Pure & Appl. Chem., Vol. 45, pp. 147–151. Pergamon Press, 1976. Printed in Great Britain.

PREVENTION OF WATER POLLUTION IN THE PETROCHEMICAL INDUSTRY

CURRENT SITUATION AND FUTURE VIEWS

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Abstract—In recent years the petrochemical industry has been faced with many environmental problems; a solution must be found to these problems in the future. This solution concerns mainly two types of problems: the first is a socio-economic one and involves the planning of industry and its future investments, the other is a technical one and concerns the means for improving the quality of the environment.

It is the object of this paper to try to outline the environmental problems that the petrochemical industry has been facing in recent years, to assess, as far as possible, its present state of pollution and, above all, to anticipate the future problems and the technical needs for their solution.

First of all let me point out that "petrochemical industry" means that production process by which, starting from a very limited number of raw materials (essentially methane, petroleum distillates, sodium chloride, hydrofluoric acid) it is possible to obtain a wide gamut of highly pure organic compounds (such as intermediates and monomers for plastics, resins, fibers, etc.) which are partly sold and partly directly transformed into semi-finished products.

Table 1 summarizes the world production of some characteristic petrochemical products. In any case, it should be pointed out that the final product of the petrochemical industry seldom becomes the object of direct consumption but rather constitutes the main material for other manufacturing industries.

This fact involves some considerations of a certain interest. On the one hand (and in particular among the public) there exists a considerable difficulty in properly evaluating the overall cost/benefit balance, on the other hand (as a consequence) there is the tendency to consider prevention measures for pollution control in the petrochemical industry as strictly related to the production plant often disregarding the socio-economic advantages deriving from the use of the finished products.

Table 1. World production of ethylene and propylene in 1970–1973 (in 1000 tonn/yr)

	1970	1972	1973
Ethylene	19·500	25·200	28·500
Propylene	9·500	12·500	13·500

World production of some organic intermediates in 1973 (in 1000 tonn/yr)

Acetone	2·100
Phenol	2·500
Methanol	6·500
DMT-Terephthalic acid	3·450
Caprolactam	1·830
Cumene	3·200
Adipic acid	1·600
Hexamethylenediamine	700
Acrilonitrile	2·150
Trichloroethylene	1·010
Tetrachloroethylene	1·050
Trichloroethane	480

This does not mean a decline of environmental responsibility by the petrochemical industry. The "environmental problem" is, as a matter of fact, an extremely complex phenomenon which cannot be limited to the production stage but should be examined in a much wider context.

It is therefore evident that we cannot talk about aqueous effluents concerning the petrochemical industry, and of the systems for their proper treatment, if firstly we do not examine the changes that have taken place in the last years in regard to the environment in which such an industry has been operating.

We think that the main environmental factors to be considered can be summarized as follows:

(1) Fair judgement of the actual situation of receiving bodies.

(2) Public opinion.

(3) Legislative provisions.

(4) Technical and economic possibilities of the petrochemical industry.

1. FAIR JUDGEMENT OF THE ACTUAL SITUATION OF RECEIVING BODIES

(a) *Typical pollutants of petrochemical industry*

Neglecting some parameters such as pH, temperature, suspended solids, salinity, mineral oils and BOD (biochemical oxygen demand), common to other industries in which they play a more relevant role or can be treated by currently practised technologies, we think that aqueous effluents originating from the petrochemical industry are essentially characterized by the presence of the following substances:

—organic substances that are not biodegradable, or only slightly so
—nitrogen compounds
—heavy metals.

The first class of substances cannot be systematically described, an exception being the organic halogen derivatives containing mainly one or two carbon atoms; we are usually dealing with a multitude of polymerization, addition, and condensation products derived from secondary reactions taking place in several production processes. Such products show a certain solubility in water due to the presence of liophilic groups in addition to being very slow towards biological oxidation.

In the second class we may include ammonium salts (typical by-products of some productions such as caprolactam, acrylonitrile, acrylates etc.) and organic substances containing nitrogen such as nitriles, cyanohydrins, amines and aromatic nitroderivatives. These products when biodegradable usually give rise, in the final effluents, to noticeable quantities of ammonium ions or eventually to nitrate ions.

The third class of pollutants is usually due to accidental losses of catalysts, to the production of chlorine by the mercury cell and partly to the corrosion of equipment; in addition to mercury, the metals which may be most frequently present in waste waters are copper, nickel, cobalt, molybdenum, chromium, zinc, bismuth and vanadium.

(b) *Knowledge on the environmental incidence of wastes*

The present knowledge is not exhaustive, in spite of the many efforts which are being made, in view of the complexity of the problem.

On the other hand, it becomes indispensable to ascertain some criteria (in addition to official regulations) for the quality demands to be satisfied; the best solution could of course be the "zero discharge" goal if we neglect the economic and technical constraints involved.

Such criteria can be briefly summarized as follows: *Reduction, to safe levels of the concentration of substances characterized by acute toxicity.* Enough knowledge is available because of the great quantity of scientific data concerning a great many compounds, and because of the simplicity and rapidity of experimental tests should these be necessary.

Reduction of discharges of substances normally present in the environment to such quantities that will not alter appreciably the pre-existing concentration. This is the case for several metals, some nitrogen and phosphorus compounds, biodegradable organic substances, salinity, etc.

Knowledge in this connection can be considered very satisfactory, and it is the belief that it is such to allow eventually the definition of the "absolute quantities" for waste waters to be discharged in relation to the quality of the receiving bodies. This consideration is fundamental in the choice of the appropriate area for new industrial installations.

Reduction to within limits approaching "zero" of the discharge of noxious, persistent and bio-accumulative substances. Clearly it is necessary to distinguish whether such substances originate from the production process only, or are also connected with the utilization of the final product. Typical examples are those concerning mercury and DDT.

While in the first case, it is always possible to intervene with appropriate antipollution processes or, even better, with changes in the production process itself, in the second case it might be necessary to reduce, or even to stop, the production process responsible.

As far as persistent and non biodegradable by-products (typical of this petrochemical industry) are concerned, the knowledge is still quite insufficient. Environmental consequences not immediately detectable, presence of compounds and of their degradation products not yet well characterized, eventual mechanisms for degradation or for bio-multiplication, are typical examples. Certainly among the thousands of compounds present in waste waters, the majority can be considered harmless; at the present moment, however, we have no means of proving this so that any justification along these lines might contribute to the reduction of unjustified depuration costs.

(c) *Phenomena of particular relevance*

Apart from what has just been said about mercury and heavy chlorinated hydrocarbons, we are not aware of other particularly significant phenomena concerning water pollution in the petrochemical industry.

From a general point of view it can be noted that, in spite of a 30% increase in the production chemicals in Europe in the period 1968–1971, the environmental situation has not undergone marked change. This is clearly due to the appropriate interventions presently adopted everywhere.

We cannot help but recall, however, that recently some worries have arisen in regard to problems due to vinyl chloride and to the eventual noxious effects of light chlorinated products in potable water.

The problem must of course be followed with great care and any explanation which might be necessary should be given in the shortest period of time possible.

2. PUBLIC OPINION

In the last years the concept of "environmental protection" has been evolving and now has a better and more adequate realistic meaning.

The new interpretation given to the principle "pollueur–payeur" represents a well-known example of such evolution. Not long ago it was practically interpreted as a coercive law against freely polluting industry rather than as a rule for the prevention of any sort of distortion of competition among industries. As a matter of fact, at present people are inclined to recognize the need of a certain environmental cost for any human activity.

Certainly to-day a petrochemical plant is not looked upon as a good neighbour. Errors made in the past in regard to plant ubication, the scarcity of adequate environmental precautions adopted, the insufficient information available on the actual contribution of the pollution load and, above all, the difficulty in properly evaluating the "cost/benefit" ratio, are among the necessary reasons.

The petrochemical industry, as with power and nuclear stations, is a type of activity characterized mainly by a low manpower demand and high environmental impact, while distributing its products on a wide national and international scale. Consequently, the local authorities become most active in requiring a strong control of pollution at stricter levels than those contemplated by the national regulations. The latter are often simply considered as reference standards.

For industry and for public administration an appealing goal is to develop methods for achieving reliable information on the acceptability of the emmission of a given quantity of a given pollutant in a defined environment.

3. LEGISLATIVE PROVISIONS

In the past the problem of environmental protection had been approached through the enforcement of proper legislation aimed at the protection of the "quality" of the receiving waters. Attention was given more to the eventual effects caused by the wastes rather than to the characteristics of the wastes involved.

The absence of damage to aquatic life or the specification of certain chemical and/or physico-chemical characteristics to be respected, are some typical examples of the meaning of "quality" of receiving waters.

Subsequently, several legislations have adopted the concept of "standards" as a measure of the quality of the effluents. Such standards are to be satisfied (usually in terms of concentration limits) regardless of the origin of the wastes and of their volumes.

This type of regulation has some advantages and disadvantages: it has the merit to provide plain rules of general validity but it does not take into account particular factors, such as the real economic and technical possibilities for a given type of production to meet the fixed standards, the environment into which the discharge is carried out, and the absolute and relative quantities of the polluting load. In any case it does not stimulate the saving of water. On the other side, some countries have avoided the use of standards and the quality of the effluent is managed by local authorities (river authorities etc.) in relation to local needs.

Finally in the U.S.A., E.P.A. has followed a quite different approach; "effluent standards", differentiated in accordance to type of production, are fixed and determined as quantity of pollutant allowed per tonn of product.

Which system is preferable? All have merits and defects, but I believe that in this field we should never forget the fundamental characteristics of the various production lines. In any case common regulations would be desirable even though local demands to be satisfied differ from place to place.

4. TECHNICAL AND ECONOMIC POSSIBILITIES OF THE PETROCHEMICAL INDUSTRY

Industry needs clear goals in order to plan properly its investments in the environmental field; I have just described some of the problems related to the definitions of these goals. I wish now to describe the technical means for their fulfilment.

In theory it is possible to satisfy any kind of regulation provided we neglect the energy consumption and relative costs. The problem, therefore, is to have regulations that can be respected with the use of practical, available, technologies which are also economically achievable.

At this point we ought to remember that the environmental problem is completely different, and consequently the costs involved in the case of ecological improvement of old plants are also very different compared with the costs of new installations. Practical legislation must, therefore, take into account these aspects. In regard to available technologies, it is fair to proceed to a rough distinction between centralized water treatment plants and technical interventions carried out at the battery limits.

(a) *Centralized waste water treatment plants*

Fundamentally these plants yield depurated effluents of different origin through a series of operational and undifferentiated steps. Wastes may be either a mixture of industrial effluents or a mixture of industrial and urban waters. Scale economy and simplicity of control are the main advantages inherent to such plants.

Normally the operational steps of a centralized plant for petrochemical wastes can be briefly summarized as follows:

Suspended solids separation. This is a very old and traditional treatment operation. The most practical technology consists in a flocculation step carried out through addition of suitable reagents and subsequent sedimentation of the flocs. In addition to organic and inorganic suspended solids abatement, partial reduction of the concentration of soluble products is also accomplished (in particular metal ions, fluorides, phosphates and organic macromolecules).

During the last years the most noticeable developments are those related to the improvement of the mechanism of flocculation, particularly through the use of most appropriate chemical additives. An example is the use of excess quantity of lime in order to improve the overall abatement of suspended and soluble substances.

BOD_5 reduction. This operational step, usually carried out through biological oxidation, does constitute the most important part of a centralized depuration plant. Biological oxidation with activated sludge is certainly the most classic system being used even though other systems, such as extended aeration, are also available.

Recently, the use of plastic media trickling filters has found a wide application especially as a first stage for the partial reduction of BOD in effluents characterized by high organic loads.

However, the high energy consumption (due to low yield in air utilization) and the need for large volume oxidation tanks (because of the low sludge concentration) represent, as far as activated sludge processes are concerned, the main drawbacks. Studies are, however, under way to overcome these drawbacks. In this respect we think that replacement of air with oxygen, and the eventual utilization of a suspension of activated carbon as a support for the biological mass, might constitute valid alternatives to the solution of the problems. Should it be possible to accomplish carbon regeneration via wet oxidation methods, this last process might become of practical interest.

In addition to BOD reduction, activated sludge biological processes allow complete elimination of residual phosphates still present in the effuent; reduction of nitrogen compounds and of non-biodegradable substances will, on the other hand, be very limited.

Final filtration and chlorination. These last steps will allow further removal of residual quantities of sludges lost in the biological stage and disinfection of the final effluent to be discharged.

Sludge disposal. Incineration, carried out in multiple-hearth or in fluidized bed furnaces, is presently regarded as the most correct method for the disposal of primary and secondary sludges derived from a water treatment plant. The solution is, however, economically not feasible in view of the considerable investment and operating costs involved (up to 40% of the overall cost of the treatment plant).

Open sea disposal is another possibility, but it is still the subject of many discussions regarding the appropriatness of the solution.

Another possible alternative appears to be that of spreading on agricultural land, either in the solid or in the liquid phase. Such an operation implies, however, some sort of pretreatment of the sludges to be disposed in order to avoid anaerobic fermentation and to reduce the initial volumes. For this purpose several techniques are available: aerobic or anaerobic stabilization, ozone or sulphur dioxide conditioning, heating in autoclave either in the presence or absence of oxygen are just a few examples. At present it is very difficult to foresee which of the methods mentioned can be considered the best.

A centralized water treatment plant, even when conceived according to the best available technology, is not capable of bringing about a satisfactory reduction in the concentration of nitrogen compounds, non-biodegradable organic substances (halogen derivatives in particular), heavy metal (such as mercury), or salinity. As far as nitrogen compounds are concerned, the problem is likely to find a solution in the near future. Practical examples on an industrial scale of processes based on nitrification and biological denitrification are presently being tested with success. Even though technically valid, such systems still require further improvement especially in regard to investment and operational costs. Three different schemes of biological denitrification are reported in Fig. 1.

In regard to non-biodegradable organic substances, future possibilities for their reduction are to be considered with less optimism. The possibility of using in biological processes pure oxygen in a loop system, could allow aseptic conditions favourable to the growth of selected bacteria strains capable of metabolizing substances of peculiar organic structure. One wishes to recall, as examples, the isolation of selected bacteria strains which are believed to be capable of metabolizing substrates such as polyacrylamide, polyvinyl chloride and DDT.

Adsorption on activated carbon or on resins after the final stage of filtration is, of course, another possibility; however, considering the high flows usually involved in petrochemical plants, we think the process economically not feasible. It could be, on the other hand, successfully applied at the battery limits of single production units.

Therefore, the presence of substances which cannot be eliminated in a centralized treatment plant or which may give rise to inhibitory or toxic effects of the biomass require specific interventions at the various stages of production involved through in-plant improvements and/or specific treatment at the battery limits.

As far as process improvements are concerned, it is probable that the problem constitutes a big job for process engineers. One would like only to point out that the final target should be the complete elimination, whenever possible, of all undesirable by-products; should this not be possible, efforts should be made to reduce their specific quantity and proceed to a proper segregation in order to achieve minimum volumes of waste with maximum concentration of pollutants.

(b) *Technical interventions at the battery limits*

These consist mainly in processes for the treatment of a given waste containing specific pollutants; after treatment, the effluent will become acceptable to a centralized treatment plant or in this extreme case can be discharged directly into a receiving body.

Any method based on physical, chemical and physico-chemical separation may be suitable for the treatment of a specific effluent. Now I will briefly describe those processes currently in use or those which may find useful application in the petrochemical industry.

Flotation. In addition to the elimination of insoluble oils, this technology may find useful application for the extraction of substances possessing tensio-active properties and perhaps for the removal of other organic products after their chemical complexation or insolubilization.

Thermal hydrolysis. This is normally used for destruction of nitriles and cyanides; another field of application might be in the breakdown of toxic or complex molecules to enhance their biodegradability.

Wet oxidation. In spite of certain technological difficulties (corrosion, scaling, etc.), wet oxidation of non biodegradable organic compounds may be considered a very attractive method. Further studies are, however, necessary for optimization of oxidation catalysts in order to lower substantially the present operating temperature (above 250°C). The process can be considered particularly promising for destruction of toxic substances or of soluble macromolecules present in high concentration in the wastes to be treated.

Adsorption. Adsorption on activated carbon or on synthetic polymers will continue to find an ever increasing application for extraction of non biodegradable substances and in particular for organic chlorinated derivatives.

Synthetic polymers above all, seem susceptible to further development inasmuch as they may be tailored

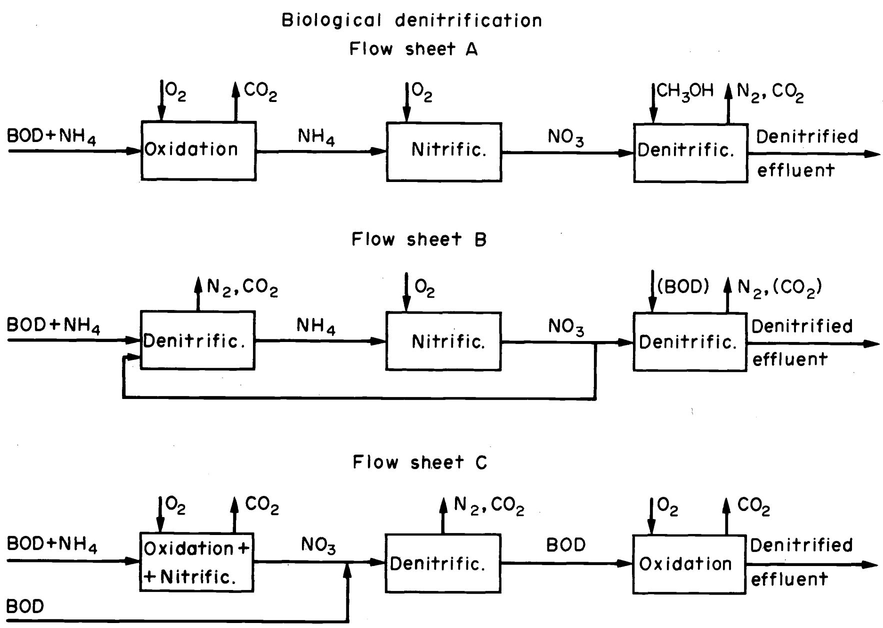

Fig. 1.

according to the specific product to be treated. Examples are chelating or complexing resins which have yielded very good results in the elimination of mercury.

Ion exchange. Normally used for inorganic ion removal, ion exchange resins have shown useful application in the treatment of wastes containing phenols. The availability of resins that can be regenerated thermally, constitutes an interesting development of this technology. This, in fact, brings the possibility of eliminating or of reducing the salinity content caused by the normal regeneration process.

Combustion. Elimination of troublesome wastes through incineration, is to be considered the last chance owing to the high costs involved. In spite of this, the number of incineration furnaces in petrochemical plants continue to increase. We hope that in the future, this technology will be applied strictly to those self-sustaining streams characterized by high concentrations of organic substances in view of the development of more specific and economic treatment process.

It is necessary in the context of this summary discussion on treatments at the battery limits to add a few words about the important problem concerning the possibility of reutilizing treated waste waters.

Surely this will be one of the biggest problems of the near future since water resources are not unlimited and cannot follow the future demands of industry. In addition, the requirements of more stringent "limits" in water quality by public authorities force and facilitate this trend.

The basic criteria for approaching the problem are still in an evolution stage: is it better to recycle water coming from a centralized treatment plant or within individual production units? Probably a sure answer is not possible but the choice will depend on environmental and technical situations.

Some examples of possible internal recycle are as follows. In Fig. 2, Schemes A and B represent two possibilities of water recovery. Condensed water and process water containing mainly an organic load, are typical examples of selected streams present at the single production units. The process water (Scheme A), could be treated on an adsorption bed and yield an effluent particularly suitable to be fed to a plant for deionized water production. Condensed water, on the other hand,

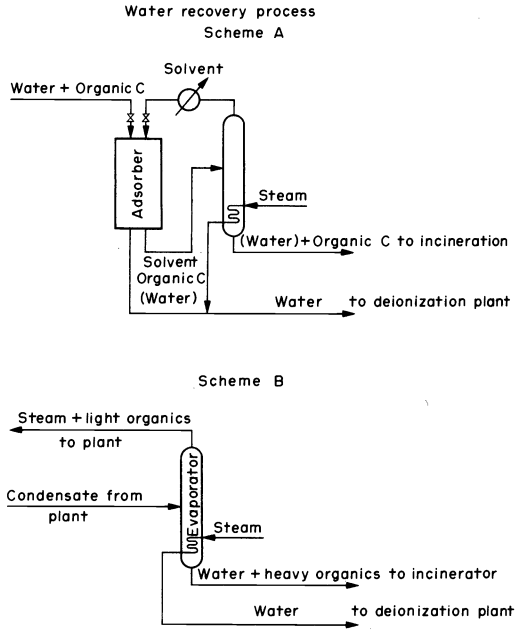

Fig. 2.

could be almost totally re-evaporated to yield a mixture of organics and steam, to be recycled to the production plant, and a residue with high concentration of heavy organics to be incinerated. Secondary condensed water, being clean, can be recycled to the deionization plant.

CONCLUSIONS

In conclusion, we can say that a great number of technologies are presently available to the petrochemical industry for a correct approach to the solution of the environmental problems which it is facing. Further developments will also help industry to meet future needs.

The economic impact of the use of the present technologies is, however, in many cases the main constraint on their utilization. And this, considering the increasing difficulties in competition, constitutes a real headache.