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# Review of the PhD Thesis

Author: **M.Sc. Juan Carlos Beltrán Prieto**

Title: **Treatment of glycerin fraction**

The review of the PhD thesis was written in response to letter by associate prof. Mgr. Milan Adámek, Ph.D. dean of the Faculty of Applied Informatics of the Tomas Bata University in Zlín. The PhD thesis by M.Sc. Juan Carlos Beltrán Prieto entitled „Treatment of glycerin fraction" comprises 135 pages of the text including bibliography, four appendices, list of publication and curriculum vitae of the author.

Due to my professional specialization in my review I will express primarily for the creation and verification of mathematical models from point of view of a control theory.

## 1. Topicality of PhD Thesis

The PhD thesis is devoted to the treatment of glycerin fraction with orientation on analysis and analytical solutions of selected deterministic mathematical models of glycerol oxidation and their verification by digital simulation and experimentally. This topic is relevant today because the research of new applications of glycerin with an emphasis on developing new products with high utility value.

I consider the selected topic up-to-date with the contribution for the further development and application of the superfluous glycerin.

## 2. Chosen Methods and Problem Solving Approach

The PhD thesis consists from the acknowledgement, the abstract in Czech and English, lists of figures, tables, appendices, abbreviations and symbols, fifteen chapters including bibliography, four appendices, list of publication and curriculum vitae of the author. The first chapter is devoted to a brief introduction. The second chapter describes the state of the arts and motivation for selected objectives. The aims of the thesis are formulated in the third chapter. In following chapters from the fourth to the ninth the author subsequently describes

and determines the mathematical models for glycerol oxidation. First the models are expressed in the form of state space models in the time domain and then on the basis of the Laplace transform in the form of transfer functions and transfer function matrices in the complex variable domain. In some cases the linearization was used. The mathematical models are analysed and the analytical solutions are obtained. The tenth chapter deals with the experimental measurements. In the eleventh chapter the theoretical and experimental results are compared. In chapters from twelfth to fourteenth the contribution of the thesis to science, the recommendation for industrial applications and overall conclusions are given. The bibliography in fifteenth chapter consists of 87 items. The appendices from I to IV contain the experimental results, the list of selected experiments, the programs developed in MATLAB and some results for uses of the PID controller. The list of author's publications contains 18 items including 9 publications in international journals with impact factor. The author's curriculum vitae concludes the thesis.

The PhD thesis shows the relatively wide knowledge of the author. Generally, it can be said that selected methods are appropriate to the intended purpose and that they were correctly used. From the conformity of analytical and experimental results it follows that the PhD thesis is worked out on very high professional level.

## 2. Reaching of objectives

The objectives of the thesis, which are formulated in chapter three, were fully reached.

## 3. Results of PhD thesis

In my opinion the most important author's results are:

- design, description and analysis of deterministic mathematical models of selected glycerol oxidations;
- analytical, numerical and experimental verification of the designed mathematical models.

Some important results of the PhD thesis were published in international journals with the impact factor.

## 4. Remarks and Defence Questions

I have some formal remarks to the PhD thesis:

Some general remarks:

- in the equations should be only one sign of equality (e.g.: p. 41 Fig. 11 (in the block), p. 42 Eqs (54), p. 47 Fig. 12 (in the block) ets.);
- it is better to use instead of the transfer function the concept the transfer function matrix (e.g.: p. 45, p. 50 and 51 ets.).

Some special remarks:

- p. 41 – in Eqs (50) and (51) the signs of derivative are missing;
- p. 47 – in Eg. (103) the sign of equality is missing ($a_{23} =$ );
- p. 69 – Egs (281) and (282) aren't written correctly;
- p. 74 – the axes are not described in Fig. 26;
- p. 100 – in Eg. (333) the complex variable $s$ is missing;
- p. 130 – the equation of the PID controller is incomplete.

During the defence it would be appropriate if the author could respond the following question:

What tuning method for the PID controllers was used (Appendix IV)?

The above given comments and remarks are formal and they do not reduce the quality of the PhD thesis which is on the high professional and formal level.

## Final Evaluation

The PhD thesis of M.Sc. Juan Carlos Beltrán Prieto is executed at the required scientific and formal level. It demonstrates the author's very good theoretical knowledge as well as qualification for independent original scientific work.

I recommend the PhD thesis for defence before relevant commission.

Ostrava 10. 2. 2015

Assoc. Prof. Monika Bakošová, PhD., Slovak University of Technology in Bratislava, Faculty of Chemical and Food Technology, Institute of Information Engineering, Automation and Mathematics, Radlinského 9, 812 37 Bratislava, Slovakia

# Opponent review of the doctoral thesis

Title: **Treatment of glycerine fraction**
Author: **M.Sc. Juan Carlos Beltrán Prieto**

Characteristics of the thesis

The doctoral thesis is devoted to study the problem of glycerol oxidation. In terms of content, the state of art is discussed in Chapter 2. In this chapter several approaches to glycerol oxidation are introduced with a lot of number of references. The author presents also reasons for control of glycerol oxidation. In Chapter 3 the aims of the thesis are formulated that are focused especially on modelling of glycerol oxidation. Chapter 4 is devoted to the exploration of the production system. Here, partial oxidation of glycerol and the kinetics of oxidation are modelled. The estimation of the thermodynamics parameters of the glycerol oxidation to glyceraldehyde with $H_2O_2$ and with $N_2O$ is one of the main results of this chapter. Transfer functions of the isothermal processes of anodic oxidation and oxidation with $N_2O$ are derived in Chapters 5 and 6. A non-isothermal reaction system for glycerol oxidation is presented and modelled in Chapter 7 and the transfer functions of the glycerol oxidation in non-isothermal conditions are derived in Chapter 8. In this chapter the temperature profiles during the glycerol oxidation are also presented. Chapter 9 is devoted to the analysis of the glycerol oxidation considering reversible reactions and again the transfer functions of the process are derived. Experimental measurements used in glycerol oxidation are presented Chapter 11 and obtained results are summarized in Chapter 12. The contribution of the thesis to science and practice is discussed in Chapter 13. Chapter 14 presents recommendation for industry.

The doctoral thesis has 135 pages. It is divided into the English and Czech abstracts, 15 chapters including introduction, conclusions and list of references. 4 appendices are added to the thesis as well as the list of author's publications and author's curriculum vitae.

Structure of the doctoral thesis is logical. The form of figures and tables is good. Text is well written with small amount of misprints. English is good; there are only small mistakes in the text.

Recency of the selected topics

The topic of the doctoral thesis devoted to the glycerol oxidation is recent and interesting, because it is strongly connected with finding renewable energy sources and biodiesel production. It is necessary to find exploitation of glycerol that is a side product of biodiesel production. The glycerol oxidation to valuable products may be one of ways as it is studied in the thesis.

Achievement the aims of the doctoral thesis and choice of methods

All aims of the doctoral thesis formulated in Chapter 3 were fulfilled. They were oriented especially on modelling of glycerol oxidation, development of an analytical method for

analysis of products of oxidation and the analysis of products of glycerol oxidation. The chosen methods correspond to the outlined aims. They are correct and actual. The HPLC is one of the most used analytical methods.

The contribution of dissertation

The main contributions of the doctoral thesis are in the field of modelling of the glycerol oxidation in various conditions and in the field of identification and analysis of products of glycerol oxidation. The derived mathematical models of the kinetics and the reaction processes are the first steps to the automatic control system implementation. The new method for identification and quantification of glycerine oxidation products by HPLC was also developed.

Publications of the author

M.Sc. Juan Carlos Beltrán Prieto is the author or the co-author of 9 publications in the international journals with impact factor and of 9 publications in the journals without impact factor or conference papers. His publication activity is good.

Comments to the doctoral thesis and questions

- P. 13 – $OH^-$ is usually considered as hydroxyl anion (hydroxide), hydroxyl radical is usually referred as $^{\cdot}HO$.
- P. 13 – $H^+$ is hydron, i.e. a cationic form of atomic hydrogen.
- P. 32 – what reactant represents A in (15)? What is the main product of the two consecutive reactions in (15)?
- P. 33 – the maximum yields of glyceraldehyde is denoted in Figs. 9 and 10. Wasn't it possible to find the maximum yield of glyceraldehyde in the situation presented in Fig. 8?
- P. 47 – nitrous oxide has the formula $N_2O$; $NO_2$ is nitrogen dioxide.
- P. 54 – What is the purpose of deriving (165)-(176) and what represent these equations? How it is possible to calculate step responses from (165)-(176)? I have the same commentary to Eqs. (303)-(308) (p. 72) and Eqs. (352)-(357) (p. 103).
- P. 64 – what is the meaning of the symbol "}" in equations in Fig. 18?
- P. 64 – the numerical values of listed parameters should be also given.
- P. 130 – The transfer function of PID controller is incorrect.
- P. 130 – What tuning methods were used for PID controller?
- The Appendix IV could be incorporated in the main text of the doctoral thesis.

Concluding statement

The aims of the doctoral thesis were fulfilled. Submitted doctoral thesis meets the requirements for this kind of work. I recommend the doctoral thesis for defence.

Bratislava, 9 February 2015

**The reviewer`s comments on the dissertation thesis Treatment of Glycerin Fraction of Juan Carlos Beltrán Prieto**

The work is motivated by the need of finding a technical application of a new source of glycerin, which is a byproduct of the production of fatty acid methyl esters (i.e. biodiesel). The aim is to develop a method for the selective oxidation of glycerol to technically usable product. The intention of the study was to find a technological process for the selective oxidation of glycerol to glyceraldehyde.

Technological research in the oxidation of glycerol to the reactive intermediate product glyceraldehyde is a difficult technical task, because of several reasons:

It is a research of a system of subsequent and side reactions, with the aim to obtain the highest possible yield of one of the intermediates. Optimization of the yield of the intermediate is a classic task of reactor engineering, which requires finding suitable reaction conditions and determination of the time of the process termination, which is optimal in economic terms. To control the state of the reaction mixture in which the reaction should be terminated and the reaction mixture processed, it is necessary to have a mathematical model describing the dependence of the reaction mixture composition on reaction time and temperature.

The author demonstrated that he is able to construct mathematical models of chemical reactors of different types and apply computational methods for the simulation of the reaction. For simulation of the course of reactions the author used analytical solution of a system of differential equations based on the application of Laplace transforms and also numerical solution of a differential equations system. He compiled models describing isothermal and non-isothermal reactors.

The ongoing reactions are exothermic. When carrying out the process in an industrial device, the cooling of the reactor can be the step which determines the security of the process. The author has demonstrated that he is able to evaluate the basic thermodynamic parameters of the reaction mixtures that determine the risk of temperature runaway in the reactor. He assessed the reaction heat of the ongoing reactions and the adiabatic temperature rise of the reaction mixture and assembled chemical reactor models that allow simulating of the reaction course in reactors with heat exchange wall.

The research of this process is complicated by the complexity of analytical determination of the reaction mixture composition. The authors developed an analytical method based on the use of liquid chromatography and used the method for approximate study of glycerol oxidation to glyceraldehyde and other products. The author carried out preliminary measurements of the course of the glycerol oxidation to glyceraldehyde and other products.

**The author should comment the following questions during the defense:**

The work is motivated by the attempt of the preparation of glyceraldehyde; however, it is not stated in the work what application the said substance can have in the chemical industry. Alternatively, in which applications can be used other oxidation products.

The technical problem is the separation of the reaction mixture. The author should state his idea about the possibilities of the separation of the reaction mixture.

Simulation models of carious reactor types have been compiled in the presented work; however, the author's idea is not presented on which reactor type could be suitable for execution of the oxidation on an industrial scale.

The author should indicate whether it is possible from the mathematical models, using the kinetic data obtained by experiments, to estimate the maximal possible yield of glyceraldehyde.

Conclusion

The author has shown the ability to construct mathematical models of different levels for the description of the course of chemical reactions in a variety of chemical reactors. He has worked out an analytical method for the analysis of a complex reaction mixture and gained initial approximate information of the reaction kinetics. The results of his work have been presented at numerous technical conferences.

The author has demonstrated that he is able to solve technical problems; I recommend that his work is submitted for defense.

Prof. Ing. Jozef Horák, DrSc.