REVIEW

For the awarding the “Doctor of Science” degree in the Professional field 4.2. Chemical Sciences, specialty "Organic Chemistry"

Applicant: Assoc. Prof. Dr. Stefan Marinov, Laboratory of “ Chemistry of Solid Fuels”, Institute of Organic Chemistry with Center for Phytochemistry, Bulgarian Academy of Sciences

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1. Personal details of the applicant

Dr. Stefan Marinov graduated from Higher Technology School of Chemistry and Metallurgy - Sofia in 1980. Since 1981 he has been enrolled as a full-time PhD student at IOCCF, BAS. In 1986 he defended his doctoral thesis and was selected as a researcher at the same institute. In 2001, he won the "Associate Professor" competition at the “Solid Fuel Chemistry” Laboratory, where he has worked so far.

2. Review of the DSc thesis

The dissertation submitted for review is written on 173 pages and contains 41 figures and diagrams, 35 tables and 212 references. After a brief introduction and a literature review, the aim and the related tasks of the investigations are formulated, followed by a detailed description of the materials, methods and instrumental techniques used, presentation of basic results and discussion, short conclusions and main contributions of the thesis, literature sources, lists of publications, conferences, citations and scientific projects related to the dissertation.

In the Introduction part of the dissertation, the candidate describes the problems related to the use of coal, in particular, the adverse effect of sulfur on the quality of the coke produced and the environmental pollution and the need to determine the type and content of sulfur-containing compounds in the organic mass. Emphasis is also placed on the difficulties associated with these studies, which result from the poor solubility and thermal instability of these materials.

In the Literature Review, after a brief overview of the basic states of sulfur in coal, the author makes a thorough and critical assessment of the traditionally applied methods for determining the composition of organic sulfur compounds. Thermal analytical methods conducted in different gas environment or in the presence of reducing solvents are discussed in detail, with particular attention to temperature-programmed reduction. The advantages and disadvantages of thermal studies in an oxidizing environment have been demonstrated. The possibilities offered by the non-destructive instrumental methods such as XPS, XANES, EXAFS, SEM-EDX, which are also used in the dissertation, are reviewed.

On the basis of a detailed analysis of the problem, the author clearly formulates the purpose of the DSc Thesis and its specific tasks. The applicant's attention is directed to the study and development of the possibilities of reduction pyrolysis as a means for effective qualitative and quantitative determination of the organic sulfur compounds before and after bio-desulfurization of coal and other natural products such as coal lithotypes, briquettes for burning and humic acids from lignites and Leonardite. Considerable attention has also been paid to the composition of volatile products from the aqueous extracts of coal leaching and gases released during pyrolysis of lignincellulose biomass.

The subject of investigations in the dissertation is low and high rank coal from various fields in Bulgaria, Turkey, Spain and Ukraine, coal products (lithotypes, humic acids) and biomass. The studies were performed using Temperature-Programmed Reduction at Atmospheric Pressure (AP-TPR) with potentiometric detector, "on-line" mass spectrometric detection and "off-line" combined gas chromatographic-mass spectral determination of the products after their pre-adsorption concentration. In more recent studies, the author also includes the Temperature-Programmed Oxidation under Atmospheric Pressure (AP-TPO) method. In this case, the analyzes are performed on-line using a mass spectrometer as a detector. Modern non-destructive methods of analysis have been used, such as X-ray Photoelectron Spectroscopy, Fourier Transform Infrared Spectroscopy, Thermal and Elemental analysis. A very good impression is made of the detailed and accurate description of the methods and procedures used for the preparation of the materials and their study, which undoubtedly proves the author's routine in the field that is the subject of the dissertation and makes the latter particularly valuable for future researchers.

The Results and Discussion section is central to the dissertation. This section identifies 8 chapters directed to the application of reduction pyrolysis for the determination of sulfur containing organic compounds and organic matter in coal (Chapter 1), lithotype lignites from Maritza East mines (Chapter 2), briquettes (Chapter 3), biodesulfurized coal (Chapter 4) and humic acids from Bulgarian lignites and Turkish leonardite (Chapter 5), products from lignite leaching (Chapter 7). Chapters 6 and 8 discuss the results of the pyrolytic determination of the organic mass of lignite and lignocellulosic biomass, respectively.

Chapter 1 of the dissertation describes the results of studies on desulphurized coal from different fields in Bulgaria, low and high rank coals from the Donbass Basin in Ukraine and lignite from Spain using the method of atmospheric pressure reduction pyrolysis with potentiometric detection combined with XANES, DTA / TGA and SEM techniques. The possibilities of different methods of coal treatment are shown, emphasizing the advantages of the alkaline melting method for the almost complete removal of organic and inorganic sulfur. The effect of the destruction of some sulfur heterocyclic compounds and the bridge-bound sulfur-containing groups using reduction pyrolysis was noted. The increase in the amount of thiol groups is attributed to the rupture of sulfide and disulfide bonds as a result of water vapor pyrolysis, which is more pronounced under reducing conditions. The candidate compares the impact of water vapor pyrolysis with that of the reducing medium, drawing significant conclusions about the possibilities for more effective desulfurization with complete removal of inorganic sulfur when using water vapor. At the same time, there is a high rate of destruction of the reduction of bridging sulfur and thiophene-type heterocyclic compounds. In water vapor pyrolysis, it has been demonstrated that sulfur-containing, non-thiophene-type compounds decrease strongly with increasing temperature, and under these conditions sulfonic acid compounds are also removed. In comparison, it has been noted that conventional pyrolysis in Ar influences more the amount of non-thiophene sulfur and removes all oxidized sulfur compounds. In the course of the investigation, the author refines the AP-TPR method by "on-line" incorporation of mass spectrometric analysis, which demonstrates the complete removal of the non-thiophene sulfur in water vapor pyrolysis and with considerable precision determines the content of aliphatic and thiophene compounds in coal from different fields in Bulgaria. The next step in the development of the AP-TPR technique is the equipment with GC / MS gas analysis. Conclusions are made about the predominant presence in coal of low grade aromatic compounds with two rings and a high degree of substitution. The advanced technique allows to determine the content of thiols, mono- and disulfides, alkyl and ω-alkenyl thiophenes, alkyl benzothiophenes and alkyl dibenzothiophenes in coal.

The advanced AP-TPR-GC / MS technique, in combination with pre-adsorption and concentration of the released gases on Tenax, was applied for the first time to determine the composition of lignite lithotypes (Chapter 2). The use of this technique allows the author to investigate in detail the presence of sulfur-containing groups in lithotypes. Significantly improved sulfur balance has been shown as a result of reading the low molecular weight sulfur compounds, which is impossible to achieve with conventional pyrolysis techniques. Similar investigations have been done on household briquettes (Chapter 3). I would like to point out some significant conclusions regarding the role of the raw materials in the production of briquettes on the content of organic compounds in them. For example, for briquettes obtained from biomass, low levels of dialkyl sulfides and aliphatic thiols have been demonstrated. For comparison, lignite coal briquettes have been found to produce flue gases containing a considerable amount of aliphatic sulfides, mixed aliphatic-aromatic sulfides, aryl sulfides, aliphatic thiols, thiophene structures, methylthiophene and methylthiol.

The formation of more complex thiophene structures in bituminous and sub-bituminous coals has been identified. The author's research on biodesulfurized coal is very interesting (Chapter 4). AP-TPR-MS studies, including in helium atmosphere, have demonstrated the presence of complex sulfur compounds such as sulfones and sulfoxides, which is the result of aliphatic sulfur oxidation during the biodesulfurization. A new, improved procedure is proposed for the determination of elemental sulfur content in microbially desulphurized coal from different fields. The capabilities of the AP-TPR-MS / GC method for the determination of a number of organic sulfur compounds in solid bituminous residues have been demonstrated. Using this method, the author finds a beneficial effect of the combined chemical / microbial desulphurization of lignite. An important point in this section of the dissertation is the research on the changes that occur in the organic mass and sulfur functionalities of solid fossil fuels after various chemical and biochemical treatments. By useing the DTA-TG technique, Dr. Marinov demonstrated better ignition rates, a slight reduction in calorific value, and a number of disadvantages, among which increased combustion time and a decrease in the auto-ignition temperature of coal as a result of biodesulfurization. The overall positive effect of bio-treatment on environmental pollution has been assumed.

A novelty in candidate studies is the application of the AP-TPR-MS / GC technique to study the organic sulfur content of humic acids (Chapter 5). The presence of dialkyl sulfides, sulfoxides and sulfones has been demonstrated. It has been demonstrated that by combining AP-TPR with TD-GC / MS detection, a large number of compounds in humic acids such as aromatic structures and other hydrocarbons, in the presence of N- and S-containing compounds, can be determined. The detailed analysis achieved is the assumption for the origin of coal from different localities in Bulgaria. Both qualitative and quantitative evaluation of the components in the non-extractable part of the organic substance of humic acids, such as phenol and its derivatives, furans and benzofurans and some N- and S-containing organic compounds such as dimethyl disulfide, dimethyl trisulfide, thiophenes and benzothiophenes.

Undoubtedly, a significant contribution of the work is the illustrated advantage of the new approach for determining the organic composition of the volatile substances of humic acids of different origin (solid fuels, soils, peats, sediments, etc.). The author also demonstrates the possibilities of this method for detailed characterization of organic mass in coal. A large number of organic compounds have been identified, such as C_6-C_{10} alkyl benzenes, C_6-C_{15} linear hydrocarbons, naphthalenes, bi-phenyls, acetnaphthalene, fluorine and their alkylated homologs, mono- and di-romatic structures, substituted phenols and sesquiterpenoids (Chapter 6).

For the first time, Dr. Marinov applied the approach of reduction pyrolysis with AP-TPR technique and off-line TD-GC / MS detection to determine the organic components in pyrolysis gases from the fractional fractions of Bulgarian lignites (Chapter 7). A simplified scheme for the isolation and fractionation of lignite rates has been implemented. The analysis showed a significant decrease in the amount of paraffinic hydrocarbons and alkyl benzenes compared to the starting lignite, as well as an increase in the content of polycyclic aromatic hydrocarbons and N-containing compounds. The conclusion was made about the absence of toxic risk of environmental hazards, but recommendations were made for their constant monitoring, proving the social commitment and importance of the candidate's studies.

Dr. Marinov's investigations on the composition of biomass waste (Chapter 8) is potentially relevant to addressing alternative fuel and environmental issues. By using the relatively recently discovered process of water vapor pyrolysis, the author establishes the beneficial effect of the addition of CO_2 to water vapor on the carbonation of biomass. It has been found that in an inert environment the yield of the solid product is increased. Applicant's studies on the use of reducing pyrolysis to investigate the composition of the lignocellulosic portion of the biomass are very relevant. For the first time, the author makes a detailed qualitative and quantitative analysis of the volatile components released under these conditions. The modification of the AP-TPR-TD-GC / MS method, by replacing hydrogen with argon and subsequent adsorption concentration of the volatile products, allows Dr. Marinov to obtain new information on the composition of the non-condensable components in the pyrolysis of cellulose, hemicellulose and lignin which are crucial for the production of biodiesel and the protection of human health. The research results have been published in 26 articles in specialized journals and 14 peer-reviewed papers in scientific forums. 14 of the articles presented are in Quartered magazines Q1, 4-Q2; 2-Q3 and 3-Q4. The results were partially reported at 30 conferences in Bulgaria and abroad. The research was funded by 2 contracts with the National Scientific Fund, 4- by the Belgian Research Fund and supported by bilateral collaborations with the Academies of Sciences of Turkey (2 projects) and Ukraine (2 projects). The significance of the obtained results is proved by the high citation of the publications included in the dissertation (328 citations of 20 articles were noted). In most publications, Dr. Marinov is first or second author. All this, as well as the carefully drafted separation protocols with the co-authors, undoubtedly prove the leading role and the significant personal contribution of the candidate in the conducted studies.

The abstract is written very well in Bulgarian and English, clearly and accurately reflecting the content of the dissertation.

Conclusion

The dissertation presented for review is a systematic exposition of Dr. Marinov's experience in the qualitative and quantitative characterization of the state of sulfur in coal and other objects, as well as the volatile organic compounds released during their thermal treatment. I believe that the development of reduction pyrolysis by combining it with new, highly sensitive analytic techniques such as MS-GC with pre-adsorption concentration of the components, and the broad demonstration of the capabilities of the methods on a large number of diverse sites (coal of different rank before and after biodesulfurization, humic acids, briquettes, lignincellulosic biomass, coal leaching products in water) can be considered as major contributions from the research described in the dissertation. Undoubtedly, the results of the studies are both methodological and of considerable practical importance for solving a number of environmental problems related to the exploitation of traditional fuels and synthesis of lignin-cellulosic biomass based fuels. Interesting emphases from the highly applied research are the conclusions regarding:

- the effect of pyrolysis temperature on the preparation of lignincellulosic biomass biofuels on the composition of the sulfur-containing compounds released in non-condensable volatile organic products;
- preserving the structure and calorific value of coal after bio-treatment.

I believe that the direct method developed for the quantification of sulfur-containing organic compounds in coal and other solid insoluble and non-volatile natural materials, as well as the method for the direct determination of elemental sulfur in coal and the determination of organic components in pyrolytic gases in combination with detailed and accurate description of sample preparation and experimental can be a valuable guide for researchers working in the field. The dissertation summarizes the vast, time-consuming research and the extensive experience, knowledge and skills of Dr. Marinov to perfect the applied technique by combining modern analytical techniques and application for solving important problems related to energy sources and human health. Evidence of the quality and usefulness of the research is the significant number of publications in prestigious publications, as well as the high number of citation.

Therefore, I highly appreciate the dissertation submitted for the review and strongly recommend to the Scientific Jury to award Ass. Prof. Dr. Stefan Marinov the Doctor of Science degree in Professional Field 4.2. Chemical Sciences, specialty "Organic Chemistry".

Sofia, 2.03.2020 Reviewer:

/Prof. DSc. Tanya Tsoncheva/