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COLLABORATIVE REPORT

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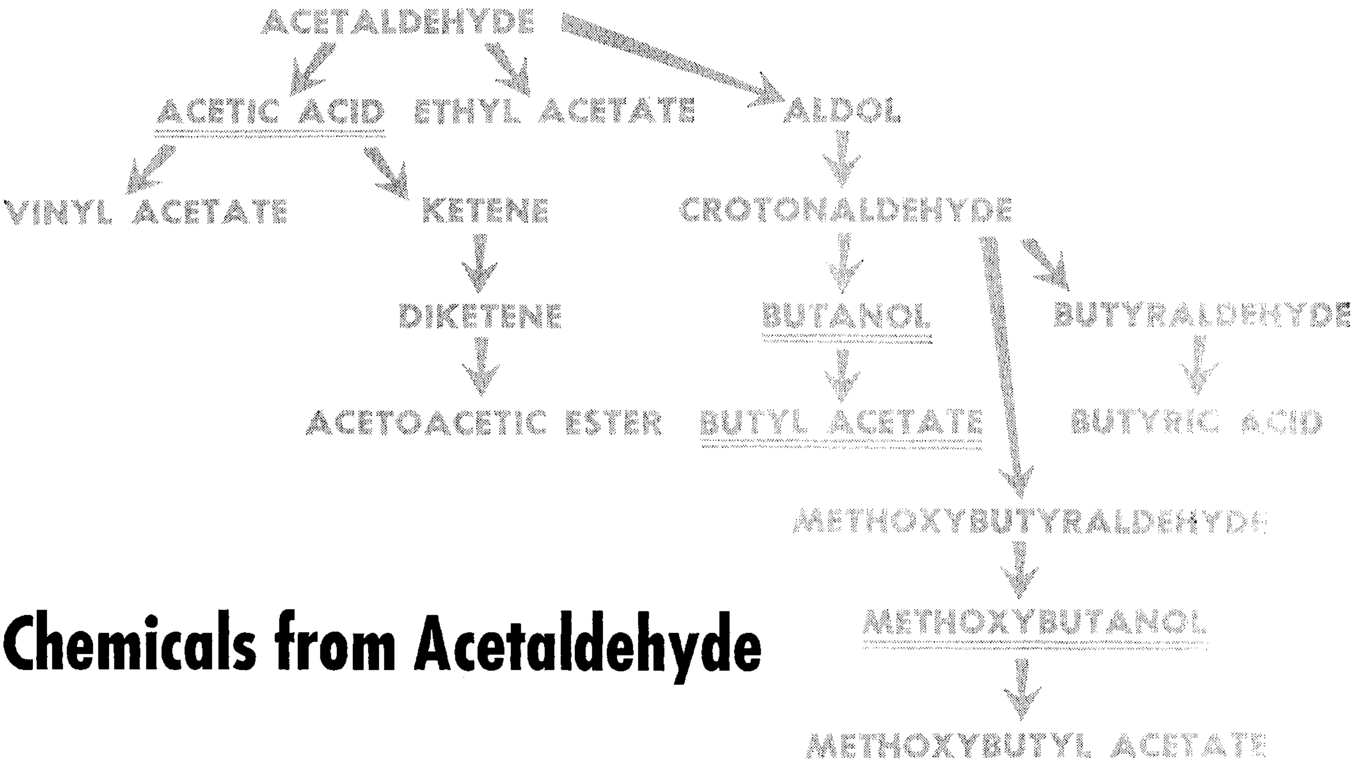
Chemicals from Acetaldehyde



LARGE-SCALE PROCESSES for making a wide range of solvents and other chemicals from acetaldehyde were developed chiefly for making aliphatic compounds from acetylene, derived from calcium carbide. Acetylene can be hydrated to acetaldehyde, which can then be converted into a long list of derivatives. Although today large quantities of aliphatic compounds are made by petrochemical processes in the United States, and to a growing extent in Europe, the acetaldehyde route is still an important one and likely to remain so (*4*).

The development of acetaldehyde chemistry on a large scale started with the need for acetone for explosives manufacture in Germany during the first World War. The first big plant for making acetaldehyde from acetylene came on stream at the Hoechst plant near Frankfurt in 1917. This acetaldehyde was converted to acetic acid, which in turn went to make acetone. After the war these processes served as the basis for a growing solvents and plastics industry.

The pioneer work which made this possible was done by Hoechst (then Farbwerke Meister, Lucius & Bruening), Chemische Fabrik Griesheim, and the Consortium fuer Elektrochemische Industrie (Waker-chemie at Burghausen am Inn).

Steps in Development of Acetaldehyde Process

The large-scale continuous manufacture of acetaldehyde through hydration of acetylene

The oxidation of acetaldehyde with oxygen to acetic acid with manganese acetate, and also a process for the simultaneous manufacture of acetic anhydride

The catalytic conversion of acetic acid to acetone

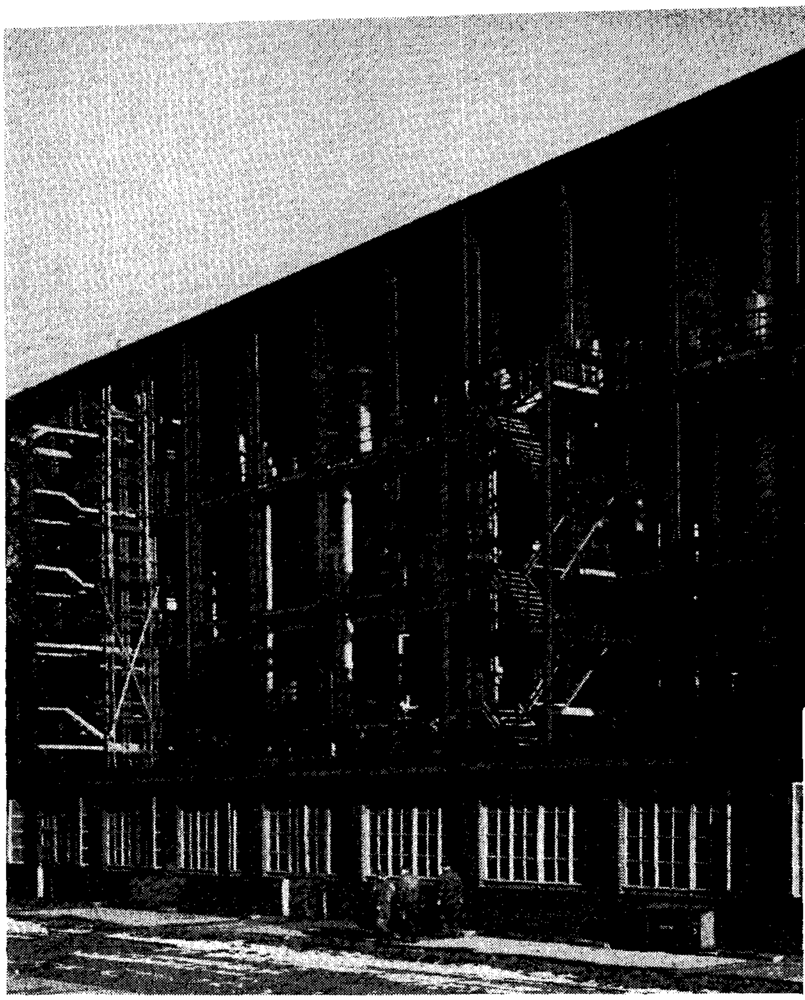
The continuous manufacture of crotonaldehyde from acetaldol and the catalytic hydration to butanol in the vapor phase

The continuous manufacture of ethyl acetate from acetaldehyde via the Tischtschenko reaction using aluminum ethylate catalyst

In order to secure its acetylene supply, Hoechst purchased an interest in a large calcium carbide factory at Knapsack near Cologne. Today this is owned by Knapsack-Griesheim, a Hoechst subsidiary. Acetaldehyde, acetic acid, and acetone factories were also set up in this plant, and were in operation by 1919. In 1933 acetaldehyde production was discontinued at Hoechst. Knapsack now sends out 3000 tons per month of its 6000 to 7000 tons per month output to Hoechst.

The Hoechst Plant

The scheme for manufacturing aldehyde derivatives at Hoechst is shown in Figure 1. The processes as operated during World War I have been described (*2*, *3*), most have been improved considerably since then. All these operations are carried out in one department of the plant. The processing equipment is set up in three adjacent buildings. These are roofed, but have no sides around most of the equipment. Towers and stills are supported on the steel framework. Access is by numerous catwalks and stairs. About 70 operators, under the supervision of four chemists, operate the department. Control is almost fully automatic. Control panels are in adjacent buildings.



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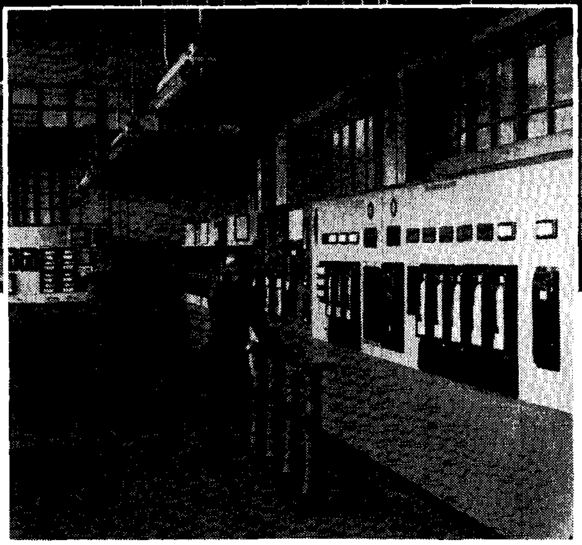
Typical plant construction in acetaldehyde chemicals section of the Farbwerke Hoechst plant. This is one of three buildings housing processes described in this article, as well as other processes. The low one-story section in front is the control room



The control room is almost fully automatic ▶

Storage tanks for raw materials and finished products are located nearby, next to the river bank. Pipelines connecting them to the plant are located in a covered trench which can be uncovered easily for maintenance work. Intermediate storage is in tanks located in the buildings.

Outlook

The development for petrochemicals does not mean that the aldehyde route to aliphatic compounds need suffer. In the first place a petrochemical process can be used merely to replace the calcium carbide process for making acetylene, which can then be converted to acetaldehyde as before. This is what is being done at the government-owned Azienda Nazionale Idrogenazione Combustibili (ANIC) plant at Ravenna, Italy. Natural gas is converted to acetylene, which is hydrated to acetaldehyde to be used for making butadiene for synthetic rubber. This route is, however, exceptional in Europe today. It was used in Germany during World War II but the other synthetic rubber plants in operation or under construction in Europe use butadiene derived from four-carbon petroleum fractions.

The acetaldehyde route can also be used with acetaldehyde made from fermentation ethyl alcohol in parts of the world where this is economical. For example, in South Africa National Chemical Products Corp., an affiliate of Distillers Limited in Great Britain makes acetic acid and other chemicals in this way; Electroquímica de Flix, a Spanish company, uses a similar process developed at Hoechst. Acetaldehyde from carbide acetylene is also used for chemical production in South Africa—by Hollands Electrochemicals, a subsidiary of a Netherlands company.

Making acetaldehyde directly from petrochemical raw materials has been made possible through a very recently discovered process for oxidation of lower olefins (*1*, *5*). Catalytic oxidation of ethylene with oxygen in the liquid- or wet-gas phase gives acetaldehyde. Copper salts can be used as catalysts. Platinum metal salts—for example, palladium chloride—are added to make the process possible on a commercial and large scale. Yields are nearly 95%. The process was developed jointly by Hoechst and Wacker-Chemie in Germany. Production plants are under construction in Hoechst and near Cologne (Wacker). These are expected to come on stream late this year.

This new process makes it easier to fit aldehyde chemistry into a system based on petrochemicals, as ethylene is cheaper to make by petrochemical processes than acetylene is.

New processes for making chemicals from acetaldehyde which were previously made by other methods keep the aldehyde route important too. For example, Knapsack-Griesheim, a subsidiary of Hoechst in Germany, has built a semiworks plant for making acrylonitrile from acetaldehyde instead

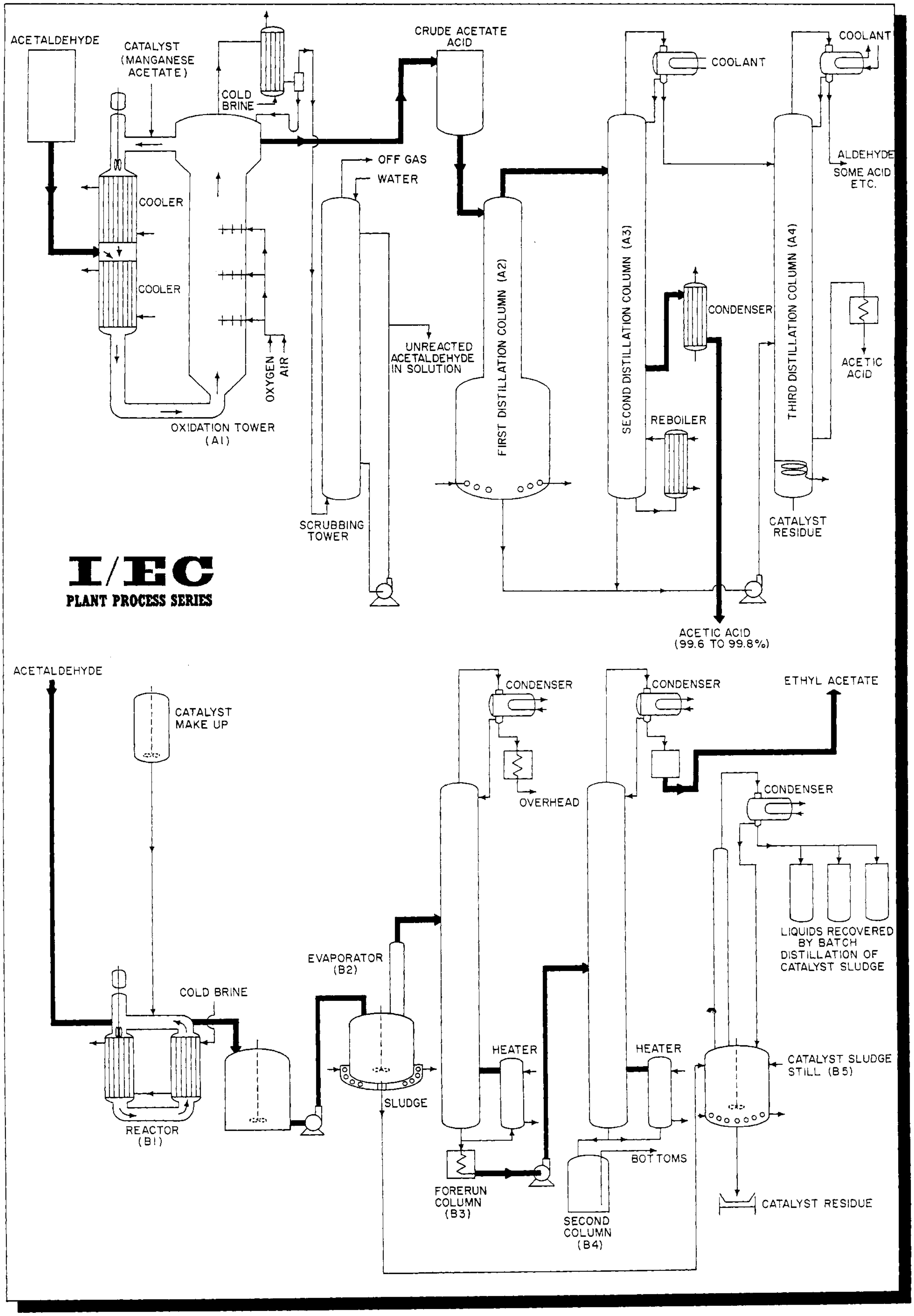


Figure 1. Flowsheet for the production of ethyl acetate and acetic acid from acetaldehyde, Farbwerke Hoechst A.G., Hoechst bei Frankfurt/Main, Germany

of from acetylene. This process is supposed to have several advantages over the usual one using acetylene. Among them is the possibility of building the acrylonitrile plant at some other location than an acetylene plant. Of course, if the process for making aldehyde from ethylene is fully developed this process would take on added significance.

Acetaldehyde to Acetic Acid

A process for the oxidation of acetaldehyde to acetic acid on a laboratory scale was carried out before the first World War, and processes had been patented by Hoechst and Wacker-Chemie. Until 1952 Hoechst carried out a batchwise oxidation in aluminum-clad steel pressure vessels of 6.5-cubic-meter capacity under a pressure of 4 atm. Oxygen was introduced through a sparger at the bottom. Manganese acetate catalyst dissolved in water was added to convert the peracetic acid formed, which is explosive.

Then danger and the higher cost of the older batch process led to the development of a continuous process. In 1928 at Knapsack a continuous process was installed with an oxidizing tower operating with air under a pressure of 6 atm. Output was 18 tons per day. In 1940 Hoechst started a pilot plant for continuous oxidation at atmospheric pressure. It gave very satisfactory results, and plans were drawn up for a 1000-ton-per-month production plant. However, because of wartime and postwar difficulties, it was not put into operation until 1952.

The continuous oxidation is carried out in one unit, which has a slightly greater capacity than the several reactors used in the batch process, and requires considerably fewer people to operate it (see top of Figure 1).

The reaction mixture is circulated upward through the oxidation tower (A1). Oxygen, diluted with 5% air to slow down the reaction and to avoid overoxidation enters through dispersing rings located at three different levels in the tower. The main reaction is:

$$2CH_3CHO + O_2 \rightarrow 2CH_3COOH$$

The aldehyde is diluted with crude acid. In practice crude acid (90 to 94%) is circulated through the tower at a rate of about 450 cubic meters per hour. Leaving the tower, the mixture passes downward through the tubes of two large coolers in series, one placed above the other. The aldehyde is fed in between these coolers. Manganese acetate solution is added as the stream leaves the top of the tower.

The circulation pump for crude acetic acid is located at the top of the coolers. Impeller and shaft are of stainless steel.

Reaction temperature can go up as high as 65° C. without getting overoxidation and excessive quantities of by-products. Test runs at very low temperatures—for example, under 30° C.—showed no advantages and required more cooling water.

The gas coming off the top of the tower contains 40 to 50% carbon dioxide, plus some nitrogen, acetic acid, and aldehyde—which is recovered. The gas goes first through a brine cooler to remove condensable materials, and then to a scrubbing tower where most of the acetaldehyde is washed out in water.

The reaction mixture is drawn off from the top of the oxidation tower and distilled continuously in three distillation columns. Crude acid is fed into the top of the first column (A2). On the way downward through the column, any acetic anhydride which is still present reacts with the water to give acetic acid.

Most of the acetic acid and the volatile components, such as aldehyde, water, methyl acetate, formaldehyde, etc., are taken off overhead. The acetic acid residue, containing the manganese acetate, is taken off the bottom.

In the second column (A3) the low boiling forerun is taken off overhead. It is:

70 to 80% acetic acid
10 to 20% acetaldehyde
about 10% water
about 1% methyl acetate, etc.

About 2 meters above the reboiler the technically pure acetic acid is taken off. It is 99.6 to 99.8% pure and can be used directly for esterification, and ketene and vinylacetate production.

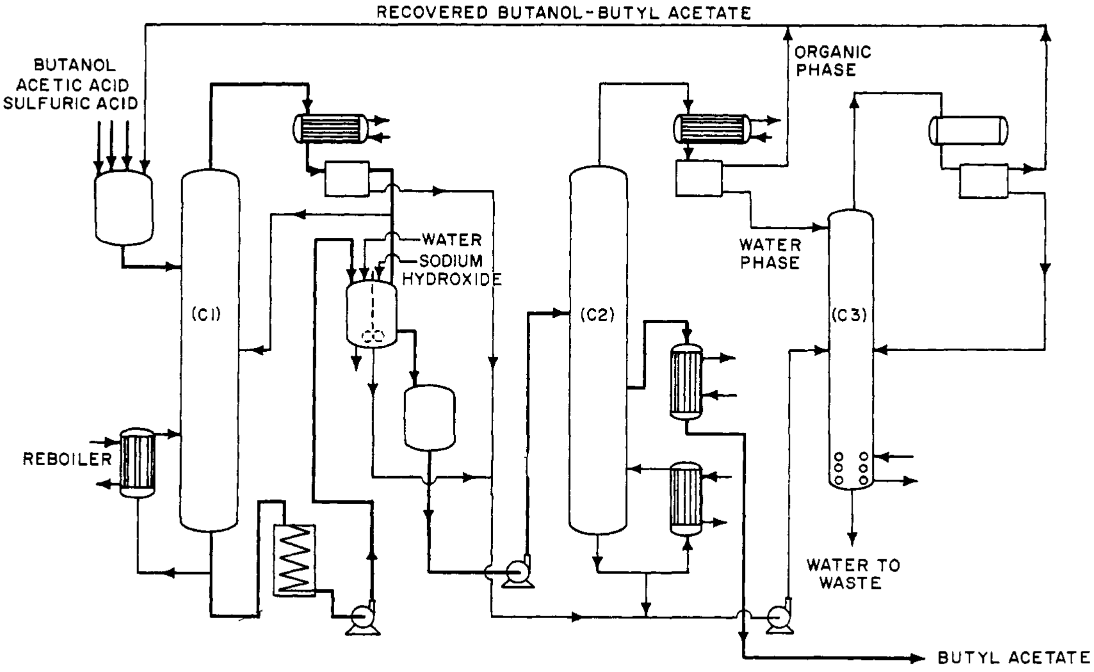


Figure 2. Flowsheet of butanol and acetic acid to butyl acetate

The overhead from the second column, together with the bottoms from the first and second columns, goes to the third column (A4). Here a greater part of the remaining acetic acid is taken off as vapor in highly concentrated form and condensed. The water, containing aldehyde with a little acetic acid, is taken off overhead. This mixture, like the bottoms is processed discontinuously. The acetic acid from the process is sent to the intermediate storage tanks.

The Old Acetic Acid Process

In the old process 1600 liters of acetaldehyde were oxidized in one batch. This material was added to 400 liters of crude acetic acid in a reaction vessel. The manganese acetate solution (containing 1.6 kg. of salt) was then added and the mixture heated to 40° C. The mixture of gases found over the liquid in the vessel consisted of nitrogen, carbon dioxide, and other gases. After warming the pressure reached about 1.2 atm. Then, very cautiously, the operator blew a little oxygen in and waited for the reaction to "go." When this happened there was a slight rise in temperature, a slight drop in pressure, and the previously colorless crude acid turned brown. Then more oxygen was blown in, and the pressure in the vessel rose because of the increase in inert gases.

Temperature was kept down to 60° C. by water cooling through coils, which had a cooling surface of 33 square meters. The end of the reaction was marked by an increase in pressure and a simultaneous drop in temperature. The oxidation lasted 9 hours. The reaction mixture then contained

93 to 94% acetic acid
2 to 3% acetaldehyde
3 to 5% acetic anhydride
1 to 2% water

The acetic acid was then purified by distillation.

Acetaldehyde to Ethyl Acetate

Ethyl acetate can be made either by the esterification of ethyl alcohol with acetic acid or by the Tischtschenko process. Formerly Hoechst made ethyl acetate by direct esterification. Raw material used was a crude acetic acid containing some acetaldehyde. To this 0.5% sulfuric acid was added, and the mixture distilled. The aldehyde came off in the overhead. Then the alcohol was run in, and the crude ester distilled off. Crude ester was washed with sodium bisulfite to remove aldehyde, and neutralized with a soda wash. After drying with calcium chloride, the ester was purified by distillation. Hoechst produced about 2000 tons per year this way from 1927 on, after first starting in 1924.

As alcohol became more expensive more interest was shown in the Tischtschenko process. In its old form this process was not too attractive. The catalyst was dissolved in a high boiling solvent, such as naphtha. The acetaldehyde was 95% converted to ethyl acetate. While it was possible to recover the unreacted acetaldehyde by distillation, the working of the crude ester was still rather involved.

However, the Consortium fuer Elektrochemie in Munich improved the process by using an ethylate catalyst with the addition of chlorine compounds such as aluminum chloride. The final breakthrough did not come until after the First World War when a process was developed for manufacturing the aluminum catalyst directly in ethyl acetate solvent. Further work at Hoechst showed that practically quantitative yields were possible with the process, so a license was obtained from the Consortium and Wacker-Chemie and in 1931 the process was put into operation. The process has remained basically the same, but now both the conversion and the purification distillation have been continuous.

Catalyst for the process is made up in an agitated vessel by mixing 160 k. of aluminum powder, 50 k. of aluminum chloride, and 20 k. of iron chloride in 5000 liters of ethyl acetate. This is then refluxed (see bottom Figure 1). After a short time the operator starts to add slowly a mixture of 2000 liters of ethyl acetate and 1000 liters of alcohol. The hydrogen developed goes through a water- and a brine-cooler and passes overhead through the reflux. Most of the heat developed is carried away.

Overheating is prevented by cooling the kettle contents, or by slowing down the flow of alcohol mixture. The ending of the reaction is apparent when the development of hydrogen stops. Heating is continued for about an hour

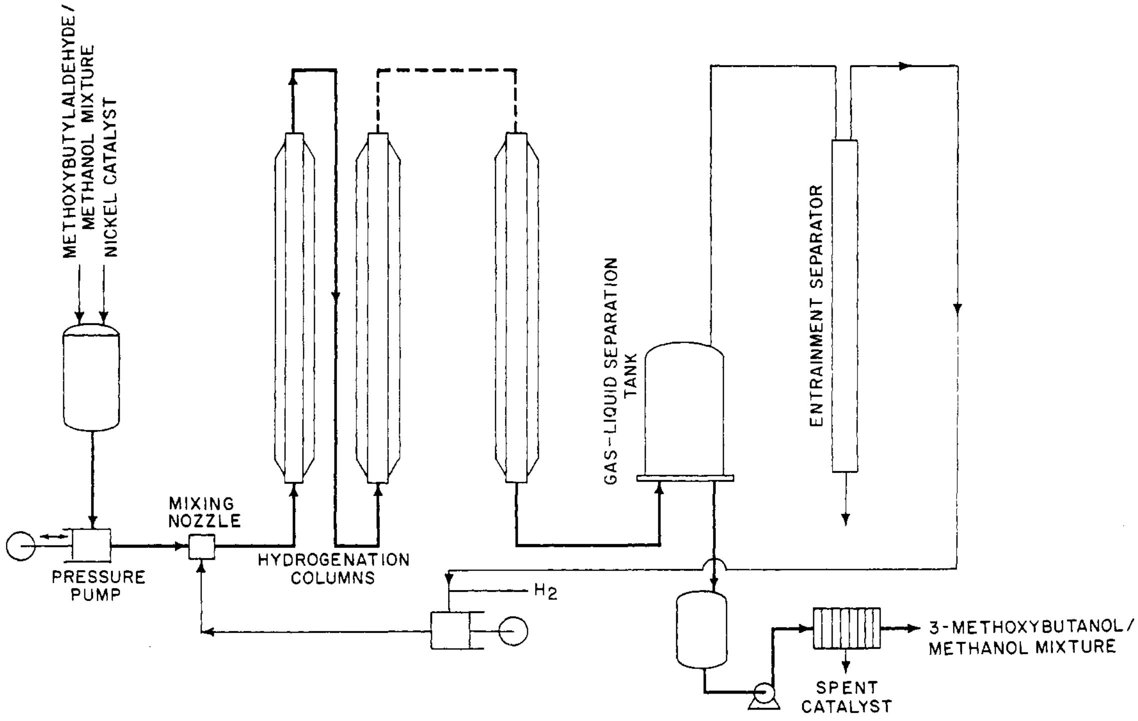
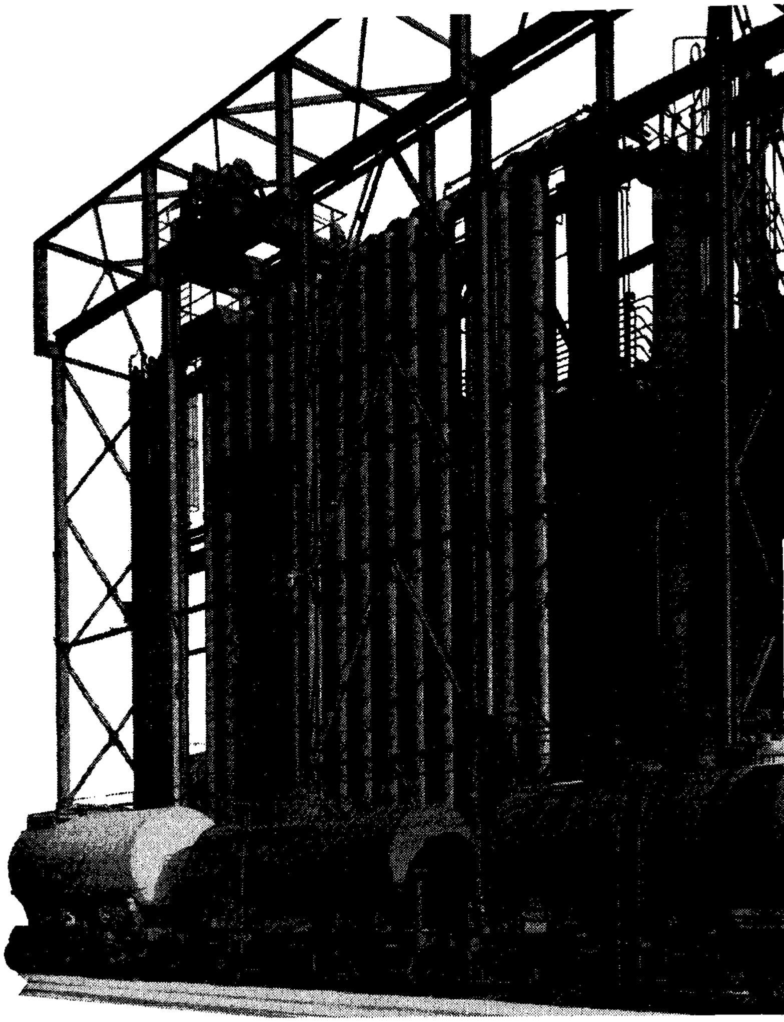


Figure 3. Flowsheet of methoxybutylaldehyde to 3-methoxybutanol



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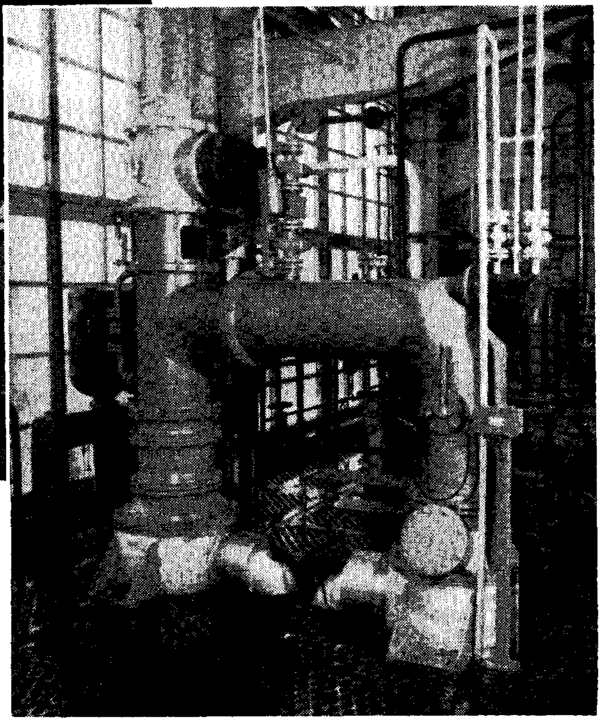
High pressure hydrogenation columns convert methoxybutyraldehyde to methoxybutanol under pressure of 250 atm. at 100° to 130° C. over a nickel catalyst. The same equipment can also be used to make butyraldehyde from crotonaldehyde



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Top of the ethyl acetate reactor. The pump on the upper left hand corner circulates the reaction mixture around the more or less rectangular tube which makes up the vessel. Tops of cooling jackets extend up just above the grating floor

or more, and then the mixture is allowed to cool. The catalyst mixture then contains about 2% aluminum in the form of a supposed ethylate complex.

The reaction for conversion of aldehyde to ethyl acetate is carried out in a special reactor (B1). This is, roughly, a vertical rectangular circuit of pipe with a circulating propeller, and with the two vertical coolers. Acetaldehyde and catalyst solution, in the ratio of about 10 to 1, are continuously fed into the circulating reaction mixture. The reaction temperature is kept between 12° to 14° C. by cooling with brine.

A contact time of 2 hours gives a 95% conversion of aldehyde. By continuous overflow of the crude ester through a large (20 cubic meters) brine-cooled kettle the reaction goes 99.5% to completion—that is until only 0.5% aldehyde is left.

This crude ester is cleaned of the catalyst by distillation to get a very pure ester fraction. This is a semicontinuous process. Crude ester is evaporated in a still (B2) and the vapor fed into a forerun column (B3). A small amount of acetaldehyde, water, and alcohol goes overhead. The bottoms are pumped into the second column (B4). Pure ester goes overhead where it is condensed and sent to storage. The bottoms—a mixture of diethylacetal (about 70%) and ethyl acetate—are taken off at intervals and processed.

This catalyst sludge, contained in 50 to 60 tons of crude ester, is distilled in a special agitated vessel (B5). The agitation has to be very powerful, because of the sludge being so thick. The remaining liquids are distilled off, then water is added and the rest of the aluminum ethylate is decomposed, the organic substances are distilled off. The remaining sludge consisting of salts and $Al(OH)_3$ (aluminum hydroxide) goes to the dump.

Capacity of the Hoechst plant is 1000 tons per month.

Butyl Acetate

Unlike ethyl acetate, butyl acetate is prepared at Hoechst by direct esterification. Butanol and acetic acid are heated in the presence of a catalyst, sulfuric acid. The process is continuous (Figure 2).

The three substances are mixed in a reaction kettle and partially esterified by heating to about 60° C. The mixture is then fed into the upper third of the first esterification column (C1). In this column the ternary mixture of water, butyl acetate, and butanol is continually distilled off, the water removed, and the organic phase returned to the column. As a result the esterification proceeds until the bottoms contain less than 1% acetic acid, and the butyl acetate content reaches 90 to 95%.

The ester is neutralized in a small tank with dilute sodium hydroxide. The stream flows through a holding tank and then into the distillation column (C2). Butyl acetate, 98 to 100% pure, is taken off under the middle of the column. Overhead is a wet mixture of butanol and butyl acetate. After separating out the water, the mixture of alcohol and ester is returned to the initial reaction kettle.

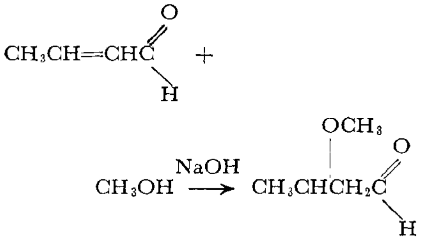
Butanol and butyl acetate entrained in the water from the esterification and distillation column condensers and from the neutralizing tank, are distilled in the recovery column (C3). The organic phase from the overhead condensate is returned to the initial reaction kettle. The solvent-free water from the bottom of the column goes to waste.

Table I. Production of Some Chemicals Derived from Acetaldehyde

	Metric Tons			
	1952	1954	1956	1957
Acetone				
West Germany	9,921	9,391	...	...
France	6,192	18,756	23,832	28,500
Italy	2,659	2,423	4,445	...
Great Britain	...	...	...	ca 40,000
Japan	2,497	3,988	4,976	6,758
U.S.A.	199,387	216,610	275,167	295,189
East Zone	3,350	...	...	...
Acetic acid (100%)				
West Germany	59,254	83,033	81,194	90,589
France	7,476	10,224	11,196	13,104
Italy	12,199	16,608	13,221	27,902
Great Britain	ca 10,000	...	...	...
Belgium	ca 1,400	...	...	...
Sweden	2,983	5,477	8,025	...
Spain	...	800	...	2,664
Poland	...	980	3,200	...
Finland	...	522	548	...
Japan (99%)	21,780	26,076	38,016	44,532
U.S.A.	173,690	200,490	249,392	237,874
Butyl acetate				
West Germany	11,306	15,780	20,862	18,020
France	575	1,317	1,781	...
Italy	2,213	3,360	3,623	3,742
Sweden	1,427	1,948	4,382	...
Japan	2,608	2,310	3,089	...
U.S.A.	24,408	35,496	37,091	32,763
Spain	...	...	...	...
Finland	...	158	284	...
Ethyl acetate				
West Germany	20,694	27,511	33,453	35,742
France	3,290	3,840	5,008	...
Italy	1,408	2,604	4,303	5,556
Sweden	807	1,368	1,711	...
Spain	...	...	...	517
Finland	...	53	47	...
Japan	5,747	6,699	8,257	...
U.S.A.	32,787	32,863	41,193	41,591
Methyl acetate				
West Germany	7,002	9,409	20,862	18,020
France	556	607	726	...
Italy	286	432	433	197
Japan	42	...	...	...
U.S.A.	1,552	1,218	5,552	3,728
Butanol				
West Germany	...	37,186	48,389	50,372
France	2,195	3,320	3,845	...
Italy	2,379	3,096	3,678	...
Great Britain	...	...	ca 11,300	...
Japan	4,200	9,036	11,179	12,300
Sweden	1,466	4,244	7,977	...
U.S.A.	138,473	184,851	233,311	220,644

Methoxybutylacetate

Methoxybutylacetate, which Hoechst sells under the name Butoxyl, is an important solvent for the paint industry in Europe. The methoxybutanol, which is used to prepare acetic ester, is made from methoxybutyraldehyde. This is made from crotonaldehyde, which is made from acetaldehyde *via* aldol according to the following reaction:



$$CH_3CH{=}CHCHO + CH_3OH \xrightarrow{NaOH} CH_3CH(OCH_3)CH_2CHO$$

An equilibrium is formed in a methanol solution. About 95% of the crotonaldehyde is converted into methoxybutyraldehyde, while about 5% remains unchanged. In practice the amount of crotonaldehyde added is just sufficient to give a 50% solution of methoxybutyraldehyde. After the reaction which takes place about 0° C. is finished, the mixture is slightly acidified with acetic acid to stabilize the aldehyde for higher temperatures.

By continuous high pressure hydrogenation with a nickel catalyst at 100° to 130° C. and 250 atm. methoxybutanol is formed. This is then esterified with acetic acid to methoxybutylacetate (Butoxyl).

The aldehyde mixture is mixed with a water slurry of nickel catalyst in a mixing tank and sent through the high pressure proportioning pump and then through the mixing nozzle, where it is mixed with the high pressure hydrogen stream (Figure 3). Then the mixture goes through a series of high pressure vessels. These are jacketed for water cooling. Reaction temperature is 100° to 130° C.

An excess of hydrogen prevents the deposition of nickel.

After the reaction is finished in the last hydrogenation column, the stream flows into a vessel where the liquid and gas are separated. Hydrogen goes into a separator to remove entrained liquid and the gas then to a recycling pump for re-use in the process.

The liquid, containing the catalyst, goes to a decanting vessel and then to a filter press. Part of the catalyst can be re-used. The crude methoxybutanol is then purified by continuous distillation.

The esterification of methoxybutanol with acetic acid is carried out by a batch process, using toluene sulfonic acid as a catalyst.

The same equipment used for making methoxybutanol can also be used for making butyraldehyde from crotonaldehyde. Hoechst has developed a new process for doing this in the gas phase. A semiworks plant for this has been built.

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