### REVIEW

# from Professor Irena Kostova Sofia University "St. Kl. Ohridski"

# Department of Geology, Paleontology and Fossil Fuels

Member of the Scientific Jury in connection with the procedure for awarding the degree of Doctor of Science, announced by the Institute of Organic Chemistry with the Center of Phytochemistry - BAS, in the professional field 4.2. "Chemical Sciences", scientific specialty "Organic Chemistry" for the needs of the Laboratory of Solid Fuels Chemistry.

Stefan Marinov completed his higher education in 1980 at the Higher Chemical Technology Institute - Sofia, Faculty of Organic Technology, Department of Technology of Organic Synthesis and Fuels. From 1981 to 1985 he was a doctoral student at the Institute of Organic Chemistry - BAS, where in 1986 he successfully defended his doctoral thesis and obtained a doctoral degree. From 1986 until today he has been working at the Institute of Organic Chemistry with the Center of Phytochemistry - BAS, where he is engaged in scientific research, and since 2001 he is an associate professor at the same institute. In 1993 he specialized at the University of Hasselt in Belgium and in the period 1994-1995 was a guest researcher at the same university. Assoc. Prof. Stefan Marinov was a scientific adviser on the Bulgarian side of a bilateral international doctoral study program between the University of Hasselt - Belgium and the Institute of Organic Chemistry with the Center of Phytochemistry - BAS, successfully defended in 2012 with a European diploma by the doctoral student Lenia Gonçalves. Assoc. Prof. Stefan Marinov has reviewed a number of articles for prestigious international journals by Elsevier and other international publishers.

## Publishing activities and scientific contributions.

For the participation in the present competition for the award of the scientific degree "Doctor of Sciences" Dr. Stefan Marinov presented a totally 40 papers and other scientific works, which include:

- Publications in Q1 issues 14;
- Publications in Q2 issues 4;
- Publications in Q3 issues 2;
- Publications in Q4 issues 3;
- Publications in other scientific issues 3;
- Extended presentations in per review conference proceedings 14.

I would like to point out in particular that Assoc. Prof. Stefan Marinov has a brilliant publishing activity and most of the scientific articles have been published in prestigious international journals with high impact factors such as Fuel, Fuel Processing Technology, International Journal of Coal Geology, Thermochimica Acta and others. The applicant's contributions, which are neatly noted in the dissertation and the thesis abstract and reflected in his publishing activity can be summarized as follows.

# Contributions of fundamental nature:

- 1. New quantitative and qualitative data about organic sulphur-containing functionalities in coals has been obtained by developing and refining the analytical approach of reductive pyrolysis.
- 2. The reductive pyrolysis method with the AP-TPR technique for the study of organic sulphur functionalities in humic acids has been applied for the first time.
- 3. Non-condensable volatile compounds by pyrolysis of the main lignocellulosic biomass building blocks have been determined for the first time.

- 4. VOCs and PAHs have been studied by reductive pyrolysis in leachates products of water-soluble lignite-based organic matter in the vicinities of some BEN endemic zones in Bulgaria for the first time.
- 5. The oxidative mechanism of microbial desulphurization in coal has been confirmed and low grade coal biodegradation has been found to occur with the formation of complex sulphur structures, including some with mixed functionality like sulphones and sulphoxides.
- 6. Knowledge on the composition of lignite aqueous extracts has been confirmed and enriched. The obtained data have environmental significance, since the presence of N-, S- and O-heteroatom containing compounds has been established, which could penetrate groundwater near to the coal basins.

## Contributions related to the new methods implementation:

- 1. A direct method for the quantitative determination of organic Sulphur compounds in coal and in other solid insoluble and non-volatile nature materials was developed.
- 2. A new protocol for the direct determination of elemental sulphur in coal is proposed and accurate data for the organic sulphur distribution have been provided.

# Contributions with applied nature:

- 1. It was found that there were not PAHs in the  $< 600^{\circ}$ C flue gases from pyrolysis of the three main components of lignocellulosic biomass. During lignin pyrolysis in the temperature range  $600^{\circ}$ C  $800^{\circ}$ C, non-condensable VOCs containing sulphur compounds, i.e. alkyl sulphones, di- and trimethyl sulphides, were tracked. The results indicate that in the preparation of biofuels by pyrolysis of waste products, sulphur-containing compounds are emitted by non-condensable VOCs at temperatures  $> 600^{\circ}$ C. The information should be considered during multi-tonnage production as emissions could pose serious environmental problems.
- 2. It was determined that the application of biotreatments by selected microorganisms and fungi did not significantly affect the coal matrix and the calorific values were maintained.

A total of 328 citations of the candidate's publications were notice in the international journals with impact factors, as well as in other foreign and national journals and scientific publications. These large number of quotes shows the importance of the research of Assoc. Prof. Stefan Marinov and the impact of his work on the international scientific community. Assoc. Prof. Stefan Marinov has presented the results of his research in connection with his dissertation at 30 international and national scientific conferences where he has a number of oral presentation or posters.

In addition to the intensive scientific and teaching activity Assoc. Prof. Stefan Marinov has been the leader of 17 national and international research projects including joint projects with scientists and teams from Belgium, Turkey and Ukraine. In these projects he was engaged in solving problems that are closely related to the topic of the present dissertation.

### **Teaching activity**

Together with his successful scientific work, Assoc. Prof. Dr. Stefan Marinov was a scientific adviser of a doctoral thesis on the following topic "Sulfur and organic Sulfur alterations in biodesulphurized low rank coals". The doctorate was bilateral between the University of Hasselt in Belgium and the Institute of Organic Chemistry with the Center for Phytochemistry - BAS, and Dr. Srefan Marinov was a leader from Bulgarian side. The PhD was successfully defended in 2012 by Lenia Gonçalves-Musakova, who received a European PhD diploma.

### Conclusion

In conclusion, I would like to emphasize that Assoc. Prof. Stefan Marinov meets all the requirements of the law, both in terms of science, as well as in his project and teaching activity for awarding the degree of Doctor of Sciences in the science specialty "Organic Chemistry" at the Institute of Organic Chemistry with a Phytochemistry Center - BAS.

I believe that Assoc. Prof. Stefan Marinov has an excellent reputation as a research scientist both among the Bulgarian and the world scientific community. He is a teacher and colleague who readily shares his experience and often helps younger colleagues.

The above mentioned gives me reason **to recommend** that Assoc. Prof. Stefan Marinov be awarded the degree of Doctor of Science in the field of Organic Chemistry. I will **vote in favor** as a members of the Scientific Jury.

Member of the Scientific Jury:

/Professor Irena Kostova/

25 March 2020