New Hybrid Process for Purification and Separation of MDI Isomers

ABSTRACT

Based on proven and long-standing experience, Sulzer has launched a new hybrid process which combines distillation and melt crystallization technology to manufacture pure monomeric MDI as well as any fraction of commercial interest. MDI from reaction is fed to the crude MDI distillation columns for purification. The purified crude MDI is sent on to the isomers distillation column, where a mixture with high 2,4'-MDI content (typically 50 to 60 % 2,4'-MDI) and pre-concentrated dimer-free 4,4'-MDI are produced. Following the distillation, pre-concentrated 4,4'-MDI is sent on to the melt crystallization section for final purification. The residue from crystallization is recycled to the distillation column. Optionally, the residue can be further depleted of 4,4'-MDI, thus allowing any dimer-free 4,4'-MDI mixture from 50 to 80 % to be produced by melt crystallization. The flexibility of Sulzer's new hybrid process makes it possible to control and modify the properties of a broad range of MDI products. Heat integration and optimum combination of distillation and crystallization equipment allow the plant to be built at a lower investment cost and to be run at lower operating costs compared to current purification technologies. Due to the efficiency of the separation train, this plant configuration is most attractive for new plants with more than 80'000 mtpy capacity. In existing plants, capacity can be expanded by adding one of the individual units to existing set-up.

Sulzer Chemtech is a world leader in mass transfer technology, and has developed extensive know-how in the hybrid distillation and crystallization process. The new process can be licensed without limitation from Sulzer and the products can be manufactured and sold worldwide without restriction.

INTRODUCTION

Methylene diphenyl diisocyanate (MDI) is manufactured from aniline by condensation with formaldehyde to produce methylene diamineline (MDA), which is in turn reacted with phosgene. The reaction forms a mixture of monomeric MDI (mainly 4,4'-MDI with an isomeric 2,4'-MDI content) and components of higher molecular weight. The crude MDI mixture is distilled to remove the components of higher molecular weight and heavy and light boilers. Conventional processes use either distillation or melt crystallization to produce a pure 4,4'-MDI from the purified isomer mixture and most already rely upon Sulzer distillation and crystallization technology. As a second product an isomer mixture with a high 2,4'-MDI concentration is produced.

Both unit operations are well understood and give a good performance but they also have drawbacks. Distillation consumes high amounts of energy and investment costs are usually high. Crystallization performs poorly with feed of high dimer content and the eutectic point of the solid-liquid equilibrium limits the recovery of 2,4'-MDI.

NEW HYBRID PROCESS

The Sulzer MDI process is characterized by three purification and separation steps (Figure 1):

1. The crude MDI distillation unit to remove components of higher molecular weight.
2. The isomers distillation unit, where a product with a high 2,4'-MDI content and a pre-concentrated, dimer-free 4,4'-MDI are produced.
3. A static melt crystallization unit for final purification of 4,4'-MDI.
Crude MDI Distillation Unit

Following the reaction, crude MDI is sent on to the crude MDI distillation column, where the Mono-MDI-Isomers and lights are separated from the MDI-oligomers and “Poly”-MDI.

Key features of the crude MDI distillation column include:

- Advanced vacuum distillation technology using Sulzer's structured high capacity packings MellapakPlus (Figure 2) and internals, resulting in excellent separation efficiencies and process advantages.
- The whole system is designed for very low pressure drop, resulting in high product yield and low degradation at moderate bottom temperature.
- The use of specially developed, highly fouling-resistant liquid distributors for MDI distillation service secures highly reliable operation (Figure 3). Shut down periods of two years and more have been achieved.
- The whole system is developed and designed to minimize stagnant zones where products could be trapped over a long period.
- The direct condensation of the distilled MDI results in a short residence time and only brief high temperature exposure. If intermediate storage is required, the MDI can be cooled down directly to low temperature levels. Very low dimer contents are achievable.
- Compact design avoids costly shell and tube condensors.

Isomers Distillation Unit

The isomers distillation unit consists of a fractionating column with 3 to 4 beds (depending on the lights concentration in the feed) of high efficiency structured packing. The design criterion for the whole system is low pressure drop and minimum residence time. The light boilers are withdrawn as top product, while the 2,4'- and the 4,4'-MDI are taken as side draws. The 4,4'-MDI is withdrawn in the vapor phase, condensed and directly cooled to less than 50 °C in a side condenser/sub-cooler. The bottom product consists of a mixture of 4,4'-MDI and oligomeric MDI. Specially designed falling film evaporators are used as reboilers.

- Compared to a single distillation system, where the 4,4'-MDI is distilled up to a purity of more than 99 %, the throughput with the hybrid system is practically doubled. Consequently the residence time is halved, reducing the formation of polymers and increasing the yield of pure 4,4'-MDI.
- In a hybrid system the isomers distillation unit is only about half as large as a single distillation unit. For large processing units (e.g. 160'000 tpy) only one distillation unit is required, instead of two.
- As the 4,4'-MDI concentration going to crystallization unit is only approx. 96 %, the reflux ratio is much lower. The energy consumption is reduced to approx. 52-60 % (exact figure depends on the recycle stream flow rate back from the crystallization unit).
- In the future high capacity wire gauze packing will further reduce the column dimensions for newly built distillation units. This packing will exhibit...
Figure 2: Two layer interface of Mellapak segments (left) and new MellapakPlus (right)

even lower pressure drop than the well known industrially widely used Sulzer BX, and will provide new possibilities to debottleneck existing distillation units. Additional benefits of a more compact column design are reduced liquid and vapor hold-up, which cut down residence time.

The use of well designed and fouling-resistant liquid distributors with a wide operating range adds additionally to operational safety and reliability of the plant.

Figure 3: Improved VEP splash-plate distributor

Residue Processing Unit

The residue processing unit can be designed to handle most of the residues from both the crude MDI and isomers distillation system. As the “Poly”-MDI is in itself a marketable product, the demands on the residue processing system depend very much on specific requirements and market demand. Depending on the capacity required, the residue processing unit consists of one or two thin film or short path distillation units, which can be flexibly operated either as independent units or in series. As the “Poly”-MDI is basically free of any light boilers, the vacuum system for the crude MDI or isomers distillation unit can be shared with the residue unit to provide the required low operating pressure. The distilled MDI from the residue stream is then recycled back to the feed of the Crude MDI column.

The residue processing unit can increase the yield of MDI significantly.

- The very gentle operation of a thin film evaporator / short path distillation unit operated at very low pressure allows MDI monomers to be distilled from a considerably viscous matrix of oligomers / polymers. This would not possible with other devices.
Static Melt Crystallization Unit

The pre-concentrated and dimer-free 4,4'-MDI from the isomers distillation is continuously fed to the melt crystallization unit. The melt crystallization section is equipped with Sulzer static crystallizers. The number of crystallizers is determined by the plant capacity. Figure 4 shows a plant with two crystallizers, which operate in an alternating mode. The crystallizers are fed batch-wise with material from a storage vessel.

The Sulzer static crystallizer (Figure 5) contains a number of vertical plates, heated or cooled by an internal circulation of heat transfer medium. The plates are suspended in the MDI feed melt to be purified. Slow cooling of the heat transfer medium below the freezing point of the melt causes a structure of 4,4'-MDI crystals to build up on the outer surface of the plates (Figure 6). Impurities, i.e. other isomers and heavies, are largely rejected from the growing crystals and are concentrated in the remaining melt.

After the desired fraction has been crystallized, the remaining liquid phase is drained from the crystallizer to the residue storage vessel. This material is recycled to the isomers distillation unit.

The purified crystalline layer remains adhered to the plates. It is further purified by sweating, which is gentle reheating close to the melting point. Trapped and adherent melt, which contains the impurities, drains off. Partial melting both washes the crystalline layer and rinses the equipment free of impure melt.

After sweating, the purified 4,4'-MDI crystal layer is totally melted and drained to the product storage vessel. From here it is pumped out continuously to downstream processes.

One crystallization stage is used to reach the desired product purity of at least 99.5 wt-%. However, any desired product purity can be reached by further sweating or by repeating the whole cycle in the same crystallizers. Countless combinations of purification algorithms can be imposed upon the crystallizers reliably and reproducibly.

The crystallizers alternate between a cooling and heating mode of operation. Brine with a temperature of 5 to 10 °C is sufficient to provide cooling energy. If brine is unavailable, the plant is equipped with a chiller. Due to the low melting point of MDI, hot water or any low pressure steam can be used to heat and melt the crystals.
Key features of static melt crystallization are:

- Excellent product quality with high color stability and high yields. Melt crystallization ensures colorless product, even in cases of process upsets in the synthesis section which generate levels of color bodies higher than those which can be handled by the distillation units.
- Proven large scale industrial technology for MDI with a wide variety of other monomer applications, from glacial acrylic acid to optical grade BPA
- Incomparably flexible operation allows products to be tailor made to suit particular applications
- Extremely robust operation and recovery from process upsets without off-spec product losses
- No moving parts except standard pumps or valves

CHARACTERISTICS AND FEATURES

The new hybrid MDI process is based on Sulzer Chemtech's proven experience in distillation and melt crystallization technology. The design of and interfacing between all plant components are optimized and heat integration is secured throughout the entire system. This allows the plant to be run most economically. Considerable reductions in high pressure steam, cooling water and electricity consumption are achieved.

High capacity distillation columns equipped with Sulzer Chemtech's structured packing enable efficient separation in a small diameter column. More separation performance per column height is achieved, which results in lower energy consumption for the specified purity. Low pressure drop is a characteristic of structured packings (especially the new Sulzer MellapakPlus), and results in decreased bottoms temperature and pressure. Heat integration becomes feasible due to the small temperature difference over the columns. Lower pressure means generally higher separation efficiency and therefore less separation stages.

Sulzer Chemtech's melt crystallization is a proven technology for MDI as well as for many organic chemicals such as p-xylene, acrylic acid, bisphenol A, tar chemicals or paraffin waxes. Crystallization is carried out without transporting crystals, eliminating the typical problems of crystallization, such as filtration or incrustation. Start-up and shut down are simple. In fact the plant can be stopped at any stage in the process and operation restarted at the same point at any time. Furthermore, the plant is designed for zero emissions.

The combination of convenient equipment allows a straightforward implementation of computer-based control systems. Only a minimum of operational supervision is required.

DESIGN AND SCALE-UP

For the distillation of MDI, Sulzer has performed numerous continuous pilot tests, mainly to predict the behavior of the isomers. However, a pilot test for MDI distillation cannot satisfactorily answer all questions regarding polymerization, product color etc. This makes feedback from industrial experience very important. Sulzer, with its decade-long history of MDI distillation, has developed extensive industrial scale know-how for this application, and thereby eliminated scale-up uncertainty.

Sulzer’s test results and industrial experience allow process simulations to be performed for a wide range of feedstock compositions. Proposals are consequently tailored to suit particular customer specifications.

Commercial process design of melt crystallization plants is always based on pilot tests. Each static crystallizer consists of a series of vertical heat transfer elements, all working under identical conditions to provide total similarity with regard to geometry and hydrodynamics, as well as to heat and mass transfer.

Pilot testing can consequently be carried out in a pilot crystallizer equipped with two of these identical elements, making scale-up clear and predictable. No uncontrolled physical or engineering dependence on the number of crystallizer elements is introduced. In this way uncertainties usually involved in scale-up are totally eliminated. Feedstock described in the case study below has been investigated in Sulzer's pilot plant in Switzerland.

CASE STUDY

The new hybrid process is interesting for both grass-roots investments and large-scale debottlenecks of existing operations. In both cases, investment and operating costs are lower than those of conventional MDI isomers separation processes, product quality is superior and operability is improved.

The case study below describes an application that uses a crude MDI stream from a typical MDI reaction plant. The goal is to produce 4,4'-MDI with a purity of at least 99.5 wt.-% and 2,4'-MDI with at least 60 wt.-%. The crude MDI capacity is 160'000 tons per year.

The composition and capacity for feed and products are listed in Table 1 for the hybrid system.

Owing to heat integration and optimum combination of distillation and crystallization, the plant runs with low operating costs. Consumption of higher pressure steam for the isomer distillation is reduced from 5.5 MW to 3.4 MW for the hybrid system (Table 3). Electric power consumption is about equal. Only a small amount of cooling water is needed for the crystallization.

The residue of the crystallization is a isomer mixture with 80 wt.-% of 4,4'-MDI and 20 wt-% of 2,4'-MDI which can be used as a product. If the residue is not recycled to the distillation, the energy consumption is reduced to 2.80 MW. The composition and capacity for feed and products are listed in Table 2 for the case that the residue is not recycled.
### Table 1: Composition and capacity of feed and product with residue recycling

<table>
<thead>
<tr>
<th>Stream</th>
<th>Crude MDI</th>
<th>Pure 4,4’-MDI</th>
<th>Rich 2,4’-MDI</th>
<th>Polymeric MDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,4’-MDI, wt-%</td>
<td>5.2</td>
<td>&lt; 0.5</td>
<td>&gt; 60</td>
<td>1.1</td>
</tr>
<tr>
<td>4,4’-MDI, wt-%</td>
<td>69.0</td>
<td>&gt; 99.5</td>
<td>&lt; 40</td>
<td>23.6</td>
</tr>
<tr>
<td>Dimer, wt-%</td>
<td>1.0</td>
<td>&lt; 0.045</td>
<td>&lt; 0.03</td>
<td>2.8</td>
</tr>
<tr>
<td>Tri and higher, wt-%</td>
<td>24.0</td>
<td>&lt; 0.02</td>
<td></td>
<td>72.3</td>
</tr>
<tr>
<td>others, wt-% (mainly 2,2’-MDI)</td>
<td>0.8</td>
<td>Traces</td>
<td>2 - 4</td>
<td>0.2</td>
</tr>
<tr>
<td>Color, APHA</td>
<td></td>
<td></td>
<td>&lt; 10</td>
<td>&lt; 10</td>
</tr>
<tr>
<td>Capacity, kg/hour</td>
<td>21,000</td>
<td>11,000</td>
<td>1,265</td>
<td>8,735</td>
</tr>
</tbody>
</table>

### Table 2: Composition and capacity of feed and product without residue recycling

<table>
<thead>
<tr>
<th>Stream</th>
<th>Crude MDI</th>
<th>Pure 4,4’-MDI</th>
<th>Rich 2,4’-MDI</th>
<th>Isomer mixture 80% 4,4’-MDI</th>
<th>Polymeric MDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,4’-MDI, wt-%</td>
<td>5.2</td>
<td>&lt; 0.5</td>
<td>&gt; 60</td>
<td>20</td>
<td>1.1</td>
</tr>
<tr>
<td>4,4’-MDI, wt-%</td>
<td>69.0</td>
<td>&gt; 99.5</td>
<td>&lt; 40</td>
<td>80</td>
<td>23.6</td>
</tr>
<tr>
<td>Dimer, wt-%</td>
<td>1.0</td>
<td>&lt; 0.045</td>
<td>&lt; 0.03</td>
<td>&lt; 0.025</td>
<td>2.8</td>
</tr>
<tr>
<td>Tri and higher, wt-%</td>
<td>24.0</td>
<td>&lt; 0.02</td>
<td></td>
<td>72.3</td>
<td></td>
</tr>
<tr>
<td>others, wt-% (mainly 2,2’-MDI)</td>
<td>0.8</td>
<td>Traces</td>
<td>2 - 4</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>Color, APHA</td>
<td></td>
<td></td>
<td>&lt; 10</td>
<td>&lt; 10</td>
<td></td>
</tr>
<tr>
<td>Capacity, kg/hour</td>
<td>21,000</td>
<td>9,700</td>
<td>750</td>
<td>2,050</td>
<td>8,500</td>
</tr>
</tbody>
</table>

### Table 3: Energy consumption for isomers distillation unit

<table>
<thead>
<tr>
<th>Process</th>
<th>MW</th>
<th>equivalent tons of steam per hour</th>
</tr>
</thead>
<tbody>
<tr>
<td>isomers separation only by distillation</td>
<td>5.5</td>
<td>11.7</td>
</tr>
<tr>
<td>hybrid process with residue recycling</td>
<td>3.4</td>
<td>7.2</td>
</tr>
<tr>
<td>hybrid process without residue recycling</td>
<td>2.8</td>
<td>5.9</td>
</tr>
</tbody>
</table>

### CONCLUSION

The new process allows the MDI-process to be optimized for maximum purity, yield and overall plant economy. Main features are:

- Reduced capital and operating costs due to optimized process integration
- High product yield and color stability, due to limited temperature/time exposure
- Maintenance cost savings, due to use of proven equipment
- Highly flexible operation matches product quality to changing market demands
BIOGRAPHIES

Manfred Stepanski

Manfred Stepanski joined Sulzer Chemtech Ltd. in 1990 in Switzerland, where he was primarily responsible for process engineering and project management. He is currently working as a Regional Sales Manager and is also responsible for design and evaluation of new melt crystallization applications. He holds a diploma in mechanical engineering from the Technical University Aachen (Germany) and a doctorate degree from the University of Bremen (Germany), where he also provided research assistance to the department of Chemical Engineering.

Peter Faessler

Peter Faessler holds a B.Sc. degree in Chemistry and Chemical Engineering of the Basle Engineering College / Switzerland. He joined Sulzer Chemtech Winterthur / Switzerland in 1982, as project and sales engineer for mass transfer products. From 1986 till 1990 he worked at Sulzer Brazil and from 1991 to 1992 at Sulzer Mexico as product manager for Sulzer Chemtech. In 1992 he took over the position of Sales Manager of Sulzer Chemtech Singapore. Since 1996 he has been responsible for all technical aspects as Technology Manager for Asia Pacific.