Attitude of Reviewer

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With respect to the Doctoral Thesis presented for awarding the degree
"Doctor of Sciences" in the Professional Field 4.2. "Chemical Sciences",
scientific specialty „Organic Chemistry"
Author: Assoc. Prof. Dr. Stefan Penchev Marinov,
Institute of Organic Chemistry with Centre of Phytochemistry, BAS
Topic: " Development and application of reductive pyrolysis in the study of organic sulphur forms in fossil fuels and biomass organic matter composition"

The documents presented by Assoc. Prof. Marinov with respect to the thesis defense procedure are in accordance with the Regulations for the Development of the Academic Staff of the Institute of Organic Chemistry with Centre of Phytochemistry, Bulgarian Academy of Sciences (IOCCP – BAS), and meet the criteria of the Institute for obtaining the scientific degree "Doctor of Sciences".

The thesis of Assoc. Prof. Marinov is dedicated to the study of the composition and forms of organic sulfur in coal and in other fossil natural products from different local and foreign fields by using the pyrolytic reduction method by means of temperature-programmed reduction in hydrogen flow at atmospheric pressure. In the course of research, this technique has been repeatedly improved in its detection part, and the replacement of hydrogen with inert gas provides an additional opportunity to study the composition of the organic mass of fossil fuels and biomass. The literature review shows an excellent knowledge of the topic by covering 205 literature sources and in details are presented the methods and techniques used to determine organic sulfur and its compounds in coal and other solid, non-volatile coal based materials. On the basis of the review, the aim and tasks of the thesis are very clearly formulated, the successful solution of which is related to the application of the reduction pyrolysis approach and its development in combination with the use of contemporary detection analytical techniques. The chosen methodological approaches comprise the use of the temperature-programmed reduction at atmospheric pressure (AP-TPR) method and its coupling with mass spectral detection techniques directly or indirectly with gas chromatographic/mass spectral detection techniques, and in combination with temperature-programmed oxidation at atmospheric pressure (AP-TPO), fully comply with the tasks set. Both classical and state-of-the-art methods in the field of chemistry and physics are applied.

The thesis contains original contributions, which can be characterized as novelty for science and expansion of the existing knowledge, as well as contributions of confirmatory nature and methodical character with undoubted potential for practical application. New quantitative and qualitative information on organic sulfur-containing functionalities in coal has been obtained with the help of the developed and sophisticated analytical approach of reductive pyrolysis. For the first time, the reductive pyrolysis method with the AP-TPR technique has been applied for

the study of organic sulphur functionalities in humic acids. For the first time have been quantified the non-condensable volatile compounds by pyrolysis of the main lignocellulosic biomass building blocks. For the first time by reductive pyrolysis have been studied the volatile organic compounds and polycyclic aromatic hydrocarbons in leachates products of water-soluble lignite-based organic matter in the vicinities of some endemic zones in Bulgaria. A direct method for the quantitative determination of organic sulphur compounds in coal and in other solid insoluble and non-volatile natural materials was developed. A new protocol for the direct determination of elemental sulphur in coal is proposed that provides accurate data for the organic sulphur distribution. The oxidative mechanism of microbial desulfurization in coal has been confirmed. The use of biodesulfurization in solid fuel processing technologies is very promising, with microbial treatments not disrupting the coal matrix and changes in the calorific values of the treated sites being negligible. The knowledge on the composition of lignite aqueous extracts has been confirmed and enriched. In Bulgarian lignite leaching products have been found nitrogen-containing compounds whose total amount is low and they do not represent a toxic environmental risk but could have a carcinogenic/mutagenic effect at prolonged exposure to the organisms and should be subject to future monitoring. For the first time polycyclic aromatic hydrocarbons in the pyrolysis fraction above 600°C have been identified in the flue gases from pyrolysis of the three main components of lignocellulosic biomass, so they should be monitored with particular care in multi-tonal industrial pyrolysis processes.

I have no criticisms and no recommendations for the thesis, I have only one minor note - no data was provided on the amount of organic sulfur compounds retained in the coal or in the tar after conducting the reduction experiments with the AP-TPR technique.

The results presented in the thesis are published in 40 publications, including 26 scientific papers with a total impact factor of 41.99 and 14 papers from scientific conferences, published in full text. The quality of the publications is demonstrated by the number of those in journals from the first quartile in the respective field (Q1) - 14, as well as by the number of citations of the papers included in the thesis - 328, or an average of more than 8 citations per publication. The thesis results are also presented at 30 scientific forums in Bulgaria and abroad. The significant personal contribution of Assoc. Prof. Marinov in the publications is undoubted, and the fact that he is the first author or corresponding author in 20 out of 40 publications is indicative. I would like to add also my personal impressions of Assoc. Prof. Marinov - I have known him for over 20 years as a competent, focused, persistent and dedicated researcher.

The thesis abstract is well worked and fully reflects in the summary the conducted research and the results obtained in the dissertation.

CONCLUSION

The thesis of Assoc. Prof. Marinov contains substantial and significant original fundamental and applied scientific contributions in the field of organic chemistry, which meet all the requirements of the Law on the Development of the Academic Staff in the Republic of

Bulgaria, the Regulations for the implementation of the same Law and fully meet the specific requirements of the corresponding Regulations of the IOCCP - BAS.

The thesis shows that Prof. Marinov possesses in-depth knowledge and professional skills in the scientific specialty "Organic Chemistry", which he has been able to demonstrate in the conducted research and summarized in the form of original and significant scientific contributions.

On the basis of the above considerations, I strongly propose to the honorable members of the scientific jury to bestow to Associate Professor Dr Stefan Penchev Marinov the scientific degree “Doctor of Sciences” in the Professional Field 4.2. Chemical Sciences, scientific specialty “Organic Chemistry”.

26.03.2020 **Reviewer**: .....

Assoc. Prof. Dr. Momtchil Dimitrov