# Catalytic semi-hydrogenation of acetylene under front end conditions – Kinetic measurement and modeling

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***Highlights***

- Catalytic testing of hydrogenation catalysts using advanced TEMKIN reactor.
- Kinetic modeling of process based on steady state kinetic data.
- Accurate simulative prediction of all components, including side products.

## 1. Introduction

The catalytic semi-hydrogenation of acetylene is of utmost importance in the chemical industry, as it is a crucial purification step during the production of ethylene. Downstream processes, mainly polymerization, demand pure ethylene streams of ~ 1ppm acetylene content. The ratio of acetylene to ethylene in the inlet stream under typical *front-end* hydrogenation conditions is around 1:100. The hydrogenation catalysts therefore must be highly active and extremely selective for safety reasons. This requires comprehensive kinetic investigations and modelling of new catalysts.[1]

Catalytic measurements of intact eggshell catalysts can be difficult to transfer from a laboratory to an industrial setting. While testing on the laboratory scale is much cheaper it provides challenges regarding mass- and heat-transport resistances. Also, certain requirements regarding the size of a packed bed in combination with pressure drop and on the other hand a high gas velocity according to industrial conditions must be met. To combat these limitations an advanced TEMKIN reactor, as described by Kuhn et al.[2], can be applied.

The goal of this work was to gain comprehensive insights into the catalyst performance of commercially available catalysts for the semi-hydrogenation of acetylene. Additionally, we developed a predictive kinetic model based on steady state kinetic data.

## 2. Methods

The catalytic testing was conducted using an advanced TEMKIN reactor integrated into a miniplant which was optimized to operate under industrial conditions. This setup has already been published.[2] The miniplant setup enables high gas velocities under otherwise concentration and temperature gradient-free conditions. The automized nature of the setup containing on-line gas chromatography analysis enables the acquisition of large amounts of data required for the development of a comprehensive kinetic model.

We tested commercially available semi-hydrogenation catalysts across a wide range of experimental parameters, such as inlet composition, temperature, pressure, as well as CO content for selective poisoning and selectivity modulation to obtain exhaustive insights on the catalytic performance. Special focus was placed on the formation of side products, such as ethane or $C_4$ components as precursor to green oil formation, as these drastically limit the applicability of the catalysts due to safety concerns and deactivation.

The kinetic modeling was done using *Presto Kinetics 11* and Python scripts, the result of which were compared and validated. Crucial parameters such as activation energy or adsorption enthalpy can be obtained as simulation parameters by parameter optimization of the temperature dependent measurements.

## 3. Results and discussion

The experimental results are highly accurate and reproducible. Depending on the exact conditions, full conversion of acetylene, as well as high selectivity towards ethylene are achieved at high temperatures of ~80 °C and above. The conversion and selectivity of the process are strongly influenced by the inlet concentration of acetylene, carbon monoxide and hydrogen. The development of a kinetic rate expression is based on these findings and contains terms for each of these components. Assuming Langmuir-Hinshelwood mechanisms for each reaction, a kinetic model is devised which is highly accurate across a broad range of reaction parameters. This allows for the exact prediction of all present $C_2$- and $C_4$ -components.

## 4. Conclusions

The highly optimized testing setup for commercially available eggshell catalysts for the semi-hydrogenation of acetylene provided large amounts of accurate and reproducible data under industrially relevant *front-end* conditions. Exhaustive insights on the kinetics of the process, especially regarding the formation of side products were gained. The resulting kinetic model provides activation energies and adsorption enthalpies of all relevant components and is accurate across the whole parameter range that was investigated.

## References

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***Keywords***
Acetylene hydrogenation, TEMKIN, kinetic modeling