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Review of the doctoral dissertation of Martino Di Serio entitled: „Catalysis, Kinetics, and Chemical Reactor Engineering for Alkoxylation Reactions”

The doctoral dissertation of Professor Martino Di Serio has been submitted for evaluation to the Chemical Sciences Discipline Council at the Poznan University of Technology. Since 2017, Martino Di Serio has been a full professor of industrial chemistry at the Department of Chemical Science at University of Naples Federico II. He is the head of the Naples Industrial Chemistry Laboratory, and his area of expertise is industrial chemistry, focusing on industrial catalysis and kinetic studies of complex reactions in multi-phase reactors [1]. He is the author of 267 papers, which have been cited over 7,000 times, and his H-index is 43 (Web of Science, 07.11.2024). The dissertation supervisor is Wiesław Hreczuch, PhD, DSc, owner of MEXEO, a company located in Kedzierzyn-Kozle, recognized for its achievements in implementing new chemical technologies. The submission of a PhD thesis by a full professor is unusual. The candidate's extensive knowledge and experience greatly enhance the value of the dissertation, which explores alkoxylation reactions, their mechanisms, and kinetics, with particular attention to reactor selection for process intensification and safety.

Among alkoxylation reactions, ethoxylation is particularly important in the chemical industry as it is widely used in the synthesis of surfactants. These processes are typically conducted in semi-batch systems; however, as production demands increase, continuous processes will become more desirable. The subject of this dissertation aligns with these trends and, in my opinion, offers an innovative solution.

The reviewed PhD thesis consists of 211 pages and is divided into two main parts: (I) *State of the Art in Alkoxylation Reactions* and (II) *Process Intensification in Alkoxylation Reactions*. It is supplemented with a table of contents, a list of abbreviations, a list of references, and two appendices containing copies of papers co-authored by the PhD candidate, as well as statements from co-authors regarding their substantive contributions to these papers.

1 https://www.docenti.unina.it/#!/professor/4d415254494e4f4449205345524 94f4453524d544e3634453136 4333363142/curriculum

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First, the author presents the scope of the thesis and defines the purpose as "*to provide the scientific basis and rationale for further work on the industrialization of oxyalkylation processes, with a focus on developing a continuous synthesis node and utilizing microreactor technology in this field*."

Literature data on alkoxylation reactions is presented across 74 pages. Four chapters cover the following topics: basic information on alkoxylation agents such as ethylene oxide and propylene oxide (Chapter 1), details on the mechanism of alkoxylation reactions, acid and base catalysts (Chapter 2), kinetics of fatty alcohol alkoxylation catalysed by metal alkali hydroxides (Chapter 3), and industrial alkoxylation reactors (Chapter 4).

The author, partly drawing on his previous valuable articles not included in the dissertation, analyses the current state of knowledge in alkoxylation processes. In the particularly valuable Chapter 4, he discusses and compares the advantages and disadvantages of industrial reactors used in alkoxylation processes, as well as safety issues in these processes (Section 4.4). In my opinion, the data presented by the candidate fully justify undertaking research into the development of an innovative continuous synthesis unit for the alkoxylation process, particularly in the modelling of new, efficient and safe reactors for this process.

In general, I have no comments on this part of the thesis. However, the titles of the subchapters in Chapter 3—*Experimental*, *Results and Discussion*, and *Conclusions*—are somewhat misleading. At first glance, they might give the impression that this is the experimental section of the research.

On the 45 pages of the second part of the dissertation, the author presents the idea of Enhanced Loop Reactor (ELR) (chapter 5), recent achievement in the field of alkoxylation in continuous systems (chapter 6), and finally an analysis of data obtained in microreactors using developed models (Chapter 7).

In Chapter 5, the Enhanced Loop Reactor, Spray Tower Loop Reactor, and Venturi Loop Reactor are compared. The Enhanced Loop Reactor's ability to operate safely at higher ethoxylation degrees is demonstrated. Additionally, a novel mathematical model developed is presented in a paper titled *"The Evolution of the Fed-Batch Ethoxylation Reactors to Produce Non-Ionic Surfactants"*, published in *Frontiers in Chemical Engineering* in 2021 (a journal with an impact factor of 2.5) (doi.org/10.3389/fceng.2021.644719). The article is multi-authored, and the statements of all co-authors have been attached. These statements are consistent and attribute to Prof. Di Serio a role in the development of the main conceptual ideas, in collaboration with co-author Riccardo Tesser.

In Chapter 6, based on both scientific literature and patents, Professor Di Serio discusses recent achievements related to alkoxylation processes in continuous reactors. This scientifically valuable discussion addresses the growing demand for surfactants, including the use of ethoxylation processes, which will likely lead to the implementation of continuous processes. The chapter is closely related to the paper co-authored by the candidate, titled *"Alkoxylation for Surfactant Production: Toward Continuous Reactors"*, published in *Frontiers in Chemical Engineering* in 2020 (https://www.semanticscholar.org/paper/Alkoxylation-for-Surfactant-Productions%3A-Toward-the-Tesser-Russo/a6b82dc93b5bf66cf4bd12f4e54c1c2dc9a34ef4). The statements of all co-authors have been attached, with each co-author declaring that Martino Di Serio conceived the initial idea for the paper and led the workgroup composed of the other authors.

At this point, I would like to inquire whether the author considered placing Chapter 6, which concerns literature data, in Part (I) *State of the Art in Alkoxylation Reactions* ?

Based on the conclusions from Chapter 6, the author began developing a laminar flow model for microreactors. The resulting model is presented both in Chapter 7 of the thesis and in the paper titled *"Design of a Continuous Device for the Ethoxylation Reaction: The Choice Between Micro and Milli Scale"*, published in 2023 in *Chemical Engineering Research and Design*, a journal with an impact factor of 3.7 (doi.org/10.1016/j.cherd.2023.04.051). The statements of all co-authors have been attached, and they all declare that the main conceptual ideas were developed by Martino Di Serio in cooperation with Wiesław Hreczuch, the supervisor of the thesis. It has been demonstrated that the laminar flow model successfully describes the experimental data reported in the literature. A simulation using a plug flow model was also performed and demonstrated the system's ability to operate safely at high conversion of the ethoxylation process through a multi-feed approach (where ethylene oxide is split along the length of the pipe).

The material presented in the dissertation was published in five papers, three of which were mentioned above. The other two were published in *Frontiers in Chemical Engineering* and *Chinese Journal of Chemical Engineering* in 2019 and 2018, respectively. Martino Di Serio is the sole author of the paper titled *"Chemical Reaction Engineering as a Bridge Between the Nano and Macro World"*, in which he explains, in an interesting way, what Chemical Reactor Engineering entails and the challenges this scientific discipline faces. In the article published in 2018, *"Polyethoxylation and Polypropoxylation Reactions: Kinetics, Mass Transfer, and Industrial Reactor Design"*, various aspects affecting the choice of a suitable reactor for alkoxylation reactions were considered, and the collected data were used for the simulation of industrial reactors.

In conclusion, I affirm that the dissertation is based on the candidate's extensive knowledge and experience in the field of alkoxylation processes, particularly in the development of appropriate mathematical models. The dissertation is supported by 86 literature references, including 21

patents. Among the cited works, at least 25 were co-authored by the candidate. The dissertation contains desirable elements of novelty, and the accomplishments have been presented in five publications in journals from the JCR list, where the candidate made a leading or significant contribution, as confirmed by the statements of the co-authors. I have no substantive comments on the presented dissertation. However, I believe that the dissertation could be sufficiently based solely on the attached publications, with an appropriately brief introduction.

In summary, I declare that the dissertation of Prof. Martino Di Serio, entitled *"Catalysis, Kinetics, and Chemical Reactor Engineering for Alkoxylation Reactions"*, meets the requirements for doctoral theses. I hereby recommend to the Chemical Sciences Discipline Council at the Poznan University of Technology that the PhD candidate be admitted to the next stages of the doctoral procedure.

Application for the Distinction of the Doctoral Dissertation of Mr. Martino Di Serio

Considering the high quality of the dissertation, I hereby apply for the distinction of the doctoral dissertation of Martino Di Serio, entitled *"Catalysis, Kinetics, and Engineering of Chemical Reactors in Alkoxylation Reactions."* The exceptional nature of the thesis is evidenced by five publications in journals from the JCR list, with a combined impact factor of 14.9, in which the candidate played a leading role. Furthermore, it is noteworthy that the results of the dissertation will serve as the foundation for designing both a pilot plant and, subsequently, a continuous industrial alkoxylation process.

Signed by / Podpisano przez:

Beata Joanna Orlińska
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Date / Data: 2024-11-08 10:21