INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 40 (2015) 15923–15932

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System optimization of cyclohexane dehydrogenation under multiphase reaction conditions using the uniform design method

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ARTICLE INFO

Article history:
Received 7 July 2015
Received in revised form
27 August 2015
Accepted 1 September 2015
Available online 24 October 2015

Keywords:
Dehydrogenation
Cyclohexane
Multiphase reaction conditions
Uniform design
Hydrogen

ABSTRACT

Hydrogen production via cyclohexane dehydrogenation catalyzed by a Raney-Ni catalyst under multiphase reaction conditions was investigated in this study. The uniform design (UD) method was employed to optimize the performance of the dehydrogenation reaction system of cyclohexane under "wet–dry" multiphase reaction conditions and to evaluate the effects of the process parameters on several response functions, such as the total amount of hydrogen produced in 2 h, the dehydrogenation conversion of cyclohexane and the relative activity of the catalyst. The results indicated that the data were well fitted by the regressed second-order polynomial models. Optimum reaction conditions for each response were obtained, under which the total amount of hydrogen produced in 2 h reached 9280 ml, the hydrogen produced through the conversion of cyclohexane was 18.63 and the relative activity of the catalyst maintained 0.91. In addition, the optimum reaction conditions for multi-response optimization were obtained, under which all three responses were expected to exhibit a relatively good performance. Confirmation experiments demonstrated that the UD method is a powerful and useful approach for optimizing the system of cyclohexane dehydrogenation under multiphase reaction conditions and is expected to provide valuable information for both efficient and economical hydrogen production.

Introduction

Hydrogen, a clean fuel in which the only by-product is water, is considered to be an ideal alternative energy source in the near-future energy revolution [1–3]. Hydrogen has the highest energy density of all energy sources [4,5]; the prospects of a hydrogen energy source are of considerable importance for the future, particularly when people are now trying to overcome the over-dependence on fossil fuels and reduce the global warming associated with carbon emissions. For engineering applications of hydrogen energy, the most intractable problem currently encountered is how to store and produce hydrogen in an efficient, economical and convenient manner [6,7].

A promising technology for hydrogen storage and production is liquid organic hydrides (LOH) [8–12]. By means of the "wet–dry" multiphase reaction mode, LOH hydrogen storage and production technology might find practical

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http://dx.doi.org/10.1016/j.ijhydene.2015.09.002

applications in on-board LOH hydrogen storage systems in the future. Under the multiphase dehydrogenation reaction conditions, the reaction not only involves vapor, liquid and solid phases but also the coupling of the dehydrogenation reaction and processes of mass and heat transport [13–15]. There exists an optimal energy balance point in the reaction system, and control over the dynamic energy balance of the reaction system is very important. The dynamic energy balance is influenced by many factors, including the reactant feed rate, the reaction temperature, the catalyst dosage, and so on. In addition, the interactions between the factors have a significant effect on the performance of the LOH multiphase dehydrogenation reaction system, as has been confirmed in previous studies [14,16]. However, due to the complexity of the interactions between the factors, determining the optimal energy balance point to enhance the performance of the dehydrogenation reaction is difficult. To date, the majority of studies on improving the hydrogen production performance have only employed a single-factor experimental design due to the lack of appropriate experimental and theoretical methods for the multiphase reaction system, and the effects of the interactions between factors have not been thoroughly investigated [13,14,16,17]. Thus, a systematic research method should be adopted to investigate the interaction between the factors and to determine the optimal energy balance point for global optimization.

The uniform design (UD) method proposed by Fang Kaitai and Wang Yuan is a unique experimental design method based on the number theory called the quasi-Monte Carlo method [18,19]. UD is a type of space-filling design that seeks the design points to be uniformly scattered on the experimental domain [20] and that can be used for computational experiments as well as for industrial experiments, particularly when the underlying model is unknown. In many cases, the model between the response (y) and the factors (e.g., x_1,x_2, … x_s) in the process is almost always unknown, and thus, one wishes for the experimental design to be robust against different model assumptions, i.e., a change in the underlying model should cause only a small change in the performance of the experimental design [19]. UD is such a method for the experimental design, with a regression model as follows: $y = g(x_1, x_2,\ldots,x_s)+\varepsilon$, where the function g is unknown and ε is the random error. When the function g is a polynomial (of first-order or second-order), the corresponding model is called a response surface model, which can be visually depicted by a 2- or 3-dimensional diagram [21,22]. Similar to orthogonal design, uniform design offers many experimental design tables for researchers to conveniently choose from. Among all the available experimental designs, uniform design accommodates the largest possible amount of levels for each factor and the UD tables of form U_n (n^s), and the number of levels can be equal to the number of experimental runs [23]. Compared with other design approaches, UD will be less laborious and time-consuming for optimizing a process, particularly when there is more than one factor in the experiment or when it is anticipated that the interactions between factors will affect the desired response. Uniform design should be an effective tool to analyze and optimize the process.

In this work, the uniform design method was used to evaluate and optimize the performance of the dehydrogenation reaction system of cyclohexane under "wet–dry" multiphase reaction conditions, and the effects of the process parameters on several response functions, such as the total amount of hydrogen produced in 2 h, the dehydrogenation conversion of cyclohexane and the relative activity of the catalyst, were studied. Consequently, the resulting optimal region of reaction conditions for these three responses was obtained. The UD strategy used for optimizing the production of hydrogen with liquid organic hydrides under "wet–dry" multiphase reaction conditions in this article is expected to provide valuable information for both efficient and economical hydrogen production.

Experimental section

Materials

The Raney-Ni catalyst used in this experiment was purchased from the Metallurgy Institute of Zhejiang Province; this catalyst possessed an apparent density of approximately 3.0 g cm^{-3} and a mean particle size of 16.58 μm. Due to the nature of the Raney-Ni catalyst, it was typically stored in deionized water prior to use. Analytical grade cyclohexane was chosen as the liquid organic hydride (LOH), and the purity of the nitrogen gas used in this experiment was greater than 99.99%.

Dehydrogenation reaction of cyclohexane under multiphase reaction conditions

The dehydrogenation of cyclohexane over a Raney-Ni catalyst was performed under pulse-spray injection conditions in a three-neck flask (100 ml) with a reaction area of 6.15 cm^2 (2.8 cm in diameter), as shown in Fig. 1.

After vacuuming, a certain amount of Raney-Ni catalyst was slowly heated using a salt bath with a pre-set temperature under the protection of nitrogen to dry the water. The N_2 gas flow was shut off after the temperature of the catalyst surface stopped increasing and reached a stable value; then, cyclohexane was intermittently injected by a high-pressure

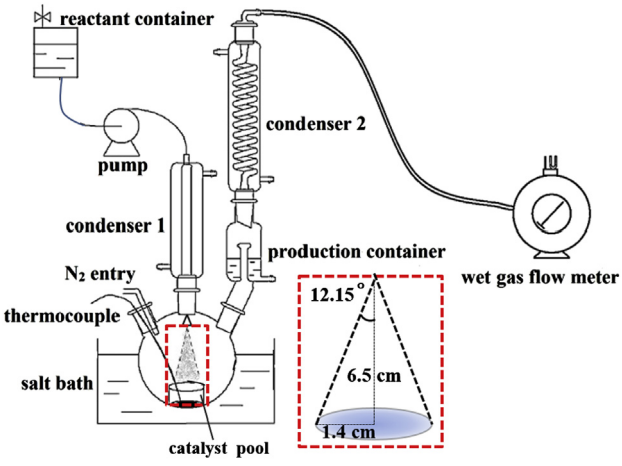

Fig. 1 – Schematic diagram of the experimental apparatus.