Dynamics of dibenzyl toluene hydrogenation and dehydrogenation reactors: design and simulation

Pietro Delogua, Elena Barberab, Andrea Mioc,e, Alberto Bertuccob,d, Maurizio Fermegliac,e \*

a. SERICHIM, Italy

b. Department of Industrial Engineering (DII), University of Padova, Italy

c. Department of Engineering and Architecture (DIA), University of Trieste, Italy

d. Centro Studi “Levi Cases” for Energy Economics and Technology, University of Padova, Italy

e. Center for Energy, Environment and Transport Giacomo Ciamician, University of Trieste, Italy

Corresponding Author: [maurizio.fermeglia@units.it](mailto:maurizio.fermeglia@units.it)

Abstract

Long-distance transport and long-term storage of H2 can be realized with Liquid Organic Hydrogen Carriers (LOHC) based on a two-step cycle: (1) hydrogenation of the LOHC molecule (i.e., H2 is covalently bound to the LOHC) and (2) dehydrogenation after transport and/or storage. Since the (optimal) LOHC is liquid at ambient conditions and shows similar properties to crude oil-based liquids (e.g. diesel and gasoline), its handling and storage is realized by well-known processes; thus, a stepwise adaptation of the existing crude oil-based infrastructure is technically possible. LOHC show economic advantages compared to compressed H2 and liquid H2 for long-term storage/long distance transport applications. The energetic efficiency of the systems depends on the dehydrogenation step. In this paper we will consider the details of thermodynamic and kinetic fundamentals of hydrogenation and dehydrogenation of a typical LOHC, namely Perhydro-Dibenzyl-Toluene. The fundamental chemical equilibrium expressions as a function of temperature and the catalytic kinetic expression for the reaction speed at different conditions are evaluated for the design of a dehydrogenation Continuous Stirred Tank Reactor. A process simulator (Aspen Plus v. 14.1™) is used to simulate the reactor at different operating conditions, focusing on the dynamic response of the reactor to any change in temperature, pressure, and inlet flow rate. The results obtained from the steady state simulation show a good agreement with experimental literature data. The results from dynamic simulation show that the time response of the reactor is compatible with the H2 production variations needed by fuel cells used for transportation.

* 1. Introduction

In recent years, liquid organic H2 carriers (LOHCs) have received a lot of interest as a viable alternative for the efficient, affordable, and secure storage of H2. Catalytic hydrogenation attaches H2 to an organic carrier molecule in LOHC systems to produce an H2-rich storage liquid that mimics a fuel. At room temperature, the latter may be handled and transported utilizing the existing petroleum infrastructure. After that, a catalytic dehydrogenation process is employed for on-demand H2 release at the time and location of energy or H2 demand. Among the possible LOHC molecules, the dibenzyl toluene (H0-DBT) and the perhydro-dibenzyl toluene (H18-DBT) have achieved significant interest. DBT is made up of many isomers in both its H2-rich (HX-DBT) and H2-lean (H0-DBT) forms. DBT has been used extensively as a heat transfer fluid since the 1960s. [1-4] A H2 capacity of up to 6.2 weight percent, or a volumetric H2 content of 56 gH2/L, is provided by the LOHC system H0-DBT/H18-DBT[5]. LOHC, and particularly DBT, show economic advantages compared to compressed H2 (CGH) and liquid H2 (LH) for long-term storage/long distance transport applications [3]. Hurskainen et al. [6]. showed the advantages of using LOHC in terms of CAPEX and net H2 payload with respect to GH2 trailers and in terms of lifetime with respect to trucks (table 1).

An example of the possibility of LOHC-based H2 transport for future international commerce of chemically bonded H2 is a tanker ship of the Suezmax class that is loaded with H18-DBT. Based on the Lower Heating Value (LHV) of the chemically bonded H2, its 150,000 metric tons of liquid load would thus contain 9,300 metric tons of H2, or 309.9 GWh of energy [5]. This indicates that a feasible alternative for the future is LOHC-based transcontinental H2 trade from wind- or sun-rich regions to industrialized nations that today import a large amount of energy is a realistic option for the future.

Table 1: Comparison of different H2 carriers [6]: LOHC tanker trailer is 36000 l; GH2 trailer is 2 x 200 bar steel bottle ISO20 containers; Advanced GH2 trailer is ISO40 HC 350 bar composite.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | Truck | LOHC tanker trailer | GH2 trailer | Advanced GH2 trailer |
| Investment cost | 180 k€ | 140 k€ | 530 k€ | 420 k€ |
| Lifetime | 8 years | 15 years | 15 years | 15 years |
| Fixed O&M |  | 4% of CAPEX | 2% of CAPEX | 2% of CAPEX |
| Net H2 payload |  | 2000 kg (1400 kg net) | 400 kg | 900 kg |
| Unloading & loading time |  | 1 h + 1 h | 1 h + 1 h | 1h + 1 h |

The introduction of global emission pricing [7] and growing electricity costs as well as an increase in the demand for electricity (for example, battery vehicle mobility) will make the import of LOHC-bound H2 appealing already in the short to medium term [3, 8, 9].

The development of the hydrogenation/dehydrogenation equilibrium and kinetic models of the H0-DBT/H18-DBT system is the focus of the current investigation. Understanding equilibrium and kinetic data is essential for sizing of the reversible hydrogenation/dehydrogenation processes. The energetic efficiency of the systems depends on the dehydrogenation step [10]. With the obtained models, the simulation of a Continuous Stirred Tank Reactor (CSTR) for the dehydrogenation process is performed and finally some preliminary results for the dynamic behaviour of the CSTR are shown.

* 1. The rection schema

H0-DBT is hydrogenated via a sequential, step-by-step process [11]. One outside benzyl ring is hydrogenated to create H6-DBT in the first stage, and the second outer benzyl ring is hydrogenated to form H12-DBT in the second step. The middle ring is hydrogenated to generate H18-DBT in the last and rate-limiting hydrogenation step. The equivalent H6-DBT, H12-DBT, and H18-DBT fractions are made up of the appropriate isomers since H0-DBT is a combination of many of them. The reactions that take place in a catalytic hydrogenation / dehydrogenation reactor of perhydro dibenzyl toluene can be summarized, both from a kinetic and thermodynamic point of view, in three fundamental steps (Figure 1) [8]. Experimental determination of the hydrogenation /dehydrogenation equilibrium of the LOHC system H0/H18 dibenzyl toluene have been recently reported using innovative methods based on 13C-NMR and GC-FID [12]. There are three phases in the system: (1) catalytic solid adsorbing reagents and products.; (2) liquid phase consisting mainly of tricyclic compounds and solubilized H2 and (3) gaseous phase containing essentially H2 and tricyclic compounds as a function of their vapor pressure in relation to the composition of the liquid phase and temperature.



Figure 1: Proposed reaction scheme for hydrogenation and dehydrogenation [8].

It can be assumed, as a first approximation, that phase and adsorption equilibria can be ideal. As a result, chemical equilibrium relationships can be represented by the following expressions:

; ; where is the equilibrium liquid-phase molar concentrations of tricyclic compounds.

The pressure of H2 is given by the difference between the total pressure and the sum of the partial pressures of the tricyclics:

(1)

but for sake of simplicity, given the low vapour pressure of these components (about 0.1 bar at a temperature of 290 °C), in the following reference is made only to the H2 pressure. The kinetics of each of the reactions taking place in the solid phase between the species adsorbed on the catalyst can be described by the following general equation:

(2)

and similar for reactions 1 and 2. The exponent is the reaction order for H2 q. Since the concentration of the catalyst appears in all equations with the same exponent, these can be simplified into the form.

(3)

The material balance of a CSTR reactor is given by:

(4)

This form can be employed to all the specific reactions. As far as H2 is concerned, the overall equation is:

(5)

Hydrogen pressure and hold-up are related to each other according to the volumes of the phases present in the reactor:

(6)

Given the similarity of the liquid compounds present in the reactor, they can be assigned a density and an average molecular weight that are the same for all, so that it can be calculated from the volume of liquid

(7)

while the total molar output flow rate must be equal to the sum of the feed flow rates

(8)

The closure constraint at 1 of the summation of molar fractions present in the liquid phase also applies.

Considering now the degree of freedom analysis, we have a total of 19 variables and 9 equations, so the system has 10 degrees of freedom. These can be saturated in various ways, but essentially the variables that could be fixed are feed rates (5), the volumes of the 3 phases (3), H2 pressure (1), temperature (1), for a total of 10 variables. The parameters of the model consist of the 3 rate constants of the direct reactions, the 3 equilibrium constants for the counter-reactions, and the H2 pressure exponent. Their estimation has been done starting from the experimental data of Dürr et al [12].

The dependence of the equilibrium constants on the temperature of the three reactions considered has been approximated by the equations.

*(9)*

*(10)*

whose adaptive parameters are e . Given the substantial identity of the 3 reactions involved in the model, a single value was used for e , while we have identified a specific value of for each reaction. The reference temperature was 493 K. Figure 2 shows the comparison between experimental [12] and calculated degree of hydrogenation (DoH) data. It can be seen how the model developed is able to reproduce the available experimental trends and can therefore be used to describe the thermodynamics in the kinetic model of the reaction.

A graph of a temperature

Description automatically generated with medium confidence

Figure 1: hydrogenation of DBT: experimental and calculated data for DoH.

The best estimation of the parameters of a kinetic model requires the availability of the evolution of the composition of the reactant system under conditions of constant temperature. Jorschick et al. [13] measured data of the composition of the reactants at constant temperature as a function of time. They used Pt on alumina as a catalyst 0.3% by weight at a single concentration of 3 g/100 g, at 30 bar absolute H2 pressure and temperatures between 201 and 311 °C. They measured the flow of H2 needed to maintain the pressure constant and calculated the degree of hydrogenation. Using the data of [12] combined with those of [13], we estimated the values of and q.

Figure 3 shows the comparison between experimental values and calculated DoH curves obtained with the equilibrium and kinetic constant derived as reported above and implemented in a batch reactor of Aspen Plus v. 14.1™ process simulator. The results obtained from the simulation show a good agreement with experimental literature data [12,13], thus allowing to state that the reactions implemented in Aspen Plus v. 14.1™ reliably describe the process of interest.

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Figure 3: dehydrogenation of DBT: experimental and calculated data for DoH

* 1. The CSTR process simulation

The output H2 pressure from the CSTR must be such that it can be fed to a fuel cell (around 4 bar). To obtain a high conversion at this pressure, it is necessary to operate at elevated temperatures, but not to exceed 300 °C, where the decomposition of dibenzyl toluene to volatile compounds become important. A temperature of 291 °C was used in the analysis and consequently it is necessary to supply the heat necessary to raise the temperature of the incoming flow up to 291 °C and the reaction heat. This heat is generated by burning some of the H2 produced. The heat to be provided for one mole of LOHC is about 38 kcal. The CSTR model available in Aspen Plus v. 14.1™ was used to simulate the dehydrogenation reactions using the equilibrium and kinetic equations developed above. We have also evaluated the transition dynamics of the CSTR between two different power demands. The model calculates the time it takes to reach the new steady state conditions starting from a steady state condition taken as a reference one and the change in the composition of the liquid effluent, taken at the same total molar flow rate as the feed.

A graph with a line

Description automatically generated

Figure 4: H2 flow rate (blue) and pressure initial changes (orange) as a function of time.

The time to reach steady state is about 5 seconds. However, this only affects the internal conditions of the reactor, as both the LOHC supply and the H2 withdrawal are constant from the beginning of the variation. In a first phase, the system produces more of the H2 withdrawn, and this leads to an increase in pressure; This is then compensated until the steady state is reached. As an example, figure 4 shows the H2 flow rate and pressure profiles as a function of time for a change in the H2 request from 10 kW to 100 kW.

* 1. Conclusions

The main result of this paper is the development of equilibrium and kinetic expressions and parameters from literature experimental data for describing hydrogenation and dehydrogenation of DBT LOHC. All chemical reactions occurring in the processes have been considered, including direct and reverse reactions. The expressions for the reactions’ rate developed compare well with the experimental data of DoH. The reactions’ rate expression has been used in the simulation of a steady state CSTR and for the dynamic simulation of a transient for the same CSTR.

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