OPINION
Submitted by Prof. PhD Alexander Eliyas at the Institute of Catalysis - BAS

on Doctor of Sciences Thesis for acquiring the scientific degree **"Doctor of Sciences"**

in professional direction 4.2 "Chemical Sciences"
scientific research specialty "Organic Chemistry"

Author: **Assoc.Prof. PhD Ing. STEFAN PENCHEV MARINOV**
(Institute of Organic Chemistry with Center of Phytochemistry - BAS)

Topic: Development and application of reduction pyrolysis in studies on the forms of organic sulfur and composition of organic mass of fossil solid fuels and biomass

1. General presentation of the procedure and of the candidate

I was appointed as member of the Scientific Jury by an Order № РД-09-19/24.01.2020, issued by the Director of IOCh CPh-BAS in connection with the procedure for acquiring the scientific degree „Doctor of Sciences" in professional direction 4.2 "Chemical Sciences", scientific research specialty "Organic Chemistry" for the needs of the Laboratory "Chemistry of Solid fuels". The order was issues on the basis of article 25 and article 26 of the Regulations about the conditions and order for acquiring research degrees at IOCh CPh-BAS and decision of the Scientific Council (Record of proceedings № 1 dated 16.01.2020). Thereafter followed a meeting of the Scientific Jury on 29.01.2020 and it was decided that I should prepare a reviewer's opinion. A set of documents and materials was given to me for this purpose:

- Scholarly essay of Doctor of Sciences Thesis on the topic „Development and application of reduction pyrolysis in studies on the forms of organic sulfur and composition of organic mass of fossil solid fuels and biomass" – in Bulgarian and in English language
- Compact disk, containing the following files: the complete text of the Doctor of Sciences Thesis, curriculum vitae, diploma certificates, statements by L. Butuzova, M. Stefanova, V. Minkova revealing the specific contributions of the coauthors in their common publications, two records dividing the contributions and explaining who is the first leading author in their joint research works, the articles upon which the Doctor thesis is based, a list of 14 participations in conferences and symposia of Assoc.Prof. Marinov, his leadership in 17 projects and a list of noticed citations – a total of 328 citations.

The set of documents and materials, submitted by Assoc. Prof. PhD Stefan Marinov is in accordance with the Regulations for the Career Development of the Academic Staff of IOCh CPh – BAS satisfying the specific criteria of IOCh CPh – BAS for acquiring of the scientific degree „Doctor of Sciences".

The Doctor of Sciences Thesis represents a summary of 40 publications, containing 41 figures, 25 tables, 1 appendix and 205 literature references. The results have been reported at 30 scientific conferences in our country and abroad.

I have no remarks concerning the materials – I would like to point out the painstaking accuracy of Assoc. Prof. PhD Stefan Marinov in the course of preparing and submitting this complete set of documents and materials материали.

Short biography data

As one can see in the data of the represented curriculum vitae he graduated from the Higher Chemical Technological University in Sofia in 1980. At first he acquired the position of "chemist" in the Scientific Research Institute for Chemistry and Pharmacy in 1980, while thereafter he became a PhD student (regular form of education) at the Institute of Organic Chemistry – BAS during the period 1980-1985 defending his PhD Thesis there in 1986 acquiring the position of "research fellow". Stefan Marinov was appointed as an "Associated Professor" at the Institute of Organic Chemistry in 2001 and now he has 40 years total length of service.

2. Actuality of the thematic research direction

The Doctor of Sciences Thesis considers a problem, which has actuality both in scientific aspect, as well as in the aspect of practical applicability, as it is focused on the use of solid fossil fuels – their combustion in electric power plants. It exerts a harmful effect contaminating the environment due to the content of sulfur-containing organic compounds. This fact imposes carrying out systematic investigations of the chemical composition of coal with the aim to prevent the liberation of sulfur oxides, leading to acidic rains, which damage the crops and in addition their inhalation is harmful for the human health. From the point of view of applying analytical methods in this respect – it is hampered due to the insolubility of sulfur-containing organic compounds in organic solvents. So it becomes necessary to seek and apply a new approach and eventually new analytical methods for this difficult for studying subject. The so far applicable traditional methods of purification cannot solve this problem. This fact makes the present Doctor Thesis very useful.

The specific experimental tasks, listed in Section II of the Doctor Thesis are arranged chronologically and they give a good idea about the scope of the investigation – the various types of coal samples and the different ways of their characterization, whereupon the method of reduction pyrolysis plays the leading role. Lignite coal samples have been studied, originating not only from Bulgaria, but also from Turkey and Ukraine, as well as coal products and microbial organisms. The applied set of methods and instrumental techniques is really impressive having a wide scope, enabling deploying studies having many aspects.

3. Knowledge on the problem

The author is well acquainted with the state of the present investigations in this field, which is clearly visible from the long list current literature references, included in the thesis and their in depth analysis and the competent interpretation of these references.

4. Methodology of the investigation

The chosen method for the investigation (reduction pyrolysis) has been developed further and considerably improved by Stefan Marinov – this is the application of temperature-programmed reduction at atmospheric pressure (AP-TPR) and respectively temperature-programmed oxidation at atmospheric pressure (AP-TPO). These are combined respectively with MS detection, as well as GC/MS analyses and XPS analyses. This combination enabled achieving the purposes, preset before starting the investigations – to follow successfully the selective desulfurization and identifying the signals in the kinematograms and attributing them to some specific functional groups containing sulfur.

5. Characteristics and evaluation of the doctoral thesis and its contributions

I would like to point out as characteristics and evaluation of the thesis that, on one side, it is extremely narrow focused on desulfurization treatments and application of reduction pyrolysis, but on the other side – the investigations have a wide scope from the point of view of the studied objects, to which it has been applied – coals from Bulgaria: „Maritza Iztok", „Elhovo", „Katrishte", „Stanyantzi", but also from „Donetzk" in Ukraine and lignites from "Mequinenza", Spain. This fact, without any doubt, determines a great variety of organic sulfur functional groups and it requires wide scope of the knowledge on behalf of the candidate, including also knowledge in the field of biology – I have in mind revealing the influence of the microbial desulfurization, and not only chemical desulfurization. As far as it concerns the contributions of the doctoral thesis in the first place I would distinguish improving and perfectioning of the analytical approach of the reduction pyrolysis and widening its scope including the application of AP-TPR. One can see here the significance as a fundamental scientific achievement, while in the aspect of applicability I would point out all the studied VOCs and PAHs in the products from leaching of the water soluble organic compounds in lignite coals, whose deposits are in immediate vicinity to endemic zones in Bulgaria. This is especially important for ecological observations and monitoring.

6. Evaluation of the publications and personal contributions of the candidate

The publications, included in the doctor thesis – a total of 26, out of them 13 are indicated in the scholarly essay to have been published in journals belonging to the first quartile Q1 – calculated as percentage (50% of all the publications) this is very impressive, 4 articles are Q2, 2 other articles are Q3 and 3 articles Q4. The response to the results of the doctor thesis in publications of other authors amounts to 325 citations (summing up the numbers indicated in Section VIII, while the summarized impact-factor makes a total of 41.99. It is difficult for me to distinguish the personal contribution of the candidate in publications in co-authorship with other researchers. Taking into account the number of the coauthors: he is the only author in 1 publication № 23; while in the rest of the papers he has three or more coauthors – in my opinion this fact gave the opportunity to the candidate to have access to apparatus abroad and access to samples, which have different composition, compared to our coals and this has a positive aspect of enriching the knowledge of the candidate. I think that we should encourage Bulgarian investigations within the framework of international cooperation and that we should not enclose ourselves within nationally restricted frameworks – collaboration during the work in a team of several members means that the candidate has compatibility and tolerance as moral qualities.

7. Scholarly essay

The style and the quality of the contents of the scholarly essay – in my opinion it is not only shaped in complete accordance with the requirements of the respective regulations, but also in concise form it gives quite a good idea about the basic results and achievements of the thesis for specialists in other fields, having in one way or another touch points with this topic.

8. Recommendations for future use of the contributions and results of the thesis

Considering the possible future use of the basic and applied research contributions of the doctor thesis I can make the following recommendation. The candidate is quite well acquainted with the properties of polycyclic aromatic hydrocarbons and sulfur-containing aromatic organic compounds especially their stability. This knowledge could be useful in case of eventual widening of the scope of the investigations in direction to applying Co-Mo, Ni-Mo and Ni-W

catalysts for hydrodesulfurization of oil fractions. Usually in such catalytic studies one uses thiophene or benzothiophene as model sulfur-containing compounds for testing the activity of synthesized in laboratory Co-Mo, Ni-Mo и Ni-W catalyst samples for hydrodesulfurization of oil fractions. Stefan Marinov could propose some other suitable model sulfur-containing aromatic organic compounds for the catalytic activity tests and he could be useful giving advice with his experience and knowledge, based on his experimental data about the stability in possible combined research work between the Institute of Organic Chemistry with Phytochemistry Center and the Institute of Catalysis – BAS.

CONCLUSION

As a member of the Scientific Jury I express my deep conviction and support for bestowing the scientific degree „Doctor of Sciences" to the candidate Assoc.Prof. PhD Eng. Stefan Marinov. The dissertation thesis contains original contributions in view of the obtained basic and applied research results and it completely satisfies the requirements of the Law for the Development of the Academic Staff in the Republic of Bulgaria (LDASRB), the State Regulations for the application of LDASRB and the Regulations for the application of LDASRB in BAS and it is in correspondence with the specific requirements and the Regulations of IOCh-PhC-BAS for observing LDASRB in professional direction 4.2 Chemical Sciences and research specialty „Organic Chemistry".

Date 16.03. 2020 **Opinion submitted by**:

…….....

(Prof. PhD Alexander Eliyas)