

Design of the Reactor, Selection of Catalyst for Ortho to Para Hydrogen Conversion and Preliminary Design of Cryogenic System for its Liquefaction

Saghatoleslami⁺, Naser and Sargolzaie, Javad*

Department of Chemical Engineering, University of Sistan and Baluchestan, Zahedan, 98164, I.R. IRAN

Moosavi, Mahmood

Department of Chemical Engineering, Ferdowsi University, Mashhad, 91775-1111, I.R. IRAN

ABSTRACT: *Hydrogen is an unusual substance in that its molecule exists in two forms, known as ortho and para, with markedly different properties. Energy level of the ortho molecule is higher than para, therefore, the latter is employed for industrial purposes. Consequently, for a high conversion of ortho to para hydrogen a catalyst reactor must be employed. Therefore, one of the main objectives of this work is to design a tubular reactor. To obtain this objective, one the parameters which should be considered is the proper selection of a catalyst that can in turn effect the price and the life of it. In this work and for an optimum of hydrogen feed and its liquefaction, the following parameters for the cryogenic apparatus in the Linde-Hampson cycle such as heat requirements, nitrogen needed for the cycle, specific capacity of refrigeration, compressor work and the cycle efficiency have been computed.*

KEY WORDS: *Orthohydrogen, Parahydrogen, Catalytic reactor, Hydrogen energy, Linde-Hampson cycle.*

INTRODUCTION

The rapid growth of the world energy consumption on the one hand and the limited source of fossil fuels on the other hand, has resulted in the search for other types of energy sources. Hydrogen may well be one of these fuels. Hydrogen can exist in what known as ortho and para states. Since the energy level of para state is less than ortho state, the latter are favoured for industrial purposes. In ortho- and para hydrogen, the spin vectors are

respectively in the same and opposite direction [1]. To convert the ortho to para hydrogen, a catalyst reactor must be employed. One of the most important criterion for the reliability of such a design is the proper selection of the catalyst which requires a good understanding in terms of reaction mechanism, heat and mass transfer for such a process. The equilibrium percentage of ortho- to parahydrogen varies with temperature [2 and 3].

* To whom correspondence should be addressed.

+ E-mail : slami@hamoon.usb.ac.ir

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Conversion of ortho to para is exothermic and slow in the liquid state [4]. In this work, in addition to the size of the reactor, a proper catalyst is selected, the extent of conversion and its kinetics are exploited and, furthermore, different parameters in the Linde-Hampson cycle for the liquefaction of hydrogen are computed.

THEORY AND DESIGN PROCEDURES FOR THE REACTOR

Fixed bed reactors are usually used for catalytic reactions. Different reactions occurs simultaneously in such a reactors [5]. Three different models are used for fixed bed reactors among which the reactor with pseudo-homogenous types are adopted in this work. The assumptions used for this model are as follows:

- (i) External resistances to heat and mass transfer are neglected
- (ii) Thermal equilibrium exists between the gas and the catalyst
- (iii) The reactor is assumed to behave as plug flow (PFR)
- (iv) Radial and axial thermal gradients are neglected

Therefore, the reactor is assumed to be tubular and in order to maintain the reactor at constant temperature, a vessel of small diameter which is submerged in a nitrogen bath is chosen. Considering the above assumptions, we can write the following material and energy balances, respectively:

$$\frac{d}{dz}(VC_A) - r_{A0}\alpha = 0 \quad (1)$$

$$V C_p \rho \frac{dT}{dz} + (-\Delta H_r) r_{A0} \alpha + U A (T - T_W) = 0 \quad (2)$$

where r_{A0} is the initial reaction rate when the catalyst is used and the activity of catalyst (i.e., α) is defined as the ratio of reaction rate at time $t = 0$ to t .

The simplest model for expressing non-activated reaction rate is the power law:

$$-r_d = k_d \alpha^d \quad (3)$$

where the rate of reaction can be calculated as follows:

$$r_A = (r_A) \alpha \quad (4)$$

From the solution of equation (3) it can be shown that:

$$\alpha = [k_d (d-1)t + 1]^{1/(1-d)} \quad d \neq 1 \quad (5)$$

$$\alpha = \exp(-k_d t) \quad d = 1 \quad (6)$$

If the integration is done in two steps for equations (1) and (2), we can obtain and plot concentration profile against the temperature (Fig. 1).

Research shows that raising the pressure would not considerably affect on the performance of the catalyst and, furthermore, the rate of these reactions may be affected by the materials which do not constitutes the reactants and products themselves. Therefore, equilibrium rate would not vary at each state. One of the most important decisive factors for the conversion of ortho, is the proper selection of the catalyst. Metal oxides' catalyst such as chromium, lead and neodymium are known to be highly effective for the conversion of ortho to para, since they possess paramagnetism properties [6]. In addition, it has been shown that since the space velocity of iron oxide III gel is high, the volume of the catalyst that is required will be reduced. Some catalysts are studied for the conversion of normal hydrogen to parahydrogen at 20 K the results of which are shown in Table 1. Studies also demonstrate that in the liquid phase, if the particle mesh sizes ranging between 20-30, they perform more effectively in the process. However, in the gas phase, if the mesh sizes varies between 10-20 and 40-50, it will increase the efficiency of the catalyst by only 5% [7]. Research also reveals that the mutual interaction between the catalyst and the absorbed hydrogen causes the nuclei to rotate in

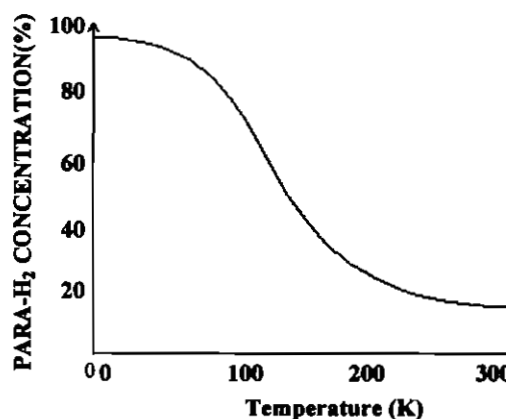


Fig. 1: Concentration of parahydrogen versus temperature

Table 1: Some catalysts used for the conversion of 25% to 90% para at 20 K and 15 psig

Catalyst	S.V. (per min.)	S.V. (w.r.t. chromium oxide)
Iron chloride with silica gel	20	0.4
Serium oxide	20	0.4
Gadollinium oxide	10	0.2
Iron oxide (paramagnetism)	20	0.2
Amonium oxide sulfate	30	0.6
Chromium oxide with alumina	50	1
Magnesium oxide with silica gel	80	1.6
Hydrous ferric oxide	330	6.6
Neodymium oxide	20	0.4

different directions which reduces the speed of the rotation. Therefore, this will act as the limiting controller for the reaction mechanism [8].

Catalyst testing and preparation

The analyzer frequently adopted for testing, employs enthalpy change properties of ortho and para molecules for estimation [8]. A typical testing apparatus are shown in Fig. 2.

Given that the reactor is adiabatic, the evolved gases causes the outlet gas temperature to raise. One can estimate the concentration of para hydrogen from the temperature difference between the incoming and outgoing gas. Research also reveals that with a temperature raise of 0.4 K, the concentration of

parahydrogen will be improved by 1% [8]. For the preparation of iron oxide III gel, aqueous solution of sodium hydroxide are added to iron chloride III in order to obtain a brownish color gel. Then the percipitate is washed with water in a decantar, the product is filtered and dried at room temperature and finally kept in 140 K for 24 hours. Moreover, to activate the catalyst before the hydrogen enters the bed it must be retained under the pressure of 1 mmHg and 110 K for 16 to 20 hours. Different parameters influence the degree of the activation of the catalyst. Presence of ions such as ferrousion can cause the degree of the activation to drop considerably and, on the other hand, addition of small amounts of hydrogen peroxide will have the reverse effect on the process.

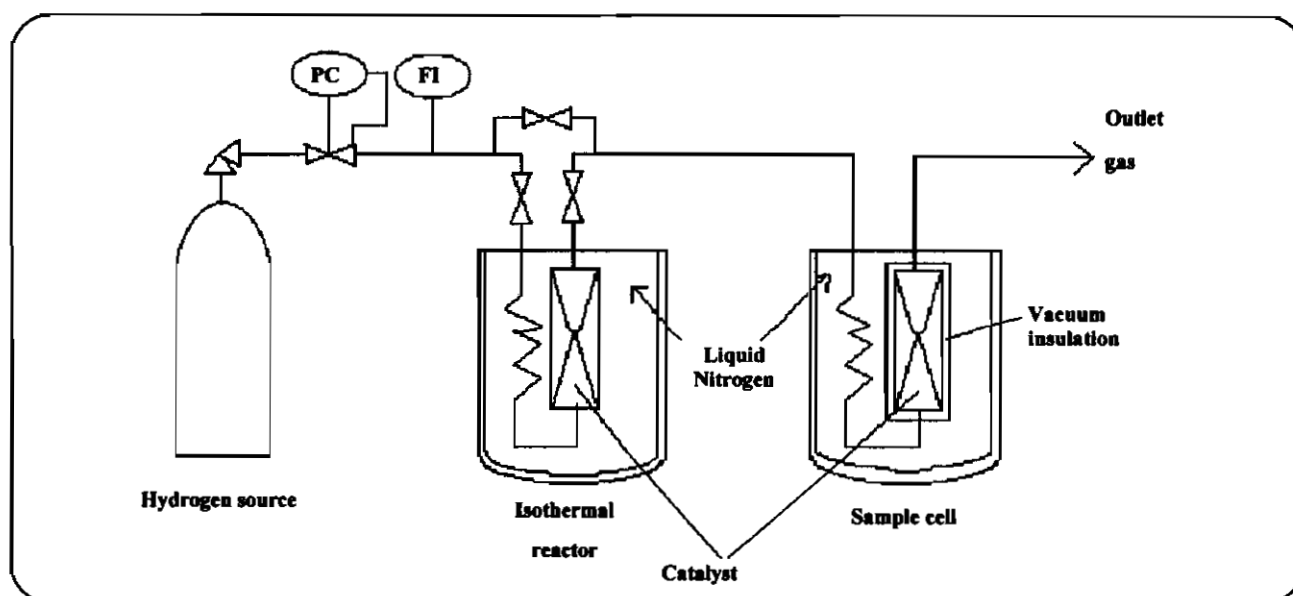
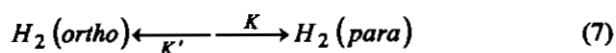


Fig. 2: Schematic flow diagram of the catalyst testing apparatus

Rate of reaction for the conversion of ortho- to parahydrogen

Reaction for the conversion in an isothermal reactor can be written as follows:



If C and $(1-C)$ are the molar species of ortho and parahydrogen respectively, the rate of reaction can be estimated by the following equations:

$$-\frac{dC}{dt} = KC - K'(1-C) \quad (8)$$

$$KC_e = K'(1-C_e) \quad (9)$$

$$K' = \frac{KC_e}{1-C_e} \quad (10)$$

If the conversion is of the first order a plot of $(C-C_e)$ versus time on a semi-log paper will result a straight line. The slope of the line will give K and the y-intercept, K' demonstrate the concentration differences between the ortho and parahydrogen of the feed at equilibrium. Fig. 3 shows the graph for the conversion of 99.8% parahydrogen which exhibit a good agreement with the experimental values [6].

The computed values are for the case of a copper made reactor of 0.25 inches in outside diameter and a thickness of 0.032 inches that holds 3 cm³ catalyst with a mesh size of 30-100. The reaction occurs in a state between isothermal and adiabatic states. To predict the temperature along the catalyst bed, further data are required on the heat transfer properties at the catalyst

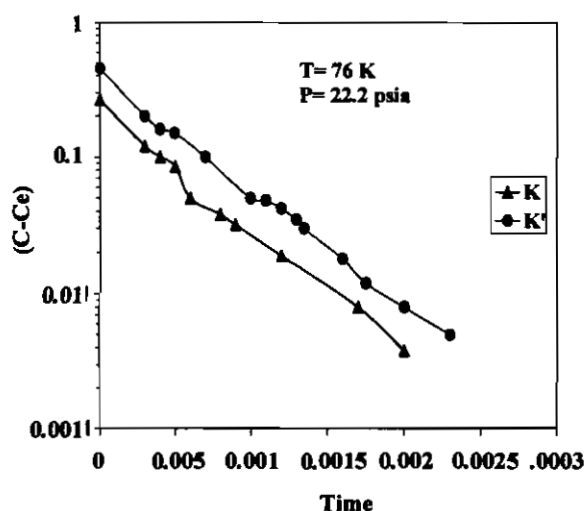


Fig. 3: Plot of $(C - C_e)$ versus time

surfaces. A further criterion which must be considered is the space linear inlet gas velocity to the reactor that varies linearly with bed length [8]. In this work, the optimum gas mass velocity to the reactor is considered to be 0.046 kg/hr which results a negligible pressure drop.

Reactor size

The size of the reactor can be estimated from the following relation:

$$\frac{V}{F_{A0}} = \int_0^x \frac{dx}{-r_A} \quad (11)$$

where x is the degree of conversion, $-r_A = KC_A - K'(1-C_A)$, F_{A0} the gas flow rate and V the size of the reactor. For this reaction and the conversion rate of 99.8% parahydrogen, the computed results are shown in Table 2.

PRELIMINARY DESIGN OF THE CRYOGENIC CYCLE

Different thermodynamic cycles are used for liquefaction of hydrogen, however, Linde-Hampson is one of the best and simplest cycle [9]. Fig. 4 shows a typical schematic flow diagram of such a process:

Therefore, the above cycle have been adopted for this work and its different parts have been computed as shown in Table 3.

For the computation of the above cycle capacity, G_i is taken as 0.53 Kg/hr and the heat liberated from the first and second catalyst bed are neglected (as they are small). Therefore, the capacity of the cycle can be computed as follows:

$$\frac{0.046 \times 0.53 \text{ Kg/hr}}{0.0000807 \text{ Kg/lit}} \cong 300 \text{ lit/hr} \quad (12)$$

Table 2: Computed results for the conversion rate of 99.8% parahydrogen

Entrance feed temperature to the reactor	80 K
Pressure on the catalyst surfaces	1.5 atm
Temperature of the liquid nitrogen bath	76 K
Forward reaction rate, K	200 min ⁻¹
Reverse reaction rate, K'	188 min ⁻¹
Volume of the reactor	16 cm ³
Pressure drop	0.12 atm

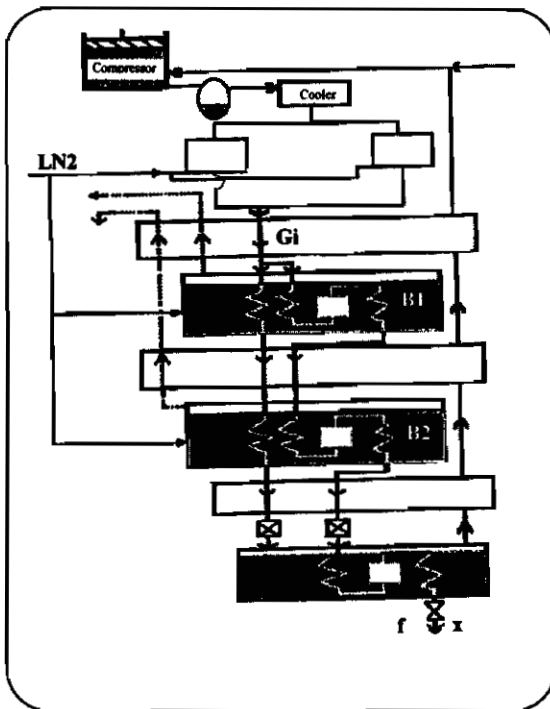


Fig. 4: Schematic flow diagram of the Linde-Hampson cycle

where the density of hydrogen is taken as 0.0807 Kg/m^3 . Consequently, through changing the G_i , a new capacity of the cycle can be computed.

CONCLUSIONS

Conversion of ortho- to parahydrogen in the presence of a catalyst is highly exothermic. Therefore, in order to maintain the process in an isothermal states, a copper reactor submerged in a liquid nitrogen bath is recommended. The design of such a reactor is analogous to PFR. With the assumption of isothermal and homogeneous flow in the gas phase, the reaction rate is of the first order. By plotting the concentration versus time and computing the slope of the line, reaction rate is estimated. It is found that for a specified space velocity through the catalyst, linear velocity varies proportionally with the bed length. Since the gas space velocity through the iron oxide III gel is high, the volume of the catalyst that required is reduced. The results reveal that for an optimum gas velocity of 0.046 kg/hr and a degree of conversion of 99.8% for ortho- to parahydrogen, a reactor with the size of 16 cm^3 is required.

For the preliminary design of Linde-Hampson cycle, given that a high rate of para hydrogen conversion is needed, three catalyst bed must be employed, i.e. more conversion can be established at low temperature than a higher one. Therefore, the heating load of the system in the hydrogen vessel storage would be higher.

Table 3: Computed results in the preliminary design of the hydrogen cryogenic cycle

Apparatus parts in Linde-Hampson cycle	Computed values
N_2 needed for the 1 st vessel (B1)	0.516 kg $\text{N}_2/\text{kg H}_2$
N_2 needed for the 2 nd vessel (B2)	0.34 kg $\text{N}_2/\text{kg H}_2$
Total N_2 needed	0.516 kg $\text{N}_2/\text{kg H}_2$
Heat needed for the 1 st vessel (B1)	215.95 KJ/Kg
Heat needed for the 2 nd vessel (B2)	125.55 KJ/Kg
Total Heat being transferred (q)	1047.5 KJ/Kg
Specific capacity of refrigeration (q_c)	181.84 KJ/Kg
Extra work needed (W_{exc})	4815 KJ/Kg
Heat absorbed through the cooler (q_k)	1673 KJ/Kg
Real compressor work (W_k)	5407.03 KJ/Kg
Specific work needed (W_o)	222.22 MJ/Kg
Ideal efficiency (ϵ_{ideal})	0.331
Cycle efficiency (ϵ_{real})	0.018
Thermodynamic efficiency (η_t)	0.0544
Fraction of liquefied hydrogen	0.046 percent

Nomenclature

A	heat transfer surface area, m ²
C _A	molar concentration of species A, kmol/cm ³
C _e	equilibrium molar concentration, kmol/cm ³
C _F	molar concentration of orthohydrogen, kmol/cm ³
C _p	heat capacity, kJ/kg.K
F _{A0}	gas flow rate, cm ³ /s
G _i	gas entrance, cm ³ /s
K	forward reaction rate
K'	reverse reaction rate
LN2	liquid nitrogen, cm ³ /s
q _k	outlet gas heat from the compressor, KJ/Kg
r _A	reaction rate for ortho- to parahydrogen conversion, kmol/m ³ .s
r _{A0}	reaction rate when the catalyst are used for the first time
t	time, min
T _w	catalyst surface temperature, K
U	overall heat transfer coefficient, W/m ² .K
V	reactor volume, cm ³
W _{exc}	work needed to compress the gas, KJ/Kg
x	degree of conversion

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