

University of Groningen

Catalytic conversion of glycerol to bio-based aromatics

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DOI:
[10.33612/diss.222277430](https://doi.org/10.33612/diss.222277430)

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2022

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):
He, S. (2022). *Catalytic conversion of glycerol to bio-based aromatics*. [Thesis fully internal (DIV), University of Groningen]. University of Groningen. <https://doi.org/10.33612/diss.222277430>

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Summary and Samenvatting

Summary

Bio-based aromatics are in high demand by the petrochemical industry to green up their business, *e.g.*, for the production of bio-based polyethylene terephthalate (bio-PET) using bio-based *para*-xylene. Biomass-derived glycerol, for example in the form of crude glycerol from the biodiesel industry, is abundantly available and is an attractive renewable platform chemical for the production of a variety of bio-based chemicals including aromatics. The research presented in this Ph.D. thesis was conducted (i) to get a better understanding of the catalytic conversion of glycerol to aromatics (GTA) process both at a molecular and reactor level; (ii) to propose and prove strategies to improve GTA performance including co-processing of glycerol and co-feeds and the use of advanced catalyst; and (iii) to demonstrate a bench-scale continuous process for crude glycerol conversion to bio-based aromatics *via* an *ex-situ* catalysis pyrolysis approach.

In **Chapter 1**, a comprehensive review of the state of the art of the catalytic conversion of glycerol to aromatics is provided, including thermal and catalytic pyrolysis of glycerol; co-conversion of glycerol with other co-feeds such as H₂O, alcohols, alkanes, vacuum gas oil, and vegetable oils; mechanisms and kinetics; catalyst development, deactivation, regeneration, and recycle; and reactor and process studies.

In **Chapter 2**, a benchmark study on the catalytic conversion of pure glycerol to bio-aromatics (namely benzene, toluene, and xylenes, bio-BTX) over an un-modified H-ZSM-5 (SiO₂/Al₂O₃ molar ratio of 23) *via* an *ex-situ* catalytic pyrolysis approach in a continuous tandem-micro fixed-bed reactor is reported. A BTX peak carbon yield of 28.1 ± 0.2% was obtained at a pyrolysis temperature of 400 °C, catalytic upgrading temperature of 500 °C, atmospheric pressure, and a WHSV of 1 h⁻¹. The total BTX productivity was about 398 ± 55 mg BTX g⁻¹ catalyst during the catalyst lifetime of 5 h (for a catalyst loading of 1 g). An oxidative regeneration of the spent catalyst was applied and 5 reaction-regeneration cycles were performed successfully. However, a drop in BTX yield after each cycle was observed, indicating an irreversible catalyst deactivation, which was related to the dealumination of the H-ZSM-5 framework.

In **Chapter 3**, a study is described to get a better understanding of the time- and space-resolved catalyst deactivation process during GTA in a continuous fixed bed reactor. Severe coking was observed at the entrance of the catalyst bed at a short time on stream (TOS) and

then throughout the catalyst bed at a longer TOS. Relevant characteristics of the catalyst such as the microporosity and acidity were also reduced with a similar time-space evolution. These results were rationalized using a conversion-zone-migration model, which includes the moving of the deactivation zone to the exit of the reactor, a conversion zone (for BTX formation), and an induction zone (giving rise to side reactions).

In **Chapter 4**, experimental studies involving the use of shaped H-ZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 28) zeolite-based catalysts in combination with various binders including Al_2O_3 , SiO_2 , and kaolinite for GTA are described. The addition of the binder (10 wt.% on catalyst formulation) has a negligible effect on the specific surface area, total pore volume, and total acidity of the catalysts. However, other relevant characteristics such as micropore volume, Brønsted acidity, and crystallinity, were significantly reduced, affecting catalyst performance. Among all catalysts, the H-ZSM-5/ Al_2O_3 catalyst showed the best performance. Compared to pristine H-ZSM-5, the H-ZSM-5/ Al_2O_3 catalyst shows a prolonged catalyst life-time (320 vs. 220 min) and a higher total BTX productivity (518 vs. 312 mg BTX g^{-1} H-ZSM-5).

In **Chapter 5**, further studies are described to improve GTA performance for the zeolite catalyst using the Al_2O_3 binder. A granular H-ZSM-5/ Al_2O_3 (60/40 wt.%) catalyst was prepared and 5 reaction-regeneration cycles were performed. With a high binder content (40 wt.%), the total pore volume and total acidity (mesopores and Lewis acidity in particular) of H-ZSM-5/ Al_2O_3 catalyst were increased compared to the virgin H-ZSM-5 catalyst. Besides the expected prolonged catalyst lifetime (8.5 vs. 6.5 h for H-ZSM-5) and higher total BTX productivity (710 vs. 556 mg g^{-1} H-ZSM-5), the addition of the Al_2O_3 binder retarded irreversible catalyst deactivation, and catalyst performance of the regenerated catalyst after 3 regenerations was still comparable to that of the fresh one. Nevertheless, after 4 regenerations, some irreversible catalyst deactivation occurred, associated with a reduction in total pore volume, crystallinity, acidity (Brønsted acidity in particular), and meso-porosity of the Al_2O_3 binder.

An experimental study using the H-ZSM-5/ Al_2O_3 (60/40 wt.%) catalyst for bio-BTX production from fatty acids, which are abundantly present in crude glycerol, is provided in **Chapter 6**. A peak BTX carbon yield of 22.7 C. % and a total BTX production of 1000 mg g^{-1} HZSM-5 within a catalyst life-time of 6.5 h were obtained for the conversion of a model compound (oleic acid). A total of 7 reaction - regeneration cycles were performed to obtain

insights into catalyst deactivation. The peak BTX carbon yield was slightly decreased with the number of cycles, however, catalyst life-time was remarkably prolonged (*e.g.*, > 24 h for the 7th reaction), leading to a significantly enhanced total BTX production (*e.g.*, 3000 mg g⁻¹ H-ZSM-5 in 24 h). These results imply that the effective hydrogen to carbon ratio (H/C_{eff} , 1.67 and 0.67 for oleic acid and glycerol) of the feed plays an important role when considering catalyst performance.

In **Chapter 7**, a catalytic co-conversion strategy for enhanced aromatics production is discussed. For this purpose, glycerol is co-processed with a second (bio-)feed with a high H/C_{eff} ratio such as fatty acids, alcohols, and alkanes. Synergistic effects of the co-feeding on catalyst performance including peak BTX carbon yield, product selectivity, total BTX productivity, catalyst life-time, and catalyst regenerability, were observed and quantified. Besides, ¹³C- and D-labeled experiments on an integrated fast pyrolysis-GC-Orbitrap MS unit showed that the aromatics are formed from both glycerol and the co-feed. Among the co-feeds studied, the best results were obtained for the co-conversion of glycerol and oleic acid (45/55 wt.%), showing a peak BTX carbon yield of 26.7 C.% and a total BTX production of 1390 mg g⁻¹ HZSM-5 for a catalyst life-time of 11 h.

The catalytic co-conversion of glycerol and oleic acid (45/55 wt.%) to bio-BTX was further investigated with special attention to catalyst deactivation phenomena using 5 reaction-regeneration cycles and the results are described in **Chapter 8**. Detailed catalyst characterization studies showed irreversible changes in the catalyst structure after reaction-regeneration cycle(s) such as textural properties, crystal structure, framework, and acidity, which impact catalyst performance.

The *ex-situ* catalytic pyrolysis of crude glycerol for the production of bio-BTX was demonstrated in a continuous bench-scale unit using a ZSM-5/bentonite catalyst (200 g loading, **Chapter 9**). A bio-BTX carbon yield of 14.6 C.% was obtained at a pyrolysis temperature of 520 °C, catalytic upgrading temperature of 536 °C, and a WHSV of 1 h⁻¹. Catalyst activity decreased with the TOS and dropped by about 8% after 4.7 h. Oxidative regeneration of the spent catalyst to remove the coke was well possible. However, the activities of the regenerated catalysts were only partially recovered. After 11 reaction-regeneration cycles, the bio-BTX carbon yield decreased to 9.7 C.%. These results indicated that special attention should be made in the future to the irreversible catalyst deactivation,

which is most likely related to the exchange of basic cations (e.g., Na⁺) of the binder and of the impurities in the crude glycerol feed with protons of H-ZSM-5 zeolite.

Samenvatting

De petrochemische industrie wil graag vergroenen en als gevolg hiervan is er een sterke vraag naar biogebaseerde aromaten (benzeen, toluen, xylenen, BTX) voor de productie van bijvoorbeeld groene plastics als polyethyleentereftalaat (bio-PET). Glycerol, bijvoorbeeld in de vorm van ruwe glycerol uit de biodieselindustrie, is overvloedig beschikbaar en is een aantrekkelijke groene voeding voor de productie van biogebaseerde chemicaliën. Het onderzoek dat in dit proefschrift beschreven wordt had als doel om glycerol om te zetten naar aromaten (GTA) en met name om (i) een beter begrip te krijgen van de katalytische omzetting zowel op moleculair als op reactorniveau; (ii) het GTA proces te verbeteren, inclusief co-processing van glycerol met andere voedingen en het ontwikkelen van geavanceerde katalysatoren; en (iii) het demonstreren van een continu proces op laboratoriumschaal voor de omzetting van ruwe glycerol naar biogebaseerde aromaten via een *ex-situ* katalytische pyrolyse aanpak.

In **Hoofdstuk 1** wordt een uitgebreid overzicht gegeven van de stand van de techniek van de katalytische omzetting van glycerol naar aromaten, inclusief i) de thermische en katalytische pyrolyse van glycerol; ii) de co-conversie van glycerol met andere voedingen zoals water, alcoholen, alkanen, vacuümgasolie en plantaardige oliën; iii) stand van zaken rond reactie mechanismen en kinetiek; iv) ontwikkeling, deactivering, regeneratie en recycling van katalysatoren; en v) reactor- en proces studies.

In **Hoofdstuk 2** wordt een benchmark studie naar de katalytische omzetting van pure glycerol naar bio-aromaten over een ongemodificeerde H-ZSM-5 katalysator (SiO₂/Al₂O₃ verhouding van 23) via een *ex-situ* katalytische pyrolyse aanpak in een continue tandem-reactor gerapporteerd. De BTX piek koolstofopbrengst was $28.1 \pm 0.2\%$ bij een pyrolyse temperatuur van 400 °C, een katalytische aromatisering temperatuur van 500 °C, atmosferische druk en een WHSV van 1 h⁻¹. De totale BTX productiviteit was ongeveer 398 ± 55 mg BTX g⁻¹-katalysator gedurende de levensduur van de katalysator (5 uur). De gebruikte katalysator kan worden geregenereerd met een oxidatieve regeneratie stap en er werden 5

reactie-regeneratie cycli met succes uitgevoerd. De BTX-opbrengst was wel minder na elke cyclus, wat wijst op een onomkeerbare deactivering van de katalysator, mogelijk als gevolg van dealuminering.

In **Hoofdstuk 3** wordt een experimentele studie beschreven om een beter begrip te krijgen van het deactiveringsproces van de katalysator tijdens het omzetten van glycerol naar aromaten in een continue vastbed reactor. Er treedt al snel coke vorming op bij de ingang van het katalysatorbed en het coke front verplaatst zich door het katalysatorbed bij een langere time on stream (TOS). Naast de vorming van coke op de katalysator werd ook een afname van de microporositeit en zuurgraad van de katalysator waargenomen. Op basis van de resultaten is een kwalitatief conversie zone-migratiemodel opgesteld dat de experimentele data goed beschrijft en verklaart.

In **Hoofdstuk 4** wordt een experimentele studie beschreven waarbij gebruik wordt gemaakt van een zeoliet gebaseerde katalysator in combinatie met verschillende binders waaronder Al_2O_3 , SiO_2 en kaoliniet. De toevoeging van de binder (10 gew.% in de katalysatorformulering) heeft een verwaarloosbaar effect op het specifieke oppervlak, het totale porie volume en de zuurgraad van de katalysatoren. Andere relevante kenmerken, zoals het microporie volume, de Brønsted-zuurgraad en de kristalliniteit, werden echter wel significant verlaagd. H-ZSM-5/ Al_2O_3 -gaf de beste resultaten en de aanwezigheid van de binder leidde tot een significante en verassend langere levensduur van de katalysator (320 vs. 220 min) en een hogere totale BTX-productiviteit (518 vs. 312 mg BTX g^{-1} H-ZSM-5) vergeleken met de H-ZSM-5 zonder de binder.

In **Hoofdstuk 5** worden additionele studies beschreven om de prestaties van de H-ZSM-5/ Al_2O_3 katalysator als beschreven in hoofdstuk 4 verder te verbeteren. Voor dit doel werd een granulaire H-ZSM-5/ Al_2O_3 (60/40 gew.%) katalysator gemaakt, en getest voor 5 reactie-regeneratie cycli. Naast de verwachte langere levensduur van de katalysator (8.5 vs. 6.5 uur voor H-ZSM-5) en een hogere totale BTX-productiviteit (710 vs. 556 mg g^{-1} voor H-ZSM-5), werd ook gevonden dat de snelheid van ongewenste onomkeerbare deactivering verminderde. Zo was na 3 regeneraties de katalysator even actief als de initieel gebruikte katalysator. Niettemin trad na 4 regeneraties wel enige onomkeerbare deactivering van de katalysator op, geassocieerd met een vermindering van het totale porievolume, kristalliniteit, zuurgraad (met name de Brønsted-zuurgraad) en de mesoporositeit van de Al_2O_3 binder.

In **Hoofdstuk 6** wordt een experimenteel onderzoek beschreven om bio-BTX te maken uit vetzuren in plaats van glycerol. Deze vetzuren zijn aanwezig in ruwe glycerol. Bij gebruik van de H-ZSM-5/Al₂O₃ (60/40 gew.%) katalysator in combinatie met oliezuur als voeding is een piek BTX koolstofopbrengst van 22.7 C.% en een totale BTX-productie van 1000 mg g⁻¹ HZSM-5 gevonden. Er werden in totaal 7 reactie-regeneratie cycli uitgevoerd om inzicht te krijgen in de mate van deactivering van de katalysator. De piek BTX-koolstofopbrengst nam enigszins af met het aantal cycli, maar de levensduur van de katalysator werd opmerkelijk verlengd (bijv. > 24 uur voor de 7e reactie), wat leidde tot een significant verhoging van de totale BTX-productie (bijv. 3000 mg g⁻¹ H-ZSM-5 in 24 uur).

In **Hoofdstuk 7** wordt een katalytische co-conversie strategie besproken om de aromaten opbrengst verder te verhogen. In dit geval werd de glycerol gevoed aan de reactor in combinatie met een andere (bio-)voeding met een hoge H/Ceff-verhouding zoals vetzuren, alcoholen en alkanen. Co-voeden leidde tot interessante en onverwachte synergetische effecten op de katalysator prestaties. Bovendien toonden ¹³C- en D-gelabelde experimenten aan dat de aromaten worden gevormd uit zowel glycerol als de co-voeding. Van de onderzochte co-voedingen werden de beste resultaten verkregen met oliezuur (45/55 gew.%), en er werd een piek BTX opbrengst van 26.7 C.% en een totale BTX-productie van 1390 mg g⁻¹ HZSM-5 voor een katalysator levensduur van 11 uur waargenomen.

De katalytische co-conversie van glycerol en oliezuur (45/55 gew.%) naar bio-BTX is verder onderzocht met de nadruk op katalysator deactiverings en de resultaten zijn beschreven in **Hoofdstuk 8**. Gedetailleerde karakteriserings studies aan de katalysator voor en na reactie-regeneratie toonden onomkeerbare veranderingen aan in de katalysatorstructuur die effect hebben op de prestaties van de katalysator.

De *ex-situ* katalytische pyrolyse van ruwe glycerol voor de productie van bio-BTX werd gedemonstreerd in een continue bench-scale unit met behulp van een ZSM-5/bentonietkatalysator (200 g belading, **Hoofdstuk 9**). Een bio-BTX opbrengst van 14.6 C.% werd verkregen bij een pyrolyse temperatuur van 520 °C, een katalytische aromatiserings temperatuur van 536 °C en een WHSV van 1 h⁻¹. De katalysator activiteit nam af met de TOS en daalde met ongeveer 8% na 4.7 uur. Oxidatieve regeneratie van katalysator om de coke te verwijderen bleek goed mogelijk te zijn. De activiteit van de geregenereerde katalysatoren bleek echter substantieel lager te zijn dan de initieel gebruikte katalysator. Na 11 reactie-

regeneratiecycli nam de bio-BTX opbrengst af tot 9.7 C.%. Deze resultaten geven aan dat in de toekomst speciale aandacht moet worden besteed aan de onomkeerbare deactivering van de katalysator, die hoogstwaarschijnlijk verband houdt met de uitwisseling van basische kationen (bijv. Na⁺) van de binder en mogelijk ook van onzuiverheden in de ruwe glycerolvoeding met protonen van de H-ZSM-5 zeoliet.

Appendices

Acknowledgments

I have been asked by friends, colleagues, and collaborators many times why I want to have a second Ph.D. degree. I do not think this curiosity can be satisfied with a few words. Therefore, I decided not to give my answer here. I will think about this question further in my future career and will likely include my thinking in one of the chapters of my life story after my retirement. Now, I would like to give my sincere thanks to those who helped and cared for me during my stay in Groningen.

The Dutch Research Council (Nederlandse Organisatie voor Wetenschappelijk Onderzoek, NWO) and the Dutch company BioBTX B.V. are acknowledged for the financial support to my Ph.D. project - Bio-p-terephthalic acid (Bio-PTA) from glycerol (NWO-LIFT programme, Grant No. 731.016.401, budget of 300 k€).

Prof. Dr. Hero Jan Heeres and Dr. André Heeres are acknowledged for being my supervisors. Dear Erik and Andre, I appreciate that you agreed that I could use the results from the NWO project to obtain a Ph.D. degree from the University of Groningen. We all believe that the results obtained in the project could be a good start for a startup company. I thank you very much for all of your input on my Ph.D. project and also for your consideration and plans for my future career. Anita, Monique, Aline, Rianne, and Danielle, thank you very much as well for the happy times at our three homes, which are memorable and make us feel like a family.

Dr. Niels Schenk and Inouk Muizebelt from BioBTX B.V. are thanked for being involved in my Ph.D. project and for valuable discussions. Your experience and insights into the industrial implementation of *ex-situ* catalytic pyrolysis were an important reference for my research. I thank you very much for initiating a creative study on crude glycerol conversion to bio-based aromatics almost 10 years ago and making a pilot demonstration operational in 2019-2020. I am very proud that I have contributed to this industry-oriented R&D.

My four master students: Kenny Zuur (2018), Frederike Klein (2018-2019), Hero Goldhoorn (2018-2019), and Thomas Kramer (2019-2020) are thanked for performing all the continuous catalytic pyrolysis experiments in the fixed bed reactors and conducting the detailed product analyses. My two bachelor students: Zhuorigebatu Tegudeer and Anshu Chandel from the Honours College (2019-2020), are thanked for performing most of the N₂

and Ar physisorption experiments. The Ph.D. student Dian Sukmayanda Santosa is also thanked for performing all the batch catalytic pyrolysis experiments using a tandem microreactor and a Pyrolysis-GC-Orbitrap MS unit. I appreciate that all of you spent a lot of time and effort in the lab to obtain a large number of duplicated or even triplicated experimental data. I do not doubt that you have learned the basics of heterogeneous catalysis. I am very proud of the outputs that we have achieved together.

The colleagues of the Faculty Technical Support: André de Groot, Harry van Driel, Hans Wagter, Willem Dresmé, Reid van der Velde, Dirk Tilman, Rudi van der Tuin, Wout Marinus, Marnick de Wolf, Frits Luimstra, Ricardo Kedah, Aad van der Weel, Maarten Vervoort, Johan Kuiper, and Gordon Roberts, and also the technicians at the Chemical Engineering department: Anne Appeldoorn, Marcel de Vries, and Erwin Wilbers, are thanked for providing technical support. Your expertise in electronics, mechanics, glass-blowing, and gases and liquid cryogenics are very precious for designing, constructing, and maintaining testing facilities efficiently, and making my laboratory work run smoothly. I am lucky that I had these important experts in different fields supporting me at the University of Groningen.

The product analyses and catalyst characterizations were performed in different laboratories. Jan Henk Marsman, Leon Rohrbach, and Thomas Ruzius (Chemical Engineering Department) are thanked for GC analysis. Hans van der Velde (Stratingh Institute for Chemistry) is thanked for elemental analysis. Dr. Marc Stuart (Electron Microscopy Facility) is thanked for the HR-TEM-EDX analysis. Jur van Dijken (Zernike Institute for Advanced Materials) is thanked for TG-DTG analysis. Prof. Dr. Evgeny Pidko, Bart van der Linden, and Chuncheng Liu (Catalysis Engineering, Delft University of Technology) are thanked for the pyridine-IR analysis. Dr. Karthick Sai Sankar Gupta (Leiden Institute of Chemistry, Leiden University) is thanked for MAS ssNMR analysis. Prof. Dr. Mirjam Kabel, Peter de Gijssel, and Dr. Gijs van Erven (Laboratory of Food Chemistry, Wageningen University & Research) are thanked for the experiments on the Pyrolysis-GC-Orbitrap MS unit. I appreciate that you shared the dedicated analytical instruments in your laboratories and helped me to obtain valuable characterization data.

During my stay in Groningen, I also participated in a one-year business development programme (Group V13, 2020-2021) provided by VentureLab North, which is highly acknowledged. Prof. Dr. Aard Groen, Dr. Cees-Jan Groen, and Aniek Ouendag are thanked for

the organization and management. Hans Cool (investment director of Eneco Ventures), Roelf Venhuizen (former director of NAM), Drs. Corina Prent and Hoang Nguyen (CEO and Investment Manager of the RUG Houdstermaatschappij) are thanked for their valuable discussions and comments on my business plan and panel presentations. Prof. Dr. Ajay Kottapalli and Dr. Amar Kamat (Advanced Production Engineering) are thanked for sharing their experience with a take-off grant application. I particularly would like to thank my private coach, Dr. Volko de Jong (founder of GGNI B.V.) for shaping my business and giving weekly one-to-one coaching on business basics and practice. Becoming an entrepreneur is the next campaign after my Ph.D. Without any doubt, I believe that I can make it and CoRe Pro will be successful.

I would like to thank my previous and current collaborators in the biorefinery domain. Paul Compagne and Ruurd van der Veen (BioMCN - OCI NV), thank you for your input in my first research project in the bio-based field to produce the bio-based H₂/syngas in BioMCN industrial plant. Dr. Bert van de Beld, Dr. Robbie Venderbosch, Elmar Holle, and Jan Florijn (BTG Biomass Technology Group), thank you for your input in the first project of CoRe Pro to explore the thermochemical conversion of fast pyrolysis bio-oil commercially produced by BTG. Gijs Jansen, Anton Bijl, Eyerusalem Gucho, and Theo Janssen (Alucha Management B.V.), thank you for your input to make the first *ex-situ* catalytic pyrolysis of paper sludge demonstrated and to support my first two grants by NWO and RVO. I look forward to our future collaborations.

I also thank my previous professors. Prof. Dr. Cheli Wang (王车礼教授, Changzhou University, PR China), thank you for supervising my bachelor's assignment in your laboratory, where I did my first research project in Chemical Engineering and published my first scientific paper in a peer-reviewed journal. Prof. Chenglin Sun (孙承林研究员, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, PR China), thank you for supervising my first Ph.D. and also offering me a faculty position in your group, which makes my academic career easy to start. Our 8-year collaboration in Industrial Catalysis for refineries led to the commercialization of a new type of long-chain paraffin dehydrogenation catalyst in PetroChina, of which the development experience benefits me in my later (and also future) projects. Prof. Dr. Gerrit Brem (Thermal Engineering, University of Twente), thank you for demonstrating the fast pyrolysis technology in a pilot plant, on which I started my first

development of *ex-situ* catalytic pyrolysis of biomass. Prof. Dr. Kulathuiyer Seshan (Catalytic Processes and Materials, University of Twente), thank you for offering my first postdoc position and bringing me to a new field - Industrial Catalysis for biorefineries. Dear Seshan, I have made it! Thank you and Jayanthi for always being with us as a family after we moved to The Netherlands.

My best friends in China, Xueming Teng (滕学明), Yan Sun (孙岩), and daughter Yiwen Teng (滕怡雯) are also thanked. Your kindness and hospitality make me feel that there is still home in Dalian, and you are always there.

My wife Joy Hou (侯佳燕) and our two sons: Tommy He (何侯闯) and Mark Hou (侯何达), are my best support. I appreciate that you are always with me, encourage me, and motivate me whenever, wherever, and forever.

Last but not the least, I thank the readers who work in the field of sustainable and renewable fuels and chemicals. I appreciate your contribution to a circular economy. I hope that this thesis can be a reference for your R&D.

Sincerely yours,

Songbo He (何松波)



Curriculum vitae

Songbo He (何松波) is a chemical engineer who develops, scales up, and industrializes catalytic processes involving heterogeneous catalysts. He believes that applied heterogeneous catalysis contributes to a circular economy. He is the founder of a Dutch startup - CoRe Pro, specializing in a Co-Refining Process for circularity.



He was born on 12th April 1981 in Jiangsu, PR China. He received his Bachelor in Chemical Engineering from Changzhou University in 2002 and his first Ph.D. in Industrial Catalysis (for refinery) from Dalian Institute of Chemical Physics, Chinese Academy of Sciences, PR China in 2009. He then joined Dalian National Laboratory for Clean Energy (DNL) as an assistant professor (July 2009 - Sept. 2011) and later became an associate professor (Oct. 2011 - Feb. 2014) and a vice-principal investigator of Group DNL0902 (April 2013 - Feb. 2014). Since 2014, he has moved to The Netherlands and worked as a postdoc at the University of Twente (April 2014 - Sept. 2016) and the University of Groningen (Oct. 2016 - Jan. 2022).

He is active in the development of catalytic technologies for the conversion of solid and liquid 'waste' streams to sustainable and renewable fuels and chemicals in The Netherlands. He has participated in several projects funded by research foundations such as TKI BBE, Horizon 2020-ABC Salt, NWO-LIFT, NWO-CatchBio, and NWO-STW, and by bio-refineries such as BioMCN - OCI NV, BioBTX BV, and Alucha Management BV.

He has obtained 4 research grants, including an RVO-TSE (No. TESN121044, in 2021) and an NWO-KIEM GoChem (No. GOCH.KIEM.KGC02.063, in 2021) and in The Netherlands, one from the National Natural Science Foundation of China (No. 21206161, in 2013) and another one from the Liaoning Provincial Natural Science Foundation of China (No. 2013020111, in 2013) in PR China. He has also won 2 Science and Technology Progress Awards by the Shandong Province Government, PR China (No. JB2015-2-41-R05, in 2016) and China Petroleum and Chemical Industry Federation, PR China (No. 2014JBR0652-3-5, in 2014).

He is the (co-)author of 52 papers and 2 chapters in international peer-reviewed journals and book series in the fields of applied heterogeneous catalysis and chemical engineering. Besides, he has 20 papers published in Chinese peer-reviewed journals and 6 granted China patents. He has participated in 7 international conferences and gave 1 keynote presentation, 3 oral presentations, and 1 poster presentation.

Since April 2019, he has been working on his second Ph.D. in Industrial Catalysis (for biorefineries) in the Department of Chemical Engineering at the University of Groningen under the supervision of Prof. Dr. H.J. Heeres and Dr. A. Heeres. The output is presented in this thesis.

Publications related to the research described in this thesis

[1] **Songbo He**, I. Muizebelt, A. Heeres, N.J. Schenk, R. Blee, H.J. Heeres. Catalytic pyrolysis of crude glycerol over shaped ZSM-5/bentonite catalysts for bio-BTX synthesis. *Applied Catalysis B-Environmental*, 2018, 235: 45-55. (Chapter 9)

[2] **Songbo He**, Frederike Gerda Hiltje Klein, Thomas Sjouke Kramer, Anshu Chandel, Zhuorigebatu Tegudeer, André Heeres, Hero Jan Heeres. Catalytic conversion of free fatty acids to bio-based aromatics: A model investigation using oleic acid and an H-ZSM-5/Al₂O₃ catalyst. *ACS Sustainable Chemistry & Engineering*, 2021, 9: 1128-1141. (Chapter 6)

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Heeres, Marc C.A. Stuart, Hero Jan Heeres. A time- and space-resolved catalyst deactivation study on the conversion of glycerol to aromatics using H-ZSM-5. *Chemical Engineering Journal*, 2022, 434: 134620. (Chapter 3)

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Attended conferences

[1] **Songbo He** and Hero Jan Heeres. Catalytic pyrolysis of crude glycerol for bio-based BTX production. **The 15th edition of the Netherlands Process Technology Symposium (NPS15)**, Enschede, The Netherlands, 30-31 May 2018. Keynote presentation.

[2] **Songbo He**, Frederike Gerda Hiltje Klein, Hero Reinder Goldhoorn, Inouk Muizebelt, André Heeres, and Hero Jan Heeres. Catalytic conversion of glycerol and fatty acids to bio-BTX over H-ZSM-5/Al₂O₃ catalyst. **The 26th meeting of the North American Catalysis Society (NAM26)**, Chicago, USA, 23-28 June 2019. Oral presentation.

[3] **Songbo He**, Kenny Zuur, Inouk Muizebelt, André Heeres, and Hero Jan Heeres. Catalytic conversion of glycerol to bio-based low molecular weight aromatics over H-ZSM-5 zeolite. **14th European Congress on Catalysis (EuropaCat 2019)**, Aachen, Germany, 18-23 August 2019. Poster.

[4] **Songbo He** and Hero Jan Heeres. Biobased aromatics and polymers from lignocellulosic biomass. **The 24th Annual Green Chemistry & Engineering (ACS GC&E) Conference**, virtual conference, 16-18 June 2020. Oral presentation.