., Microwave heating characteristics of selected minerals and components, Minerals and Metallurgical Processing. p.39-42. (Feb 1988).

[12] Chen T.T.,1984, The relative transparency of minerals to microwaves, Canadian Metallurgical Quarterly, Vol. 23, No3, p.349-351.

[13] McGill S.L.,1988, The effect of power levels on the microwave heating of selected chemicals and minerals, Materials Research Society proceedings. Vol. 124, pp247-252.

[14] Weng SH. Mossbauer analysis of the microwave desulfurization process of raw coal. J ApplPhys 1993;73, p.4690–2.
[15] Zavitsanos PD, Bleiler KW. Coal desulfurization induces thermochemical, in situ reactions between sulfur and other elements in coal, US Patent 4076607; 1978.
[16] Chironis N.P., Microwave Dry Fine Coal, Coal age, pp64-65, (1986).
[17] Dutta SN, Dowerah D, Frost DC. Fuel 1983;62:840.
[18] Taghiei MM, Huggins FE, Shah N, Huffman GP. Energy Fuels 1992;6:293.
[19] Van Aelst J, Yperman J, Franco DV, Mullens J, Van Poucke LC, Palmer SR. Fuel 1997;14/15:1377.
[20] E. Jorjania, B. Rezai, M.Vossoughic, M. Osanloo, Desulfurization of Tabas coal with microwave irradiation/peroxyacetic acid washing at 25, 55 and 85 ^{o}C, Fuel 83 (2004),p. 943–949.
[21] LichaoGe, Yanwei Zhang , Zhihua Wang, Junhu Zhou, Kefa Cen, Effects of microwave irradiation treatment on physicochemical characteristics of Chinese low-rank coals, Energy Conversion and Management 71 (2013) ,p.84–91.

[22] C.A. Pickles, F. Gao, S. Kelebek, Microwave drying of a low-rank sub-bituminous coal, Minerals Engineering, online version, (2013).

[23] Wencheng Xia, JianguoYang ,Chuan Liang, Effect of microwave pretreatment on oxidized coal flotation, Powder Technology 233 (2013) 186–189.

[24] ArashTahmasebi, Jianglong Yu , Xianchun Li, ChatpholMeesri, Experimental study on microwave drying of Chinese and Indonesian low-rank coals, Fuel Processing Technology 92 (2011) ,p.1821–1829.

[25] T.Uslu, U.Atalay, Microwave heating of coal for enhanced magnetic removal of pyrite, Fuel Processing Technology 85 (2003), p.21– 29.

[26] Gonsalvesh L, Dinler-Ddoganay G, Kolankaya N, Sam M, Carleer R, Reggers G, Yperman J, Biodesulfurized subbituminous coal by different fungi and bacteria studied by reductive pyrolysis. Part 1: Initial coal. Fuel 2008;87, p.2533-43.
[27] Gonsalvesh L, Marinov SP, Stefanova M, Carleer R, Yperman J. Organic sulfur alteration in biodesulfurized low rank coals. Fuel;2012; 97,p.489-503.

[28] Gonsalvesh L, Marinov SP, Stefanova M, Carleer R, Yperman J. Biodesulfurized low rank coal: Maritza east lignit and its "Humus-Like" product. Fuel 2013; 103, p.1039-50.

[29] International Standard, ISO 334, Solid mineral fuels—determination of total sulfur—Eschka method; 1992. p. 1–5.

[30] International Standard, ISO157, Coal-determination of forms of sulfur. 1992. p. 1–15.

[31] Jorjani E, Yperman J, Carleer R, Rezaei B., Reductive pyrolysis study of sulfur compounds in different Tabas coal samples (Iran). Fuel 2006;85, p.114-20.

[32] Rutkowski P, Mullens S, Yperman J, Gryglewicz G., AP-TPR investigation of the effect of pyrite removal on the sulfur characterization of different rank coals. Fuel processing technology 2002; 76, p.121-38.

[33] Marinov S, Stefanova M, Stamenova V, Carleer R, Yperman J. , sulfur functionality study of steam pyrolyzed "Maquineza" lignite using reductive pyrolysis technique coupled with MS and GC/MS detection systems. Fuel processing technology 2005; 86, p.523-34.

[34] Marinov SP, Tyuliev G, Stefanova M, Carleer R, Yperman J., Low rank coals sulfur functionality study by AP-TPR/TPO coupled with MS and potentiometric detection and by XPS. Fuel processing technology 2004;85(4), p.267-77.

[35] Stefanova M, Marinov S, Yperman J, Carleer R., Reductive pyrolysis of Miocene-aged lignite lithotyped using MS and GC/MS detection systems for analysis of organic sulfur groups. Fuel 2005; 84 (1), p.71-9.

[36] Mullens S, Yperman J, Carleer R, Bozdemir T, Durusoy T, Yurum Y, Sulfur analysis of Bolu-Mengen lignite before and after Microbiological treatment using reductive pyrolysis and Gas chromatography/Mass spectrometry. Energy & Fuel 2005; 19 (3), p.1029-36.

[37] Marinov SP, Stefanova M, Stamenova V, Gonsalvesh L, Carleer R, Yperman J., Sulfur analysis of household briquettes using MS and GC/MS detection systems after reductive pyrolysis. RanlianoHuaxuexuebao/journal of fuel chemistry and technology 2006; 34(3), p.257-64.

[38] S. Marland, B. Han, A. Merchant, N. Rowson, The effect of microwave radiation on coal grindability, Fuel 79 (2000), p.1283–1288.

Chapter 4

Changes and removal of different sulfur forms after chemical desulfurization by peroxyacetic acid on microwave treated coals

The results discussed in this chapter have been published in the Journal under title of fuel : Sh. Mesroghli , J. Yperman , E. Jorjani , J. Vandewijngaarden , G. Reggers , R. Carleer , M. Noaparast , Changes and removal of different sulfur forms after chemical desulfurization by peroxuacetic acid on microwave treated coals.

4.1 Introduction

Coal is still a major energy source for the foreseeable future, however the sulfur in coal has greatly limited its utilization and much attention has been paid to the air pollution caused by direct combustion of coal in recent years.

Sulfur removal is one of the most important problems in coal industry. Basically, coal cleaning methods are grouped into physical and chemical processes. Inorganic sulfur is removed during a physical process such as flotation or magnetic separation. Organic sulfur can be removed during chemical treatment, but the reaction conditions are relatively severe [1].

The potential application of microwave irradiation to coal desulfurization is suggested by many authors and scope for further research in this area is vast [2-17].

Elsamak et al (2003) investigated the effect of HI in the chemical desulfurization of Cayirhan lignite under microwave irradiation and also in a thermal heating system. They showed that the extremely short times was needed for desulfurization in the case of microwave experiments. The kinetics of the desulfurization reactions with microwave heating in concentrated HI was due to localized superheating which made HI more effective in the reactions with thioethers and thiols that normally resisted to cleavage by HI under thermal heating conditions [12].

Uslu and Atalay (2004) examined the amenability of Askale coal to desulfurization by magnetic separation following microwave heating in presence of of 5% magnetite as a microwave absorber mineral; the pyritic sulfur content of coal was reduced by 55.1%, using magnetic separation at magnetic field intensity of 2 T [15].

Singh and McWhinnie (1995) studied the organic sulfur removal of coal using microwave irradiation in presence of $Fe_3(CO)_{12}$. They showed that microwave heating accelerates the reaction of $Fe_3(CO)_{12}$ with thiophene, which leads to the removal of sulfur from the ring [16].

Jie and Jiankang (1994) investigated coal pyrolysis desulfurization by microwave radiation under a nitrogen flow stream. The dissociation of pyrite in coal to pyrrhotite and/or troilite, to different degrees, occurred at varying radiation times [17].

Use of peroxyacetic acid (PAA) as a mild oxidative agent for coal desulfurization has been reported by many authors [14,18-24].This reagent is believed to produce the hydroxyl cations that are strong electrophiles and reacts with sulfur atoms because they are considerably more nucleophilic than carbon atoms.

Ishak et al (2003) investigated chemical desulfurization of Indonesian sub-bituminous coal with PAA at 50 °C of reaction temperature. They reported that total sulfur, including both organic and inorganic sulfur, decreased from 3.46 to 1.29% by weight and approximately 44 % of ash was removed [23].

Borah et al. (2005) attempted to understand the probable pathways for the formation of oxidized sulfur species as well as the type of organic sulfur compounds responsible for desulfurization by PAA. The experiments were undertaken both in absence and in the presence of added metal ions. Study of model sulfur compounds (methionine and di-benzothiophene) reveals that the desulphurization reaction under the studied experimental conditions is primarily due to aliphatic sulfur compounds [24].

Jorjani et al. (2004), showed that microwave irradiation have a positive effect on coal desulfurization with peroxyacetic acid; the effects of irradiation time and power, peroxyacetic acid reaction time and temperature, and particle size on reduction of sulfur were investigated. According to the mentioned work, the achieved optimized leaching temperature and time were 55°C and 90 minutes, respectively. Based on the achieved results for <300 mm size fraction, after irradiation, the reduction enhanced from 49.9 to 86.6% for pyritic sulfur, 23.8 to 35% for organic sulfur and 36 to 61.9% of total sulfur. FT-IR spectroscopy of coal structure before and after desulfurization has shown significant changes in the peak corresponding to pyrite while the bands related to coal organic matrix showed only minor changes. The results have shown that this method can be used as a secure process for removal of inorganic and organic sulfur without destruction of coal organic matrix [14].

In previous studies, researchers have mainly focused on the optimization of sulfur reduction processes and determination of total, pyritic and organic sulfur forms and their quantitative changes after chemical desulfurization[2-24]; however there was no information about the different forms of organic sulfur and their changes after desulfurization, nor quantitatively nor qualitatively.

The aim of this investigation is to assess the changes in sulfur forms and functionalities of microwave treated coal samples, with a post chemical desulfurization using PAA. AP-TPR method is used to determine these changes. For the first time the study of the qualitative and quantitative changes of organic sulfur forms as a function of microwave irradiation conditions is determined for treated and desulfurized samples. The results of this assessment may lead to a better understanding of coal desulfurization after a microwave treatment- PAA chemical desulfurization.

4.2 Materials and methods

4.2.1. Coal sample

About 40 Kg of high sulfur coal sample was collected from active stopes in C1 seam of Tabas coal mine. The sampling techniques similar to those of Jones riffles, conning and quartering methods were adapted and representative (initial) samples were prepared for further studies. Proximate, ultimate analysis and sulfur determination have been performed as describe in the Chapter 2.

4.2.2. Microwave irradiation

For the pretreatment by microwave irradiation, coal samples (minus 75µm) were spread on the Pyrex glass container (8 gr). The irradiation was performed by a Samsung microwave oven with 2.45 GHz frequency and 0-1250 Watt power, with different irradiation times (2,4,6 and 8 minutes) and at different irradiation powers (300,600 and 900 watt). The microwaved samples were cooled in the desiccator, weighed, and used for post chemical desulfurization by PAA. The microwave treated samples are labeled in the following way, for example: “753002” is related to the sample fraction size under 75 μm, treated with microwave power of 300 W and for 2 minutes.

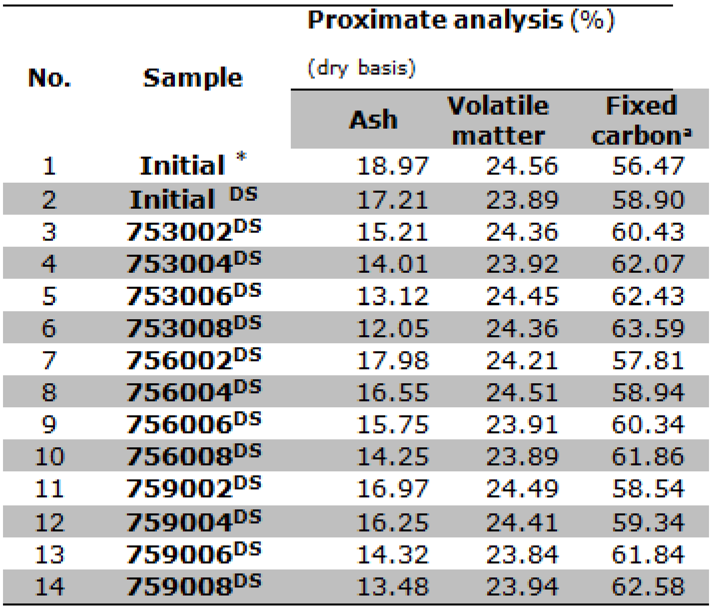
4.2.3. Chemical desulfurization

After microwave irradiation at different operating conditions (time and power), the prepared sample was desulfurized with PAA. The procedure involved dispersing 8 gr of microwaved 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% W/V) and holding temperature at 55 °C [20].The experiments were performed in 500 ml, Pyrex reactor isolated with glass wool, equipped with a thermometric probe and stirred. Based on the previous study [14], identical optimized parameters for desulfurization of Tabas coal by PAA were applied: desulfurization time of 90 min and temperature adjusted at 55 °C.

After 90 min of reaction, the reactor was cooled down and the residue solution was filtered. The desulfurized sample was washed with hot distilled water, dried in an oven at 100 °C for 3 hours and analyzed (by ISO methods 334 and 157 in duplication) for sulfate, pyrite and total sulfur content. All chemical reagents were obtained from Merck manufacturer.

Proximate and ultimate analysis has been conducted for initial and all desulfurized coal samples. The results are shown in Table (4.1) and Table (4.2).

Table (4.1). Proximate analysis of initial, initial-desulfurized and preirradiated-desulfurized samples.



No.	Sample	Proximate analysis (%) (dry basis)		
		Ash	Volatile matter	Fixed carbon^a
1	**Initial** *	18.97	24.56	56.47
2	**Initial** ^{DS}	17.21	23.89	58.90
3	**753002**^{DS}	15.21	24.36	60.43
4	**753004**^{DS}	14.01	23.92	62.07
5	**753006**^{DS}	13.12	24.45	62.43
6	**753008**^{DS}	12.05	24.36	63.59
7	**756002**^{DS}	17.98	24.21	57.81
8	**756004**^{DS}	16.55	24.51	58.94
9	**756006**^{DS}	15.75	23.91	60.34
10	**756008**^{DS}	14.25	23.89	61.86
11	**759002**^{DS}	16.97	24.49	58.54
12	**759004**^{DS}	16.25	24.41	59.34
13	**759006**^{DS}	14.32	23.84	61.84
14	**759008**^{DS}	13.48	23.94	62.58

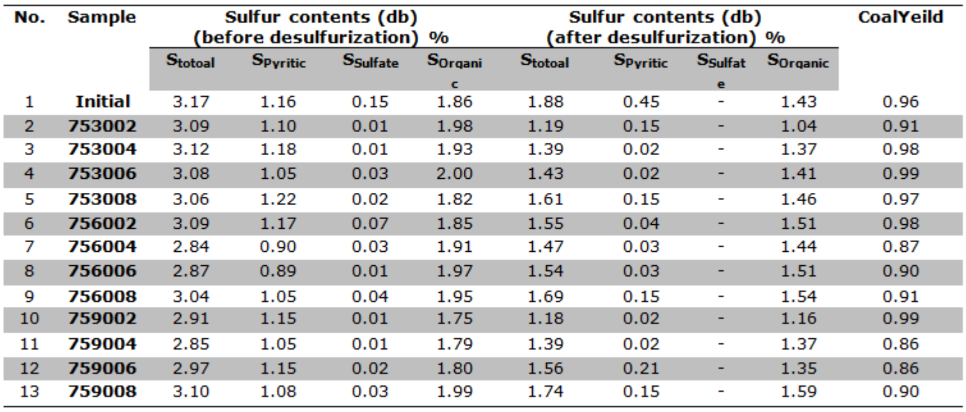
*: not irradiated and not desulfurized, a : by difference , DS: Desulfurized

Table(4.2). Ultimate analysis of initial, initial-desulfurized and preirradiated-desulfurized samples.

		Ultimate analysis (%) daf					
No.	**Sample**	**C**	**H**	**N**	**S**	**O** (by diff.)	**Calorific value ($MJ.kg^{-1}$)**
1	**Initial**	82.30	5.01	3.21	3.37	6.11	34.64
2	**Initial** ^{DS}	84.35	3.71	2.37	1.95	7.62	33.19
3	**753002**^{DS}	83.78	3.11	2.11	1.53	9.47	32.05
4	**753004**^{DS}	84.43	3.25	2.19	1.68	8.45	32.57
5	**753006**^{DS}	83.66	2.87	1.97	1.72	9.78	31.72
6	**753008**^{DS}	83.39	3.15	1.87	1.77	9.82	31.96
7	**756002**^{DS}	83.21	3.15	2.15	1.74	9.75	31.89
8	**756004**^{DS}	83.33	3.07	2.10	1.68	9.82	31.83
9	**756006**^{DS}	83.81	3.41	2.13	1.72	8.93	32.49
10	**756008**^{DS}	83.55	3.05	2.21	1.81	9.38	31.94
11	**759002**^{DS}	84.18	2.73	2.30	1.64	9.15	31.79
12	**759004**^{DS}	84.39	2.91	2.28	1.49	8.93	32.08
13	**759006**^{DS}	83.91	3.07	2.31	1.73	8.97	32.12
14	**759008**^{DS}	83.10	3.19	2.17	1.81	9.73	31.91

The sulfur contents of the samples before and after desulfurization are also shown in Table (4.3).

Table(4.3).Comparison between sulfur contents of initial and pre-irradiated samples before and after desulfurization.



No.	Sample	Sulfur contents (db) (before desulfurization) %				Sulfur contents (db) (after desulfurization) %				CoalYeild
		S_{totoal}	$S_{Pyritic}$	$S_{Sulfate}$	$S_{Organic}$	S_{totoal}	$S_{Pyritic}$	$S_{Sulfate}$	$S_{Organic}$	
1	**Initial**	3.17	1.16	0.15	1.86	1.88	0.45	-	1.43	0.96
2	**753002**	3.09	1.10	0.01	1.98	1.19	0.15	-	1.04	0.91
3	**753004**	3.12	1.18	0.01	1.93	1.39	0.02	-	1.37	0.98
4	**753006**	3.08	1.05	0.03	2.00	1.43	0.02	-	1.41	0.99
5	**753008**	3.06	1.22	0.02	1.82	1.61	0.15	-	1.46	0.97
6	**756002**	3.09	1.17	0.07	1.85	1.55	0.04	-	1.51	0.98
7	**756004**	2.84	0.90	0.03	1.91	1.47	0.03	-	1.44	0.87
8	**756006**	2.87	0.89	0.01	1.97	1.54	0.03	-	1.51	0.90
9	**756008**	3.04	1.05	0.04	1.95	1.69	0.15	-	1.54	0.91
10	**759002**	2.91	1.15	0.01	1.75	1.18	0.02	-	1.16	0.99
11	**759004**	2.85	1.05	0.01	1.79	1.39	0.02	-	1.37	0.86
12	**759006**	2.97	1.15	0.02	1.80	1.56	0.21	-	1.35	0.86
13	**759008**	3.10	1.08	0.03	1.99	1.74	0.15	-	1.59	0.90

db : dry basis

4.2.4. AP-TPR analysis

4.2.4.1. 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 pre-microwave treated and desulfurized coals to assess the changes after chemical desulfurization by PAA. These analyses are performed in the AP-TPR set-up described previously [25]. Briefly, 40 mg of desulfurized 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. TPR reactor is coupled "on-line" with a mass spectrometer (FISONS-VG ThermolabMS) 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.

4.2.4.2. 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 [26-30]. In order to improve qualitative and quantitative interpretation of volatile sulfur compounds released during pyrolysis experiment in this study, the Tenax tubes are replaced by tubes filled with a set of sorbents selective for volatile sulfur compounds adsorption. The outlet of AP-TPR reactor is connected to a set of ice-cooled metal adsorption tubes with Silcosteel coating, filled with Tenax/Carbpack B/Carbosieve SIII (Markes). The volatiles are trapped in the temperature range from ambient temperature up to 700 °C in temperature intervals of 100 °C. H_2S is not adsorbed at all, nor on the Tenax tubes, nor on the Silcolsteel coated tubes making them optimal for all other volatile sulfur compounds to be adsorbed (no problem of saturation, nor competition with a compound present in high amounts). The adsorption tubes were then desorbed systematically and analyzed by a TD-GC/MS. The total experimental strategy for this study is shown in Fig (4.1).

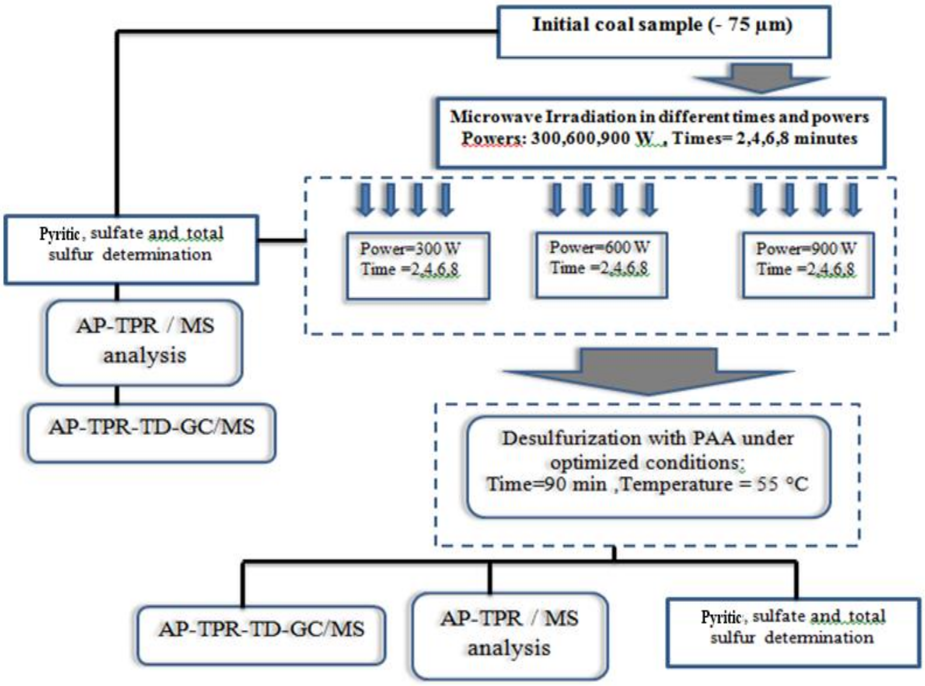


Fig (4.1). Experimental set-up for experimental sequence.

4.3 - Results and discussion

The different sulfur species after chemical desulfurization are determined and the results are shown in Table (4.4). Implementing pre-microwave irradiation at 300 W and for 2 min before chemical desulfurization by PAA, resulted in a maximum total sulfur and organic sulfur reduction of about 63% and 49% respectively. It can be noticed from Table (4.4) that the pyrite reduction for the initial desulfurized coal compared to the pre-microwave treated samples were not only specifically different, but the percentage of desulfurization degree increased always as a result of the microwave pre-treatment. According to the previous studies, pyrite showed higher dielectric properties than any other coal associated mineral tested. Due to significant differences in the dielectric properties of bulk coal and pyrite, microwave can selectively heat the pyrite phase resulting in increased pyrite reduction without adversely affecting the physical properties of the coal [31-40]. It can be also seen that the pyrite reduction in the initial desulfurized sample is about 63% and in all microwave pretreated coals is more than 84%. A 21% pyrite removal improvement can thus be noticed.

Table(4.4). Sulfur reduction (%) of initial and irradiated samples after PAA chemical desulfurization

No.	Sample	Sulfur reduction (%) (db)				Coal Yeild (%)
		S_{Total}	$S_{Pyritic}$	$S_{Organic}$	$S_{Sulfate}$	
1	**Initial** ^{DS}	43.07	62.75	26.19	100	96
2	**753002** ^{DS}	63.41	86.64	48.52	100	98
3	**753004** ^{DS}	56.31	89.20	30.43	100	98
4	**753006** ^{DS}	54.50	98.11	30.25	100	99
5	**753008** ^{DS}	48.96	85.68	22.19	100	97
6	**756002** ^{DS}	50.84	96.65	20.01	100	98
7	**756004** ^{DS}	54.96	97.10	34.40	100	90
8	**756006** ^{DS}	51.70	96.97	31.02	100	86
9	**756008** ^{DS}	49.41	87.00	28.13	100	91
10	**759002** ^{DS}	59.81	98.27	34.38	100	99
11	**759004** ^{DS}	55.13	98.36	34.96	100	86
12	**759006** ^{DS}	52.73	84.29	35.50	100	86
13	**759008** ^{DS}	49.48	87.50	28.09	100	90

DS: Desulfurized

Maximal pyritic sulfur reduction (98%) is achieved at 900 W and 4 minutes. Sulfate sulfur was completely removed after chemical desulfurization by PAA. Indeed, chemical desulfurization causes also a clear ash reduction and consequently removed completely its sulfate sulfur. The applied chemical desulfurization decreased the heating value of the samples by 1 to 3 MJ/kg, calculated according to the formula of Channiwala [41], as can be noticed in Table (4.2), which can be considered as beneficial in view of practical applications of this treatment beneficial.

4.3.1. AP-TPR experiments coupled “on-line” with mass spectrometry detection

The H_2S kinetograms of AP-TPR/MS of initial sample before and after desulfurization are visualized in Fig (4.2A and B). Because m/z 34 (H_2S^+) and m/z 33 (HS^+) exhibit the same evolution profiles, only m/z 34 ion profiles of investigated samples are shown and discussed. Two dominant peaks for initial samples before and after desulfurization can be seen, with the first peak T_{max} about 450-470 °C and for the second at about 650-660 °C. The peak in the lower temperature region can be assigned to the presence of di-alkyl sulfides, alkyl-aryl sulfides and reactive di-aryl sulfides [42]. The second peak maximum at the higher temperature region (Fig (4.2)), refers to the presence of less reactive di-aryl sulfides and simple and less complex thiophenic structures. According to these profiles, there is no proof for the presence of thiols because of the absence of an H_2S signal below 300°C as well for the initial (Fig (4.2A)) and for the desulfurized coal sample (Fig (4.2B)).

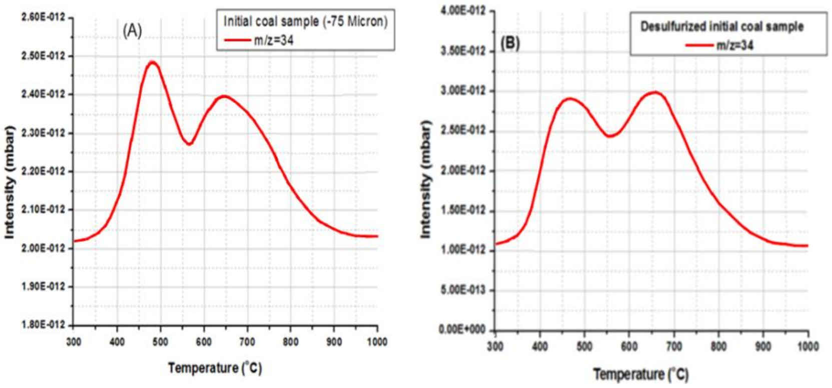
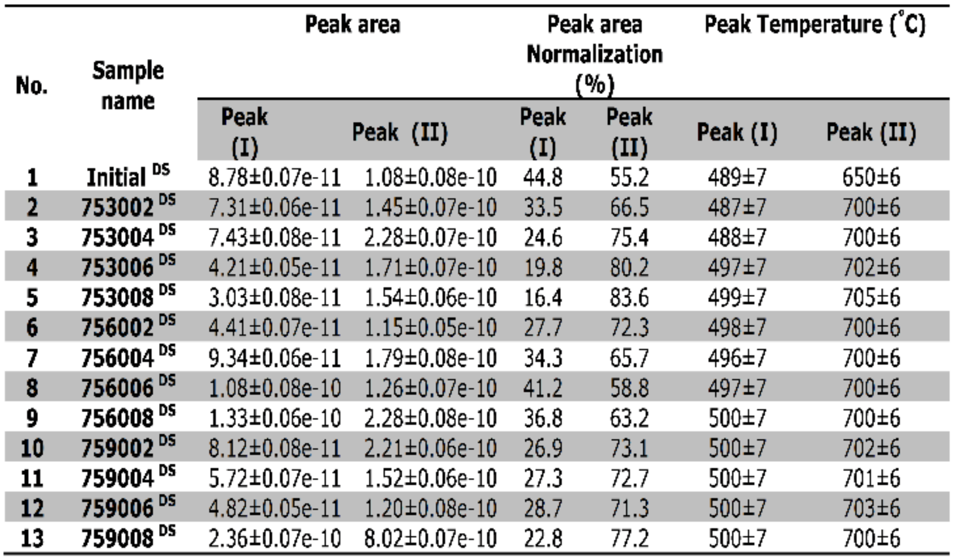


Fig (4.2). AP-TPR/MS (H_2), m/z=34 kinetograms of Tabas coal sample (initial coal) (before and after desulfurization)

Absolute MS intensities of obtained signals from different AP-TPR experiments cannot be compared with each other, since total recorded MS intensity changes for each experiment. For this reason it is necessary to normalize the profiles when a comparison of selected dominant peaks between different samples is considered. The area under each dominant H_2S peak is determined by a deconvolution strategy of the H_2S profiles using multiple Gaussian functions (using Origin software (version 8)). Percent of peak area is calculated for each AP-TPR experiment according to: (Area P_i/Area P_{tot})×100. The calculated areas and the relevant peak temperatures for desulfurized pre-irradiated and initial coal samples are illustrated in Table (4.5). For the initial coal sample the first and second peak appeared at 479°C and 650°C respectively, corresponding with an area of 36% and 64%. (The peak areas are expressed in: (°C.mbar)). It should also be mentioned that the goodness of fits (Coefficient of determination (R^2)) for all fitted curves is around 97-98%.

Table (4.5). Sulfur peak areas and relevant peak temperatures for initial and pre-irradiated desulfurized samples.



No.	Sample name	Peak area		Peak area Normalization (%)		Peak Temperature (°C)	
		Peak (I)	Peak (II)	Peak (I)	Peak (II)	Peak (I)	Peak (II)
1	Initial ^{DS}	8.78±0.07e-11	1.08±0.08e-10	44.8	55.2	489±7	650±6
2	753002 ^{DS}	7.31±0.06e-11	1.45±0.07e-10	33.5	66.5	487±7	700±6
3	753004 ^{DS}	7.43±0.08e-11	2.28±0.07e-10	24.6	75.4	488±7	700±6
4	753006 ^{DS}	4.21±0.05e-11	1.71±0.07e-10	19.8	80.2	497±7	702±6
5	753008 ^{DS}	3.03±0.08e-11	1.54±0.06e-10	16.4	83.6	499±7	705±6
6	756002 ^{DS}	4.41±0.07e-11	1.15±0.05e-10	27.7	72.3	498±7	700±6
7	756004 ^{DS}	9.34±0.06e-11	1.79±0.08e-10	34.3	65.7	496±7	700±6
8	756006 ^{DS}	1.08±0.08e-10	1.26±0.07e-10	41.2	58.8	497±7	700±6
9	756008 ^{DS}	1.33±0.06e-10	2.28±0.08e-10	36.8	63.2	500±7	700±6
10	759002 ^{DS}	8.12±0.08e-11	2.21±0.06e-10	26.9	73.1	500±7	702±6
11	759004 ^{DS}	5.72±0.07e-11	1.52±0.06e-10	27.3	72.7	500±7	701±6
12	759006 ^{DS}	4.82±0.05e-11	1.20±0.08e-10	28.7	71.3	500±7	703±6
13	759008 ^{DS}	2.36±0.07e-10	8.02±0.07e-10	22.8	77.2	500±7	700±6

DS:desulfurized

The sharp peak in the lower temperature region, visible in Fig (4.2A), is not only determined by the mentioned organic sulfur compounds but also dominated by the reduction of pyritic sulfur (1.16 wt% or 37% of the total sulfur presence, Table (4.3)) into troilite with the formation of H_2S. After desulfurization by PAA, the sharp first peak changed (Fig (4.2B)) in shape and became broader. Not only because of an absolute decrease in its pyritic sulfur form amount (0.45 wt% or 24% of total sulfur presence, Table (4.3)) but also because of its higher removal % (62%) compared to the removal % of the organic sulfur fraction. This fraction is removed for only 26% and therefore increased in relative contribution from 59 up to 76% of the total sulfur amount. Further on, as can be noticed from Table (4.6), where the sulfur recovery as H_2S during an AP-TPR experiment is calculated, sulfur recovery as H_2S during an AP-TPR experiment decreases for the initial sample from 88% [43] to only 65% for the PAA treated. This could point to a less accessibility of H_2 towards the organic sulfur groups or to the relative higher presence of less-reactive aromatic sulfur compounds (as the more-reactive ones were removed to a higher extend).

Table (4.6). Measured sulfur amount for initial and pre-irradiated desulfurised samples from AP-TPR/MS (H_2) measurements.

No.	Sample	S_{total} (%)	$S_{(T+C)}$ (%)	$S_{AP\text{-}TPR}$ (%)	AP-TPR Recovery(%)	Sulfur 1st peak (mgS/g)	Sulfur 2nd peak (mgS/g)
1	**Initial** $_{DS}$	1.88	0.66	1.22	65	5.50	6.70
2	**753002** $_{DS}$	1.19	0.11	1.08	91	3.70	7.13
3	**753004** $_{DS}$	1.39	0.20	1.19	85	2.96	8.86
4	**753006** $_{DS}$	1.43	0.28	1.15	80	2.29	9.15
5	**753008** $_{DS}$	1.61	0.23	1.38	86	2.22	11.63
6	**756002** $_{DS}$	1.55	0.35	1.20	77	3.34	8.60
7	**756004** $_{DS}$	1.47	0.20	1.27	86	4.30	8.34
8	**756006** $_{DS}$	1.54	0.32	1.22	79	4.99	7.18
9	**756008** $_{DS}$	1.69	0.39	1.30	77	4.81	8.20
10	**759002** $_{DS}$	1.18	0.10	1.08	92	2.93	7.93
11	**759004** $_{DS}$	1.39	0.19	1.20	86	3.23	8.72
12	**759006** $_{DS}$	1.56	0.31	1.25	80	3.62	8.86
13	**759008** $_{DS}$	1.74	0.39	1.35	78	3.12	10.45

It could also point to the relative increased presence of untouched complex thiophenic structures which are not hydrogenated under AP-TPR conditions into H_2S and thus results in a lower overall H_2S yield in the AP-TPR experiment. Additionally, PAA seems to be unable to breakdown these more complex thiophenic structures. Further on, PAA not only removes other sulfur compounds, but can also oxidize them into other sulfur functionalities as a result of a specific reaction mechanism that should result in a removable complete oxidized sulfur compound in the final state. However, if the end state is not reached, it is left in a sulfur form not leading to the formation of H_2S during an AP-TPR experiment or at least to a much lesser extend [22,45,46]. Therefore, these sulfur forms will be present in an oxidized state as organic sulfon, sulfoxide or organic sulfonic acid compounds. During an AP-TPR experiment, these forms can generate sulfur oxides, detectable by MS as m/z 64 (SO_2^+) and 48 (SO^+). Using the off-line setup, these oxides can also be captured by the adsorbents in the tubes and (semi-)quantitatively determined. Therefore, in the on-line detection also m/z 64 and 48 are visualized in Fig (4.3).

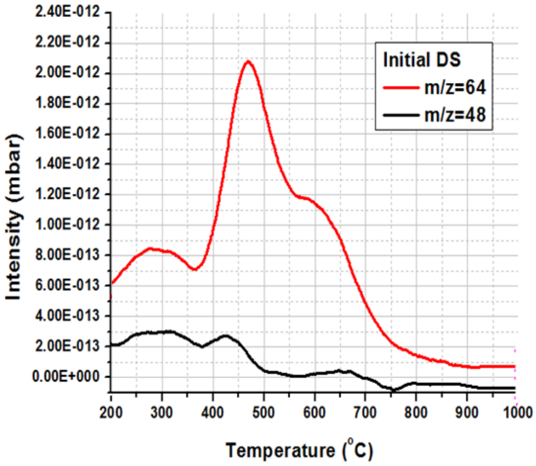


Fig (4.3).AP-TPR-MS (H_2) , m/z=48 (SO^+) and m/z=64 (SO_2^+) kinetograms of initial desulfurized coal sample.

Only when m/z 64 and 48 exhibit the same trend, absolute confirmation of formed sulfur oxides can be proved. From Fig (4.3) it is clear that this is not the case. Partly they show similar profiles, but at the higher temperature range this is less obvious. M/z 64 certainly refers also to other CH-fragments. As can be seen in Fig (4.3), the first peak in the m/z 64 as in the m/z 48 exhibited the same trend. This first peak refers to the presence of organic sulfonic acid. Peak two (425°C) in the m/z 48 profile as the third peak (650°C) could be correlated with the m/z 64 signal the second peak and the shoulder at higher temperature, respectively and therefore could be attributed to some presence of organic sulphones and sulfoxides, respectively. It should be additional noticed, that in the case of organic sulfoxides almost no m/z 64 is to be expected, only m/z 48.

However, m/z 48 is not an unique fragment referring only to SO^+ and therefore cannot be correlated with the presence of sulfoxides alone.

4.3.2. Effect of power and time of pre-irradiation on sulfur removal by PAA.

4.3.2.1 Qualitative approach.

AP-TPR profiles for microwaved and post-desulfurized coals are illustrated in Fig (4.4). From Table (4.5), for all applied power irradiation experiments, it can be deduced that the peak temperature for the dominant first H_2S signal in all desulfurized samples shows no specific shifting.

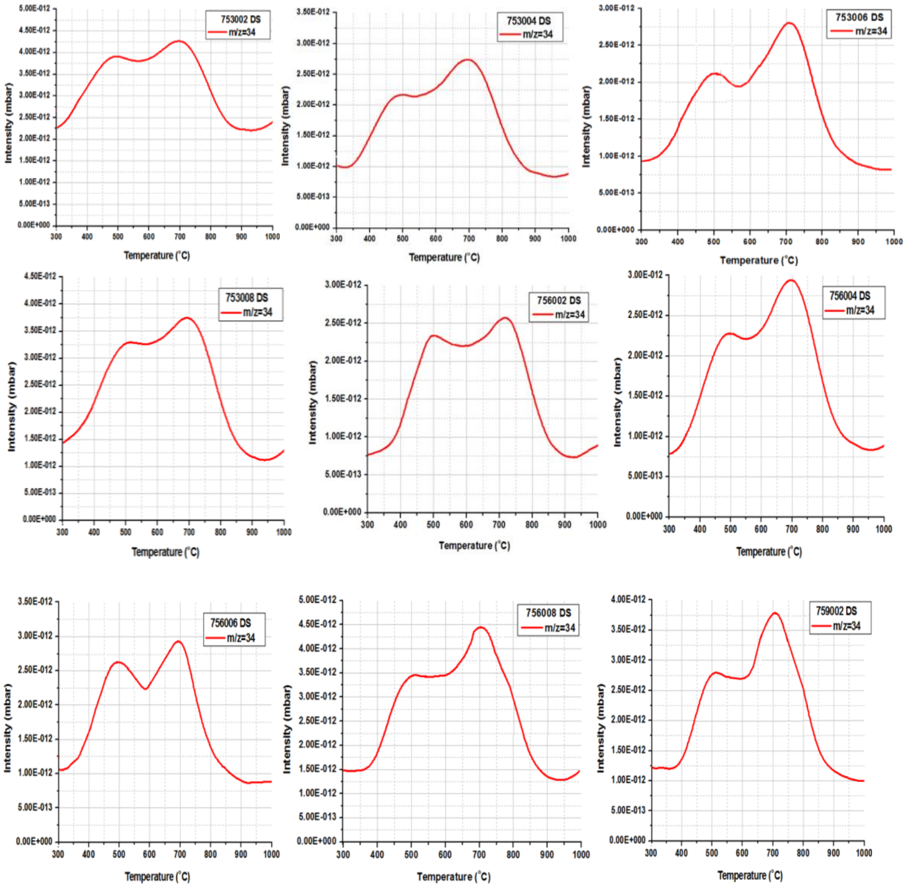


Fig (4.4). AP-TPR/MS (H_2), m/z=34 kinetograms of desulfurized Tabas coal samples (pre-microwave treated samples)

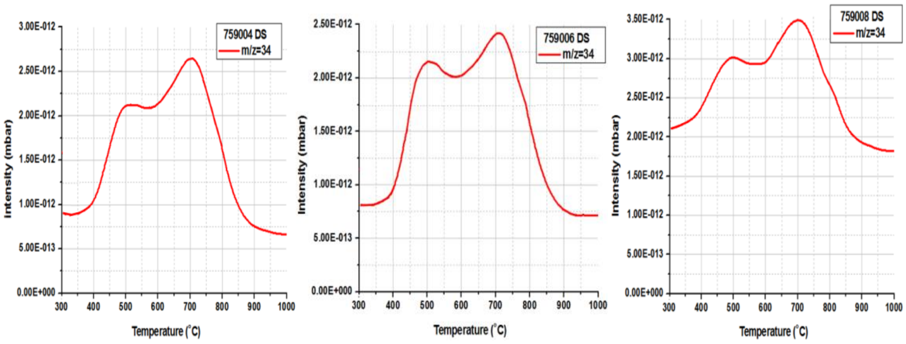
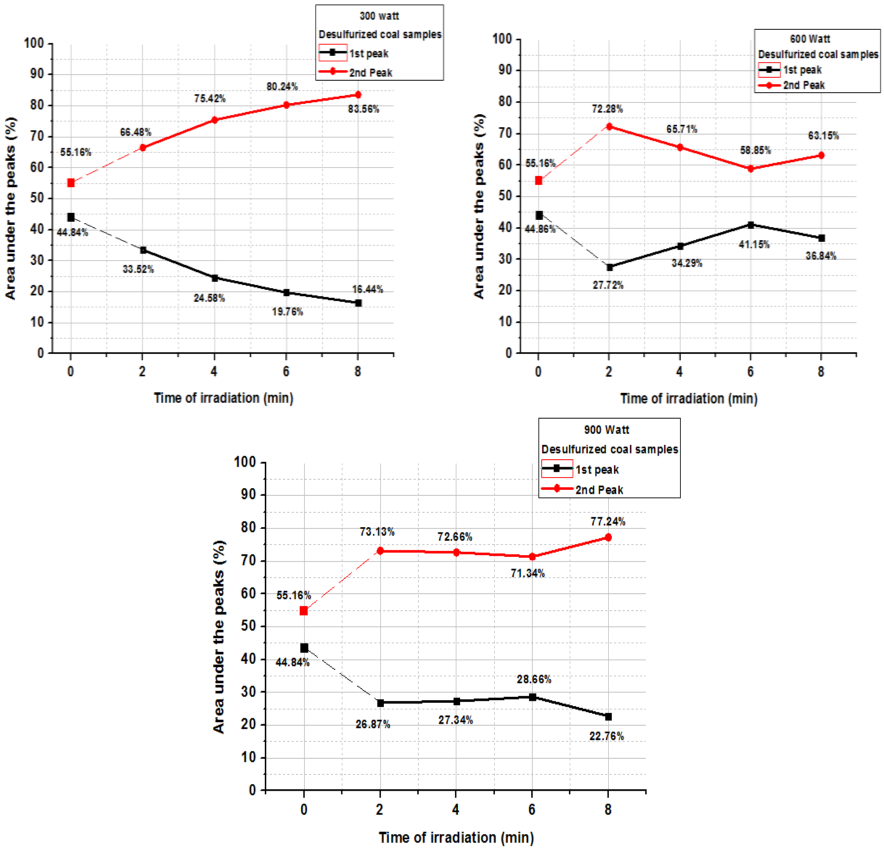


Fig (4.4). AP-TPR/MS (H_2), m/z=34 kinetograms of desulfurized Tabas coal samples (pre-microwave treated samples) (continue)

On the other hand, the temperature shift for the second main peak compared with the initial post-desulfurized coal sample is 50 °C higher. The normalized second H_2S peak % area increased apparently random up to a range of 59% - 84%, compared to the second H_2S peak % area of the initial post-desulfurized coal sample, being 55%. This means that microwave pre-irradiation has a definite but difficult to determine influence on the chemical desulfurization process and on the desulfurization impact by PAA in the coal sample.

In the Fig (4.5), deduced from Table (4.5), a comparison of the calculated normalized % area under the two dominant H_2S peaks for irradiated and initial but post-desulfurized samples are visualized.



Fig(4.5). Normalized area under the two dominant peaks in the H_2S profiles for pre-irradiated and post-desulfurized samples (for the time =0 the percentage of 1^{st} and 2^{nd} peak is 45 and 55% respectively).

In Fig (4.6) similar normalized H_2S peak % area of coal samples only irradiated are shown from our previous paper [43]. We believe, it makes the discussion more handsome.

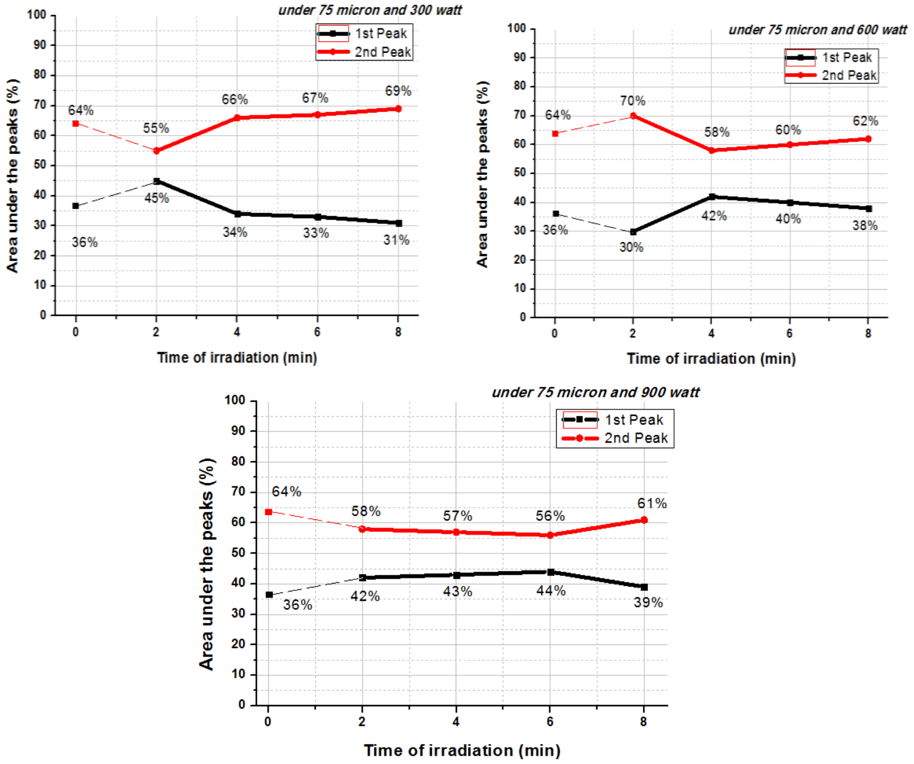


Fig (4.6). Normalized area under the two dominant peaks in this H_2S profiles for all microwave treated samples (for the time = 0 the percentage of 1st and 2nd peak is 36 and 64% respectively) (before desulfurization) [43]

Based on Table (4.4), for the 300 W pre-irradiation treatment, the highest sulfur reduction is achieved for the 2 minutes time period: 63.4% for total and 48.5% for organic sulfur. From Fig (4.6) it was concluded [43] that due to this 2 minutes pre-irradiation, more-reactive aromatic sulfur compounds were formed (increase of the first H_2S peak % area and decrease consequently of second H_2S peak % area). It is believed that the more-reactive aromatic sulfur compounds are also more PAA sensitive and thus resulted in a higher sulfur removal degree compared to the longer irradiation times at the same 300W power. Indeed, according to Fig (4.6) the second H_2S peak % area of these samples increased systematically as a function of pre-irradiation time and even higher than the initial sample. This means that, due to the longer pre-irradiation time more less-reactive aromatic sulfur compounds were formed and thus being less PAA sensitive and resulting in a lower desulfurization degree of organic sulfur as is demonstrated by Table (4.4). According to Fig (4.5), 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 the less-reactive aromatic sulfur compounds as thiophenic structures unaltered. As stated in our first publication [43], also coal matrix was altered by the pre-irradiation treatment, this combined effect resulted for the PAA treatment to a lower sulfur reduction % for S_{org} (22%) for the 8 minutes pre-irradiation treatment compared to the initial sample (26%). Nevertheless S_{tot} removal for this sample is higher (49%) than for the initial one (43%). From Table (4.4) one can further notice that S_{org} as S_{tot} removal % systematically decreased as a function of this 300W pre-irradiation time from 48.5 to 22.2%, and from 63.4 to 49.0%, respectively. From this it can already be concluded that a longer pre-irradiation time than 2 minutes at 300W is not beneficial for the PAA desulfurization process.

According to Table (4.4), it can be further seen that the smallest organic sulfur reduction using a PAA treatment is achieved for the 600W pre-irradiation treatment also for 2 minutes and being only 20.0%, compared with the initial PAA treated sample, being 26%. This can again be explained based on Fig (4.6), where now for the 600W pre-irradiation experiment, a clear increase in the second H_2S peak % area for the 2 minutes treatment compared to the initial sample can be noticed. This was due, as discussed in [43], by an increased amount of less-reactive aromatic sulfur compounds at the cost of more-reactive aromatic sulfur compounds PAA desulphurization was less effective in their removal. From Table (4.4) it can also be noticed that for S_{tot} its reduction degree compared to the initial desulfurized sample is higher, 51% compared to 43%. Taking into account the effect of irradiation on the coal matrix alteration, an apparent strange effect is noticed in Fig (4.5). An increase in the second H_2S peak %area compared to the initial samples is measured. Increasing pre-irradiation time at 600W, always higher S_{org} and S_{tot} reduction % are obtained compared with the initial sample (Table (4.4)), in contrast to decreasing as irradiation time increased. For S_{org} a decrease from 34.4 down to 28.1%, and for S_{tot} from 55.0 down to 49.4% is observed. According to Fig (4.6), increasing pre-irradiation time resulted in a systematic increase in the second H_2S peak %

area, but never reaching the value of the initial coal sample [43]. This points out again that more less-reactive sulfur compounds resist the PAA desulphurization treatment. In Fig (4.5) this systematic change is not followed. First, the second H_2S peak % area decreased and then increased again at the longest pre-irradiation time. For this 8 minute pre-irradiation time this tendency seems to be true for all power settings. The combined effects of sulfur form changes and coal matrix alteration due to pre-irradiation treatment seems to result in a none absolute systematic change in second H_2S peak % area, with of course a consequently first H_2S peak % area change. As stated in paper [43], the first 2 minutes pre-irradiation has, independently of used power, the biggest impact on the coal in view of sulfur form changes and matrix effects.

For 900 W, again a different trend occurred, an intermediate amount of S_{tot} and S_{org} removal by PAA is found compared to the 2 min 300 and 600W pre-irradiation experiments. For S_{tot} a systematic decrease as a function of the pre-irradiation time is found and for S_{org} a systematic increase is found, except for the 8 min pre-treatment (Table (4.4)). Also for the normalized % area under the second H_2S peak for the 900W and 2 min, an intermediated value is noticed compared to the 2 min ones of the 300 and 600W pre-irradiation experiment (Fig (4.6)). Within the 900 W results of the pretreatment the first H_2S peak % area decreased continuously (64 to 58 down to 56%) (Fig (4.6)), resulting in a decrease in less-reactive aromatic sulfur compounds [43] in favor of more-reactive ones. This could explain the increase of S_{org} removal by PAA as given in Table (4.4). But during 8 minutes of pre-irradiation its second H_2S peak % area increases again (Fig (4.6), 61%) and resulted in a smaller S_{org} and S_{tot} removal by PAA, as is found in Table (4.4). However, Fig (4.5) as Table (4.5) indicated that the normalized H_2S peak % area apparently do not completely confirm this conclusion. The impact of the coal matrix effect combined with the change in sulfur form due to the pre-irradiation experiment on the PAA treatment could be a reason for this adverse behavior.

4.3.2.2 Quantitative approach

The total sulfur amount as the percentage of different sulfur forms in all pre-irradiated and initial coals before and after desulfurization have been summarized in Table (4.3). The amount of sulfur in tar and char, which were remaining in the reactor after the AP-TPR experiment were determined as well. In this way, all sulfur forms which reacted with hydrogen during the AP-TPR experiment forming H_2S can be quantitatively calculated and can thus be quantitatively related to the % area under the H_2S peak profiles. The amount of sulfur in tar and char (S_{T+C}) and sulfur, which reacted with hydrogen ($S_{AP\text{-}TPR}$) are given in Table (4.6). Except for the non-microwave (MV) treated sample, the AP-TPR recoveries are very high. MW treatment makes the hydrogenation of sulfur compounds in this coal more accessible, resulting in a higher AP-TPR H_2S recovery. As already mentioned, due to this MW pre-treatment also more complex thiophenic structures will be degraded in less complex ones, better accessible towards hydrogenation reaction in AP-TPR conditions. But also PAA desulphurization treatment seems to play a positive role within the AP-TPR recovery degree. Looking in more detail to Table (4.6), for all power and time settings of the MW pre-treatment followed by a desulfurization treatment with PAA, the second sulfur peak areas in AP-TPR profile are always much larger than the first sulfur peak areas compared to the initial desulfurized sample. This supports the idea that in general and taking into account the AP-TPR recovery indeed more complex thiophenic structures are transformed in less complex ones (but still not removed by PAA), additionally available for hydrogenation under AP-TPR conditions. Within the 300W power setting at longer irradiation time, the second sulfur peak area continuously increased and the first sulfur peak area decreased accordingly. For the 600W setting we get the reversed effect with a decrease in the second sulfur peak and an increase in the first sulfur peak up to 6 minutes of pre-irradiation, at 8 minutes this trend changes. For 900W again a different trend, with for both sulfur peaks an increase in sulfur amount, except for the first sulfur peak area at 8 minutes where it decreased. As discussed in the previous chapter, power and time setting of MW pre-treatment resulted in a complex change in sulfur compound forms combined with coal matrix alteration having a different impact on the ability of PAA to remove the different sulfur groups. This is not in contradiction with the increased S_{org} sulfur removal noticed in Table (4.4) as a function of pre-irradiation time with for all 8 min experiments again a much lower S_{org} as S_{tot} sulfur reduction % values.

4.3.2.3 Oxidized sulfur compounds formation

It is known that in AP-TPR experiments, the oxidized sulfur forms present in the sample are not entirely reduced into H_2S [44-46]. 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 evolution), the sulfur distribution of oxidized sulfur forms in coal can be revealed. Therefore the profiles of both, m/z=48 (SO^+) and 64 (SO_2^+), are tracked. Fig (4.7), partly visualizes the evolution of oxidized sulfur functionalities during AP-TPR experiments in hydrogen atmosphere for pre-microwave treated and desulfurized samples. As the transient signal from these ions partly exhibits different trends, these ion profiles most likely correspond also to other organic CH-fragments with mentioned masses. Pre-irradiation also seems to affect the amount of formed oxidized sulfur compounds by the PAA treatment. Indeed, this signal shows some differences in pre-microwaved treated samples as a function of power and time setting.

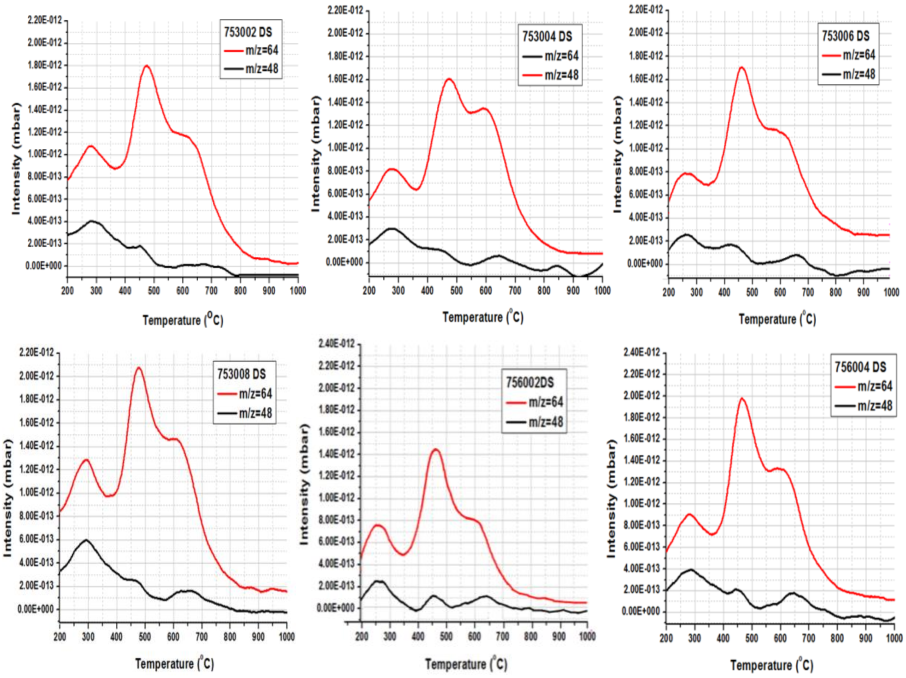


Fig (4.7). AP-TPR-MS (H_2) , m/z=48 (SO^+) and m/z=64 (SO_2^+) kinetograms of pre-microwaved desulfurized coal samples

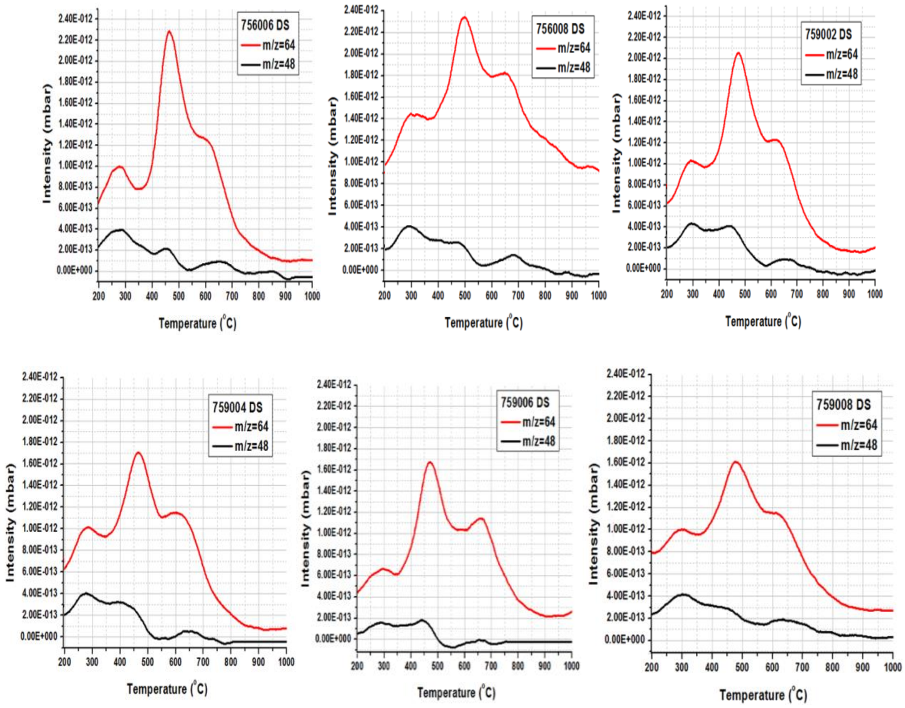


Fig (4.7). AP-TPR-MS (H_2) , m/z=48 (SO^+) and m/z=64 (SO_2^+) kinetograms of pre-microwaved desulfurized coal samples (continue)

Based on Fig (4.7), the lower temperature maximum around 200-300°C for m/z=48 profile and m/z=64 profile exhibit the same trend for all pre-irradiated and desulfurized samples certainly refers to the organic sulfonic acid group decomposition [46]. At higher temperature range (above 300 °C) m/z=64 and 48 profiles clearly demonstrate apparently not fully the same trend. For all samples the second peak maximum at around 430 °C as the shoulder at around 600°C in the m/z profile of 64 finds its analogue in the m/z 48 profile but sometimes in a very weak intensity. Therefore, besides organic sulfonic acid also sulfones (second peak) as sulfoxides (shoulder) are present in the PAA treated samples, although in minor amounts. It is as clear that these profiles give us ground to suppose that m/z=48 and 64 profiles not only refer to SO^+ and SO_2^+ but also to other CH-fragments. For this reason only the first peak in the lower temperature region (200-300 °C), has been quantized and the normalized % area of the first maximum has been evaluated. We expected that the changes in the organic sulfonic acid occurred due the desulfurization by PAA. It is found

[43] that in the pre-irradiated samples as in the initial samples no proof for the presence of oxidized sulfur compounds was observed as m/z profiles did not exhibit the same trend and this for the whole AP-TPR temperature range (see further off-line experiments, Table (4.8) and (4.9)). Table (4.7), which is deduced only from the profile of the m/z 64 ion of Fig (4.3) and (4.7), shows the quantized and normalized organic sulfonic acid peak amounts in the lower temperature range for all initial and pre-microwaved desulfurized coals.

Table (4.7). Organic sulfonic acid group amounts and normalized peak area%, for initial and pre-irradiated desulfurized coal samples

No.	**Sample**	**Total area under peaks for m/z=64 profile**	**Area under the peak in lower temperature region (200-300 ˚C)**	**Normalized area (%)**
1	**Initial DS**	3.63±0.06E-10	1.61±0.07E-11	4.4
2	**753002 DS**	2.91±0.07E-10	1.40±0.06E-11	4.8
3	**753004 DS**	3.32±0.06E-10	1.92±0.06E-11	5.8
4	**753006 DS**	3.14±0.05E-10	2.08 ±0.07E-11	6.6
5	**753008 DS**	3.88±0.06E-10	3.23±0.06E-11	8.3
6	**756002 DS**	4.85±0.07E-10	3.65±0.08E-11	7.3
7	**756004 DS**	3.39±0.07E-10	2.61±0.06E-11	7.7
8	**756006 DS**	3.15±0.07E-10	2.42±0.08E-11	7.7
9	**756008 DS**	2.75±0.07E-10	2.13±0.08E-11	7.8
10	**759002 DS**	3.13±0.05E-10	2.37±0.05E-11	7.6
11	**759004 DS**	2.50±0.07E-10	1.97±0.08E-11	7.9
12	**759006 DS**	2.48±0.08E-10	1.71±0.08E-11	8.0
13	**759008 DS**	2.35±0.07E-10	1.85±0.06E-11	8.2

DS: Desulfurized

Table (4.7) shows that the normalized first peak % area of the organic sulfonic acid group presence increases with increasing time of pre-irradiation of all desulfurized samples, mostly for the 300W pre-irradiation and less pronounced for the 600 and 900W pre-irradiation. Higher power (600 and 900W) seems to change immediately the optimal condition for oxidized sulfur group formation by PAA, longer time of pre-irradiation has only a minor positive effect. For pre-irradiation power of 300W, the duration of the pre-irradiation time improves the oxidizing efficiency towards sulfur compounds by the PAA treatment (first peak m/z 64 normalized % area goes from 4.8% up to 8.3%, the highest value of all samples) more than in the cases of 600 and 900W, 7.3 up to 7.8% and 7.6 up to 8.2%, respectively.

For all pre-irradiated samples the normalized peak % area is clearly higher compared to the initial desulfurized coal proving that irradiation indeed favors the oxidizing potential of PAA towards the present sulfur compounds.

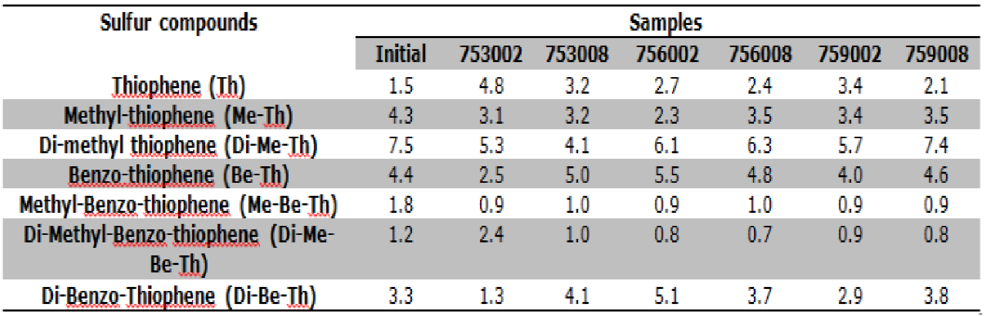
4.3.3. AP-TPR “off-line” TD-GC/MS experiments

Volatile organic sulfur compounds, different from H_2S, during pyrolysis can also be quantitatively determined by AP-TPR “off-line” TD-GC/MS 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-benzothiophene and dimethyl- benzothiophene.

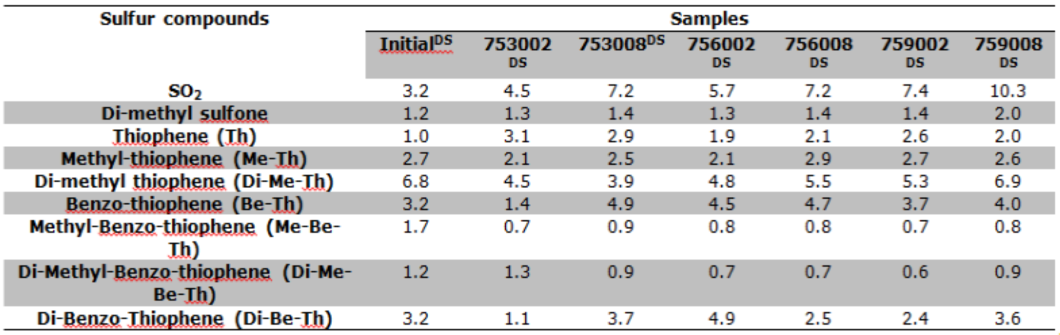
GC-MS spectra are quantitatively interpreted by spiking with 0.5µg d_6-benzene as internal standard. The “off-line” experiments have only been performed in both extreme times of irradiation treatment: 2 and 8 minutes. The higher homologues, like three/tetra/penta substituted thiophenes and three substituted benzothiophene 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 (Table (4.8) and (4.9)).

Table (4.8). Organic sulfur compounds determined by AP-TPR/GC-MS <u>before</u> desulfurization, in µg S/g.



Sulfur compounds	Samples						
	Initial	753002	753008	756002	756008	759002	759008
Thiophene (Th)	1.5	4.8	3.2	2.7	2.4	3.4	2.1
Methyl-thiophene (Me-Th)	4.3	3.1	3.2	2.3	3.5	3.4	3.5
Di-methyl thiophene (Di-Me-Th)	7.5	5.3	4.1	6.1	6.3	5.7	7.4
Benzo-thiophene (Be-Th)	4.4	2.5	5.0	5.5	4.8	4.0	4.6
Methyl-Benzo-thiophene (Me-Be-Th)	1.8	0.9	1.0	0.9	1.0	0.9	0.9
Di-Methyl-Benzo-thiophene (Di-Me-Be-Th)	1.2	2.4	1.0	0.8	0.7	0.9	0.8
Di-Benzo-Thiophene (Di-Be-Th)	3.3	1.3	4.1	5.1	3.7	2.9	3.8

Table (4.9). Organic sulfur compounds determined by AP-TPR/GC-MS <u>after</u> desulfurization, in µg S/g.



Sulfur compounds	Samples						
	Initial^{DS}	753002 DS	753008^{DS}	756002 DS	756008 DS	759002 DS	759008 DS
SO_2	3.2	4.5	7.2	5.7	7.2	7.4	10.3
Di-methyl sulfone	1.2	1.3	1.4	1.3	1.4	1.4	2.0
Thiophene (Th)	1.0	3.1	2.9	1.9	2.1	2.6	2.0
Methyl-thiophene (Me-Th)	2.7	2.1	2.5	2.1	2.9	2.7	2.6
Di-methyl thiophene (Di-Me-Th)	6.8	4.5	3.9	4.8	5.5	5.3	6.9
Benzo-thiophene (Be-Th)	3.2	1.4	4.9	4.5	4.7	3.7	4.0
Methyl-Benzo-thiophene (Me-Be-Th)	1.7	0.7	0.9	0.8	0.8	0.7	0.8
Di-Methyl-Benzo-thiophene (Di-Me-Be-Th)	1.2	1.3	0.9	0.7	0.7	0.6	0.9
Di-Benzo-Thiophene (Di-Be-Th)	3.2	1.1	3.7	4.9	2.5	2.4	3.6

The amount of the SO_2 and sulfones products recorded by "off-line" experiments in different temperature intervals have been expressed in µg S/g coal in Table (4.10).

Table(4.10). Amount of SO_2 and dimethyl-sulfone compounds determined by AP-TPR/GC-MS in µgS/g, in different temperature intervals for initial and pre-irradiated desulfurized coal samples

NO	Sample	Sulfur dioxide and dimethyl-sulfones (µgS/g)							
			25-200 °C	200-300 °C	300-400 °C	400-500 °C	500-600 °C	600-700 °C	Total
1	Initial DS	***So_2***	0.1	2.1	0.5	0.3	0.1	0.1	3.2
		Dimethyl -Sulfone	-	-	0.2	0.8	0.1	0.1	1.2
2	753002DS	***So_2***	0.3	3.4	0.5	0.2	0.1	-	4.5
		Dimethyl -Sulfone	-	-	0.1	0.9	0.2	0.1	1.3
3	753008 DS	***So_2***	0.5	5.9	0.5	0.2	0.1	-	7.2
		Dimethyl -Sulfone	-	-	0.1	1.1	0.2	-	1.4
4	756002 DS	***So_2***	0.2	4.9	0.3	0.2	0.1	-	5.7
		Dimethyl -Sulfone	-	-	0.1	1.1	0.1	-	1.3
5	756008 DS	***So_2***	0.7	6.1	0.2	0.1	0.1	-	7.2
		Dimethyl -Sulfone	-	-	0.2	1.1	0.1	-	1.4
6	759002 DS	***So_2***	0.7	6.5	0.2	-	-	-	7.4
		Dimethyl -Sulfone	-	-	0.1	1.2	0.1	-	1.4
7	759008 DS	***So_2***	0.9	8.6	0.3	0.2	0.2	0.1	10.3
		Dimethyl -Sulfone	-	0.1	0.2	1.6	0.1	-	2.0

DS:desulfurized

For pre-irradiated samples no indication of presence of oxidized sulfur was found by AP-TPR "off-line" TD-GC/MS experiments (Table (4.8)). Quantitative data of desulfurized coals: (Table (4.9)), proved by the presence of sulfur dioxide and even dimethyl sulfone showed that m/z 48 and m/z 64 profiles exhibiting partly similar tendency referred to the presence of organic sulfonic scid, sulfoxides and sulfones. As PAA is a mild oxidizing reagent, the oxidation of the sulfur compounds could be expected. However, no simple sulfoxides or organic sulfonic acid were detected by the off-line set-up, it could be therefore that the adsorption medium used in the tubes is not optimal for these compounds or that they were decomposed in its organic and SO_2 part. The amount of sulfur dioxide showed an increasing tendency with increasing power and time of irradiation (confirming the normalized peak % area values of Table (4.7)). The amount of dimethyl sulfone showed also an increasing tendency with increasing power and irradiation time compared with the initial state. The highest amounts of sulfur dioxide and sulfone are detected for 900W, certainly for the longest irradiation time. This additionally explained, beside the formation of less complex thiophenic structures, the differences in observed H_2S peak % area changes in the AP-TPR on-line experiment compared with the 300W and 600W treatment. For the 600W treatment this kind of tendency in peak % area changes could already be noticed. Further on, the quantitatively recorded amounts of the sulfur dioxide in different temperature intervals (off-line experiments) (Table (4.10)), showed that the amount of sulfur dioxide maximized in the range of 200-300°C.This can be confirmed by Fig (4.3) and (4.7) with the first evolved peak in the lower and identical temperature region for the initial desulfurized and pre-microwave desulfurized samples. Sulfur dioxide amounts in the case of 300W for 2 and 8 min showed increasing tendency from 4.4 to 7.1 μg S/g, respectively. For 600W and 2 min increasing tendency for the amount of the sulfur dioxide compared with the 300W and 2 min can be seen (5.4 μg S/g); moreover, for 600W and 8 min nonspecific changes were noticed (7.1μg S/g). For 900W, 2 and 8 min, recorded sulfur dioxide showed dramatically increasing tendency compared with the other samples (7.2 and 10.1 μg S/g, respectively).This confirms the normalized peak % area values of Table (4.7). Based on Table (4.10), an increasing tendency for sulfur dioxide was noticed as a result of time and power of pre-irradiation. Identical tendencies can be seen for the amount of dimethyl sulfone recorded by the "off-line" experiment. The maximum recorded values for dimethyl sulfone could be noticed in the range of 400-500°C and can be verified by Fig (4.3) and (4.7) with the second evolved peak in the same temperature region.

Based on the data from AP-TPR "off-line" TD-GC/MS (Table (4.8)), for all powers, the amount of thiophene detected, was always higher than for the initial state, but decreased as irradiation time increased. On the other hand, the amount of methyl and dimethyl thiophene were always lower than for the initial state, but slightly increased as pre-irradiation time became longer (except for the 300W condition). This observation holds also for methyl and dimethyl benzothiophene (except for 300W and 2 min), and slightly increased for methyl-Be-Th, but slightly decreased for dimethyl-Be-Th as pre-irradiation time became longer. This transformation could be related to the de-methylation process occurred as an impact of microwave treatment on coal matrix compared to the initial state. The change in amount of benzo and di-benzo thiophenes due to pre-irradiation was rather randomly. This again demonstrates the effects of power setting and irradiation time on sulfur form changes and on coal matrix changes, resulting in an apparently controversial but complex change in AP-TPR profiles.

The results from the AP-TPR "off-line" TD-GC/MS for desulfurized samples, Table (4.9), showed amounts of thiophene for all pre-irradiation samples to be always higher than the initial sample. However, for methyl-Th and dimethyl-Th they were mostly lower than the initial sample. Pre-irradiation time shows no clear tendency for these sulfur compounds as a result of a desulfurization treatment. For the methyl-Be-Th and the dimethyl-Be-Th again always lower amounts (except again the 300W and 2 min condition) were detected compared to the initial state. For benzo-Th always higher amounts were detected as pre-irradiation power (except again the 300W condition) and time increased due to desulfurization. For dibenzo-Th this tendency was not observed, again demonstrating the effects of power setting and irradiation time on sulfur form changes and on coal matrix changes, resulting in an apparently controversial but complex fluctuations in the AP-TPR profiles.

4.4 Conclusion

The total sulfur reduction after chemical desulfurization in this study is achieved in the range of 49-63%. Based on the discussed literature, inorganic sulfur (sulfate and pyrite) was mainly attacked by PAA after microwave treatment. The pyritic sulfur reduction achieved around 85-98% due to the dielectric characteristic of pyrite interacting efficiently with microwave irradiation. In all prepared samples, sulfate sulfur is totally removed after PAA desulfurization. Higher chemical desulfurization are achieved for the 300W and 2 minutes condition being around 63% and 48% for total and organic sulfur, respectively. AP-TPR coupled with different detection systems (MS and TD-GC/MS) gives us an opportunity to trace a broad range of organic sulfur species present in the Tabas coal. For the first time organic sulfur changes as a result of pre-microwave treated, followed by PAA desulfurization have been investigated. The information obtained by AP-TPR "off-line" (TD-GC/MS) show some quantitatively changes in the refractory aromatic sulfur forms as a results of microwave treatment before and after desulfurization. Opposite of the pre-irradiated and desulfurized samples, for the solely irradiated samples no indication of oxidized sulfur was found. This is a clear result of the PAA treatment as a mild oxidizing agent. Based on the "off-line" experiments for the desulfurized samples, the presence of sulfur dioxide and even dimethyl sulfone have been noticed quantitatively. The direct impact of the pre-MW treatment conditions (time and power) on the chemical desulfurization to produce oxidized sulfur products has been noticed, both qualitatively and quantitatively. AP-TPR "off-line" (TD-GC/MS) showed some controversial and more complex changes in organic sulfur forms which again demonstrates the direct but complicated impact of microwave irradiation on coal matrix.

4.5 - References

[1] World coal institute, Coal power for progress, 4th ed. ; 2000. p. 1–29.

[2] Zavitsanos P.D, Golden J.A, Bleiler, K.W, Kinkend K, (1978). Coal Desulfurization Using Microwave Energy. In: EPA-600/7-78-089, US Environmental Protection Agency (1978).

[3] Ferrando A.C, Andrés J.M, Membrado L, Coal desulphurization with hydroiodic acid and microwaves Coal Science and Technology, Volume 24, 1995, p.1729-1732.

[4] Yan J, Xu L, Yang J, A study on the thermal decomposition of coal-derived pyrite Journal of Analytical and Applied Pyrolysis, Volume 82, Issue 2, July 2008, p. 229-234.

[5] Butcher D.A and Rowson N.A , IChemE Research Event (1995), p. 580.

[6] Rowson N.A , Huang J. H, Hydrometallurgical decomposition of pyrite and marcasite in a microwave field Hydrometallurgy, Volume 64, Issue 3, June 2002, p.169-179.

[7] Rowson N.A , Huang J. H, Heating characteristics and decomposition of pyrite and marcasite in a microwave field Minerals Engineering, Volume 14, Issue 9, 2001, p. 1113-1117.

[8] Rowson N.A , Huang J. H., Rowson N.A, Hydrometallurgical decomposition of pyrite and marcasite in a microwave field Hydrometallurgy, Volume 64, Issue 3, June 2002, p. 169-179.

[9] Kusakabe K, Morooka S, Aso S, Chemical coal cleaning with molten alkali hydroxides in the presence of microwave radiation Fuel Processing Technology, Volume 19, Issue 3, October 1988, p. 235-242.

[10] Hayashi J, Oku K, Kusakabe K, Morooka S, The role of microwave irradiation in coal desulphurization with molten caustics Original Research Article Fuel, Volume 69, Issue 6, June 1990, p. 739-742.

[11] Ferrando A.C, Andrés J.M, Membrado L, Coal desulphurization with hydro-iodic acid and microwaves Coal Science and Technology, Volume 24, 1995, p. 1729-1732.

[12] Elsamak G, Altunta Özta N, Yürüm Y, Chemical desulfurization of Turkish Cayirhan lignite with HI using microwave and thermal energy Fuel, Volume 82, Issue 5, 1 March 2003, p. 531-537.

[13] Al-Harahsheh M, Kingman S.W, The influence of microwaves on the leaching of sphalerite in ferric chloride. Chemical Engineering and Processing: Process Intensification, Volume 46, Issue 10, October 2007, p. 883-888.

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

[15] Uslu T, Atalay Ü, Microwave heating of coal for enhanced magnetic removal of pyrite, Fuel Processing Technology, Volume 85, Issue 1, 15 January 2004, p. 21-29.

[16] Singh K, Mcwhinnie WR, Novel Methods for the Organic Desulfurisation of Coal, Coal Science and Technology, 1995;24,p.1725–1728.

[17] Jei W, Jiankang Y, Behavior of coal pyrolysis desulfurization with microwave energy, Fuel, 73, 2, 1994, p.155–159.

[18] Palmer SR, Hippo EJ, Kruge MA, Crelling C. (1994) Coal Prep 1992;10:93.

[19] Palmer SR, Hippo EJ, Dorai A. Fuel,p.73:161.

[20] Palmer SR, Hippo EJ, Dorai A. Selective oxidation pretreatment for enhanced desulfurization of coal. Fuel 1995;74(2),p.193–200.

[21] Sonmez O, Giray ES. The influence of process parameters on desulfurization of two Turkis Lignites by selective oxidation. Fuel Processing Technology 2001;70,p.159–69.

[22] Aelst JV, Yperman J, Franco DV, Mullens J, Van Poucke LC, Palmer SR. Sulfur distribution in Illinois No.6 coal subjected to different oxidation pre-treatments. Fuel 1997;76(14/15),p.1377–81.

[23] M.A.M. Ishak, K. Ismail,M.A.M. Nawi,A.F.(2003) Ismail, Chemical desulfurization of sub-bituminous high sulfur Indonesian coal via peroxyacetic acid treatment, AJSTD Vol. 20 Issue 1, p. 27-36.

[24] Dipu Borah, Mrinal K. Baruah,T, Inamul Haque, (2005), Oxidation of high sulphur coal. 3. Desulphurisation of organic sulphur by peroxyacetic acid (produced in situ) in presence of metal ions, Fuel Processing Technology 86,p. 959– 976.

[25] Yperman J, Maes II, Van den Rul H, Mullens S, Van Aelst J, Franco DV, et al. Sulfur group analysis in solid matrices by atmospheric pressure–temperature programmed reduction. Anal Chin Acta 1999; 395,p.143–55.

[26] Mullens S, Yperman J, Carleer R, Bozdemir T, Durusoy T, Yürüm Y. Sulfur analysis of Bolu-Mengen lignite before and after microbiological treatment using reductive pyrolysis and gas chromatography/mass spectrometry. Energy Fuels 2005;19,p.1029–36.

[27] Stefanova M, Marinov SP, Yperman J, Carleer R. Reductive pyrolysis of Miocene-aged lignite lithotypes using MS and GC/MS detection system for analysis of organic sulfur groups. Fuel 2005;84,p.71–9.

[28] Marinov SP, Stefanova M, Stamenova V, Carleer R, Yperman J. Sulfur functionality study of steam pyrolyzed ‘‘Mequinenza’’ lignite using reductive pyrolysis technique coupled with MS and GC/MS detection systems. Fuel Process Technol 2005;86,p.523–34.

[29] Marinov SP, Stefanova M, Stamenova V, Gonsalvesh L, Carleer R, Yperman J. Sulphur analysis of household briquettes using MS and GC/MS detection systems after reductive pyrolysis. J Fuel Chem Technol 2006;34(3),p.257–64.

[30]Gonsalvesh L, Marinov SP, Stefanova M, Yürüm Y, Dumanli AG, Dinler-Doganay G, et al. Biodesulphurized subbituminous coal by different fungi and bacteria studied by reductive pyrolysis. Part 1: initial coal. Fuel 2008;87,p.2533–43.

[31] Hu H, Chen Q, Yin Z, Zhang P, Zou J, Che H, Study on the kinetics of thermal decomposition of mechanically activated pyrites Thermochimica Acta, Volume 389, Issues 1-2, 1 July 2002, p. 79-83.

[32] Hu H, Chen Q, Yin Z, Zhang P, Thermal behaviors of mechanically activated pyrites by thermogravimetry (TG) Thermochimica Acta, Volume 398, Issues 1-2, 5 March 2003, p. 233-240.

[33] Hu G, Dam-Johansen K, Wedel S, Hansen J.P, Decomposition and oxidation of Pyrite Progress in Energy and Combustion Science, Volume 32, Issue 3, 2006, p. 295-314.

[34] Maxwell E, Kelland D.R, Jacobs I.S, Levinson L.M, Magnetic separation and thermo-magneto-chemical properties of coal liquefaction mineral participates Original Research Article Fuel, Volume 61, Issue 4, April 1982, p. 369-376.

[35] Marland S, Merchant A, Rowson N.A, Dielectric properties of coal Fuel, Volume 80, Issue 13, October 2001, p. 1839-1849.

[36] Marland S, Han B, Merchant A, Rowson N.A, The effect of microwave radiation on coal grindability Fuel, Volume 79, Issue 11, September 2000, p. 1283-1288.

[37] Weng S, Wang J, Exploration on the mechanism of coal desulfurization using microwave irradiation / acid washing method Fuel Processing Technology, Volume 31, Issue 3, September 1992, p. 233-240.

[38] Butcher D.A and Rowson N.A , IChemE Research Event (1995), p. 580.

[39] Uslu T, Atalay Ü, Arol A.I, Effect of microwave heating on magnetic separation of pyriteColloids and Surfaces A: Physicochemical and Engineering Aspects, Volume 225, Issues 1-3,15 September 2003, p. 161-167.

[40] Shuey R.T. Semiconductor Ore Minerals (Developments in Economic Geology 4) Elsevier, Amsterdam (1976).

[41] Channiwala SA, Parikh PP, A unified correlation for estimating HHV of solid, liquid and gaseous fuels. Fuel 2002;81 (8),p.1051-63.

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

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

[44] Rutkowski P, Mullens S, Yperman J, Gryglewicz G. AP-TPR investigation of the effect of pyrite removal on the sulfur characterization of different rank coals. Fuel processing technology, 2002; 76,p.121-38.

[45] Van Aelst J,Yperman J,Franco DV, Van Poucke LC, Buchanan AC, Britt PF. Study of silica-immobilized sulfur model compounds as a calibrants for the AP-TPR study of oxidized coal samples. Energy and Fuels 2000;14(5),p.1002-8.

[46] Mullens S, Yperman J, Reggers G, Carleer R, Buchanan Iii AC, Britt PF , A study of the reductive pyrolysis behavior of sulfur model compounds. Journal of analytical and applied pyrolysis 2003;70 ,20,p.469-91.

Chapter 5

Evaluation of the impacts of sonication on organic sulfur species and desulfurization by reductive pyrolysis

5.1 Introduction

Sonication is a process in which sound waves are used to agitate particles in solution. Ultrasound is cyclic sound pressure with a frequency greater than the upper limit of human hearing. It starts from the frequency of 20 kHz. Ultrasound behaves differently in liquid and liquid–solid media compared to gas medium. Ultrasound in aqueous medium produces highly reactive species such as OH radicals, H_2O_2 and ozone that are strong oxidizing agents of high oxidation potential. These radicals are capable of initiating and enhancing oxidation and reduction reactions. Oxidation occurring due to ultrasound is called "advanced oxidation process" (AOP). Sonication enhances mass transfer and chemical reaction and is expected to reduce or eliminate chemical usage, resulting in minimum disposal problems [1].

Several methods have been considered for removal of total sulfur and different forms of sulfur from coal. The processes of sulfur removal from coal prior to combustion can be subdivided into physical and chemical methods. Irrespective of already mentioned chemical desulfurization methods in previous chapter, a number of methods have been presented in Table (5.1) [2-22].

Very few researchers have focused on ultrasonic coal desulfurization, existing literature fails to explain the mechanisms involved in the ultrasonic-assisted coal desulfurization. Conclusions drawn by researchers are very general in nature. The ultrasonic desulfurization methods studied are either aqueous or chemical based. The biggest advantages of ultrasonic method are simultaneously removal of ash and sulfur. Regarding to chemical coal desulfurization some cases have been reviewed as shown in Table (5.1).

Table (5.1) Various reagents used to remove ash and sulfur from coal

Author	Reagent	Time	Sulfur removal
Steinberg et al. [2]	O_3 and O_2	1 h	20% sulfur removed
Aarya et al. [3]	NaOH	8 h	30% sulfur removed
Chandra et al. [4]	Atmospheric oxidation	106 days	44% sulfur removed (36% organic sulfur removal)
Krzymien [5]	Aqueous $CuCl_2$	48 h	$CuCl_2$ at 200 °C, 100% sulfur removed
Chaung et al. [6]	Combination of dissolved oxygen and alkalis $NaHCO_3$, Na_2CO_3 and Li_2CO_3	1 h	0.2 M alkali solution with 3.4 atm. O_2 partial pressure at 150 °C : Na_2CO_3: 72% of sulfur removed Li2CO$_3$: 73.1% of sulfur removed At 0.4 M $NaHCO_3$: 77% of sulfur removed
Yang et al. [7]	NaOH	60 min	Using 10 wt% NaOH at 250°C: 55% sulfur removed (95% pyritic and 33% organic sulfur removed)
Kara and Ceylan [8]	Molten NaOH at Different temperatures	30 min	Using 20 wt% NaOH at 450 °C: 83.5% sulfur removed
Ahnonkitpanit and Prasassarakich [9]	Aqueous H_2O_2 and H_2SO_4	2 h	Using 15% H_2O_2 and 0.1 N H_2SO_4 at 40 °C: 48.7% total sulfur removed (97% pyritic, 89% sulfate and 7.1% organic sulfur removed)
Ozdemmir et al. [10]	Chlorine in $CCl_4 + H_2O$	6 h	Using 0.033 l/min chlorine flow rate at ambient temperature and pressure: All pyritic and sulfate sulfur removed and 30% organic sulfur removed
Ali et al. [11]	H_2O_2, NH_4OH, $K_2Cr_2O_7$ and CH_3COOH	90 min	50–90% of sulfur removed, depending on concentration and solvent

Author	Reagent	Time	Sulfur removal
Prasassarakich and Thaweesri [12]	Sodium benzoxide		Using 600 ml sodium benzoxide at 205 °C, 45.9% sulfur removed (83.7% sulphate, 68.6% pyritic, 33.3% organic sulfur removed)
Rodriguez et al. [13]	HNO_3	2 h	Using 20% HNO_3 at 90 °C, 90% inorganic and 15% organic sulfur removed
Hamamci et al. [14]	Acidic Fe $(NO_3)_3.9H_2O$	12 h	Using 50 ml of 1 M solvent at 70 °C, 72.2% sulfur removed (96.6% pyritic sulfur removed)
Aacharya et al. [15]	Thio-bacillas ferrooxidants	30 days	91.81% sulfur removed from lignite 63.17% sulfur removed from polish bituminous coal 9.41% sulfur removed from Assam coal
Mukherjee and Borthakur [16]	$H_2O_2 + H_2SO_4$	4 h	Using 15% (vol) H_2O_2 and 0.1 N H_2SO_4: 45% of total sulfur removed (complete removal of inorganic sulfur and 31% removal of organic sulfur)
Ratanakandilok et al. [17]	Methanol/water and methanol/KOH	90 min	Using 2% methanol and 0.025 g KOH/g coal at 150 °C: 58% total sulfur removed (77% sulfate, 47% pyritic and 42% organic sulfur removed)
Sonmez and Giray [18]	Peroxy acetic acid (PAA)	72 h	45% sulfur removed from Gediz Lignite 85% sulfur removed from Cayirhan lignite
Jorjani et al. [19]	Microwave irradiation and desulfurization by Peroxy acetic acid	90 min	62% total sulfur 86.6% pyrite sulfur 35% organic sulfur

Author	Reagent	Time	Sulfur removal
Aacharya et al. [20]	Aspergillus	10 days	78% sulfur removed with 2% pulp Density
Baruah et al. [21]	Water	120 h	77.59% pyritic sulfur removed with aqueous leaching at 45 °C
Liu et al. [22]	Aeration + NaOH, HCl	5 h	Using 0.25 M NaOH at 90 °C with aeration rate of 0.136 m3/hr and 0.1 N HCl solution 73% organic sulfur removed 83% sulfide sulfur removed 84% pyritic sulfur removed

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 sulfur removal was higher for samples sonicated at a lower temperature. The shear forces produced by the ultrasound energy are responsible for exposing the finely disseminated sulfur sites in coal to alkali attack. 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. One hundred g of Zibo coal and 300 ml of water mixture were sonicated for 10 min using 20 kHz frequency and 200 W power. Then, the sample was wet screened. The same procedure was followed without sonication. Yield, sulfur and ash analysis were performed, and results revealed that ultrasonic conditioning can drive physical separation of pyrite and eliminated from coal. Based on this investigation they have concluded that ultrasonic conditioning can, in general, enhance the performance of coal flotation methods used for desulfurization.

In another investigation in the presence of ultrasound irradiation, 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; was studied as well [25]. It was found that the use of formic acid in the presence of ultrasonic irradiation was effective in promoting hydrogenation and desulfurization at very mild conditions. (i.e.

ambient temperature and pressure). Several carbon-based sorbents 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 CuCl and metallic Pd. The saturated sorbent with sulfur compounds was regenerated by desorption assisted by ultrasound with a solvent (mixture of benzene and n-octane with 30 and 70 wt% respectively). Sulfur desorption by ultrasound showed increasing desorption capacities (65 wt% and 45 wt% with and without ultrasound assistance respectively in a static system at 50 °C).

In the other study, 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 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 about combination of microwave irradiation and sonication as a pre-treatment method to produce ultra clean coal has been done [28]. A comparison between sulfur content of samples before (1.89%) and after leaching (HF followed by HNO_3) shows that the sulfur content of non-pretreated sample decreased down to 1.26%, whereas this reduction for microwave-ultrasonic pretreated sample was more noticeable and decreased down to 0.8%.

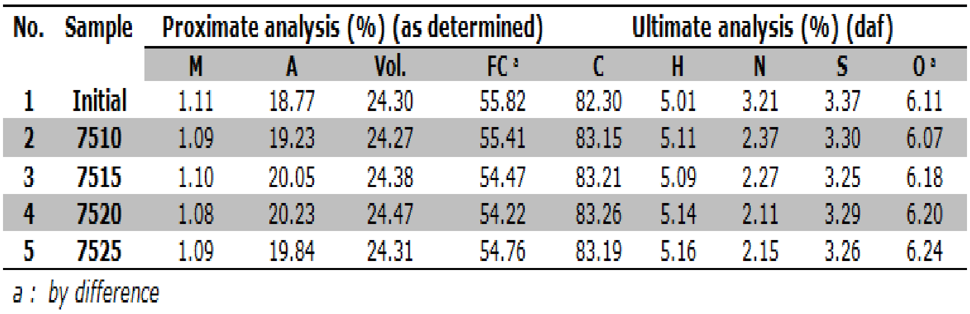
In this chapter, the impact of pre-sonication at different times of irradiation on high sulfur Tabas coal sample before optimized chemical desulfurization by peroxyacetic acid (PAA) has been studied. The main purpose is to define the differences in the effects of different sonication time settings on the organic sulfur forms and specially production of oxidized organic sulfur compounds as a result of sonication process. The same investigation for sonicated and desulfurized samples is considered. For this reason an analytical method called "AP-TPR" is used to determine all mentioned changes.

5.2 Experimental section

5.2.1 Coal sample characteristics

Forty kg of coal samples from active stopes in C1 seam of Tabas coal mine with high sulfur content were 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 the chemical treatment by PAA. Proximate and ultimate analysis has been conducted for all sonicated and desulfurized sonicated coal samples. The results are shown in Table (5.2) and Table (5.3) respectively.

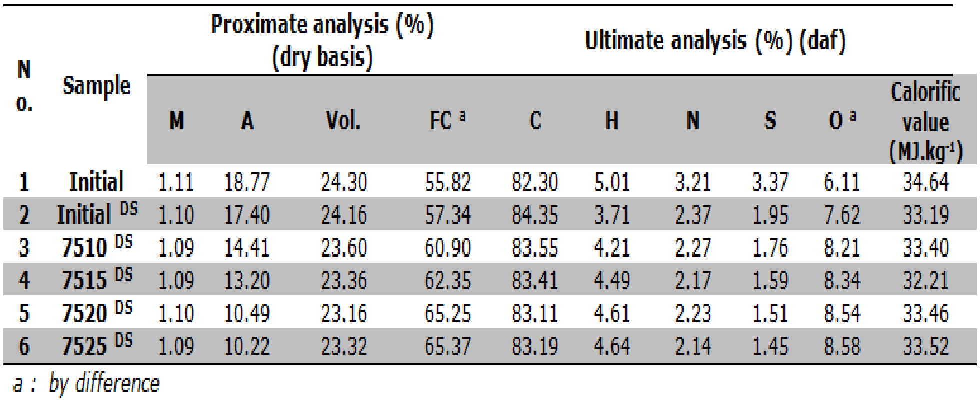
Table(5.2). Proximate and ultimate analysis of initial and sonicated samples.



No.	Sample	Proximate analysis (%) (as determined)				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 (5.3). Proximate and ultimate analysis of initial and desulfurized initial and desulfurized_sonicated samples.



No.	Sample	Proximate analysis (%) (dry basis)				Ultimate analysis (%) (daf)					
		M	A	Vol.	FC [a]	C	H	N	S	O [a]	Calorific value (MJ.kg^{-1})
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*

The ultrasound treated samples are labeled in the following way, for example: “7510” is related to the sample fraction size under 75 μm for 10 minutes.

5.2.2 Sonication process

Ultrasound as sonication pretreatment can be used for the removal of sulfur from coal. Ultrasonic is a series of vertical waves which are alternating unevenly. There are two effects of cavitation's 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 formed 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].

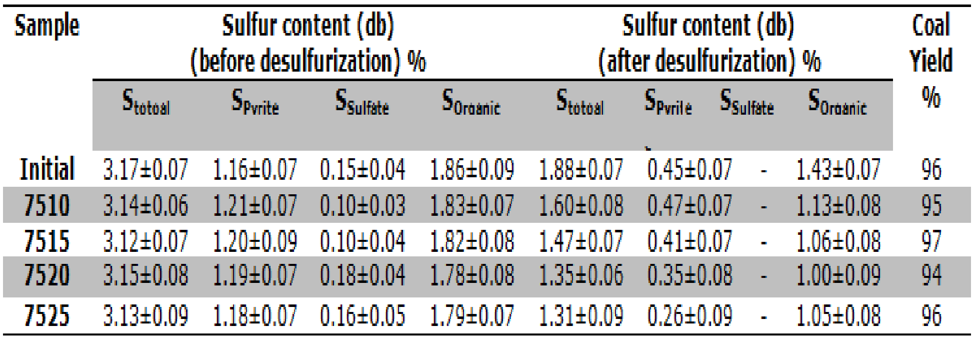
In this study, a Q280 multifunction ultrasonic transmitter was used for coal sample pretreatment. The frequency of its ultrasonic head was 43 kHz and the power of its ultrasonic transmitter was 225 W. Around 10 gram of coal (less than 75 μm) was mixed with 150 ml of distilled water into the beaker. The 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 dried in an oven at 100±10 °C for 3 hours. To evaluate the effects of irradiation time on organic sulfur functionalities, the coal samples were irradiated for 10, 15, 20 and 25 minutes. The dried sonicated samples were weighed and its sulfur forms were determined. Afterwards a post chemical desulfurization by PAA was applied.

5.2.3 Chemical desulfurization

After sonication at different times, the sample was 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% W/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 stirred. 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 residue solution was filtered. The desulfurized coal was washed with hot distilled water and dried in an oven at 100 °C for 3 hours and analyzed for sulfate, pyritic and total sulfur content. All chemical reagents (p.a.) were

obtained from Merck manufacturer. The results of sulfur content before and after desulfurization are shown in Table (5.4). The measurements have been done at least twice for each sample.

Table(5.4). Comparison of the sulfur content before and after desulfurization of initial and sonicated samples.



Sample	Sulfur content (db) (before desulfurization) %				Sulfur content (db) (after desulfurization) %				Coal Yield %
	S_{totoal}	S_{Pyrite}	$S_{Sulfate}$	$S_{Organic}$	S_{totoal}	S_{Pyrite}	$S_{Sulfate}$	$S_{Organic}$	
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
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
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
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
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 study regarding the impact of different particle sizes on the total and organic sulfur reduction % in 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 (5.1)).

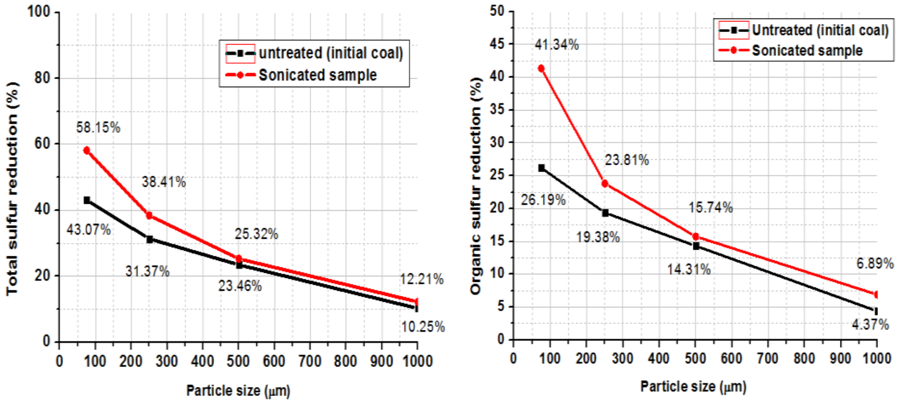


Fig (5.1). Relationship between particle size and total and organic sulfur reduction by PAA.

5.2.4 AP-TPR analysis

5.2.4.1 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 sonicated coals and to assess the sulfur forms changes by a post chemical desulfurization using PAA. These 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 ThermolabMS) 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.

5.2.4.2AP-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 ones 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 on the Tenax tubes, nor on the SilcoSteel coated ones. 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 and analyzed by a TD-GC/MS.

5.3 Results and discussion

The different kinds of sulfur forms after chemical desulfurization are determined and the results are shown in Table (5.5) with $\Delta S_i = S_{initial} - S_{DS}$ (i= total, pyrite or organic sulfur).

Table(5.5 a). Effects on sulfur form content of desulfurised initial and desulfurised sonicated samples , in % (dry basis)

No	Sample	Sulfur reduction (%) (db)			
		S_{Total}	$S_{Pyritic}$	$S_{Organic}$	$S_{Sulfate}$
1	**Initial ^{DS}**	40.70	61.21	23.12	100
2	**7510 ^{DS}**	49.04	61.16	38.25	100
3	**7515 ^{DS}**	52.88	65.83	41.76	100
4	**7520 ^{DS}**	57.14	70.59	43.82	100
5	**7525 ^{DS}**	58.15	77.97	41.34	100

DS: Desulfurized

Table(5.5 b). Effects on sulfur form content of desulfurised initial and desulfurised sonicated samples , in % (dry basis)

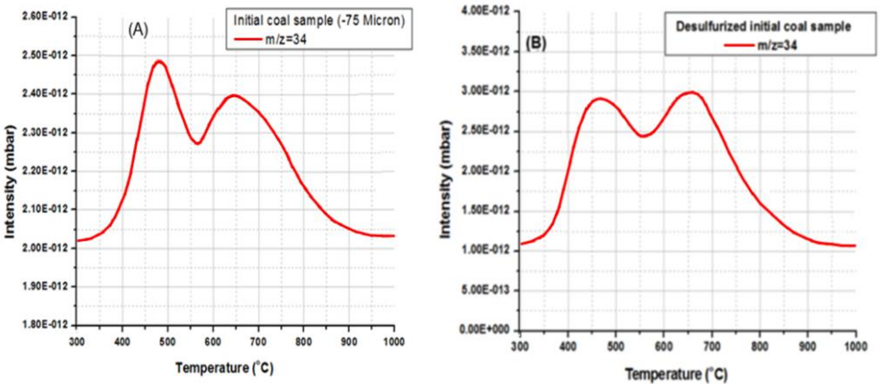
No	Sample	$\Delta S/S_{initial}$ (%)(dry basis)		
		S_{Total}	S_{Pyrite}	$S_{Organic}$
1	**Initial^{DS}**	-	-	-
2	**7510 ^{DS}**	20.49	0.08	65.44
3	**7515 ^{DS}**	29.93	7.55	80.62
4	**7520 ^{DS}**	40.39	15.32	89.53
5	**7525 ^{DS}**	42.87	27.38	78.81

DS: Desulfurized

Executing the ultrasound irradiation at a constant power (225 W) and followed by a chemical desulfurization by PAA resulted in a overall total sulfur reduction, with a maximum for the 25 minutes treatment of about 58% (from 3.13 down to 1.31%). Pyritic sulfur reduction increased and reached also a maximum at 25 minutes 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 minutes of about 44% (from 1.79 down to 1.05%). In global, not that much difference is found between the 25 and 20 min treatment. Economical speaking, by taking additionally into account that $S_{Organic}$ is more difficult to remove than S_{Pyrite}, the 20 min sonication time is more interesting and even more beneficial when taking energy cost aspects into account. It can be noticed from Table (5.5b) that the pyrite reduction is less pronounced compared to the organic sulfur reduction as a function of the pre-sonication time. As pyrite can be removed more easily by physical methods (in general), this pre-irradiation is an interesting beneficial, 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 (5.3) 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 approach is important, interesting and beneficial.

5.3.1 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 (5.2 A and B) and the detailed discussion can be found in previous chapter. The peak in the lower temperature region can be assigned to the presence of di-alkyl sulfides, alkyl-aryl sulfides, reactive di aryl sulfides and pyrite [40]. (The peak areas are expressed in: (°C.mbar)). It should also be mentioned that the goodness of fits (Coefficient of determination (R^2)) for all fitted curves is around 97-98%.



Fig(5.2). AP-TPR/MS (H_2), m/z=34 kinetograms of initial and desulfurized sample

In order to compare different AP-TPR experiments (see chapter 3 and 4), profiles are normalized. The area under each dominant H_2S peak is determined by a deconvolution strategy of the H_2S profiles using multiple Gaussian functions (using Origin software (version 8)). Percent of peak area is calculated for each AP-TPR 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 Table (5.6) and Table (5.7), respectively. The results are achieved based on at least two experiments.

Table (5.6). H_2S 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
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

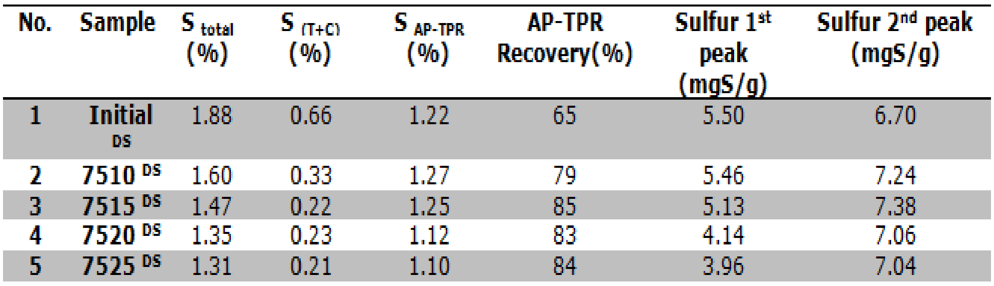
Table (5.7). H_2S peak areas and relevant peak temperatures for desulfurized initial and desulfurized sonicated samples.

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 (5.2 A) for the initial sample, the sharp first peak changed and became broader after chemical desulfurization by PAA (Fig (5.2 B)). Not only because of an absolute decrease in its pyritic sulfur form amount (37% down to 24% of total sulfur) (Tables (5.4) and (5.5 a and b)), but also because of its higher pyrite sulfur removal percentage 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]. As can be noticed from Table (5.8), sulfur recovery as H_2S during AP-TPR experiment decreases to only 65% for the PAA treated initial sample. Compared to the initial sample, a H_2S recovery of up to 85% [41] is noticed.

Table (5.8). Measured sulfur amount in desulfurized initial and desulfurized sonicated samples before and after AP-TPR/MS (H_2) measurements.



No.	Sample	S_{total} (%)	$S_{(T+C)}$ (%)	$S_{AP\text{-}TPR}$ (%)	AP-TPR Recovery(%)	Sulfur 1st peak (mgS/g)	Sulfur 2nd peak (mgS/g)
1	**Initial** DS	1.88	0.66	1.22	65	5.50	6.70
2	**7510** DS	1.60	0.33	1.27	79	5.46	7.24
3	**7515** DS	1.47	0.22	1.25	85	5.13	7.38
4	**7520** DS	1.35	0.23	1.12	83	4.14	7.06
5	**7525** DS	1.31	0.21	1.10	84	3.96	7.04

Ds:desulfurized

This could point to a less accessibility of H_2 towards the organic sulfur groups due to the PAA treatment and to be unable to break down complex thiophenic structures. In addition, PAA not only remove other sulfur compounds, but can also oxidize them into combined S-O-functionalities as a result of a specific reaction mechanism that in its end state should result in a removable oxidized sulfur compound, i.e. SO_2 and SO_3. However, if the end state is not reached, it is left in a sulfur form not leading to the formation of H_2S during an AP-TPR experiment or at least to a much lesser extend [42, 43, 44]. Therefore, these sulfur forms will be present in an oxidized state as organic sulfoxide, sulfone or sulfonic acid compounds [45]. During an AP-TPR experiments this will lead rather to the formation of sulfur dioxides and is detectable by MS as m/z 64 (SO_2^+) and 48 (SO^+). By the off-line setup, these oxidized compounds (as others) can also be captured by the absorbents in the SilcoSteel coated tubes and (semi-) quantitatively determined. For the desulfurized initial sample (in the on-line detection system) m/z 48 and 64 are visualized in Fig (5.3).

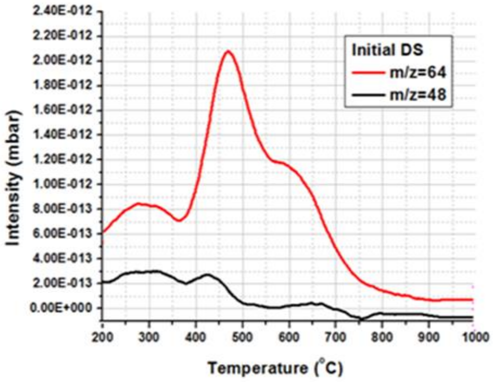


Fig (5.3). AP-TPR-MS (H_2) , m/z=48 (SO^+) and m/z=64 (SO_2^+) kinetogram of the desulfurized initial coal sample.

Only when m/z 48 and 64 exhibit the same profile absolute confirmation of formed combined S-O-functionalities can be proved. Based on a similar study on the initial coal, it was clear that for the initial coal, no specific peaks or profiles can be seen for these combined S-O-functionalities. This means that no oxidized sulfur compounds are present. On the other hand for desulfurized initial sample by PAA (Fig (5.3)), a clear 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 combined S-O-functionalities. The weak first peak around 300°C for both m/z profiles refers to the presence of organic sulfonic acids [45]. As discussed in chapter 4, for m/z 48, peak two around 425 °C, as as well as the third peak around 650°C, could be correlated to some extend with the m/z 64 second peak signal and its shoulder at higher temperature, respectively and therefore could be attributed to the presence of minor 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 combined S-O-functionalities alone.

For sonicated samples in the on-line detection also m/z 48 and 64 are visualized in Fig (5.4).

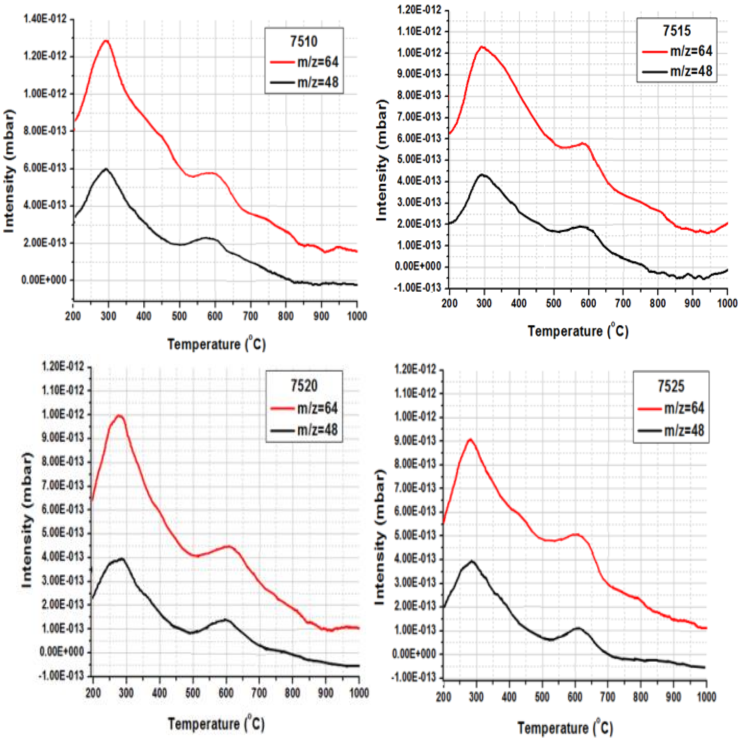


Fig (5.4). AP-TPR-MS (H_2), m/z=48 (SO^+) and m/z=64 (SO_2^+) kinetograms of sonicated coal samples.

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 clearly means that the sonication process has a direct impact on the increased oxidation degree in terms of the formation of combined S-O 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 [45]. The mentioned process is related to the ultrasound behavior in the liquid and liquid-solid interfaces. As already mentioned, ultrasound in aqueous medium produces highly reactive species such as OH radicals, H_2O_2 and ozone that are strong oxidizing reagents with high oxidation potential. These oxidation agents are capable of initiating and enhancing oxidation reactions [46-56]. Using PAA, m/z 48 and m/z 64 profiles are even more pronounced and systematically simultaneously changed over the whole temperature range as is demonstrated in Fig (5.5) for the desulfurized sonicated samples (in the on-line detection mode).

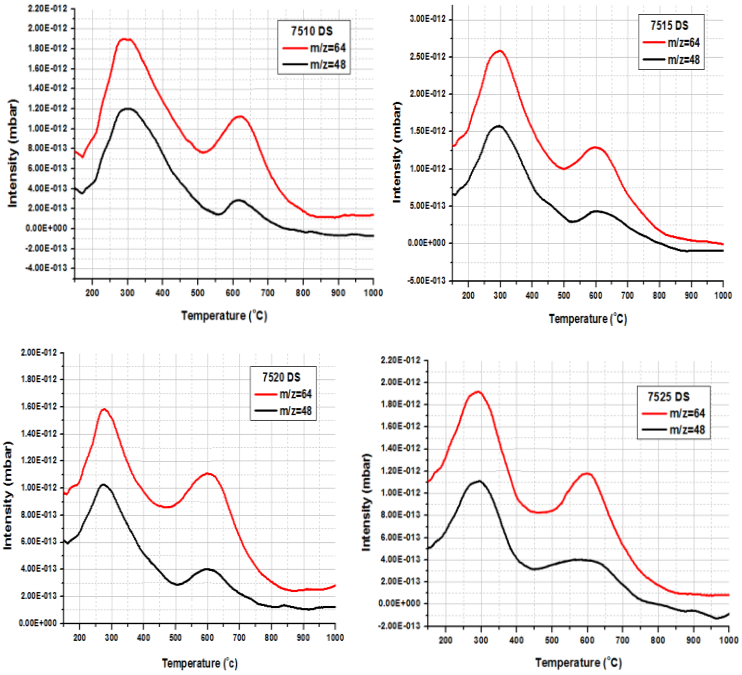


Fig (5.5). AP-TPR-MS (H_2) , m/z=48 (SO^+) and m/z=64 (SO_2^+) kinetograms of desulfurized sonicated coal samples.

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 (5.4) are noticed. This could be related to the increased "catalytic" oxidizing impact on the coal samples in using PAA after sonication, which will be discussed in the next subchapter.

5.3.2 Effect of sonication time on sulfur removal by PAA

5.3.2.1 Qualitative approach

Comparison between the AP-TPR profiles for the sonicated (Fig (5.6)) and desulfurized sonicated coal samples (Fig (5.7)) showed 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.

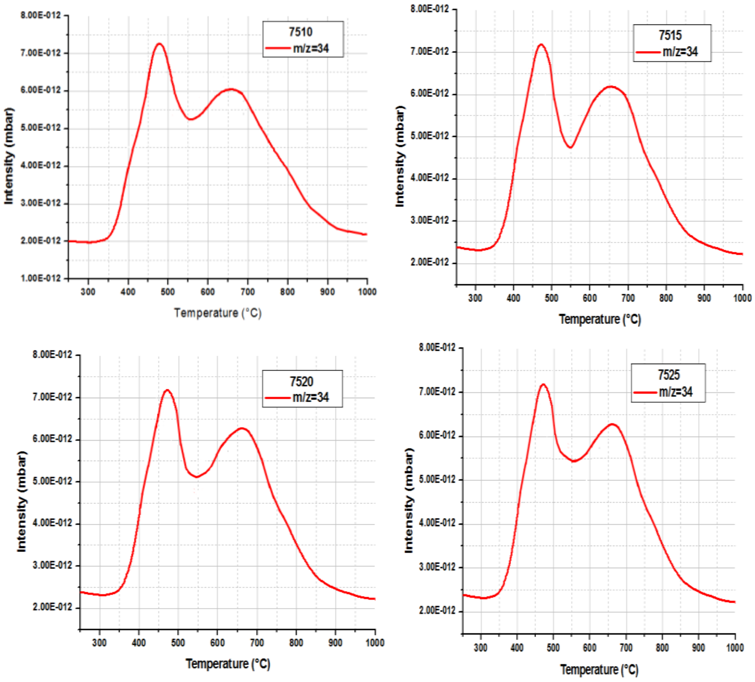


Fig (5.6). AP-TPR/MS (H_2), m/z=34 kinetograms of sonicated samples.

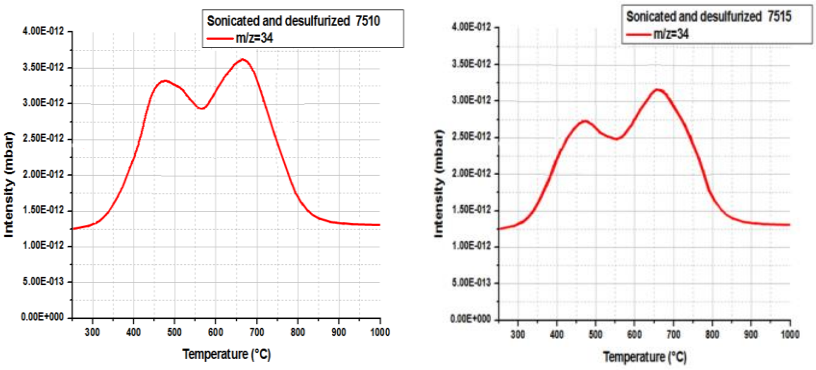


Fig (5.7). AP-TPR/MS (H_2), m/z=34 kinetograms of desulfurized sonicated samples

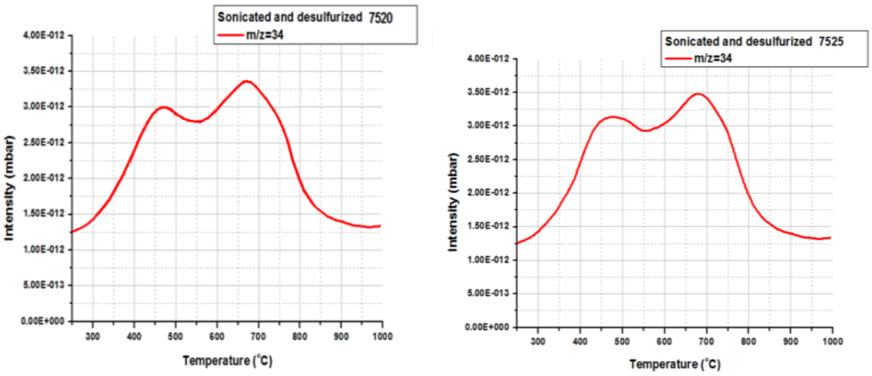


Fig (5.7). AP-TPR/MS (H_2), m/z=34 kinetograms of desulfurized sonicated samples (continue).

From Fig (5.6), for all applied time settings of sonication experiments, it can be deduced that both peak temperatures in the H_2S signal showed no specific temperature shifting. 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%. The first peak % area increased accordingly up to 45%-43% compared to the initial one, being 36%. According to the Table (5.7), the reversed is found for the desulfurized sonicated samples, as is already suggested in Fig (5.7). This means that the sonication process has definite an impact on the chemical post-desulfurization process by PAA.

Based on the Table (5.4) and (5.5 a and b), the total sulfur reduction is flattening for sonication times up to 20-25 min with a maximum 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 (5.6) 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 of around 45% and decrease consequently of second H_2S peak % area around 55%). It is believed that the more-reactive aromatic sulfur compounds are also more PAA sensitive and thus resulted in a higher sulfur removal degree. In accordance with Table (5.6), 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 decreased tendency and reached only 41% compared with the 25 min of sonication condition, reaching almost 44% sulfur reduction. Based on Table (5.6), with increasing the sonication time from 10 to 20 min, the less-reactive di aryl sulfur compound showed decreasing tendency coinciding with an increase of more-reactive di aryl sulfur compounds, also compared with initial coal. Consequently the organic sulfur reduction % by PAA showed an increasing tendency as a function of sonication time. According to the Table (5.7) 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.

5.3.2.2 Quantitative approach

The total sulfur amount as the percentage of different sulfur forms in all sonicated and initial coals before and after desulfurization has been summarized in Table (5.4). The amount of sulfur in the tar and the char left in the reactor after the AP-TPR experiment was determined as well. In this way, all sulfur forms which reacted with hydrogen during the AP-TPR 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 ($S_{AP\text{-}TPR}$) are given in Table (5.8). Except for the non-sonicated sample, the AP-TPR recoveries are relatively high. Probably, the sonication process makes the hydrogenation of sulfur compounds also more accessible as found in the case of the microwave treatment [59], resulting in a higher AP-TPR H_2S recovery after PAA treatment. Looking in more detail to Table (5.8), for all desulfurized sonicated samples by PAA, the second H_2S peak amount is always more intense than the one for the desulfurized initial sample. Further on, the first H_2S peak amount showed a rather clear decreasing tendency as a function of sonication time from 5.46 down to 3.96 mgS/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 reactive di aryl sulfur compounds, which are identified by the first peak in the AP-TPR H_2S profile. For the second peak sulfur amounts, a rather constant quantity 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 or PAA has no removal impact on these latter sulfur compounds.

5.3.3 Oxidized sulfur compound formation

5.3.3.1 Oxidized sulfur compound formation in sonicated samples

It is known that in AP-TPR experiments, oxidized sulfur forms present in the sample are only partly reduced into H_2S [57-59]. 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. Therefore both m/z 48 (SO^+) and 64 (SO_2^+) profiles are tracked. For the sonicated samples, in Fig (5.4) these evolution profiles during AP-TPR experiments are visualized. As can be seen, the output signals of these ions clearly exhibit the same trend. Sonication affects the amount of formed combined S-O functionalities by the "AOP" process (discussed in detail in chapter two) which occurred during sonication in the liquid-solid phase [46-56]. Based on Fig (5.4), a huge peak at lower temperature maximizes around 300°C is noticed for m/z 48 and for m/z 64, which certainly refers to the presence of organic sulfonic acids [45,59] and its weak shoulder at the right side towards sulfones (aliphatic, mixed aliphatic-aryl and more-reactive di aryls, Fig (5.8)). At the higher temperature range (more than 500°C), m/z 48 and 64 profiles keep demonstrating the same trends. At around 600°C, a second peak is visible for all sonicated samples assigned to organic sulfones as to sulfoxides (rather less-reactive di aryl ones, Fig (5.8)).

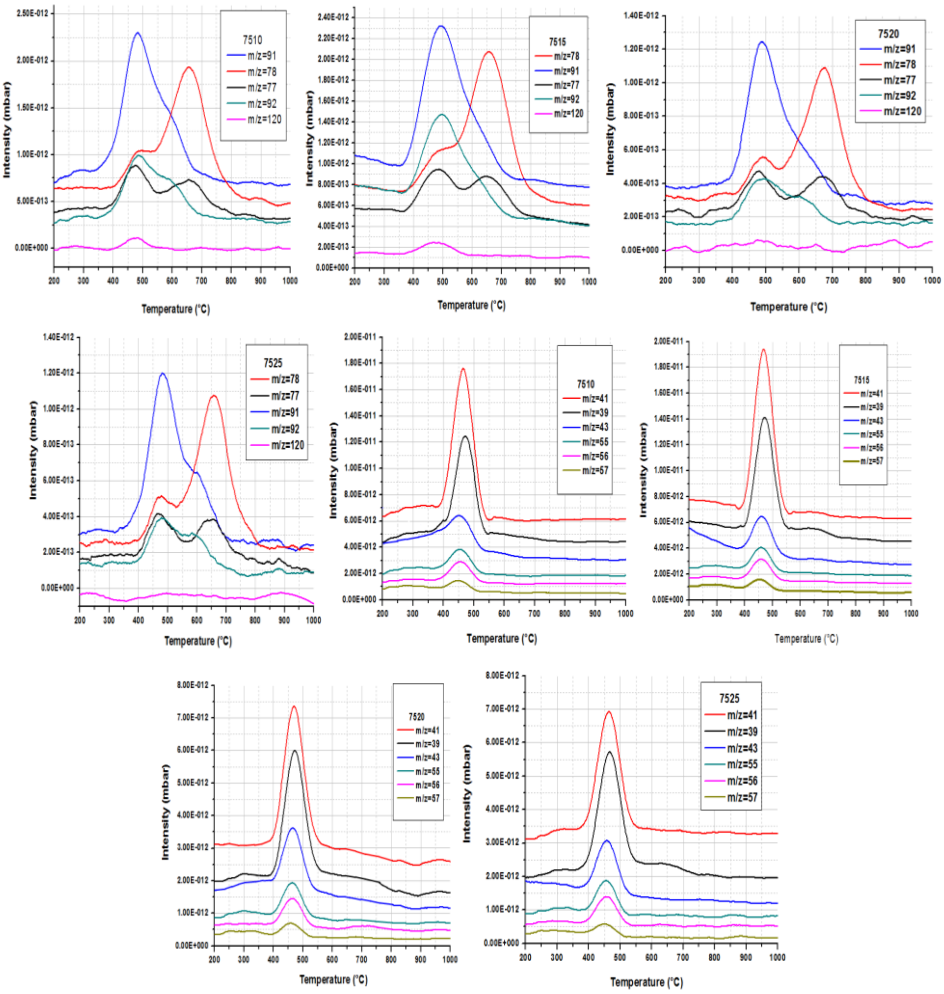


Fig (5.8) AP-TPR/MS (H_2) evolution profiles of sonicated samples, for saturated, unsaturated hydrocarbon chains and aromatic compounds (alkanes and alkenes: m/z= 39, 41, 43, 55, 56 and 57, aromatics: m/z=77, 78, 91 and 92)

It is obvious that these profiles of figures 5.4 and 5.5 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 refer also to other CH-fragments. Despites this, it makes sense to quantize both peaks. The normalized peak % area has been calculated and is summarized in Table (5.9) and Table (5.10).

Table (5.9). 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 (5.10). 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 (Table (5.9) and (5.10)) 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 related rather to the aliphatic, mixed aliphatic-aryl and di aryl sulfones than to sulfoxides (for both sulfur oxide is the representative ion) an increasing tendencies is found (for m/z 48, from 22 to 30%, for m/z 64, from 21 to 27%). (See further off-line experiments, Table (5.13) and Table (5.14)).

5.3.3.2 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 Fig (5.3) and Fig (5.5) respectively. A simple comparison between Fig (5.3) and Fig (5.5) 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 di-alkyl, mixed alkyl 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 clear and new peak appears in the higher temperature region around 600°C. This huge first peak at around 300°C (Fig (5.5)) certainly refers to a further oxidation of the above mentioned sulfones into organic sulfonic acids [45]. As no aliphatic fragments were found in this temperature range, the decomposition of only the S-O-functional group from the coal matrix as SO_2 is evolved, proving that it can only come from organic sulfonic acids.

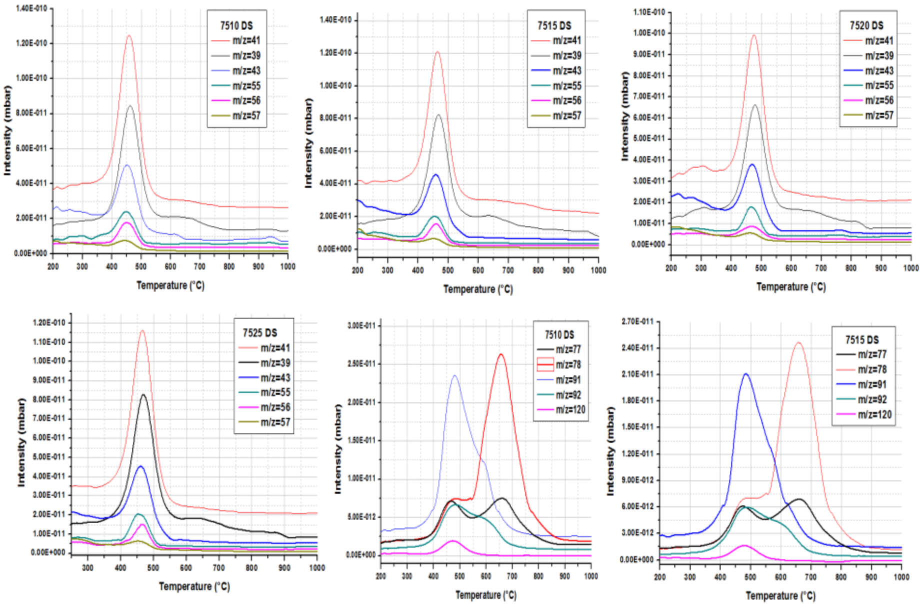


Fig (5.9) AP-TPR/MS (H_2) evolution profiles of <u>desulfurized sonicated</u> samples, for saturated, unsaturated hydrocarbon chains and aromatic compounds (alkanes and alkenes: m/z= 39, 41, 43, 55, 56 and 57, aromatics: m/z=77, 78, 91 and 92

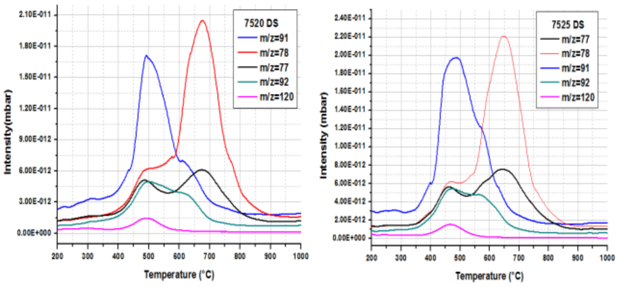


Fig (5.9) AP-TPR/MS (H_2) evolution profiles of desulfurized sonicated samples, for saturated, unsaturated hydrocarbon chains and aromatic compounds (alkanes and alkenes: m/z= 39, 41, 43, 55, 56 and 57, aromatics: m/z=77, 78, 91 and 92 (continue)

An even complete removal of combined S-O-functionalities combined with an additional oxidation of other organic sulfur compounds in its sulfoxide and sulfone form can occur, rather as less-reactive di aryl compounds, Fig (5.9).

Fig (5.5) visualizes indeed the evolution of oxidized sulfur functionality fragments during AP-TPR experiments in hydrogen atmosphere for desulfurized sonicated samples. As the signal output of these ions entirely exhibits identical trends, these ions profiles correspond to the presence of organic sulfonic acids, sulfones and/or sulfoxides. Further on, the sonication process also seems to affect the amount of formed oxidized sulfur compounds by PAA treatment acting as a mild oxidative agent. Based on Fig (5.5), it is clear that the first and second peak in the lower (300 °C) and higher temperature region (600°C) showed higher intensities compared with obtained profiles of only sonicated samples (Fig (5.4)). Therefore it is obvious that these profiles give us ground to suppose an enhanced oxidative impact of PAA. Both peaks have been quantized. Normalized peak % area for m/z 48 and 64 are given in Table (5.11) and Table (5.12), respectively.

Table (5.11). Normalized (%) peak areas and relevant peak temperatures of m/z 48 (SO^+) for desulfurised 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$_{\text{DS}}$	8.91±0.07e-11	1.43±0.07e-11	86.2±0.5	13.8±0.5	300±8	612±8
2	7515$_{\text{DS}}$	8.62±0.06e-11	1.91±0.07e-11	81.9±0.5	18.1±0.5	299±7	602±9
3	7520$_{\text{DS}}$	7.63±0.08e-11	1.84±0.07e-11	80.6±0.6	19.4±0.6	298±8	602±6
4	7525$_{\text{DS}}$	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 (5.12). 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	7510$_{\text{DS}}$	9.47± 0.07e-11	2.21± 0.08e-11	81.1±0.5	18.9±0.6	298±7	610±9
2	7515$_{\text{DS}}$	1.11± 0.08e-10	4.25± 0.08e-11	72.1±0.5	27.9±0.5	300±6	601±8
3	7520$_{\text{DS}}$	1.02± 0.06e-10	4.34± 0.07e-11	70.2±0.6	29.8±0.5	295±8	603±8
4	7525$_{\text{DS}}$	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 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 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, Table (5.13) and Table (5.14)).

5.3.3.3 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_2S) nor captured into its char/tar fractions. These volatile organic sulfur compounds release 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.

GC-MS spectra are quantitatively interpreted by spiking with 0.5µg d_6-benzene. The “off-line” experiments have only been performed in both extreme times of sonication: 10 and 25 minutes. The higher homologues, like three/tetra/penta substituted thiophenes and three substituted benzothiophene 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: Table (5.13) and (5.14).

Table (5.13). 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

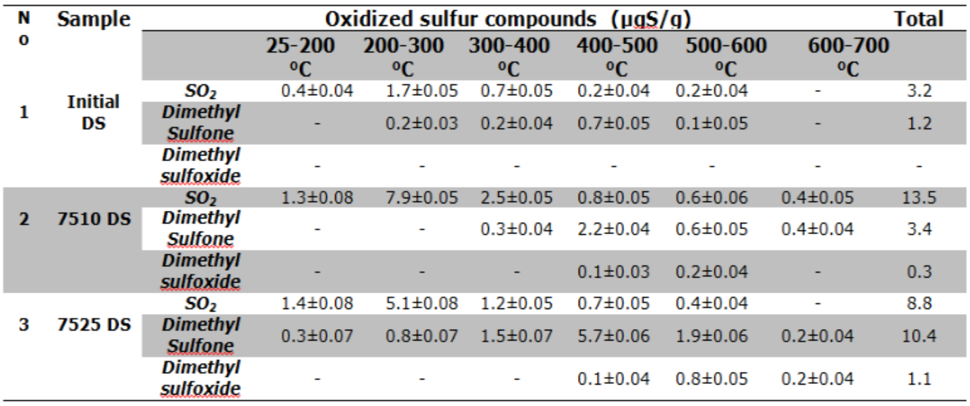
Table (5.14). Organic sulfur compounds determined by AP-TPR/GC-MS in initial and sonicated samples after desulfurization, in µg S/g.

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

Besides SO_2, also alkyl substituted sulfones and sulfoxides are recorded, demonstrating indeed the presence of combined S-O-functionalities (see further Table (5.17-19)). 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 µgS/g coal per temperature interval in Table (5.15).

Table (5.15) Amount of SO_2, dimethyl-sulfone and dimethyl sulfoxide compounds determined by AP TPR/GC-MS in µgS/g, in different temperature intervals for desulfurized initial and desulfurized sonicated samples.



No	Sample	Oxidized sulfur compounds (µgS/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

The quantitatively recorded amounts of the oxidized sulfur compounds in different temperature intervals (off-line experiments) (Table (5.15)), showed that the amount of sulfur dioxide maximized in the range of 200-300°C for all studied samples. This confirmed Table (5.11) and Table (5.12) findings concerning the first huge evolved peak in 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 that of the dimethyl sulfoxides at higher temperature range of 500-600°C. This confirms early findings using model compound work [43] 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 into a higher extend. These results confirm the findings of the AP-TPR on-line findings in m/z profiles 64 and 48 from deduced tables Table (5.11) and (5.12).

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

Based on the data from AP-TPR "off-line" TD-GC/MS (Table (5.13)), the amounts of all other kinds of volatile organic sulfur compounds did not change that much (or rather fluctuated randomly) in contrast to the combined S-O-functionalities, 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 (5.14), 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)) compounds have been illustrated in Fig (5.10). As can be seen their profiles show all two peaks, one in the lower (around 350 °C) and one in the higher (550 °C) temperature region.

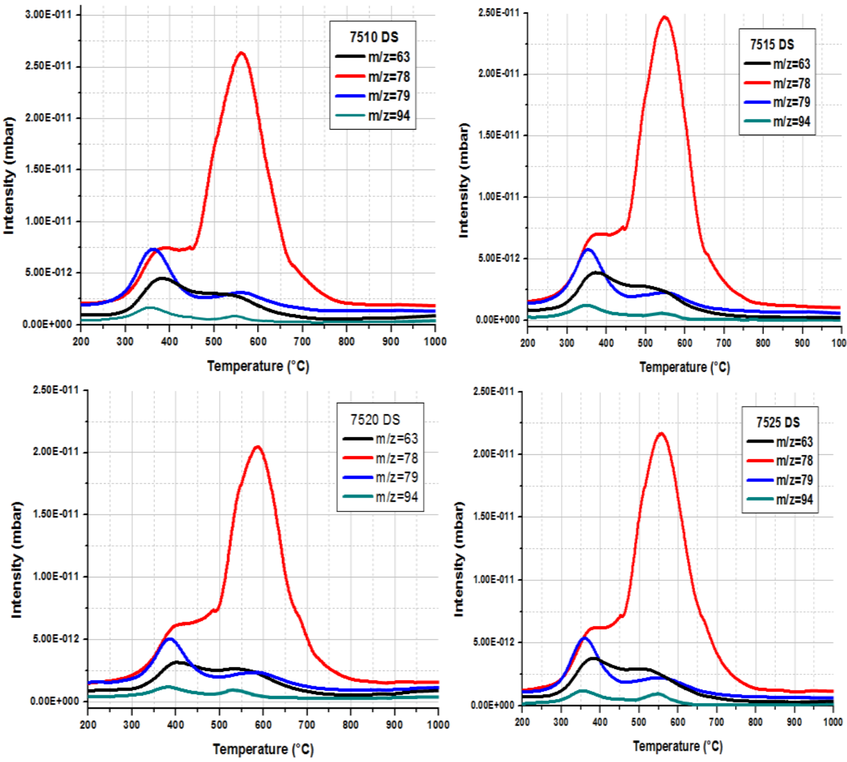


Fig (5.10) AP-TPR/MS (H_2) evolution profiles of desulfurized sonicated samples, for m/z= 63, 78, 79 and 94.

As expected, the signal for m/z 94 and 78 should be more intense than the ones for m/z 79 and 63, both signals exhibiting the same trend. Only for the combination m/z 94 and 79 this is clearly the case. For the combination m/z 78 and 63 this is only partly the case. For m/z 78, certainly the second peak is completely in disharmony with m/z 63. This means that certainly 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 the Table (5.17-20).

Table (5.17). 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 (5.18). 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	**7510** ^{DS}	4.10±0.07e-10	8.85±0.07e-11	82.2±0.6	17.8±0.6
2	**7515** ^{DS}	3.45±0.06e-10	7.71±0.07e-11	81.8±0.5	18.2±0.5
3	**7520** ^{DS}	2.64±0.08e-10	7.80±0.07e-11	77.2±0.6	22.8±0.6
4	**7525** ^{DS}	2.71±0.07e-10	7.20±0.06e-11	76.3±0.5	23.7±0.5

DS: Desulfurized

Table(5.19). 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	**7510** ^{DS}	2.70±0.06e-10	2.44±0.08e-9	9.9±0.5	90.1.±0.5
2	**7515** ^{DS}	1.50±0.08e-10	2.17±0.06e-9	6.5±0.7	93.5±0.6
3	**7520** ^{DS}	7.50±0.07e-11	1.72±0.08e-9	4.2±0.5	95.8±0.7
4	**7525** ^{DS}	8.21±0.08e-11	2.31±0.08e-9	3.4±0.6	96.6±0.6

DS: Desulfurized

Table (5.20). 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	**7510** ^{DS}	6.74±0.06e-11	7.31±0.08e-12	90.2±0.5	9.8±0.6
2	**7515** ^{DS}	5.81±0.06e-11	8.10±0.06e-12	87.8±0.6	12.2±0.6
3	**7520** ^{DS}	4.53±0.08e-11	8.23±0.08e-12	84.7±0.5	15.3±0.5
4	**7525** ^{DS}	3.71±0.07e-11	8.55±0.07e-12	81.23±0.7	18.8±0.6

DS: Desulfurized

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

5.3 Conclusion

In this study the total sulfur reduction after chemical desulfurization by PAA is achieved in the range of 49 to 58%. The results showed that the sulfate and pyritic sulfur were mainly attacked by PAA after sonication: resulting in a 100% of sulfate sulfur removal and 61% to 78% pyritic sulfur removal. The results showed that the maximum organic sulfur reduction was obtained for the longer sonication time of 20 up to 25 minutes being around 41-44%. The sonication process in the liquid-solid phase happens via an "AOP" process, producing oxidizing reagents resulting in more oxidized coal samples as oxidized sulfur compounds. The profiles obtained by AP-TPR (on-line) experiments for m/z 48 and 64 for sonicated and desulfurized sonicated samples exhibited over the whole temperature range the same trend, demonstrating the high amounts of different oxidized sulfur functionalities. For the first time organic sulfur changes by AP-TPR 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 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 for the role of sonication process on the oxidation of organic sulfur compounds.

5.3 References

[1] Suslick, Kenneth S. The Chemical Effects of Ultrasound. Scientific American (1989), p.62-68.

[2] Steinberg M, Yang RT, Horn TK, Berlad AL (1977) Desulfurization of coal with ozone: an attempt. Fuel 56:p.227–228.

[3] Araya PE, Ohlbaum RB, Droguett SE (1981) Study of the treatment of sub bituminous coals by NaOH solutions. Fuel 60,p.1127–1130.

[4] Chandra D, Chakrabarti JN, Swamy YV (1982) Auto-desulfurization of coal. Fuel 61:p.204–205

[5] Krzymien LL (1982) Complete removal of sulfur from coal using solutions containing cupric ions. Fuel 61,p.871–873.

[6] Chaung KC, Markuszewesky R, Wheelock TD (1983) Desulfurization of coal by oxidation in alkaline solutions. Fuel Process Technol 7,p.43–57.

[7] Yang RT, Das SK, Tsai BMC (1985) Coal demineralization using sodium hydroxide and acid solutions. Fuel 65,p.735–742.

[8] Kara H, Ceylan R (1988) Removal of sulfur from four central anatolian lignite's by NaOH. Fuel 67,p.170–172.

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

[10] Ozdemmir M, Bayrakceken S, Gurses A, Gulaboglu S (1990) Desulfurization of two Turkish lignite's by chlorinolysis. Fuel Process Technol 26,p.15–23.

[11] Ali A, Srivatsava SK, Haque R (1992) Chemical desulfurization of high sulfur coals. Fuel 71,p.835–839

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

[13] Rodriguez RA, Jul CC, Limon DG (1996) The influence of process parameters on coal desulfurization by nitric leaching. Fuel 75,p.606–612.

[14] Hamamci C, Kahraman F, Diiz MZ (1997) Desulfurization of southeastern anatolian asphaltites by the Meyers method. Fuel Process Technol 50,p.171–177.

[15] Aacharya C, Kar RN, Sukla LB (2001) Bacterial removal of sulfur from three different coals. Fuel 80,p.2207–2216.

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

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

[18] Sonmez O, Giray ES (2001) The influence of process parameters on desulfurization of two turkish lignite's by selective oxidation. Fuel Process Technol 70,p.159–169.

[19] E. Jorjani, B. Rezai, M.Vossoughic, M. Osanloo, Desulfurization of Tabas coal with microwave irradiation/peroxyacetic acid washing at 25, 55 and 85 ^{o}C, Fuel 83 (2004),p. 943–949.

[20] Aacharya C, Sukla LB, Misra VN (2005) Biological elimination of sulfur from high sulfur coal by aspergillus-like fungi. Fuel 84,p.1597–1600.

[21] Baruah BP, Saikia BK, Kotoky P, Rao PG (2006) Aqueous leaching on high sulfur subbituminous coals, in Assam, India. Energy Fuels 20,p.1550–1555.

[22] Liu K, Yang JJ, Wang Y (2008) Desulfurization of coal via low temperature atmospheric alkaline oxidation. Chemosphere 71,p.183–188.

[23] Zaidi SAH (1993) Ultrasonically enhanced coal desulfurization. Fuel Process Technol 33,p. 95–100.

[24] Ze KW, Xin XH, Tao CJ (2007) Study of enhanced fine coal desulfurization and de-ashing by ultrasonic floatation. J Chin Univ Min Technol 17,p.358–362.

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

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

[27] Mello PA, Duarte FA, Nunes MAG, Alencar MS, Moreira EM, Korn M, Dressler VL, Flores ÉMM (2009) Ultrasound-assisted oxidative process for sulfur removal from petroleum product feedstock. Ultrason Sonochem 16,p.732–736.

[28] M.M.Royaei, E.Jorjani, S.Chehreh Chelgani, Combination of microwave and ultrasounic irradiation as a pretreatment method to produce ultra clean coal, International journal of coal preparation and utilization, April 2012.

[29] Vieira, M. A., B. Welz, and A. J. Curtius. 2002. 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. Spectrochimica Acta Part B 57,p. 2057–2067.

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

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

[32] Palmer SR, Hippo EJ, Dorai A. Selective oxidation pretreatment for enhanced desulfurization of coal. Fuel 1995;74(2),p.193–200.

[33] Yperman J, Maes II, Van den Rul H, Mullens S, Van Aelst J, Franco DV, et al. Sulfur group analysis in solid matrices by atmospheric pressure–temperature programmed reduction. Anal Chin Acta 1999;395,p.143–55.

[34] Mullens S, Yperman J, Carleer R, Bozdemir T, Durusoy T, Yürüm Y. Sulfur analysis of Bolu-Mengen lignite before and after microbiological treatment using reductive pyrolysis and gas chromatography/mass spectrometry. Energy Fuels 2005;19,p.1029–36.

[35] Stefanova M, Marinov SP, Yperman J, Carleer R. Reductive pyrolysis of Miocene-aged lignite lithotypes using MS and GC/MS detection system for analysis of organic sulfur groups. Fuel 2005;84,p.71–9.

[36] Marinov SP, Stefanova M, Stamenova V, Carleer R, Yperman J. Sulfur functionality study of steam pyrolyzed ‘‘Mequinenza’’ lignite using reductive pyrolysis technique coupled with MS and GC/MS detection systems. Fuel Process Technol 2005;86,p.523–34.

[37] Marinov SP, Stefanova M, Stamenova V, Gonsalvesh L, Carleer R, Yperman J. Sulphur analysis of household briquettes using MS and GC/MS detection systems after reductive pyrolysis. J Fuel Chem Technol 2006;34(3),p.257–64.
[38] Gonsalvesh L, Marinov SP, Stefanova M, Yürüm Y, Dumanli AG, Dinler-Doganay G, et al. Biodesulphurized subbituminous coal by different fungi and bacteria studied by reductive pyrolysis. Part 1: initial coal. Fuel 2008;87,p.2533–43.
[39] Channiwala SA, Parikh PP, A unified correlation for estimating HHV of solid, liquid and gaseous fuels. Fuel 2002;81 (8),p.1051-63.
[40] L.Gonsalvesh,S.P.marinov, M.Stefanova,R.Carleer, J.Yperman, Biodesulfurized low-rank coal: Maritza east lignite and its "humus-like" by product, Fuel 2013;103,p.1039-1050.
[41] Sh. Mesroghli, J. Yperman, E. Jorjani, R. Carleer, M. Noaparast , Evaluation of microwave treatment on coal structure and sulfur species by reductive pyrolysis- mass spectrometry method, 2014 , Fuel processing technology (accepted).

[42] Aelst JV, Yperman J, Franco DV, Mullens J, Van Poucke LC, Palmer SR. Sulfur distribution in Illinois No.6 coal subjected to different oxidation pre-treatments. Fuel 1997;76(14/15),p.1377–81.
[43] Van Aelst J,Yperman J,Franco DV, Van Poucke LC, Buchanan AC, Britt PF. Study of silica-immobilized sulfur model compounds as a calibrants for the AP-TPR study of oxidized coal samples. Energy and Fuels 2000;14(5),p.1002-8.

[44] Mullens S, Yperman J, Reggers G, Carleer R, Buchanan Iii AC, Britt PF , A study of the reductive pyrolysis behavior of sulfur model compounds. Journal of analytical and applied pyrolysis 2003;70 ,20,p.469-91.

[45] A.P. Terzyk, J. Colloid Interface Sci. 268 (2003) ,p.301–329.

[46] Lindstrom O, Lamm O (1951) The chemical effects produced by ultrasonic waves. J Phys Chem 55,p.1139–1146
[47] Webster E (1963) Cavitation. Ultrasonics 1,p.39–48.

[48] Makino K, Mossoba MM, Riesz P (1982) Chemical effects of ultrasound on aqueous solutions evidence for OH- and H+ by spin trapping. J Am Chem Soc 104,p.3537–3539.

[49] Riesz P, Berdahl D, Christman CL (1985) Free radical generation by ultrasound in aqueous and non-aqueous solutions. Environ Health Perspect 64,p.233–252.

[50] Christman CL, Carmichael AJ, Mossoba MM, Riesz P (1987) Evidence for free radicals produced in aqueous solutions by diagnostic ultrasound. Ultrasonics 25,p.31–34.

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

[52] Misik V, Riesz P (1996) Peroxyl radical formation in aqueous solutions of ndimethylformamide,n-methylformamide, and dimethylsulfoxide by ultrasound. Free Radical Biol Med 20,p.129–138.

[53] Entezari MH, Krus P (1994) Effect of frequency on sono chemical reaction. Ultrason Sonochem 1,p.75–79.

[54] Luche JL (1994) Effect of ultrasound on heterogeneous system. Ultrason Sonochem 1,p.111–118.

[55] Henglein A (1995) Chemical effects of continuous and pulsed ultrasound in aqueous solutions. Ultrason Sonochem 2,p.115–121.

[56] Hoffmann MR, Hua I, Hochemer R (1996) Application of ultrasonic irradiation for the degradation of chemical contaminants in water. Ultrasonic Sonochemistry 3,p.163–172.

[57] Rutkowski P, Mullens S, Yperman J, Gryglewicz G. AP-TPR investigation of the effect of pyrite removal on the sulfur characterization of different rank coals. Fuel processing technology, 2002; 76,p.121-38.

[58] Sh. Mesroghli, J. Yperman, E. Jorjani, J. Vandewijngaarden, G. Reggers, R. Carleer, M. Noaparast, Changes and removal of different sulfur forms after chemical desulfurization by peroxyacetic acid on microwave treated coals, Fuel,2015,154,p.59-70.

[59] Mullens S, Yperman J, Reggers G, Carleer R, Buchanan Iii AC, Britt PF , A study of the reductive pyrolysis behavior of sulfur model compounds. Journal of analytical and applied pyrolysis 2003; 70, 20,p.469-91.

Chapter 6: Contribution and perspectives

Following dissertation contributions can be formulated based on the experimental data and their in-depth interpretation:

- Two types of the irradiation pre-treatments effects achieved for all sulfur forms present in the studied coal are precisely evaluated. By applying an appropriate experimental strategy and analytical techniques, the organic sulfur transformation mechanisms, as a results of applied treatments, are explained and clarified to a certain extent.
- Qualitative influences of applied pre-treatments on post chemical desulfurization with PAA were explained precisely.
- Impacts of the execution of microwave and sonication pre-treatments on coal matrix were considered.
- For the first time the reliable sulfur balance of pyrolysis experiments in this thesis was considered.
- Desulfurized pre-treated coal using PAA result in complex sulfur form changes.
- Oxidized organic sulfur compounds are present in desulfurized microwave pre-treated samples using PAA were considered.
- De-methylation reactions occur in desulfurized microwave pre-treated coal samples.
- For the first time quantitative organic sulfur forms changes were determined.
- For the first time the influences of advanced oxidation process (AOP) on the changes of organic sulfur forms after sonication pre-treatment were considered.

Based on the literature overview and analysis of the obtained in the thesis results it is obvious that the applied pre-treatment methods are not yet sufficiently effective as a pre-treatment methods before chemical desulfurization by PAA. Despite the considerable progress in the elucidation of the mechanisms of the irradiation pre-treatments on the chemical desulfurization processes of organic sulfur functionalities and the efforts to increase the rate of the organic sulfur removal, the registered chemical desulfurization effects concerning organic sulfur can be increased. Therefore, additional study in this field is required. This research can comprise:

- Discovery and selection of combined pre-treatment methods to investigate the influences on post chemical desulfurization and coal matrix.
- To evaluate the interaction of applying different (and/or extreme) irradiation conditions, on coal matrix and organic sulfur functionalities and post chemical desulfurization.
- Assessment of simultaneous different irradiation methods and chemical desulfurization in different settings on organic sulfur removal and organic sulfur functionalities.
- Using chemical thermodynamics approaches to evaluating the organic sulfur transformation mechanisms during pre-treatment and post chemical desulfurization.
- Using complementary instrumental analysis to evaluate sulfur structures and coal matrix changes after pre-treatments and post chemical desulfurization such as: NMR, FTIR, TGA, GC, HPLC and etc.

Summary and general conclusions

Sulfur is an undesirable constituent of coal. Technological utilization of sulfur-containing coal, i.e. combustion, dry distillation or hydrogenation, creates air pollution. During combustion of coal, most of the sulfur (pyritic, elemental (not seen in the present research) and organic sulfur) is emitted as SO_2, while during dry distillation and hydrogenation H_2S, CS_2, COS and sulfur-containing volatile organic compounds are released. In addition, sulfur in coal induces supplemental operational problems, i.e. boiler fouling, corrosion and equipment damage, poisoning of catalysts and production of metallurgical coke steel manufacture with low quality.

Environmental legislation norms regarding sulfur emission from coal combustion is already in place in many countries and is under consideration in others. Therefore in the last years, in order to comply with the strict environmental requirements for coal combustion, desulfurization of fossil fuel has become extremely important. Recently there is keen interest to use the pre-treatment by irradiation before chemical desulfurization as a method with high potential toward sulfur removal. There is lack of information about the pre-treatment influences on chemical structure of coal matrix, organic sulfur functionalities changes and also post chemical desulfurization. From the other side, it is very attractive approach due to the relatively mild experimental conditions (pre-irradiation and post chemical desulfurization with PAA) and lack of additional pollutants. However, the current limitation (higher energy consumption of microwave treatment) can hinder their industrial application. In order to promote this kind of pre-treatment methods before chemical desulfurization for future industrial exploitation, there is need to perform additional research resulting in increased desulfurization rates and scale up experiments.

It is believed that deeper knowledge in organic sulfur transformation in coal during (microwave and sonication) pre-treatment and after chemical desulfurization will reflect in better understanding of post chemical desulfurization in coal. This will assure a greater success in chemical sulfur removal. Therefore the main goal of the present study is tracking the changes that occur with sulfur, its forms and functionalities and coal organic compounds/matrix after pre-treatment and chemical desulfurization.

The current thesis comprises six chapters.

Chapter 1 is an introduction describing the importance of sulfur removal from coal, sulfur forms and general literature regarding the recent studies about sulfur forms and post desulfurization assisted by irradiation have been considered. Simultaneously, an in-depth literature study and an overview is presented. Finally the research objectives, necessities and novelties are formulated.

Chapter 2 describes the sample under consideration, used pre-treatment methods and their related conditions, sulfur forms analysis standards, chemical desulfurization conditions and analytical methods such as AP-TPR/MS and AP-TPR-TD-GC/MS.

Chapter 3 describes the influences of microwave pre-treatment on coal matrix and organic sulfur forms transformation. Organic sulfur functionality alteration as a result of applied microwave pre-treatment is traced by atmospheric pressure-temperature programmed reduction (AP-TPR) technique coupled with different detection systems: Mass spectrometry, thermal desorption-gas chromatography/mass spectrometry (TD-GC/MS).

The following conclusions can be formulated:

AP-TPR device coupled with MS detection system (AP-TPR/MS) demonstrates the opportunity to elucidate organic matrix and organic sulfur species alteration in the microwave treated high sulfur coal samples (Tabas, Iran). For the first time, organic sulfur alterations are investigated qualitatively and quantitatively. According to the present state and the obtained profiles using AP-TPR method, the 2 minutes irradiation time has the most significant impact for all used power settings. Changes in H_2S peak profiles due to microwave treatment can be mainly explained by conversion of less-reactive and more-reactive aromatic sulfur compounds into each other and by coal matrix effects. Peak maxima of all aromatic carbon fragments shifted towards higher temperature region, due to the poly cyclic aromatic ring formation as a result of microwave treatment. The irradiation treatment used on the coal samples, resulted in coal matrix degradation and also changes in terms of physical characteristics and causing a simultaneous degradation of the organic matrix. Microwave irradiation of coal can cause phase changes and also expansion which is creating internal pressures within the coal matrix and possibly weakening the structure can creating fracture, therefore the positive effects reported for microwave irradiation on the post desulfurization probably related to this mentioned phenomena and easy access of leaching reagent to sulfur targets. Based on above mentioned physico-chemical phenomena and the effects of irradiation treatment on coal matrix, this will influence the effect and efficiency of further desulphurization of organic sulfur compounds as will be proved in the next paper.

Chapter 4 describes impacts of pre-treatment (discussed in chapter 3) on post chemical desulfurization (with peroxyacetic acid: PAA), organic sulfur functionalities changes and organic sulfur reduction with respect to the aliphatic and aromatic sulfur forms and their related changes. Based on the achieved results in Chapter 3, the following conclusions can be formulated for Chapter 4:

The total sulfur reduction after chemical desulfurization in this study is achieved in the range of 49-63%. Based on the discussed literature, inorganic sulfur (sulfate and pyrite) was mainly attacked by PAA after microwave treatment. The pyritic sulfur reduction achieved around 85-98% due to the dielectric characteristic of pyrite interacting efficiently with microwave irradiation. In all prepared samples, sulfate sulfur is totally removed after PAA desulfurization. Higher chemical desulfurization is achieved for the 300W and 2 minutes condition being around 63% and 48% for total and organic sulfur, respectively. AP-TPR coupled with different detection systems (MS and TD-GC/MS) gives us an opportunity to trace a broad range of organic sulfur species present in the Tabas coal. For the first time organic sulfur changes as a result of pre-microwave treated, followed by PAA desulfurization have been investigated. The information obtained by AP-TPR "off-line" (TD-GC/MS) show some quantitatively changes in the refractory aromatic sulfur forms as a results of microwave treatment before and after desulfurization. Opposite of the pre-irradiated and desulfurized samples, for the solely irradiated samples no indication of oxidized sulfur was found. This is a clear result of the PAA treatment as a mild oxidizing agent. Based on the "off-line" experiments for the desulfurized samples, the presence of sulfur dioxide and even dimethyl sulfone has been noticed quantitatively. The direct impact of the pre-MW treatment conditions (time and power) on the chemical desulfurization to produce oxidized sulfur products has been noticed, both qualitatively and quantitatively. AP-TPR "off-line" (TD-GC/MS) showed some controversial and more complex changes in organic sulfur forms which again demonstrate the direct but complicated impact of microwave irradiation on coal matrix.

Chapter 5 irrespective of achieved results in the previous chapters, in this chapter the impacts of sonication on the post chemical desulfurization and organic sulfur functionalities and their changes were considered qualitatively and quantitatively. Hence, the following conclusions can be formulated for Chapter 5:

The sonication as another pre-treatment method in constant power/frequency and different time settings was used and the influences of this treatment on coal matrix and sulfur functionalities were evaluated. Sulfur reduction after chemical desulfurization by PAA is achieved in the range of 49-58%. The results showed that the sulfate and pyritic sulfur was mainly attacked by PAA after sonication: 100% of sulfate sulfur removal and 63%-74% pyritic sulfur removal. The results showed that the maximum organic sulfur reduction was obtained for the longer sonication time of 20 up to 25 min around 39%. The sonication process in the liquid-solid phase happens via an "AOP" process, producing oxidizing reagents resulting in more oxidized coal samples as oxidized sulfur compounds. The profiles obtained by AP-TPR (on-line) experiments for m/z=48 and 64 for sonicated and desulfurized sonicated samples exhibited over the whole temperature range the same trend, demonstrating the high presence amounts of different oxidezed sulfur compounds. For the first time organic sulfur changes by AP-TPR 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 aromatic sulfur forms as a result of sonication time settings before and after desulfurization.

Chapter 6 comprises the dissertation contributions and perspectives for future investigations.

Samenvatting en algemene conclusie.

Zwavel in steenkool is een ongewenst element. Technologisch gebruik van zwavelhouden steenkool geeft heel wat problemen: bij verbranding, bij droge destillatie of hydrogenatie en leidt tot luchtverontreiniging. Tijdens verbranding van steenkool zal de meeste zwavel (pyriet, elementaire (niet aanwezig in de hier bestudeerde steenkool) en organische zwavel) leiden tot SO_2 uitstoot, terwijl gedurende droge destillatie of hydrogenatie H_2S, CS_2, COS en zwavelhoudende vluchtige organische verbindingen worden vrijgemaakt. Bijkomend induceert zwavel operationele problemen: blokkering verwarmingsketels, corrosie verschijnselen en toestelbeschadigingen, vergiftiging van katalysatoren en productie van laagwaardig staal. Milieunormregularisaties naar zwavel emissies toe van steenkoolverbranding zijn al in vele landen van toepassing of worden in overweging genomen in de resterende landen. Dit heeft voor gevolg dat in de laatste jaren het halen van deze normen, de ontzwaveling van steenkool zeer belangrijk werd. Recentelijk is een voorbehandeling via "bestraling" van de steenkool vóór een chemische ontzwaveling als de methode beschouwd met de meeste potentie voor een optimale verdere chemische zwavelverwijdering. Het ontbreekt echter aan informatie wat de invloed is van deze vorm van voorbehandeling zowel op de chemische structuur van de steenkool matrix, de organische zwavelvormveranderingen als op de chemische ontzwavelingsbehandeling achteraf. Het dient vermeld te worden dat deze totale benadering een relatieve vrij zachte experimentele conditie is ("voor-bestraling" gevolgd door een chemische ontzwaveling middels peroxy-azijnzuur (PAA)) en geen bijkomende polluenten genereert. Echter het hoge energieverbruik door een microgolf- en geluidsgolfbehandeling kan een hinderpaal zijn in het industrieel gebruik van deze benadering. Om deze methode toch ingang te kunnen geven dient een verder bewijs geleverd te worden van een optimalere ontzwaveling, wat bijkomend onderzoek vergt en opschaling dient eveneens bestudeerd te worden.

We zijn ervan overtuigd dat een betere kennis in de organische zwavelvormverandering in steenkool gedurende microgolf- en geluidsgolfvoorbehandeling een beter inzicht geeft in het effect en de keuze van de post chemische ontzwaveling van steenkool. Dit moet resulteren in een meer succesvolle verwijdering van de zwavel. Vandaar dat de hoofdopzet van deze studie het nagaan is van de veranderingen die plaatsgrijpen rond de zwavel aanwezigheid in steenkool, zowel naar vorm als naar bindingsaard, als naar de verandering in de steenkoolmatrix zelf als zijn organische componenten ten gevolge van deze voorbehandeling en verdere ontzwaveling. De thesis is ingedeeld in zes hoofdstukken.

<u>Hoofdstuk 1</u> is de inleiding die een beschrijving geeft van het belang van ontzwaveling, de aard van het zwavelvoorkomen en de algemene literatuur rond recente studies over zwavelvormvoorkomen en ontzwavelingsmethoden voorafgegaan door een "bestraling". Terzelfdertijd wordt een diepgaande literatuurstudie en overzicht hierrond gegeven. Tot slot worden de onderzoekobjectieven, de nood ervan en de vernieuwende aspecten geformuleerd.

<u>Hoofdstuk 2</u> beschrijft de bestudeerde monsters, de gebruikte voorbehandelingsmethoden en hun omstandigheden, de verschillende zwavelvormbepalingsmethoden, de chemische ontzwavelingsomstandigheden en de gebruikte analytische methoden zoals atmosferische druk temperatuur geprogrammeerde reductie gekoppeld met massa spectrometrie (AP-TPR/MS) en via thermische desorptie gas chromatografie massa spectrometrie (AP-TPR-TD-GC/MS).

<u>Hoofdstuk 3</u> beschrijft de invloed van de microgolf voorbehandeling op de steenkool matrix en op de organische zwavelvormveranderingen in steenkool met een hoog zwavelgehalte (Tabas, Iran). Deze veranderingen konden nagegaan worden door gebruik te maken van een unieke analytische methoden: AP-TPR/MS en AP-TPR-TD-GC/MS. De volgende conclusies konden geformuleerd worden: middels AP-TPR/MS kon een opheldering gegeven worden van organische steenkoolmatrixverandering en de organische zwavelvormverandering. Voor de eerste maal kon zowel kwalitatief als kwantitatief zwavelgroep veranderingen bepaald worden. Op basis van het huidige onderzoek kan gesteld worden dat de 2 minuten microgolfbehandeling al voldoende is om de grootste veranderingen te induceren voor alle aangewende watt-instellingen. De verandering in de H_2S profielen ten gevolge van de microgolf behandeling kan hoofdzakelijk verklaard worden door een omzetting

van weinig-reactieve en meer-reactieve aromatische zwavelcomponenten in elkaar en door steenkool matrixeffecten. Piek maxima van alle aromatische koolwaterstoffragmenten verschoven naar een hogere temperatuur ten gevolge van polycyclische aromatische ringvorming ten gevolge van de microgolf behandeling. De bestralingsbehandeling van de steenkool resulteerde in een steenkool en organische matrix afbraak en ook in veranderingen van hun fysische karakteristieken. Microgolfbestraling van de steenkool resulteerde ook in een faseverandering en uitzetting ten gevolg van de interne druk verhoging in de steenkool matrix en daardoor mogelijks de complete structuur verzwakt en barsten creëert. Dit veroorzaakt zo een positief ontzwavelingspercentage ten gevolge van de gemakkelijkere toegang van het PAA tot de zwavelfunctionaliteiten. Ten gevolge van deze fysicochemische verschijnselen en het effect van de bestraling op de steenkool matrix zal dit het effect en de efficiëntie van de vervolg ontzwavelingbehandeling gunstig beïnvloeden.

Hoofdstuk 4 beschrijft de impact van de voorbehandeling op de chemische ontzwaveling met PAA, de organische zwavelfunctionaliteitsverandering en de organische zwavelreductie in zijn alifatische en aromatische vorm als hun onderlinge relatie op basis van de bekomen AP-TPR/MS resultaten. Baserend op de resultaten van hoofdstuk 3 konden voor hoofdstuk 4 volgende conclusies geformuleerd worden: de totale zwavelreductie lag in de grootte orde van 49-63%. Anorganische zwavel zoals sulfaat werd door PAA volledig verwijderd en de pyriet verwijdering lag tussen 85 en 98%. Het hoog percentage aan pyriet verwijdering dient gezocht te worden in de zeer efficiënte wisselwerking ervan met de microgolfbehandeling waardoor de optimale verwijderingscondities ervan werden gerealiseerd. De hoogste post-chemische ontzwaveling werd verkregen voor de 300W en 2 minuten behandeling met 63% verwijdering van het totaal zwavelgehalte en 48% verwijdering van het organisch zwavel gehalte. Bijkomende informatie verkregen met de AP-TPR "off-line" opstelling (TD-GC/MS) toonde kwantitatieve veranderingen aan in aromatische zwavelvormverbindingen. In tegenstelling tot de microgolf behandeling gaven nu de ontzwavelde stalen een duidelijke aanwezigheid van geoxideerde zwavelverbindingen. PAA is immers een zacht oxiderend reagens. De "off-line" resultaten toonden ook duidelijk de vorming van zwaveldioxide aan en zelfs van dimethyl sulfonen en dit dus op kwalitatief als op een kwantitatieve wijze. Dit bevestigde de niet volledig overtuigende m/z 48 en m/z 64 AP-TPR/MS resultaten. Anderzijds toont AP-TPR sommige controversiële en meer complexe veranderingen in zwavelvormvoorkomen aan wat wederom de gecompliceerde impact van microgolf behandeling aangeeft.

Hoofdstuk 5 wordt de impact van geluidsgolfbehandeling op verder te ontzwavelen steenkool middels PAA beschreven. Ook op de verandering in organische zwavel functionaliteiten zowel kwalitatief als kwantitatief kon aangetoond worden. De volgende conclusies kunnen geformuleerd worden: geluidsgolfbehandeling bij constant wattage en frequentie maar voor verschillende behandelingstijd geeft een totaal zwavel reductie van 49 tot 58%. 100% sulfaat zwavelverwijdering werd wederom gerealiseerd en voor pyriet zwavelverwijdering werd een percentage tussen 63 en 74 % behaald. De maximale organische zwavelverwijdering werd bekomen voor een langere behandelingstijd van rond 20-25 min met een percentage van 39%. Geluidsgolfbehandeling gebeurt in de vloeibare-vaste fase toestand via een AOP proces. Wat resulteert in de vorming van een oxiderend reagens en in meer geoxideerde zwavelverbindingen als in een meer geoxideerde steenkool matrix. De AP-TPR/MS profielen voor m/z 48 en 64 vertoonde in tegenstelling tot de microgolf behandelde stalen nu een duidelijk parallel verloop over gans het temperatuurgebied en met vrij intense signalen. Net zoals voor hoofdstuk 4 werd voor de eerste maal organische zwavelvormveranderingen in kaart gebracht als een gevolg van een geluidsgolfbehandeling gevolgd door een PAA ontzwavelingsprocedure. AP-TPR "off-line" toonde ook kwantitatieve veranderingen aan in meer bestendige aromatische zwavelverbindingen als een gevolg van de geluidsgolfbehandeling zowel voor als na ontzwaveling.

Hoofdstuk 6 geeft ten slotte een overzicht van al de behaalde resultaten en mogelijke perspectieven naar de toekomst toe wat betreft verder wetenschappelijk onderzoek en de toepassingsmogelijkheden.

Curriculum vitae and list of publications:

- **Education**

- Ph.d in Mine engineering in field of mineral processing engineering from Science and research branch of IAU (Iran/Tehran) (2015)

- Ph.d candidate in chemistry at Hasselt University (Belgium).

Title of thesis (Ph.d):

Evaluation of irradiation effects on coal sulfur forms and chemical desulfurization using AP-TPR method. (Atmospheric Pressure – Temperature Programmed Reduction)

- Mine Engineering in field of mineral processing (M.Sc) Science and research Open University (Tehran) **(2005-2007)**

Title of thesis (M.Sc):

Prediction of coal calorific value by means of mathematical methods with regard to proximate,
ultimate and elemental analysis data (Kentucky Coal Samples)

- Mine Engineering in field of extracting (B.Sc) Tehran Open University **(2000-2004)**

Title of thesis (B.Sc):

Recognition of Tehran faults by studying on underground water situations

- **Language and computer skills:**

A: Language: English *(IELTS BAND : 6.5)*
Turkish *(Fluent)*
Persian *(Native language)*
B: Mathematical software: *Matlab, SPSS , NCSS , Microsoft Office* (level : expert), Origin
C: Graphical software: *Autocad* (level : expert)

- **Scientific/Technical accomplishments**

a. - Recovery of Barite from drilling mud residue (Present project)
b. - Passive treatment system for acid mine drainage
c. - Flotation of low solubility salts
d. - Biological pretreatment for gold recovery from refractory resources
e. - Reagent interaction in flotation and leaching process
f. Effects of irradiation on coal sulfur forms by AP-TPR
g. Evaluation and modeling of Ash fusion temperature (AFT) of coals in energy plants.

- **Honors/Awards**

  - Excellent student in M.Sc with (A+) average (2007).
  - Got the excellent researcher award in 2008. (Science and research open university Tehran)
  - Got (A+) score in comprehensive exam (2009).

- **Publication (ISI Journals)**

1- Simultaneous prediction of coal rank parameters based on ultimate analysis using regression and artificial neural network, S. Chehreh Chelgani,Sh. Mesroghli, James C. Hower, International Journal of Coal Geology, Accepted date: 25 March 2010.

2- Estimation of gross calorific value based on coal analysis using regression and artificial neural networks, Sh. Mesroghli, E. Jorjani, S. Chehreh Chelgani, International Journal of Coal Geology 79 (2009) 49 54.

3- Prediction of coal response to froth flotation based on coal analysis using regression and artificial neural network, E. Jorjani, H. Asadollahi Poorali, A. Sam, S. Chehreh Chelgani, Sh.Mesroghli, M.R. Shayestehfar , Minerals Engineering 22 (2009) 970 976.

4- Prediction of operational parameters effect on coal flotation using artificial neural network, E. Jorjani, Sh. Mesroghli, and S. Chehreh Chelgani, Journal of University of Science and Technology Beijing Volume 15, Number 5, October 2008, Page 528.

5- Application of artificial neural networks to predict chemical desulfurization of Tabas coal, E.Jorjani, S. Chehreh Chelgani, Sh. Mesroghli, Fuel 87 (2008) 2727 2734.

6- Prediction of yttrium, lanthanum, cerium, and neodymium leaching recovery from apatite concentrate using artificial neural networks, E. Jorjani, A.H. Bagherieh, Sh. Mesroghli, and S. Chehreh Chelgani, Journal of University of Science and Technology Beijing Volume 15, Number 4, August 2008, Page 367.

7- Studies of relationship between petrography and elemental analysis with grindability for Kentucky coals, E. Jorjani, James C. Hower , S. Chehreh Chelgani Mohsen A. Shirazi, Sh.Mesroghli, Fuel 87 (2008) 707 713.

8- Prediction of coal grindability based on petrography, proximate and ultimate analysis using multiple regression and artificial neural network models, S. Chehreh Chelgani, James C. Howerb, E. Jorjania, , Sh. Mesroghlia, A.H. Bagherieh, Fuel processing technology 89 (2008) 1 3 2 0.

9- Prediction of microbial desulfurization of coal using artificial neural networks, E. Jorjani, S.Chehreh Chelgani, Sh. Mesroghli, Minerals Engineering 20 (2007) 1285 1292.

10- Multivariable Regression and Adaptive Neurofuzzy Inference System Predictions of Ash Fusion Temperatures Using Ash Chemical Composition of US Coals, Sh. Karimi, E. Jorjani, S.Chehreh Chelgani, and Sh.Mesroghli, Hindawi Publishing Corporation Journal of Fuels. 16 April 2014.

11- Evaluation of microwave treatment on coal structure and sulfur species by reductive pyrolysis-mass spectrometry method, Sh. Mesroghli , J. Yperman, E. Jorjani, R. Carleer, M. Noaparast, Fuel Processing Technology 131 (2015) 193–202.

12- Changes and removal of different sulfur forms after chemical desulfurization by peroxyacetic acid on microwave treated coals, Sh. Mesroghli, J. Yperman, E. Jorjani, J. Vandewijngaarden , G. Reggers, R. Carleer, M. Noaparast, Fuel 154 (2015) 59–70.

13- Evaluation of the impacts of sonication on organic sulfur species and desulfurization by reductive pyrolysis, Sh. Mesroghli , J. Yperman , E. Jorjani , R. Carleer , Fuel (Under review)

The last three papers, have been extracted from the Ph.d thesis.

Conference papers

1- Estimation of coal calorific value with petrography, ultimate analysis, moisture, Rmax and ash using regression and artificial neural network methods**,** E. Jorjani1*, James C. Hower2, Sh.Mesroghli1, Mohsen A. Shirazi3, S. Chehreh Chelgani, *24th International Pittsburgh Coal Conference*, September 10 14, 2007.

2- Application of ANN to predict combustible value and recovery of coal flotation concentrate, E.Jorjani, SH.Mesroghli,SC.chelgani, Mineral processing conference, cape town, 2-3 August 2007.

3- Coal Grind-ability prediction based on petrography with multiple regression and artificial neural network models, E.Jorjani,JC.Hower, SC.Chelgani, SH.Mesroghli, Mineral processing conference, cape town, 2-3 August 2007.

4- Evaluation of microwave pre-concentration on coal matrix and sulfur forms by AP-TPR method, Sh. Mesroghli , J. Yperman, E. Jorjani, R. Carleer, M. Noaparast, accepted for oral presentation, international conference of clean energy 2014, at Istanbul.

5- Evaluation of the effects of microwave pretreatment on coal sulfur forms and post chemical desulfurization by AP-TPR method, accepted for oral presentation, Sh. Mesroghli, J. Yperman, E. Jorjani, J. Vandewijngaarden , G. Reggers, R. Carleer, M. Noaparast, BIT's 4th annual international symposium of clean coal technology, 24-26 September 2015.

Last two mentioned papers have been extracted from the Ph.d thesis.