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Computer Modeling To Improve The Process of Manufacturing Ammonia From Natural Gas

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Keywords:
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Simulation
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ABSTRACT

One of the most basic aspects of ammonia production is the optimal direction for manufacturing a final product called urea, which is a very important fertilizer that contains a high percentage of nitrogen, which in turn works to improve agricultural soil fertility. Many processes have been invented to achieve optimal ammonia production. Currently, ammonia is produced primarily through the Haber-Bosch process in which nitrogen and hydrogen react in the presence of an iron catalyst to form ammonia. Hydrogen is formed from natural gas and steam reaction at high temperatures and nitrogen is supplied from the air. Other gases (such as water vapour and carbon dioxide) are removed from the reactor inlet gas stream and nitrogen and hydrogen are passed over the iron catalyst at high temperature and pressure to form ammonia. In this work, a simulation of the ammonia manufacturing process was performed on Aspen Hysys 3.1 software. Using (294) kg mol/h for methane flow, (10253) kg mol/h for hydrogen gas, and (3418) kg mol/h for nitrogen gas, about (3663) kg mol/h of ammonia was produced, which is equivalent to (67248) kilogram/h at a concentration of (0.9883). It was also found that ammonia production increases with higher flow pressure in the feed line of the industrial unit. I also use the Peng-Robinson model to better adjust the thermodynamic equilibrium process.

النمذجة الحاسوبية لتحسين عملية تصنيع الأمونيا من الغازالطبيعى

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الكلمات المفتاحية:
الأمونيا
أسبن هيسيس
الأسمدة
المحاكاة
هابر بوش

الملخص

من أهم الجوانب الأساسية لإنتاج الأمونيا هو الاتجاه الأمثل لتصنيع منتج نهائي يسمى اليوريا، وهو سماد مهم جداً يحتوي على نسبة عالية من النيتروجين، والذي بدوره يعمل على تحسين خصوبة التربة الزراعية. تم اختراع العديد من العمليات لتحقيق الإنتاج الأمثل للأمونيا. حاليًا، يتم إنتاج الأمونيا بشكل أساسي من خلال عملية هابر بوش التي يتفاعل فيها النيتروجين والهيدروجين في وجود محفز حديدي لتكوين الأمونيا. يتكون الهيدروجين من تفاعل الغاز الطبيعي والبخار عند درجات حرارة عالية ويتم توفير النيتروجين من الهواء. وتزال الغازات الأخرى (مثل بخار الماء وثاني أكسيد الكربون) من تيار الغاز الداخل للمفاعل ويمرر النيتروجين والهيدروجين فوق المحفز الحديدي عند درجة حرارة وضغط مرتفعين لتكوين الأمونيا. في هذا العمل، تم إجراء محاكاة لعملية تصنيع الأمونيا على برنامج Aspen Hysys 3.1. بإستخدام (294) كجم مول/ساعة لتدفق غاز الميثان، (10253) كجم مول/ساعة لغاز الهيدروجين، و(3418) كجم مول/ساعة لغاز النيتروجين، تم إنتاج حوالى (3663) كجم مول/ساعة أمونيا أى ما يعادل (67248) كيلو جرام/ ساعة وبتركيز (0.9883). كما وجد أن إنتاج الأمونيا يزداد مع ارتفاع ضغط تدفق خط التغذية للوحدة الصناعية. وأستخدم كذلك نموذج Peng-Robinson لضبط عملية التوازن الثيرمو ديناميكى بشكل أفضل.

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1. Introduction

Ammonia has had a studied global impact since its hydrogen-nitrogen mixture was discovered by Haber and Bosch in Germany before the 20th century. Ammonia's primary role today is its use as an essential raw material for inorganic fertilizers, which currently support food production for approximately half of the world's population [1]. Ammonia is synthesized from hydrogen (at first from natural gas) and nitrogen (at first from air). Ammonia is a colour less gas, lighter than air, which liquefies easily at room temperature under a pressure of about 10 atm. It has a strong odor with an alkaline or foamy taste. If suddenly inhaled it causes watering of the eyes and irritation of the upper respiratory tract. Ammonia can be used in numerous applications such as fertilizers (an essential element for growth), nitric acid, industrial refrigeration, rubber and leather (latex stabilizing factor), metal processing operations (nitrating and carbonitriding), water boiling (O_2 scavenger) and wastewater (pH control). The first commercial plant with a capacity of 30 tons per day was built by the German chemical giant BASF in Germany [2]. Ammonia is a base component, both straight and indirectly, for synthesizing many pharmaceutical products and is used in a lot of commercial clean-up products. Although ammonia is widely used, it is corrosive and dangerous. Global ammonia production is expected to be 198 million tons in 2012, up 35% from the estimated global production of 146.5 million tons in 2006. Commercially used ammonia is often referred to as anhydrous ammonia [3]. This period emphasizes the absence of water in the matter. Since NH_3 boils at (-33.34 °C) and a pressure of 1.0 atmosphere, the liquid must be stored at high pressure [4] or low temperature.“Ammonium hydroxide” or “household ammonia” is a solution of NH_3 in water. The concentration of such solutions is measured in units of the Baumé scale (density), with 26 degrees Baumé (about 30% by weight ammonia at 15.5°C) being the typical highly concentrated commercial product. The concentration of ammonia in your home varies from 5 to 10% ammonia by weight. In this research, a detailed study of the process is carried out via simulation in Aspen Hysys V3.1[5]. The Hysys properties package can display accurate forecasts of physical and thermodynamic properties for hydrocarbons, non-hydrocarbons, chemical liquids, and petrochemicals. Hysys database contains many components, exactly more than 1500 components and more than 16000 embedded binary coefficients, and the creation of hypothetical components is done when the database does not contain any components [6]. Since the Haber process is often used for maximum ammonia production, we simulated the process based on the Haber process [7]. While simulation does not provide real performance or a real manufacturing environment when the underlying process is known and associated data is available, it is certainly the best way to gain insights into an industrial process without having to experiment. The Haber-Bosch process produces 150 million tons of ammonia per year, about five times that higher than before the Haber-Bosch process. Ammonia synthesis involves the production of hydrogen from natural sources. Nitrogen gas and production are produced from atmospheric air [8].

Simulation is used to simulate operations in both a steady state (time is ignored) and a dynamic state. (Time is not ignored). The simulation also serves to illustrate the processes and effects of other diseases.

2. Methodology

The ammonia production process was simulated using Aspen Hysys V 3.1 simulation software. The Aspen Hysys process simulator is a key component of Aspen Tech engineering applications. It provides fairly accurate results, making it an effective simulator. It provides a comprehensive thermodynamic framework for the precise determination of physical properties, transport properties, and phase behaviour. Aspen Hysys can be used to determine the output conditions of a process if input conditions such as temperature, pressure, and composition are specified. In this simulation, we use the Peng-Robinson model to better tune the equilibrium process.

3. Process Description

The simplified process flow diagram of ammonia synthesis in Figure 1 is given below.

After completing the basic stages of hydrogen production, nitrogen addition, water removal, and carbon oxide gases, as shown by the chemical reactions shown in the following equations:

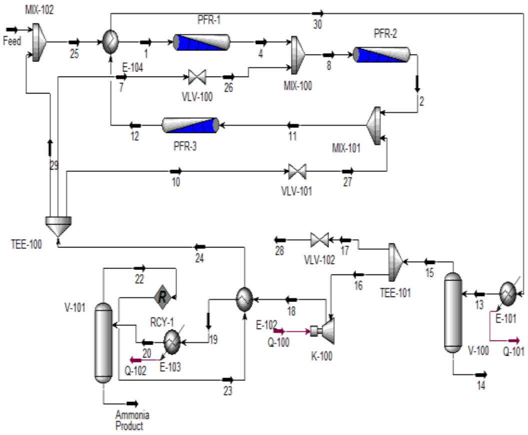

Fig. 1: Hysys Process Flow diagram of ammonia synthesis [9]

1) Hydrogen production step,

$$ZnO + H_2S = ZnS + H_2O$$
$$O_2 + 2CH_4 = 2CO + 4H_2$$
$$O_2 + CH_4 = CO_2 + 2H_2$$
$$2O_2 + CH_4 = 2H_2O + CO_2$$

2) Carbon monoxide removal step,

$$CO + H_2O = CO_2 + H_2$$
$$CO + 3H_2 = CH_4 + H_2O$$
$$CO_2 + 4H_2 = CH_4 + 2H_2O$$

3) Ammonia synthesis step,

$$N_2 + 3H_2 = 2NH_3$$

The gas mixture is now cooled, compressed, and introduced into the ammonia manufacturing cycle. A mixture of ammonia and unreacted gases around the annulus is mixed with the incoming gas stream and cooled to a temperature of 50°C. The ammonia present is removed and the unreacted gases are heated to 400°C at a pressure of 330 bar and passed over an iron catalyst. Under these conditions, 26% of the hydrogen and nitrogen are converted to ammonia. The outlet gas is cooled from the ammonia converter from 220°C to 300°C.

This cooling process condenses half of the ammonia, which is then separated. The remaining gas is mixed with more cooled and compressed incoming gas. The reaction takes place in an ammonia converter. The ammonia is quickly decompressed to 24 barg. At this pressure, impurities such as methane and hydrogen turn into gases. The gas mixture above the liquid ammonia (which also contains significant ammonia) is removed and sent to an ammonia recovery unit. This is an absorption and stripping system that uses water as the solvent. The remaining gas (purge gas) is used to heat the primary repair device. The remaining pure ammonia is mixed with pure ammonia from the above primary condensation and is ready to be used in urea production, stored, or sold directly [9].

4. Results and Discussions

After simulation, the influence of various process parameters such as (temperature and pressure of steam, temperature and pressure of natural gas, etc.) on the production speed of the process is observed, and optimal ammonia production can be achieved by controlling these parameters. Based on the simulation results, these effects are described below.

Figure 2 shows the change in the concentration of the reactants hydrogen and nitrogen in reactor PFR-1 as showing in figure 1, and the final product ammonia with the length of the reactor. Therefore, the length of the reactor has little effect on the concentration of these materials in this case. This is due to the increased speed of the reactant flow. This type of reaction is also considered fast and does not allow the reactor length to affect the concentration of the materials significantly in this case, in addition to the short retention time of the reactants inside the reactor.

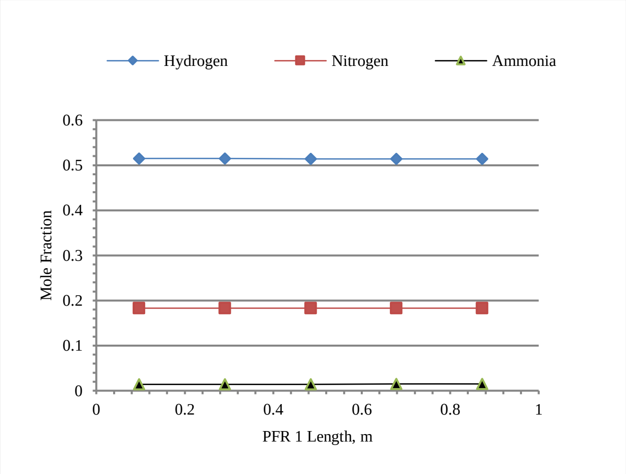

Fig. 2: Mole Fraction vs PER-1 Length

Both Figure 3 and 4 shows the change in the rate of conversion to ammonia in the reactor PFR-1 and the molar flow rate of ammonia, respectively, with the length of the reactor. We notice from the two figures that the mentioned variables have the same change behaviour, that is, they rise to half the length of the reactor and after that they stabilize and remain constant along the length of Reactor. To increase the product concentration of ammonia, the industrial unit is equipped with two reactors for this purpose. Increasing the length of the reactor as the size of the reactor increases, the time the reactants remain in the reactor increases, leading to a rise in the conversion rate. In a tubular flow reactor, the reactants move gradually through the reactor, and the longer the path, the more time the reaction has to reach equilibrium, leading to an increase in the conversion rate [9].

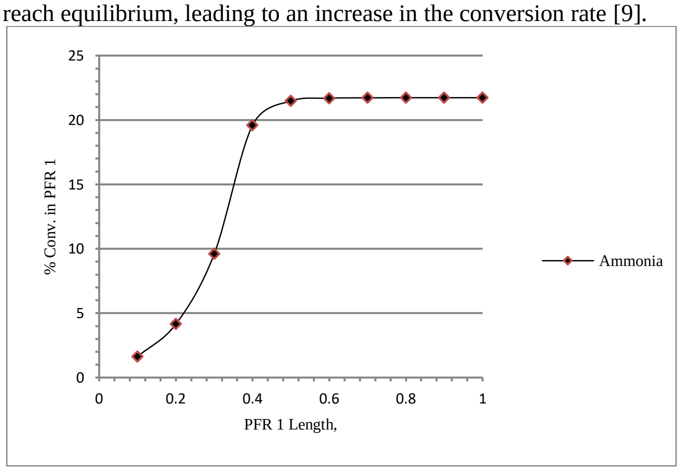

Fig. 3: % Conversion of ammonia vs PER-1 Length

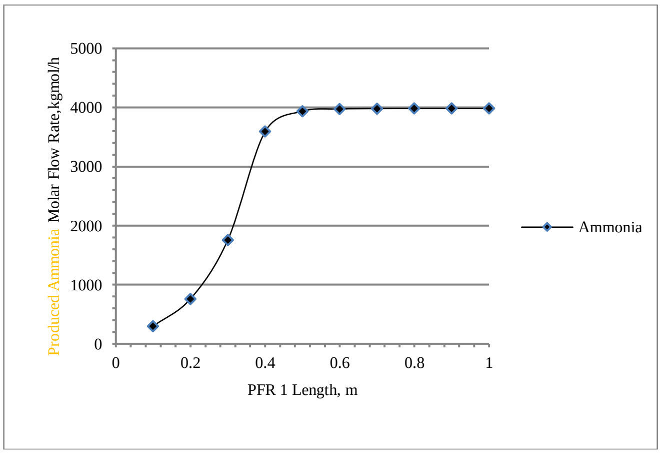

Fig. 4: Molar Flow Rate of ammonia vs PER-1 Length

From Figure 5 we note that the effect of the natural gas pressure in the feed stream. That is, by increasing the pressure, the rate of ammonia production increases in this case. Pressure has a significant effect on the rate of ammonia production, as the reaction depends on the ideal conditions to obtain the highest conversion rate and production efficiency. The higher the pressure, the more collisions between nitrogen and hydrogen molecules occur, which increases the chances of the reaction occurring. This leads to an increase in the rate of ammonia production [6].

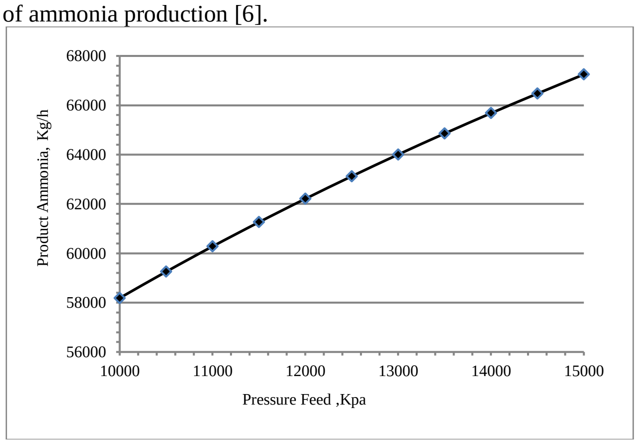

Fig. 5: Product of ammonia vs Feed Pressure

Figure 6 shows the ammonia productivity rate versus the temperature of the nutrients. We noticed that productivity increases up to the optimum temperature for ammonia production, after which the production process begins to decrease. This is due to the geometry and dimensions of the reactor, and the temperature gradient for ammonia production is an exothermic reaction, so as the reaction proceeds, heat build up may slow the reaction. Longer systems may require axial cooling to avoid a decrease in reaction efficiency due to higher temperatures [6].

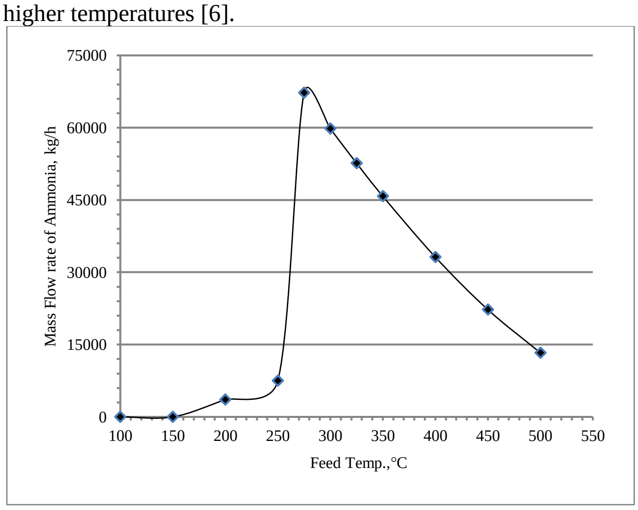

Fig. 6: Product of ammonia vs Feed Temperature

Table 1 describes the initial condition of the natural gas inlet line, including pressure, temperature, and flow rates.

Table 1: Title of the table.

Vapor / Phase Fraction	1
Temperature [°C]	400
Pressure [kPa]	15000
Molar Flow [kg mole/h]	14098.60
Mass Flow [kg/h]	126481.7
Std Ideal Liq. Vol. Flow [m^3/h]	434.28
Molar Enthalpy [kJ/kg mole]	9673.64
Heat Flow [kJ/h]	1.36E+08

Table 2 also shows the change in ammonia concentration at the inlet line and the product line. The results showed an increase in the purity of the ammonia product to about 0.9883 as a result of choosing the optimal conditions for the operating process and developing some lines using the recycling technology shown in the process flow diagram in Figure 1 to increase the ammonia concentration in this simulation.

Table 2: Title of the table.

Component	Feed Stream	Product Stream
Methane	0.0209	0.0038
H_2O	0.0000	0.0000
CO	0.0000	0.0000
CO_2	0.0000	0.0000
Hydrogen	0.7272	0.0043
Nitrogen	0.2424	0.0008
Oxygen	0.0000	0.0000
Ammonia	0.0000	0.9883
Argon	0.0095	0.0028

Appendix A also shows the numerical values related to the operating conditions of pressures, temperatures, flow rates and molar concentrations for all lines and the design process paths for ammonia production shown in Figure 1.

5. Conclusion

The Ammonia Manufacturing Simulation Model provides a practical description of how ammonia is manufactured and produced. The simulation is developed using several Aspen Hysys capabilities, including standard operating models, and engineering data related to pressures and temperatures. The model provides accurate information about the mass and energy balance of ammonia production and can be used to support conceptual process design. An important feature of this software is the ability to impose and operate the parameters necessary to achieve the optimal operating conditions for the production process. The model can also be used to develop reaction simulations using a modified plug flow reactor. This model is intended to serve as a guide for modelling ammonia production. It can also be used as a starting point for more advanced models. It is considered an initial starting point for developing cost and design feasibility for such production units. Ammonia production is a vital process that affects many sectors, and by implementing the above recommendations, more efficient and sustainable production can be achieved while reducing environmental and economic impacts.

6. Recommendations

Ammonia production is a complex and necessary process, requiring the implementation of technical, economic, and environmental recommendations to ensure its sustainability and efficiency. Here are some key recommendations related to ammonia production:

6.1 Improving the efficiency of technological processes:

Using modern technologies: Relying on new technologies such as advanced catalysts to accelerate the reaction and reduce energy consumption in the Haber-Bosch process, which is the most widely used process for ammonia production. Improving efficiency reduces production costs and fuel consumption.

Control of operating conditions: Improving control of temperatures and pressures inside the reactor to ensure the best conversion ratio of hydrogen and nitrogen to ammonia, which reduces the loss of unconverted reactants.

6.2. Reducing energy consumption:

Using renewable energy sources: Since ammonia production requires large amounts of energy, using clean energy sources such as solar or wind energy can reduce the carbon footprint of the process.

Improving the efficiency of fossil fuel consumption: If natural gas is used as a source of hydrogen, the efficiency of natural gas consumption should be improved and heat recovery processes should be applied to reduce energy consumption.

6.3. Reducing carbon emissions:

Transition to green hydrogen: Replacing hydrogen extracted from fossil fuels with green hydrogen produced from the electrolysis of water using renewable energy. This will help reduce CO_2 emissions associated with production.

Carbon capture and storage (CCS): Carbon capture and storage technology can reduce CO_2 emissions from the use of natural gas in hydrogen production. This will help reduce the climate change impacts associated with traditional ammonia production.

6.4. Improving catalyst efficiency:

Research and development in catalysts: It is recommended to continue research into more efficient catalysts for the reaction between nitrogen and hydrogen. New catalysts can enable the reaction to occur at lower temperatures and pressures, reducing energy consumption.

Use of nanocatalysts: Nanocatalysts may be more effective in accelerating the reaction and reducing energy and material consumption.

6.5. Water resource management:

Reducing water consumption: Since ammonia production requires large amounts of water to extract hydrogen, technologies that reduce water consumption or rely on recycling the water used in the process should be developed.

Water Reuse: Treating and reusing wastewater in industrial processes to reduce waste and achieve greater sustainability in the use of water resources.

6.6. Increasing safety in production:

Improving safety protocols: Ammonia production is associated with the risk of using highly reactive materials such as hydrogen. It is necessary to apply strict safety standards and conduct periodic training for workers to deal with any emergency.

Corrosion control: Since some stages in production require handling high-pressure gases and high temperatures, anti-corrosion materials must be used to ensure the longevity and safety of equipment.

6.7. Expanding the use of ammonia as a clean fuel:

Using ammonia as an alternative fuel: It is recommended to invest in technologies for using ammonia as a clean fuel, whether in fuel cells or in internal combustion engines, which reduces dependence on fossil fuels and contributes to reducing carbon emissions.

6.8. Enhancing cooperation between industries and governments:

Environmental legislation: Governments and industries must work together to develop strict legislation that limits polluting emissions and encourages the use of environmentally friendly ammonia production technologies.

Supporting research and development: Encouraging public-private sector collaboration to support research focused on developing more efficient and environmentally friendly production technologies.

6.9. Recycling reactants:

Recycling hydrogen and nitrogen: In production units, it is recommended to recycle unconverted hydrogen and nitrogen in the cycle to reduce waste and increase reaction efficiency.

6.10. Investing in education and training:

Training human resources: Providing specialized training programs for industry workers to ensure adherence to best practices in operation, safety, and equipment maintenance.

Supporting innovation: Investing in educational programs that support innovation in ammonia production technologies and improve process efficiency.

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Appendix A

A. Conditions and Results of all Material Streams of the Simulation Program as shown in the Figure 1

Name of Stream →	**Feed**	**1**	**4**	**7**	**8**	**10**	**11**	**12**	**13**	**14**	**15**	**17**
Vapour Fraction	1.00	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	0.0	1.0	1.0
Temperature [°C]	400.00	250.00	252.73	25.00	252.73	25.00	255.10	255.35	34.98	34.98	34.98	34.98
Pressure [kPa]	15000	15000	14985	15000	14985	15000	14970	14955	14940	14940	14940	14940
Molar Flow [kgmole/h]	14099	1149526	1147639	19	1147658	27	1146041	1145874	1145874	0	1145874	360
Mass Flow [kg/h]	1.26E+05	1.07E+07	1.07E+07	1.75E+02	1.07E+07	2.51E+02	1.1E+07	1.07E+07	1.07E+07	0.00E+00	1.07E+07	3364.84
Liquid Volume Flow [m^3/h]	4.34E+02	3.58E+04	3.57E+04	5.86E-01	3.57E+04	8.38E-01	3.6E+04	3.57E+04	3.57E+04	0.00E+00	3.57E+04	11.20
Heat Flow [kJ/h]	1.36E+08	3.97E+09	3.97E+09	-6.54E+04	3.97E+09	-9.35E+04	4.0E+09	3.97E+09	-3.79E+09	0.00E+00	-3.79E+09	-1191330.07
Comp Mole Frac (CH_3)	0.02	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04
Comp Mole Frac (H_2O)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Comp Mole Frac (CO)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Comp Mole Frac (CO_2)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Comp Mole Frac (H_2)	0.73	0.70	0.70	0.70	0.70	0.70	0.70	0.70	0.70	0.70	0.70	0.70
Comp Mole Frac (N_2)	0.24	0.24	0.23	0.24	0.23	0.24	0.23	0.23	0.23	0.23	0.23	0.23
Comp Mole Frac (O_2)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Comp Mole Frac (NH_3)	0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Comp Mole Frac (Ar)	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01

Name of Stream →	**18**	**19**	**20**	**Ammonia Product**	**22**	**23**	**24**	**25**	**26**	**27**	**28**	**16**
Vapour Fraction	1.00	1.00	1.00	0.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Temperature [°C]	35.81	-28.64	-39.95	-39.95	-39.95	-39.95	25.00	29.53	25.00	24.99	34.88	34.98
Pressure [kPa]	15045	15030	15015	15015	15015	15015	15000	15000	14985	14970	14500	14940
Molar Flow [kgmole/h]	1.15E+06	1.15E+06	1.15E+06	3.66E+03	1.14E+06	1.14E+06	1.1E+06	1.15E+06	1.88E+01	2.69E+01	3.60E+02	1.15E+06
Mass Flow [kg/h]	1.07E+07	1.07E+07	1.07E+07	6.24E+04	1.07E+07	1.06E+07	1.1E+07	1.07E+07	1.75E+02	2.51E+02	3.36E+03	1.07E+07
Liquid Volume Flow [m^3/h]	35668.00	35668.00	35668.00	101.68	35566.31	35367.01	35367.0	35799.87	0.59	0.84	11.20	35668.00
Heat Flow [kJ/h]	-3.76E+09	-6.06E+09	-6.53E+09	-2.61E+08	-6.27E+09	-6.24E+09	-4E+09	-3.81E+09	-6.54E+04	-9.3E+04	-1.19E+06	-3.79E+09
Comp Mole Frac (CH_3)	0.04	0.04	0.04	0.00	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04
Comp Mole Frac (H_2O)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Comp Mole Frac (CO)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Comp Mole Frac (CO_2)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Comp Mole Frac (H_2)	0.70	0.70	0.70	0.00	0.70	0.70	0.70	0.70	0.70	0.70	0.70	0.70
Comp Mole Frac (N_2)	0.23	0.23	0.23	0.00	0.24	0.24	0.24	0.24	0.24	0.24	0.23	0.23
Comp Mole Frac (O_2)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Comp Mole Frac (NH_3)	0.01	0.01	0.01	0.99	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Comp Mole Frac (Ar)	0.01	0.01	0.01	0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01

Name of Stream →	**29**	**2**	**30**
Vapour Fraction	1.00	1.00	1.00
Temperature [°C]	25	255	35
Pressure [kPa]	15000	14970	14955
Molar Flow [kgmole/h]	1.14E+06	1.15E+06	1.15E+06
Mass Flow [kg/h]	1.06E+07	1.07E+07	1.07E+07
Liquid Volume Flow [m^3/h]	35365.59	35683.89	35679.20
Heat Flow [kJ/h]	-3.95E+09	3.97E+09	-3.81E+09
Comp Mole Frac (CH_3)	0.04	0.04	0.04
Comp Mole Frac (H_2O)	0.00	0.00	0.00
Comp Mole Frac (CO)	0.00	0.00	0.00
Comp Mole Frac (CO_2)	0.00	0.00	0.00

Comp Mole Frac (H_2)	0.70	0.70	0.70
Comp Mole Frac (N_2)	0.24	0.23	0.23
Comp Mole Frac (O_2)	0.00	0.00	0.00
Comp Mole Frac (NH_3)	0.01	0.01	0.01
Comp Mole Frac (Ar)	0.01	0.01	0.01