Maciej Szwast, PhD DSc
Faculty of Chemical and Process Engineering
Warsaw University of Technology
00-645 Warsaw, Waryńskiego 1

Warsaw, 08.04.2024

Review Report on Ph.D. Thesis of Mr. Guoqiang Li, MSc
entitled
Polymeric membranes and mixed matrix membranes (MMMs) for carbon dioxide separation
Supervisor: Prof. Wojciech Kujawski, PhD DSc
Co-supervisor: Joanna Kujawa, PhD DSc

I have prepared this review report at the request of Professor Iwona Łakomska, Dean of the Faculty of Chemistry at Nicolaus Copernicus University in Toruń, expressed in the letter dated March 15, 2024.

The PhD thesis of Mr. Guoqiang Li entitled "Polymeric membranes and mixed matrix membranes (MMMs) for carbon dioxide separation" consists of 204 pages. The main substantive part of the work is presented as a collection of 6 scientific papers, copies of which have been attached to the thesis printout. These publications are accompanied by a concise description of approximately 40 pages. The thesis has been prepared entirely in English.

The doctoral thesis includes the following scientific papers:

1. G. Li, W. Kujawski*, R. Válek, S. Koter, A review of the development of hollow fiber membranes for gas separation processes, International Journal of Greenhouse Gas Control, 104 (2021) 103195.
2. G. Li, W. Kujawski*, K. Knozowska, J. Kujawa, The effects of PEI hollow fiber substrate characteristics on PDMS/PEI hollow fiber membranes for CO2 /N2 separation, Membranes, 11 (2021) 56.
3. G. Li, K. Knozowska, J. Kujawa, A. Tonkonogovas, A. Stankevičius, W. Kujawski*, Fabrication of polydimethylsiloxane (PDMS) dense layer on polyetherimide (PEI) hollow fiber support for the efficient CO2/N2 separation membranes, Polymers 13 (2021) 756.

4. G. Li, W. Kujawski*, K. Knozowska, J. Kujawa, Thin film mixed matrix hollow fiber membrane fabricated by incorporation of amine functionalized metal-organic framework for CO2/N2 separation, Materials, 14 (2021) 3366.
5. V. G. Li, W. Kujawski*, A. Tonkonogovas, K. Knozowska, J. Kujawa, E. Olewnik-Kruszkowska, N. Pedišius, A. Stankevičius, Evaluation of CO2 separation performance with enhanced features of materials - Pebax® 2533 mixed matrix membranes containing ZIF-8-PEI@[P(3)HIm][Tf2N], Chemical Engineering Research and Design, 181 (2022) 195-208.
6. VI. G. Li, W. Kujawski*, K. Knozowska, J. Kujawa, Pebax® 2533/PVDF thin film mixed matrix membranes containing MIL-101 (Fe)/GO composite for CO2 capture, RSC Advances, 12 (2022) 29124-29136.

The total Impact Factor (IF) of these 6 papers is 24.3. In all of these papers, Mr. Guoqiang Li is the first author. Mr. Guoqiang Li's declared contribution to these papers, confirmed by statements from co-authors, ranges from 45% to 65%.

The reviewed doctoral thesis addresses a highly important and current issue of management of carbon dioxide (CO_2) produced in various processes, particularly combustion. The current policy of the European Union mandates the exploration of technologies to reduce CO_2 emissions. Membrane technologies utilizing polymer membranes seem to align well with this industrial development trend. However, based on the literature analysis, the doctoral candidate rightly observes that polymer membranes have significant limitations, which could be overcome by developing polymer-inorganic heterogeneous membranes (MMMs - mixed matrix membranes). Therefore, the aim of Mr. Guoqiang Li's doctoral thesis is to produce and examine a new type of MMM membrane. Specific objectives of the thesis include:

i. to fabricate polyetherimide (PEI) HFMs by using the dry-jet-wet spinning technique and to investigate the effects of spinning parameters on the morphology, pore structure, and gas permeance of HFMs;
ii. to fabricate PDMS/PEI TFC-HFMs by using dip-coating method and to investigate the effects of coating conditions on the morphology and thickness of PDMS layer and the gas permeance of TFC-HFMs;
iii. to synthesize and characterize ZIFs (pristine and modified ZIF-8), MOFs (UiO-66-HN2, MIL-101 (Fe)), and MOF@GO composite (MIL-GO composite);

iv. to fabricate and characterize Pebax® 2533 based HF-MMMs and FS-MMMs containing pristine and modified ZIFs, MOFs or MOF@GO composite;

v. to investigate the effects of pristine and modified ZIFs, MOFs or MOF@GO composite on the morphology, structure, thermal stability, mechanical strength, and gas transport properties of MMMs.

At this point in the review, I can already state that all these objectives have been achieved.

The division of the descriptive part of the thesis presented for review could be discussed. It would be more convenient for the reader to have a brief introduction, followed by the presentation of the motivation and objectives of the work, and then the presentation of relevant theoretical information and state-of-the-art in the field of the doctoral thesis. The doctoral candidate decided to start the dissertation with a literature review spanning several dozen pages (over 80 literature references). Reading this part without knowing the scope of the work makes it difficult to assess whether the information contained in this chapter is in line with the scope and whether it is sufficient. The current structure of the content forces the reader to return to section 1.1. after reading section 1.2.

The substantive part of the doctoral thesis is contained in the reviewed scientific articles published in reputable journals. These materials have already been reviewed by several individuals, which means that the results of these studies are well-described and comprehensive. However, there are several questions, which I would like the doctoral candidate to provide answers to.

1. Why did you not choose to study the CO_2+N_2 gas mixture? The phenomenon of membrane swelling in the presence of CO_2 is known in the literature. This could significantly affect the actual separation factor. Did you consider this aspect?
2. In addition to CO_2 and N_2, flue gases often contain other gases, such as NO_x, SO_x, or even VOCs. Even small amounts of these gases can affect separation efficiency and cause membranes to age faster. Did you consider this aspect?
3. Do the membranes you produced have significantly better processing properties compared to existing membranes (especially commercially available ones)? In the descriptive part of the thesis, a summary in the form of a Robeson-like chart for all the membranes you produced would be appreciated.

4. How do you assess the possibility of producing the membranes you developed on an industrial scale? Will scaling up production be easy? Will the manufacturing costs of such membranes be justified?
5. The "gutter layer" is a very interesting aspect presented in your work. I feel a bit unsatisfied with your description of the significance of this technological solution. Could you please present the advantages of this technological approach?

The above comments are of a discussion nature and stem from the reviewer's curiosity. They do not affect my very high assessment of the doctoral thesis.

The reviewed doctoral is undoubtedly one of the best I have had the opportunity to read. It deserves positive recognition for its well-defined research plan and consistent pursuit of the set objectives. The research presented in the thesis was carefully planned and conducted using modern research methods. The description of the research and presentation of the author's scientific achievements are done in a very clear and transparent manner.

Final conclusion

I highly recommend Mr. Guoqiang Li's doctoral thesis. The work significantly contributes to the advancement of science and technology in the field of membrane manufacturing for gas separation processes.

I affirm that the reviewed thesis **meets the requirements** set forth in the Law on Higher Education and Science (Journal of Laws 2018, item 1668, with changes) for doctoral dissertations. Therefore, I submit a request to the Discipline Council of Chemical Sciences at the Faculty of Chemistry, Nicolaus Copernicus University in Toruń, for the thesis **to be approved for public defense**.

Proposal for distinction of the doctoral thesis

I submit a proposal to the Discipline Council of Chemical Sciences at the Faculty of Chemistry, Nicolaus Copernicus University in Toruń, to distinguish Mr. Guoqiang Li's doctoral thesis.

The dissertation is based on 6 publications with a cumulative Impact Factor of 24.3 and 720 points from the Ministry of Science. These works have already been cited 109 times (Scopus), indicating a very high level of scientific quality. Furthermore, the oral and poster presentations by the doctoral candidate related to the dissertation topic have been repeatedly

awarded at scientific meetings. I consider these achievements to be significantly above average for doctoral dissertations. Therefore, this justifies the request for distinction.