REFEREE REPORT

By Prof. Ekaterina Georgieva Filcheva, 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", Author: Assoc. Prof. Stefan Penchev Marinov, PhD. Topic: "Development and application of reductive pyrolysis in the study of organic sulphur forms in fossil fuels and biomass organic matter composition"

1. Subject of review

The production of Assoc. Prof. Dr. Eng. Stefan Marinov has been established with the requirements of Art. 26 paragraph 2 and 3 of the Law on the Development of Academic Staff in the Republic of Bulgaria and the Regulations for its implementation, as well as the criteria presented in an annex to the Regulations for the Application of the Law in the Institute of Organic Chemistry with the centre of phytochemistry (IOCCP), BAS for the scientific degree "Doctor of Sciences" and significantly exceeding the minimum requirements by more than 750 points (Total: A, B, D, E, E = 1673 points (882 points minimum).

The pack of documents presented for review in paper and electronic form contains: CV (European standard), DSc thesis, thesis abstract (Bul. and Engl.), reference for compliance with the criteria for the scientific degree "Doctor of Sciences", copies of diplomas for PhD and Assoc. Professor degrees, a list of 26 publications in scientific journals, 14 reports in the scientific conferences with full texts of related with the presented thesis, a list of 30 conferences where the results have been reported, a list of citations, information about participation in research projects, supper visor of phD student Lenia Gonsalvesh-Musakova, titled „Sulphur and organic sulphur alterations in biodesulphurized low rank coals", 2012, Hasselt University and Institute of Organic Chemistry with Centre of Phytochemistry, BAS, List of National (5) and International projects (10), Separation protocols (5). The materials 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".

2. Brief Biographical data

Assoc. Prof. Dr. Stefan Marinov was born on 12.02.1955. In 1980 he graduated the Chemical Technology Metallurgy University - Sofia and continued his education (1980-1985) at the IOCCP, Bulgarian Academy of Sciences, where he acquired a phD degree (1986). The same year he started his scientific carrier as Assistant Prof. In the same Institute she consecutively occupies all academic positions from "chemist" to "Assoc. Prof." in 2001.

Assoc. Prof. Dr. Stefan Marinov holds Post Doc Position in Belgium: in 1993 for 3 months and 2 times was "Invited scientist": 1994-1995 for 6 months and in 2000 for 2 months. Preparation as a full-time doctoral student, habilitation through 2001, visiting and working in prestigious laboratories, the management of national and international projects formed Assoc. Prof. Dr. Stefan Marinov as an experienced specialist in working with precision equipment, ability to interpret results as well as good communication and teamwork skills.

3. Actuality of the thesis topic.

In Bulgaria, the main pollutants, depending on the region, are dust, sulfur dioxide, nitrogen oxides, lead aerosols, ammonia, phenol, hydrogen sulfide. The latter is the cause of acid rain, affecting plants, metals, destroying rocks, buildings, cultural monuments, and killing animals in rivers and lakes. This is a significant environmental problem when burning fuels, especially high sulfur coal. To determine the properties of solid fossil fuels, a methodology and accurate technique are needed to characterize the content of sulfur compounds and other groups of individual organic compounds in coal and other solid natural products before and after desulphurization treatments, and to determine the volatiles of lignin cellulose biomass. This is clearly formulated aim and the five experimental tasks in the dissertation. The studies performed are methodological contributions related to the determination of the sulfur compounds content,

conclusions and environmental contributions. They relate to the goals set and the topics discussed in the EU and also to the “Green Deal”, particularly relevant at the moment, which emphasizes the relevance of the thesis.

4. Familiarity with the scientific problem

The candidate's very well-informed knowledge is evident from the literature review, made very critically, which gives an idea of the author's personal opinion as well as the literature used. The literature review covers 14 pages, about 1/10 of the dissertation. 205 references were cited, 45% of which were published after 2000. This proves both the actuality of the problem being developed and the author's very good awareness of the presence and quantitative determination of sulfur in various forms and the removal of organic sulfur from coal, methods of pyrolysis, and the application of non-destructive, direct instrumental techniques for this purpose.

This section published scientific findings covering developments in methods for the determination of organic sulfur and its compounds in coal and other solid, non-volatile, coal-based materials. In the laboratory of Fuel Chemistry, IOCCP-BAS, the determination of organic sulfur and its functionality in coal was carried out by so-called “wet chemical” methods. By refining the methods, organic sulfur compounds are determined by pyrolysis. The major compounds quantified by GC/MS detection technique are volatile sulfur compounds formed, i.e. H_2S, COS, CH_2S and SO_2. Later on, a thermo kinetic approach was applied to the qualitative and quantitative determination of sulfur functionalities. Subsequently, a modified version of the reduction method, the "APP TPR", is proposed. AP-TPR, in the presence of sulfur-specific detectors, provides qualitative and quantitative information on the types of sulfur and sulfur functionality in volatile substances in coal pyrolysis. Later, it went through various stages and introduced the AP-TPR technique implemented in combination "on-line" with the MS analyzer and the original enhancement: GC/MS detection system connected "off-line" with the AP-TPR technique. Quantitative studies are performed for the content of sulfur functional compounds at the molecular level using N_2 or Ar with a starting sample of 10-30 mg.

5. Methodology of the study

The chosen research methodology allows achieving the set goal and the five tasks that are solved in the dissertation.

1. Materials A. Coal samples: Lignites “Maritza East”, “Elhovo”, “Katrishte”, “Stanianci” - Bulgaria; “Kairhan-Beypazar”-Turkey and “Mequinenza”-Spain; Sub-bituminous coal “Bobov Dol” and “Pirin”- Bulgaria, Low and high rank coal " Donetsk “, Donbass basin, Ukraine. **B**. Coal products (lithotypes, humic acids) and biomass: Lithotypes from “Maritza East” lignites; Humic acids from “Maritza East” lignites, “Stanianci” and from leonardite; Humus-like products from biodesulfurized lignites “Maritza East”; House-hold briquettes for burning based on coal and sawdust; Waste biomass products; The following materials were supplied from the commercial experimental testing network: Cellulose - ARBOGEL BE 600/30 from JRS.EU; Lignin - №470996 - 100G, Sigma-Aldrich; Xylan (hemicellulose analogue and substitute) - No.95588, Wood – “Fluka” birch. **C.** Microbial organisms. The following microorganisms were used: Trametes versicolor (ATCC No. 200801), (TV-1), (TV-2), fungi; Pleurotus Sajor-Caju, (PSJ) fungi; Phanerohaeta Chrysosporium (ME446), (PC), fungi; Mixed cultures of microorganisms (ATCC No. 39327), (MC), bacterium; Sulfolobus Solfataricus - (ATCC No. 35091) (SS) a thermophilic and acidophilic bacterium; Acidothiobacillus ferrooxidans (A. ferrooxidans) bacterium; Pseudomonas putida (PP) bacterium; Pure cultures of microorganisms were obtained from the American microbial bank ATCC (American Type Culture Collection).

2. Methods and Instrumental Techniques: The method of reduction pyrolysis over a 25-year period has been applied and refined, with improvements to the pyrolytic reduction method and the corresponding AP-TPR technique. A potentiometric detection system was used to track and semi-quantify the H_2S formed from the pyrolysis reactions at specific temperatures for the various sulfur-containing compounds. An advanced AP-TPR reactor was used in the improvement of the AP-TPR technique. The AP-TPR technique is combined with a pyrolysis gas potentiometric detection system. At this stage, Assoc. Prof. Dr. Marinov joins a team to refine the

reduction AP-TPR method and apply the appropriate detection technique to study sulfur organic functionality in coal. The next step in the AP-TPR-MS pyrolysis reactor is the on-line coupling, which avoids the pyrolysis gases to condense until they enter the mass spectrometer. The AP-TPR-GC/MS "off-line" incorporates a powerful GC/MS analytical detection system. The AP-TPR pyrolyzer is connected “off-line” to a GC/MS apparatus for the analysis of pyrolisis gas emissions. The pyrolysis gases released from the TPR reactor pass through tubes filled with Tenax absorbent which are cooled in ice. The tubes were replaced at 50^{o}C temperature intervals in the range of 250 to 950 ^{o}C, depending on the sample tested. The absorbent gases are directed for analysis by thermal desorption, etc. TD-GC/MS. This approach of study with the AP-TPR technique makes it possible to investigate a plurality of sulfur-containing compounds at the molecular level and, under the replacement of H_2 by an inert gas stream, solid and non-volatile organic-containing materials, also at molecular level, under standard conditions. Direct studies of sulfur-containing compounds were performed by XPS analysis. Differentially thermogravimetric (TGA) and differential thermal (DTA) analyzes were performed to characterize coal samples resulting from chemical and microbial desulphurization treatments applied.

6. Characterization and evaluation of the thesis

The dissertation is written on 172 pages, of which 142 pages are text with 25 tables and 42 figures, conclusions and contributions, all lists described in item 1 and Annex 1 with tables of volatile products of pyrolysis of cellulose, xylan and lignin in three temperature ranges: 250-600^{o}C, 600-800^{o}C, 800-900^{o}C. The thesis is structured as follows:

Introduction - a short, concise introduction to the topic of the study.

I. Literary Review - The critically presented literature review gives an idea of the dissertation II. 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.

III. Materials, methods and instrumental techniques - are presented in detail in item 5.

IV. Results and discussion

IV.1. Desulphurization treatments and research by reductive pyrolysis of organic sulfur-containing compounds and coal organic matter. Both unclear issues and the search for and implementation of an effective methodology for qualitative and quantitative determination of changes in organic sulfur of feed stocks and desulphurized coal at different study sites are presented.

IV.1.1. Desulphurisation treatments and reductive pyrolysis of “Maritza East” lignite. Six desulphurization treatments have been applied. It has been found that selective desulfurization can be successfully monitored by reducing AP-TPR assays. The resulting product, after treatment with alkaline melting, is almost completely desulfurized, removing organic and inorganic sulfur, and its calorific value for coal is much higher.

IV. 1. 2. Desulphurization treatment of low and high rank coal “Donetsk”, Donbass basin, Ukraine. Thermochemical treatment was done in a stream of water vapor and reduction treatment with alkali metals. Coal pairs of different genetic types (reduced and low reduced) of low and high rank coal from the Donbass Basin with different sulfur content were investigated. In the case of pyrolysis with water vapor, the interactions between sulfur groups in coal and water vapor have been found to increase the amount of thiol groups, an indication for sulfide and disulfide bonds cleavage; In the case of thermochemical treatment in a stream of water vapor, inorganic sulfur is almost completely removed, while in the case of reduction desulfurization, bridged sulfur and sulfur heterocycles of thiophene type are destroyed,

IV. 1. 3. Desulphurization treatments and reductive pyrolysis in low rank coal exploration from Elhovo and Katrishte, Bulgaria. AP-TPR and XPS analyzes have proved completely remove the non-thiophene sulfur during water vapor pyrolysis. AP-TPR with potentiometric detection and

AP-TPR-MS "on-line" profiles show that Elhovo coal contains more aliphatic sulfur compounds, and from Katrishte they are enriched in more complex thiophene structures.

IV. 1. 4. Desulfurization treatments and reductive pyrolysis of demineralized Elhovo lignites, Bulgaria. The main structural units in low rank coal have been found to be aromatic compounds with two rings and a high degree of substitution and nearly 58% of the organic sulfur is represented by thiophene structures. The high content of disulfides in Elhovo lignites is due to the major aliphatic sulfur species from the structural elements of the organic coal substance.

IV. 1. 5. Desulfurization treatments and reductive pyrolysis of “Mequinenza” lignite, Spain. Various forms of organic sulfur compounds have been determined in demineralized lignite testing using the off-line AP-TPR-GC/MS technique. Benzo[b]thiophene and its alkylated homologs have been registered at temperatures above 450 °C. Alkylated thiophenes were most abundant. Reduction pyrolysis with AP-TPR/TPO-MS "on-line" and AP-TPR-GC/MS "off-line" techniques is proven to be a good approach for determining sulfur functionality in organic coal mass, and for obtaining reliable information about the organic forms of sulfur in various geological sites.

IV. 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.

IV. 3. Investigation by reductive pyrolysis of organic sulfur functionality and organic matter composition of house-hold briquettes is an environmentally important issue. Combustion of coal in small industrial installations as well as in domestic stoves without efficient filters resulted in environmental pollution and creation of health problems. This can be avoided by using approaches to reduce their high sulfur and ash content and turn them into high quality solid fuels. The content of dialkyl sulfides and aliphatic thiols was found to be low in biomass briquettes. Bituminous/sub-bituminous coal briquettes are characterized by more complex thiophene structures, but no oxidized sulfur compounds have been detected. Organic sulfur compounds in analyzes of household briquettes are unaltered organic molecules released into the atmosphere. Some of them are monitored through monitoring programs of European legislation. Using AP-TPR with MS and GC/MS detectors, quantitative determination of all organic compounds present in briquette combustion emissions at home is achieved.

IV. 4. Study by reductive pyrolysis of organic sulfur functionalities and organic matter composition of biodesulphurized coal:

IV. 4.1. Investigation of local and foreign high sulfur coal. Coal biodesulfurization with selected fungal preparations and mixed bacterial cultures provides a reduction of up to 24% for organic sulfur compounds and up to 79% for inorganic sulfur. The AP-TPR "off-line" GC/MS proves that complex sulfur compounds are converted to sulfones and sulfoxides by biodesulfurization of coal.

IV. 4.2. Procedure for direct determination of elemental sulfur in coal. There is no analytical method for the determination of organic sulfur (So) in coal and it is calculated differently from the values for total sulfur (St) and inorganic sulfur (Sp + Ss + Sel). The dissertation proposes a procedure for the determination of Sel in coal, which provides direct data.

IV. 4.3.Study by reductive pyrolysis of organic sulfur functionalities and organic matter composition of biodesulfurized technological samples from local high-sulfur coal. Samples of Maritza East lignites, the Troyanovo-North mine and sub-bituminous coal from the Bobov Dol deposit with high sulfur content were investigated. Acidothiobacillus ferrooxidans and Pseudomonas putida microorganisms were used. It has been found that the sulfide content is decreasing. By reducing pyrolysis with AP-TPR technique, online and off-line modes with MS and GC/MS detection techniques, organic sulfur compounds in solid bituminous residues are determined. It was found that A. Ferrooxidans - F3 bacterium significantly reduces pyrite sulfur, and Ps.putida - B2 bacterium affects pyrite sulfur.

IV. 4.4. Study by reductive pyrolysis of organic sulfur functionalities and organic matter composition of lignites with high-sulfur content treated by combined chemical/microbial desulfurization techniques. By applying chemical and microbial desulphurization treatments on lignite, desulphurisation of 71%, pyrite desulphurisation of 90.6% and organic desulphurisation of 49.4% were achieved. Using the AP-TPR "on-line" MS technique, a qualitative specification of a wide range of sulfur and mixed C-O compounds was made and a decrease in the thiol content was found in all samples.

IV. 4. 5. Study of the influence of microbial treatments on the combustion behavior of biodesulfurized coal. For biotreated samples, better ignition rates, a slight decrease in calorific value, were found. Lowering the auto-ignition temperature (Tsh) increases the risk of spontaneous uncontrolled burning (Maritza East - B). Notwithstanding the disadvantages mentioned, the reduction of sulfur emissions is a major advantage of biodesulfurization.

IV. 4. 6. Study of organic sulfur functionalities and organic matter composition of “humus-like” products from “Maritsa East” lignite biodesulfurization. Changes with organic sulfur in Maritza East lignite after microbial treatment with Pseudomonas putida microorganisms and AP-TPR technique combined with “on-line” MS and “off-line” with TD-GC/MS analyzes were determined qualitatively and quantitatively. Aliphatic and aromatic sulfur have been found to be affected by the treatments carried out, some of the organic sulfur is transformed into a water-soluble state, which is highly volatile under the applied AP-TPR conditions. The “humus-like” by-product (HL) resembles to HA compared with HA isolated from the same coal sample.

IV. 5. Study by the reductive pyrolysis of the organic matter composition of humic acids (HA) from Bulgarian lignites and Turkish leonardite. For the first time to study organic sulfur in HA in the pyrolytic study of HA, a GC-MS detection technique coupled “on-line” with an AP-TPR was applied. Later, an AP-TPR with TD-GC/MS "off-line" was applied for qualitative/quantitative determination of organic compounds. The lignite HA from Maritza East and Stanyantsi were investigated. Aromatic structures, low hydrocarbons content, presence of N- and S-heteroatom-containing compounds predominate in HA pyrolysates. HA Maritza East are characterized by a higher content of phenolic structures than HA-Stanyantsi. It is proven that carbohydrates are present in HA, which is more typical of HA Stanyantsi. These HAs are structured by units with 1-2 condensed or combined rings with a high content of (N and S) compounds - important for environmental impact when using preparations made on their basis. HAs were compared with pyrolytic studies of humovitrain lithotypes of the same lignites - Maritza East and HA of Turkish leonarditis. AP-TPR off-Line Reduction Pyrolysis with TD-GC/MS detection apparatus is applied which provides qualitative and quantitative molecular-level information for the non-extractable portion of the organic matter of HA. Alkyl aromatic compounds are the products of the humification of primary plant materials and microbial metabolites that form the structures of HA. The linear hydrocarbons nC$_6$-nC$_{14}$, including pairs of *n*-alkenes and *n*-alkanes have a quantitative presence in HA. Alkylated naphthalenes are only determined in the high temperature range 550 ^{o}C - 950^{o}C, and PACs with a higher degree of condensation are not detected. As the pyrolysis temperature increases during the reduction analysis, the alkylated aromatic compounds are gradually replaced by phenolic structures, furan and benzofuran are reported. The proven sulfur compounds are linear and aliphatic polysulfides (dimethyl disulfide and dimethyl trisulfide) and cyclic sulfur compounds (thiophenes and benzothiophenes). Reduction pyrolysis with the AP-TPR "off-line" TD-GC/MS technique can be applied to characterize and compare at molecular level the whole range of organic functionalities in the composition of volatile humic acids of different origin, incl. from fossil fuels, soils, peat, sediment etc.

IV. 6. Pyrolytic study of the organic matter of “Stanyantsi” lignites. By applying the AP-TPR "off-line" TD-GC/MS instrumental technique for the determination of sulfur compounds in coal, the individual compounds in coal are determined at the molecular level. A high number of individual organic compounds were identified in a sample of 40 mg of “Stanyantsi” lignite.

IV. 7. Reductive pyrolysis of aqueous leachates from “Maritsa East” and “Stanyantsi” lignites Coals are not carcinogenic and mutagenic, but water-soluble lignite organic substances have a marked mutagenicity. Drinking water at low concentrations of lignite-leached organic compounds and they have some suspicions to be one of the probable causes of the Balkan Endemic Nephropathy (BEN) disease. The author found that, for the time being, the amounts of certain carcinogenic/mutagenic compounds did not pose a serious toxic environmental risk, but the N-containing compounds in the lignites of Stanyantsi must monitor their concentrations.
IV. 8. Pyrolytic studies of waste vegetation products and three main components of ligno cellulosic biomass. Due to the limited global reserves of quality and low-emission fossil fuels, the interest of scientists in the search and use of alternative sources of energy and fuels is determined. Such an energy source is environmentally friendly biomass and is therefore considered to be a source of clean or green energy. Non-condensable volatile compounds (VOCs) were studied by AP-TPR "off-line" with TD-GC/MS and PAHs, in the pyrolysates of the three major components of ligno cellulose biomass. The volatile amounts of cellulose and xylan volatiles are comparable and significantly lower for lignin; PAHs are present in small amounts in the non-condensable VOCs in the pyrolysis gas. They need to be monitored for industrial pyrolysis processes, as PAHs formed can create serious problems for environmental and human health. No noticeable quantities of PAHs have been detected in the temperature range of 250-600 ^{o}C, which is important for biodiesel production.

Characteristic of the dissertation is 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 at the molecular level applied to different study materials and sampling regions. Each section concludes with a brief conclusion of what I find to be a very positive and well-realized idea.

7. Contributions and importance of the results to science and practice

The conclusions and contributions are formulated briefly and clearly. Of environmental importance are: conclusion 10 (acidification of the environment can be difficult to manage), as well as the text of Chapter IV, Page 117 (for the study with reducing pyrolysis of lignite leaching products from Maritza East and Stanyantsi).
I note conclusion 4 - of fundamental importance, and conclusion 5 fundamental, but also of an applied character; Conclusions 7 and 8 - applied. Novelty is the presence of PAHs in the pyrolysis gases from the studied lignite coal rates in conclusion 11. Conclusion 12, related to the determination of nitrogen-containing compounds in the leaching products of Bulgarian lignites from the Maritza-East and Sofia basins with prolonged exposure to organisms can lead to carcinogenic/mutagenic action and is important for the protection of human health. Conclusion 13 - of environmental importance, PAHs were determined for the first time in the fraction of 600-900 °C in non-condensable volatile compounds by pyrolysis of the main components - cellulose, xylan and lignin. Conclusion 14 has an applied character and is related to the production of biodiesel. I accept the formulated contributions in Area I, containing new and original information for science; Confirmatory contributions (Area II) - The results obtained are of ecological significance, since the presence of N-, S- and O-heteroatom-containing compounds, which may enter groundwater in the areas of the studied coal basins, has been established; Two methodological contributions (Area III) have been formulated, which I consider to be important, which should take the top position!; The contributions from Area IV are clearly applied: IV. 1 is also described in conclusion 4 related to biodiesel production; IV.2 clearly emphasizes that the applied treatments do not affect the calorific values of the coal.
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.

8. Assessment of the papers related with the thesis. The total number of publications has been summarized in two directions, all written in English:

I. Scientific papers published in scientific journals –26 бр. (Q1 – 14; Q2 – 4; Q3 – 2; Q4 – 3, in non-refereed edition - 3). Total IF 41.99

II. Reports of scientific conferences, published in full text in the materials of conferences after review by the editorial board - 14, of which international scientific conferences abroad 12; articles in national journals - 1 issue; papers in Proceedings at international scientific conferences in Bulgaria - 2 issues. By number of co-authors: independent - 1 issue (N 23); with three or more co-authors –39; first author of 16 publications and second author of 13 publications. Separation protocols (5) are attached, which certify the personal participation of Assoc. Prof. Dr. Stefan Marinov in the development of the attached publications. List of noted citations related to the dissertation material are 328 citations of 20 papers: № 3 - Q1 (first author) - 35 citations, № 5 (second author) - 136 citations, № 11 - Q1 (second author) –27 citations; No. 16 - Q1 (first author) - 38 citations.

9. Personal participation of the author

I believe that writing the dissertation, forming the conclusions and the contribution, which is also evident from the published papers in reputable, high IF journals, is the personal work of Assoc. Prof. Dr. Stefan Marinov. They are parts of a dissertation that is very well designed, illustrated with tables and figures. Each section concludes with a summary and a conclusion, especially important and in my opinion very positive when it is summarizing a large volume of experimental material. Although most of Assoc. Prof. Dr. Marinov papers are published in co-authorship with Bulgarian and foreign scientists, the leading role are obvious.

10. Thesis abstract

The abstract in Bulgarian and English accurately and completely reflects the materials of the dissertation. It contains the main results of the large experimental work, conclusions and contributions and all the lists, applied in the dissertation, while complying with the requirements of the regulations of the IOCCP-BAS.

11. Critical remarks and recommendations

A. The author concludes that the bacterial culture of Sulfolobus Solfataricus is a good biodesulfurization agent for elemental sulfur and is recommended for future biotechnological studies. Properly, he refrains from recommending Acidothiobacillus Ferrooxidans, a bacterium that can cause additional environmental problems when used in agriculture. Similar to the known utility model patent No. 2981 / 04/24/2018 "Plant Biostimulator", when treated with Leonardite with Pseudomonas putida, very good results were obtained, as well as in these experiments. B. On page 32, in the Methodical section, when humic acids are prepared, they are dried at 105 ° C. I think that temperatures of 40-60 ^{o}C, max 80^{o}C, as recommended by Kononova, Orlov, Ponomareva and Plotnikova, would be good to observe, as some changes in the HA may occur. C. Pages 106, 124 peats - in plural, instead of peat. D. A mixture of Latin and Cyrillic literary sources is found in the literature. E. I were found absence or excess of intervals in some places.

The noted do not diminish the value of the work submitted for review and can be considered as recommendations.

12. Personal impressions

I am familiar with his scientific research articles Assoc. Prof. Dr. Stefan Marinov presented at the conferences organized by the Bulgarian Humic Substances Society (BHSS) in 2003, 2011, 2016 and in the 19 IHSS Meeting hosted by the BHSS in 2018, from the joint development article I presented at the 2017 conference in Kudowa-Wroclaw, Poland with in-depth research and interpretation of the results obtained.

13. Recommendations for future use of dissertation results and achievements

The results obtained, the formulated conclusions and the contributions are of great importance for the use (utilization) of the method of pyrolysis to analyzing different materials. In this regard, other materials may be explored in the future, e.g. coal from other basins, soil and peat HA could also be investigated in cooperation with ISSAPP N. Poushkarov.

CONCLUSION

The dissertation is written in a concise manner, the abstract, reflecting the main chapters of the dissertation with scientific, applied contributions and conclusions, and the annexed publications, published in prestigious journals with high IF, as well as the materials from the conferences with the presented parts. This dissertation has an original contribution to the science. Management of national and international projects, Assoc. Prof. Dr. Eng. Stefan Marinov 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. The dissertation shows that the candidate Assoc. Prof. Dr. Eng. Stefan Penchev Marinov possesses deep theoretical knowledge in the scientific specialty organic chemistry, demonstrates qualities and skills to present research with obtaining original and significant scientific and applied contributions. The topic of the dissertation is up-to-date and is related to contemporary environmental requirements.

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".

10.03.2020

Reviewer: .....

(Prof. Ekaterina Filcheva, PhD)