

# Waste Reduction in Alkyl Pyridine Production: Solving the Root Problem Pays off

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**Abstract:** The production process for 5-ethyl-2-methyl-pyridine (MEP) is the largest single source of total organic carbon and total nitrogen in the feed of the capacity-limited wastewater treatment plant at LONZA's major production site. According to LONZA's integrated waste treatment concept, efforts were made to reduce the amount of critical components in the MEP process wastewater. Detailed analysis of causes and effects revealed the formation of small amounts of ethylamines in the reaction unit as the root cause not only for the ecological but also for the economical problems such as high catalyst consumption and reduced MEP yield. Separation of interfering ethylamines from the process in combination with recycling of catalyst and catalyst byproduct-containing process water can solve all problems.

**Keywords:** Alkyl pyridines · Catalysis · Ethylamines · Green chemistry · Recycling · Separation · Waste reduction

## Introduction

LONZA utilizes an integrated waste treatment concept at its major production site for organic fine chemicals, 'Valais Works' ('Walliser Werke') in Visp, Switzerland [1]. The waste issue is handled by the following measures in decreasing priority:

- *avoid* waste by suitable choice of process
- *reduce* waste by process optimization with regard to minimizing the amount of waste
- *reuse* waste by recycling, sale to third party, or energy recovery
- *treat* waste in the factory's own waste treatment plants (Scheme 1): waste-

water treatment plant, incineration of residues, land fill, ammonia recovery.

As the result of the lively development of the fine chemical business in the last years, the wastewater treatment plant has reached its capacity limit. In order to avoid a high investment into enlargement of the existing wastewater treatment plant or restriction of future business development, solutions have to be found to reduce the amount of wastewater, and in particular the carbon and nitrogen content. The analysis of the major originators of wastewater suggested that evaluation start with the production process for 5-ethyl-2-methyl-pyridine (MEP), which is responsible for nearly 40% of total organic carbon and 50% of total nitrogen in the total feed of wastewater treatment plant.

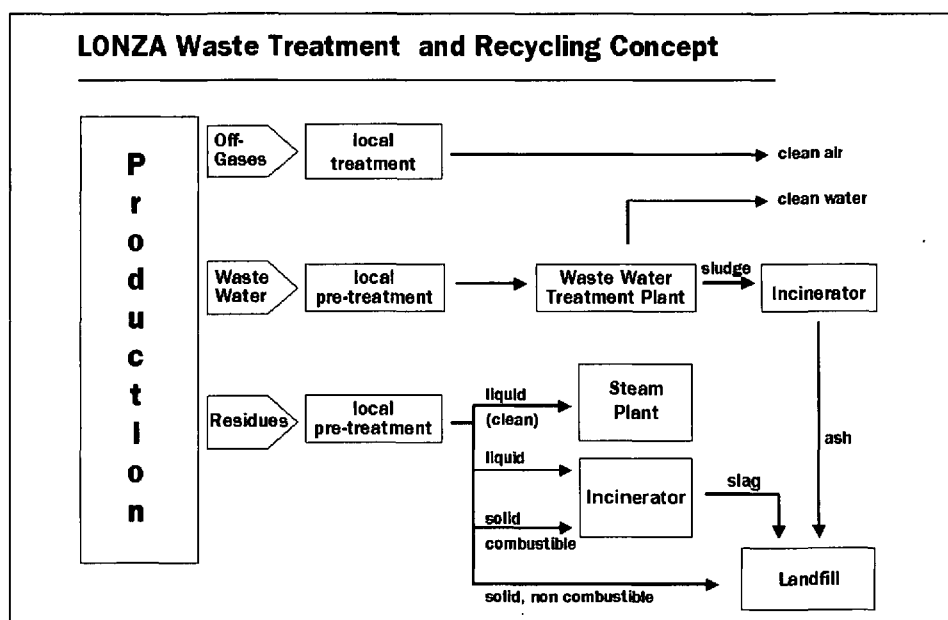
The present paper is therefore concerned with the reduction of total organic carbon and nitrogen in the wastewater of the MEP process and shows how the LONZA integrated waste treatment concept is implemented in practice.

## 2. MEP Process [2]

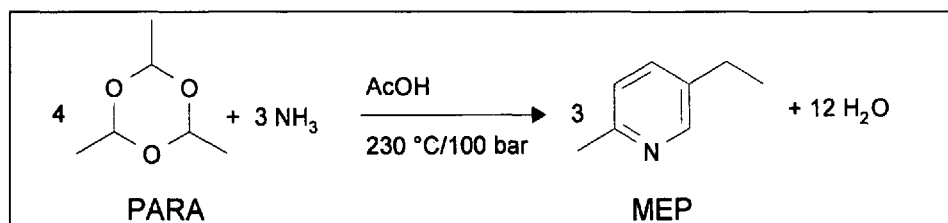
LONZA has produced MEP in a dedicated plant as an important intermediate for the production of the vitamin nicotinic acid (niacin) [3] for many years. MEP is formed according to the reaction in Scheme 2. In the liquid-phase reaction, acetic acid (AcOH) is used as a catalyst. The overall yield of MEP relative to the raw material paraldehyde (PARA) is 70–74% depending on reaction conditions. For each mole of MEP, four moles of reaction water have to be removed from the process.

According to the simplified process flow sheet (Scheme 3) following the reaction, the major part of unconverted ammonia is separated as gas, recycled, and recovered by absorption. From the next step (liquid/liquid separation), the major part of catalyst is recycled with the water phase to the absorption unit. The organic phase contains the raw MEP which is purified by extraction with water to remove residues of catalyst and catalyst byproducts (see below). In the

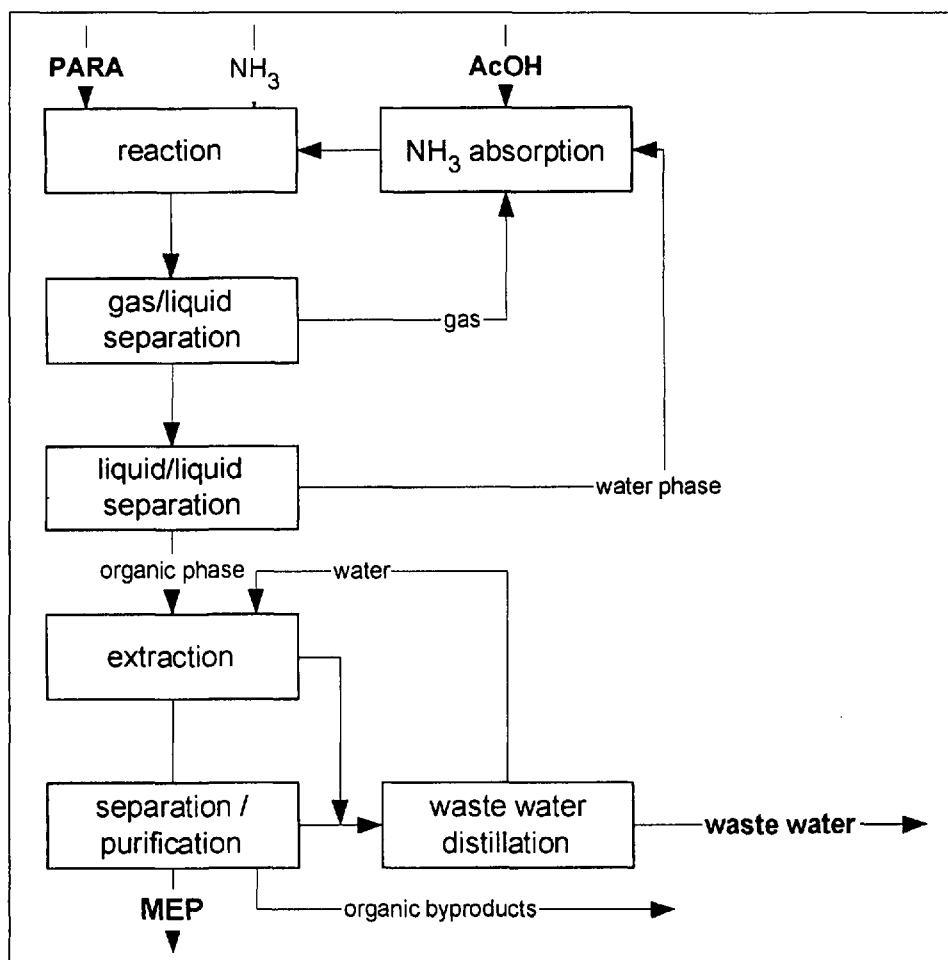
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Scheme 1.



Scheme 2.



Scheme 3. Simplified flow sheet of the MEP process

following separation steps, water and organic byproducts are removed. Excess process water leaves the process after recovery/separation of pyridine derivatives by distillation.

Beside the less than satisfactory yield, the process has the following weak points:

- a considerable consumption of catalyst (around 100 kg AcOH/+MEP)
- a critical wastewater with a high load of total organic carbon (about 35 kg C/+MEP) and of total nitrogen (about 15 kg N/+MEP).

Analysis of the wastewater composition shows that the major components which are responsible for the high organic carbon and nitrogen content are derivatives or byproducts of the catalyst (ammonium acetate, acetamide, N-ethylacetamide and N-diethylacetamide) as explained below. Both problems 'high C/N content of wastewater' and 'consumption of catalyst' are therefore coupled.

The obvious solution of recycling the catalyst and mono- and diethylacetamide-containing process waters from extraction to the internal water cycle around the reaction and absorption unit failed. Earlier plant trials showed an increase of the mono- and diethylacetamide concentrations, simultaneously a decreased MEP yield and problems with liquid/liquid phase separation. Therefore the disturbing components have had to be removed in form of wastewater up to now.

### 3. Ethylamine as the Root Cause of Problems in the MEP Process

In order to tackle the wastewater problem and the consumption of catalyst at its roots, the chemistry of the catalyst was studied under the conditions of the MEP reaction. Detailed investigations show the existence of different temperature-dependent chemical equilibria according to Scheme 4. Under the reaction conditions, equilibria are reached within a fraction of the resident time in the reactor. From the results it can be concluded that:

- because of reversible chemical equilibria, acetamide works as a catalyst as well as acetic acid,
- formation of mono- and diethylacetamide can be explained by transamination of acetamide in the presence of small amounts of monoethylamine and diethylamines, which could be detected in the water phase from liquid/liquid separation as well as in the gas phase from gas/liquid separation.

The different amines are assumed to be formed during MEP formation according to reaction Scheme 5.

Investigations of factors influencing the MEP yield show that monoethyl- and diethylamines have a severe negative effect even in small concentrations. This result could explain why earlier plant trials to recycle the wastewater containing the catalyst and mono- and diethylacetamide failed, as the components generate the free corresponding amines in the reaction unit because of the existing equilibria.

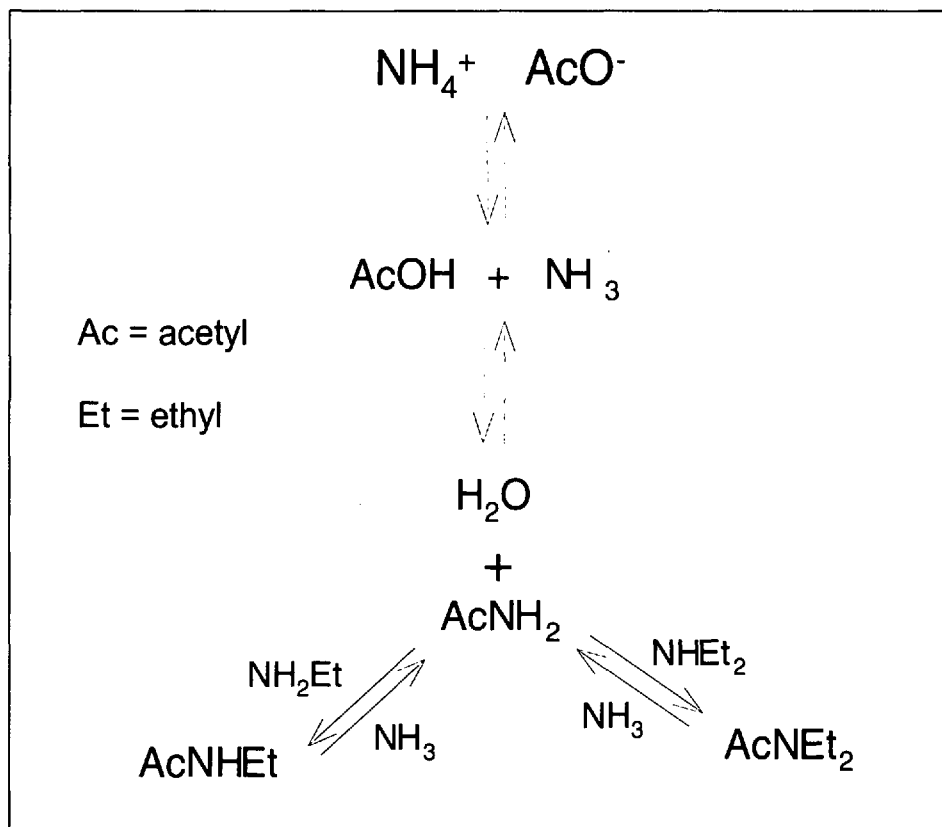
Therefore the formation of amines during the MEP reaction is the root cause of the wastewater problem and the high raw material consumption (PARA, AcOH). In the current process, the side reaction of the catalyst is an unsatisfactory way to trap and to transfer the disturbing amines outward.

#### 4. Problem Solution

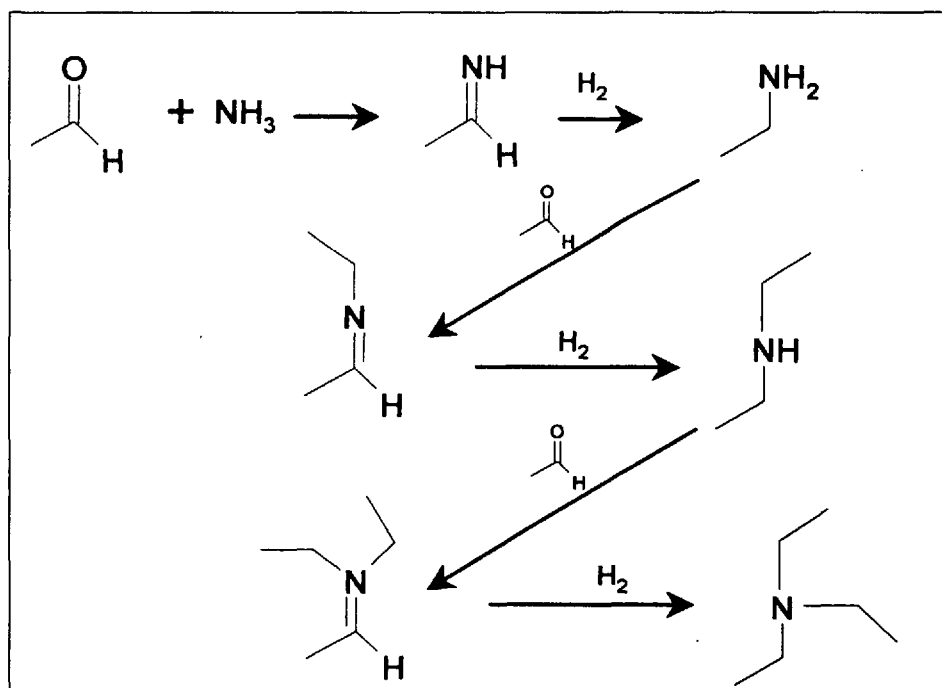
As it was not possible to suppress or diminish the formation of amines during the MEP reaction or to simply recycle the wastewater containing the catalyst and mono- and diethylacetamide, possible measures were evaluated to separate or eliminate the disturbing amines.

In a first step a mass balance of the amines was recorded to determine the rate of formation, to choose the best point for separation in the process and to get experimental values as a basis for later process modeling. The results show that:

- The observed concentrations of the different ethylamines and N-alkylacetamide derivatives in the gaseous process stream and/or water stream from liquid/liquid separation can be explained by a steady state resulting from the slight formation of amines in the reaction unit, a considerable internal recycling to the reaction unit, the outlet of amines in form of the corresponding acetamide derivatives *via* the organic phase from liquid/liquid separation and the adjustment of the above-mentioned chemical equilibria of all components in the reaction unit.
- The best point for separation (highest concentration of amines, simplest composition concerning other components) is the gaseous process stream from the gas/liquid separation unit.
- As the rate of formation of diethylamine and triethylamine is much lower than for monoethylamine (about 20 kg ethylamine/kg MEP)



Scheme 4. Reaction and chemical equilibria of the catalyst in the MEP reaction



Scheme 5. Assumed reaction path for the formation of ethylamines in the MEP reaction

the problem could be basically reduced to the latter component. The amount of ethylamine which is recycled in form of free ethylamine or bound in form of N-ethylacetamide to the reaction unit is six times as much as the amount of ethylamine which is formed in the reaction unit.

For the separation problem (separate ethylamine at a low percent level from a mixture with large excess of ammonia and water vapor), different unit operations and its combinations were considered.

As a final solution (Scheme 6) condensation followed by a fractional distillation in combination with a partial recycle of the water phase (solvate) from the extraction step was selected as the best procedure with regard to the different selection criteria (reduction of waste, investment and operation cost, financial benefit from reduced raw material consumption, flexibility, technical risk).

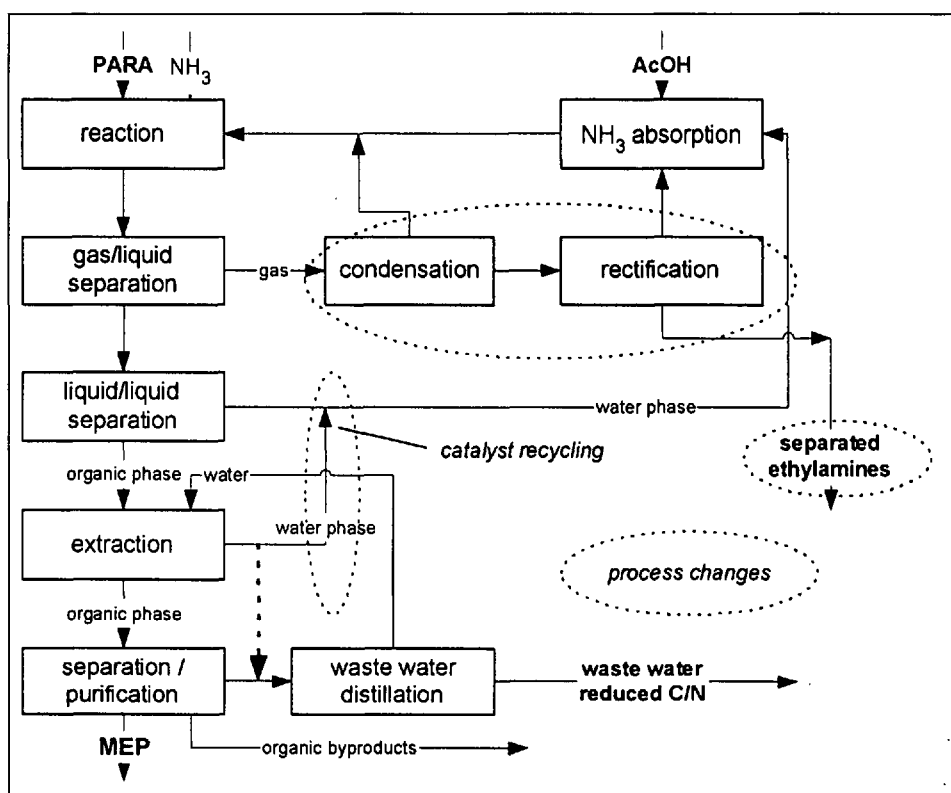
As the separation and outlet of the different ethylamines will change their concentrations at the location of separation as soon as the separation and catalyst recycling is started, the most reasonable operating point and the corresponding separation unit had to be developed by an iterative process for the design of the additional unit operations, in which steady-state concentrations as a function of the degree of ethylamine separation, catalyst recycling and other parameters were estimated by calculation.

Results of steady-state simulations and plant trials with recycling of the water phase from the extraction step showed that the selected solution (with a degree of ethylamine separation of 85%) reduces the consumption of acetic acid and the TOC and N-content in wastewater by about 70%.

From the results of the investigations of the factor influencing the MEP yield we also expect a 2% higher MEP yield at the planned operating point for the designed solution because of the diminished concentrations of the disturbing ethylamines in reaction unit.

## 5. Conclusion

By solving the root problem of the MEP process instead of possible end-of-pipe solutions, different ecological and economical goals can be achieved simultaneously, so that once more an investment into the ecological performance of a production process will prove profitable in the end.



Scheme 6. Simplified flow sheet of the MEP process with ethylamine separation and catalyst recycling

The additional plant units for the separation of the disturbing ethylamines are presently being designed. The start-up is expected in the year 2001.

As we are not able to predict the exact composition of the separated amines because of the limited accuracy of our calculations, the small amount of separated amines will be incinerated in the first phase. As soon as the exact composition is known after start-up and after steady operation conditions have been achieved, a reasonable utilization will be evaluated.

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