Nitration and Sulfuric Acid Recovery: Effective Reaction Control and Efficient Acid Recycling for Economic Production

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Introduction

Nitration of aromatic organics is one of the key processes of modern chemical industry. It produces various precursors of chemicals and products (i.e. nitrobenzene, nitrotoluene or chloronitrobenzene). The nitration is performed with a mixture of sulfuric and nitric acid which is brought into contact with the organic compounds by intensive mixing. Therefore, the process involves the handling of corrosive acids as well as potentially hazardous, toxic and explosive organics. Downstream of the nitration unit a product washing and separation is required (see Figure 1).

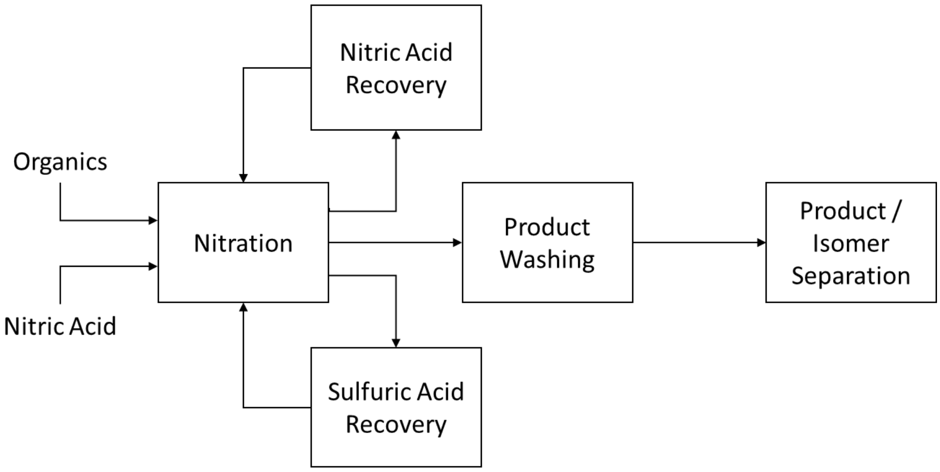

Figure 1: Overview of the nitration process with acid recovery and product purification.

The design and operation of nitration plants requires a balancing of various design aspects. Those aspects can be expressed by a tension triangle (Figure 2) where safety, CAPEX and OPEX are located on opposite sides. The main driver for the investment cost of nitration plants is the requirement to use corrosion resistant materials like glass-lined steel, fluoropolymer-lining or tantalum for the major part of the nitration process. Instrumentation required for a safe and reliable operation further increases the CAPEX. An efficient recovery of acids (sulfuric & nitric acid) and an efficient reaction control to achieve high product yield allows to optimize OPEX. By applying advanced processes with optimized (tubular) reactors as well as optimized downstream processing of the product mixture all design aspects can be considered.

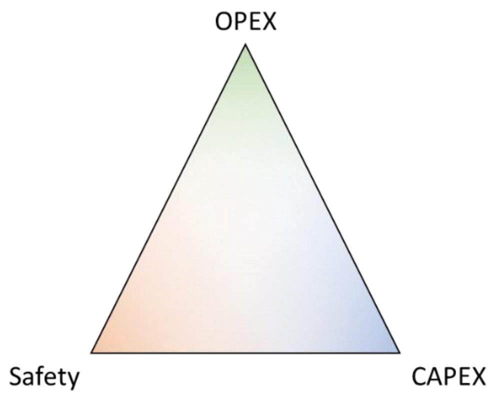

Figure 2: Tension triangle for the plant design and operation.

Nitration Reaction

Nitration describes the addition of one or more nitration groups to an aromatic compound involving a reactive mixture of sulfuric and nitric acid (so called nitration acid). The sulfuric acid is used as dehydration agent and promotes the formation of reactive nitronium ions (Eq. 1). The nitration as addition of the nitronium ion to the aromatic compound occurs in the aqueous acid phase. Thus, the reaction rate is determined by the mass transfer rate between the organic and the acid phase (Figure 3). An increase of the surface area and therefore dispersion of the organic phase in the acid phase is required for an efficient reaction. This can be achieved by intensified mixing. The overall nitration reaction (Eq. 2 as example for benzene) is exothermal, consumes nitric acid and dilutes the sulfuric acid with the produced water.

$H_2SO_4 + HNO_3 \rightarrow HSO_4^- + H_2O + NO_2^+$	**Eq. 1**
$C_6H_6 + HNO_3 \xrightarrow{H_2SO_4} C_6H_5NO_2 + H_2O + heat$	**Eq. 2**

Nitration reactions can be realized in isothermal and adiabatic reactors. Isothermal reactors provide the opportunity to effectively control the reactor conditions in terms of temperature, acid concentrations and stirring speed. However, relatively large heat exchange areas are required for the nitration reactors to maintain the isothermal conditions. Furthermore, the recovery of the sulfuric acid requires a subsequent heating and evaporation of the produced mixture. Adiabatic reactors, as developed and successfully commercially applied by KBR, allow for an efficient use of the reaction heat released by the nitration (Eq. 2).

With this type of systems, heat is utilized to flash the excess water and recover the sulfuric acid under vacuum conditions. Furthermore, adiabatic tubular reactors provide the possibility to efficiently disperse the organic phase by applying shear forces on the organic droplets within the acid phase without use of stirrers. An improved dispersion reduces the formation of byproducts and increases the yield. For that reason, tubular reactors are commonly used for the adiabatic nitration of benzene [1].

A further transfer of that reactor concept to other aromatic compounds is possible and still ongoing. In many cases intensive screening studies are required to determine the necessary operation conditions of the tubular reactor (acid concentrations, temperature, flow rates). Such studies can be performed in small tubular reactors as done for benzene, chlorobenzene and toluene [2].

Although the control of adiabatic reactors is more challenging, they integrate all design aspects by combining an efficient use of the reaction heat (reduced OPEX), the integration of two plant units in one (reduced CAPEX) and reliable transfer of the reaction heat (increased safety). By achieving a high yield and a complete conversion of the nitric acid, the costs for product purification and acid recovery are reduced.

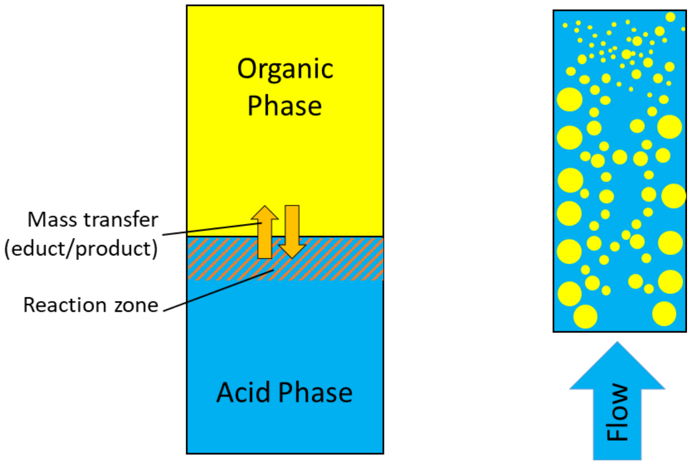

Figure 3: Scheme of the nitration reaction as sequence of mass transfer between immiscible phases and the reaction (left side). The mass transfer is promoted with the application of tubular reactors which increase the dispersion of the organic phase in the acid phase (right side)

Acid Recovery

Traditionally the sulfuric acid recovery is an addon to the isothermal nitration (e.g., in the case of mono- and dinitrotoluene production). For those plants several waste streams consisting of spent sulfuric acid and washing liquid (yellow water) must be treated which contain residual nitric acid, sulfuric acid and organics. An efficient separation in the sulfuric acid recovery is required to return valuable compounds like acids and organics to the nitration process. Various processes involving stream stripping (denitration) and acid concentration are available to recover the acids and organics from those waste streams.

For adiabatic nitration plants the sulfuric acid recovery is directly integrated into the process and the same building (see Figure 4). These systems allow an efficient use of the reaction heat to evaporate water in the acid recovery step. Sulfuric acid, that is separated from the organic products, is discharged to glass-lined evaporators operating under vacuum conditions to flash the water and recover the sulfuric acid. To achieve higher sulfuric acid concentrations two or more evaporation steps equipped with tantalum heat exchangers can be used. The concentration of the sulfuric acid is adjusted by a combination of temperature and vacuum.

Although nitration processes target a complete conversion of the nitric acid and a high yield, some nitrogen oxides are formed in all nitration reactions. Effluent gases can be treated by catalytic reduction or alkaline washing to remove nitrogen oxides. However, such off-gas treatment techniques destroy a valuable source of nitric acid. Pressure absorption is an established solution to recover nitric acid from nitration off-gases. Similar to nitric acid production, nitrogen monoxide is oxidized and absorbed into water. For nitration plants the use of liquid ring compressors allows an efficient absorption within the compressor and the absorption column equipped with cooled trays.

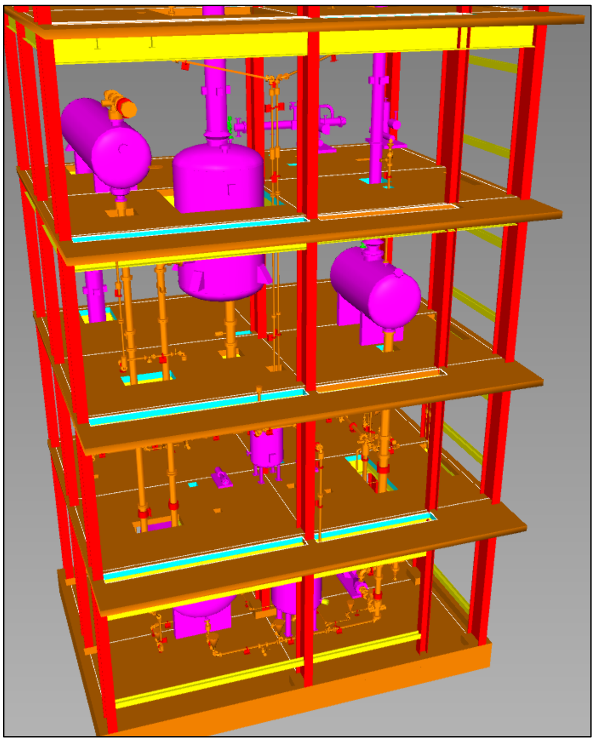

Figure 4: 3D model of a typical adiabatic benzene nitration (70'000 tons per year) with integrated sulfuric acid recovery. Equipment is indicated in pink and process pipes in orange.

Product Purification

The product separated from the sulfuric acid after the nitration reactor contains residual sulfuric acid, nitric acid, nitrogen oxides and other byproducts like nitrophenols in case of benzene nitration. With optimized reaction conditions, the formation of byproducts can be reduced but not eliminated. Therefore, acidic substances as well as unwanted byproducts must be removed before a further use of the product. Additionally, many nitration processes operate with an excess of the educts, which must be separated.

The purification of the crude nitration product is a sequence of two or more steps like washing to remove acids and phenolic byproducts, rectification or stripping to remove the unreacted organics, and the separation of the product's isomers. The washing process includes various steps of acidic, alkaline and neutral washing [3]. Removing the acid compounds, transfer the weakly acidic phenols into the aqueous phase and lowering the temperature, allows a change of the construction material. Stainless steel as material of construction instead of corrosion resistant glass- or fluoropolymer-lined steel reduces the investment costs for the purification step, significantly. Accordingly, the various washing steps allow for a purification in a rectification or stripping column without corrosion problems.

Conclusion

Nitration plants combine various challenging process steps. Their design and operation require detailed knowledge of corrosion resistant materials, advanced reaction technology and the integration of the various processing steps. Adiabatic nitration systems, as offered by KBR, provide the most efficient design in terms of optimized CAPEX, OPEX and plant safety.

Literature

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[3] H. Winterbauer, (2004). New Process to Minimize Effluent Water in the Production of DNT. Engineering in Life Sciences 4(1), 97-100.