Electrified dehydrogenation of the LOHC pair methylcyclohexane – toluene: reactor modeling and process simulation.

Luca Vergani, Matteo Ambrosetti, Gianpiero Groppi*

Dipartimento di Energia, Politecnico di Milano. Via Lambruschini 4, 20156, Milano, Italy

*Corresponding author: gianpiero.groppi@polimi.it

Highlights
- MCH to TOL is considered as an LOHC hydrogen release process.
- A 1-D model of an electrified reactor is applied to MCH dehydrogenation.
- Reactor-process integration allows quantitative performance evaluation.

1. Introduction

Liquid organic hydrogen carriers (LOHC) have been proposed as a promising solution to address the critical issues of hydrogen storage and transportation since they store hydrogen in liquid form under ambient conditions. Hydrogen release from LOHC is an endothermic catalytic reaction characterized by considerable energy demand. It is possible to fulfill this demand via electrification (Joule effect) by applying a potential difference to a ceramic foam characterized by an electric resistivity, which is loaded with the catalyst (packed or washcoated). Our group has already demonstrated the effectiveness of this technology applied to SMR using washcoated SiSiC foams [1]. We aim to apply the same reactor concept to model methylcyclohexane (MCH) dehydrogenation into toluene (TOL). Moreover, we aim to integrate the reactor into a process layout and evaluate its performance through the defined KPIs.

2. Methods

We propose a steady-state 1-D pseudo-homogeneous model of an electrified catalytic reactor where the catalytic particles are packed inside a SiSiC foam to which a voltage is applied. A literature equation has been selected for the reaction rate [2], and packed foam configuration is herein proposed, given the slow kinetics of the reaction. The model consists of mass balance equations for the reacting components, an energy balance equation for the reacting phase (gas + catalytic pellets), and an energy balance equation for the solid foam. The inlet mass fraction of each component, the inlet gas temperature, and zero heat flux for the foam phase are imposed as boundary conditions. A Similar model has been applied to electrified SMR in a previous work of our group [3]. The equations are implemented into the simulation software gPROMS. Subsequently, the reactor model is integrated into a process layout that delivers hydrogen at 50 bar. The process includes MCH pumping, a recuperative preheating section in which the heat of the reaction products is recovered to evaporate the MCH and bring it to the reactor inlet temperature, a condenser where hydrogen is separated from hydrocarbons, and a multistage inter-cooled hydrogen compressor. The condenser and compression stages inlet temperatures are set to 40 °C, the final hydrogen pressure is set to 50 bar, and the number of compression stages is determined to avoid discharge temperatures higher than 150 °C. Different KPIs are defined to evaluate the process and they are reported in Table 1.

Specific EE consumption [kWh $kg_{H_2}^{-1}$]	$\dfrac{\sum EP}{F_{H_2,out} \cdot MW_{H_2}}$	Hydrogen Recovery [%]	$\dfrac{F_{H_2,out}}{3 \cdot F_{MCH,in}} \cdot 100$
Hydrogen purity [%]	$\dfrac{F_{H_2,out}}{\sum F_{gas,out}} \cdot 100$	Reaction PC fraction [%]	$\dfrac{P_{reactor}}{\sum EP} \cdot 100$

Table 1. Process evaluation KPIs

3. Results and discussion

Figures 1.a,b represent the MCH conversion and temperature profiles along the reactor bed. The simulation is carried out with a reactor inlet temperature and pressure of 250 °C and 2.7 bar, respectively, a space velocity (GHSV) of 600 Nl h^{-1} kg$_{cat}$$^{-1}$, and pure MCH in the feed. The conditions are chosen to reach an MCH target conversion of 95%. The conversion profile shows that the reaction is kinetically

limited due to the slow reaction rate. The calculated catalyst productivity is 7.7 $mol_{H2}\,g_{Pt}^{-1}\,h^{-1}$, which is in good agreement with the literature [4]. The temperature profiles present a cold spot at the reactor inlet where the reaction rate is at its maximum; proceeding along the axial coordinate, the reaction rate decreases, and so does the energy demand, while the external power input remains almost constant, as a result, the temperature increases. A limit on the maximum temperature is set to 400°C to avoid catalyst deactivation (coking) and carrier degradation. The reacting phase–foam temperature difference is limited due to the high heat transfer coefficient between the two phases. The thermal duty of the reactor is 1 $MW\,m^{-3}$.
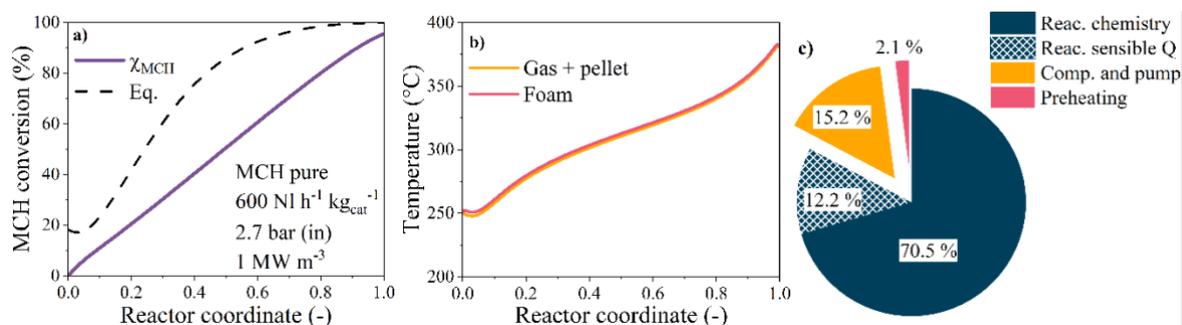

Figure 1. a) reactor conversion profile, b) reactor temperature profiles, c) process consumption components.

The process is designed to produce 1400 $Nm^3\,h^{-1}$ of hydrogen, with ten tubular reactor units (L = 3.3 m, D = 0.24 m) working in parallel. The hydrogen recovery is 95.5%, the specific energy consumption is 14.3 $kWh\,kg_{H2}^{-1}$, 82.7% of which is due to the reaction section, and the purity of the released hydrogen is 99.6%. Figure 1.c represents process consumption components. The reactor, particularly the reaction enthalpy, represents the largest share. The second source of consumption is hydrogen compression (MCH pumping is almost negligible). The preheating slice in Figure 1.c is due to an electrical heater, which adjusts the reactants' temperature after the recuperative preheating. The high specific power consumption and the purity of the released hydrogen remain critical for the process deployment. The power consumption can be reduced by optimizing the process layout and parameters; however, the reaction enthalpy is almost independent of this optimization. An adsorption step after the condenser is needed to increase the hydrogen purity; as an alternative, LOHC pairs characterized by a higher difference in volatility with respect to hydrogen can be investigated.

4. Conclusion

We have successfully applied the 1-D model of an electrified catalytic reactor to the reaction of methylcyclohexane dehydrogenation as an example of hydrogen release from LOHC. We have demonstrated that this reactor can reach the target value of 95% conversion without exceeding the maximum temperature of 400°C, with a catalyst productivity of 7.7 $mol_{H2}\,g_{Pt}^{-1}\,h^{-1}$. Moreover, we have extended the model's capabilities by integrating the reactor in a process layout. The obtained process has been simulated to produce 1400 $Nm^3\,h^{-1}$. The process performances were evaluated through specific energy consumption, hydrogen recovery, impact of the reaction on the process consumption, and hydrogen purity. The high specific electric consumption and the purity of the released hydrogen remain critical aspects of the process. The process layout and parameters must be optimized to improve the performance further, and different LOHC couples can be considered.

References

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