

# Design of an Plant for Manufacturing of Acetaldehyde

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## Abstract

*Production of acetaldehyde is declining and since it is used as a precursor in the manufacturing of pentaerythritol, which is a fundamental resource to Perstorp AB, it is important to secure the assets of acetaldehyde. The aim with this study is to investigate the possibility to convert a formaldehyde plant in Bruchhausen into an acetaldehyde plant. Perstorp also has a site in Gent with two available units. There are several different ways to produce acetaldehyde; the focus in this report will be on the silver process where acetaldehyde is produced by oxidation of ethanol. An overall process simulation, made in ChemCAD, was used as a base for the sizing of the different units and for the economical calculations. The study shows that it is possible to use the absorption column and the distillation column from Bruchhausen and both the reactor and mixing condenser from Gent. There will be a need to invest in a saturator, a distillation column for acetaldehyde and several heat exchangers. The recirculation back to the absorption columns needs to be cooled down to 2 °C hence a cooling machine is needed. The plant has an overall yield of ethanol to acetaldehyde of 93 %. Calculation of the process economy shows that the proposed process is economically viable. The total investment costs will be 40.0 million SEK and the operating cost per ton acetaldehyde is 7 081 SEK. This results in a payback time of 2.6 years.*

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## Introduction

Perstorp is the largest producer of pentaerythritol in Europe. The precursors for pentaerythritol are formaldehyde and acetaldehyde. Since acetaldehyde production in the world is declining and the prices are increasing it is important for Perstorp to explore the possibility of captive production. The aim with this study is to investigate the possibility to convert one of the groups formaldehyde plant into an acetaldehyde plant. The finished plant has to be economically viable and the aim is to produce 16 000 tons per year.

## Theory

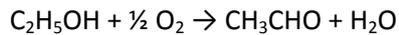
There are several different ways to produce acetaldehyde, precursors that are commonly used are ethylene, ethanol and acetylene. The focus in this report will be on the silver process where acetaldehyde is produced by

oxidation of ethanol. There are several reasons for this choice. Ethylene is produced in the petrochemical industry and is hence not classified as a green product. The production of acetaldehyde from acetylene includes a catalyst containing mercury, hence this method is discarded. Moreover the plant in Bruchhausen, in focus for reconstruction, produces formaldehyde from methanol using a silver catalyst and these processes are similar.

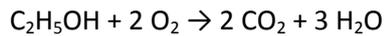
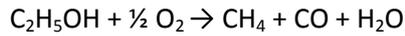
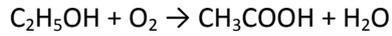
## Acetaldehyde Production

The main difference between the silver process for acetaldehyde production and the one for formaldehyde production is that two distillation columns are needed to produce acetaldehyde. The following section will describe a silver process for acetaldehyde production from ethanol [1]. Air and preheated ethanol goes into a saturator. The air leaving is saturated with ethanol and

overheated before entering the reactor. The main reactions that take place are:



The by-products are formed according to following reactions:



The overall reaction is exothermic and the temperature in the reactor is 550 °C. The

products are cooled instantly and the heat of reaction is used to produce steam. Further cooling is done before the products enter the absorber. The bottom stream is sent to the distillation column where acetaldehyde is removed in the top. The bottom from the distillation column is sent to an ethanol column to recover unconverted ethanol.

### Available Units

The different units chosen from the plants in Bruchhausen and two units from a plant in Gent are shown in the following table.

Table 1. Dimensions, material and building year of the different units. I stands for inner and O for outer.

Unit	Saturator	Reactor	Abs column	Mixing condenser	Distillation column
From	Bruchhausen	Gent	Bruchhausen	Gent	Bruchhausen
Height (m)	4.9	8.847	9.8	9.2	11.2
Diameter (m)	I/O = 0.99/1.0	I/O = 1.24 /1.25	I/O = 0.99/1.0	2.0	I/O = 1.49/1.5
Material	1.4541	1.4571 and 316	Al 99.5	304 L and 316	1.4571
Building year	1989	Assumed 1970	1960	Assumed 1970	1960
	Column with random packing		Column with random packing	Column with random packing	60 bubble cap trays

## Material and Method

Simulations are conducted in ChemCAD.

### Simulation Work

A simulation of the overall process is performed. The results are used as base in the sizing and economic calculations.

One of the most important things in order to perform accurate simulations is the choice of an appropriate physical properties model.

The methods best suited for this kind of system would be Wilson, NRTL or UNIQUAC [2]. The thermodynamic wizard in ChemCAD suggests the NRTL model for this system and vapour phase association when acetic acid is present [3] so hence this model is used.

Figure 1 shows the overall process simulation. Detailed descriptions can be seen in the master thesis with the same title as the article.

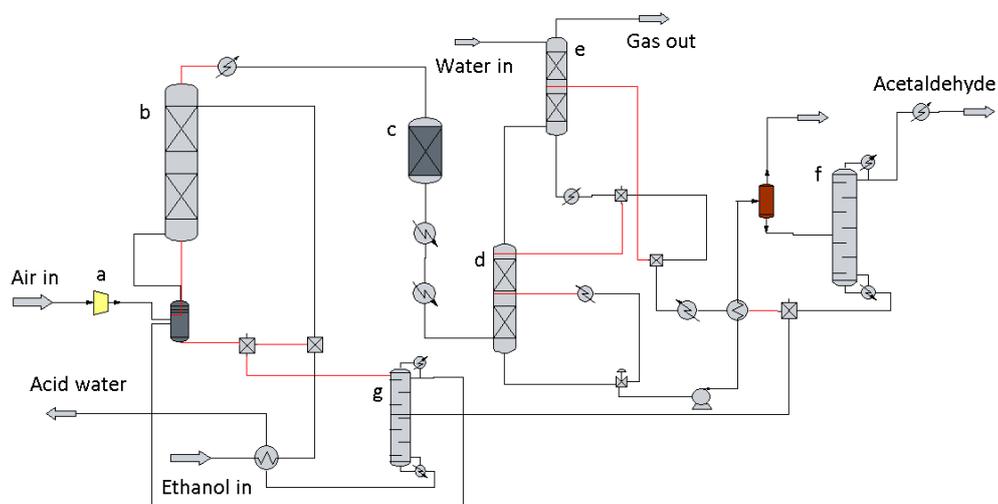


Figure 1. Flow sheet for the overall simulation. a) Compressor; b) Saturator; c) Reactor; d) Absorption column; e) Mixing condenser; f) Acetaldehyde distillation column; g) Ethanol distillation column.

## Changes in the Simulations

When comparing the equilibrium curve for acetaldehyde and water to experimental data found in literature it was found that they differed a lot. According to Faúndez et al. the deviation in percent for the system acetaldehyde and water is greater for NRTL than for UNIFAC [4]. Hence the NRTL parameters are regressed to match UNIFAC data and the regression was then compared to reliable articles. The results were similar [5; 6].

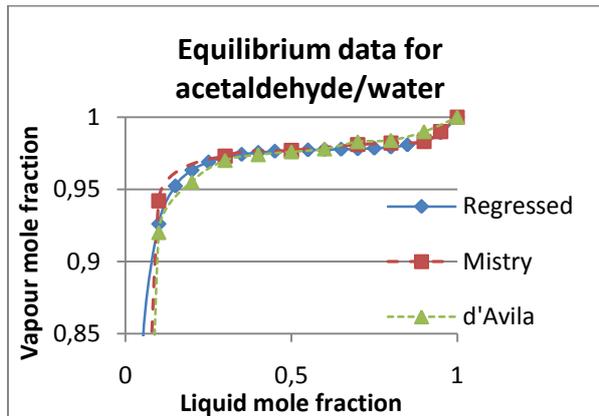


Figure 2. The equilibrium curve for acetaldehyde and water from the two articles and the regressed curve.

Table 2 shows the BIPs used in the simulations.

Table 2. Binary interactive parameters used in the simulations.

i	j	B <sub>ij</sub>	B <sub>ji</sub>	Alpha
Water	EtOH	670.441	-55.1681	0.3031
Water	HAc	424.019	-110.568	0.2997
Water	Acet	323.0035	531.4352	0.3999429
EtOH	HAc	-147.787	105.313	0.2992
EtOH	Acet	466.825	-317.713	0.4078
HAc	Acet	190.383	-98.3092	0.3006

## Results and Discussion

The proposed process, see figure 3, will be using a silver catalyst and partial oxidation of ethanol. First ethanol and air is sent to a saturator and the gases leaving are saturated with ethanol. The reaction is carried out in a fixed bed reactor over a bed of silver catalyst. The stream from the reactor is sent to an absorption column where water is used to

absorb acetaldehyde and the unconverted ethanol.

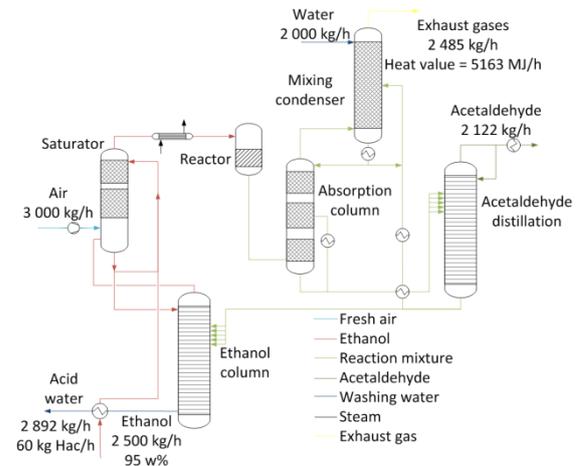


Figure 3. Flow diagram over the selected process with in and out flows.

Then a two stage distillation is performed. In the first column pure acetaldehyde is retrieved in the top and the bottoms containing ethanol, water, and acetic acid is divided. One part is sent to the mixing condenser to improve the absorption and the rest is sent to the second column where the unconverted ethanol is removed in the top and sent back to the process. The saturator acts as a condenser for the ethanol column.

## Simulation of the Overall Process

The simulations showed that the maximum capacity of the saturator from Bruchhausen was around 4 000 tons per years. This is the bottleneck in the plant therefore a new saturator is needed.

During communications with the staff in Bruchhausen it was determined that the distillation column in Bruchhausen cannot handle a pressure over 2 bara [7]. The acetaldehyde distillation is preferably run at a pressure of 3 bara. This in combination with that the distillation column was not able to handle full production results in the need to invest in a new distillation column. The consumption figures for the process can be seen in table 3. The plant has an overall yield of ethanol to acetaldehyde of 93 %.

Table 3. Consumption figures for the overall process, both per hour and per kg acetaldehyde.

	Per hour		Per kg acet	
Ethanol	2500	kg/h	1.18	kg
Electricity	1254	kWh	0.59	kWh
Steam	3071	kg/h	1.44	kg
Cooling water	114.7	m <sup>3</sup> /h	54.08	kg
Waste water	2.97	m <sup>3</sup> /h	1.36	kg
Acetic acid	60	kg/h	0.03	kg
Exhaust gases	2485	kg/h	1.17	kg
Heat value	5136	MJ/h	2.433	MJ
Fresh water	2.0	m <sup>3</sup> /h	0.94	kg

## Process Design and Economy

The units that need to be bought are a saturator, a distillation column and several heat exchangers. The circulation in the absorption units needs to be cooled to 2 °C therefore a cooling machine is needed.

To avoid flooding all the columns are designed for a flooding factor of around 60 %. If flooding would occur this would lead to a high differential pressure resulting in that the efficiency of the packing or trays goes, down resulting in that the mass transfer would be greatly diminished [8].

The simulations of the saturator show that the packing should be 4 m high and 1 m in diameter. The vessel needs to be 7 m high and 1.01 m in diameter.

The simulation shows that the packing height in the acetaldehyde column needs to be 15 m and 1 m in diameter.

The packing material in the columns is metallic Super Raschig rings #0.7 and the total amount needed is 50 m<sup>3</sup>. The cooling machine needs to remove 809 kW/h and the total amount of catalyst needed is 70 kg.

The total investment costs will be just below 40.0 million SEK and the operating cost per ton acetaldehyde is 7 081 SEK. The price for acetaldehyde is 7 996 SEK per ton. This results in a payback time of 2.6 years.

## Conclusions

This study shows that the problem with the declining acetaldehyde quantities can be solved by captive production. By using ethanol, which can be derived biologically, as a precursor acetaldehyde will be a green product.

It is possible to use an absorption column and a distillation column from Bruchhausen and a reactor and a mixing condenser from Gent. There will be a need to invest in a saturator, a distillation column and heat exchangers. The recirculation back to the absorption columns needs to be cooled to 2 °C hence a cooling machine is needed.

The proposed process is economically viable. The total investment costs will be 40.0 million SEK and the payback time will be 2.6 years.

## References

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