TABLE XI

Substances in the Rhine (Yearly Averages, German-Dutch Border)

	1976	1977	1978	1979	1980
Mercury (μg/L)	0.5	0.4	0.3	0.3	0.2
Cadmium (μg/L)	3.0	2.0	1.5	1.2	0.9
Chloroform (μg/L)	67	28	22	8.4	4.5
Dichloromethane (μg/L)	–	18	15	0.09	nn
1,1,1-Trichloroethane (μg/L)	2.2	0.27	0.08	<0.1	0.2
Trichloroethylene (μg/L)	0.56	0.50	0.32	0.13	0.23
HCB (μg/L)	0.051	0.051	0.024	0.019	0.01
α-HCH (μg/L)	0.026	0.025	0.015	0.007	0.01
Hexachlorobutadiene (μg/L)	–	0.063	0.023	0.008	nn
Nitrobenzene (μg/L)	–	0.38	0.12	<0.01	–
Fluoranthene (μg/L)	–	0.21	0.21	0.096	0.076
3,4-Benzopyrene (μg/L)	–	–	0.058	0.041	0.033
Amount of water (m^3/s)	1341	2208	2361	2541	2552

The industry is forced to plan on a long-term basis. Therefore, waste reduction measures obviously have been taken even without actual administrative regulations.

OUTLOOK ON FUTURE DEVELOPMENTS

However, possible risks of these proceedings become more and more obvious. Again and again, additional substances are brought into discussion by various groups. For a sensible examination, first their content in the surface waters as well as in possible discharges has to be ascertained via analysis. For this purpose, the authorities – as, of course, the dischargers, too – have to make series analyses in the trace range. With regard to these substances, possible points of discharge, waste reduction techniques, control measures, etc., have to be found. All this has to be done at a time when the extensive sanitation measures become evident, as shown at the Rhine. There is a danger that bureaucratic perfectionism is liable to turn this necessary EEC directive into an end in itself. The selection of substances should be reasonable and implementation of the directive should still be possible. Therefore, selection should strictly concentrate on those substances for which an ecological necessity for regulation is definitely recognizable.

Large-Scale Production and Application of Highly Concentrated Ozone

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ABSTRACT

With the new, very efficient generating plants, ozone can be produced in high concentrations, at low cost and with high reliability. This versatile reagent is therefore destined, in the near future, to play a more important role in the oleochemical industry than today, since it can help to solve different problems in the synthesis of chemicals as well as in the treatment of waste.

INTRODUCTION

Ozone is an extraordinarily powerful oxidizing agent which has been used in drinking water treatment for more than 80 years. Its outstanding properties–high oxidation potential (2.07 V), high reactivity even below room temperature, pronounced selectivity and no residues after reaction–make ozone a reagent which can be used to solve various problems. Ozone has many possible applications in synthesis and in the treatment of wastewater, and off-gases are being studied in laboratory and pilot plant experiments. Nevertheless, ozone lacks large-scale application in the chemical industry. The only known process, where ozone is used in amounts of hundreds of kilograms per hour, is the ozonolysis of unsaturated long-chain fatty acids for the production of bifunctional compounds such as dicarboxylic acids, aldehydes, ketons and alcohols (1,2). There are several reasons for this shortcoming:

Ozone is very often considered to be an expensive, dangerous substance which cannot be produced with the reliability demanded for industrial production processes. The concentrations in which ozone could be produced in the feed gas were restricted to about 1.5 wt-% in air and 3 wt-% in oxygen. This resulted in the handling of large gas volumes and an unfavorable reaction kinetic. Moreover, ozone cannot substitute for other oxidants without an adaption of the whole process.

It is the aim of this paper to show that modern large-scale ozone generating plants can produce ozone according to the requirements of the oleochemical industry, i.e., cheaply, reliably and in high concentrations.

PRINCIPLES OF OZONE PRODUCTION

Today ozone is produced on a commercial scale exclusively by a silent electrical discharge in an oxygen-containing gas. An alternating current with a high voltage is applied between 2 electrodes separated by a dielectric of glass and a narrow gap. While the feed gas is flowing through the gap, the silent electrical discharge produces ozone in it. The discharge causes a dissociation of oxygen molecules into 2 oxygen atoms, which recombine with oxygen molecules and form ozone.

The production and destruction of atomic oxygen and ozone from an initial mixture of electrons and oxygen has to be described by more than 40 different reactions. It has been shown that only about 7 reactions, which are listed in Figure 1, are dominant (3). In air, even more reactions have to be considered.

In practice, the 2 electrodes are concentric tubes, the outer electrode made from stainless steel, the inner electrode formed by a metallic layer on the inner glass surface. The ozone generator consists of a large number of such electrode pairs, assembled in a vessel as shown in Figure 2.

$$\boxed{(1)\quad e+O_2 \xrightarrow{K_1} 2O+e}$$

$$\boxed{(2)\quad e+O_3 \xrightarrow{K_2} O_2+O+e}$$

$$\boxed{(3)\quad O+O_2+O_2 \xrightarrow{K_3} O_3+O_2}$$

$$\boxed{(4)\quad O+O_3 \xrightarrow{K_4} 2O_2}$$

$$\boxed{(5)\quad O+O+O_2 \xrightarrow{K_5} O_2+O_2}$$

$$\boxed{(6)\quad e+O_2 \xrightarrow{K_6} O_2^{+}+2e}$$

$$\boxed{(7)\quad e+O_2 \xrightarrow{K_7} O^{-}+O}$$

FIG. 1. Dominant reactions of ozone formation by a silent electrical discharge in oxygen.

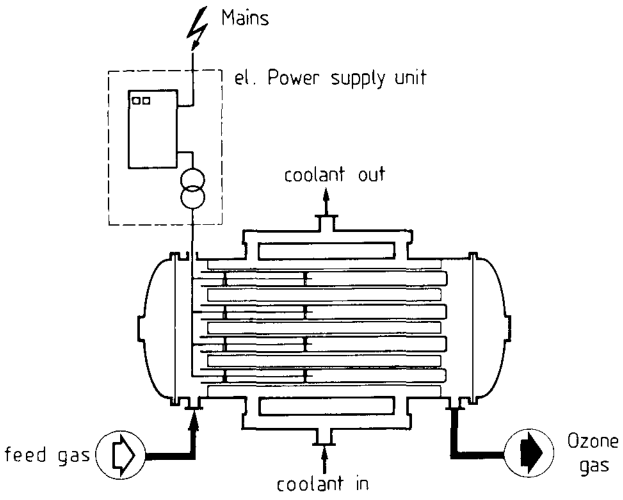

FIG. 2. Schematic diagram of an ozone generator.

PERFORMANCE DATA OF MODERN OZONE GENERATING PLANTS

Different essential developments have improved the economy and reliability of ozone plants.

Frequency of Electrical Supply (4)

To make ozone cheaper, it has to be produced at high density, to reduce the size and the investment, and with a minimum of specific energy consumption.

Under given boundary conditions, such as type and composition of the feed gas, gas pressure, gap width, coolant temperature, etc., the ozone production (or ozone concentration) is a function of the energy supplied per unit of the discharge surface or, expressed in other terms, the resulting power density. The higher this parameter, the

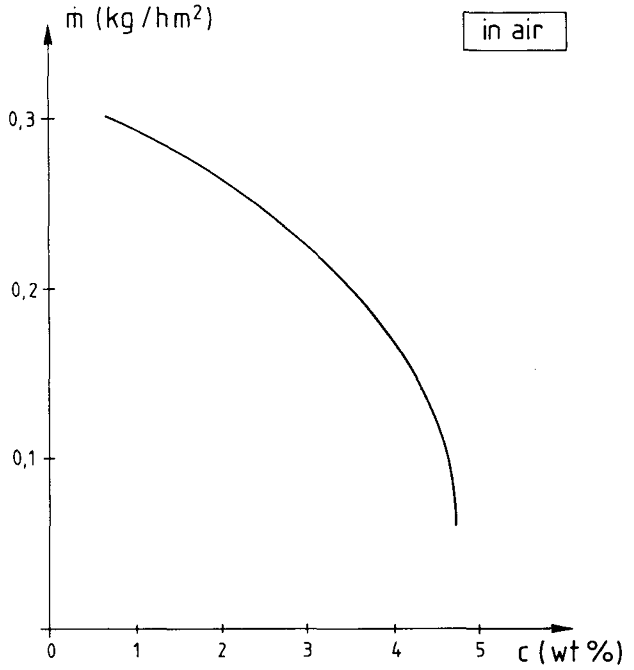

FIG. 3. Ozone production density ($\dot{m}$) of an ozone generator as a function of the ozone concentration (c) in air.

greater the ozone production. The power density can be increased by increasing the voltage or the frequency, but the maximum possible applicable voltage is limited to about 14 kV. Above this, voltage sparking occurs in the gap, causing stresses and breakage of the dielectric glass tubes.

Therefore, higher production densities for a reliable continuous operation can be achieved only with higher operational frequencies and correspondingly lower voltages. The appropriate frequencies of 600-1000 Hz are easily achieved by power electronics. A modern ozone generator, working on this basis, runs with a power density of 3-4 KW/ M^2 and a corresponding ozone production density of 0.2-0.25 kg/M^2/h in air. This is a multiple of that of classical ozone generators with 50 Hz operational frequency.

Cooling of the Ozone Generator

The plasmachemical process of the ozone formation is very sensitive to the gas temperature. Higher temperatures mean lower yield and lower ozone concentrations. Better cooling of the gas is achieved by a narrow gap since the heat release from the gap is limited by the thermal conductivity of the gas. As a result, the specific energy consumption is minimized and high ozone concentration is possible. In Figure 3, the ozone production is plotted as a function of the

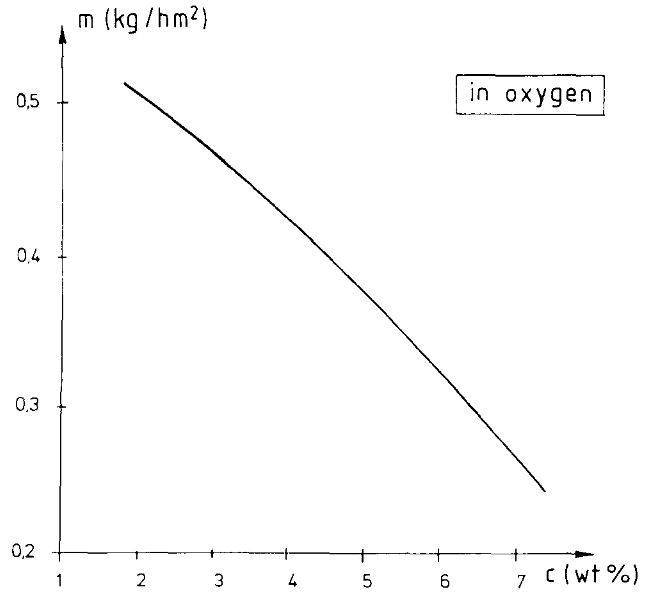

FIG. 4. Ozone production density ($\dot{m}$) of an ozone generator as a function of the ozone concentration (c) in oxygen.

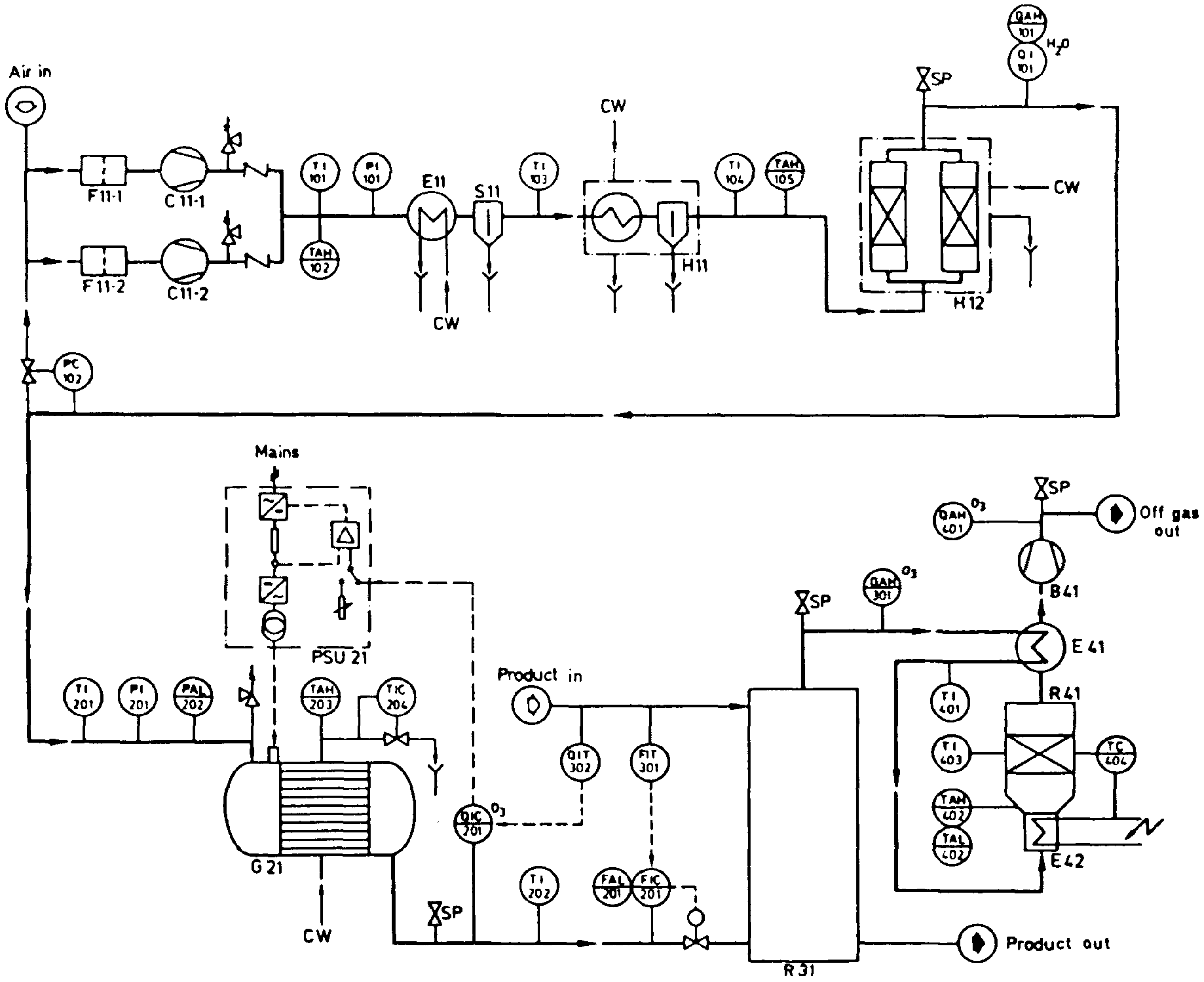

FIG. 5. Flow diagram of an ozone plant with air conditioning. F 11—Filter; C 11—Compressor; E 11—Water cooler; S 11—Water separator; H 11—Refrigerating dryer; H 12—Adsorption dryer; G 21—Ozone generator; PSU 21—Power supply unit; R 31—Ozone reactor; E 42,41—Economizer; R 41—Residual ozone destruction unit; B 41—Blower.

ozone concentration for air as a feed gas. Ozone concentrations of up to 3.5% can be produced with a good yield. For higher concentrations, the production decreases sharply and reaches zero at the cut-off concentrations of about 5%. In oxygen, ozone concentrations of up to 7% are obtained with good production yield (Fig. 4).

Optimum System Design

Besides the ozone generator, an ozone plant consists of the feed gas preparation, the ozone reaction and, if necessary, the residual ozone destruction in the off-gas. These elements are shown in the flow diagram, of an ozone plant using air as a feed gas, in Figure 5. A careful system design is an essential requirement for optimum ozone generation. The feed gas of the ozone generator has to be prepared to the appropriate quality, i.e., with the right pressure, free from dust and organic impurities and with low humidity. Even a small amount of humidity reduces the yield drastically. Therefore, the dew point of the feed gas has to be lower than −50 C. Traces of hydrogen or hydrocarbons reduce ozone production to an unacceptable level if they are present in the range of 10 ppm (5) (Fig. 6).

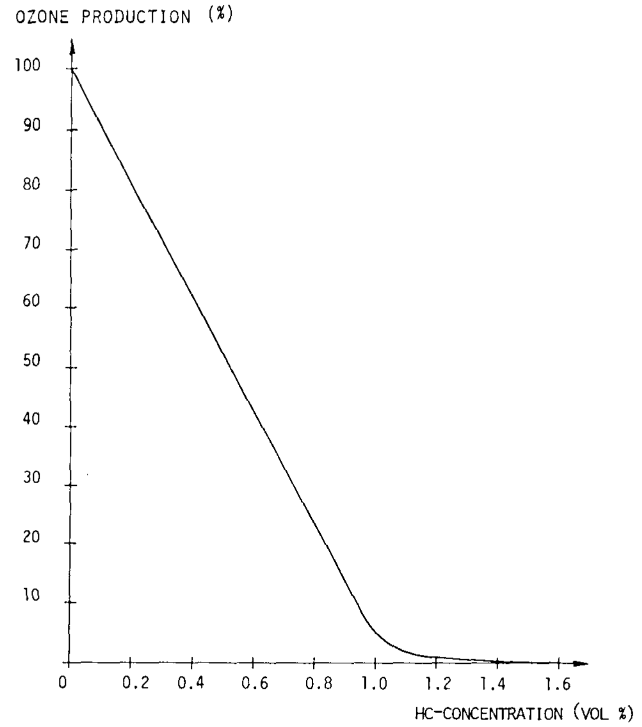

FIG. 6. Effect of hydrocarbons (HC) on the ozone production according to Inoue and Sugino (5).

The reactor, where the oxidation process takes place, has to be adapted to each specific reaction and process. But there are a few general rules. A fast reaction and an almost complete utilization of the applied ozone can be achieved best with a high ozone concentration in the carrier gas. The reaction of ozone, as well as its mass transfer from the gas phase to the liquid phase, are accelerated by higher ozone concentrations, which are therefore an important contribution to the efficiency of the ozone plant. Since the formation and destruction of ozonides are very strong exothermic processes, careful control of the temperature and efficient cooling of the reactor are necessary.

CHOICE OF THE FEEDGAS

A comparison of the specific energy consumption for the ozone generation from air and oxygen (Fig. 7) favors use of oxygen. The same is true from the point of view of high ozone concentrations. But this advantage is balanced by the economic necessity of recovering the oxygen, which is not converted to ozone, from the ozone reactor by a recirculation cleaning system.

Figure 8 shows the basic flow chart of 3 versions of ozone plants. Variant 1 uses air as feed gas. In variant 2, the feed gas is oxygen. The off-gas from the reactor passes through a cleaning system before re-entering the ozone generator. This cleaning consists of washing, mostly with an alkaline solution, and drying. Variant 3 is the most elegant because the oxygen does not come into contact with

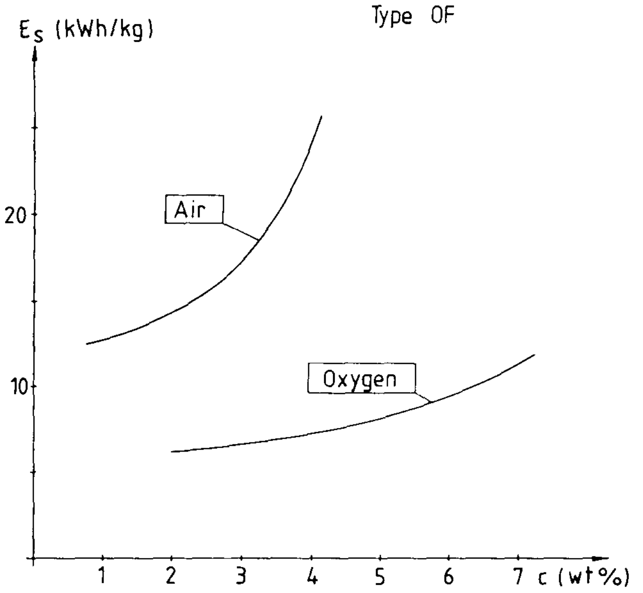

FIG. 7. Specific energy consumption (E_S) as a function of the ozone concentration (c) for BBC Ozone Generators Type OF. Feedgas air and oxygen.

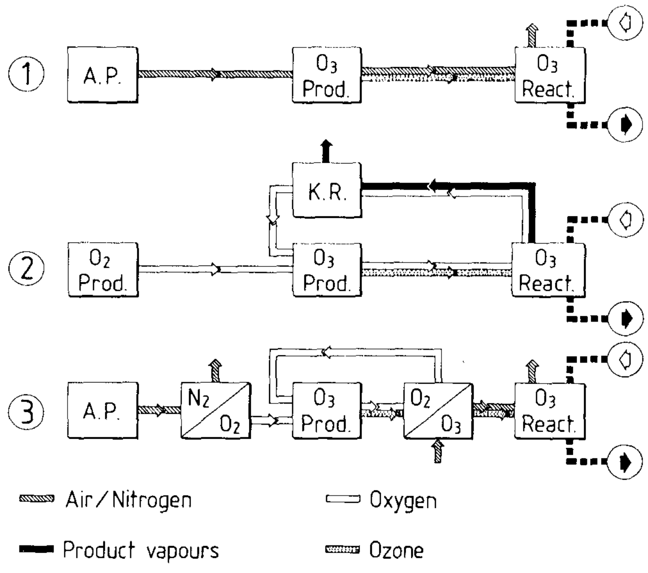

FIG. 8. Basic flow diagram of an ozone plant: variant 1: once through system with air as a feed gas; variant 2: oxygen system with a recirculation cleaning unit (KR); variant 3: pressure swing adsorption system for oxygen/nitrogen and oxygen/ozone gas mixtures and with air as the feed gas.

the reaction products. This is achieved by employing appropriate adsorption agents, which separate nitrogen of the air from the oxygen by adsorption before it enters the ozone generator, and ozone from oxygen after the ozone production. The unconverted oxygen is fed back to the ozone generator. In a second step the nitrogen and ozone are desorbed and fed to the reactor (4).

OZONE PLANT FOR 200 kg/hr

With the described technology, ozone plants with production capacities of 200 kg/hr, and more, are possible. Figure 9 shows the layout of a 200 kg/hr plant. The feed gas is air and the ozone concentration 20 g/NM^3. The plant consists of 6 ozone generators each with a 34 kg/hr production capacity. For the preparation of the air, about 10,000 M^3 of N_2/hr, 2 independent lines are provided. The air preparation unit with compressors, coolers and the large dryers needs about half of the required space. The total plant for this large-scale concept covers an area of 36 X 18 sq m and is 8 m high.

COST OF OZONE

The most important question for large-scale ozone application is related to the cost per kg of ozone. On the basis of the presented technology, the result for ozone production from air is shown in Table I. For the given design basis and the corresponding energy and cooling water consumption, the cost per kg of ozone is \$1.03 for a 200 kg/hr plant and \$1.13 for a 50 kg/hr plant.

The values obtained for ozone production from oxygen can be seen in Table II. With the chosen prices for oxygen and energy the costs are just the same as for air.

TABLE I

Cost per kg of Ozone Produced from Air for 50 kg/hr and 200 kg/hr Production Plants

Design basis:			
Feed gas		air	
Ozone concentration		1.5 wt % (20 g/M^3)	
Cooling water temperature		18 C	
Consumption data per kg ozone			
Energy		17.7 kilowatt hr	
Cooling water		2.6 M^3	
Ozone production	kg/hr	50	200
Investment	\$ million	0.85	2.77
Cost per kg ozone in \$/kg (8400 hr operation per year)			
Annuity 20% (12%/8 years)		0.40	0.33
Labor cost (\$20,000/year)		0.05	0.01
Maintenance (2% of investment)		0.04	0.03
Fixed cost		0.49	0.37
Energy (\$0.03/kilowatt hr)		0.53	0.53
Cooling water (\$0.05/M^3)		0.13	0.13
Total cost		1.15	1.03

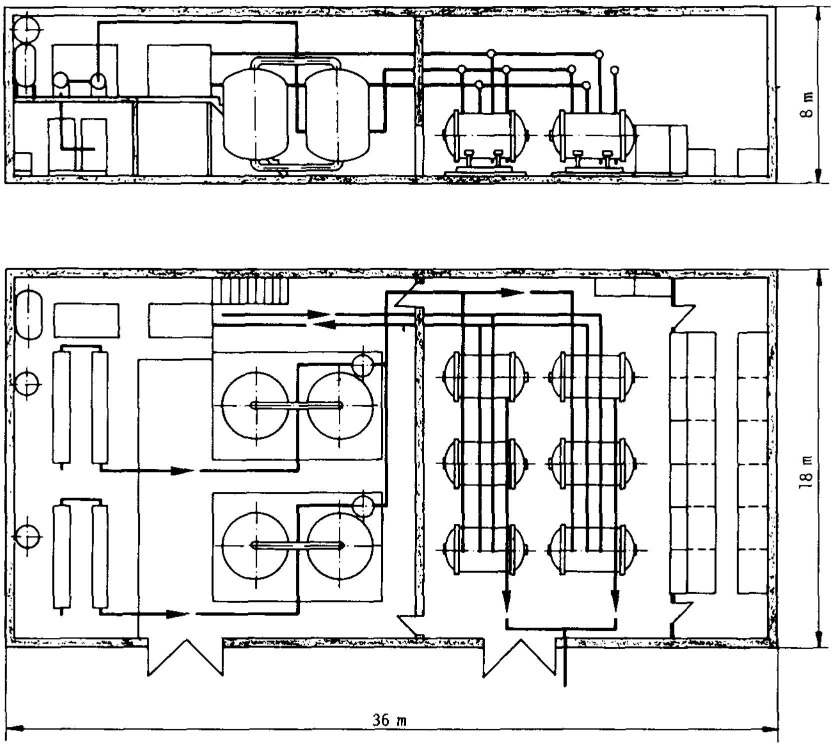

FIG. 9. Layout of an ozone plant for 200 kg/hr production rate from air. Ozone concentration 1.5 wt-%, cooling water temperature 20 C.

TABLE II

Cost per kg of Ozone Produced from Oxygen for 50 kg/hr and 200 kg/hr Production Plants

Design basis:			
Feed gas		oxygen	
Ozone concentration		6 wt %	
Cooling water temperature		18 C	
Consumption data per kg ozone			
Oxygen (with 10% purge)		2.7 kg	
Energy		11.6 kilowatt hr	
Cooling water		1.5 M^3	
Ozone production	kg/hr	50	200
Investment	$ million	0.74	2.44
Cost per kg ozone in $/kg (8400 hr operation per year)			
Annuity 20% (12%/8 years)		0.35	0.29
Labor cost ($20,000/year)		0.05	0.01
Maintenance (2% of investment)		0.04	0.03
Fixed cost		0.44	0.33
Energy ($0.03/kilowatt hr)		0.35	0.35
Cooling water ($0.05/$M^3$)		0.08	0.08
Oxygen ($0.1/kg)		0.27	0.27
Total cost		1.14	1.03

APPLICATION OF OZONE IN THE OLEOCHEMICAL INDUSTRY

The ozone-oxidation of unsaturated fatty acids is a technique applied only to a limited extent in industry. Yet the first large-scale application of ozone in the industry, by Emery Industries, was the ozonolysis of oleic acid to yield azelaic acid and pelargonic acid (1). In this process the double bond reacts first with ozone, forming an ozonide. The basic mechanism of the reaction of ozone with the double bond was formulated by Criegee (Fig. 10) (6).

This assumption describes the process with the formation of a relatively unstable primary ozonide which cleaves to a ketone or aldehyde and a carbonyl oxide called the Criegee intermediate or zwitterion. Recombination of these 2 molecules produces the final ozonide. In a subsequent oxidation or reduction process this ozonide breaks into 2 molecules with terminal functionality. As an example of oxidative ozonolysis, the abovementioned production of azelaic acid and pelargonic acid from oleic acid is shown in Figure 11. Ozonolysis is a versatile technique by which to cleave unsaturated fatty acids at the double bond and produce molecules, with one and 2 terminal functional groups, from fatty acids. It is a very "clean" and fast oxidation process and has high yields. Moreover, the selectivity of the ozone reaction allows the synthesis of products which could otherwise hardly be produced economically.

Vegetable oils which contain a high amount of unsaturated fatty acids and which are therefore destined for ozonolysis are listed in Table III. Fatty acids with more than one or 2 double bonds are not so suited for ozonolysis since the corresponding ozone consumption is relatively high and a preceeding separation process is often necessary for economic reasons. The same is true for some of the animal fats which exhibit a particularly high degree of unsaturation. The carboxylic acids obtained by the ozonolysis of fatty acids are shown in Table IV. Azelaic acid today is mainly produced by ozonolysis, since this process has proven to be the most economical. With the above calculated ozone costs, the corresponding costs amount to about $0.30 to produce 1 kg azelaic acid. Azelaic acid itself is a versatile intermediate that is used in a large number of different applications in the form of diesters and polymer intermediates (2). Simple polymer additives, like plasticizers and softeners for PVC and varnishes, synthetic lubricants for a wide temperature range and very special high standard nylons and polyesters are the final products. Sebacic acid and undecanedioic acid can be used in the same way as azelaic acid as intermediates for plasticizers, synthetic ester lubricants, polyesters and polyamides (7). Quiana, a polyamid fiber of Dupont, is derived from dodecanedioc acid. Brassilic acid is obtained by the ozonolysis of erucic acid which is contained in crambe abyssinia oil (8) at ca. 90% concentration. It is an intermediate for the synthesis of nylon 13/13 and nylon 6/13 which both exhibit extraordinary water resistance (9).

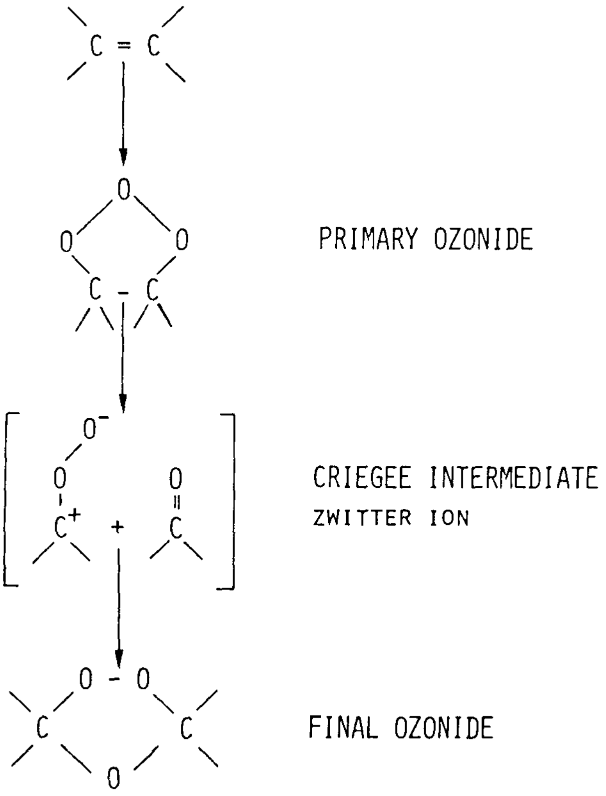

FIG. 10. Criegee mechanism of ozonolysis of alkenes.

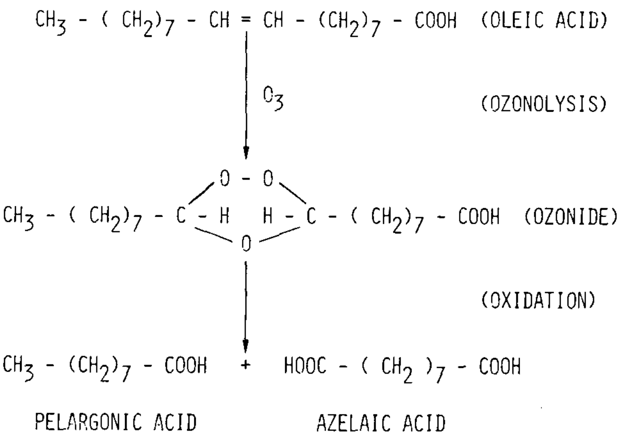

FIG. 11. Formation of azelaic acid and pelargonic acid from oleic acid by oxidative ozonolysis.

TABLE III

Vegetable Fats and Oils for Ozone Chemistry

Fats and oils	Approximate usable portion for ozonolysis
1-2 Double bonds	
Peanut oil	85%
Olive oil	90%
Palm oil	55%
Maize oil	90%
Rice oil	85%
Mustard oil	95%
Rapeseed oil	95%
Soybean oil	85%
Crambe oil	90%
Castor oil	95%
Cotton oil	75%
Sesame oil	85%
Sunflower oil	85%
Safflower oil	90%
Niger seed oil	85%
Poppy-seed oil	90%
1-3 Double bonds	
Hemp seed oil	85%
Oiticica oil	90%
Linseed oil	90%
Tung oil	95%

TABLE IV

Carboxylic Acids Formed by Ozonolysis of Unsaturated Fatty Acids

Dicarboxylic acids:	
Azelaic acid	C_9
Sebacic acid	C_{10}
Undecanedioic acid	C_{11}
Dodecanedioic acid	C_{12}
Brassilic acid	C_{13}
Monocarboxylic acids:	
Caproic acid	C_6
Pelargonic acid	C_9

Reduction of the ozonide yields ketones, aldehydes and alcohols. Cleavage of the ozonides with ammonia results in amines.

The monocarboxylic acids are not such useful products but they are used as plasticizers and lubricants and moreover, can be used advantageously as solvents for the ozonolysis process. They help to remove the heat and to get a uniform reaction with a moderate reaction velocity. In contrast to water, these acids react with the ozonides to form intermediates which are much more stable to heat than normal ozonides. Therefore, ozonation of the real solution of oil in the carboxylic acid results in higher yields than ozonation of oil-in-water emulsions.

The significance of this process lies in the fact that it provides an alternative to the petrochemical industry for the manufacture of products from cheap and naturally renewable raw materials. Lower prices for ozone by this technology could expand the application considerably.

WASTEWATER TREATMENT WITH OZONE

Different wastewaters are produced during the extraction and refining of fats and oils (10,11). These effluents contain a high load of organic materials in a bulky, complex and somewhat untreatable form. Different methods of reducing the organic load of the effluents have been proposed, but ozone has never been taken into account until now.

Ozone treatment for oxidation and/or disinfection is a well known technique in water and wastewater treatment. Of course, ozone cannot be used for complete oxidation of the organic matter due to economics. But it can help to increase the biodegradability, break emulsions and increase the protein production of the waste (12).

If effluent from a biological treatment stage still contains a high COD value caused by refractory organic material, a partial oxidation with ozone can crack these molecules and make them biodegradable. A subsequent second biological treatment yields a substantial reduction in COD.

Another technique uses the effluents produced during the extraction of palm oil as a substrate from microbial protein production by fungi (12). Moreover, small doses of ozone have been shown to stimulate growth of yeast on sewage by a factor of 10 or more if the pH is in the right range (14). This effect is correlated to the change in permeability of the cell membrane, enabling the cell's faster and more effective uptake of the nutrient.

These facts have resulted in the proposal for wastewater treatment for the edible oil industry. The effluent of the biological treatment stage is treated by ozone to break down the refractory organics and simultaneously enhance the protein production by fungi or yeast. After separation of the protein, an effluent with a substantial reduction in the COD should be obtained.

Another potential application of ozone in wastewater treatment arises from its ability to break oil emulsions. The mechanism is a destabilization of the emulsion by oxidation of the emulsifier. The effectiveness of this process has been proven for different types of oil emulsions.

DEODORIZATION WITH OZONE

Deodorization with ozone is a very common technique in the industry. Malodorous compounds in the exhaust gas, such as phenols, mercaptans or hydrogen sulfides are transformed quickly into odorless compounds. Toxic sulfur oxides and nitrogen oxides contained in off-gases can be oxidized to SO_3 and N_2O_5 which are then removed easily by washing with water.

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