RATIONAL DESIGN OF NOVEL CATALYTIC SYSTEM FOR UPGRADATION OF BIOMASS-DERIVED FURFURAL TO VALUE-ADDED CHEMICALS AND FUELS

DEBARUN BANERJEE

INDIAN INSTITUTE OF TECHNOLOGY DELHI

AND

THE UNIVERSITY OF QUEENSLAND

JULY 2026

© Indian Institute of Technology Delhi (IITD), New Delhi, 2026

RATIONAL DESIGN OF NOVEL CATALYTIC SYSTEM FOR UPGRADATION OF BIOMASS-DERIVED FURFURAL TO VALUE-ADDED CHEMICALS AND FUELS

by

DEBARUN BANERJEE

Submitted

in fulfilment of the requirements for the joint degree of

DOCTOR OF PHILOSOPHY

to the

INDIAN INSTITUTE OF TECHNOLOGY DELHI

&

THE UNIVERSITY OF QUEENSLAND

JULY 2026

Dedication

To my parents Mrs. Anima Banerjee and Mr. Debasis Bandyopadhyay.

To my grandfathers Late Mr. Biswanath Chakraborty and Late Mr. Pankaj Kumar Bandyopadhyay.

To my grandmothers Late Mrs. Shefali Chakraborty and Mrs. Puspanjali Bandyopadhyay.

SUPERVISOR CERTIFICATION

This is to certify that the thesis entitled "**Rational Design of Novel Catalytic System for Upgradation of Biomass-derived Furfural to Value-added Chemicals and Fuels**" being submitted by **Mr. Debarun Banerjee** to the **Indian Institute of Technology Delhi** and **The University of Queensland** for the award of a joint degree of **Doctor of Philosophy** is a record of Bonafide research work carried out by him. **Debarun** has worked under our guidance and supervision and has fulfilled the requirements for the submission of this thesis, which to our knowledge has reached the requisite standard. The results contained in this thesis are original and have not been submitted, in part or full, to any other University or Institute for the award of any other degree or diploma.





Prof. Sreedevi Upadhyayula
Professor
Department of Chemical Engineering
Indian Institute of Technology Delhi
Hauz Khas, New Delhi, India- 110016

Prof. Jack K. Clegg
Professor
School of Chemistry & Molecular Biosciences
The University of Queensland
St. Lucia, QLD, Australia - 4076

ACKNOWLEDGEMENTS

First and foremost, I would like to express my sincere gratitude to my PhD supervisors, Prof. Sreedevi Upadhyayula and Prof. Jack K. Clegg, for accepting me as a co-advised student in the UQ–IITD Joint PhD Program. I am deeply thankful for their continuous guidance, encouragement and support throughout this research journey. Their mentorship has not only strengthened my technical understanding but also empowered me to grow as an independent researcher, while consistently nurturing my ideas and providing invaluable insights.

I extend my sincere thanks to the Academy Student Milestone Committee members, Prof. Divesh Bhatia, Prof. Manjesh Kumar and Prof. Jingwei Hou, for their constructive feedback, valuable suggestions and encouragement during the course of my doctoral journey. I am also grateful to the Professor-in-Charge of the Academy, Prof. Vigneswara Ilavarasan and former Professors-in-Charge, Prof. Neetu Singh and Prof. Nidhi Jain, for their support. I would like to acknowledge the assistance of the UQ–IITD Research Academy staff, Ms. Ragini Gill, Ms. Aashita Apoorva, Dr. Nidhi Dubey, Ms. Sumita Chakrabortty and Mr. Anil, for their administrative support throughout my PhD journey.

I gratefully acknowledge the support of the academic and technical staff at the Central Research Facility and the Departmental Research Facility of the Department of Chemical Engineering, IIT Delhi, as well as the research facilities at the School of Chemistry and Molecular Biosciences at The University of Queensland, for their assistance with material characterization and data analysis. I am also thankful to my scientific collaborators, Prof. Jithin John Varghese and Dr. Ajin Rajan, for their valuable discussions, insights, and contributions that significantly enriched this work.

I would also like to thank my seniors, colleagues and lab mates, Dr. Meenakshi Pokhriyal, Dr. Ambereen Niaze, Dr. Surya Chandra Tiwari, Dr. Aloka Kumar Sahu, Dr. Caitlin Setter, Aakash Bhardwaj, Chitrangda Singh, Sushant Yadav, Swagat Sabyasachi Sahoo, Rupali Gautam, Srivardhan Grandhi and Anindya Kanti Roy, for their support and camaraderie. I am especially grateful to my friends Kaushik Kundu, Pranit Samanta, Sourav Chowdhury, Gautam Kumar Saw and Debkrishna Dey for the joyful moments and constant encouragement that made this journey lighter and more enjoyable.

Finally, I express my deepest gratitude to my family for their unwavering support, love and encouragement. Thank you, Maa and Baba, for your trust and belief in me. Above all, I thank the Almighty for providing me with the strength and perseverance to complete this journey.

FINANCIAL SUPPORT

This research was supported by the Prime Minister's Research Fellowship (PMRF ID: 1402118) awarded by the Ministry of Education, Government of India. I gratefully acknowledge the financial support provided by the Indian Institute of Technology Delhi, the UQ-IITD Research Academy, and the School of Chemistry and Molecular Biosciences at The University of Queensland. I also acknowledge the Department of Science and Technology (DST), Government of India, for funding support under the FIST project (SR/FST/ET-II/2017/133, dated 27 August 2018) in the Department of Chemical Engineering, IIT Delhi. Additionally, I acknowledge funding support from the SPARC project (No. P3427) from the Ministry of Education, Government of India.

ABSTRACT

The transition toward sustainable chemical production has intensified the need for efficient utilization of lignocellulosic biomass as a renewable carbon source. Among biomass-derived platform molecules, furfural has emerged as a key intermediate due to its large-scale availability from agricultural residues and its versatility for conversion into fuels and value-added chemicals. One of the most promising routes for furfural valorization is its conversion to 2-methylfuran (2-MF), a high-energy-density biofuel with superior combustion properties compared to conventional fuels. Catalytic transfer hydrogenation (CTH), employing alcohols such as isopropanol as hydrogen donors, offers a hydrogen-free, safer, and potentially more sustainable alternative to conventional hydrogenation processes that rely on molecular hydrogen. However, despite significant progress in catalyst development, challenges related to catalyst stability, mechanistic understanding and process integration continue to limit the industrial implementation of this approach.

This thesis presents a comprehensive, multi-scale investigation into the catalytic transfer hydrogenation of furfural to 2-MF, integrating catalyst design, mechanistic and kinetic analysis, and process-level evaluation. Chapter 1 introduces furfural upgradation, biofuel production and the research gaps and the thesis objectives. Further, this chapter provides an understanding of transfer hydrogenation processes and reviews the state-of-art in furfural transfer hydrogenation. In particular, a detailed discussion was carried out regarding the plausible mechanisms, the influence of catalyst properties, hydrogen donor characteristics and reaction conditions governing activity, selectivity and overall process efficiency.

In Chapter 2, the development of Cu-based catalysts derived from the pyrolysis of a Cu-BTC metal organic framework (MOF) was focussed. Controlled pyrolysis was employed to tailor the physicochemical properties of the catalyst, particularly the distribution of Cu^0 and Cu^+ species and surface acidity. The optimized catalyst (CBP-310) exhibited a balanced Cu^0/Cu^+ ratio (~0.22), high surface area, and mesoporous structure, enabling efficient tandem hydrogenation–hydrogenolysis pathways. Under optimized reaction conditions (250 °C, 5 bar), complete furfural conversion with a 2-MF yield of 77% was achieved. The superior performance was attributed to the synergistic interaction between metallic Cu^0 sites and Lewis acidic Cu^+ sites. However, catalyst

stability studies revealed gradual deactivation due to the in situ reduction of Cu^{+} to Cu^{0}, disrupting the metallic–acidic balance and highlighting the limitations of monometallic systems.

In Chapter 3, bifunctional Cu–ReO_x/SiO_2 catalysts were developed via sequential wet impregnation followed by photoreduction. The incorporation of ReO_x significantly enhanced catalytic performance by improving Cu dispersion, reducing particle size, and introducing oxophilic sites capable of facilitating hydrogen transfer. The optimized 6Cu–4ReO_x/SiO_2 catalyst achieved complete furfural conversion with an 81% yield of 2-MF at 225 °C and 10 bar (N_2 atmosphere) within 5 hours. Additionally, high combined yields (> 90%) of furanic alcohols and deoxygenated hydrocarbons were observed across various substrates, demonstrating the versatility of the catalyst system.

Building on the experimental findings, a detailed mechanistic kinetic model was developed in Chapter 4 to quantitatively describe the furfural CTH reaction network. Langmuir–Hinshelwood–Hougen–Watson (LHHW)-type kinetic formulations representing multiple mechanistic scenarios were evaluated against experimental concentration–time data. The analysis revealed that the reaction proceeds predominantly via a stepwise dual-site mechanism over Cu–ReO_x/SiO_2, wherein O–H bond cleavage of isopropanol occurs on ReO_x sites, while C–H activation and hydrogenation reactions occur on Cu sites. The model successfully captured concentration profiles across a temperature range of 210–240 °C with high predictive accuracy (R^2> 0.9). Kinetic parameter estimation indicated that the hydrogenolysis of furfuryl alcohol to 2-MF is the rate-limiting step, with an apparent activation energy of ~67.9 kJ mol^{-1}, significantly higher than that for furfural hydrogenation (~34.6 kJ mol^{-1}). Adsorption thermodynamics further revealed strong adsorption of furfuryl alcohol and weak adsorption of 2-MF, explaining intermediate accumulation and high product selectivity. In contrast, monometallic Cu catalysts were found to follow a concerted single-site mechanism with higher activation barriers, resulting in lower activity and limited hydrodeoxygenation.

In Chapter 5, the process-level feasibility of the CTH pathway was evaluated through integrated process simulation, techno-economic analysis (TEA) and life cycle assessment (LCA). The kinetic model developed in this work was incorporated into process simulations to establish realistic reactor and separation models. The TEA results indicated that the minimum selling price of 2-MF produced via the CTH route is approximately 14.1 US$/kg, which is competitive with

conventional direct hydrogenation processes (12.5–13.8 US$/kg), particularly when the value of coproduct acetone is considered. The analysis also identified solvent circulation and furfural consumption as key contributors to operating costs. The LCA revealed that the environmental performance of the process is strongly influenced by the source of the hydrogen donor, with waste-derived feedstocks significantly reducing greenhouse gas emissions and cumulative energy demand. Additionally, coproduct valorization through system expansion provided further environmental benefits for CTH.

Overall, this thesis establishes a comprehensive framework linking catalyst design, reaction kinetics, and process sustainability for the catalytic upgrading of furfural to 2-MF. The findings highlight the critical role of bifunctional catalysis, mechanistic understanding, and integrated process analysis in advancing biomass conversion technologies. This work provides valuable insights and design principles for the development of efficient, scalable, and sustainable pathways for biofuel and chemical production from renewable resources.

सारांश

सतत रासायनिक उत्पादन की दिशा में बढ़ते प्रयासों ने नवीकरणीय कार्बन स्रोत के रूप में लिग्नोसेलुलोसिक बायोमास के कुशल उपयोग की आवश्यकता को और अधिक महत्वपूर्ण बना दिया है। बायोमास से प्राप्त प्लेटफ़ॉर्म अणुओं में, फर्फुरल एक प्रमुख मध्यवर्ती के रूप में उभरा है, क्योंकि यह कृषि अवशेषों से बड़े पैमाने पर उपलब्ध है और इसे ईंधनों तथा उच्च-मूल्य रसायनों में परिवर्तित करने की बहुमुखी क्षमता रखता है। फर्फुरल के वैलोराइज़ेशन के लिए सबसे आशाजनक मार्गों में से एक इसका 2-मेथिलफ्यूरान (2-MF) में रूपांतरण है, जो एक उच्च ऊर्जा घनत्व वाला जैव-ईंधन है और पारंपरिक ईंधनों की तुलना में बेहतर दहन गुण प्रदर्शित करता है।

कैटालिटिक ट्रांसफर हाइड्रोजनेशन (CTH), जिसमें आइसोप्रोपेनॉल जैसे अल्कोहल को हाइड्रोजन दाता के रूप में उपयोग किया जाता है, आणविक हाइड्रोजन पर आधारित पारंपरिक हाइड्रोजनेशन प्रक्रियाओं की तुलना में एक सुरक्षित, हाइड्रोजन-मुक्त और संभावित रूप से अधिक सतत विकल्प प्रदान करता है। तथापि, उत्प्रेरक विकास में उल्लेखनीय प्रगति के बावजूद, उत्प्रेरक स्थिरता, तंत्र की समझ तथा प्रक्रिया एकीकरण से संबंधित चुनौतियाँ अभी भी इस तकनीक के औद्योगिक कार्यान्वयन को सीमित करती हैं। यह शोध प्रबंध फर्फुरल के 2-MF में कैटालिटिक ट्रांसफर हाइड्रोजनेशन का एक व्यापक, बहु-स्तरीय अध्ययन प्रस्तुत करता है, जिसमें उत्प्रेरक डिजाइन, यांत्रिक एवं गतिज विश्लेषण, तथा प्रक्रिया-स्तरीय मूल्यांकन को एकीकृत किया गया है। अध्याय 1 में फर्फुरल अपग्रेडेशन, जैव-ईंधन उत्पादन, शोध अंतराल तथा शोध उद्देश्यों का परिचय दिया गया है। इसके अतिरिक्त, इस अध्याय में ट्रांसफर हाइड्रोजनेशन प्रक्रियाओं की समझ विकसित की गई है और फर्फुरल ट्रांसफर हाइड्रोजनेशन की वर्तमान स्थिति की समीक्षा प्रस्तुत की गई है। विशेष रूप से, संभावित अभिक्रिया तंत्र, उत्प्रेरक गुणों का प्रभाव, हाइड्रोजन दाता की विशेषताएँ तथा अभिक्रिया स्थितियों का गतिविधि, चयनात्मकता और समग्र प्रक्रिया दक्षता पर प्रभाव का विस्तृत विश्लेषण किया गया है।

अध्याय 2 में Cu-BTC मेटल ऑर्गेनिक फ्रेमवर्क (MOF) के पायरोलिसिस से प्राप्त Cu-आधारित उत्प्रेरकों के विकास पर ध्यान केंद्रित किया गया है। नियंत्रित पायरोलिसिस के माध्यम से उत्प्रेरक के भौतिक-रासायनिक गुणों को अनुकूलित किया गया, विशेषकर Cu^0 और Cu^+ प्रजातियों के वितरण तथा सतही अम्लता को। अनुकूलित उत्प्रेरक (CBP-310) में संतुलित Cu^0/Cu^+ अनुपात (~0.22), उच्च सतह क्षेत्र तथा मेसो-पोरस संरचना पाई गई, जिससे प्रभावी टैंडम हाइड्रोजनेशन-हाइड्रोजेनोलिसिस मार्ग संभव हुआ। अनुकूलित

अभिक्रिया स्थितियों (250 °C, 5 bar) पर पूर्ण फर्फुरल रूपांतरण के साथ 77% 2-MF प्राप्त हुआ। यह उच्च प्रदर्शन धात्विक Cu^0 साइट्स और लुईस अम्लीय Cu^+ साइट्स के बीच सहक्रियात्मक अंतःक्रिया के कारण था। हालांकि, स्थिरता अध्ययन में पाया गया कि समय के साथ Cu^+ का Cu^0 में इन-सिटू अपचयन होने से उत्प्रेरक निष्क्रिय होता गया, जिससे धात्विक-अम्लीय संतुलन बिगड़ गया और एकधात्विक प्रणालियों की सीमाएँ स्पष्ट हुईं।

अध्याय 3 में, द्वि-कार्यात्मक $Cu–ReO_x/SiO_2$ उत्प्रेरकों का विकास क्रमिक वेट इम्प्रेग्नेशन और फोटो-रिडक्शन विधि से किया गया। ReO_x के समावेशन से उत्प्रेरक प्रदर्शन में उल्लेखनीय वृद्धि हुई, क्योंकि इसने Cu के प्रसार में सुधार किया, कण आकार को कम किया और ऑक्सोफिलिक साइट्स प्रदान किए जो हाइड्रोजन स्थानांतरण को सुगम बनाते हैं। अनुकूलित $6Cu–4Re/SiO_2$ उत्प्रेरक ने 225 °C और 10 bar (N_2 वातावरण) पर 5 घंटे में पूर्ण फर्फुरल रूपांतरण के साथ 81% 2-MF प्राप्त किया। इसके अतिरिक्त, विभिन्न सब्सट्रेट्स पर फ्यूरैनिक अल्कोहल्स और डीऑक्सीजनयुक्त हाइड्रोकार्बनों की उच्च संयुक्त उपज (>90%) प्राप्त हुई, जो इस उत्प्रेरक प्रणाली की बहुमुखी क्षमता को दर्शाती है।

अध्याय 4 में, प्रयोगात्मक निष्कर्षों के आधार पर एक विस्तृत यांत्रिक गतिज मॉडल विकसित किया गया, जो फर्फुरल CTH अभिक्रिया नेटवर्क का मात्रात्मक वर्णन करता है। विभिन्न यांत्रिक परिदृश्यों को दर्शाने वाले Langmuir–Hinshelwood–Hougen–Watson (LHHW) प्रकार के गतिज मॉडल को प्रयोगात्मक सांद्रता-समय डेटा के साथ परखा गया। विश्लेषण से स्पष्ट हुआ कि अभिक्रिया मुख्यतः $Cu–ReO_x/SiO_2$ पर एक क्रमिक द्वि-साइट तंत्र के माध्यम से होती है, जिसमें आइसोप्रोपेनॉल का O–H बंध टूटना ReO_x साइट्स पर होता है, जबकि C–H सक्रियण और हाइड्रोजनेशन प्रतिक्रियाएँ Cu साइट्स पर होती हैं। मॉडल ने 210–240 °C तापमान सीमा में सांद्रता प्रोफाइल को उच्च सटीकता ($R^2 > 0.9$) के साथ प्रदर्शित किया। गतिज मापदंडों से ज्ञात हुआ कि फुरफ्यूरिल अल्कोहल से 2-MF का हाइड्रोजेनोलिसिस दर-सीमित चरण है, जिसका सक्रियण ऊर्जा (~67.9 kJ mol^{-1}) फर्फुरल हाइड्रोजनेशन (~34.6 kJ mol^{-1}) की तुलना में अधिक है। अवशोषण ऊष्मागतिकी से यह भी ज्ञात हुआ कि फुरफ्यूरिल अल्कोहल का अवशोषण मजबूत है, जबकि 2-MF का कमजोर, जिससे मध्यवर्ती संचय और उच्च चयनात्मकता की व्याख्या होती है। इसके विपरीत, एकधात्विक Cu उत्प्रेरक एकल-साइट तंत्र का अनुसरण करते हैं, जिनमें अधिक सक्रियण अवरोध होने के कारण गतिविधि कम और डीऑक्सीजनशन सीमित होता है।

अध्याय 5 में, CTH मार्ग की प्रक्रिया-स्तरीय व्यवहार्यता का मूल्यांकन प्रक्रिया सिमुलेशन, टेक्नो-इकोनॉमिक विश्लेषण (TEA) और लाइफ साइकल असेसमेंट (LCA) के माध्यम से किया गया। इस कार्य में विकसित गतिज मॉडल को प्रक्रिया सिमुलेशन में सम्मिलित किया गया, जिससे यथार्थवादी रिएक्टर और पृथक्करण मॉडल स्थापित किए जा सके। TEA परिणामों से ज्ञात हुआ कि CTH मार्ग से उत्पादित 2-MF का न्यूनतम विक्रय मूल्य लगभग 14.1 US$/kg है, जो पारंपरिक प्रत्यक्ष हाइड्रोजनेशन प्रक्रियाओं (12.5–13.8 US$/kg) के तुलनीय है, विशेष रूप से सह-उत्पाद एसीटोन के मूल्य को ध्यान में रखते हुए। विश्लेषण में यह भी पाया गया कि सॉल्वेंट पुनर्चक्रण और फर्फुरल की खपत संचालन लागत के प्रमुख कारक हैं। LCA से यह स्पष्ट हुआ कि प्रक्रिया का पर्यावरणीय प्रदर्शन हाइड्रोजन दाता के स्रोत पर अत्यधिक निर्भर करता है, जहाँ अपशिष्ट-आधारित फीडस्टॉक्स ग्रीनहाउस गैस उत्सर्जन और ऊर्जा मांग को महत्वपूर्ण रूप से कम करते हैं। इसके अतिरिक्त, सह-उत्पाद के उपयोग द्वारा प्रणाली विस्तार से अतिरिक्त पर्यावरणीय लाभ प्राप्त होते हैं।

समग्र रूप से, यह शोध प्रबंध फर्फुरल से 2-MF में रूपांतरण के लिए उत्प्रेरक डिजाइन, अभिक्रिया गतिशीलता और प्रक्रिया स्थिरता को जोड़ने वाला एक व्यापक ढांचा प्रस्तुत करता है। निष्कर्ष द्वि-कार्यात्मक उत्प्रेरण, यांत्रिक समझ और एकीकृत प्रक्रिया विश्लेषण की महत्वपूर्ण भूमिका को उजागर करते हैं, जो बायोमास रूपांतरण तकनीकों को आगे बढ़ाने में सहायक हैं। यह कार्य नवीकरणीय संसाधनों से ईंधन और रसायनों के कुशल, विस्तार योग्य और सतत उत्पादन मार्गों के विकास के लिए महत्वपूर्ण अंतर्दृष्टि और डिजाइन सिद्धांत प्रदान करता है।

Declaration by Author

This thesis is composed of my original work and contains no material previously published or written by another person except where due reference has been made in the text. I have clearly stated the contribution of others to jointly authored works that I have included in my thesis.

I have clearly stated the contributions of others to my thesis as a whole, including statistical assistance, survey design, data analytics, significant technical procedures, professional editorial advice, financial support and any other original research work used or reported in my thesis. The content of my thesis is the result of work I have carried out since the commencement of my higher degree by research candidature and does not include a substantial part of work that has been submitted to qualify for the award of any other degree or diploma in any university or other tertiary institution. I have clearly stated which parts of my thesis, if any, have been submitted to qualify for another award.

I acknowledge that an electronic copy of my thesis must be lodged with the University Library and, subject to the policy and procedures of The University of Queensland, the thesis be made available for research and study in accordance with the Copyright Act 1968 unless a period of embargo has been approved by the Dean of Graduate School.

I acknowledge that the copyright of all material contained in my thesis resides with the copyright holder(s) of that material. Where appropriate, I have obtained copyright permission from the copyright holder to reproduce material in this thesis and have sought permission from co-authors for any jointly authored works included in this thesis.

Publications and Statement of Contributions

Publications included in this thesis

1. **Debarun B**, Aloka KS, Jack KC, Sreedevi U. Recent Advances in 2-Methylfuran Production via Catalytic Transfer Hydrogenation of Biomass-derived Furfural. *Chemical Engineering Journal,* 493, 152552, **2024**. (Incorporated in Chapter 1)

Contribution statement

Debarun Banerjee: Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. Aloka Kumar Sahu: Writing – review & editing, Methodology, Formal analysis. Jack Kay Clegg: Writing – review & editing, Supervision, Conceptualization. Sreedevi Upadhyayula: Writing – review & editing, Supervision, Conceptualization.

2. **Debarun B**, Sushant Y, Aloka KS, Jack KC, Sreedevi U. Transfer Hydrogenation of Furfural to 2-Methylfuran over a Cu-BTC-derived Catalyst with Isopropanol as a Hydrogen Donor. *Energy Fuels*, 38, 11, 9814-9826, **2024**. (Incorporated in Chapter 2)

Contribution statement

Debarun Banerjee: Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. Sushant Yadav: Writing – review & editing, Methodology, Investigation. Aloka Kumar Sahu: Writing – review & editing, Formal analysis, Conceptualization. Jack Kay Clegg: Writing – review & editing, Supervision. Sreedevi Upadhyayula: Writing – review & editing, Project administration, Funding acquisition, Conceptualization.

3. **Debarun B**, Aloka KS, Ajin R, Agrim S, Jithin JV, Jack KC, Sreedevi U. Reductive Transfer Hydrogenation of Furfural to 2-Methylfuran over a Re-assisted Cu Catalyst. *Chemical Engineering Journal*, 525, 169866, **2025**. (Incorporated in Chapters 3 and 4)

Contribution statement

Debarun Banerjee: Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. Aloka Kumar Sahu: Writing – review & editing, Formal analysis,

Conceptualization. Ajin Rajan: Writing – review & editing, Methodology, Investigation. Agrim Singh: Methodology. Jithin John Varghese: Writing – review & editing, Supervision. Jack Kay Clegg: Writing – review & editing, Supervision. Sreedevi Upadhyayula: Writing – review & editing, Project administration, Funding acquisition, Conceptualization.

Unpublished manuscripts included in this thesis

1. **Debarun B**, Jack KC, Sreedevi U. Mechanistic Kinetic Model of Furfural Transfer Hydrogenation.

Contribution statement

Debarun Banerjee: Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. Jack Kay Clegg: Writing – review & editing, Supervision. Sreedevi Upadhyayula: Writing – review & editing, Project administration, Conceptualization.

2. **Debarun B**, Jack KC, Sreedevi U. Conceptual Process Design, Techno-economics and Lifecycle Analysis of 2-Methylfuran Production.

Contribution statement

Debarun Banerjee: Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. Jack Kay Clegg: Writing – review & editing, Supervision. Sreedevi Upadhyayula: Writing – review & editing, Project administration, Conceptualization.

Conferences

Contributed talks

1. Debarun B, Jack KC, Sreedevi U. Synergistic Cu-ReO_x Catalysis for Hydrogen-Free Transfer Hydrogenation of Furfural: Pathway to Value-Added Chemicals and Fuels. 29th North American Catalysis Society Meeting (NAM29) **2025**, Atlanta, GA, USA.

2. Debarun B, Jack KC, Sreedevi U. Selective and Cost-Effective Hydrogen-Free Deoxygenation of Furfural Using a Copper Catalyst. IIChE CHEMCON **2024**, Jalandhar, India.

3. Debarun B, Sushant Y, Jack KC, Sreedevi U. Copper-based Catalysts for Sustainable Furanic Biofuel Production via Transfer Hydrogenation Reaction. National Conference on Catalysis for Energy, Environment & Sustainability (CEES) **2024**, Hyderabad, India.

4. Debarun B, Sreedevi U, Jack KC. Designing robust Cu-based catalysts for sustainable biofuel production: Balancing metallic and acid sites for enhanced performance. ACS Fall **2024**, Virtual.

Poster Demonstration

1. Debarun B, Jack KC, Sreedevi U. Beyond Molecular Hydrogen: Multifunctional Catalysts for Selective Upgrading of Furanic Aldehydes to Sustainable Biofuels. Gordon Research Seminar & Conference: Biomass to Biobased Chemicals and Materials **2025**, Newry, ME, USA.

2. Debarun B, Jack KC, Sreedevi U. Furfural transfer hydrogenation over metal organic framework-derived catalyst. 18th International Congress on Catalysis (ICC) **2024**, Lyon, France.

3. Debarun B, Jack KC, Sreedevi U. Catalytic Transfer Hydrogenation of Biomass-based Furfural over Copper Catalyst. 15th European Congress on Catalysis (EuropaCat) **2023**, Prague, Czechia.

4. Debarun B, Sreedevi U, Jack KC. Sustainable Production of Biofuel from Biomass-derived Furfural using Heterogeneous Catalyst. Global Bioeconomy Alliance Conference **2023**, Brisbane, Australia.

Keywords: Furfural, Catalysis, Transfer hydrogenation, 2-Methylfuran, Biomass conversion, Reaction Mechanism, Techno-economic analysis, Lifecycle analysis

Australian and New Zealand Standard Research Classifications (ANZSRC)

ANZRSC code: 400408- Reaction engineering (excl. nuclear reactions), 40%

ANZRSC code: 400499- Chemical engineering not elsewhere classified, 25%

ANZRSC code: 340601- Catalysis and mechanism of reactions, 15%

ANZRSC code: 340607- Reaction kinetics and dynamics, 10%

ANZRSC code: 401105- Life cycle assessment and industrial ecology, 10%

Fields of Research Classification

FoR code: 4004, Chemical engineering, 65%

FoR code: 3406, Physical chemistry, 25%

FoR code: 4011, Environmental engineering, 10%

Table of Contents

Acknowledgements i
Financial Support ii
Abstract iii
सारांश vi
Declaration by Author ix
Publications and Statement of Contributions x
Conferences xii
Australian and New Zealand Standard Research Classifications xiii
Field of Research Classification xiii
Table of Contents xiv
List of Figures xviii
List of Tables xxii
List of Abbreviations xxiv
Chapter 1 Introduction & Literature Review 1
1.1. Background 2
1.2. Research gaps and motivation 4
1.3. Objectives of the Thesis 5
1.4. Outline of the Thesis 6
1.5. Overview of the literature review 7
1.6. Mechanistic pathways of 2-MF formation via catalytic transfer hydrogenation of furfural.. 8
1.7. Catalyst families for furfural transfer hydrogenation to 2-MF 11
1.7.1. Noble metal-based catalysts 12
1.7.1.1. Ru-based catalysts 12
1.7.1.2. Pd-based catalysts 15
1.7.1.3. Ir-based catalysts 19
1.7.2. Non-noble metal-based catalysts 20
1.7.2.1. Ni-based catalysts 20
1.7.2.2. Cu-based catalysts 22
1.7.2.3. Other non-noble metal-based catalysts 27

1.8. Effect of properties of H-donor solvents on 2-MF production via furfural transfer hydrogenation 29

1.9. Reactor types and configurations used for 2-MF production via furfural transfer hydrogenation 32

1.10. Impact of operating parameters on 2-MF yield and furfural conversion 34

1.11. Summary 38

Chapter 2 Transfer Hydrogenation of Furfural to 2-Methylfuran over a Cu-BTC-derived Catalyst with Isopropanol as a Hydrogen Donor 39

2.1. Introduction 40

2.2. Materials and methods 42

2.2.1. Materials and chemicals 42

2.2.2. Synthesis of Cu-BTC and CBP-T sample 42

2.2.3. Structural characterization 43

2.2.4. Catalytic activity tests 44

2.3. Results and discussion 45

2.3.1. Catalyst characterization 45

2.3.2. Reaction evaluation of CBP-T samples toward furfural transfer hydrogenation 51

2.3.3. Optimization of reaction parameters toward 2-MF production via furfural transfer hydrogenation 53

2.3.4. Transfer hydrogenation reactions of furfural aqueous solution 57

2.3.5. Kinetic investigations into catalytic transfer hydrogenation of furfural 58

2.4. Conclusions 59

Chapter 3 Reductive Transfer Hydrogenation of Furfural to 2-Methylfuran over a Re-assisted Cu Catalyst 61

3.1. Introduction 62

3.2. Materials and methods 63

3.2.1. Materials and chemicals 63

3.2.2. Catalyst synthesis 63

3.2.3. Catalyst characterization 65

3.2.4. Transfer hydrogenation reactions 66

3.3. Results and discussion 67

3.3.1. Characterization of catalysts 67

3.3.2. Reaction activity evaluations toward CTH of furfural 74
3.3.3. Catalytic transfer hydrogenation of furanic aldehydes 85
3.4. Conclusions 87
Chapter 4 Mechanistic Kinetic Modeling of Furfural Transfer Hydrogenation to 2-Methylfuran 88
4.1. Introduction 89
4.2. Methodology 90
4.2.1. Experimental details 90
4.2.2. Power law kinetics of furfural transfer hydrogenation 90
4.2.3. Langmuir-Hinshelwood-Hougen-Watson kinetic model of furfural transfer hydrogenation 91
4.3. Results and discussion 93
4.3.1. Power law-based kinetic model of furfural transfer hydrogenation 93
4.3.2. Langmuir-Hinshelwood-Hougen-Watson kinetic model of furfural transfer hydrogenation 95
4.3.3. Mechanistic validation and elucidation of Re-mediated bifunctional pathway in furfural transfer hydrogenation 99
4.4. Conclusions 103
Chapter 5 Conceptual Process Design, Techno-economics and Life Cycle Assessment of 2-Methylfuran Production from Furfural 105
5.1. Introduction 106
5.2. Methodology 107
5.2.1. Process simulation and design 107
5.2.2. Economics analysis 109
5.2.3. Life cycle assessment 110
5.3. Results and discussion 112
5.3.1. Process simulation 112
5.3.2. Economics analysis 115
5.3.3. Life cycle assessment 121
5.3.4. Overall economics-environmental impact analysis 126
5.4. Conclusions 127

Chapter 6 Conclusions and Future Recommendations 129
6.1. Conclusions 129
6.2. Future recommendations 130
References 133
Appendices A1
Appendix 1 ..... A1
Appendix 2 ..... A9
Appendix 3 ..... A17
Appendix 4 ..... A27
References A31
Curriculum Vitae

List of Figures

Figure 1.1. Possible products of furfural conversion

Figure 1.2. Conceptual illustration comparing catalytic transfer hydrogenation and conventional direct hydrogenation routes

Figure 1.3. Overall workflow of the thesis

Figure 1.4. Mechanistic pathways of 2-MF formation via furfural transfer hydrogenation

Figure 1.5. Catalyst families for 2-MF production via furfural transfer hydrogenation

Figure 1.6. (a) Adsorption configurations of furfural on transition metals. (b) Effect of N-doping amount in carbon on Ru nanoparticle size of Ru-N@carbon catalyst. (c) Effect of Ru-loading in the Ru-$NiFe_2O_4$ catalyst on 2-MF yield and furfural conversion. (d) STEM images and corresponding elemental maps of filtered-washed and impregnated Pd-Ni-TUD-1 catalysts

Figure 1.7. (a) X-ray diffraction spectra of Ni-activated carbon catalysts, where symbols indicate the respective crystalline phase. (b) Product yield and furfural conversion over 10wt.% Ni catalyst-loaded over different supports. (c) 2-MF formation via successive hydrogenation-hydrogenolysis of furfural over bimetallic Ni-Cu-Al_2O_3 catalyst. (d) Cu LMM XAES spectra of Cu-Al catalysts reduced under varying temperatures. (e) High-resolution TEM image and X-ray diffraction spectra of Cu-Zn-Al_2O_3 catalyst

Figure 1.8. Spectrum of H-donor solvents used in furfural transfer hydrogenation to 2-MF

Figure 1.9. List of most widely used reactors in furfural transfer hydrogenation reaction for 2-MF production

Figure 1.10. Effects of operating parameters: (a) operating temperature, (b) operating pressure, (c) liquid reactant flowrate, (d) contact time on furfural conversion and 2-MF yield

Figure 2.1. PXRD patterns of Cu-BTC and CBP-T catalysts

Figure 2.2. FE-SEM images of (a) Cu-BTC and (b) CBP-310. (c) HR-TEM image of CBP-310.

Figure 2.3. XPS full spectra of CBP-310 catalyst. High-resolution XPS spectra corresponding to (b) Cu 2p orbital, (c) Cu LMM and (d) C 1s orbital of CBP-310

Figure 2.4. (a) Raman spectra and (b) NH_3-TPD profiles of CBP-T catalysts

Figure 2.5. Catalytic performance of (a) different samples and (b) CBP-T samples toward furfural transfer hydrogenation. 2-MF yield as a function of (c) Cu(0):Cu(I) ratio and (d) total acidity of the catalysts

Figure 2.6. Furfural conversions and product yields using CBP-310 catalyst in furfural transfer hydrogenation as a function of (a) operating temperature, (b) time, and (c) catalyst concentration. (d) Recyclability tests of CBP-310 catalyst in furfural transfer hydrogenation.

Figure 2.7. (a) PXRD patterns and (b) Cu LMM XPS spectra of fresh and spent CBP-310 catalyst after four cycles of reaction

Figure 2.8. Transfer hydrogenation reaction of crude furfural containing 0-10 wt.% water over CBP-310 catalyst

Figure 2.9. Results of kinetic studies of (a) furfural and (b) FFA conversion via transfer hydrogenation

Figure 3.1. PXRD patterns of as-synthesized catalysts

Figure 3.2. TEM images of (a) 6CS PR and (b) 6C4RS PR catalysts. (c) HR-TEM image of 6C4RS PR catalyst. (d) HAADF-STEM image of 6C4RS PR and corresponding mapping of (e) Cu and (f) Re

Figure 3.3. (a) XPS full spectra of 6C4RS PR catalyst. High-resolution XPS spectra of 6CS Calc, 6CS PR, 6C4RS Calc and 6C4RS PR corresponding to (b) Cu 2p orbital and (c) Cu LMM Auger transition. High-resolution XPS spectra of 6C4RS Calc, 6C4RS PR and 4RS PR corresponding to (d) Re 4f orbital

Figure 3.4. NH_3-TPD profiles of catalysts

Figure 3.5. (a) Furfural conversions and product yields using different photoreduced catalysts toward furfural transfer hydrogenation, (b) Radar plot illustrating the structure-activity relationships in different photoreduced catalysts.

Figure 3.6. Concentration profiles of furfural and products over time in the presence of 6CS PR catalyst at (a) 210 °C, (b) 225 °C, (c) 240 °C and in the presence of 6C4RS PR catalyst at (d) 210 °C, (e) 225 °C and (f) 240 °C.

Figure 3.7. Effects of (a) hydrogen donor, (b) furfural-to-hydrogen donor molar ratio, (c) N_2 pressure, and (d) catalyst-to-furfural mass ratio on furfural conversions and product yields using 6C4RS PR catalyst toward furfural transfer hydrogenation

Figure 3.8. (a) PXRD patterns, (b) Cu LMM and (c) Re 4f XPS spectra and (d) TG-DTG profiles of fresh and used 6C4RS PR catalyst after five cycles of reaction

Figure 3.9. Comparative analysis of the 6C4RS PR catalyst with existing state-of-the-art catalysts for CTH of furfural to 2-MF

Figure 4.1. Experimental and simulated concentration profiles based on the pseudo-first-order power law kinetic model at (a) 210 °C, (b) 225 °C and (c) 240 °C

Figure 4.2. Experimental and simulated concentration profiles for the LHHW kinetic model (Scenario 3) at (a) 210 °C, (b) 225 °C and (c) 240 °C over Cu-ReO_x/SiO_2 catalyst

Figure 4.3. Van't Hoff plots corresponding to adsorption equilibrium constants of (a) furfural, (b) FFA, (c) 2-MF and (d) water, as determined from LHHW model fitting (Scenario 3)

Figure 4.4. *In situ* FTIR spectra of isopropanol adsorption on (a) 6CS and (b) 6C4RS catalyst, furfural adsorption on (c) 6CS and (d) 6C4RS catalyst and FFA adsorption on (e) 6CS and (f) 6C4RS catalyst over a temperature range of 25-240 °C

Figure 5.1. Generic block flow diagrams of the 2-MF production processes from furfural

Figure 5.2. Distribution of total operating costs among the major contributing categories for 2-MF production from furfural via (a) CTH, (b) liquid phase direct hydrogenation and (c) gas phase direct hydrogenation

Figure 5.3. Sensitivity analysis of MSP of 2-MF produced via (a) CTH, (b) liquid phase direct hydrogenation and (c) gas phase direct hydrogenation process

Figure 5.4. Greenhouse gas emissions of the six process scenarios studied for 2-MF production based on (a) economic allocation and (b) system expansion

Figure 5.5. Cumulative energy demands of six process scenarios studied for 2-MF production based on (a) economic allocation and (b) system expansion

Figure 5.6. Uncertainty analysis of (a) GHG emissions and (b) CED of 2-MF production pathways based on different allocation methods

Figure 5.7. (a) GHG emissions versus MSP and (b) CED versus MSP for the six different 2-MF production scenarios

Figure A1.1. N_2 adsorption-desorption isotherm and pore size distribution of Cu-BTC

Figure A1.2. TGA profile of pristine Cu-BTC

Figure A1.3. N_2 adsorption-desorption isotherms and pore size distributions of (a) CBP-300, (b) CBP-310, (c) CBP-320 and (d) CBP-330

Figure A1.4. Cu LMM XPS spectra of (a) CBP-300, (b) CBP-320 and (c) CBP-330

Figure A1.5. C 1s XPS spectra of (a) CBP-300, (b) CBP-320 and (c) CBP-330

Figure A1.6. Variation of $sp^3{}_{C-C}$: $sp^2{}_{C=C}$ ratio in the CBP-T catalysts as a function of Cu-BTC pyrolysis temperature

Figure A1.7. Effect of pyrolysis temperature on total acidity of CBP-T catalysts

Figure A1.8. Furfural conversions and product yields using CBP-310 catalyst in transfer hydrogenation reaction as a function of N_2 pressure

Figure A1.9. GC-MS spectra of furfural transfer hydrogenation products by CBP-T catalysts

Figure A1.10. TGA profiles of fresh and spent CBP-310 catalyst after 4 cycles of reaction

Figure A1.11. Plots of -ln(1-X) versus time for (a) furfural and (b) FFA conversion via transfer hydrogenation over CBP-310 catalyst

Figure A2.1. PXRD patterns of (a) 6C4RS catalysts photoreduced for different durations and (b) photoreduced catalysts with various Cu-Re compositions

Figure A2.2. (a) N_2 adsorption-desorption isotherms and (b) pore size distributions of the catalysts

Figure A2.3. FE-SEM images and corresponding elemental maps of (a-c) 6CS PR and (d-g) 6C4RS PR samples

Figure A2.4. H_2-TPR profiles of calcined catalysts

Figure A2.5. Effect of stirring speed on furfural conversion and product yields using 6C4RS PR catalyst

Figure A2.6. TOF of different photoreduced catalysts toward furfural transfer hydrogenation

Figure A2.7. Furfural conversions and product yields toward furfural transfer hydrogenation over different catalysts

Figure A2.8. Gibbs free energy change of the major reactions as a function of temperature at 10 bar_{abs}

Figure A3.1. Schematic representation of the reaction network for CTH of furfural

Figure A3.2. Arrhenius plots corresponding to the pseudo-first-order power law kinetic model for individual reaction steps: (a) furfural hydrogenation to FFA, (b) FFA hydrodeoxygenation to 2-MF, (c) FFA ring hydrogenation to THFA and (d) 2-MF ring hydrogenation to 2-MTHF

Figure A3.3. Eyring plots corresponding to the pseudo-first-order power law kinetic model for key reaction steps: (a) furfural hydrogenation to FFA, (b) FFA hydrodeoxygenation to 2-MF

Figure A3.4. Schematic representation of the proposed mechanism for Scenario 1 (concerted single site model), involving concerted hydride transfer on Cu sites

Figure A3.5. Schematic representation of the proposed mechanism for Scenario 2 (concerted dual site model), involving concerted hydride transfer across adjacent Cu and ReO_x sites

Figure A3.6. Schematic representation of the proposed mechanism for Scenario 3 (stepwise dual site model), highlighting bifunctional Cu-Re catalysts involving O-H bond cleavage on ReO_x sites and C-H bond activation on Cu sites

Figure A3.7. Experimental and model-predicted concentration profiles for the LHHW kinetic model (Scenario 1) at (a) 210 °C, (b) 225 °C and (c) 240 °C over Cu-Re/SiO_2

Figure A3.8. Experimental and model-predicted concentration profiles for the LHHW kinetic model (Scenario 2) at (a) 210 °C, (b) 225 °C and (c) 240 °C over Cu-Re/SiO_2

Figure A3.9. Experimental and model-predicted concentration profiles for the LHHW kinetic model (Scenario 1) at (a) 210 °C, (b) 225 °C and (c) 240 °C over Cu/SiO_2

Figure A3.10. Furfural conversions, product yields, acetone formation and hydrogen transfer efficiencies of (a) 6CS PR and (b) 6C4RS PR catalyst

Figure A3.11. FFA conversions and product yields toward transfer hydrogenation and direct hydrogenation

Figure A4.1. Process flow diagram of the 2-MF production process via CTH

Figure A4.2. Process flow diagram of the 2-MF production process via liquid phase direct hydrogenation

Figure A4.3. Process flow diagram of the 2-MF production process via gas phase direct hydrogenation

List of Tables

Table 1.1. Ru-based catalysts for furfural transfer hydrogenation to 2-MF

Table 1.2. Pd-based catalysts for furfural transfer hydrogenation to 2-MF

Table 1.3. Ni-based catalysts for furfural transfer hydrogenation to 2-MF

Table 1.4. Cu-based catalysts for furfural transfer hydrogenation to 2-MF

Table 1.5. Mg and Fe-based catalysts for furfural transfer hydrogenation to 2-MF

Table 1.6. Effects of operating parameters on furfural transfer hydrogenation to 2-MF

Table 2.1. Physicochemical properties of Cu-BTC and CBP-T catalysts

Table 3.1. Physicochemical properties of catalysts

Table 3.2. The susbtsrate scope of furanic aldehydes for transfer hydrogenation over 6C4RS PR catalyst

Table 4.1. Kinetic parameters, including rate constants and apparent activation energies for individual reaction steps obtained from LHHW model fitting (Scenario 3) and subsequent Arrhenius evaluation

Table 5.1. Economic assumptions and parameter values for TEA of 2-MF production from furfural

Table 5.2. Scenario-wise product, co-product and displaced product with respective allocation shares

Table 5.3. Process model results for the CTH and direct hydrogenation processes

Table 5.4. Capital and operating costs of 2-MF production via CTH and direct hydrogenation processes

Table A1.1. Comparison of catalytic activities of CBP-310 with the literature-reported catalysts in furfural transfer hydrogenation to 2-MF

Table A1.2. Composition of Cu-BTC and CBP-T samples

Table A1.3. Catalytic performance of various samples toward furfural transfer hydrogenation

Table A1.4. Results of kinetic studies of furfural conversion via transfer hydrogenation

Table A1.5. Results of kinetic studies of FFA conversion via transfer hydrogenation

Table A2.1. Comparison of the activity of the 6C4RS PR catalyst with the literature-reported catalysts for CTH of furfural to 2-MF

Table A2.2. Eco-score evaluation for CTH of furfural to 2-MF using 6C4RS PR catalyst

Table A3.1. Major catalyst and reaction parameters considered for the calculation of Mears number

Table A3.2. Major catalyst and reaction parameters considered for the calculation of Weisz-Prater number

Table A3.3. Pseudo first-order-based power law rate constants and activation energies

Table A3.4. Surface reaction and adsorption/desorption steps involved and corresponding kinetic equations for Scenario 1

Table A3.5. Surface reaction and adsorption/desorption steps involved and corresponding kinetic equations for Scenario 2

Table A3.6. Surface reaction and adsorption/desorption steps involved and corresponding kinetic equations for Scenario 3

Table A3.7. Adsorption thermodynamic parameters, including equilibrium constants and corresponding enthalpy and entropy values, obtained from LHHW model fitting (Scenario 3) and Van't Hoff analysis

Table A4.1. Process stream table for the CTH process

Table A4.2. Process stream table for the liquid phase direct hydrogenation process

Table A4.3. Process stream table for the gas phase direct hydrogenation process

List of Abbreviations

FFA – Furfuryl alcohol

2-MF – 2-Methylfuran

2-MTHF – 2-Methyltetrahydrofuran

TRL – Technology readiness level

CTH – Catalytic transfer hydrogenation

MOF – Metal-organic framework

TEA – Techno-economic analysis

LCA – Life cycle assessment

MPV – Meerwein-Ponndorf-Verley

THFA – Tetrahydrofurfuryl alcohol

BTC – Benzene-1,3,5-tricarboxylic acid

DI – De-ionised

PXRD – Powder X-ray diffractometer

ICP-MS – Inductively coupled plasma mass spectrometry

FE-SEM – Field emission scanning electron microscope

HR-TEM – High-resolution transmission electron microscope

XPS – X-ray photoelectron spectroscopy

TPD – Temperature programmed desorption

TCD – Thermal conductivity detector

TGA – Thermogravimetric analysis

GC – Gas chromatography

FID – Flame ionization detector

TOF – Turnover Frequency

LHHW – Langmuir–Hinshelwood–Hougen–Watson

TCI – Total capital investment

FCI – Fixed capital investment

MSP – Minimum selling price

NPV – Net present value

GHG – Greenhouse gas

CED – Cumulative energy demand