High-purity liquefied gases: Aspen Dynamics simulation of a purification process in a middle-vessel batch distillation column

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Abstract. The paper explores the use of Aspen Plus and Aspen Dynamics for simulating and optimising a high-precision process of liquefied gases high purification in a middle-vessel packed distillation column. The example studied involves the removal of lower- and higher-boiling impurities from the upper- and lower rectifying sections and maintaining the purified product in the middle vessel. Total reflux operation is studied in the pressure range between the normal boiling point of the purified product and the critical point. Among the considered aspects are the column design and sizing, hydrodynamics study (flooding calculations), the effect of operating pressure and temperature on the thermodynamics of vapour-liquid equilibrium and mass-transfer kinetics in a wide range of operating conditions. The paper demonstrates that the effects and dependencies observed previously through the experiments and by using user-developed custom models are adequately reproduced in the commercial simulator (Aspen Plus) by setting up a fictitious steady-state continuous process with rigorous built-in models. The optimised flowsheet can be converted to Aspen Dynamics as a pressure-driven process where a rigorous dynamic simulation gives a realistic dynamic response, and alternative control structures can be explored.

1. Introduction

The increasing demand for specific applications involving high-purity gases across the globe promises a positive industry outlook for specialty gases in the next decade [1]. Many industries, including analytical, pharmaceutical, electronics and petrochemical benefit from the unique properties of high-purity gases that help to improve yields, optimise performance and lower costs [2–4]. The purity of process-specialty gases is critical to success in the specific fields of their application, where they must be rigorously free of trace impurities that will alter the processes.

The most universal and widely used method for high purification of liquefied gases is batch distillation in high-efficient packed columns. The method is versatile, offers high performance and is characterised by simplicity of technological scheme and the possibility of maintaining high chemical sterility of the process. A middle-vessel distillation column allows removing higher-boiling and lower-boiling impurities from the purified product in one technological stage. It shortens the duration of the purification process and reduces the contact time of the purified media with the material of the
equipment. Two independently operating columns (upper and lower sections) are combined in one apparatus with a middle vessel for purified product. The organisation of the purification process with the removal of impurities reduces the possibility of contaminating the product during accidental disruption of the column operating mode.

In recent years, commercial chemical engineering simulators have been developed that provide rigorous built-in models of distillation unit operations. A large library of physical property data and a reliable selection of rigorous numerical integration algorithms are also provided. However, the vast majority of studies consider the control of continuous steady-state processes. There is no built-in middle-vessel batch distillation column unit in commercial simulators. Studies of batch processes have used user-developed models and solution methods, Aspen Custom Modeler, Aspen Batch Modeler, hybrid systems combining Aspen Plus and Matlab, involving complex programming and multiple steps with scripts [5].

William L. Luyben has recently proposed a novel straightforward approach for modelling a middle-vessel batch distillation column combining a fictitious steady-state continuous process in Aspen Plus and a subsequent dynamic simulation with a realistic control structure in Aspen Dynamics [5]. Separation of a ternary hydrocarbon mixture (30 mol% benzene, 30 mol% toluene and 40 mol% o-xylene) in a tray column under a constant pressure has been considered, and alternative control strategies have been explored using various control functions. The advantage of employing rigorous Radfrac distillation column model which gives realistic predictions of column hydraulics together with Aspen Dynamics control model library has been demonstrated.

The current paper is aimed at exploring the feasibility of using Aspen Plus and Aspen Dynamics for simulating and optimising a high-precision process of high purification of liquefied gases in a middle vessel packed distillation column. Literature survey shows that information on this subject in the public domain remains scarce. The process of interest implies the removal of impurities from upper- and lower rectifying sections and maintaining the purified product in the middle vessel. A variety of important aspects needs to be considered including column design and sizing (e.g. size and liquid holdups of impurity-enriched fraction collectors - reflux drum and lower sump), hydrodynamics study (pressure drops and flooding calculations), the effect of operating pressure and temperature on the thermodynamics of vapour-liquid equilibrium (VLE) and mass-transfer kinetics.

2. Methods and materials

2.1 Model mixture

The vast majority of studies consider the separation of equimolar hydrocarbon-based mixtures. The modelling of a high-purity gases distillation process in commercial simulators has not received a considerable attention. As an example, the process of ammonia high purification with the removal of higher-boiling and lower-boiling impurities would be an interesting case study for simulating a batch distillation in a packed column with a middle-vessel. The numerical example studied has a ternary feed mixture based on ammonia with impurities of water and acetylene at an initial concentration of 0.1 mol%.

During the preliminary studies, it was determined that Peng Robinson equation of state with Michelsen-Huron-Vidal mixing rules (PRMHV2 thermodynamic method) describes quite accurately the behaviour of vapour-liquid equilibrium of ammonia-acetylene and ammonia-water binary systems in the dilute region over a large pressure and temperature range between the normal boiling point of ammonia and the critical point. Table 1 shows the concentration and temperature ranges for the experimental VLE data obtained from the literature [6,7]. Figure 1 presents a VLE analysis covering the temperature and pressure range from the normal boiling point of ammonia up to the critical point. For the convenience, the K-value (vapour-liquid distribution coefficient) data is plotted in Arrhenius coordinates (natural logarithm of K-value against inverse temperature). The experimental data are presented by marks. The simulation results are obtained with Aspen Plus V9 (lines).
Table 1. The experimental VLE data for the ammonia-based binary system.

| Impurity    | K-value at 293K | Impurity mole fraction | Temperature range, K | Reference |
|-------------|-----------------|------------------------|----------------------|-----------|
| Water       | 450±150         | 0.0001 – 0.1150        | 293.15 – 405.71      | [6]       |
| Acetylene   | 2.7±0.2         | 0.0280 – 0.0890        | 238.15 – 405.5       | [7]       |

Taking into account the normal boiling point of ammonia (-33.34 °C), it is advisable to employ high-pressure distillation [2,3] to permit the condensation process at ambient temperature and avoid using energy-intensive and expensive cryogenic refrigeration systems. The increase of temperature also lowers the enthalpy of vaporisation thus promoting the further reduction of energy intensity, while the increasing pressure gives an opportunity to raise the productivity of the purification process [2].

Carrying out the distillation under higher pressure promotes the intensification of the mass transfer kinetics [2]. However, it is inevitably accompanied by a significant change in phase equilibrium[8,9]. That is why a comprehensive modelling of a purification process in a middle-vessel packed distillation column is required in a wide pressure range to identify the best set of operating parameters.

2.2 Process design procedure
The structuring of a technological scheme and configuring the column units are carried out according to the properties of the chosen model mixture and defined the range of operating conditions. Table 2
summarises the range of operating pressure, temperature and load, as well as the geometric parameters of the simulated column.

**Table 2. Column operating conditions and parameters during the simulations**

| Parameter                                  | Value          |
|--------------------------------------------|----------------|
| Operating pressure, $P$ ($10^5$ Pa)        | 5–50           |
| Operating temperature, $T$ (K)             | 278–362        |
| Vapour and liquid load ($\text{kg h}^{-1}$) | 10–20          |
| Column diameter (m)                        | 0.05           |
| Total packing height (m)                   | 1              |
| Column packing type                        | Sulzer CY      |
| Middle vessel volume ($\text{m}^3$)        | 1              |
| Reflux drum volume ($\text{m}^3$)          | 0.002          |
| Lower sump volume ($\text{m}^3$)           | 0.002          |

The general design procedure follows the approach described in detail elsewhere [5,10]. At the first step, a steady-state simulation in Aspen Plus is set up with required pieces of equipment. Fig. 2 presents the initial Aspen Plus steady-state flowsheet with fictitious streams. A Radfrac rectifier model (condenser but no reboiler) is used for the upper column. A Radfrac stripper model (reboiler but no condenser) is used for the lower column. The Aspen model used for the middle vessel is a Flash2 separator model so that realistic pressures will be predicted during the dynamic simulation. The vapour and liquid flow in the column is set to maintain the load at 80% of flooding under the given pressure and temperature.
Figure 2. Aspen Plus steady-state flowsheet of a middle-vessel distillation column.

At the second step, the Aspen Plus steady-state simulation file is exported to Aspen Dynamics as a pressure-driven dynamic simulation (Figure 3). The valves VF, VB, VVENT, VD, and VVAP are set to be closed to simulate a total reflux batch distillation. The vapour flow from a lower section leaving the valve VV is connected to the upper section.

Figure 3. Aspen Dynamics flowsheet and its control structure.

The control structure is established so that the two reflux flowrates are maintained constant (80% of flooding) under given pressure and temperature during the total reflux operation. The level controllers LCtop, LBase, and LCbot are installed to maintain constant holdup in impurity fraction collectors (reflux drum and lower sump). The flow controller FCmid sets a constant liquid flow rate from the middle vessel to the lower rectifying section (80% of flooding), while the LCbot controls the corresponding vapour boil-up by adjusting the reboiler duty. The pressure controller Pc maintains a constant column pressure by adjusting the condenser duty.

3. Results and discussion
Setting up the adequate vapour and liquid load in the column is required to assure the best surface area and mass transfer efficiency. Since the maximum packing throughput is known to be increasing with pressure [2], a preliminary hydrodynamic simulation was carried out for Sulzer CY packing to determine maximum throughput of rectifying sections according to the operating pressure. Fig. 4 represents simulation results on the vapour flow corresponding to the 80% of flooding point depending on the operating pressure.
Figure 4. Vapour load corresponding to 80% of flooding point depending on the operating pressure.

As can be seen from the graph higher loads can be achieved when pressure increases. A similar dependence of a flooding vapour flow rate on pressure was also reported previously for various packings [2,10,11]. All further separation efficiency studies are conducted under total molar reflux conditions maintaining a fixed distance from the flooding point according to pressure and temperature. This approach also ensures that the packing is completely wetted, and only the liquid in dead zones is not involved in the mass transfer.

A dynamic simulation of a batch distillation process in Aspen Dynamics allows estimating the time required to achieve a near-stationary state in a total-reflux operation. Figure 5 shows the variation of acetylene and water impurity concentration at the top and at the bottom of the column, correspondingly, over time. The column is operated at 10 bar and 298 K; the liquid and vapour flow through the rectifying sections are 13.7 kg h\(^{-1}\), which corresponds to 4.5 kW reboiler duty. It takes approximately 30 hours for acetylene and over 60 hours for water impurity to achieve a stable value.

The studied case demonstrates a separation process at high pressure when the condensation process occurs at a temperature near the ambient one, which helps to avoid using energy-intensive and expensive cryogenic refrigeration systems required for atmospheric ammonia distillation. Alongside this, carrying out the distillation under elevated pressure leads to a significant change in phase equilibrium and mass transfer kinetics. A complicating factor is the influence of loading rate affecting hydrodynamics, interfacial area, phase velocities and contact time. Since the packing capacity increases with the operating pressure and the loading zone becomes more extended, the process is carried out at a constant distance from the flooding point maintaining the work in the loading region. In that case, simulation of the simultaneous impact of increasing pressure, temperature and loading on the overall column separation efficiency is of immediate interest.

The simulations have been repeated for different operating pressures. The range of simulated operating conditions include values of pressure (temperature) from near the normal boiling point of ammonia to near the critical one (Table 2). For each simulation run the vapour pressure of the separated mixture in the column was calculated according to the set temperature, and it corresponded
to that of the pure ammonia due to the relatively low initial concentration of impurity components. Since the packing throughput correlated with physical properties of the mixture, the loading was adjusted according to established pressure and temperature to keep the operation in the loading region (80% of flooding point) for the best surface area and mass transfer efficiency.

Figure 5. Achieving a near-stationary state in total-reflux operation at 10 bar: 1 – liquid mole fraction of acetylene in the reflux drum; 2 – liquid mole fraction of water in the lower sump.

The simulation results show that pressure has a significant effect on the column separation performance. Fig. 6 shows the variation of a height equivalent to a theoretical plate (HETP) simulated with rate-based modelling approach and plotted against operating pressure. This diagram reflects the influence of simultaneously increasing pressure, temperature and loading on mass transfer in the packed section. The evidence is that an increase in pressure and temperature with accompanying the growth of load results in a steady reduction of HETP signifying intensification of mass transfer. Similar trends of pressure-HETP behaviour in the loading region were observed and discussed in detail elsewhere [2]. The improvement of mass transfer kinetics compensates the negative impact of decreasing relative volatility resulting in extreme behaviour of column separation efficiency with simultaneously increasing pressure, temperature and loading. Figure 7 reflects the influence of pressure on overall column separation efficiency represented by the variation of a separation degree (initial water impurity concentration divided by the concentration of water at the top of the column). At first, the separation efficiency increases with increasing pressure (temperature), reaches a maximum under certain operating conditions and then starts to decrease as pressure and temperature become closer to the critical point of the matrix. The results obtained in this work through Aspen Plus simulation for a middle-vessel batch distillation column (figures 6, 7) follow quite well the tendency of previously reported experiments on separation efficiency of high-pressure distillation in packed columns [2,3].
Figure 6. Simulated HETP depending on column pressure with loading kept at 80% of flooding.

Figure 7. Simulation of the influence of operating pressure on the overall column separation performance.
4. Conclusions
This study contributes towards exploring the feasibility of using Aspen Plus and Aspen Dynamics simulators for designing and optimising a high-precision process of liquefied gases high purification in a middle-vessel packed distillation column. There is no built-in middle-vessel batch distillation column unit in commercial chemical engineering simulators. The paper demonstrates that the effects and dependencies observed previously through the experiments and by using user-developed custom models are adequately simulated by setting up a fictitious steady-state continuous process based on rigorous built-in models in Aspen Plus. The simulation results concerning the qualitative aspects of the general behaviour of high-pressure column separation performance in total-reflux operating conditions can be applied for optimisation procedure defining the optimal operating parameters for distillation of high-purity gases. This allows identifying the optimal set of operating parameters for the distillation process in a wide range of operating conditions. The optimised flowsheet can be converted to Aspen Dynamics as a pressure-driven process where a rigorous dynamic simulation gives a realistic dynamic response, and alternative control structures can be explored.

The future work would involve the dynamic simulation of a high purification process with different impurity withdrawal approaches (continuous/periodical withdrawal) and various control structures, validating the performance of simulations by comparing to experimental data.

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