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# การศึกษาการสังเคราะห์แอมโมเนียบนตัวเร่งปฏิกิริยาประเภทเหล็กโดยการใช้แบบจำลอง Aspen Plus®

**ศิริพร พวงอุบล, อุณาโลม เวทย์วัฒนะ***

## บทคัดย่อ

สภาวะที่เหมาะสมสำหรับการสังเคราะห์แอมโมเนียบนตัวเร่งปฏิกิริยาประเภทเหล็กได้ศึกษาด้วยแบบจำลอง ASPEN PLUS® ในงานวิจัยนี้ โดยมีสารตั้งต้นเป็นก๊าซไนโตรเจนและไฮโดรเจนจากก๊าซสังเคราะห์ที่มีอัตราส่วนของไฮโดรเจนต่อคาร์บอนมอนอกไซด์เท่ากับสามต่อหนึ่ง ซึ่งก๊าซสังเคราะห์นี้ได้มาจากปฏิกิริยาสตีมรีฟอร์มมิงของวัตถุดิบที่หาได้ง่ายในประเทศไทย โรงงานอุตสาหกรรมการผลิตแอมโมเนียได้จำลองขึ้นโดยการใช้เตาปฏิกรณ์ประเภทแบบเบดนิ่งชนิดเอเดียแบติกโดยใช้วิธี Sauve-Redlich-Kwong Property ก๊าซตั้งต้นประกอบด้วยไฮโดรเจน 59.4%, ไนโตรเจน 19.8%, คาร์บอนมอนอกไซด์ 19.8% และ อาร์กอน 1.0% โดยโมล ผลการทดลองพบว่าอุณหภูมิและความดันที่เหมาะสมกับการสังเคราะห์แอมโมเนียด้วยวิธี Haber คือ 231 °C และ 150 บรรยากาศตามลำดับ เนื่องจากการเพิ่มความดันจะทำให้สภาวะสมดุลถูกเลื่อนไปข้างหน้าส่งผลให้ได้ปริมาณแอมโมเนีย ที่มากขึ้น เช่นเดียวกันกับการลดอุณหภูมิ อย่างไรก็ดีการลดอุณหภูมิอย่างไม่เหมาะสมจะส่งผลกับอัตราการเกิดปฏิกิริยา ตัวเร่งปฏิกิริยาประเภทเหล็กได้เลือกมาใช้ในการทดลองนี้ เนื่องจากได้รับความเชื่อถือว่ามีความสามารถที่จะเร่งอัตราเร็วของปฏิกิริยานี้ได้โดยการไปช่วยลดพลังงานก่อกัมมันต์ ที่สภาวะดังกล่าวนี้ จะผลิตแอมโมเนียได้ $21.9\times10^{2}$ กิโลโมลต่อชั่วโมง ที่อัตราการไหลของไฮโดรเจนและไนโตรเจนเท่ากับ $11.9\times10^{3}$ และ $39.6\times10^{2}$ กิโลโมลต่อชั่วโมง ตามลำดับ

**คำสำคัญ** : ASPEN PLUS®, การสังเคราะห์แอมโมเนีย, ตัวเร่งปฏิกิริยาประเภทเหล็ก, ก๊าซสังเคราะห์

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หลักสูตรวิศวกรรมเคมีและกระบวนการ, บัณฑิตวิทยาลัยวิศวกรรมศาสตร์นานาชาติสิรินธร ไทย-เยอรมัน, มหาวิทยาลัยเทคโนโลยีพระจอมเกล้าพระนครเหนือ

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# A Study of Ammonia Synthesis over Iron-based Catalyst using Aspen Plus®

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## Abstract

Optimal operating conditions of ammonia synthesis over iron catalyst were studied using ASPEN PLUS®. Reactant of this reaction was assumed to be $N_2$ and $H_2$ from synthesis gas which could be obtained from steam reforming of available feedstocks in Thailand with ratio of $H_2$/CO = 3:1. The ammonia plant simulation was based on an adiabatic plug-flow reactor (PFR) and modeled using Sauve-Redlich-Kwong Property Method. The feed composition was fixed at 59.4% $H_2$, 19.8% $N_2$, 19.8% CO and 1.0% by mole Ar. Optimal temperature and pressure for ammonia synthesis via the Haber process were found to be at 231 °C and 150 atm, respectively, since an increase of pressure would cause the equilibrium position to move forward resulting in a higher yield of ammonia, as well as decreasing the temperature. However, inappropriately low temperature would show a negative effect on rate of the reaction. Iron catalyst was selected in this study as it is believed to speed up the reaction by lowering the activation energy. To produce $21.9\times10^2$ kmol/hr of $NH_3$, the system required a feed of $11.9\times10^3$ and $39.6\times10^2$ kmol/hr of $H_2$ and $N_2$, respectively.

**Keywords :** ASPEN PLUS®**,** Ammonia synthesis, Iron catalyst, Synthesis Gas

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## 1. Introduction

Ammonia is one of the most important chemicals produced and employed in the manufacture of fertilizers. Fertilizer use in Thai agriculture has increased from 4.3 to 4.4 million tons during 2003 and increased by 2.7-3.1% in 2007 [1], however ammonia is difficult to produce on an industrial scale due to its energy intensive process and it is not currently produced in Thailand. This report will focus on ammonia synthesis for use in the fertilizer industry of Thailand. Ammonia contributes significantly to the nutritional needs of terrestrial organisms by serving as a precursor to food and fertilizers. Because of its many uses, ammonia is one of the most highly produced inorganic chemicals. Chemical plants worldwide produce ammonia, global ammonia production in 2004 was 109 million metric tons and was about 130.0 million metric tons in 2010. The People's Republic of China produce 28.4% of the worldwide production (increasingly from coal as part of urea synthesis) followed by India with 8.6%, Russia with 8.4%, and the United States with 8.2%. About 80% or more of the ammonia produced is used for fertilizing agricultural crops [2].

The Haber process is considered to be one of the most significant scientific discoveries in the 20th century. Fritz Haber established the conditions under which nitrogen and hydrogen would combine using

- Medium temperature (300 - 550 °C)
- Very high pressure (150 - 250 bar)
- A catalyst (a porous iron catalyst prepare by reducing magnetite, $Fe_3O_4$).

Osmium is a much better catalyst for the reaction but very expensive.

This process produced an ammonia, $NH_3$ (g), yield of approximately 10-20%.

The Haber process was improved to be used as an industrial process by Carl Bosch. Operating pressure was normally fixed constant at approximately 200 atm. The reaction between nitrogen gas and hydrogen gas to produce ammonia gas as shown in Eq. (1) is an exothermic equilibrium reaction, releasing 92.4 kJ/mol of energy at 298 K.

$$N_2\,(g) + 3\,H_2\,(g) \rightleftharpoons 2\,NH_3\,(g) \qquad (1)$$

Synthesis of ammonia is a kinetically simple reaction, a straightforward synthesis with no side reaction, and the product is stable. Hydrogen used in the process can be produced through steam reforming. The steam reforming feedstocks can be biomass and wastes such as waste glycerol from biodiesel production, ethanol etc. Steam reforming reactions are environmentally friendly because they can help reducing waste or convert waste into higher value products such as $H_2$ and $NH_3$

Steam reforming is the most widespread process for the generation of hydrogen-rich synthesis gas from feedstock including natural gas, refinery off-gases, LPG, and naphtha. Steam methane reforming (SMR) is the most common process of producing commercial bulk hydrogen as well as hydrogen used in the industrial synthesis of ammonia. At high temperatures (700 – 1100°C) and in the presence of a metal-based catalyst (nickel), steam reacts with methane to yield carbon monoxide and hydrogen as shown in Eq. (2), [3].

$$CH_4 + H_2O \rightleftharpoons CO + 3\,H_2 \qquad (2)$$

Additional hydrogen can be recovered by the gas-shift reaction with carbon monoxide. The reaction is summarized by:

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad (3)$$

The reaction (2) is strongly endothermic, and the reaction (3) is mildly exothermic. One readily available feedstock for the steam reforming reaction is waste glycerol obtained as a by-product of bio-diesel production. Due to the significant increase of biodiesel production, more waste glycerol is produced. Additionally, glycerol is a potential feedstock to produce $H_2$ as 1.0 mol of glycerol can theoretically produce up to 4.0 mol of hydrogen. $H_2$ is mostly used in refinery hydrotreating operations, for ammonia production, and in fuel cells [4]. Steam reforming reaction of any oxygenated organic compounds such as glycerol and acetaldehyde proceed according to the following equation

$$C_nH_mO_k + (n\text{-}k)\ H_2O \rightleftharpoons n\ CO + [(n+m/2\text{-}k)]\ H_2 \qquad (4)$$

## 2. Experimental Methodology

The synthesis gas which is the product from steam reforming or other processes was used as a feedstock in Haber process to produce ammonia. The ammonia plant simulation by ASPEN PLUS® was based on an adiabatic plug-flow reactor (PFR) and modeled with the Sauve-Redlich-Kwong Property Method, shown in Figure 1. Iron catalyst was selected in this study because it is a well-known material that was used to speed up the reaction by lowering the activation energy so that the $N_2$ bonds and $H_2$ bonds can be more readily broken [5]. The reactor consisted of three adiabatic beds; the reactor feed consisted of two sources. The first of which was a make-up feed stream of $20.0\times10^3$ kmol/hr at 25°C and 150 atm containing mainly hydrogen and nitrogen in the stoichiometric molar ratio of 3:1, it contained small concentrations of carbonmonoxide (CO) from synthesis gas and argon (Ar) from purge. The second feed was a recycle stream that recovered after removing the ammonia product. The converter consisted of three cylinders which 2.0m diameter adiabatic beds, packed with catalyst for bed lengths of 1.5m, 2m and 2.5m, respectively, because one cylinder can produce ammonia in the fewer amounts. The first length was the minimal length and increased length in the next step to increase ammonia product. The reactor feed was split into three branches, with the first branch as the main feed entering the first bed after being preheated by the hot reactor effluent from the third bed. The second and third branches were controlled by adjusting valves VLV-1 and VLV-2, and provide cold-shot cooling at the first and second bed effluents, respectively.

The effluent from the converter bed was introduced into the heat exchanger before transferred to a following reactor which used the produced ammonia as the refrigerant to cool down the process stream before entering the flash vessel. The flash vessel was also operated at -30°C and had a pressure drop of 5 atm. The compressor was an ideal two stage compressor and increased the pressure of the recycle stream to 150 atm before merging with the feed stream and entering the reactor.

**Table 1:** The input feed stream for the ammonia process

| Component | Mole percentages |
|---|---|
| $H_2$ | 59.4 % |
| $N_2$ | 19.8 % |
| CO | 19.8 % |
| Ar | 1.0 % |
| $NH_3$ | 0.0 % |

### 2.1 Rate expression

Ammonia was synthesized in a reversible reaction, whose rate was correlated by the Tempkin equation [6], expressed in terms of the partial pressures, in atmospheres, of the reacting species.

$$R\alpha = 10^4 e^{-91,000/RT}[P_{N_2}]^{0.5}[2P_{H_2}]^{1.5} - 1.3\times10^{10} e^{-140,000/RT}[P_{NH_3}] \qquad (5)$$

Where $R\alpha$ is the rate of nitrogen disappearance in kmol/$m^3$-s, T is the temperature in Kelvin (K), $P_i$ are the partial pressure of the reacting species in atm, and the activation energies for the forward and reverse reactions are in kJ/kmol.

The species partial pressures can be expressed in terms of the ammonia mole fraction, $x_{NH_3}$, and the original feed composition. The species partial pressures can be expressed in terms of the ammonia mole fraction, ($x_{NH_3}$), and the original feed composition as following:

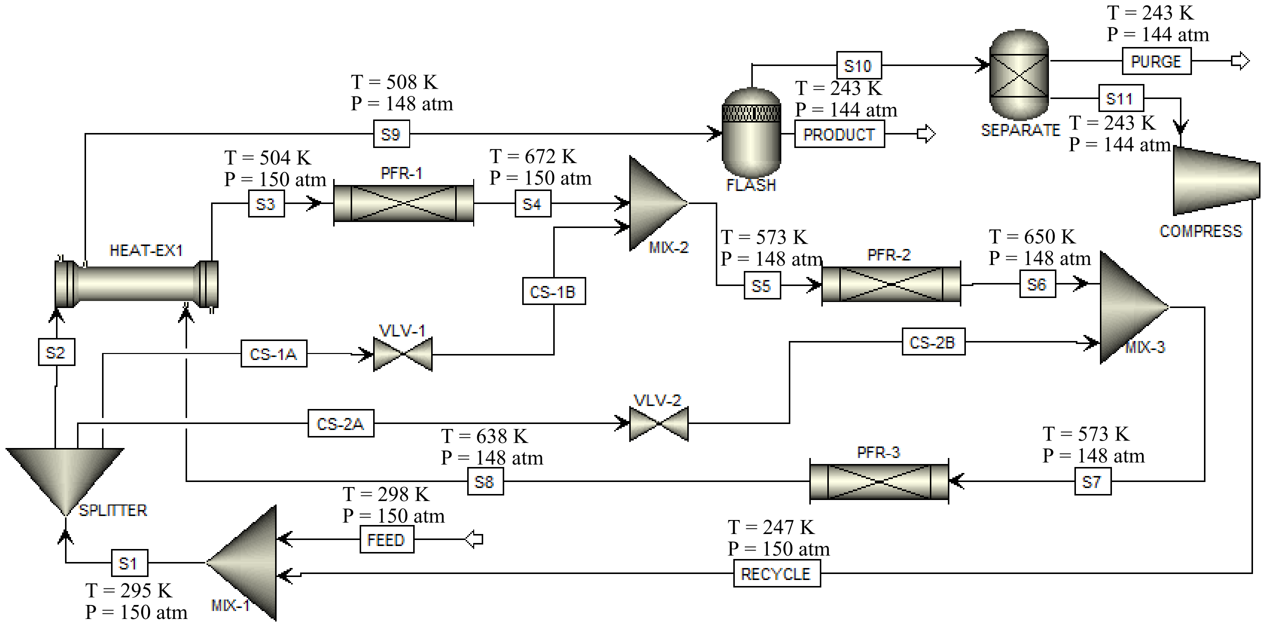

**Fig. 1** Schematic of Ammonia Plant in Aspen with adiabatic plug flow reactors

$$P_{H_2} = \left\{\frac{F_0 X_{f,H_2} - 1.5\xi}{F_0 - \xi}\right\} P$$

$$P_{N_2} = \left\{\frac{F_0 X_{f,N_2} - 1.5\xi}{F_0 - \xi}\right\} P$$

$$P_{NH_3} = \left\{\frac{F_0 X_{f,NH_3} + \xi}{F_0 - \xi}\right\} P = X_{NH_3} P \qquad (6)$$

Where $F_0$ is the total molar flow rate of the combined reactor feed, $\xi = F_0(x_{NH_3} - x_{f,NH_3})/(1 + x_{NH_3})$ is the molar conversion, P is the operating pressure, and $x_{f,i}$ is the feed mole fraction of species i. Consequently, the rate of reaction can be computed as a function of temperature and $x_{NH_3}$ for an operating pressure of 150 atm. The ridge of maximum reaction rate in composition-temperature space defines an optimal decreasing temperature progression that is to be approximated by the appropriate design and operation of the converter.

### 2.2. Kinetics Parameter

Ammonia was formed by the reversible reaction between nitrogen and hydrogen, Power-Law rate expression given previously as shown in Eq. (5), [7];

$$R\alpha = k_1 [P_{N_2}]^{0.5} [P_{H_2}]^{1.5} - k_2 [P_{NH_3}] \quad \text{kmol/m}^3\text{-s} \qquad (7)$$

Forward reaction: $k_1 = 5.844\times10^{-7} \exp[-91{,}000/RT]$

Reverse reaction: $k_2 = 76980 \exp[140{,}000/RT]$

### 2.3 Optimal condition

The production of ammonia depended on the temperature of feed gas at the top of the reactor, the partial pressures of the reactants (nitrogen and hydrogen) and the reactor length. Amount of the ammonia was found to be favored by high pressure and low temperature. The operating temperature and pressure of ammonia synthesis were varied and investigated yield of ammonia.

### 2.3.1 The effect of temperature

The temperature was varied in the range 230-350°C since this range enables the system to produce ammonia in the large amount. Optimal design for ammonia synthesis in terms of temperature was investigated.

### 2.3.2 The effect of pressure

The pressure was varied and investigated in the range 130-240 atm as ammonia production was found to occur at high pressure according to Le Chaterlier's principle.

## 3. Results and Discussions

### 3.1 Optimal condition

#### 3.1.1 The effect of temperature

The effect of temperature on the product yield during the ammonia synthesis was shown in Figure 2. The operating temperature was varied while holding the pressure of the feed constant. With an increase of temperature from 230 to 240°C, the molar flow rate of ammonia increased from $15.7\times10^{2}$ to $21.6\times10^{2}$ kmol/hr. On the other hand, as increasing temperature from 240 to 350°C, the result showed a decrease of ammonia production rate. This was possibly due to the fact that a decrease of temperature caused the equilibrium position moving to the right resulting in a higher yield of ammonia [8].

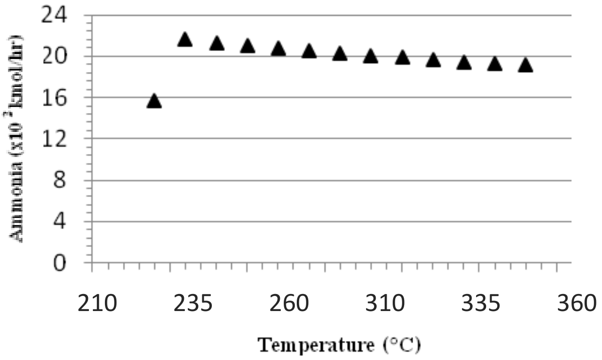

**Fig. 2** The effect of temperature on the product yield during the ammonia synthesis at 150 atm when the temperature range was varied from 230 to 350°C

Therefore, temperature in a range of 230-241°C was chosen to be investigated further as it showed a steep increase of molar flow rate of ammonia. It is noticed from Fig. 3 that the highest rate of ammonia production occurred at 231°C.

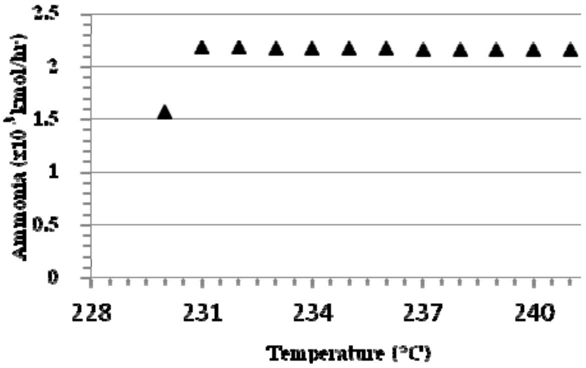

**Fig. 3** The effect of temperature on the product yield during the ammonia synthesis at 150 atm when the temperature range was varied from 230 to 241°C

#### 3.1.2 The effect of pressure

From the previous results, the temperature at 231°C was selected and fixed constant to study the effect of the operating pressure. Ammonia yield was found to increase with higher pressure.

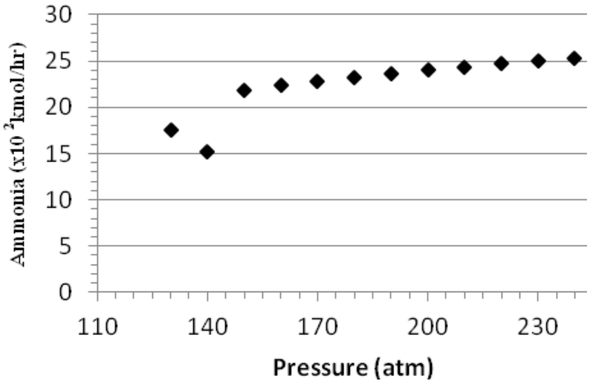

**Fig. 4** The effect of pressure on the product yield during the ammonia synthesis at 231.0°C when the pressure range was varied from 130 to 240 atm,

From Fig. 4, it was found that ammonia yield approximately from $20\times10^{2}$ to $25\times10^{2}$ kmol/hr was obtained when the operating pressure is higher than 150 atm. However, the operating with high pressure is expensive and complicated. The pressure at 150 atm was then chosen as an optimum since the ammonia yield at this pressure is only 0.9% less than at 200 atm. The optimal condition of Haber process was found to be at 231°C and 150 atm.

### 3.2 Simulated ammonia plant

The final ammonia plant simulated by ASPEN PLUS® was based on adiabatic Plug-Flow reactor operated at a pressure of 150 atm and 230°C. The input feed stream for the process was $20×10^3$ kmol/hr with 59.4% of $H_2$, 19.8% of $N_2$, 19.8% of CO and 1% by mole Ar. Table 2 shows the operating conditions, molar flow rate of each component and other properties of feed and product streams, respectively.

**Table 2** Simulation results obtained using ASPEN PLUS®

| Stream ID | Feed | Product |
|---|---|---|
| Temperature (K) | 298.1 | 243.2 |
| Pressure (atm) | 150.0 | 143.7 |
| Mole flow (kmol/hr) | $20.0×10^3$ | $23.5×10^2$ |
| Mass flow (kg/hr) | $25.4×10^4$ | $41.7×10^3$ |
| Enthalpy (MMkcal/hr) | -104.5 | -41.2 |
| **Mole flow (kmol/hr)** | | |
| $H_2$ | $11.9×10^3$ | 7.2 |
| $N_2$ | $39.6×10^2$ | 4.6 |
| $NH_3$ | 0.0 | $21.9×10^2$ |
| Ar | 200.0 | 0.7 |
| CO | $39.6×10^2$ | 151.9 |

## 4. Conclusions

The synthesis gas with a ratio of $H_2$/CO = 3:1 and $N_2$ was used as a feedstock to produce ammonia via Haber process over iron-based catalyst. The ammonia plant simulation by ASPEN PLUS® was based on an adiabatic Plug-Flow reactor model. The reactor consisted of three adiabatic beds. The feed consisted of two sources, the first of which was a make-up feed stream of $20×10^3$ kmol/hr at 25°C and 150 atm containing 59.4 % $H_2$, 19.8 % $N_2$, 19.8 % CO and 1.0 % Ar and the second was a recycle stream that recovered after removing the ammonia product. Iron catalyst was selected in this study because it was believed to speed up the reaction by lowering the activation energy so that the $N_2$ bonds and $H_2$ bonds can be more readily broken. Operating condition of Haber process was found to be optimal at 231°C and 150 atm which agreed with previous results [9] since an increase of pressure would cause the equilibrium position to move forward resulting in a higher yield of ammonia, as well as decreasing the temperature. However, inappropriately low temperature would show a negative effect on rate of the reaction. Iron catalyst was selected in this study as it is believed to be able to speed up the reaction by lowering the activation energy. At this condition, this process was able to produce $65.3×10^3$ kg/day ($23.5×10^2$ kmol/hr) of ammonia.

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