

# Optimizing Reaction Conditions for the Hydrogenation Kinetics of 2-Methylquinoline as a Heterocyclic Liquid Organic Hydrogen Carrier (LOHC) Using Ru/Al<sub>2</sub>O<sub>3</sub> Catalyst

Emilija Rakić <sup>a,e</sup>, Jošt Oblak <sup>a</sup>, Blaž Likozar <sup>a,b,c,d,\*</sup>

<sup>a</sup> Department of Catalysis and Chemical Reaction Engineering, National Institute of Chemistry, Hajdrihova, 1001 Ljubljana, Slovenia

<sup>b</sup> Pulp and Paper Institute, Bogišičeva, 1000 Ljubljana, Slovenia

<sup>c</sup> Faculty of Polymer Technology, Ozare, 2380 Slovenj Gradec, Slovenia

<sup>d</sup> Faculty of Chemistry and Chemical Technology, University of Ljubljana, Večna pot, 1001 Ljubljana, Slovenia

<sup>e</sup> Faculty of Chemistry and Chemical Engineering, University of Maribor, Smetanova ulica, 2000, Maribor, Slovenia

\*Corresponding author: [blaz.likozar@ki.si](mailto:blaz.likozar@ki.si)

## Highlights

- LOHCs present a cost-effective, and promising solution for sustainable hydrogen storage.
- At higher temperatures, the reaction accelerates, enhancing selectivity for the desired product.
- The study produced a detailed kinetic model with calculated activation energies and kinetic rates.

## 1. Introduction

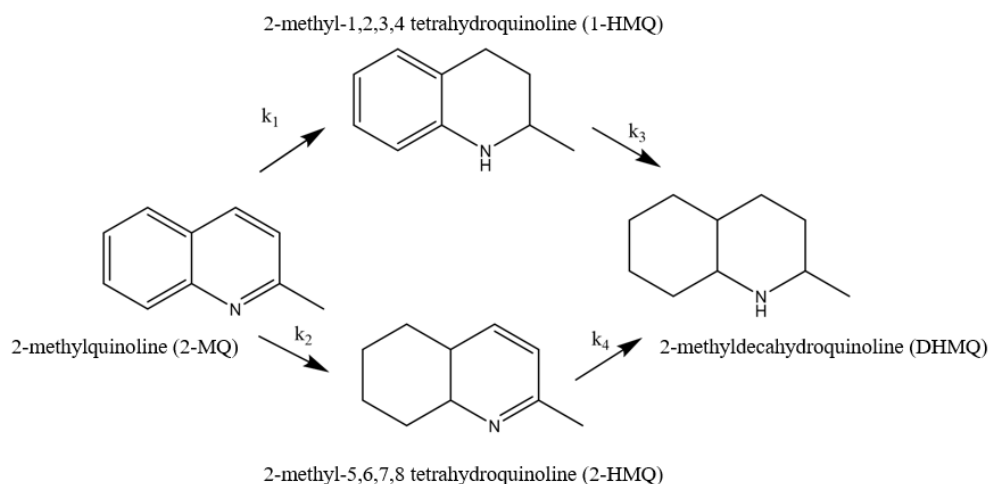
Hydrogen has recently emerged as a highly promising "green carrier" for renewable energy, serving diverse purposes like fuel cell vehicles and various stationary and mobile electrical devices. However, the predominant practice involves burning hydrogen at the production site, with only a minimal 5% freely traded in the market. This limitation stems from the challenging transportation of hydrogen due to its unfavorable properties as a gas. Consequently, there has been considerable focus on liquid organic hydrogen carriers (LOHCs) in recent years. LOHCs are organic substances where hydrogen is chemically bound through covalent bonds via the exothermic process of catalytic hydrogenation [1]. Understanding the kinetics of the hydrogenation process is imperative for optimizing the utilization of LOHCs and enhancing their overall efficiency [2].

## 2. Methods

The activity test of catalytic hydrogenation of liquid organic hydrogen carriers was carried out in a 75 mL Parr 5000 multiple reactor system at a temperature range between 120 - 180 °C and hydrogen pressure of 25-75 bar with magnetic stirring of 850 rpm over 5 wt% Ru/Al<sub>2</sub>O<sub>3</sub> catalyst over a 6-hour time period. The reaction mixture consists of 2 -methylquinoline, n-hexane as a solvent, and dodecane as an internal standard, with the desired mass of the catalyst. Sample analysis was conducted by gas chromatography coupled with mass spectrometry (Shimadzu, GCMS-QP2010 Ultra, Kyoto, Japan) equipped with a capillary column (60 m × 0.25 mm × 0.25 μm, Zebron ZB-5, Phenomenex, Torrance, CA, USA).

## 3. Results and discussion

In the first part of this research, we examined a commercial catalyst to study the conversion process itself. The results obtained were modelled according to the reaction mechanism shown in Figure 1. The reaction proceeds through two possible pathways via two distinct intermediates. It was noted that higher temperatures, especially up to 180 °C, had a substantial impact. The developed model showed good agreement with the experimental results with an error of ±10%. Such systems often require a continuous supply of hydrogen, which was not the case in this instance. The main challenge in this system was the presence of hydrogen as a limiting reactant, as a continuous supply was not ensured in this case.



**Figure 1.** Reaction mechanism for hydrogenation of 2-methylquinoline.

#### 4. Conclusions

In summary, our study involved the collection and analysis of experimental data to formulate a comprehensive kinetic model. This model enabled us to determine reaction rates and activation energies for each phase of the hydrogenation process. The findings provide valuable insights into the factors influencing the hydrogenation kinetics of 2-methylquinoline, contributing to an enhanced understanding of the relationship between reaction conditions and the conversion efficiency. Importantly, these results emphasise the significant potential of the compound under investigation.

#### References

- [1] M. Niermann, S. Timmerberg, S. Drünert, M. Kaltschmitt, Liquid Organic Hydrogen Carriers and alternatives for international transport of renewable hydrogen, *Renew. Sustain. Energy Rev.* 135 (2021). <https://doi.org/10.1016/j.rser.2020.110171>.
- [2] W. Xue, H. Liu, B. Mao, H. Liu, M. Qiu, C. Yang, X. Chen, Y. Sun, Reversible hydrogenation and dehydrogenation of N-ethylcarbazole over bimetallic Pd-Rh catalyst for hydrogen storage, *Chem. Eng. J.* 421 (2021) 127781. <https://doi.org/10.1016/j.cej.2020.127781>.

#### Acknowledgements

The authors gratefully acknowledge financial support by the Slovenian Research Agency (research program P2-0152 and basic research project J2-1723).

#### Keywords

Catalysis, liquid organic hydrogen carriers (LOHCs), kinetic modeling