Improvements in Waste Minimization, Process Safety, and Running Costs by Integrated Process Development

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Abstract. By the development of a new recycling process for spent acid in the manufacture of the 1-chloro-2,4-dinitrobenzene (CDNB) effective improvements in the waste balance and the process safety were achieved. Under the old process, the sulfuric acid generated could not be sold to the low strength sulfuric-acid market, because it had a high concentration of organic contaminants. The resulting waste stream had long been a costly issue. A laboratory feasibility study followed by pilot evaluation qualified continuous extraction as an appropriate technology for purifying the acid. With the change from a batch extraction process to a continuous extraction on a column, the quality of the acid could be improved such that use without further regeneration is possible now. Thus, the continuous extraction column offered improved efficiency, safety, and product consistency as compared to the corresponding batch process.

The Process

An overview of the CDNB process may assist in understanding the formation of the acid phase and the acid-phase treatment (*Fig. 1, a*). Monochlorobenzene (MCB) is nitrated with nitric acid in the presence of sulfuric acid to form chloro-(mono)nitrobenzene (CMNB), then nitrated again in the same reactor to form CDNB. After completion of the nitration, the acid phase is allowed to separate from the organic phase. The acid phase is pumped from the reactor to a holding tank. This untreated acid contains sulfuric acid, nitric acid, nitrous acid, and a small amount of CDNB, as given in *Table 1*. An overall material balance is shown in *Table 2*.

The content of organic material prevents the direct reuse of the acid. Therefore, the untreated acid has to be purified.

Previous Waste Acid Purification Technology

In the old process, this was achieved by batch extraction with MCB to remove nitric acid and CDNB. Finally, nitrous acid was removed from the untreated acid by reaction with urea to yield a treated acid stream.

The batch extraction using a single stirred tank did not produce a high purity waste acid stream. There were several reasons for the low purity. Firstly, the tank was inadequately agitated for reaching mass transfer equilibrium. Secondly, a one-tank system did not allow countercurrent contacting to conserve driving force. Thirdly, driving force was further sacrificed by multiple extractions with a single MCB charge.

This meant significant costs associated with both the extraction (MCB phase) and raffinate (acid phase) streams were incurred. The raffinate had a high level of organic contaminates (0.2–0.7%) and had to be regenerated off-site at considerable expense. Another cost associated with the raffinate was the follow-up, labor-intensive batch reaction of the nitrous-acid component with urea powder. The higher cost of the extract was due to the special batch procedure required for conversion to CDNB. This special procedure was labor-intensive because of the high amount of CMNB and CDNB in the extract.

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Table 1. *Material Balance* (per 100 kg of CDNB)

	Old process		New process	
Input				
MCB	58.0– 61.3 kg		55.1 kg	
Urea solution	70.9– 74.9 kg		67.8 kg	
Nitric acid	123.7–130.7 kg		114.5 kg	
Sulfuric acid	amounts varied		1.1 kg	
Output		Recycle status		Recycle status
CDNB	100 kg		100 kg	
Treated acid (as-is basis)	ca. 163 kg	100% regenerated	ca. 144 kg	100% sold
Gas/vapor	**	not scrubbed	**	scrubbed/recycled
Waste* (as-is basis)	ca. 127 kg	0–20% recycled	ca. 31 kg	100% recycled

*   spent CDNB wash water
** data not available

Table 2. *Contaminate Content in the Treated and Untreated Acid Streams*

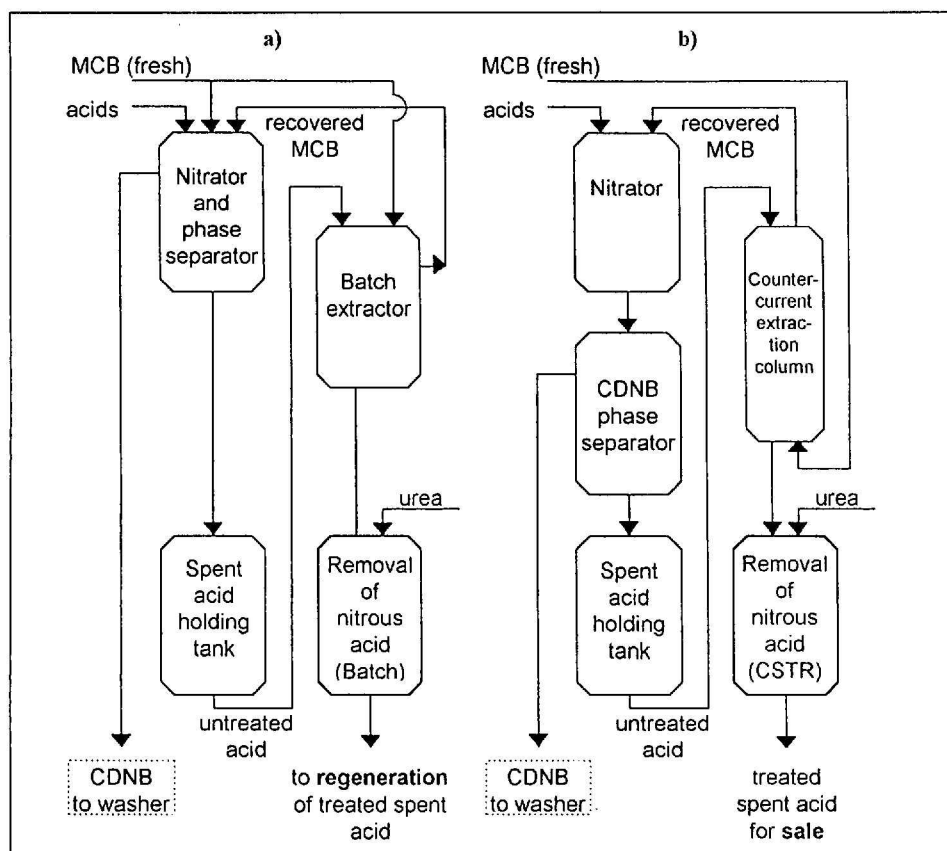| Component	Untreated	Previous extraction	Specification for process design	New extraction (pilot plant)	New extraction (production)
Nitric acid	3.5%	< 0.1%	< 0.1%	< 0.1%	< 0.1%
Nitrous acid	1.0%	< 0.2%	< 0.2%	< 0.1%	< 0.15%
Organics	3.5%	0.2–0.7%	< 0.05%	< 0.02%	< 0.04%
Sulfuric acid	74%	79–81%	74–77%	75–77%	74–77%

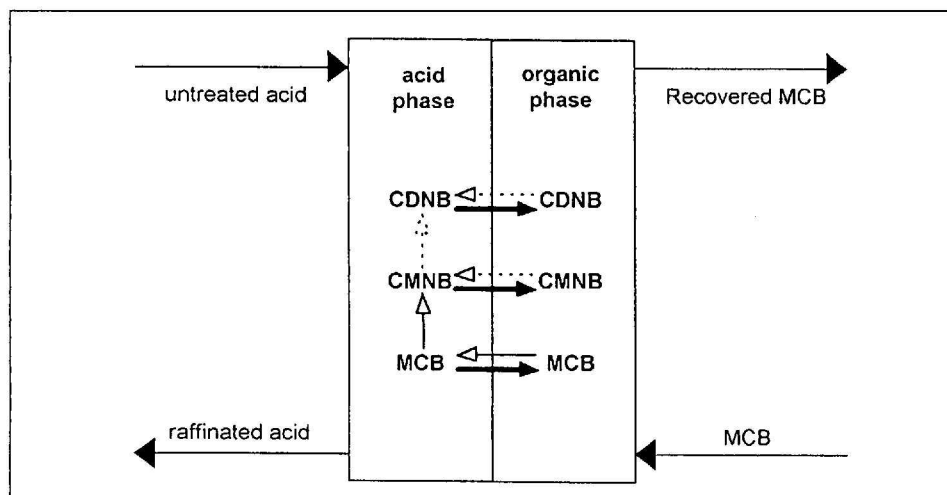Fig. 1. *Process flow diagram:* a) *old and* b) *new process*

Fig. 2. *Modeling scheme showing the phase equilibria* (as a function of the position along the column) *and the chemical reaction.* Nitration of MCB occurs in the acid phase due to residual content of nitric and nitrous acid.

Developing a New, Improved Technology

To solve the problem mentioned above, the development of a continuous extraction process was envisaged. For the design of this new extraction process, fundamental process data was measured in the laboratory using liter-scale batch equipment. Distribution coefficients were determined from simple, sequential equilibrium batch extractions.

Despite the detailed experimental characterization of the extraction in the laboratory, the development of a continuous extraction process turned out to be very challenging. First, a modeling approach was chosen to design a continuous extraction column. Several simulation programs were applied. However, the extraction combined with a simultaneous chemical reaction (*i.e.*, the mononitration of MCB due to the residual nitric acid in the untreated sulfuric acid, see *Fig. 2*), where the reaction generated more material to be extracted, posed considerable difficulties for the simulation.

The first modeling approach used simplistic, in-house computer modeling software. This software was not capable of handling the complication of chemical reaction with extraction. Unsuccessful modeling attempts were also made with two commercially available state-of-the-art simulation software packages, which were successfully applied to similar problems before [1].

As an alternative piloting was chosen to be the approach for column design. Two stages of piloting were identified: The first was a feasibility study by *Otto York* using a *York-Scheibel* continuous extraction column. The column was constructed of glass and stainless steel, had 36 stages, was three inches (7.6 cm) in diameter, and had variable speed agitation. That test proved continuous extraction was feasible. During the study, it was determined that a cooling jacket on the column was necessary, because the reaction of MCB and residual nitric acid was highly exothermic. A second stage of piloting for process optimization was performed in the *Clariant* pilot-plant column (*Fig. 3*). The pilot-plant column was the same as the *Otto York* column with the addition of a cooling jacket. Using this column, final design parameters and operating conditions were generated. This in-house design parameter generation allowed competitive bidding for construction of the production extraction column.

Continuous extraction allowed for the development of a continuous system for

the elimination of the nitrous acid in the acid stream by reaction with urea. A continuous stirred-tank reactor (CSTR) was designed based on laboratory liter-scale batch data followed by verification at the *Clariant* pilot-plant in a CSTR. The use of a liquid urea-metering system was the key component to develop a reliable, less labor-intensive process.

Fig. 1, b shows the flowsheet of the new CDNB production. In addition to the development of the new extraction process, the wash process of the organic CDNB phase was redesigned too: Wash water was reduced by 70%, and this reduction allowed a full utilization of this 'waste' in an other process; thus, leaving zero liquid waste.

Material of Construction

The selection of materials of construction was an important aspect of the project, because corrosion of the numerous rotating agitator parts risked column failure. If the column fails, the entire CDNB process would be shut down. Corrosion mechanisms studied were general etching, pitting, and crevice corrosion. Materials of construction were tested in the pilot-plant laboratory by exposing coupons of each material to the acid phase in an agitated batch reactor. A corrosion consultant was hired to analyze the coupons. Based on the results of the analysis, the following materials were chosen: shell of the column should be 316 l stainless steel, internal moving parts should be Alloy 20 Cb-3, and thermoplastic parts should be Rulon J.

Thermal Safety

The safety of the dinitration process was assessed, based on calorimetric data obtained in Contalab and RC-1 calorimeters in the safety laboratory. As shown in *Fig. 4, a*, the nitration is strongly exothermic (660 kJ/kg reaction mass). Under the process conditions applied, the reaction is essentially dosage-controlled, *i.e.*, no accumulation occurs. The differential thermoanalysis (DTA) of the reaction mixture was investigated SEDEX (stirred), using closed test autoclaves (*Fig. 4, b*). The reaction mass is stable for at least 8 h up to 110°. The exothermic decomposition with a potential of about 1200 kJ/kg reaction mass is initiated at temperatures above 300 K but may occur at lower temperatures in case of contamination with metal ions, in particular with iron.

In case of cooling failure or stoppage of the stirrer, self-heating of the reaction
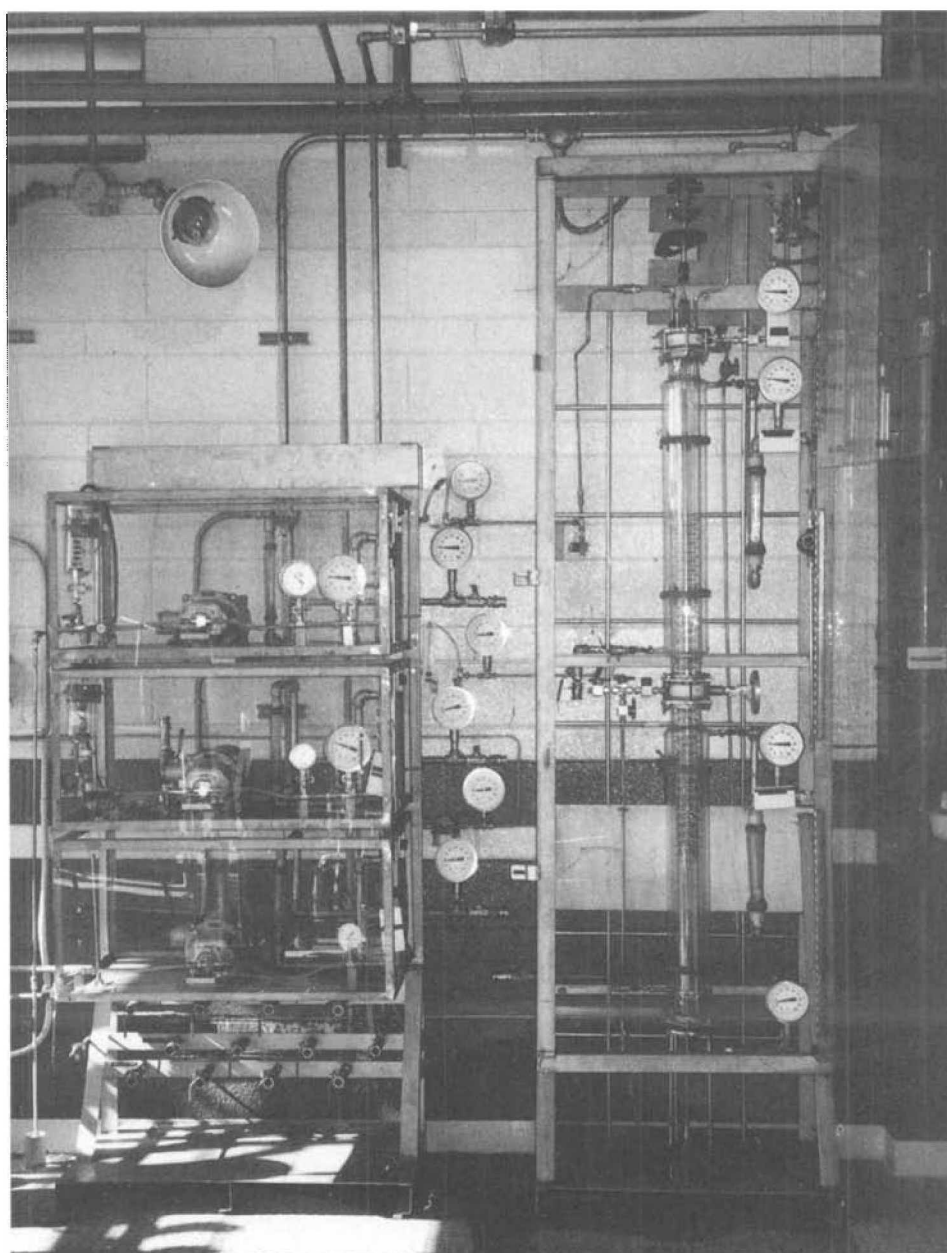

Fig. 3. *Pilot-plant column showing at the left* (top-down) *the three pumps for spent acid, MCB, and treated spent acid* (raffinate). The outlet for the MCB-containing CDNB and CMNB is at the top right of the column.

mass can be prevented by interruption of the addition of the aromatic compound. Furthermore, the dosage is interlocked with the stirrer in order to prevent accumulation in case of unintended stoppage of the stirrer.

Moreover, special care is taken to ensure fast mixing of MCB in order to avoid the formation of local hot spots at the feed point.

Beside small amounts of CDNB, the untreated acid still contains nitric acid. As the CDNB is extracted from the acid into the organic phase, also nitration of the MCB occurs. Due to the low nitric-acid concentration mostly mononitration to CMNB will occur. Nevertheless, the heat production of 170 kJ/mol CMNB has to be taken into account for the design of the extraction process.

Comparison of the Old and the New Process

Improvements are evident from the material balance (*Table 1*): Decrease of raw-material consumption, and the complete elimination of liquid waste by recycling. Since the new technology was started up, the treated acid has met all of the design specifications. The *Clariant* Safety and Environmental Department developed the new specifications for contaminants in the treated acid stream based on current and anticipated regulatory standards along with the requirements of potential customers. *Table* 2 summarizes the contaminate content in the untreated acid and the treated acid stream from various sources.

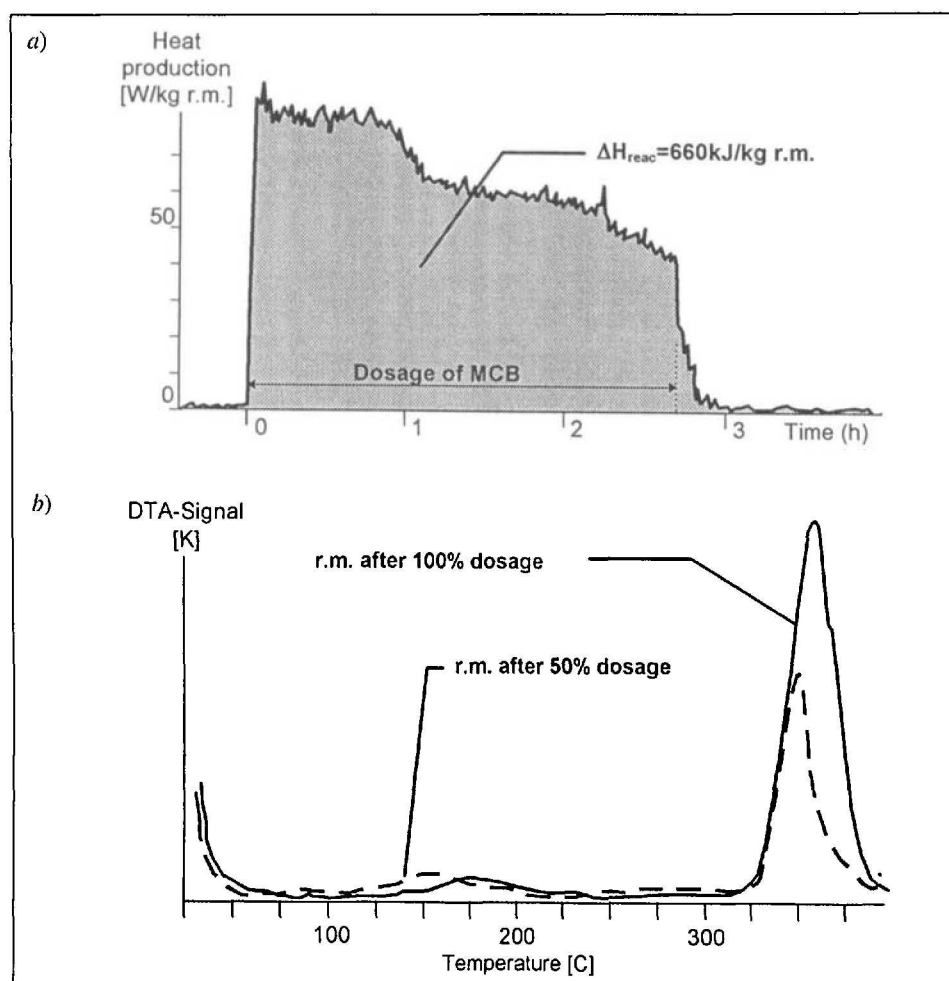A relevant safety aspect is that the total holdup in production decreased slightly

Fig. 4. a) *Reaction Calorimetry of the dinitration process.* The heat production almost immediately drops to zero after termination of MCB dosage, *i.e.*, there is only negligible accumulation of unreacted MCB. b) *Dynamic differential thermoanalysis* (DTA) *of the reaction mixture* (r.m.). After 50% of MCB addition, the small exothermic signal above 110° is attributed to the nitration of unreacted MCB/CMNB. The main exothermic signal above 300° results from the decomposition of the nitro compounds [2].

although throughput was considerably increased.

Concluding Remarks

The higher purity of treated acid stream produced by the new process is not classified as a hazardous waste stream by the authorities. This ruling allows the transportation and use of the treated acid without extra regulatory constraints other than those applying to acids in general.

An attractive rate of return is being realized on the capital investment: The savings of using the extraction column are such that the return on investment is as short as one year. 80% of this savings result from the cost avoidance associated with off-site regeneration. Instead of a paying for regeneration, the treated acid is being sold to cover transportation costs. Another 20% is contributed by improved CDNB yield, resulting from better organic recovery in the extraction column.

[1] J. Wiss, C. Fleury, V.Fuchs, 'Modeling and optimization of semi-batch and continuous nitration of chlorobenzene from safety and technical viewpoints', *J. Loss. Prev. Ind.* **1995**, *8*, 205.
[2] T. Grewer, O. Klais, 'Exotherme Zersetzung', VDI, Düsseldorf, 1988.

Electrostatic Hazards in Powder Handling Operations

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Abstract. Charge build-up is observed in most powder handling operations as soon as the powder is highly insulating or the equipment is made from highly insulating material. The ignition probability by discharges due to static electricity can drastically be reduce in practice, if only conductive material is used for all parts of the equipment and installations and if all these parts are safely earthed. The question remains, however, whether the charge retained on a highly insulating product in powder form will be able to ignite this powder, even if the powder is handled and processed in conductive and earthed equipment. Based on extensive research performed during the last decade in this field, ignition of highly insulating powder must be expected under certain circumstances (formation of so-called cone discharges), even if the powder is handled or processed in metallic and earthed equipment.

1. Charge Build-up on Powders

Charge build-up is intrinsically related to the handling and processing of electrically insulating powders. In most physical operations with powders such as filling, emptying, sieving, grinding, mixing, dust separation, pneumatic transfer, *etc.*, separation processes between the powder particles themselves and the walls of installations occur. As a result, the powder as well as parts of the installations may become charged. Different types of discharges may be generated from charged installation parts and from the charged product. The charge build-up on insulating powders is

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