Energy Consumption Optimization of a Synthetic Ammonia Process Based on Oxygen Purity

Jianrong Jiang[a], Xiao Feng[a,*], Mingzhe Duan[b], Zhigang Zhang[b]

[a]Xi'an JiaoTong Univ., Dep. Chemical Engineering, Xianning West Rd. 28, 710049 Xi'an, China
[b]Shaanxi Coal and Chemical Technology Institute Co., Ltd., Keji Fifth Rd. 8, 710075 Xi'an, China
 xfeng@xjtu.edu.cn

The energy consumption of an ammonia process is huge, and it occupies a large proportion in the industrial energy consumption. The air separation unit is an important energy-consuming unit in the process of ammonia synthesis. For the ammonia process with pure oxygen gasification, the purity of oxygen products in the air separation unit is generally 99.6%. If the oxygen purity from the air separation is reduced properly, its energy consumption will decrease effectively, and the energy consumption of the whole ammonia process may further decrease, as the nitrogen element is needed for ammonia synthesis. However, with the increase of the flow rate, the operating cost of the subsequent unit would increase, so there is an optimal purity that could minimize the energy consumption of the whole process. In this paper, the process simulation software, ASPEN PLUS, is used to model and analyse the process of ammonia synthesis to determine the process energy consumption with different inlet oxygen purity. With the reduction of oxygen purity, the oxygen compressor power consumption increases, nitrogen compressor power consumption decreases, and the refrigeration energy consumption of the purification unit increases. The relations between the three kinds of energy consumption and oxygen purity are linear. Combined with the relation between oxygen purity and the energy consumption of air separation unit, the optimal oxygen purity that makes the process energy consumption minimal is 92%. Compared with the current process used 99.6% purity oxygen, the energy saving is about 13.3% as much as air separation energy consumption.

1. Introduction

The main materials for ammonia synthesis are coal, natural gas, coke and heavy oil. Coal is an important fossil fuel and has a huge reserve (Bassani et al., 2017). Coal gasification is a process that convert the combustible part of coal or char into combustible gas at high temperature, with oxygen, water vapour or hydrogen as gasification agent. According to the different oxygen purity, the process using oxygen as gasification agent can be divided into air gasification, enriched oxygen gasification, and pure oxygen gasification. In an ammonia synthesis process using pure oxygen gasification, the air separation unit is an important energy-consuming unit and the purity of its oxygen product is mostly 99.6 %. However, high purity oxygen consumes more energy, considering that the nitrogen mixed in oxygen is the element needed for ammonia synthesis.

Due to the development of computers and process simulation software, many scholars have applied ASPEN PLUS to study the related processes of ammonia synthesis. In the studies of coal gasification, He et al. (2013) modelled and analysed a Lurgi fixed-bed coal gasifier of an SNG plant using ASPEN PLUS. Duan et al. (2015) built a model of coal integrated gasification combined blast furnace slag waste heat recovery system using the residual heat of blast furnace gas. In the studies of gas purification for ammonia synthesis, Aroua et al. (2002) used ASPEN PLUS to model the CO_2 absorption process by MDEA; Field et al. (2011) modelled and analysed the two section Selexol absorption process; Sun and Smith (2013) simulated the Rectisol wash process, and compared the energy consumption of the single-stage and the two-stage processes. In the studies of water gas shift, Amran et al. (2017) simulated the process of water gas shift for hydrogen production. Due to the excellent applicability of ASPEN PLUS in ammonia process simulation, we use ASPEN PLUS to simulate ammonia process in this paper.

In this paper, ASPEN PLUS is used to model a process of ammonia production from coal to study the relationship between the energy consumption of the process and the purity of oxygen from the air separation unit, and finally determine the optimal oxygen purity that makes the energy consumption minimal. Similar studies have not been reported.

2. Process description

Generally, there are coal gasification, water gas shift, syngas purification and ammonia synthesis units in a coal to ammonia plant. Texaco coal gasification is a mature process with high efficiency of carbon conversion (Wang et al., 2007). Co-Mo sulphur-tolerant shift catalysts have a wide temperature range and long using lifetime (ChandraRatnasamy and Wagner, 2009). Rectisol wash is for H_2S, COS, CO_2, HCN and NH_3 removal simultaneously (Sun and Smith, 2013). Besides, it has good energy saving effect when combined with liquid-nitrogen washing process. So, Texaco coal gasification, two-stage sulphur-tolerant water gas shift, Rectisol wash process and liquid-nitrogen washing process are selected as the research process in this paper.

Texaco gasification process can be divided into gasification, cooling and dust removal. Pressurized gasification is used in the process; the pressure of the furnace is 6.5 MPa. The volume fraction of the oxygen from the air separation unit is 99.6 %, which is compressed by compressor CP1 to 1-2 MPa higher than the gasifier GR and transported to the gasifier with coal water slurry to react. The reaction product enters the quench chamber, and the syngas is sent from the upper part of the quench chamber. Next, it is transferred to the carbon-washing column GT for cooling and dedusting.

The temperature of the syngas from the gasification unit is 235 °C. After separated from condensate and a small amount of slag in the gas water separator SF1, the syngas is heated to 260 °C in the heat exchanger SE1. Then, it is sent into the first reactor SR1, which has Co-Mo sulphur-tolerant shift catalysts. The temperature of the syngas from the first stage reactor is 450 °C. After cooled to 230 °C in the heat exchanger SE2, the water gas is sent into the second stage reactor SR2. The dry basis of the syngas from the second stage reactor is 98.6 %. After a series heat exchange, the syngas is cooled to 40 °C, and then transported to the subsequent gas purification process.

The syngas from the shift unit is cooled to -21 °C in the heat exchanger RH. Next, it is sent into the bottom of the absorber RT. The solubility of H_2S and COS in cryogenic methanol is much greater than that of CO_2. Therefore, the absorber is divided into two parts. The upper part of the tower is mainly used to absorb CO_2, and the lower part is mainly used to absorb H_2S, COS and other sulfides. As H_2S and CO_2 absorption in methanol is an exothermic process, in order to prevent the temperature of the absorption liquid too high, the absorber RT has liquid-side draw cooling loops returning liquid at -34 °C. Practical absorption normally has 3-4 loops.

After the Rectisol wash process, the syngas enters the NB molecular sieve absorber for CO_2, H_2O and CH_3OH removal. Next, the syngas is cooled in heat exchangers NE2 and NE1. Then the syngas enters the bottom of the nitrogen-washing column to remove CO, CH_4 and Ar. The nitrogen is generated from the air separation unit and compressed to 5.5 MPa by compressor CP2. The refined gas from the top of the nitrogen-washing column NT is adjusted the proportion of nitrogen to hydrogen by nitrogen flow. After being reheated, the proportion of nitrogen to hydrogen is adjusted again, which finally reaches to 1:3. Then, the syngas is sent to the ammonia synthesis process. The flowsheet of ammonia production from coal is shown in Figure 1.
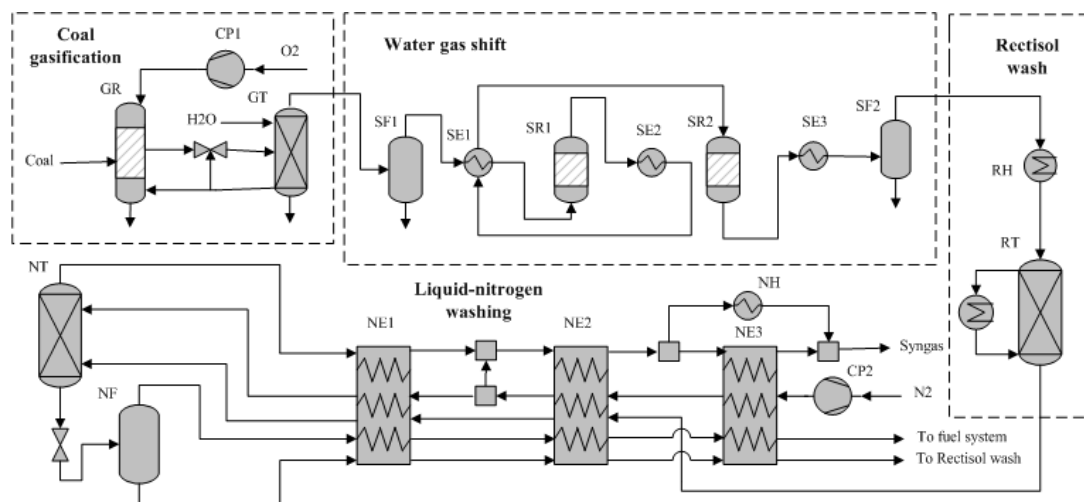

Figure 1: Flowsheet of ammonia production from coal

3. Process simulation

The model RK-BM is chosen as the physical property method of gasification process. The process of coal gasification includes two parts: pyrolysis and gasification. The module RYieid is chosen to simulate pyrolysis unit (Duan et al., 2015), which decomposes coal into H_2O, H_2, N_2, CL_2, O_2, S, C and Ash. Meanwhile, the pyrolysis heat is transferred to the gasification unit. The RGibbs reaction module is selected as the gasification unit GG. The oxygen entering the gasification unit is considered as only nitrogen and oxygen. The flash module Flash2 is used as the quench chamber GF, the temperature of which is set to 235 °C. The Radfrac module is used as the carbon-washing column.

The model PENG-ROB is chosen for the physical property of the water gas shift unit. The HeatX module is selected as the heat exchangers and the flash module Flash2 is selected as the water separators in the process. The RStoic reactor module is adopted in the two-stage reactor. The pressure drop of the first stage reactor is 0.03 MPa, the outlet temperature is 450 °C, and the conversion rate of CO is 72 %. The pressure drop of the second stage reactor is 0.02 MPa, the outlet temperature is 343.5 °C, and the conversion rate of CO is 86 %.

The RK-ASPEN model is selected for the physical properties of the Rectisol wash process. The absorber is split into four columns (Sun and Smith, 2013), RT1, RT2, RT3 and RT4 in the model for more convenience of the simulation convergence. The module Radfac is selected as the four columns. The Heater module is chosen as the two side coolers, the outlet temperature of which is set to -36 °C.

The RK-ASPEN model is selected for the physical properties of the liquid-nitrogen washing process. NE1, NE2 and NE3 are multi-flow heat exchangers, so the module MheatX is selected as the three heat exchangers (Amanm et al., 2009). The model Radfrac is selected for the nitrogen washing column, the pressure of which is set to 5.3 MPa. The module Flash2 is selected as the circulating gas flash tank.

4. Results and verification

4.1 Simulation results and verification of the gasification unit

The simulation results are validated by comparison with industrial data, using the oxygen purity of 99.6 % as an example. Because the gasification unit of the process of ammonia production from coal is the same as that of methanol production from coal, the industrial data of Yankuang Shandong 500,000 tons coal to methanol project is used to compare with the simulation results. Due to the different scale of the two process, the emphases of the comparison are the mole fraction of the components. The comparison between simulation results and industrial data is show in Table 1. The differences are mainly due to the selection of the gasifier module. The gasifier module, RGibbs, only considers thermodynamic factors, but ignores kinetic factors. But, the main components, H_2O, CO and H_2, are almost the same as the industrial data. So the simulated result is acceptable.

Table 1: Comparison between simulation results and industrial data of the coal gasification

Mole fractions of components	Simulation results /mol %	Industrial data /mol %
H_2	14.69	13.07
N_2	0.34	2.37
CO	25.06	28.48
CH_4	0	-
CO_2	5.26	2.37
H_2S	0.33	2.37
COS	0.03	-
HCL	0	-
H_2O	54.29	53.45
Total	100	100

4.2 Simulation results and verification of liquid-nitrogen washing process

The syngas generated by the gasification unit contains many impurities, which have toxic effects on the ammonia synthesis catalysts and must be thoroughly removed before entering the ammonia synthesis device. Besides, after the adjustment of the proportion between nitrogen and hydrogen in the liquid-nitrogen washing process, the raw material proportion of ammonia synthesis unit is determined. Therefore, whether the composition of the syngas from the liquid-nitrogen washing process reaches the industrial requirements is an important reference index for the smooth operation of the ammonia production from coal process. From Table 2, it is known that the removal of CO and CH_4 reaches the industrial requirements. In addition, the ratio of H_2 to N_2 has reached 3:1 after nitrogen washing.

Table 2: Comparison between simulation results and industrial requirements of the liquid-nitrogen washing process

Components	CO	CH$_4$	N$_2$	H$_2$
Simulation results (mol)	2PPM	trace	25%	75%
Industrial requirements (mol)	<20PPM	<27PPM	-	-

5. The optimal oxygen purity

In the process to reduce the oxygen purity of air separation, the capital cost of the air separation unit will reduce. Meanwhile, as the amount of gas entering the gasification unit increase, the capital cost of the gasification unit and its subsequent processes will increase. The total result of the two parts is relatively small compared with the operation cost. So the operation cost is the main optimization objective, which is basically proportional to the energy consumption of the process. Therefore, it is reasonable to considerate the process energy consumption as the optimization objective.

The purity of the oxygen product of most current air separation units is 99.6 %, which is relatively too high. If the purity of the oxygen product is reduced, it will reduce the energy consumption of the air separation unit. Besides, nitrogen is the element needed for ammonia synthesis. However, the operation cost of the following processes, including compression and refrigeration processes, will increase due to the excess nitrogen mixed in the oxygen. In this way, there is an optimal oxygen purity that makes the energy consumption of the complete ammonia process minimal.
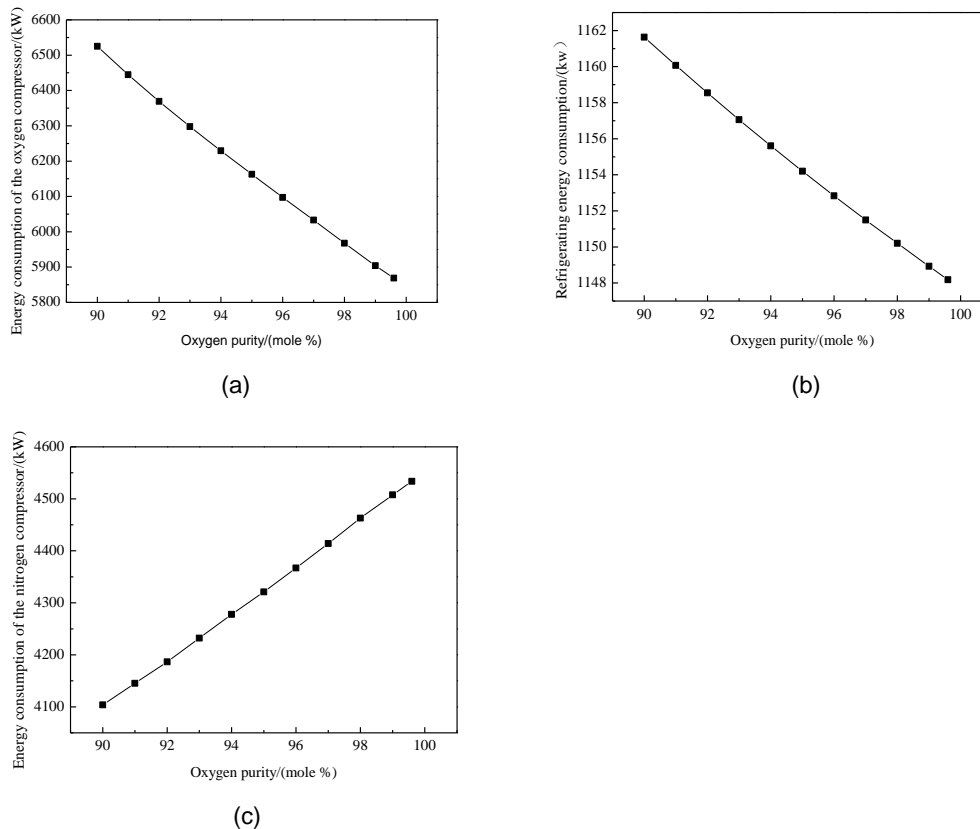
(a)

(b)

(c)

Figure 2: Relations between (a) energy consumption of oxygen compressor and oxygen purity; (b) energy consumption of refrigeration power and oxygen purity; (c) energy consumption of nitrogen compressor and oxygen purity

In order to ensure the effect of coal gasification, the inlet oxygen flow to the gasification unit should be kept unchanged and the flow of nitrogen need to be increased. Then, the process energy consumption under different inlet oxygen purity is obtained. Because the reaction**s** in the process are mainly exothermic reactions, the main process energy consumption is considered as the oxygen compression power consumption, the nitrogen compression power consumption and the refrigeration power consumption. The energy consumption at different

inlet oxygen purity is shown in Table 3. The refrigeration power is based on the refrigeration capacity which is obtained in ASPEN PLUS combined with the refrigerating cycle (Smith, 2005).

The relations of the three kinds of power consumption with the purity of the inlet oxygen are obtained by fitting the data in Table 3. With the decrease of oxygen purity, more and more nitrogen is mixed in the oxygen, which makes the power consumption of the oxygen compressor and the refrigeration increase. Besides, observing from the Figures 2(a) and 2(b), the two kinds of power consumption have a linear relation with oxygen purity. Due to the increase of the nitrogen added in the gasification process, the nitrogen needed in the liquid-nitrogen washing unit can be reduced accordingly, which reduces energy consumption of the nitrogen compressor. Observing from Figure 2(c), the relationship between the energy consumption of the nitrogen compressor and oxygen purity is also linear.

Table 3: Relations between operating power consumption and oxygen purity

Oxygen purity /mol %	Oxygen flow rate /Nm$_3$·h^{-1}	Oxygen compression /kW	Nitrogen compression /kW	Refrigeration capacity/kW	Refrigeration power /kW
99.6	20000	5868.7	4533.8	2873.02	1148.18
99	20121.21	5903.98	4507.66	2874.9	1148.93
98	20326.53	5967.45	4462.91	2878.08	1150.2
97	20536.08	6033.19	4414.08	2881.33	1151.5
96	20750	6097.23	4367.12	2884.67	1152.83
95	20968.42	6162.62	4321.01	2888.1	1154.2
94	21191.49	6229.41	4277.7	2891.62	1155.61
93	21419.35	6297.63	4232.17	2895.24	1157.06
92	21652.17	6369.34	4186.35	2898.95	1158.54
91	21890.11	6444.58	4145.23	2902.77	1160.07
90	22133.33	6525.12	4103.74	2906.7	1161.63

According to the relation between the oxygen purity and the energy consumption provided by the Air Liquide, the relation between the oxygen purity and the consumption coefficient is shown in Table 4. The unit consumption of oxygen is 0.42 kW·h·m^{-3}. Combined with the inlet flow rate of oxygen to the gasification unit, the energy consumption of the air separation unit corresponding to the oxygen flow can be calculated. Then the relation between the energy consumption of air separation and oxygen purity is obtained. Except for the 4 points in Table 4, all the data in the Figure 3(a) are fitted.

Table 4: Relation between energy consumption coefficient and oxygen purity

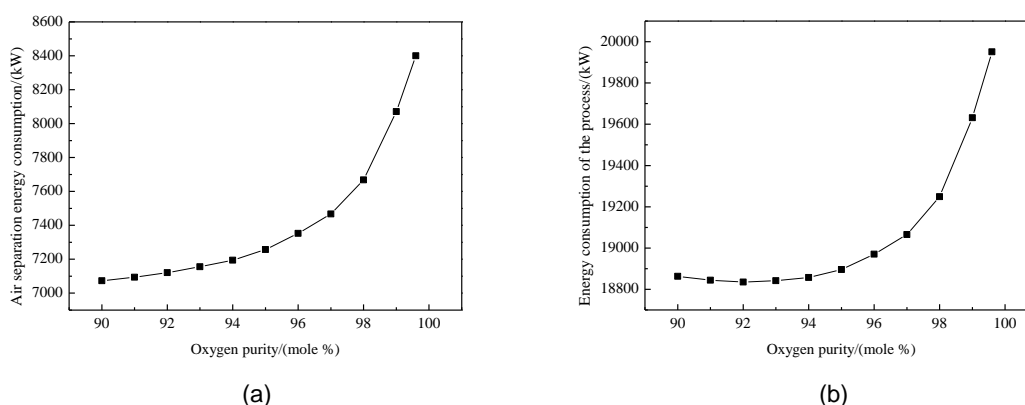| Oxygen purity /mole %	99.6	98	95	90
Energy consumption coefficient	1	0.913	0.864	0.842

(a)　　　　　　　　　　　(b)

Figure 3: Relations between (a) air separation energy consumption and oxygen purity (b) the total energy consumption of the process and oxygen purity

Combined with the three kinds of energy consumption calculated above, the energy consumption of the complete process varied with oxygen purity is obtained, as shown in Figure 3(b). With the reduction of oxygen purity, the total energy consumption of the process decreases first and then increases. When the purity of

oxygen is 92 %, the total energy consumption of the whole process is the lowest. Due to the decrease of the energy consumption of the air separation unit and the nitrogen compressor, the total energy consumption of the complete process decreases in the high purity area. The decreasing speed of the energy consumption of the air separation unit decreases in the low purity area, while the increase of the energy consumption of the oxygen compression and the refrigeration is still linear, which makes the energy consumption of the whole process increase in the low purity area. Compared with the current process using the oxygen purity of 99.6 %, it can save 13.3 % of the energy consumption of the air separation.

6. Conclusion

In this paper, in order to determine the influence of oxygen purity on the energy consumption of the ammonia synthesis process with pure oxygen gasification, the ammonia process is modelled and simulated by ASPEN PLUS. By adjusting the oxygen purity of air separation unit and considering the energy consumption of the oxygen compression, the nitrogen compression and the refrigeration power, the total energy consumption of the process under different operating conditions is obtained by simulation calculation. The optimal oxygen purity minimizes the total energy consumption of the ammonia process is 92 %. Compared with the current process using the oxygen purity of 99.6 %, it can save 13.3 % of the energy consumption of the air separation.

References

Amann J.M., Kanniche M., Bouallou C., 2009, Natural gas combined cycle power plant modified into an O_2/CO_2 cycle for CO_2 capture. Energy Conversion & Management, 50(3), 510-521.

Amran U.I., Ahmad A., Othman M.R., 2017, Kinetic based simulation of methane steam reforming and water gas shift for hydrogen production using aspen plus. Chemical Engineering Transactions, 56, 1681.

Aroua M.K., Haji-Sulaiman M.Z., Ramasamy K., 2002, Modelling of carbon dioxide absorption in aqueous solutions of AMP and MDEA and their blends using Aspenplus. Separation & Purification Technology, 29(2), 153-162.

Bassani A., Frau C., Maggio E., Pettinau A., Cali G., Ranzi E., Manenti F., 2017, Devolatilization of organo-sulfur compounds in coal gasification, Chemical Engineering Transactions, 57, 505-510 DOI: 10.3303/CET1757085

ChandraRatnasamy, Wagner J., 2009, Water gas shift catalysis. Catalysis Reviews, 51 (3), 325-440.

Duan W., Yu Q., Wang K., Qin Q., Hou L., Yao X., Wu T., 2015, Aspen plus simulation of coal integrated gasification combined blast furnace slag waste heat recovery system. Energy Conversion & Management, 100, 30-36.

Field R.P., Brasington R., 2011, Baseline flowsheet model for IGCC with carbon capture. Industrial & Engineering Chemistry Research, 50(19), 11306-11312.

He C., Feng X., Chu K.H., 2013, Process modeling and thermodynamic analysis of Lurgi fixed-bed coal gasifier in an SNG plant. Applied Energy, 111(11), 742-757.

Smart S., Lin C.X.C., Ding L., Thambimuthu K., Costa J.C.D.D., 2010, Ceramic membranes for gas processing in coal gasification. Energy & Environmental Science, 3(3), 268-278.

Smith, R. (Ed), 2005, Chemical process design and integration, McGraw Hill, Manchester, UK

Sun L., Smith R., 2013, Rectisol wash process simulation and analysis. Journal of Cleaner Production, 39(1), 321-328.

Wang F., Zhou Z., Dai Z., Gong X., Yu G., Liu H., Wang Y., Yu Z., 2007, Development and demonstration plant operation of an opposed multi-burner coal-water slurry gasification technology. Frontiers of Energy & Power Engineering in China, 1(3), 251-258.

Zheng L., Furinsky E., 2005, Comparison of shell, Texaco, BGL and KRW gasifiers as part of IGCC plant computer simulations. Energy Conversion & Management, 46, 1767-1779.