

# MEASURES AGAINST WATER POLLUTION IN INDUSTRIES PRODUCING PETROCHEMICALS INCLUDING POLYMERS

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## ABSTRACT

Because of the breadth of the subject, the problems concerning the treatment of waste water are limited to those of (i) the production of organic chemicals which are produced on a petrochemical basis in chemical plants, (ii) the production of various derivatives selected according to their importance and (iii) the production of some of the more important vinyl polymers. Specific quantities of waste water per ton of product are derived using examples and specifying the pollutants.

The waste water from these processes can be purified mainly by mechanical, physical, chemical or biological methods. Technological difficulties in waste water treatment, which arise in some cases producing highly refined products, must be eliminated by modifying the process.

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The term petrochemicals is variously defined. In the broadest sense it is understood to mean chemical compounds or elements (*e.g.* sulphur) which are produced from petroleum or natural gas or which are entirely or partly derived from the hydrocarbons of petroleum or natural gas (Römpf). According to this definition most of the products of organic chemistry and some inorganic products, such as ammonia which is produced from natural gas, are today termed petrochemicals.

The following account is limited to organic primary chemicals which are produced on a petrochemical basis in chemical plants. It will include a discussion of some of the most important vinyl polymers. Using the Federal Republic of Germany and the USA as examples, *Table 1* shows the most important products. The data presented in the table refer to total production, independent of the source of the raw materials.

## MONOMERIC HYDROCARBONS

After petroleum largely replaced coal as a raw material in the chemical industry of today, ethylene became the most important starting material for organic synthesis. The production of ethylene and its higher homologues, of which the C<sub>3</sub> and C<sub>4</sub> compounds are the most important, is shifting more

Table 1. Production of important organic chemicals in 1000 metric tons/year

Product	West Germany		USA	
	1966	1968	1966	1968
ethylene	892	1 534	5 099	7 451
propylene	467	680	2 122	3 669
butadiene, butylene	257	449	1 933	2 532
acetylene	273	264	526†	(635)†
methanol	633	614	1 483	1 748
formaldehyde	260	320	623	688
carbon tetrachloride	42	(53)	294	(345)
acetaldehyde	283	259	590	(680)
acetic acid	155	190	639	749
ethylene oxide	163	220	1 056	1 186
ethylene glycol	77	120	944	—
vinyl chloride	415	618	1 134	1 199
vinyl acetate	(90)	—	275	321
styrene	(290)	—	1 448	1 677
acrylonitrile	(47)	—	325	463
isopropanol	(75)	—	778	—
acetone	(85)	—	603	578
polyethylene	342	593	1 614	2 060
polypropylene	(17)	(35)	250	397
polyvinyl chloride‡	410	623	981	1 101
polyvinyl acetate	(83)	(98)	146	161
polystyrene	(230)	(310)	732	805

† Of this amount, acetylene for chemical synthesis in USA: 1966 = 324 000 tons, 1968 = 215 000 tons

‡ For West Germany polyvinylidene chloride is included.

The figures in brackets are estimates.

and more to the refineries. Light naphtha, which is cracked in a middle temperature pyrolysis process, serves as the starting material.

The main source of acetylene is still calcium carbide, which is produced on the basis of coal. However, in various chemical works, processes are also being employed which are based on the cracking of hydrocarbons at very high temperatures (2000 to 2500°C) and extremely short residence times.

Heating is carried out either in reactors (direct heat transfer), in cracking furnaces (indirect heat transfer), or in an electric arc. Depending on process and starting material, other products of cracking are formed in greater or smaller amounts, for example, ethylene, methane, hydrogen, oxides of carbon and soot. After the cracking process the gas mixture is quickly cooled in any case, in order to avoid undesirable polymerization reactions and the decomposition of acetylene. During this procedure, called quenching, one of the materials employed is water, which must be removed again as relatively highly polluted waste water.

An old plant, for example, produces 28 m<sup>3</sup> waste water per ton C<sub>2</sub> hydrocarbons. First, undissolved hydrocarbons and polymers are removed in a settling tank, leaving a hydrocarbon concentration of 1.5 g/l, consisting principally of benzene. By stripping with air, the hydrocarbon content is reduced by 85–90 per cent. The stripping gas is passed through a

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combustion plant. The pre-cleaned waste water, together with processing water from plastics and solvent works, is then fed into a biological purification plant, where it is no longer a source of disturbing odours.

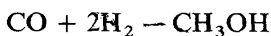
In a newer plant of the same type, the amount of waste water produced is reduced to only 10 m<sup>3</sup> per ton C<sub>2</sub> hydrocarbons by decreasing the amount of water used in quenching and by partial recirculation of the quenching water.

## MONOMERIC DERIVATIVES OF HYDROCARBONS

### (a) C<sub>1</sub> derivatives

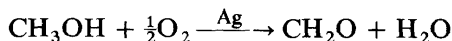
The most important products are methanol, formaldehyde, methylene chloride, and carbon tetrachloride.

Methanol synthesis starts with a mixture of carbon monoxide and hydrogen (synthesis gas), which is produced today mainly by cracking of petroleum fractions or natural gas. The reaction



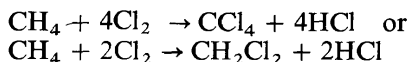
occurs in the presence of a mixed catalyst of zinc oxide and oxide of chromium in the high pressure reactor at 200 kg/cm<sup>2</sup> and approx. 370°C. This process does not create any major waste water problems.

A large part of the methanol is processed further to formaldehyde, an important starting material for synthetic resins and special plastics. In this process methanol reacts with oxygen from the air in the presence of a silver crystal catalyst at temperatures of 600 to 700°C, according to the equation:



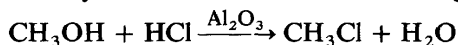
There is also no source of difficulty for waste water technology.

Carbon tetrachloride and methylene chloride are produced by the chlorination of methane, which comes either from natural gas or from cracked petroleum. Synthesis occurs at about 400°C according to the reaction equations



and necessarily produces hydrochloric acid as a byproduct. When carbon tetrachloride, which serves as the starting material for the production of propellants and refrigerants, gained in importance, the hydrochloric acid could not always be disposed of because of seasonal fluctuation of the market capacity and in part was discharged into the waste water. The obvious step of electrolytically decomposing the hydrochloric acid into chlorine and hydrogen could not be taken for a long time due to the problem of corrosion and for lack of a suitable material for diaphragms. Finally in 1964 it was possible to put into operation the first plant for the electrolysis of hydrochloric acid on an industrial scale<sup>1, 2</sup>. In this plant decomposition occurs at bipolar graphite electrodes. The cathode and anode compartments are separated by diaphragms of special PVC that are made up in a special weave and density. In this way a serious waste water problem has been solved by means of chemical engineering.

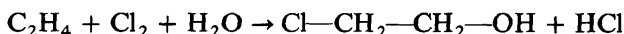
The recently developed methanol esterification represents another interesting possibility for the utilization of hydrochloric acid. Methanol vapour and hydrogen chloride react under pressure and at 300 to 350°C in the presence of a stationary bed catalyst of aluminium oxide according to the equation:



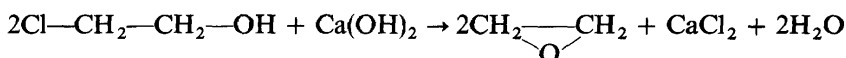
The process does not involve any waste water. The methyl chloride that is produced is processed further to more highly chlorinated products.

### (b) C<sub>2</sub> derivatives

The possibility of producing ethylene cheaply from natural gas or petroleum greatly influenced the synthesis of C<sub>2</sub>-derivatives. One of the materials affected was ethylene oxide, the starting material for the production of ethylene glycol, of almost all glycol derivatives, including polyester fibres, and of nonionogenic detergents. In this case, a process became important, which, although it brings a smaller yield, does produce a decidedly improved waste water situation. In the old chlorohydrin process, ethylene, chlorine, and water were converted to ethylene chlorohydrin at 70°C according to the equation:

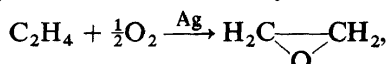


Then, in a second stage, ethylene oxide is formed by boiling with lime, with the splitting off of hydrogen chloride:



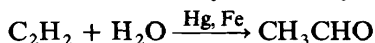
For each ton ethylene oxide this process produced 60 m<sup>3</sup> waste water containing 2500 kg calcium chloride, 275 kg excess calcium hydroxide, and 110 kg ethylene glycol<sup>3</sup>.

In the modern process, which is based on the direct oxidation of ethylene with oxygen in the presence of a silver catalyst, according to the equation:



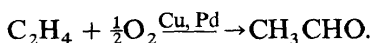
the quantity of waste water per ton ethylene oxide is reduced to 1 m<sup>3</sup>. This 1 m<sup>3</sup> waste water contains only 10–15 kg sodium bicarbonate and 5–10 kg organic products which are easily decomposed biologically.

Acetaldehyde, also an important intermediate product of organic chemistry, was produced in Germany until a few years ago exclusively by the hydration of acetylene in the presence of a mercury-iron catalyst:



The use of mercury led to considerable difficulties. The loss of mercury amounted to (1943) 500 kg per 1000 tons acetaldehyde. Part of it was given into the waste water. Along with the dehydrogenation of alcohol, which is practised in other countries, this process has today receded into the background and been replaced largely through the oxidation of ethylene with air or pure oxygen in the presence of copper and palladium chloride, according to the equation:

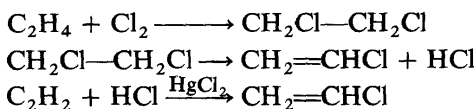
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One plant which is operated with oxygen produces per ton acetaldehyde 7.5 m<sup>3</sup> waste water and another produces 10 m<sup>3</sup> waste water, with a total five day B.O.D. load of 17.5 and 27 kg, respectively. The water can be purified without difficulty in a biological treatment plant together with waste water from other production processes. If oxidation is carried out with air, the five-day B.O.D. load remains unchanged and the quantity of waste water decreases. The waste water, which is accordingly more concentrated, also contains more organic chlorine compounds, for example mono- and dichloroacetaldehyde, which, because of their toxicity to bacteria, have to be saponified with alkali before a biological treatment is applied.

Part of the acetaldehyde is oxidized to acetic acid with oxygen in the presence of heavy metal acetates. The process produces only a little waste water. A plant operating with manganese acetate produces per ton acetic acid 26 litres waste water with a five-day B.O.D. load of 0.5 kg.

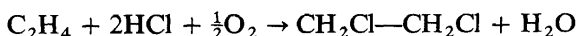
Vinyl chloride, the starting product for the production of PVC, is produced at several places in the Federal Republic according to the combined ethylene-acetylene process. First, from ethylene and chlorine, ethylene dichloride is formed. This product is cracked at a high temperature in the presence of activated carbon or aluminium oxide to vinyl chloride and hydrogen chloride. More vinyl chloride is formed by the addition of the hydrogen chloride to acetylene at 150–220°C in the presence of a mercury chloride catalyst on activated carbon:



When separating out the vinyl chloride by distillation after the cracking of ethylene dichloride, residues containing chlorinated hydrocarbons result which are partly burned in special furnaces with the recovery of hydrochloric acid.

For the entire process 0.15 m<sup>3</sup> and 1 m<sup>3</sup> waste water per ton vinyl chloride were determined for two plants. The waste water accrues from scrubbers and contains common salt and sodium hydroxide or hydrogen chloride, and further small amounts of chlorinated hydrocarbons, which mostly can be stripped by air.

The combined process is becoming less important and will be replaced in the future by the package unit process, which is based solely on ethylene. In this process, the hydrogen chloride formed by the cracking of ethylene dichloride is again converted to ethylene dichloride in an oxychlorination reaction with ethylene and oxygen from the air:



The water, which is separated by distillation, still contains chlorinated hydrocarbons and may have to be purified, for example, by stripping.

Another important vinyl ester is vinyl acetate, the raw material for polyvinyl acetate and polyvinyl alcohol. In the Federal Republic of Germany it is

produced by the reaction of acetylene and acetic acid in the gas phase at about 170°C in the presence of a zinc-containing carbon catalyst. No waste water accrues from this process.

By the addition of ethylene to benzene according to a Friedel Crafts reaction using aluminium chloride as a catalyst, ethyl benzene is formed, from which principally styrene is produced:

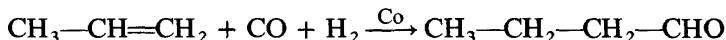


Before processing is carried on, the catalyst and small quantities of hydrogen chloride must be washed out with water and caustic soda solution. Calculated on the basis of data taken from the literature<sup>4</sup>, the wash water per ton product amounts to 4.6 m<sup>3</sup> acidic waste water with 0.2 per cent AlCl<sub>3</sub> and 0.3 per cent HCl as well as 0.6 m<sup>3</sup> alkaline waste water with 0.3 per cent NaOH and 0.3 per cent NaCl. These wash waters contain 0.13 per cent benzene hydrocarbons, which are removed in a benzene stripping plant by nitrogen. They are then eliminated from the recirculated nitrogen by activated carbon adsorbers. In another plant the specific amount of waste water equals 0.36 m<sup>3</sup> with 5 kg AlCl<sub>3</sub> as well as minute amounts of sodium hydroxide and highly volatile hydrocarbons.

For the dehydrogenation of ethyl benzene to styrene, which occurs in the presence of zinc oxide catalysts at about 600°C, a waste water production rate of 2.8 m<sup>3</sup> per ton styrene was reported. It contains 0.2 per cent dissolved hydrocarbons, which can be removed almost completely by stripping.

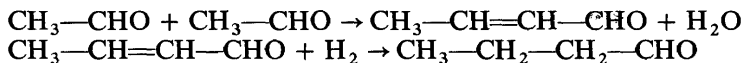
### (c) C<sub>3</sub> derivatives

C<sub>3</sub>-derivatives are obtained from propylene. The hydroformylation of propylene, which leads to butyraldehyde, is increasing in importance. In this process propylene reacts with synthesis gas (carbon monoxide and hydrogen) in a high pressure reactor at 260 to 300 kg/cm<sup>2</sup> and 140 to 180°C in the presence of cobalt catalysts:



The dimerization and hydrogenation of butyraldehyde yields ethyl hexanol, of which the phthalic ester is used on a large scale as a plasticizer of PVC. Butanol, which is important as a solvent and intermediate product, is produced by the hydrogenation of butyraldehyde.

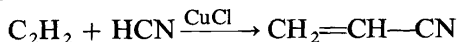
Butyraldehyde was formerly produced from acetaldehyde by aldol condensation, with crotonaldehyde as an intermediate stage:



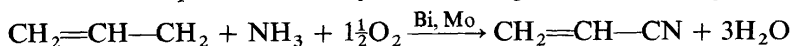
This process produced highly polluted waste water at the rate of about 1 m<sup>3</sup> per ton n-C<sub>4</sub> product with a five-day B.O.D. load of 42.5 kg. Oxo synthesis has led to a substantial improvement of the waste water situation. The specific amount of waste water in a modern plant with various technical improvements, after the C<sub>4</sub> product has been processed, is 2 m<sup>3</sup>/ton. It contains 5–7 kg five-day B.O.D. per ton product and can be purified without difficulty in a biological purification plant together with waste water from other production processes.

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Another example of synthesis starting with propylene is the Sohio process for producing acrylonitrile, which is contained in the oil-insoluble rubber, Perbunan, but which serves principally as a raw material for making polyacrylonitrile fibres. This process has replaced the addition of hydrogen cyanide to acetylene in aqueous, acidic cuprous chloride solution, which is still the customary method used in old plants:



In the Sohio process, propylene reacts with ammonia and oxygen in the air at about  $480^\circ$  in the presence of catalysts containing bismuth and molybdenum:



In this process a high-percentage aqueous solution of organic substances is formed which can be burned, just as acetonitrile, which is formed as a by-product. Besides there accrues a weak waste water that is relatively difficult to handle and which contains polymeric products, nitriles of dicarboxylic acids and some cyanide. In one German plant this waste water is purified biologically in a mixture with other, principally petrochemical, waste waters. The specific amount of waste water here is about  $3 \text{ m}^3$  per ton acrylonitrile with a five-day B.O.D. load of in all about 15 kg per ton. In another plant the toxic nitriles are saponified under pressure. Excess ammonia can be removed from the reaction gases with sulphuric acid and discharged as ammonium sulphate.

## POLYMERIC DERIVATIVES OF HYDROCARBONS

In the last few years the production of thermoplastics has risen sharply. Polyethylene has moved into first place among them. In the high pressure process, ethylene with a minute quantity of oxygen added, is polymerized at 1000 to 2000 kg/cm<sup>2</sup> and about  $200^\circ\text{C}$ . This process involves practically no waste water.

Polymerization according to the low pressure process is carried out at atmospheric pressure and low temperature in the presence of a mixed catalyst of aluminium and titanium and with liquid hydrocarbon as the dispersing agent. After polymerization was concluded in the processes previously employed, the catalysts were made soluble with alcohol and extracted with water. In the factory of Farbwerke Hoechst AG. these processes produced per ton polyethylene 5 to  $6 \text{ m}^3$  weak acidic waste water which had to be clarified mechanically to separate the dispersing agent and which afterwards, apart from the dissolved catalyst, still contained a relatively high organic load of about 15 kg five-day B.O.D. per ton. After neutralization and separation of the metallic hydroxides, the waste water can easily be purified biologically. It is economically advantageous to give the concentrated portions of the waste water a preliminary treatment by stripping or distillation.

Meanwhile technical developments have made it possible in certain cases to reduce substantially the quantity of catalyst employed in the low pressure process. The catalyst can then remain in the product. This improves the quality of the waste water considerably. The waste water produced is free of metal salts and no longer contains any organic load worth mentioning.

The production of polypropylene is similar to that of high low polyethylene. As larger quantities of alcohol must be used to wash out the catalyst, the load in the waste water is at present still higher than for the old polyethylene process.

Polyvinyl chloride (PVC), another important thermoplastic, is formed by emulsion, suspension, or mass polymerization of vinyl chloride at about  $15 \text{ kg/cm}^2$  and  $50^\circ\text{C}$  in the presence of peroxides as catalysts. The most important of these processes is emulsion polymerization. In this process the monomer is finely distributed in water with emulsifier and polymerized to a latex, which is then spray dried. Waste water is formed only by the cleaning of apparatus and the rinsing of the latex filter, which retains coarse particles as sludge. Such a plant produces per ton PVC, for example,  $7 \text{ m}^3$  waste water, which still contains, after precipitation of emulsified and suspended components, a total organic load of about  $0.2 \text{ kg}$  five-day B.O.D. (per ton PVC).

The figures for suspension polymerization are somewhat higher. Here the aqueous phase is separated out after conclusion of polymerization to become waste water. The specific quantity of waste water is thereby raised, for example, to  $14 \text{ m}^3$  per ton PVC. After precipitation with lime and alum, the five-day B.O.D. load amounts to  $0.85 \text{ kg}$  per ton PVC and is caused chiefly by the dispersing agent. Mass polymerization occurs without the use of water or solvents. Waste water is produced only by occasional rinsing procedures.

Polyvinyl acetate (PVA) cannot be used as a raw material for plastics because of its low softening point, but is used on a large scale in the form of aqueous dispersions, chiefly as a raw material for glue, paints and lacquers. It is mainly emulsion polymerized at atmospheric pressure and  $80$  to  $90^\circ\text{C}$ . Waste water is produced only through the cleaning of apparatus, especially from rinsing the filter through which the product is fed after the conclusion of polymerization. In a relatively large plant, for example, about  $5 \text{ m}^3$  waste water are produced per ton PVA raw product (50 per cent polymer). The C.O.D. load of about  $20 \text{ kg}$  per ton PVA raw product is caused essentially by the polymer and can be reduced by about 95 per cent through precipitation with lime and ferrous sulphate. The five-day B.O.D. load amounts to about  $1.5 \text{ kg}$  per ton PVA raw product and results from additions of protective colloids and emulsifiers. After treatment with lime, the water is biologically purified together with water from other production processes, at times with the addition of defoamers.

## **FURTHER PROCESSING OF PETROCHEMICAL PRIMARY CHEMICALS**

For the production of primary chemicals it is possible to keep the waste water situation fairly well in view. The examples just presented show that the waste water from manufacturing processes in so far as it contains organic substances is amenable to biological purification after suitable preliminary treatment in some cases. In existing biological plants five-day B.O.D. decomposition rates between 85–99 per cent are attained, depending on the concentration and composition of the raw water. The largely constant composition and the mostly rather continuous production of waste water facilitate treatment.



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On the other hand, however, further processing of the primary chemicals to dyes, plant protecting agents, pharmaceuticals, textile auxiliaries, organic chemicals and the like frequently leads to waste water which cannot be purified by the usual procedures of waste water technology or only unsatisfactorily. This includes waste water which contains, apart from organic substances, inorganic salts, acids, or bases in high concentrations. Mainly in chemical works near the coast, shipping such waste water out to sea will assume increasing importance. Where this method is not possible, the chemical industry must seek to improve the quality of the water by changing its manufacturing processes. In the future, where new developments of chemical processes are concerned, waste water technology will be a more important consideration than ever before.

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- <sup>3</sup> H. Engelhardt and W. Haltrich. *Chem.-Ing.-Techn.* **40**, 275 (1968).
- <sup>4</sup> K. J. Bock and W. Lukaschek. *Chem.-Ing.-Techn.* **40**, 284 (1968).