

## REFEREE REPORT

By Prof. DSc Pavlinka Aleksandrova Dolashka, Institute of Organic Chemistry with Centre of Phytochemistry, Bulgarian Academy of Sciences for PhD of Doctoral Thesis in the field of higher education: 4. "Natural Sciences, Mathematics and Informatics"; professional area: 4.2. "Chemical Sciences"; scientific specialty "Organic Chemistry",

**Applicant:** Assoc. Prof. Stefan Penchev Marinov, PhD, Laboratory of "Chemistry of Solid Fuels", Institute of Organic Chemistry with Center for Phytochemistry, Bulgarian Academy of Sciences

**Topic:** "Development and application of reductive pyrolysis in the study of organic sulphur forms in fossil fuels and biomass organic matter composition"

### **I. Biographical data of the applicant**

In 1980 Dr. Stefan Marinov graduated from Higher Technology School of Chemistry and Metallurgy. He defended his doctoral thesis in 1986 as a full-time PhD student at IOCCF, BAS 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

### **II. Review of the DSc thesis**

The pack of documents presented for review in paper and electronic form have been prepared in accordance with the Law for the Scientific Development in Bulgaria, the Rules of its Application as well as of the Internal Rules and Regulations of the Institute of Organic Chemistry with Centre of Phytochemistry (IOCCP) for acquiring the scientific degree "Doctor of Sciences".

Actuality of the thesis topic is a significant environmental problem when burning fuels, especially high sulfur coal. The studies performed are methodological contributions related to the determination of the sulfur compounds content, conclusions and environmental contributions.

#### ***Characterization and evaluation of the thesis***

The dissertation submitted for review is written on 172 pages, of which 142 pages are text with 25 tables and 42 figures, conclusions and contributions. A dissertation is very well designed, illustrated with tables and figures. Each section concludes with a summary and a conclusion, especially important summarizing a large volume of experimental material.

Introduction - a short, concise introduction to the topic of the study. The literature review covers 14 pages, 205 references were cited, 45% of which were published after 2000.

Aim and Objectives - the main objective of applying the reduction pyrolysis approach in its development, and in combination with modern detection analytical techniques is to track qualitatively and quantitatively the available and quantified organic sulfur functionalities and other groups of individual organic compounds in coal and in other solid natural products are convincingly solved and are completed on 5 tasks.

Materials, methods and instrumental techniques - are presented in detail in item. The materials are coal samples: lignites, coal products and microbial organisms.

### ***Results and discussion***

The dissertation represents the consistent examination of the method of pyrolysis in its development and improvement by applying different detection techniques in the atmosphere of different gases and achieving qualitative and quantitative results. Each section concludes with a brief conclusion which is a very positive and well-realized idea.

1. Desulphurization treatments and research by reductive pyrolysis of organic sulfur-containing compounds and coal organic matter.
2. Study by reducing pyrolysis of organic sulfur functionalities and the organic matter composition of Maritza East lithotypes. It has been found that the combination of different AP-TPR techniques the information about the presence of different sulfur groups in lithotypes was achieved. It should be noted that the application of the AP-TPR-GC/MS "off-line" analytical study clarifies the issues of low-grade organic sulfur in coal, as well as completes information on the specification of sulfur in solid organic sulfur-containing materials.
3. Investigation by reductive pyrolysis of organic sulfur functionality and organic matter composition of house-hold briquettes is an environmentally important issue.
4. Study by reductive pyrolysis of organic sulfur functionalities and organic matter composition of biodesulphurized coal:

6. Pyrolytic study of the organic matter of "Stanyantsi" lignitec by applying the AP-TPR "off-line" TD-GC/MS instrumental technique and determination of sulfur compounds in coal and individual compounds at the molecular level.
7. Reductive pyrolysis of aqueous leachates from "Maritsa East" and "Stanyantsi".
8. Pyrolytic studies of waste vegetation products and three main components of ligno cellulosic biomass.

#### ***Contributions and importance of the results to science and practice***

The conclusions and contributions are formulated briefly and clearly. The presented conclusions and contributions, which with the novelty and originality of science, in addition to being fundamental and methodical in nature, are applied in practice and are highly appreciated.

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

### **III. Personal impressions**

I know Assoc. Prof. Dr. Stefan Marinov and his scientific research articles since many years. Although most of Assoc. Prof. Dr. Marinov papers are published in co-authorship with Bulgarian and foreign scientists, the leading role are obvious.

### **III. CONCLUSION**

The dissertation is written in a concise manner and has an original contribution to the science. The topic of the dissertation is up-to-date and is related to contemporary environmental requirements. Assoc. Prof. Dr. Eng. Stefan Marinov possesses deep theoretical knowledge in the scientific specialty organic chemistry, demonstrates qualities and skills and fully complies with the requirements of the Law for Scientific Development in Bulgaria, the Rules of its Application and the Regulations for its implementation, as well as the Internal Rules for the implementation of the Law at IOCCP-BAS.

In view of the above, I fully believe in my positive assessment of the research presented by the dissertation, abstracts, results and contributions reviewed above, and propose to the Honorable Scientific Jury to award the degree of Doctor of Science to Assoc. Prof. Dr. Stefan Penchev Marinov, PhD in Higher Education: 4. "Natural Sciences,

Mathematics and Informatics, Professional, area Chemical Sciences - 4.2., scientific specialty  
– “Organic Chemistry”

25.03. 2020. г.



Reviewer:.....

(Prof. Pavlina Dolashka, DCs)