PEER REVIEW

of the thesis paper “Development and Application of Reductive Pyrolysis in the Study of Organic Sulphur Forms in Fossil Fuels and Biomass Organic Matter Composition”

Peer Reviewer: Prof. Dr. Jordan Ivanov Kortenski

Assoc. Prof. Dr. Stefan Penchev Marinov graduated the Higher Institute of Chemical Technology, Sofia, in 1980. After graduation he started work as a chemical engineer at the Research Institute of Chemical Pharmaceuticals and in 1981 he became a Ph.D. student at the Institute of Organic Chemistry with a Centre of Phytochemistry at the Bulgarian Academy of Sciences (BAS). In 1986 he defended his doctoral thesis and was appointed a junior research associate at the same institute at the Laboratory “Chemistry of Solid Fuels”. Since 2001 he has been an associate professor at the same laboratory.

The thesis paper is mainly relevant with regard to limiting the harmful effects of sulphur on the environment by reducing its content in coal combustion emissions. Coal desulphurisation is also crucial when used for technological purposes. Part of the pyrite sulphur could be removed in the process of coal treatment, the other part by demineralisation and depiritisation, while the amount of organic sulphur remains unchanged. Therefore, the dissertation studies the organic sulphur compounds in lithotype from Maritza East, briquettes and biodesulphurised coal by using reduction pyrolysis. The results of the study of organic lignite and lignocellulosic biomass are presented.

The dissertation submitted is of 142 pages, which include 42 figures, 26 tables and 205 reference titles. It is developed in 7 parts as follows: Part 1. Literature Review - 13 pages; Part 2. Aim and tasks - 1 page; Part 3. Materials, methods and instrumental techniques - 15 pages; Part 4. Results and Discussion - 91 pages. This part contains 8 chapters, each of which concludes with a conclusion; Part 5. General conclusions – 3 pages; Part 6. Scientific contributions - 2 pages; Part 7. References - 14 pages. The dissertation ends with separate lists of Assoc. Prof. Marinov’s scientific works related to the topic of the dissertation, the conferences at which the results were presented, the noted citations and projects related to the topic of the dissertation. .

The introduction justifies the need for the purification of sulphur from coal and emphasises the complex relationship between the organic sulphur and the organic matter of coal.

Part I discusses the achievements in the development of methods for the determination of organic sulphur and its compounds in coal and other solid, non-volatile, coal-based materials, using about 200 literature sources. It is worth noting the in-depth description of the temperature-programmed atmospheric pressure reduction (AP-TPR) proposed by Yperman (1987). Improvements have been made therein (Marinov et al., 2001a), enabling all volatile sulphur organic compounds to be investigated.

Part II describes the aims and tasks of the dissertation. The aim is to follow, by applying the reduction pyrolysis approach in its development and in combination with modern detection analytical techniques, the qualitatively and quantitatively available and changed organic sulphur functionalities and other groups of individual organic compounds in coal and in other solid natural products before and after desulphurisation treatments, and to determine the composition of volatile products from pyrolytic treatment of lignincellulose biomass. The following processes have been implemented: investigation, by reduction pyrolysis, of the forms of organic sulphur and the composition of the organic mass in high sulphur coals, lithotypes, briquettes for burning, in representative technological samples of sulphur coal before and after carrying out various biodesulfurisation treatments, etc.

The third part is devoted to the materials and the research methods. The studied objects and the various methods used are described in detail. The methodology of temperature-programmed atmospheric pressure oxidation (AP-TPO) and the additions made thereto is particularly well described. The peer reviewer has the following remarks on this part: In the description of the studied coal the international classifications are mixed up with the Bulgarian classification. The Donbass coal is incorrectly described as low- and high-rank - they are of low and medium rank. This basin is incorrectly written as Donbass - it is correct to write Donetsk or Donbass.

Part IV summarises the results of the studies carried out. They are reviewed in six chapters. Chapter IV.1 discusses the desulphurisation treatments and the results from studies by reduction pyrolysis of organic sulphur-containing compounds and the organic mass of coal. Section 1 of this chapter establishes that the product obtained after the alkaline melting treatment of Maritza East lignites is almost completely desulphurised and its calorific value is significantly higher than that of the starting coal. Section 2 reflects the desulphurisation treatments and the results from the studies of Donbass coal. The thermochemical treatment with water vapour and the reduction treatment with K/THF have shown to be effective with respect to bridge sulphur and the pyrolysis with water vapour increases the thiol groups, which is an indication of rupture of the sulphide and disulphide bonds. It is noted that the main difference between the thermochemical treatment in a stream of water vapour and the reduction treatment is that in the thermochemical treatment, inorganic sulphur is almost completely eliminated, while the reduction desulphurisation destroys not only the bridge sulphur but also the sulphur heterocycles of thiophenic type. The data presented in Table 3 shows that only one sample of KUL2 is from low-rank coal and the other 3 are from medium-rank coal. I would like to recommend to Assoc. Prof. Marinov to pay attention to the macerated composition of the coal, since the data in the table show a clear dependence between the amount of inertinite macerals and the sulphur content, especially pyrite. Section 3 of this chapter sets out the results of desulphurisation treatments and the reduction pyrolysis of low-rank coal from the Elhovo basin and the Katrishte deposit. The results from the AP-TPR and XPS analyses demonstrate complete removal of non-thiophene sulphur in the water vapour pyrolysis. The conducted AP-TPR with potentiometric detection and AP-TPR-MS "on-line" profiles show significant differences in the presence of organic sulphur groups in the two types of coal. The Elhovo lignites contain more aliphatic sulphur compounds, while more complex thiophene structures are found in the coal from the the Katrishte deposit. This is completely natural because of the different source vegetation for the coal formation. The demineralisation of the sulphur content is reflected in a different way, since the inorganic sulphur has a higher content in the Elhovo lignites, while the organic sulphur prevails in the Katrishte coal. What is striking is the unusually large amount of sulphate sulphur in the Elhovo lignites, which is probably due to the fact that the sample is taken from heavily weathered coal. Section 4 of this chapter is devoted to the studies of organic sulphur functionalities in demineralised Elhovo lignites by reduction pyrolysis. The basic structural units of the organic mass in this coal have been found to be aromatic compounds with two rings and a high degree of substitution, with the disulphides being the major aliphatic sulphur species. About 58% of the organic sulphur is represented by thiophene structures. The last fifth section of this chapter deals with the results from the desulphurisation treatments and the reduction pyrolysis of Spanish lignites from the Mequinenza deposit. These lignites have high sulphur content and as can be seen from Table 8 the predominant form of sulphur is organic, with a minimal amount of mineral sulphur. Therefore, demineralisation has little effect on the total sulphur content. The off-line AP-TPR-GC/MS technique has demonstrated that in the demineralised lignites there are: thiols; mono- and disulphides; alkyl and ω-alkenyl thiophenes, alkyl benzo[b]thiophenes and alkyl dibenzo[bd]thiophenes. At temperatures above 450°C, the predominance of benzo[b]thiophene and its alkylated homologues was recorded. Classical pyrolysis in Ar currents has a greater effect on the amount of non-thiophene sulphur and removes all oxidised sulphur compounds compared to water vapour pyrolysis at the same process parameters. The pyrolysis temperature is important for the removal of the non-thiophene sulphur.

Chapter 2 of Part IV is devoted to the study of organic sulphur functionalities and the organic mass of lithotype from Maritza East lignites by reduction pyrolysis. In xylene and humovitren, aliphatic sulphur, thiols and dimethyl sulfides were found to be predominant. The non-sulphate and humiclare are dominated by disulphides, in the almost complete absence of sulphides. The proposed AP-TPR-GC/MS "off-line" analytical study allows the separation of dimethyl sulphides, polysulphides, and disulphides. It would be good to have a humodurein sample in these studies, even though it is a high-ash lithotype. The formation of lithotypes is not related to the process of carbonation, so another explanation for the lower content of aliphatic sulphur functionalities in lipten and humoclarain should be sought.

Chapter 3 presents the results of studies of organic sulphur functionalities and the organic mass of household briquettes by reduction pyrolysis. Briquettes produced from biomass have low content of dialkyl sulphides and aliphatic thiols. The dominant components are cellulose degradation products. Lignite briquettes are characterised by volatile aliphatic sulphides, mixed aliphatic-aromatic sulphides, aryl sulphides, aliphatic thiols, thiophene structures, methyl thiophene and methyl thiol. Bituminous/sub-bituminous coal briquettes are characterised by more complex thiophene structures, but no oxidised sulphur compounds have been detected. The presence of aliphatic thiols and sulphides, mixed alkyl aryl sulphides, diaryl sulphides and more complex thiophenes has been reported in mixed briquettes of different ranks of coal. All organic sulphur compounds in household briquettes can be considered as unchanged organic molecules released into the atmosphere. As a side note to the terminology used, I can point out that coal is not properly characterised by its rank. According to the international classifications, lignite and brown coal is low-rank, black coal is medium-rank and anthracite coal is high-rank. The concepts of brown coal and sub-bituminous coal are similar, the first being the Bulgarian State Standard (BDS) coal classification and the second one - the same coal in the US and international classification.

Chapter 4 - Study by Reductive Pyrolysis of Organic Sulphur Functionalities and Organic Matter Composition of Biodesulphurised Coal - includes 6 sections. The first one is devoted to the investigation of local and foreign high-sulphur coal. Low-rank coal from two Bulgarian and one Turkish deposits has been explored. Coal biodesulphurisation with selected fungi and mixed bacterial microorganisms contributes to a maximum reduction of organic sulphur functionalities by up to 24% and a reduction of up to 79% of inorganic sulphur. No coal matrix violation is reported for biotreated coal samples, with a slight decrease in calorific values, the AP-TPR off-line GC/MS study has confirmed the oxidative biodegradation mechanism in coal biodesulphurisation and the conversion of complex sulphur compounds to sulphones and sulphoxides. Section two of this chapter proposes a procedure for the direct determination of the elemental sulphur in coal, thus reducing the error when determining the amount of organic sulphur. Section 4.3 presents the results of the study by reduction pyrolysis of organic sulphur functionalities and organic matter composition of biodesulphurised technological samples from local high-sulphur coal. Low-rank coal samples from the Maritza East and the Bobov Dol basins were treated with two bacteria A. *Ferrooxidans* - F3 and *Ps.putida* - B2. The studies of the initial and the treated samples show a decrease in the amount of pyrite sulphur, and for the Maritza East lignites – for the elemental as well. It is recommended both types of coals to be treated with the two bacteria for comparability of the results. There is a contradiction in the comments on the results in the text and the conclusion. In the text it is stated that the sample treated with the bacterium *Ps.putida* - B2 shows a significant decrease in the amount of pyrite sulphur, and this can be seen from Table 13, whereas in the conclusion it is said that this is a result from the treatment with the bacterium *A. Ferrooxidans* - F3. In section 4.4. the results of the study by reduction pyrolysis of organic sulphur functionalities and the organic mass of high-sulphur lignite treated with combined chemical/microbial desulphurisation are presented. In addition to the Maritza East lignites, it is recommended to investigate also the Elhovo lignites, which are known for their high sulphur content. As a result of applying a combination of chemical and microbial desulphurisation treatments of Maritza East lignites, a maximum total desulphurisation of 71%, pyrite desulphurisation of 90.6% and organic desulphurisation of 49.4% have been achieved. Using the AP-TPR "on-line" MS technique, a qualitative specification of a wide range of sulphur and mixed oxygen-containing functional forms has been made. A decrease in the content of thiols has been found in all oxidised and bio-treated samples. Section 4.5. is devoted to the study of the influence of microbial treatments on the combustion indicators of biodesulphurised coal from Maritza East, Bobov Dol and Pirin. Better ignition performance has been determined for bio-treated samples; a slight decrease in calorific value and a decrease in peak temperature for maximum weight loss rate (T_{max}). A disadvantage is that the bio-treated samples show a decrease in combustion by increasing the combustion time (tq) and the final combustion temperature (T_{ec}) and the decrease in the auto-ignition temperature (T_{sh}). In Section 4.6. the results from the study of organic sulphur functionalities and the organic mass of humus-like lignite biodesulphurisation products from Maritza East are reflected. As a result of microbial treatment with *Pseudomonas putida*, aliphatic and aromatic sulphur has been found to be affected by the treatments. Thus, much of the organic sulphur is transformed into a water-soluble state, which is highly volatile. The current desulphurisation mechanism is oxidative. The transformation of BzTh and Th during processing may take place through the S-atom oxidation mechanism or through the C-atom oxidation mechanism that is dominant. Since the humus-like by-product (HL) exhibits an outward resemblance to the humic substances (HA), it is compared with humic acids obtained from the same coal sample.

Chapter 5 of Part IV sets out the results from the study by reduction pyrolysis of the organic mass of humic acids from Maritza East and Stanyanci lignites and from Turkish leonardite. The presence of dialkyl sulphides, sulphoxides and sulphones has been found. No sulphates and sulphonates have been reported, since during the preliminary demineralisation with mineral acids, they were removed together with pyrite sulphur and carbonates. Humic acids derived from Maritza East lignites are characterised by a predominant structure with coniferous vegetation of lignin structures, while highly microbially processed carbohydrates are included in the organic matter of Stanyanci deposit. From a chemical point of view, both types of humic acids are made up of structural units with 1-2 aromatic condensed or combined rings. For the industrial application of humic acids from the Maritza East and Stanyanci lignites, the high content of heteroatom-containing compounds (N and S) and their environmental impact must be taken into account when applying preparations based on them.

Chapter 6 is devoted to a pyrolytic study of the organic mass of Stanyanci lignites. In the whole temperature range from 250°C to 950°C, the content of alkyl benzene is the highest, i.e. C6-C10. They make up the largest proportion (44%) of all registered volatile products. In the low temperature range (250°C - 550°C) their distribution is dominated by toluene, while benzene predominates in the high temperature range (550°C - 950°C). Linear hydrocarbons *n*C6-*n*C15, which are second in content (21.7%) in the lignites tested, i.e. *n*-alkene/*n*-alkane pairs, have been identified only in the low temperature range, with short-chain aliphatic compounds predominating in the pyrogram. Symmetrical isoprenoids have also been identified, including regular isoprenoids *iso*-C14, *iso*-C15 and *iso*-C16. Naphthalenes, biphenyls, acenaphthalenes, fluorines and their alkylated homologues are recorded in the high temperature range. Mono- and diromatic structures, including alkylated benzenes and naphthalenes, are accompanied by significant amounts of their sulphur analogues, i.e. thiophenes/benzothiophenes (7%). Aliphatic S-containing compounds have also been found, i.e. dimethyl- and di-/trisulphides. As the pyrolysis temperature increases, alkyl aromatic compounds are accompanied by substituted phenolic structures, among which vanillyl phenols predominate, i.e. 2-methoxy and methyl-2-methoxy phenols. A range of sesquiterpenoids is also recorded in the low-temperature interval, i.e. dihydrocurcumene, cedrane, cuparene, cadinatrienes and cadalene. In the Stanyanci lignite study of 40 mg of starting material, a large number of individual organic compounds are identified.

Chapter 7 sets out the results from studies by reductive pyrolysis of aqueous leachates from Maritza East and Stanyanci lignites. At this stage, the identified and quantified compounds in these products do not pose a serious toxic risk to the environment. However, nitrogen-containing compounds could be of concern and their amount should be monitored, especially in Stanyanci lignites. The simplified scheme for the isolation and fractionation of lignite leachates enables the identification of a wide variety of functional groups on their surface. A number of organic compounds have been identified and quantified at the molecular level, some of them being potential environmental pollutants with a threat to human health.

Chapter 8 provides information on the pyrolytic studies of waste vegetation products and model lignocellulosic biomass. The determined quantities of volatile cellulose and xylan products are comparable (3141-3409 μg / g) and significantly lower for lignin (667 μg / g). They constitute the following percentage of the pyrolysed samples: 0.31 wt.% for cellulose, 0.32 wt.% for xylan and 0.0067 wt.% for lignin. PAHs are present in small amounts in non-condensable VOCs in the pyrolysis gas: 105 μg/g for cellulose, 168 μg/g for xylan, and 27 μg/g for lignin, which are dangerous for the environment and the human health. No noticeable amounts of PAHs are detected in the low pyrolysis temperature range of 250-600°C.

Additional notes and recommendations to Part IV:

- The term "Donetsk", "Elhovo", "Katrishte" and others is misused throughout the text. It is correct to say, e.g. Donetsk coal or coal from Donbass, etc.;

- There are many different coal studies from several Bulgarian and foreign basins and deposits. However, a large part of this research has not been done for all types of coal. It is recommendable to do this and compare the results;

- Different contents of a number of compounds in the different types of coal have been identified. In future research, it is recommended to Assoc. Prof. Marinov to extend the age range of coal and look into the causes for these differences.

Part V sets out the conclusions which are based on the results of the studies carried out. They are summarised by the conclusions of the individual chapters and sections in Part IV. There are three main groups: Composition and forms of organic sulphur in coal and natural fossil products; Clarifying the mechanism of low-rank biodesulphurisation of coal and Environmental observations and monitoring. The conclusions are logical, well-founded and fully reflect all results.

Part VI presents the scientific contributions of the dissertation. They are briefly and concisely formulated and relate to:

Contributions containing new and original information for science:

- By developing and refining the analytical approach of reduction pyrolysis, new quantitative and qualitative information on organic sulphur-containing functionalities in coal is obtained.
- For the first time, the reduction pyrolysis method with the AP-TPR technique for the studying the organic sulphur functionalities in humic acids is applied.
- For the first time, non-condensable volatile compounds of pyrolysis of the main building components of lignincellulose biomass is quantified.
- VOCs and PAHs are studied for the first time by reduction pyrolysis in leachate products of water-soluble lignite organic matter located in close proximity to endemic zones in Bulgaria.

Contributions of a confirmatory nature:

- The oxidative mechanism of microbial desulphurisation in coal is confirmed. Biodegradation of low-rank coal is found to occur with the formation of complex sulphur structures, i.e. with mixed functionality, e.g. sulphones and sulphoxides.
- The knowledge of the composition of the lignite aqueous extracts is confirmed and enriched. The results obtained are of ecological significance, since the presence of N-, S- and O-heteroatom-containing compounds has been established, which could penetrate groundwater near the coal basins.

Methodological contributions:

- A direct method is developed for the quantitative determination of organic sulphur compounds in coal and in other solid insoluble and non-volatile natural materials.
- A new methodology for the direct determination of elemental sulphur in coal is proposed, which provides more accurate data on the content of organic sulphur in them.

Applied contributions:

- It is found that no PAHs are released together with the volatile gases during the pyrolysis of model lignincellulose biomass at temperatures <600 °C. In pyrolysis of lignin at a temperature range of 600°C to 800°C, non-condensable VOCs containing sulphur heteroatoms in the molecule are released in minimal amounts, i.e. alkyl sulphones, di- and trimethyl sulphides. These results indicate that when biofuels are obtained by pyrolysis of plant waste products, sulphur-containing compounds are released at non-condensable VOCs at temperatures above 600°C.
- The applied biotreatments do not significantly affect the coal matrix, while maintaining their calorific value.

The thesis is well-presented, the aims are clearly stated, the research results are correctly interpreted and summarised, the overall layout of the work is of a high standard, the contributions are correctly and accurately formulated and the claims are fully justified. My critical remarks do not in any way diminish the qualities of the thesis paper.

Assoc. Prof. Dr. Marinov has provided a list of 26 articles in international journals, with their total impact factor being 41.99 and 14 full-text papers at scientific forums related to the topic of the dissertation. There are a total of 328 citations of published articles. Assoc. Prof. Marinov is the lead author of 10 of these articles and 7 papers. The total number of Assoc. Prof. Marinov's papers and posters at international and national scientific forums where the results of the dissertation have been presented is impressive, in 12 of them he is the lead author. Assoc. Prof. Marinov's research work related to the dissertation is based on 10 projects, where he is the project manager.

I have known Assoc. Prof. Dr. St. Marinov for more than 30 years, we have worked together on research projects and have published several joint articles that are not related to the topic of the dissertation. I highly respect him as a researcher and a well-renowned scientist.

CONCLUSION

The presented thesis paper and the overall research work characterise Assoc. Prof. Dr. Marinov as a well-established scientist. The merits and contributions of the dissertation are indisputable, which gives me reason to recommend to the honourable members of the Scientific Jury to award the scientific degree "Doctor of Sciences" to Assoc. Prof. Dr. Stefan Penchev Marinov.

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Sofia (Prof. Dr. J. Kortenski)