# Separations and Reaction Engineering
# Design Project

## Production of Ammonia

Your assignment is to continue evaluating the details of a process to produce 50,000 tonne ammonia per year from synthesis gas. This ammonia synthesis loop is to be integrated with a larger process that converts coal into synthesis gas (syngas), adjusts the composition of the syngas, and produces ammonia. Ammonia is one of the top five commodity chemicals produced by the chemical industry. It is used as a raw material for nitrogen oxides and fertilizers, among other products. As the final part of the feasibility study, we would like you to study the details of the reactor and separation section of proposed plant and then optimize the complete process. Your final design should be an optimized process and should include all unit operations necessary to produce the desired amount and purity of ammonia.

### Chemical Reaction

To provide an initial guess for the integration of the ammonia synthesis loop into the overall process, the syngas feed is assumed to have been pretreated to yield stoichiometric amounts of nitrogen and hydrogen. The syngas is available at 1000 kPa and 200°C. The syngas feed specifications are 24.4 mole % nitrogen, 73.3 mole % hydrogen, 2.3 mole % methane, and 5.6 ppm carbon dioxide. In the pretreatment, oxygen-containing compounds like $CO_2$ must be removed, because amounts above 10 ppm in the reactor poison the catalyst. One method for accomplishing this is by methanation, hence the small amounts of methane in the feed syngas. If carbon dioxide must be removed from the process feed, monoethanolamine or diethanolamine (pure or dissolved in water) are recommended solvent candidates for a scrubber. The solvent can be recovered by stripping. These amines may require non-typical materials of construction.

The reaction is reversible and described by:

$$N_2 + 3H_2 = 2NH_3 \qquad (1)$$

Detailed kinetics for the reaction are described in Appendix 2. The ammonia product stream is to have an ammonia content of greater than 99.9 weight % as a liquid that can be pumped to a nearby rail loading facility. For additional information on ammonia production, consult the literature. Some possibilities are suggested.[1,2] It is highly recommended that you read about ammonia production before proceeding with this assignment. Many chemical prices are available at http://www.icis.com/StaticPages/a-e.htm. The value of syngas is $0.10/kg.

## Specific Assignments

### 1. Separations Design – (ChE 312)

You are to determine the number of distillation columns required, their locations, their sequence, and enough information for each column to determine their costs. The distillation column that purifies the ammonia should be designed in detail. A detailed design of a tray tower includes number of trays, tray spacing, diameter, reflux ratio, weir height, top and bottom pressure specifications, and design of auxiliary equipment (heat exchangers, pump, reflux drum, if present). A detailed design of a packed tower includes height, packing size and type, and the same other specifications as in a tray tower. For all columns in this project, you may assume that HETP = 0.6 m. For the distillation column, the better economical choice between a packed and tray tower should be determined. For either a packed or a tray distillation column, the optimum reflux ratio should be determined.

Note that a tower consists of a vessel with internals (trays or packing). The constraints on a vessel are typically a height-to-diameter ratio less than 20. However, it is possible to extend this ratio to 30 as long as the tower is less than about 3 ft (1 m) in diameter. For larger-diameter towers, stresses caused by wind limit the actual height. Extra supports are needed for a height-to-diameter ratio above 20, even for smaller diameter columns. Therefore, there is a capital cost "penalty" of an additional 25% (only on the vessel) up to a ratio of 25, and a "penalty" of an additional 100% up to a ratio of 30.

You must choose the operating pressures for each column subject to constraints of operating temperature and available utilities. If vacuum columns are needed, pressure drop becomes a significant concern. As an alternative to tray towers, packed towers with a low-pressure-drop structured packing may be used. The packing factor as defined in Wankat[3], p. 336, is that for Koch Flexipac #2. Assume the HETP for the structured packing to be 0.6 m (see the definition of HETP in Wankat[3], p. 332, and the relationship between HETP and $H_{OG}$ in Equation (15.36) in Wankat[3].), and that the pressure drop is 0.2 kPa/m (0.245 inch water/ft).

### 2. Reactor Design – (ChE 325)

Several reactor types may be considered for use in this design. They are an adiabatic, packed bed reactor (a series of these with interstage cooling, if needed), an "isothermal," packed bed reactor, and a packed bed reactor with heat exchange. An "isothermal" reactor is defined here as one with a specified outlet temperature, not necessarily the inlet temperature, and some form of heat exchange is needed to add or remove the heat of reaction to maintain constant temperature. Chemcad will model the entire reactor as "isothermal" at that temperature. It must be understood that this situation is not physically realistic. In a reactor with heat exchange, the temperature along the length of the packed-bed reactor is not constant. The temperature can be controlled by varying the temperature and flowrate of the heat-transfer fluid, heat-transfer area, and the catalyst/inert ratio. The suggested heat-transfer fluid is Dowtherm A™. If a heat-transfer fluid is used, it is circulated in a closed loop through the reactor where its temperature is increased (if the reaction is endothermic) or decreased (if the reaction is exothermic). Then, heat is added (removed) from the fluid in a heat exchanger (or fired heater, if needed). The heat-transfer fluid is then pumped back to the reactor. Properties of the Dowtherm A™ can be obtained from Chemcad.

For your best case, you should include a discussion of the temperature, pressure, and concentration profiles obtained from Chemcad.

**Other Information**

It should be assumed that a year equals 8000 hours. This is about 330 days, which allows for periodic shutdown and maintenance.

## Deliverables

***General***

The entire ammonia process should be optimized using decision variables of your choosing. Decision variables should be chosen as those most strongly affecting the objective function. There are topological optimization and parametric optimization. In topological optimization, which is usually done first, the best process configuration is chosen. Parametric optimization involves varying operating variables and should be done after topological optimization is complete. Some examples of parameters that can be used as decision variables are reactor temperature, pressure, conversion, and distillation column reflux ratio.

**Economic Analysis**

When evaluating alternative cases, the equivalent annual operating cost (EAOC) objective function should be used. The EAOC is defined as

EAOC = -(product value - feed cost – utility costs – waste treatment cost - capital cost annuity)

A negative EAOC means there is a profit. It is desirable to minimize the EAOC; i.e., a large negative EAOC is very desirable.

The capital cost annuity is an ***annual*** cost (like a car payment) associated with the ***one-time***, fixed cost of plant construction.

The capital cost annuity is defined as follows:

$$\textit{capital cost annuity} = FCI\,\frac{i(1+i)^n}{(1+i)^n - 1} \tag{5}$$

where *FCI* is the installed cost of all equipment; *i* is the interest rate (take $i$ = 0.15) and *n* is the plant life for accounting purposes (take $n$ = 10).

### Other Information

Unless specifically stated in class, the information in this document is valid for this project only. Any information in the sophomore projects not specifically stated in this document is not valid for this project.

## Deliverables

### Written Reports

Each group must deliver a report written using a word processor. Two identical copies should be submitted, one for each instructor. The written project reports are due by 11:00 a.m. Wednesday, April 21, 2010. Late projects will receive a minimum of a one letter grade deduction.

The report should be clear and concise. For the correct formatting information, refer to the document entitled *Written Design Reports*. The report must contain a labeled process flow diagram (PFD) and a stream table, each in the appropriate format. The preferred software for preparing PFDs is Corel Draw. A PFD from Chemcad is unacceptable; however, it should be included in the appendix along with a Chemcad report for the base case. Figure 1 should be used as a template for your PFD. When presenting results for different cases, graphs are superior to tables. For the optimal case, the report appendix should contain details of calculations that are easy to follow. These may be hand written if done neatly. Alternatively, Excel spreadsheets may be included, but these must be well documented so that the reader can interpret the results. Calculations that cannot be easily followed and that are not explained will lose credit.

Since this project involves two “mini-designs,” it is suggested that the report be organized with the following sections. There should be a general abstract and introduction. Then, there should be a results section followed by a discussion section for each of the major components of this design project, namely the design of the reactor and separation strategy. General conclusion and recommendation sections should follow. At a minimum, there should be separate appendices for each class, ChE 312 and ChE 325, each containing detailed calculations that are clearly written, easy to follow, and appropriate for the respective class.

In order to evaluate each group member’s writing skills, the results and discussion sections for each mini-design should be written by a different group member. The authorship of each of these mini-reports should be clearly specified in the report. Although the individual written portions of the reports must be authored by a single group member, it is the intent of the instructors that group members should help each other in writing different sections. To this end, we recommend that you seek input, such as proofreading and critiques, from other members of your group.

The reports will be evaluated as follows:

- course-specific technical content – 50%
- oral presentation – 20%

- written report – 20%
- technical quality of general sections (safety, simulation, etc.) – 10%

For a more detailed set of evaluation criteria that we will use, see the following web site (design project assessment, oral report assessment, written report assessment):
http://www.che.cemr.wvu.edu/ugrad/outcomes/rubrics/index.php

Each report will be assessed separately by both instructors. A historical account of what each group did is neither required nor wanted. Results and explanations should be those needed to justify your choices, not a litany of everything that was tried. Each mini-report should be limited to 4-5 double space pages plus figures and tables.

This report should conform to the Department guidelines. It should be bound in a folder that is not oversized relative to the number of pages in the report. Figures and tables should be included as appropriate.

The written report is a very important part of the assignment. Poorly written and/or organized written reports may require re-writing. Be sure to follow the format outlined in the guidelines for written reports. Failure to follow the prescribed format may be grounds for a re-write.

The following information, at a minimum, must appear in the main body of the final report:

1. a computer-generated PFD (not a Chemcad PFD) for the recommended optimum case,

2. a stream table containing the usual items,

3. a list of new equipment for the process, costs, plus equipment specifications (presented with a reasonable number of significant figures),

4. a summary table of all utilities used,

5. a clear summary of alternatives considered and a discussion, supported with figures, of why the chosen alternative is superior,

6. a clear economic analysis which justifies the recommended case

7. a discussion section pertinent to each class plus a general discussion section for optimization of the entire process

8. a Chemcad report only for your optimized case (in the Appendix). This must contain the equipment connectivity, thermodynamics, and overall material balance cover pages; stream flows; equipment summaries; tower profiles; and tray (packing) design specifications (if you use Chemcad to design the trays (packing)). It should not contain stream properties. Missing Chemcad output will not be requested; credit will be deducted as if the information is missing.

**Oral Reports**

Each group will give an oral report in which the results of this project will be presented in a concise manner. The oral report should be between 15-20 minutes, and each group member must speak. Each group member should speak only once. A 5-10 minute question-and-answer session will follow, and all members must participate. Refer to the document entitled *Oral Reports* for instructions. The oral presentations will be Wednesday April 21, 2010, from 11:00 a.m. to 1:00 pm. Attendance is required of all students during their classmates' presentations (this means in the room, not in the hall or the computer room). ***Failure to attend any of the above-required sessions will result in a decrease of one-letter grade (per occurrence) from your project grade in ChE 312 and ChE 325***.

## Teams

This project will be completed in teams of 3 or 4. More details of group formation and peer evaluation will be discussed in class.

## Revisions

As with any open-ended problem (*i.e*., a problem with no single correct answer), the problem statement above is deliberately vague. The possibility exists that, as you work on this problem, questions from the class will require revisions and/or clarifications of the problem statement. You should be aware that these revisions/clarifications might be forthcoming.

## References

1. Eggeman, T., "Ammonia," *Kirk-Othmer Encyclopedia of Chemical Technology*, on-line version, 10/18/2001. (This encyclopedia is accessible from any University computer at http://www.libraries.wvu.edu/databases. An older print version is available in the Evansdale Library reference section.)

2. Quartulli, Orlando J., William Turner, and Keith W. Padgett, "Ammonia," in *Encyclopedia of Chemical Processing and Design*, (J. J. McKetta, ed.), Marcel Dekker, New York, vol. 3, 256-278 (1977). (This collection is available in the reference section of the Evansdale Library, first floor, back and to the right.)

3. Wankat, P., *Separation Process Engineering*, Second Edition, Prentice Hall, Upper Saddle River, NJ, 2007.

# Appendix 1
# Economic Data

## Equipment Costs (Purchased)

Note: The numbers following the attribute are the minimum and maximum values for that attribute. For a piece of equipment with a lower attribute value than the minimum, the minimum attribute value should be used to compute the cost. For a piece of equipment with a larger attribute value, extrapolation is possible, but inaccurate. To err on the side of caution, the price for multiple, identical, smaller pieces of equipment should be used.

Pumps $\log_{10}(\text{purchased cost}) = 3.4 + 0.05\log_{10} W + 0.15[\log_{10} W]^2$
$W$ = power (kW, 1, 300)
assume 80% efficiency

Heat Exchangers $\log_{10}(\text{purchased cost}) = 4.6 - 0.8\log_{10} A + 0.3[\log_{10} A]^2$
$A$ = heat exchange area ($m^2$, 20, 1000)

Compressors $\log_{10}(\text{purchased cost}) = 2.3 + 1.4\log_{10} W - 0.1[\log_{10} W]^2$
$W$ = power (kW, 450, no limit)
assume 70% efficiency

Compressor Drive $\log_{10}(\text{purchased cost}) = 2.5 + 1.4\log_{10} W - 0.18[\log_{10} W]^2$
$W$ = power (kW, 75, 2600)

Turbine $\log_{10}(\text{purchased cost}) = 2.5 + 1.45\log_{10} W - 0.17[\log_{10} W]^2$
$W$ = power (kW, 100, 4000)
assume 65% efficiency

Fired Heater $\log_{10}(\text{purchased cost}) = 3.0 + 0.66\log_{10} Q + 0.02[\log_{10} Q]^2$
$Q$ = duty (kW, 3000, 100,000)
assume 80% thermal efficiency
assume it can be designed to use any organic compound as a fuel

Vertical Vessel $\log_{10}(\text{purchased cost}) = 3.5 + 0.45\log_{10} V + 0.11[\log_{10} V]^2$
$V$ = volume of vessel ($m^3$, 0.3, 520)

Horizontal Vessel $\log_{10}(\text{purchased cost}) = 3.5 + 0.38\log_{10} V + 0.09[\log_{10} V]^2$
$V$ = volume of vessel ($m^3$, 0.1, 628)

Catalyst $2.25/kg

| | |
|---|---|
| Packed Tower | Cost as vessel plus cost of packing |
| Packing | $\log_{10}(\text{purchased cost}) = 3 + 0.97\log_{10} V + 0.0055[\log_{10} V]^2$<br>$V$ = packing volume ($m^3$, 0.03, 628) |
| Tray Tower | Cost as vessel plus cost of trays |
| Trays | $\log_{10}(\text{purchased cost}) = 3.3 + 0.46\log_{10} A + 0.37[\log_{10} A]^2$<br>$A$ = tray area ($m^2$, 0.07, 12.3) |
| Reactors | For this project, the reactor is considered to be a vessel. |
| Storage Tanks | $\log_{10}(\text{purchased cost}) = 4.85 - 0.397\log_{10} V + 0.145[\log_{10} V]^2$<br>$V$ = volume of tank ($m^3$, 90, 30000) |

It may be assumed that pipes and valves are included in the equipment cost factors. Location of key valves should be specified on the PFD.

**Additional Cost Information**

Piping straight pipe $/m = 5.0 (nominal pipe diameter, in)(1+(sch #)/20)$^{0.25}$
sch = schedule number for pipe
use the same sch number for fittings and valves

fittings (except valves) $/fitting = 50.0 (nominal pipe diameter, in)(1+(sch #)/20)$^{0.25}$

Valves for gate (isolation) valves $100 (nominal pipe diameter, in)$^{0.8}$ (1+(sch #)/20)$^{0.25}$
for control valve use $1000 (nominal pipe diameter, in)$^{0.8}$(1+(sch #)/20)$^{0.25}$

**Utility Costs**

| | |
|---|---|
| Low-Pressure Steam (618 kPa saturated) | $13.28/GJ |
| Medium-Pressure Steam (1135 kPa saturated) | $14.19/GJ |
| High-Pressure Steam (4237 kPa saturated) | $17.70/GJ |
| Natural Gas (446 kPa, 25°C) | $11.00/GJ |
| Fuel Gas Credit | $9.00/GJ |
| Cost of syngas | $0.10/kg |
| Cost of monoethanolamine | $2.42/kg |
| Cost of diethanolamine | $2.75/kg |

| | |
|---|---|
| Electricity | \$0.06/kWh |
| Boiler Feed Water (at 549 kPa, 90°C) | \$2.45/1000 kg |
| Cooling Water<br>available at 516 kPa and 30°C<br>return pressure ≥ 308 kPa<br>return temperature is no more than 15°C above the inlet temperature | \$0.354/GJ |
| Refrigerated Water<br>available at 516 kPa and 10°C<br>return pressure ≥ 308 kPa<br>return temperature is no higher than 20°C | \$4.43/GJ |
| Deionized Water<br>available at 5 bar and 30°C | \$1.00/1000 kg |
| Waste Treatment of Off-Gas | incinerated - take fuel credit |
| Low Temperature Refrigeration<br>Coolant stream at -20°C | \$7.89/GJ |
| Very Low Temperature Refrigeration<br>Coolant stream at -50°C | \$13.11/GJ |
| Wastewater Treatment | \$56/1000 $m^3$ |

**Equipment Cost Factors**

Total Installed Cost = Purchased Cost (4 + material factor (MF) + pressure factor (PF))

| | | |
|---|---|---|
| Pressure (absolute) | < 10 atm, PF = 0.0<br>10 - 20 atm, PF = 0.6<br>20 - 40 atm, PF = 3.0<br>40 - 50 atm, PR = 5.0<br>50 - 100 atm, PF = 10 | does not apply to turbines, compressors, vessels, packing, trays, or catalyst, since their cost equations include pressure effects |

Carbon Steel MF = 0.0
Stainless Steel MF = 4.0

# Appendix 2
# Information on Reaction Kinetics

The main reaction in the catalytic synthesis of ammonia is

$$N_2 + 3H_2 = 2NH_3 \tag{A2-1}$$

Experimental analysis of the performance of this catalyst has been reported to give the following expression for the net rate of reaction of nitrogen:

$$-r_{N_2} = k_f \frac{p_{N_2} p_{H_2}^{1.5}}{p_{NH_3}} - k_r \frac{p_{NH_3}}{p_{H_2}^{1.5}} \tag{A2-2}$$

where $k_f$ and $k_r$ are the reaction rate constants for the forward and reverse reactions, the rate units are kmol/(m$^3$ catalyst hr), the partial pressure is in atm, and the gas constant is in kcal/mol. In Chemcad, chose the activation energy in kcal, the volume in m$^3$, the molar flow in kmol, the mass flow in kg, and the time unit of hr. The rate constants were reported as follows:

$$k_f = 582.3\exp\left[-\frac{17{,}307}{RT}\right] \tag{A2-3}$$

and

$$k_r = 1.77 \times 10^{14} \exp\left[-\frac{40{,}765}{RT}\right] \tag{A2-4}$$

where the activation energy is given in kcal/kmol and temperature is in Kelvins. The catalyst is promoted iron oxide, with a specific gravity of 2.6 and a packing void fraction of 0.44. Remember that the required units in Chemcad for the reaction rate are kmol/m$^3$reactor hr.

You may wish to consider several reactor configurations. Some suggested configurations are shell-and-tube packed bed with heat removal, adiabatic reactor, and staged adiabatic packed beds with intercooling. There are other possibilities.