A Study on the Application of Computer Process Simulation Technology in Ammonia Synthesis

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A chemical process simulation software, AspenPlus, is applied to simulate the ammonia synthesis in the ammonia production process. A reasonable unit operating model is selected, and the RKS-BM thermodynamic method is adopted for calculations. The simulation results are in favorable agreement with the actual operation results, and the simulation data has a guiding significance on the actual production. Meanwhile, this paper analyzes the influence of the changes in the synthesis pressure, the outlet gas temperature of the synthesis tower, the hydrogen/nitrogen ratio of fresh air and other operating parameters on the ammonia synthesis section. The net profit of the synthetic section is taken as the objective function to optimize the operating parameters. The optimal process operating parameters are obtained: the synthesis pressure is 20MPa, the convertor outlet temperature is 313°C, and the H_2/N_2 ratio of fresh air is 3.0.
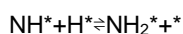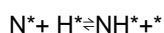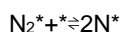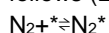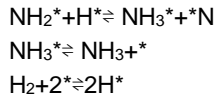
1. Introduction

Synthetic ammonia is the main raw material for the production of urea, phosphoric acid, nitric acid and other chemical fertilizers (Penkuhn et al., 1997; Upreti and Deb, 1996). For a long time, synthetic ammonia has been a large energy consumer in the chemical industry. In China, the equipment for ammonia synthesis has been through repeated raw material route transformation and energy-saving transformation, such as oil to coal, coal to oil, oil to gas, and anthracite to powdered coal. Tens of major large transformations are carried out on the hydrocarbon steam conversion section, shift section, decarburization section, and control system, etc. (Kirova, 2004; Annable, 1952; Gaines, 1079). However, due to plant raw material route, resource supply, transportation, capital, technology maturity and other reasons, the effect of synthetic ammonia energy-saving technological transformation has failed to reach the expected goals (Lísal et al., 2005; Sadeghi and Kavianiboroujeni, 2009; Azarhoosh et al., 2014). Process simulation and optimization technology is one of the main means to address these problems. How to apply process simulation and optimization technology to guide the operation of the actual production equipment has become a major research topic in the petrochemical industry today (Babu and Angira, 2005; Peng et al., 2005; Fischer and Iribarren et al., 2012).
This paper selects the core part of ammonia production process-ammonia synthesis system as the research object, employs process simulation and optimization techniques as research tools, brings about energy saving and consumption reduction of ammonia production, and provides an example and a reference for other sections of ammonia production.

2. A theoretical study on simulation and optimization of ammonia synthesis system

2.1 Reaction mechanism of ammonia synthesis

Ammonia synthesis reaction generally adopts the molten iron catalyst, and the reaction mechanism is as follows (Lin et al., 2015):

$N_2 + * \rightleftharpoons N_2*$

$N_2* + * \rightleftharpoons 2N*$

$N* + H* \rightleftharpoons NH* + *$

$NH* + H* \rightleftharpoons NH_2* + *$

$NH_2*+H* \rightleftharpoons NH_3*+*N$

$NH_3* \rightleftharpoons NH_3+*$

$H_2+2* \rightleftharpoons 2H*$

The symbol * in each reaction step represents a blank activity.

2.2 Optimization method of the nitrogen synthesis system

This paper applies a feasible path method (also called black box method) based on the sequential module method for optimization (Xu et al., 2015). The general formula of the objective function for ammonia synthesis system optimization is:

$$N = \sum g_1 Q + \sum g_2 W + \sum g_3 FL \tag{1}$$

Specifically, Q represents energy flow. W stands for power consumption. FL means logistics flow. g_1, g_2 and g_3 are coefficients that are determined according to the actual situation.

This paper takes the net income of the ammonia synthesis section as the objective function and studies how the net income changes with the synthetic pressure, the outlet gas temperature of the synthesis tower, the recirculating ratio, the hydrogen/nitrogen ratio of fresh air and the adiabatic efficiency of the circulating compressor. Table 1 illustrates the reference price for each indicator of net income.

Table 1: The reference price of the net income indications

Index	Ammonia /(Yuan·t^{-1})	cooling water /(Yuan·t^{-1})	boiler water /(Yuan·t^{-1})	Steam /(Yuan·t^{-1})	Electricity /(Yuan·KW^{-1}·h^{-1})
price	2500	0.25	2.5	120	1.0

The calculating formula for net income is:

$N=2500L+120G-2.5D_g-0.25D_s-2500Da-1.0P-C_o$

In the formula, N is the net benefit. L is the ammonia yield. G is the steam consumption of the by-products. D_g is the water supply of waste heat boiler. D_s is the water consumption of cooling water. D_a is the frozen ammonia consumption of the ammonia condenser. P is the power consumption of compressor. C is the amount of consumption of hourly fresh feed gas.

2.3 Ammonia synthesis section process

The liquid ammonia project, with an annual output of 180,000 tons, of the ammonia synthesis section in a certain factory is taken as an example, and its process flow chart is illustrated in Figure 1.
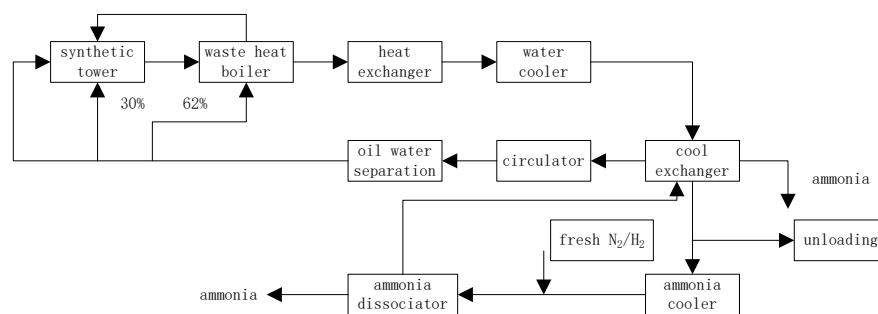

Figure 1: The simple flow chart of the ammonia synthesis process

The fresh H_2/N_2 mixture gas supplied from the alkylation system and the gas after the reaction in the ammonia cooler are mixed into the ammonia dissociator to separate the trace debris such as water and oil. The dissociated gas enters the cool exchanger tube and exchanges heat with the gas that is cooled down by the water between the pipes. After passing through the oil water separator, the exchanged gas is divided into three parts. One part exchanges heat with the hot gas that are reacted in the heat exchanger and the waste heat boiler and then enters the synthesis tower. The other two parts of gas directly enter the synthesis tower. Outlet reaction gas enters the waste heat boiler for waste heat recovery of the by-product steam, passes through the heat exchanger, enters the water cooler for further cooling, then enters the cool exchanger, and

passes through the cyclone separator at the lower part of the cool exchanger for ammonia separation, so that most of the liquid ammonia in the gas is separated. The dissociated gas and a small amount of ammonia enter the ammonia cooler, come out and enter the ammonia dissociator together with the qualified alkylated nitrogen and hydrogen mixture for re-cycling.

The main process parameters of ammonia synthesis are indicated in Table 2.

Table 2: The main process parameters of ammonia synthesis process

Fresh gas component	H_2	N_2	AR	CH_4
mole fraction / %	75.61	22.39	0.5	1.5
fresh gas flow ($m3 \cdot h^{-1}$)	78168			
fresh gas temperature/ °C	83			
fresh gas pressure/MPa	18.88			
adiabatic efficiency of compressor	0.553			
synthesis pressure/Mpa	20.37			
out tower gas temperature/ °C	298			
H_2/N_2	337			

3. Simulation process for ammonia synthesis system

This paper adopts the Aspen Plus software to simulate and optimize the ammonia synthesis system.

3.1 Simulation process

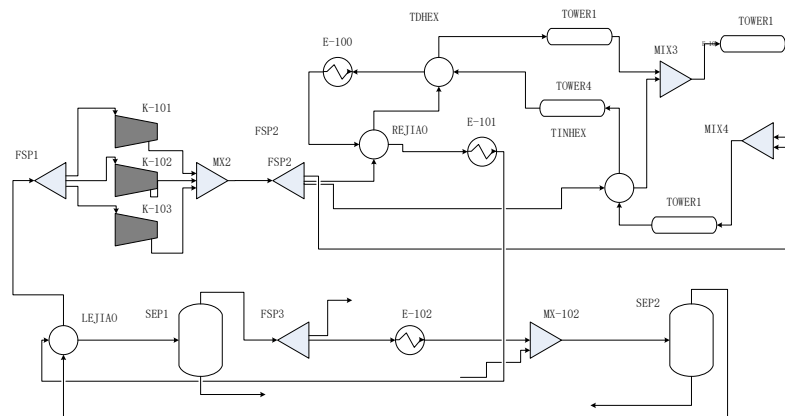The simulation flow chart for the ammonia synthesis system is demonstrated in Figure 2.

Figure 2: The process simulation chart of ammonia synthesis process

The ammonia synthesis tower is a JD2000 four-stage reactor. RPlug is selected as the unit model of the ammonia synthesis reactor TOWER1 ~ TOWER4l. Two-stream heat exchanger HEATX is employed by heat exchangers (REJIAO), cold exchangers (LEJIAO), heat exchangers at tower bottom(TDHEX) and in-tower heat exchangers (TINHEX), etc. The HEATER model is adopted for waste heat boilers (E-100), water coolers (E-101) and ammonia coolers (E-102). The circulating compressor (K-101 to K-103) adopts the COMPR model. The cyclone separator at the lower part of the cool exchanger (SEP1) and the ammonia dissociator (SEP2) adopt the FLASH2 model. MIXER and FSPLIT models are used for the mixing and splitting operations.

3.2 Model selection

Concerning the equipment of ammonia synthesis, the physical methods recommended by Aspen are the state equations (with binary interaction parameters) employed in the high pressure hydrocarbon application, which

mainly involve RKS-BM, PR-BM, LK-PLOCK and BWR-LS4. The comparison of simulation results and actual measured data of the ammonia synthesis section by means of four different thermodynamic model calculation methods is demonstrated in Table 3.

Table 3: The comparison of simulation results and actual plant data

Parameters	Actual plant data	RKS-BM	PR-BM	LK-PLOCK	BWR-LS
Towe income flow (Kmol·h^{-1})	14709.00	15039.70	15070.79	15532.79	15349.88
NH3 volume fraction of tower outpu (%)	14.30	14.40	14.98	14.52	14.01
NH3 yield	25.00	25.52	25.53	25.19	25.27
Unloading gas (Kmol·h^{-1})	475.28	489.65	491.54	510.80	502.66
Inlet temperature of compressor (°C）	6.05	7.08	7.67	7.63	6.99
Iutlet temperature of compressor (°C）	19.70	19.93	19.76	19.97	20.23

The results in Table 2 suggest that the results calculated by the RKS-BM thermodynamic calculation model have the best agreement with the actual data. Therefore, the simulated calculations of the ammonia synthesis section adopt the RKS-BM thermodynamic calculation model.

4. A study on the optimization of ammonia synthesis system

This paper takes the net income of ammonia synthesis section as the objective function, studies how net income changes with the net operating income, the outlet gas temperature of the synthesis tower, the H_2/N_2 ratio of fresh air and the adiabatic efficiency of the circulating compressor, and optimizes various parameters.

4.1 Synthesis pressure

Given the other conditions stay unchanged, the synthesis pressure is changed. ASPEN software is adopted for the simulation calculation of the ammonia synthesis section. The results indicate that, as the synthesis pressure moves up from 19MPa to 21MPa, the mole fraction of ammonia in the ammonia synthesis tower increases from 14.33% to 14.45%; the ammonia yield climbs from 25.46t·h^{-1} to 25.54t·h^{-1}; the compressor power consumption goes up from 1322.07kW to 2404.43kW; the cooling water consumption changes from 1728.00t·h^{-1} to 1735.58t·h^{-1}; the amount of ammonia used in the ammonia cooler drops from 5.69t·h^{-1} to 5.57t·h^{-1}; the by-produced steam fluctuates between 19.34t·h^{-1} and 19.59t·h^{-1}. Figure 3 illustrates the relationship between the net income of the ammonia synthesis section and synthesis pressure.
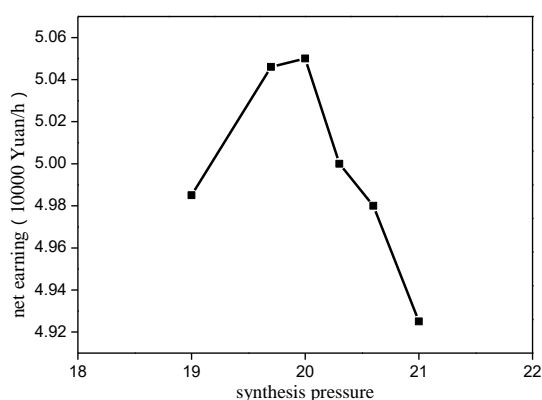

Figure 3: The relationship of net income against synthesis pressure

According to this figure, when the synthesis pressure extends from 19MPa to 21MPa, the net income increases first and then decreases. When the pressure is 20MPa, the maximization of the net income can be realized and the net income is 50,500 Yuan·h^{-1}.

4.2 Converter outlet temperature

Given the other conditions remain unchanged, when the temperature of the reaction gas at the converter outlet is changed from 295°C to 313°C, the mole fraction of ammonia in the outlet ammonia tower moves up from 14.34% to 14.75%; the ammonia yield rises from 25.49t·h^{-1} to 25.67t·h^{-1}; the compressor power consumption reduces from 1803.28kW to 1756.99kW; the consumption of cooling water drops from 1733.19t·h^{-1} to 1714.97t·h^{-1}; the consumption of frozen ammonia in the ammonia cooler goes down from 5.57t·h^{-1} to 5.35t·h^{-1}; the by-product steam augments from 18.90t·h^{-1} to 21.88t·h^{-1}. Figure 4 indicates the relationship between the net income of the section and the outlet gas temperature of the synthesis tower.
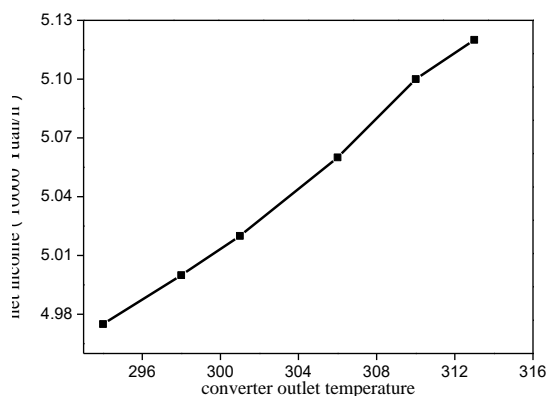

Figure 4: The relationship of net income against converter outlet temperature

As seen from Figure 4, the net income is on the rise with the increase of outlet temperature. The higher the outlet temperature is, the lower the temperature of the to-be-reacted gas in the first bed of the inlet synthetic tower is, which is favorable for the synthesis of ammonia in the tower. The temperature range of the catalyst used in this section is 425°C to 500°C. When the outlet temperature is 313 °C, the temperature of the first bed of the inlet synthetic tower is 425.34 °C. Therefore, the outlet temperature of the tower should be controlled below 313 °C, and the net income at this point is 51,200 Yuan·h^{-1}.
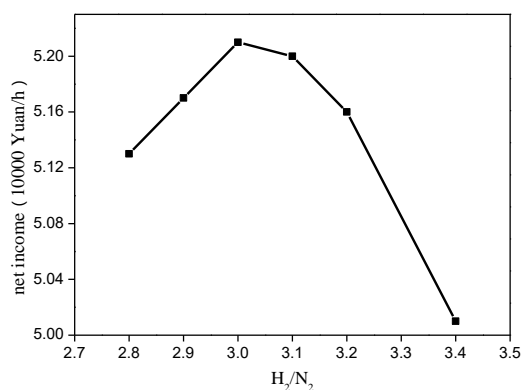
4.3 A study on hydrogen and nitrogen ratio

Figure 5: The relationship of net income against H$_2$/N$_2$

With the addition of fresh air, the H$_2$/N$_2$ ratio changes from 2.8 to 3.4. The molar content of ammonia in the outlet synthetic tower decreases from 15.83% to 14.40%. The ammonia yield fells down from 25.58t·h^{-1} to 25.52t·h^{-1}. The compressor power consumption increases from 1635.16kW to 1795.72kW. The consumption of cooling water rises from 1688.96t·h^{-1} to 1730.23t·h^{-1}. The ammonia consumption of ammonia cooler moves up from 5.51t·h^{-1} to 5.53t·h^{-1}. By-product steam climbs from 18.73t·h^{-1} to 19.34t·h^{-1}. It is indicated that, with the increase of the ratio of hydrogen and nitrogen in the fresh gas, the amount of by-product steam augments. But at the same time, the amount of ammonia production drops; the consumption of cooling water rises; the consumption of cold ammonia increases; the power consumption of the compressor moves upward. Figure 5 demonstrates the relationship graph of net income against the H$_2$/N$_2$ ratio. When the H$_2$/N$_2$ ratio is 3.0, the net income is 51,200 Yuan·h^{-}.

5. Concluding remarks

(1) Aspen Plus is applied to simulate the section of ammonia synthesis. It is planned to select RPlug as the unit model of the ammonia synthesis tower, and the RKS-BM thermodynamic method is used for calculations. The simulation results are in good agreement with the actual operation results, which proves the creditability of various data given by the simulation. The model can be used to guide the transformation, design and operational optimization of similar devices.

(2) This paper analyzes the influence of the changes in synthesis pressure, outlet gas temperature of the synthesis tower, the hydrogen/nitrogen ratio of fresh air and other operating parameters on the system. The net income of the synthetic section is taken as the objective function to optimize various operating parameters. The results have indicated that when the synthesis pressure is 20MPa, the net income can reach the maximum value of 50,500 Yuan·h^{-1}. The net income goes up with the increase of the outlet gas temperature of the synthesis tower. When the outlet temperature is 313°C, the income is up to 51,200 Yuan·h^{-1}. When the H_2/N_2 ratio is 3.0, the net income reaches a maximum value of 52,100 Yuan ·h^{-1}.

Acknowledgment

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