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GEA MDI Splitting Process

A novel hybrid combination of evaporation/distillation and melt crystallization

Application

Methylene diphenyl diisocyanate (MDI) is an organic chemical which is one of the main components for the production of polyurethanes. Crude MDI is still only commercially produced via the phosgene route and contains three diisocyanate isomers, oligomeric polyisocyanates (tri,tetra,penta ,etc isocyanates), byproducts and impurities. The present market requires separate products or blends thereof to make polyurethanes with a wide range of properties. The MDI splitting plant is responsible for producing the commercially viable fractions from this crude feed.
The typical MDI fractions of commercial importance can be generally classified as:

(a) Polymeric MDI (mixtures of oligomeric and 2,4 / 2,2 & 4,4 MDI),
(b) Pure MDI (mostly 4,4 with some 2,4 MDI) and
(c) Mixed MDI Isomers (a range of 2,4 / 2,2 & 4,4 MDI excluding oligomeric)

Features

This novel hybrid configuration provides significant advantages over the conventional process; more than 50% energy reduction can be realized through the combination of optimized distillation with an efficient crystallization system and reduced vacuum load The product quality is improved by reducing temperature related product degradation, less generation of toxic light impurities and reduced dimer formation. Fewer and smaller components provide for reduced CAPEX.
Flexible operation is key to the design; higher 2,4 MDI compositions can be realized depending on the crude feed composition. The crystallization capacity is based on a pure 4,4 MDI output and increased 2,4 MDI can easily be handled on the same equipment (filtrate flow is not limiting). The ratio of 2,4 MDI in the feed to 2,4 MDI in the Pure 4,4 MDI product is thus maximized resulting in a high overall rejection in the Pure 4,4' MDI fraction of the close boilers that are not removed in the distillation process.

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Process Description

Traditionally, MDI splitting plants are set up as multi-step distillation plants to split the various MDI fractions. Occasionally melt crystallization (as final step with low purification ratio) is used for the Pure 4,4 MDI production. The GEA hybrid process solution does not separate the isomers by distillation and therefore offers low energy consumption, improved product quality and lower capital cost through the novel combination of evaporation/distillation processes and continuous suspension-based melt crystallization to produce the specific MDI fractions.

A general principle in MDI process design is to avoid water or steam as direct utility to avoid the risk of water ingress in the MDI process. Appropriate heat transfer fluids are used as intermediates.

This distillation unit must operate under rather extreme vacuum (2-10 mBar) to minimize operating temperature and preserve product quality. The proprietary GEA vacuum utility is designed with ejectors driven by monochlorobenzene (MCB) vapors, thus complying with the need to avoid any moisture inside the MDI process.

The first step in the splitting process is always the separation of the higher oligomers from a part of the three diisocyanate isomers. The only possible route is by evaporation/distillation. Commercial crude MDI feedstocks can vary in their specific composition, the GEA process allows control of the diisocyanates concentration in the Polymeric MDI bottoms product to give the desired viscosity.

The mixed diisocyanate isomer vapors are condensed via the top of the column. The condenser design allows the rapid cooling of the diisocyanate vapor stream and avoids liquid holdup, thus strongly reducing the formation of unwanted dimers.

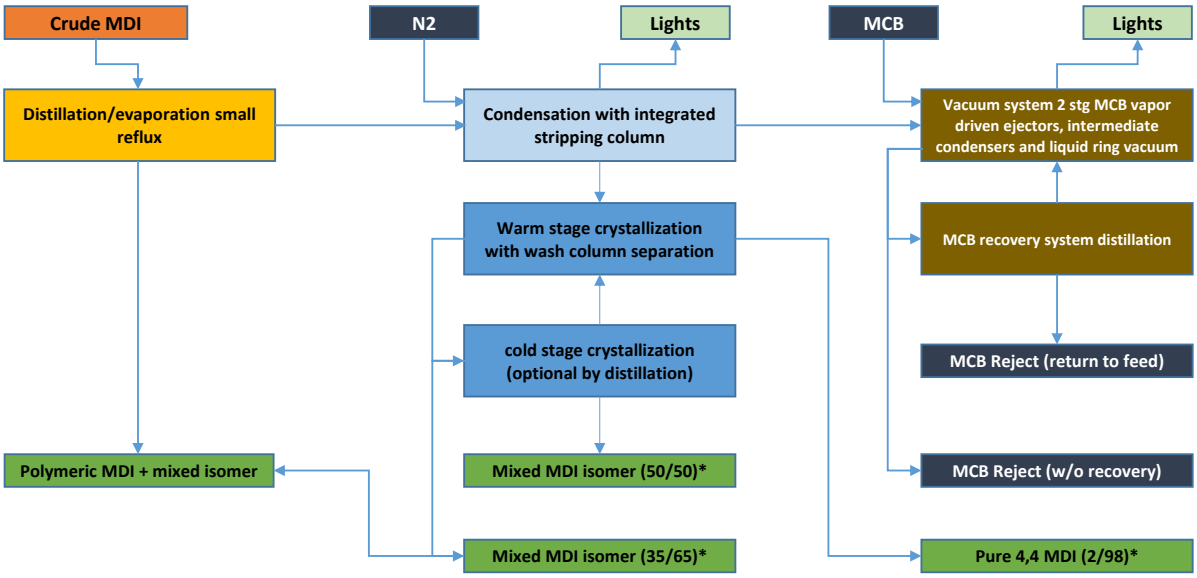
The concentration of the toxic phenyl isocyanates and other lights is reduced to below necessary limits by a stripping element or a low energy distillation step.

The condensed diisocyanate mixed isomers stream (distillate) free of oligomers and light impurities is fed via a small buffer tank continuously to the crystallization step.

The GEA process uses a patented two stage suspension crystallization unit with wash columns for the final solid/liquid separation and this unit produces the Pure 4,4 MDI and the Mixed isomer fractions (b & c mentioned above). The distillate is fed to the crystallization unit where the final product purity is simply controlled by the equilibrium temperature of the slurry produced in the crystallizer. The wash column efficiently separates the Pure 4,4 MDI crystal from the 2,4/2,2 enriched liquid. The liquid filtrate is crystallized at a lower temperature in a second cold stage crystallizer generating the so called 50/50 MDI consisting of about half 2,4 (plus some 2,2 isomer) MDI and half 4,4 MDI. Since this is near the eutectic point of the mixture higher concentrations of 2,4 MDI are not possible with crystallization and if needed, this second crystallization step can be totally or partially replaced with GEA distillation. Due to the high separation efficiency in the wash columns, there is no need for an intermediate distillation step to reach the desired composition of the pure (4,4) MDI.

GEA can design the hybrid plant configuration adjacent to the crude production complex or alternatively as a standalone unit.

GEA has in house a unique combination of evaporation, distillation, vacuum and crystallization technologies that are needed in the hybrid MDI splitting plant. Proprietary process and equipment design coupled with the required know-how results in a process with the highest possible asset productivity.



* Composition of 2,4+2,2 MDI / 4,4 MDI

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