

REVIEW ARTICLE

PRODUCTION OF AMMONIA AT RELATIVELY LOW P,T: ASPEN PROCESS ECONOMIC ANALYSIS

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ARTICLE DETAILS

ABSTRACT

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The process of ammonia production from N₂ and H₂ with recycling of unreacted materials is investigated. The process is examined at relatively low pressure (48 bar) and temperature (190°C). CSTR isothermally runs under equilibrium condition. With recycling, it was found that a liquid product of NH₃ with a purity of 99.3 wt. % was achieved. The waste is minimized with potential use as a fuel. Aspen process economic analysis was also carried out. It was found that such an investment project is profitable with a payout (payback) period of 4.2 years and modified internal rate of return (MIRR) of 21.5 %. The total capital cost was found to be \$ 10,300,600 and the total operating cost to be \$ 15,439,500/year for an annual production of ammonia of 30,046 tonne/year.

KEYWORDS

Ammonia Production, Aspen Plus, Economic Analysis, Investment, Modified Internal Rate of Return, MIRR, Payout Period, Hydrogen, Nitrogen

1. INTRODUCTION

Ammonia is synthesized from hydrogen (originally from natural gas) and nitrogen (originally from air). Ammonia is a colorless gas, lighter than air, easily liquefied at room temperature by applying a pressure of about 10 atm. and it has a pungent odor with an alkaline or soapy taste. When suddenly inhaled, it brings tears into the eyes and causes irritation in the upper respiratory tract. Ammonia can be used in numerous applications, like fertilizers (an essential element for growth), nitric acid, industrial refrigeration, rubber and leather (stabilizing factor for latex), metal-treating (nitriding and carbo-nitriding) operations, water boiling (O₂ scavenger), and wastewater (pH control). The first commercial plant with a capacity of 30 tons/day was set up by the German chemical giant BASF in Germany.

In UAE, the natural gas comes from oil fields at Buhasa, Bab, and Habshan to ammonia plants. The ADNOC- and TOTAL-owned Ruwais Fertilizer Industries (FERTIL) achieved a record production of ammonia and urea in 2003, resulting in higher exports, especially to Asian markets. In terms of production, new records were achieved with an annual production of ammonia and urea of 473,987 and 653,943 metric tons, respectively [1]. FERTIL's production, at Ruwais complex, comprises of ammonia with 3,310 metric tons per day (MTPD) and granulated urea with 5,800 MTPD [2].

The researchers carried out simulation for chemical reaction equilibrium of ammonia synthesis in MCM-41 pores and pillared clays, based on reactive canonical Monte Carlo (RCMC) method [3]. They found that the yield of ammonia increased with pressure and the maximum ammonia mole fraction was attained at 100 bar and 573 K in both MCM-41 pores

and pillared clays. When the feed mole ratio of N:H of the bulk phase declined from 4:13 to 4:15, the yield of ammonia in the pore phase also decreased.

The researchers examined ruthenium (Ru) catalysts for ammonia synthesis at high pressures. The strong inhibition by H₂ was found to require a lower molar H₂:N₂ ratio in the feed gas than 3:1 in order to achieve a high effluent NH₃ mole fraction [4]. They also recommended alkali-promoted Ru catalysts as candidates to substitute the conventionally used Fe catalysts for NH₃ synthesis, carried out at high pressure.

The researchers presented an application of the developed Monte Carlo method for simulations at fixed total enthalpy, combined with the reaction ensemble Monte Carlo method, for the direct prediction of equilibrium ammonia synthesis in an adiabatic plug-flow reactor [5]. They performed direct simulations of the equilibrium reaction temperature and the composition of the exit stream as a function of the temperature and pressure of the inlet stream. The chemical species of the system were represented by all-atom potentials with interaction parameters taken from the literature. The accuracy of the molecular model was validated by comparing simulation results with experimental data. They also compared the simulation results with a macroscopic thermodynamic model based on the Soave-Redlich-Kwong equation of state.

The researchers examined ammonia production in N₂/H₂ direct current glow discharge plasmas, with nitrogen concentrations varying from 1.5% to 33%, using different wall materials (tungsten, stainless steel and aluminum as a proxy for beryllium) and varying surface temperatures up

to 350°C [6]. The results indicated weak wall temperature dependence in tungsten and stainless steel. However, wall temperatures above 300°C had a very clear influence on aluminum walls, as almost all the molecular N₂ depleted from the gas phase was converted into ammonia. The amount of implanted N seemed to have a direct impact on the ammonia formation yield, pointing to the competition between N implantation and N/H-N/N recombination on the walls as the key mechanism of the ammonia formation.

The researcher reported that the typical conversion, for a high-pressure ammonia production process, falls in the range of 8–15%, depending on the used catalyst [7]. The ammonia production process utilizes iron-based catalyst operates at temperatures between 400–700°C and pressures over 300 atm. Moreover, he indicated that there has been a decrease in the operating pressure from about 300 down to 80 atm, attributed to engineering improvement in the construction of the plant. He further pointed out that the replacement of iron-based catalyst by ruthenium catalyst, deposited on active graphite, showed a significant improvement in activity, which enabled further reduction in both operating temperature and pressure down to 40 atm.

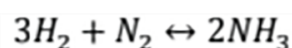
In this work, a process flowsheet for ammonia production based on equilibrium conditions is proposed. It is mainly made of a pre-compressor, CSTR, flash drum, post-compressor, and purge tank. In addition, recycle of un-reacted materials to the inlet of the reactor is also maintained. Aspen Plus process economic analysis is also carried out.

2. METHODOLOGY

The following paragraph, quoted from the researcher, describes what Aspen Plus is all about: “Aspen Plus, a flowsheet simulation, is a computer software that is used to quantitatively model a chemical processing plant, which in addition to the core reactor unit, it also includes pre-treatment and post-treatment steps, as well [8]. Thus, simulation of an entire chemical process, starting from the raw material side down all the way to the final, finished product side, is symbolically represented by different icons where each icon stands for a unit operation, chemical process, input/output material stream, input/output energy stream, or

input/output electric/pneumatic signal”. Given reliable thermodynamic data, sensible operating conditions, and rigorous equipment models, Aspen Plus enables us to run many tasks, like carrying out optimization case studies.

Figure 1 shows the process flowsheet for ammonia production. The feed stream entering at room temperature and 20 atm with a total flow rate of 400.5 kmol/hr (30,051 tonne/year) with 300, 100, and 0.5 kmol/hr for H₂, N₂, and CO₂, respectively. The presence of CO₂ is a demonstration for impurities originally present in H₂ stream. The feed pressure is elevated to a pressure of 48.5 bar where it is mixed with the recycled stream, mainly H₂ and N₂, at the same pressure. The compressor is driven by an electric motor. In the first heat exchanger, the combined feed is heated up to the reaction temperature 190°C, using high-pressure steam (phase change at 250°C). The CSTR is isothermally run at 190°C under equilibrium conditions with a pressure of 48 bar. The reactor volume is set to 12 m³. The following equilibrium gas-phase reaction is assumed to take place in CSTR:



The catalyst is assumed to be present inside CSTR with an amount of 1 tonne (metric ton) and bed voidage of 0.5. The exothermic heat of reaction is utilized to generate medium-pressure steam (phase change at 175°C).

In the second heat exchanger, the reaction products are cooled down to 135°C to allow generation of low-pressure steam (phase change at 125°C) before being sent to the flash drum. Flashing process is carried out in the flash drum at -35°C and 40 atm. The cooling takes place utilizing type 2 refrigeration (i.e., a phase change temperature of -40°C). The liquid main product is almost pure ammonia with a mass fraction of 0.993 and 0.006 CO₂. A tiny amount of the flash drum off vapor is purged with a split fraction of 0.0015 and the 0.9985 remaining fraction is sent to the inlet of the post compressor where its pressure is elevated to 48.5 bar reactor. The compressed recycled stream is finally mixed with the compressed fresh feed prior to introduction to the reactor.

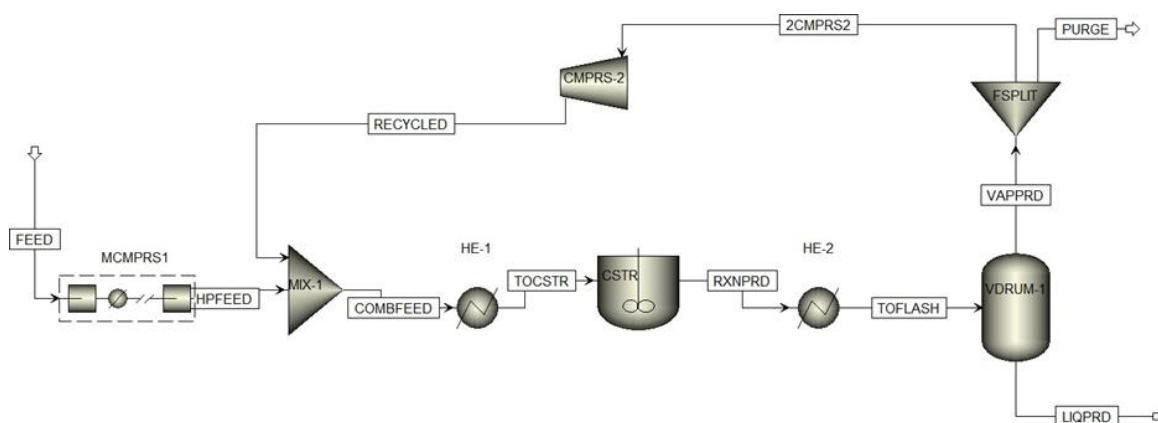


Figure 1: The process flowsheet for gas-phase ammonia production with recycling of unreacted H₂ and N₂.

The following bulk rate unit prices are used for both feed and product streams as shown in **Figure 2**. It is worth-mentioning here that the price for ammonia is calculated, based on a report prepared by the researchers [9]. On the other hand, the unit price of liquid nitrogen adjusted to 2018, is \$ 0.187/L, (density of liquid nitrogen is 0.807 kg/L; hence, \$ 0.232/kg)

$$x_{H_2} \times H_2 \text{ Unit Price} + x_{N_2} \times N_2 \text{ Unit Price} = 0.1775 \times 1.123 + 0.8225 \times 0.232 = \frac{\$ 0.390}{\text{kg}} \cong \frac{\$ 400}{\text{tonne of feed}}$$

For the purge stream, one can roughly say that it can be sold/utilized as a source of fuel with a price equivalent to that of LNG or LPG, while taking into account the BTU value of each fuel. Currently as of 2108, LNG prices vary as low as \$ 2.75 /MMBtu and as high as \$ 8.7/MMBtu[12]. Notice that

[10]. As of 2002, most hydrogen is produced on site and the cost is approximately \$0.70/kg [11]. This being the case, the unit price will be adjusted to 2018 and with an annual inflation rate of 3%, the new price will be \$ 1.123/kg. Consequently, the mass fraction-weighted unit price of the feed stream will be:

MBTU stands for one million BTUs, which can also be expressed as one dekatherm (10 therms). For a more conservative approach, the lowest value will be taken as the unit price for the given fuel.

For H₂ [13]: 1 pound of hydrogen = 51,892 BTU

$$\frac{51,892 \text{ BTU}}{1 \text{ lb H}_2} \times \frac{1 \text{ lb H}_2}{0.45359 \text{ kg H}_2} = \frac{114,403 \text{ BTU}}{\text{kg H}_2} \times \frac{\$2.75}{1 \times 10^6 \text{ BTU}} = \frac{\$0.3146}{\text{kg H}_2}$$

For NH₃ [14]: 1 pound of NH₃ = 41,700 BTU

$$\frac{41,700 \text{ BTU}}{1 \text{ lb NH}_3} \times \frac{1 \text{ lb NH}_3}{0.45359 \text{ kg NH}_3} = \frac{91,933 \text{ BTU}}{\text{kg NH}_3} \times \frac{\$2.75}{1 \times 10^6 \text{ BTU}} = \frac{\$0.2528}{\text{kg NH}_3}$$

The purge stream has 42.49 weight percent of a combined H₂ (33.73 wt. %) and NH₃ (8.76 wt. %), which can be used as a fuel with mass fraction-

weighted bulk rate value of 145 \$125/tonne, as shown in the following equation

$$x_{\text{H}_2} \times \text{H}_2 \text{ Unit Price} + x_{\text{N}_2} \times \text{N}_2 \text{ Unit Price} = 0.1775 \times 1.123 + 0.8225 \times 0.232 = \frac{\$0.390}{\text{kg}} \cong \frac{\$400}{\text{tonne of feed}}$$

$$x_{\text{H}_2} \times \text{H}_2 \text{ Unit Price} + x_{\text{NH}_3} \times \text{NH}_3 \text{ Unit Price} = 0.3373 \times 0.3146 + 0.0876 \times 0.2528 = \frac{\$0.128}{\text{kg}} \cong \frac{\$125}{\text{tonne of purge}}$$

Stream ID	Source	Destination	Basis	Price	Unit
FEED		CMPRS1	Mass	400	\$/tonne
LIQPRD	VDRUM-1		Mass	750	\$/tonne
PURGE	FSPLIT		Mass	125	\$/tonne

Figure 2: Bulk rate unit prices for feed and product streams.

3. RESULTS AND DISCUSSION

Figure 3 shows the executive summary of Aspen Process Economic Analyzer (APEA) for the investment project of ammonia production. As can be seen, the payout (or, payback) period is about 4.17 years, which means the number of accounting periods needed to repay the 1 company's initial investment.

Enabled by Aspen Process Economic Analyzer (APEA)	
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Summary	Utilities Unit operation Equipment Cer
Total Capital Cost [USD]	10,300,600
Total Operating Cost [USD/Year]	15,439,500
Total Raw Materials Cost [USD/Year]	12,018,100
Total Product Sales [USD/Year]	22,531,300
Total Utilities Cost [USD/Year]	350,814
Desired Rate of Return [Percent/Year]	20
P.O. Period [Year]	4.17297
Equipment Cost [USD]	2,523,600
Total Installed Cost [USD]	3,407,100

Figure 3: The executive summary of APEA being applied to ammonia production investment project.

Table 1 shows numerous profitability indices for such an investment project. For further information about such profitability indices, please, refer to CHAPTER SEVENTEEN: Aspen Process Economic Analyzer (APEA) [8].

Table 1: Profitability indices for ammonia production investment project.

IRR (Internal Rate of Return)	47.7883 %
MIRR (Modified Internal Rate of Return)	21.4617 %
NRR (Net Return Rate)	13.3235 %
PO (Payout Period)	4.17297 Year
ARR (Accounting Rate of Return)	71.3984 %
PI (Profitability Index)	1.12871

Figure 4 shows the purchased cost (\$), the installed cost (\$), the bare equipment weight (lbs), the installed weight (lbs) and the utility rate (\$/HR) associated with each unit operation.

Notice that the negative sign for utility tailored to HE-2 is due to generation of the low-pressure steam.

Summary	Utilities	Unit operation	Equipment	Centrif gas compr	Agitated reactor	TEMA HEX	Cryogenic tank	Vertical vessel	Jac
Name	Equipment Cost [USD]	Installed Cost [USD]	Equipment Weight [LBS]	Installed Weight [LBS]	Utility Cost [USD/HR]				
CMPRS-2	805,100	913,900	9700	18809	0.867225				
FSPLIT	41,600	164,800	7800	19218	0				
CSTR	256,100	432,700	57300	81841	0				
MIX-1	23,400	102,400	6900	14907	0				
HE-2	26,000	108,200	6900	25386	-1.1397				
HE-1	8,800	68,300	2970	13519	2.37724				
MCMPRS1	1,305,200	1,429,100	19500	30347	28.9075				
VDRUM-1	57,400	187,700	13400	26505	0				

Figure 4: The purchased cost (\$), the installed cost (\$), the bare equipment weight (lbs), the installed weight (lbs) and the utility rate (\$/HR) associated with each unit operation.

If the purge stream is incinerated prior to being dumped it into the atmosphere, then the 1annual loss will be:

$$\frac{\$0.061638}{\text{hr}} \times \frac{8,000 \text{ hr}}{\text{year}} \cong \frac{\$500}{\text{year}}$$

4. CONCLUSIONS

Ammonia production with a high degree of purity can be achieved at relatively low pressure (48 bar) and temperature (190°C) with recycling of unreacted materials. A liquid product of NH₃ with a mass purity 99.3 % was achieved. The waste is also minimized with a potential use as a fuel. With the aid of Aspen process economic analysis, it was found that such an investment project is profitable with a payout (payback) period of 4.2 years and a modified internal rate of return (MIRR) of 21.5 %. The total capital cost was found to be \$ 10,300,600 and the total operating cost to be \$15,439,500/year for an annual production of ammonia of 30,046 tonne/year.

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