Systems & Control Transactions

**Research Article - Peer Reviewed Conference Proceeding**
ESCAPE 35 - European Symposium on Computer Aided Process Engineering
Ghent, Belgium. 6-9 July 2025
Jan F.M. Van Impe, Grégoire Léonard, Satyajeet S. Bhonsale,
Monika E. Polańska, Filip Logist (Eds.)

PSE PRESS

# Energy Efficient Process Designs for Acrylonitrile Production by Propylene Ammoxidation

**Qing Li[a], Alexandre C. Dimian[b], and Anton A. Kiss[a]***

[a] Delft University of Technology, Department of Chemical Engineering, Delft, The Netherlands
[b] University Politehnica of Bucharest, Department of Chemical and Biochemical Engineering, Bucharest, Romania
* Corresponding Author: a.a.kiss@tudelft.nl.

## ABSTRACT

Acrylonitrile is a critical commodity chemical used to produce a variety of industrial polymers, such as carbon fibers, plastics, etc. Currently 90% of the global acrylonitrile production is based on propylene ammoxidation. However, there is no literature reporting the whole process holistically in detail, and which also looks into the energy utilization of the whole process including the reaction heat as well as the energy demands of the downstream separation. This original study provides a rigorous process design of the full process from a holistic viewpoint, covering 7 sections of acrylonitrile production (reaction, acid quenching, absorption-desorption, hydrogen cyanide recovery, acrolein recovery, acrylonitrile-acetonitrile-water separation, acetonitrile recovery sections). In order to further improve the energy efficiency, three energy integration strategies are proposed (1) Energy integrated downstream processing; (2) Systematic heat integration utilizing the heat of reaction; (3) Power generation by process surplus heat. Design 1 employs a direct heat exchanger network, recovering 30.1 MW heat through multiple heat exchanges, saving 86.91% fuel gas, 17.38% low pressure steam and 43.96% cooling utilities. Design 2 and 3 recovers 58.39 MW heat, and 12.20 MW low pressure steam is output as waste heat recovery in design 2, whereas 11.06 MW low pressure steam and 7.8 MW electricity are generated in design 3. The pro/con each options are also discussed for further guidance. As the first comprehensive description of the design of the entire acrylonitrile production process, this work highlights the potential for improved energy efficiency in the acrylonitrile production.

**Keywords**: Process Design, Process Intensification, Distillation, Energy Efficiency, Heat Exchanger Network

## 1. INTRODUCTION

Acrylonitrile (AN) is a widely used commodity chemical in industry, primarily as a monomer for the production of acrylic fibers, acrylonitrile-butadiene-styrene (ABS) resins, adiponitrile, acrylamide, nitrile rubbers, and carbon fibers. Driven by the increasing demand for acrylonitrile from end-use industries, such as construction,, the global acrylonitrile market size valued at USD 11.87 billion in 2021 is expected to grow at a compound annual growth rate (CAGR) of 1.3% from 2022 to 2030 [1].

Over 90% of the world's acrylonitrile is commercially manufactured via the propene ammoxidation process, described by Equation 1:

$$CH_2{=}CHCH_3 + NH_3 + 3/2O_2 \rightarrow CH_2CHCN + 3H_2O \quad (1)$$

However, this global reaction involves a complex reaction mechanism and is accompanied with the formation of acetonitrile, hydrogen cyanide, acroleine, acrylic acid, carbon oxides (COx), and large amounts of water. Therefore, to separate the products, the whole process can be described as the following sections, according to the descriptions given by Dimian and Bildea [2]: (1) reactor, (2) acid-quench, (3) absorption-desorption, (4) removal of hydrogen cyanide (5) separation of acrolein, (6) separation of acrylonitrile, (7) separation of acetonitrile.

The reaction is performed at temperatures of 400-510°C and pressures of 1.5-3 bar. The high exothermicity of the reactions involved ($\triangle H = -123$ kcal/mol) requires very efficient cooling to maintain the reaction temperature in the desired range. The downstream separation and purification of AN involves several distillation

columns, which are very energy intensive, however, energy costs and environmental concerns associated with energy consumption were not critical in the past, the energy consumption and the improvement of the energy usage and integration did not draw much attention. Thus, in the current climate, better utilization of the energy for the whole process is essential, and before investigating this, a detailed design of the whole process is also necessary.

The objectives of this study are: (1) to develop an optimized complete process flowsheet using thermodynamic analysis and literature information, (2) to implement process intensification technologies for downstream processing (DSP), such as dividing wall columns, exploring also the mechanical vapor recompression heat-pumping potentials, (3) to explore heat integration potentials by heat exchanger network design, utilizing the heat from reactions for the whole process, (4) to evaluate and compare different designs in terms of the energy intensity of each process.

## 2. PROBLEM STATEMENT

Acrylonitrile production process by propylene ammoxidation involves high exothermicity reactions, multi co-products which need to be separated, and complex downstream separation and purification processes. Developing a comprehensive flowsheet involving both reactions and separations to understand the whole process is essential, and energy integrated options should be considered in order to develop more energy-efficient flowsheets. Different designs should be evaluated and compared based on key performance parameters such as economics and sustainability, and suggestions are given based on the different advantages and disadvantages of each design.

## 3. DESIGN AND SIMULATION APPROCH

### 3.1 Process design

Aspen Plus V12 is used for rigorous simulations in this work. According to the process proposed by Dimian and Bildea [2], fifteen components are present in the process: acetonitrile, acrolein, acrylic acid, acrylonitrile, ammonia, ammonium sulphate, carbon dioxide, carbon monoxide, hydrogen cyanide, nitrogen, oxygen, propane, propylene, sulfuric acid, and water. The UNIQUAC-RK model is selected in Aspen Plus as suitable property model to calculate all physical properties required for the process simulation. The stoichiometric reactor model is used to model the reactions based on the activity data for a molybdenum/bismuth-modified catalyst reported in the patent (US 6,596,897 B1, 2003 [3]), in order to achieve a reliable description of the conversion of reactants into products, co-products, and other impurities. The simulation is developed based on VLE data, ternary diagrams combined with RCM, reaction conditions, separation specifications, and product purity requirements. Plant production capacity is 120 ktpy (acrylonitrile 99.4 wt% purity, 99.9 wt% recovery) with a corresponding reactor production rate of 272.34 kmol/h acrylonitrile.

### 3.2 Energy integration methodology

#### 3.2.1 Process intensification opportunities for DSP to enhance energy efficiency

Process intensification (PI) technologies are considered to have great potential in reducing the high costs and energy requirements of the separation and purification step, enhancing productivity while improving process safety, reducing waste without sacrificing product quality. The intensified distillation technologies considered in this work include dividing wall column (in which one column shell with the middle wall is used to replace the conventional two columns and avoid re-mixing effect); and heat pump assisted distillation (in which the overhead vapor can be upgraded and re-used to heat the bottom reboiler), which addresses heat transfer bottlenecks by increasing the temperature of cold streams to create a feasible temperature driving force, thereby expanding heat transfer opportunities for integration.

#### 3.2.2 Heat exchanger network (HEN) design to utilize the heat of the process

The HEN is synthesized by a stage-wise superstructure optimization approach, integrating systematically direct heat integration and heat pumps. In addition, it allows the integration of multiple hot utility options, waste heat recovery, and mechanical heat pump applications, to enhance energy efficiency and reduce costs. Direct stream-stream transfer, indirect transfer via heat pumps, and utility-mediated heat transfer for waste heat are automatically selected for each heat transfer match. Heat exchangers are positioned at optimal locations between hot and cold streams, enabling efficient heat recoveries. A detailed description of this HEN synthesis method can be found in literature [4]. Initial and target temperatures of the streams, heat capacities, and stream film heat transfer coefficients are required for a new HEN design. The superstructure formulation is modelled as a mixed-integer nonlinear program (MINLP) and solved by BARON/GAMS, the objective function of this model is minimizing the total annualized cost (TAC). The fixed and area costs of heat exchangers, compressor size costs, and utility costs are considered as the cost-related parameters. The capital costs related to heat exchangers are taken from the literature [5]. The minimum approach temperature difference for heat transfer is set at 10°C.

## 4. RESULTS AND DISCUSSIONS

### 4.1 Base case design

Figure 1 presents the base-case flowsheet comprising the reaction and separation section. The fluid-bed reactor operates at 2.0 bar and 440°C. The reactants - propylene, ammonia, and air - are separately fed in the molar ratio 1, 1.2, 9.8 to fulfill reaction chemistry and safety constraints. After cooling at 220°C, the reaction mixture enters the quench column A-Q operated at 1.9 bar with a view to removing the excess ammonia as ammonium sulphate through neutralization with sulfuric acid (30 mol%). The bottom stream is sent to the recovery of ammonium sulphate that is a co-product of this process. After acid quenching and cooling at 30°C, the cleaned gas enters the absorption/desorption section. First, the column ABS equipped with 24 stages and operating at 1.6 bar, separates non-condensable components ($N_2$, $O_2$, $CO_2$, CO and propene) by absorption in water at 5°C. Next, the recovery of acrylonitrile from the aqueous bottom stream is sent to the column REC (36 stages). Top-vapor condensation at 30°C followed by liquid-liquid splitting in the DECANT1 ensures the recovery of the organic components (acrylonitrile, acetonitrile, hydrogen cyanide, and acrolein) in the organic phase and recycles the aqueous phase to the stripper.

The organic phase enters the column ACR for splitting the mixture in acrylonitrile/acetonitrile and HCN / acrolein fractions (1.1 bar). In the hydrogen cyanide section, hydrogen cyanide is recovered from the hydrogen cyanide-acrolein overhead (1.01 bar). The product stream leaving the bottom of the acrolein section is fed to the acrylonitrile-acetonitrile-water section, operating around atmospheric pressure, targeting the recovery of acrylonitrile as desired product. An extractive distillation is performed using water as mass-separating agent. The feed stream from the previous separation is combined with the aqueous stream from the decanter and the entrainer water stream to form the combined stream. The combined stream is separated in the first column to obtain a near-azeotropic distillate at the top, water at the bottom, and an acetonitrile-water mixture as a side stream. The organic phase from the decanter is sent to a second column (C2) to obtain a near-azeotropic distillate at the top and pure acrylonitrile at the bottom.

Finally, the side stream from the acrylonitrile-acetonitrile-water section is fed to the acetonitrile recovery section, which performs a pressure-swing distillation. Extractive distillation has good performance for recovering acetonitrile from water, yet there is only 4% acetonitrile in the feed resulting in low absolute value of the separating duties. Therefore the difference between different separation methods is small. Pressure swing distillation does not require introducing a third component so this is preferable. The pressure of the columns are 4.4 bar and 1.1 bar respectively. Overall 48.42 MW hot utilities and 43.15 MW cold utilities are needed by the process (after the heat recovery by HX1, 11.88 MW). Of the total 43.15 MW cold utility requirement, 3.39 MW of refrigerant is needed to cool the “ABS-H2O” stream in the absorption-desorption section (25°C–5°C), while 0.16 MW of chilled water is required for HCN column condenser (25.7°C–24.7°C). The remaining cooling duties are covered by cooling water. As the temperatures of ABS-H2O stream and the HCN condenser are too low for heat integration, they are excluded from the heat exchanger network (HEN) optimization process but re-added as cooling utilities in the optimized solution. Thus the refrigerant and chilled water requirements remain constant across all designs.

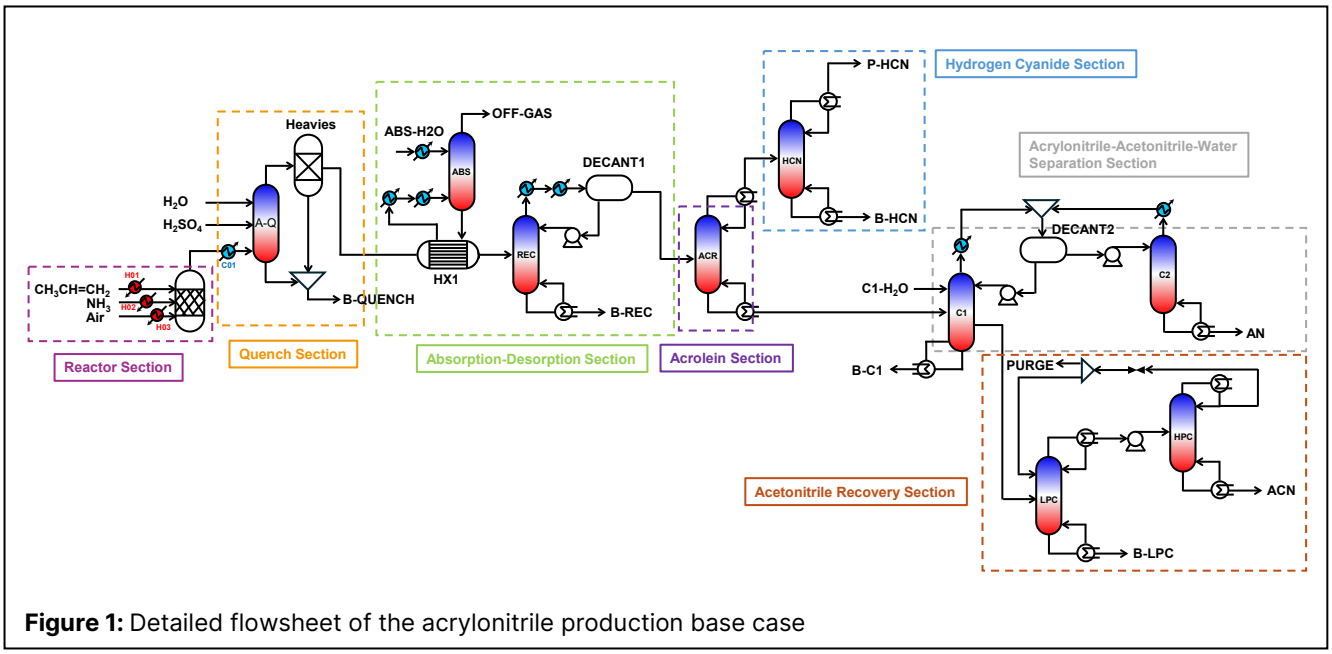


**Figure 1:** Detailed flowsheet of the acrylonitrile production base case

## 4.2 Process Energy integration

Propylene ammoxidation is an exothermic reaction - the reactor operates at 440°C and generates surplus heat amounting to 59.74 MW, which must be removed using a heat medium to ensure process stability. The heat can be removed directly by cooling medium to ensure effective cooling *(Section 4.2.1)*, the focus of the energy integration is then on the downstream separations; or the heat of the reaction can also be integrated into the process *(Section 4.2.2)*, by transferring its heat to a utility stream (hot oil, 400°C), and a heat exchanger network is developed by utilizing the reaction heat as well as the process to process heat integration;

Alternatively, the heat generated from the reaction can be utilized to produce power (very high pressure (VHP) steam to a steam turbine) and low-pressure (LP) steam. The generated power can be exported, while the LP steam serves as a hot utility within the process. The optimal heat integration solutions are presented through a HEN, as detailed in *(Section 4.2.3)*.

### 4.2.1 Energy integration of DSP taking into account process intensification options – Design 1

As heat pump assisted distillation has great potential to be able to enhance the energy efficiency, it is involved in the systematic heat integration approach. Taking vapor recompression as an example, the overhead vapor from the distillation column is compressed to a higher pressure, and used as heat source for the reboiler. However, when the process in complex (e.g., has multiple heat exchangers as well, providing heat integration potentials), a systematic heat exchanger network design is necessary, as an effective process to process heat transfer could also be potentially more effective than using heat pumps.

For heat pump assisted distillation, the lower the temperature lift (i.e., the temperature difference between the overhead vapour and the condenser), the higher the coefficient of performance [6,7]. When analysing the process, there are three potentials opportunities by integrating heat pumps in the acrylonitrile production process: (1) The overhead vapour from the recovery column (89°C) and the reboiler of the ACR column (81°C); (2) The overhead vapor of the first column of ACN/AN/$H_2O$ separation section (BD-C1, 76°C) to its reboiler (113°C); (3) The overhead vapor of second column of ACN/AN/$H_2O$ separation section (BD-C2, 76°C) to its reboiler (82°C).

However, an effective process to process heat integration might integrate the heat well without heat pumps, therefore a systematic heat exchanger network design (described in Section 3.2.2) is carried out, which includes the flexibility of choosing to use heat pumps is it brings more benefits. **Figure 2** presents the optimal heat exchanger network design of the process, and shows that in this case no heat pumps are needed. The target HEN configuration includes 10 hot streams, 11 cold streams, and two hot utilities: fuel gas and low-pressure steam. The heat exchanger HX1 (11.88 MW) in the conventional design was released as a degree of freedom in the new HEN design. Cooling water (20-25°C) and chilled water (5-15°C) refrigerant (-20°C) are employed to meet the cooling demands of system [8]. 10 heat exchangers are installed with a total heat transfer area of 3706 m², strategically placed within the network.

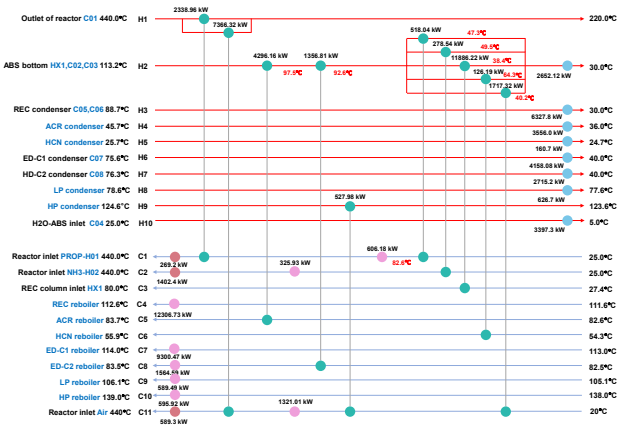


**Figure 2.** Heat exchanger network design via systemetic energy utilization for downstream processing without reaction-separation integration

These exchangers enable heat recovery of 30.41 MW, comparing to the conventional process. 28.87 MW hot utilities are needed (2.26 MW fuel gas, 26.61 MW LP steam), and 23.60 MW cold utilities are needed. Overall 20.60 MW hot utilities and 20.60 MW cold utilities are saved comparing to the conventional process, effectively utilizing heat from the reactor outlet stream (H1) and the ABS bottom stream (H2). The number and ratio of stream splits are shown in the HEN, maximizing the use of temperature driving forces to efficiently transfer heat to multiple cold streams. LPS is placed at the intermediate stage of cold stream C1, C2 and C11 by multiple utility optimization, to avoid the extra usage of fuel gas.

Note that the option of using dividing wall columns in this process does not bring benefits after calculations, therefore it will not be discussed further.

### 4.2.2 Systematic heat integration utilizing the heat of reaction – Design 2

Differently, the surplus heat from the reaction can also be first utilized to preheat the reactor feed inlets - propylene, NH3, and air - from 420°C to 440°C. The remaining surplus heat is then transferred to generate hot oil (200°C–400°C, 301.8 t/h), which is introduced as a new hot stream. The use of hot oil allows the HEN to operate with single-phase heat transfer, avoiding operational challenges associated with phase-change heat transfer in steam networks. A new HEN synthesis is

proposed in **Figure 3**, incorporating the hot oil stream. This design problem involves 11 hot streams, 11 cold streams, and two hot utilities. Additionally, LPS is used as a cold utility for automated waste heat recovery (steam generation). The LPS generated by the hot oil stream is exported from the system, further increasing energy benefits and enhancing overall efficiency.

**Figure 3** illustrates the optimal HEN design, which includes a total of 16 heat exchangers with a total heat transfer area of 2308 m². This improves process energy efficiency by achieving 58.39 MW of heat recovery compared to Section 4.2.1. The hot oil (59.74 MW) heat transferred by the reaction surplus heat covers all the hot utilities needed in this process, and additionally 12.20 MW LPS is generated/output as a form of waste heat recovery. 43.15 MW cold utilities are needed.

The previous design relied on a complex HEN with stream branches to utilize H1 and H2, yet the HEN in this section focuses on maximizing cost efficiency by utilizing the hot oil stream (H11). Half of the heat exchangers are placed in the hot oil stream, recovering 47.54 MW to cold streams. Overall, this HEN achieves complete heat integration without requiring any hot utility input, showcasing efficient energy utilization and cost-effectiveness.

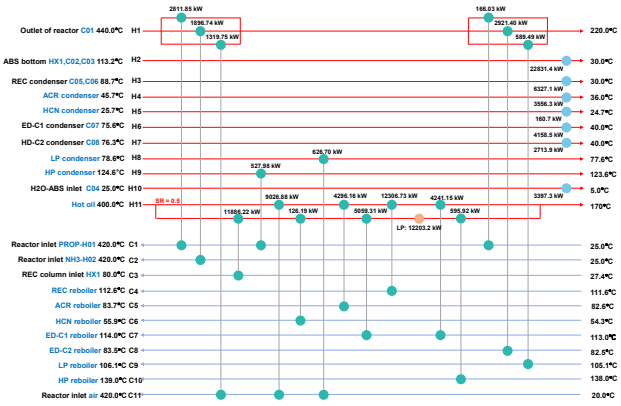


**Figure 3.** Reaction-separation integration via hot oil (to take the reaction surplus heat for integration) and systematic heat exchanger network design

### 4.2.3 Taking the reaction heat to generate power – Design 3

A steam network is established to generate electricity and provide heating for cold streams. The surplus heat (59.74 MW) from the reactor is first used to generate VHP steam (40 barg, 251.8°C), with 1.40 MW of heat transferred to the reaction inlet (air, C3) stream. The remaining VHP steam (58.35 MW) is passed through a steam turbine to generate electricity and produce LP steam (6 barg, 160°C) for process heating requirements. A partial HEN is synthesized using an optimization approach, incorporating only H1, C1, C2, and C11 within a multiple utility system. The remaining cold streams are directly heated by the steam network, simplifying the overall configuration while ensuring efficient energy utilization.

In this case, the steam network sufficiently meets the main heating requirements of 42.02 MW for cold streams C3–C10. Cold streams C1, C2, and C11 require an additional 5.28 MW from the steam network, while H1 compensates for the remaining 9.71 MW of heating. Overall 58.39 kW heat recovery can be achieved by this HEN. The key advantage of this solution is that the steam network not only meets heating demands but also generates 7.8 MW of electricity and 11.06 MW of LP steam as waste heat recovery. The turbine is simulated in Aspen Plus V12, with isentropic efficiency of 0.85 and mechanical efficiency of 0.98. However, integrating a steam network into the whole design introduces added complexity, particularly regarding control and safety considerations.

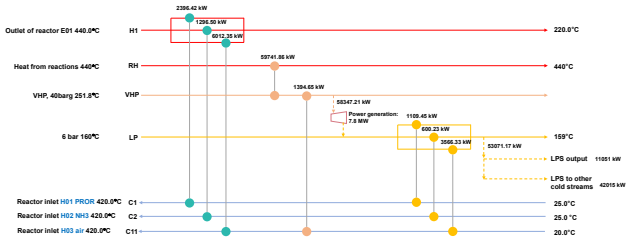


**Figure 4.** Reaction-separation integration via steam network and power generation (to take the reaction surplus heat for integration) by systematic heat exchanger network design; Hot (cold) streams that are directly cooled (heated) are not included in this diagram.

## 4.3 Comparisons of different design cases

The comparison of the different design cases is shown in Table 1 and 2. Overall, Design 1 employs a direct HEN that recovers 30.1 MW through multiple heat exchangers, balancing network investment and energy efficiency. This solution requires multiple stream splits to maximize the utilization of driving forces, resulting in a more complex network. Compared to the non heat integrated case, all the heat is needed by the fuel gas (assuming that no multiple-utility is used in heat exchangers), however in Design 1 (see figure 2), part of the heat is provided by heat recovery, therefore less fuel gas is required.

Design 2 introduces a hot oil stream to heat cold streams, enabling single-phase heat exchange and increasing heat recovery to 58.39 MW. This substantial improvement demonstrates that incorporating alternative heat transfer fluids can significantly enhance energy efficiency by extracting energy from exothermic reactions. Design 3 integrates a steam network to achieve multifunctional energy utilization. It generates both electricity and low-pressure steam while meeting the primary heating demands, offering a comprehensive solution for energy recovery and utilization.

Both Design 2 and 3 meet the heating requirements

for cold streams while generating low-pressure steam (LPS) of 12.2 MW and 11.06 MW, respectively. However, Design 3 relies on a steam turbine and high-pressure systems, which introduce additional complexities in control, safety, and integration with existing process streams, despite its ability to generate 7.8 MW electricity. In contrast, Design 2 includes additional equipment, such as hot oil loops and associated heat exchangers. This approach simplifies the challenges associated with phase-change heat transfer, offering a more straightforward and manageable solution for heat integration.

**Table 1:** Comparison between the conventional design and the Design 1 (downstream separations only)

| | Conv. | Design 1 | Savings |
|---|---|---|---|
| CU for reactor (MW) | 59.74 | 59.74 | - |
| Fuel gas (MW) | 17.26 | 2.26 | 86.91% |
| LP steam (MW) | 32.21 | 26.61 | 17.38% |
| CU (MW) | 44.20 | 23.60 | 43.96% |
| Area ($m^2$) | - | 3706 | - |
| No. HEx | - | 10+19 | - |
| Power Gen. (MW) | - | - | - |
| Energy ($kWh/kg_{AN}$) | 3.42 | 1.99 | 41.81% |

**Table 2:** Comparison between the Design 2 and 3 (including the reactions surplus heat)

| | Design 2 | Design 3 |
|---|---|---|
| Hot oil (t/h) | 301.8 | - |
| HU (MW) | 0 | 0 |
| CU (MW) | 43.15 | 44.30 |
| Area ($m^2$) | 2308 | 3036.2 |
| No. HEx | 16+8 | 3+12 |
| LPS Gen. (MW) | 12.20 | 11.06 |
| Power Gen. (MW) | - | 7.8 |
| Energy ($kWh/kg_{AN}$) | -0.84 | -1.30 |

**Note:** HU - hot utility required; CU – cold utilities required; Area – heat exchangers area; No. HEx – Number of heat exchangers, the number of heat exchangers for utilities is underlined; LPS Gen – low pressure steam generated; Power Gen. – power generated; AN production 120 ktpy

## 5. CONCLUSIONS

The comprehensive process developed in this study demonstrates the efficiency of integrated process design, coupling rigorous reaction modeling with thermodynamically and economically optimized separation strategies. Systematic heat integration can save around a half of the utility requirements compared to the conventional design. When utilizing the surplus reaction heat, generating LP steam and associated power has the lowest energy intensity, comparing to taking the reaction heat by heat oil and use it again as a hot stream in the process. However, relying on steam turbines and high-pressure systems might not be favorable due to the additional complexities. The energy integration strategies proposed in this research can be chosen based on different needs.

Including different designs and the quantification of their associated trade-offs ensure reliable performance and applicability in industrial processes. The flexibility of the resulting heat exchanger networks and utility configurations ensures that the findings can be appropriate to specific operational requirements. The results not only bridge an important knowledge gap in acrylonitrile production design but also offer a solution for optimizing similar exothermic processes characterized by complex product distributions and energy-intensive separations.

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