Multi-objective performance optimization of ammonia decomposition thermal storage reactor

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Abstract. Heat storage technology plays an essential role in the stable operation of solar thermal power generation. In this paper, a one-dimensional model of a tubular filled bed heat absorption reactor for ammonia decomposition is established by applying finite time thermodynamics. Taking the inlet temperature, the outside diameter and the length of the reactor as optimization variables, the multi-objective particle swarm optimization is used to perform multi-objective optimization considering the maximum heat absorption rate and the minimum total entropy generation rate, and the Pareto Fronts are determined under different reactor outer wall temperatures. Finally, three optimized reactors' design parameters and performance indicators are obtained by LINMAP, TOPSIS and Shannon Entropy decision methods, and the cross-sectional comparison of the optimal reactors at different outer wall temperatures. Compared to the reference reactor, the three optimized reactors improve heat absorption rate by 58%-143%, while the total entropy generate rate is reduced by 26.4%-38.8%. The obtained results have some guidance for optimal designs of ammonia decomposition reactor in real engineering.

1 Introduction

In order to achieve the strategic goal of reaching the carbon peak by 2030 and becoming carbon neutral by 2060, China will intensify efforts to promote the transformation of the energy industry during the 14th Five-Year Plan period. Solar energy will be exploited to new heights.

Thermal storage systems are essential for the stable operation of solar thermal power generation. And amino thermochemical heat storage is a promising solar thermal storage technology. ANU's Luzzi [1] developed the world's first solar-powered experimental plant that used ammonia for thermal storage, and achieved 24-hour stable power generation.

In the simulation and analysis of ammonia decomposition reactor performance, Deng et al. [2] established a three-dimensional physical model of a tubular packed bed reactor and found that smaller catalyst particle sizes were effective in enhancing ammonia decomposition rates and reducing maximum wall temperatures. Wang et al [3] designed a self-heating shell and tube reactor with the hydrogen combustion catalyst attached to the inner tube, which increases the ammonia decomposition rate considerably by consuming hydrogen. Besides numerical analyses, Li et al. [4] used COMSOL software to carry out simulation modeling for the ammonia decomposition reactor. Membrane reactors have attracted the attention of researchers due to their ability to

filter out hydrogen to drive the ammonia decomposition reaction towards a positive reaction. Abashar et al. [5] developed a mathematical model of a small-scale membrane reactor and found that improved inlet ammonia feeding could significantly reduce the reactor length. Li and Liu [6] showed that a high performance new structure composite palladium membrane reactor can achieve complete decomposition of ammonia at 673K.

Since its inception in the mid-1970s [7], Finite Time Thermodynamics (FTT) has made important progresses in both physics and engineering. In the FTT studies of ammonia decomposition reactors, Hu et al. [8] developed a one-dimensional ammonia decomposition reactor model and determined the reactor diameter and length for the highest ammonia decomposition rate. Badescu et al. [9] obtained the optimum distribution of temperature along the pipe wall, the pipe diameter and the catalyst particle size distribution with the objectives of maximizing the ammonia decomposition rate and minimizing the heat flux under a predetermined ammonia decomposition rate.

As can be seen above, the former analysis and optimisation of ammonia decomposition reactors focused mainly on the ammonia decomposition to hydrogen scenario and was usually carried out with the single objective of maximising the ammonia decomposition rate or minimising the heat flux etc. However, as a heat storage reactor, the important performance indicator of maximum heat absorption was not fully considered. Besides, the multi-objective optimisation of minimum entropy generation rate and maximum heat absorption was also lacking. Therefore,

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this paper will further develop a multi-objective optimisation for minimising the total entropy yield and maximising the heat absorption rate for the practical application scenarios of ammonia decomposition heat storage reactors with finite rate heat transfer and chemical reaction.

2 Materials and Methods

A schematic diagram of the reactor model is shown in Figure 1. The ammonia gas flows axially, absorbs heat from the wall of the tube and undergoes a decomposition reaction.

Figure 1 Ammonia decomposition reactor model

Table 1 Reference reactor model parameters [8,9]

Physical quantities	Symbols	Value
Reactor outer diameter	D_o	16 mm
Reactor wall thickness	δ_w	1 mm
Reactor length	L	3 m
Reactor outer wall temperature	T_w	800 K
Reactor wall thermal conductivity	λ_w	100 W/m · K
Reactor wall specific heat capacity	c_w	700 J/kg · K
Reactor wall density	ρ_w	4000 kg/m ³
Catalyst density	ρ_c	2355.2 kg · m ⁻³
Catalyst particle diameter	d_p	2.23 mm
Catalyst porosity	ε_p	0.59
Catalyst thermal conductivity	λ_c	0.3489 W · m ⁻¹ · K ⁻¹
Inlet ammonia molar flow rate	N_{NH_3}	0.025 mol/s
Inlet hydrogen molar flow rate	N_{H_2}	0.001 mol/s
Inlet nitrogen molar flow rate	N_{N_2}	0.001 mol/s
Reaction pressure	p	10 MPa
Inlet gas temperature	T_0	350 K

With pressures up to 10 MPa during the ammonia decomposition reaction, the ideal gas state equation does not hold on. Tian [10] combined the actual gas compression factor and a trial method to obtain a single constant actual gas equation of state, which was very fit for hydrogen, nitrogen and ammonia.

$$V = \frac{nRT}{p} \left\{ 2 - e^{\frac{p_i}{T_i} \left[c \frac{T}{903.65} \right]^{2.75} - \left(\frac{T - T_{tri}}{903.65} \right)^2 (p_i - T_i)^2} \right\} \quad (1)$$

$$p_r = \frac{p_{cr}}{p} \quad (2)$$

$$T_r = \frac{T_{cr}}{T} \quad (3)$$

where p_r is the reduced pressure, and p_{cr} is the critical pressure. T_r is the reduced temperature, and T_{cr} is the critical temperature. T_{tri} is the three-phase point temperature in K. c is a parameter related to the substance only and the corresponding values of H_2 , N_2 and NH_3 are 0.28, 0.415 and 0.98, respectively [10].

According to the first law of thermodynamics, the equation for energy conservation is:

$$\frac{dT}{dz} = \frac{\pi D_i q - A_c \rho_c (1 - \varepsilon_p) \sum_j \eta_j r_j \Delta_r H_j}{\sum_k F_k C_{p,k}} \quad (4)$$

where A_c is the cross-sectional area inside the reactor in m². $\Delta_r H_j$ is the enthalpy of reaction j in kJ/mol. η_j is the effective factor of internal diffusion. r_j is the intrinsic reaction rate of reaction j in mol/s. $C_{p,k}$ is the molar constant pressure heat capacity of the component k . F_k is the molar flow rate of the component k in mol/s. q is the heat flow density in W.

The Hicks pressure drop equation is used to describe the momentum conservation properties in the reactor, as follows:

$$\frac{dp}{dz} = -6.8 \frac{(1 - \varepsilon_p)^{1.2}}{\varepsilon_p^3} \text{Re}^{-0.2} \frac{\rho_m v_m^2}{d_p} \quad (5)$$

where ρ_m is the density of the reaction mixture in kg/m³. v_m is the average flow rate of the reaction mixture in m/s.

The mass conservation equation can be expressed using the differential equation for the rate of conversion as follows.

$$\frac{d\xi_j}{dz} = \frac{A_c \rho_c}{F_{k,in}} \sum_j \eta_j r_j \quad (6)$$

Ammonia decomposition reactions obey the Temkin-Pyzhev reaction rate equation:

$$r_A = k \left[\left(\frac{p_{NH_3}^2}{p_{H_2}^3} \right)^\beta - \frac{p_{N_2}}{K_{eq}^2} \left(\frac{p_{H_2}^3}{p_{NH_3}^2} \right)^{1-\beta} \right] \quad (7)$$

$$k = k_0 e^{-E_a/RT} \quad (8)$$

where r_A is the kinetic rate of ammonia decomposition reaction in mol/s. k is the reaction rate constant in mol/(s bar^β). k_0 is its correlation factor, taking the value of 13.51×10^6 [mol/(s bar^β)]. β is the dimensionless constant and takes the value of 0.166. E_a is the activation energy of the ammonia decomposition reaction, the value is 107.1 kJ/mol. R is the gas constant, and the corresponding value is 8.314 kJ/(mol·K). p_i are the sub-pressure of H_2 , N_2 and NH_3 . The chemical reaction equilibrium constant K_{eq} are read from the HSC software.

The thermal resistance of thermal conductivity from the outer to the inner wall of the reactor is:

$$R_w = \frac{\ln \frac{D_o}{D_i}}{2\pi\lambda_w \Delta L} \quad (9)$$

For convective heat transfer between the reactor walls and the reaction mixture, the Nu is calculated using the Gnielinski equation [11]:

$$Nu = \frac{\left(\frac{f}{8}\right)(Re-1000)Pr}{1+12.7\sqrt{\frac{f}{8}}\left(\frac{Pr}{3}-1\right)} \left[1+\left(\frac{d}{l}\right)^{\frac{2}{3}}\right] \left(\frac{T_f}{T_w}\right)^{0.45} \quad (10)$$

the flow resistance coefficient f is calculated using the Filonenko formula:

$$f = (1.82 \log_{10} Re - 1.64)^{-2} \quad (11)$$

and the Re is calculated by:

$$Re = 0.354 \times \frac{Q_m}{D_i \mu} \quad (12)$$

where Q_m is the mass flow rate of the gas mixture in kg/h, D_i is the inner diameter of the reactor in mm, and μ is the kinetic viscosity of the gas in Pa·s.

The total local entropy generation rate for finite temperature differential heat transfer, finite rate chemical reactions and finite differential pressure flow in the reactor is:

$$\sigma = \pi \cdot d_{r,in} J_q \cdot \left[\left(\frac{1}{T_{in}} - \frac{1}{T_w} \right) + \left(\frac{1}{T} - \frac{1}{T_{in}} \right) \right] + A_c \rho_c r_A \frac{\Delta G}{T} + A_c c_g \frac{1}{T} \frac{dp}{dz} \quad (13)$$

The total entropy generation rate of the reactor is the integral of the total local entropy generation rate along the tube length.

$$SG = \int_0^L \sigma dz \quad (14)$$

As mentioned earlier, this paper will apply a multi-objective particle swarm optimization to carry out a multi-objective optimization with the objective of maximizing the heat absorption rate and minimizing the total entropy generation rate of the reactor. The objective function of the optimization problem is:

$$\min(-Q, SG) \quad (15)$$

The constraints are:

$$350 \text{ K} < T_o < 450 \text{ K} \quad (16)$$

$$0.01 \text{ m} < D_o < 0.02 \text{ m} \quad (17)$$

$$2 \text{ m} < L < 20 \text{ m} \quad (18)$$

3 Results & Discussion

650K, 700K, 750K, 800K, 850K and 900K are chosen as the outer wall temperature of the reactor, respectively, and 6 Pareto Fronts are obtained. Figure 2 shows the Pareto Front when the outer wall temperature of the reactor is 900K. As seen in Figure 2, the optimal frontier space can be divided into four quadrants using the reference reactor point as the origin. According to the physical significance of the coordinate axes, the optimal reactors distributed in the first quadrant have both higher total entropy generation rate and higher heat absorption rate compared to the reference reactor; the optimal reactors distributed in the third quadrant have both lower heat absorption rate and total entropy generation rate; the optimal reactors

distributed in the fourth quadrant have higher heat absorption rate with lower total entropy generation rate.

Figure 2 The Pareto Front with 900K outer wall temperature

Three decision methods, TOPSIS, LINMAP and Shannon Entropy(SE) are further applied to 6 Pareto Fronts under different reactor outer wall temperatures, respectively, 18 optimal reactors' design parameters and performance indexes are obtained.

In order to determine better operating temperatures and to narrow the selection space of optimal reactors to guide engineering practice more precisely, optimal reactors at different temperatures are compared horizontally in Figure 3 to 5.

Figure 3 Performance indicators for LINMAP optimal reactors

Figure 4 Performance indicators for TOPSIS optimal reactors

Figure 5 Performance indicators for SE optimal reactors

As seen in Figure 3, the entropy generation rate of the corresponding LINMAP optimum reactor decreases more significantly than the heat absorption rate as the temperature of the outer wall of the reactor increases from 700 K to 750 K. Moreover, the heat absorption rate does not increase more significantly than the entropy generation rate all the way from 750 K to 900 K. Therefore, the LINMAP optimum reactor at 750 K is a better choice. Similarly, the TOPSIS optimal reactors at 650K and 750K, and the Shannon Entropy optimal reactor at 650K are all preferable options (The Shannon Entropy optimal reactor and the TOPSIS optimal reactor are identical at 650K). The final three best choices are listed in Table 2.

Table 2 The parameters of three final choices

Parameters	Choice 1	Choice 2	Choice 3
Outer wall temperature(K)	750	650	750
Outer diameter(m)	0.02	0.02	0.02
Length(m)	5.7	20	9.5
Inlet temperature(K)	427	449	389
Heat absorption rate(W)	906.0	1292.5	1392.7
Entropy generation rate(W/K)	18.4	15.3	25.6

4 Conclusions

In this paper, finite time thermodynamics is applied to analyze the heat absorption decomposition process in a tubular packed-bed ammonia decomposition reactor under constant external wall conditions. The effects of three parameters, reactor inlet temperature, reactor outer diameter and length on the heat absorption rate and entropy generation rate of the reactor were analyzed. And the results show that:

(1) Within the given constraints, the multi-objective optimized reactors tend to have a bigger reactor diameter to effectively enhance the heat absorption rate.

(2) The comparison of multi-objective optimal reactors for different temperatures shows that the outer wall temperatures are not the higher the better, while 650K and 750K are two better choices.

(3) Through the comparison of 18 optimal reactors at

different outer wall temperatures, three better choices were obtained. Compared to the reference reactor, the three optimal reactors improve heat absorption rate by 58%-143%, while the total entropy generate rate is reduced by 26.4%-38.8%.

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