Hydrogen Peroxide: A Key Chemical for Today's Sustainable Development

Rosaria Ciriminna,[a] Lorenzo Albanese,[b] Francesco Meneguzzo,[b] and Mario Pagliaro*[a]

This article is dedicated to Professor Laura Maria Ilharco, University of Lisboa, for all she has done for the progress of sol–gel science and technology.

The global utilization of hydrogen peroxide, a green oxidant that decomposes in water and oxygen, has gone from 0.5 million tonnes per year three decades ago to 4.5 million tonnes per year in 2014, and is still climbing. With the aim of expanding the utilization of this eminent green chemical across different industrial and civil sectors, the production and use of hydrogen peroxide as a green industrial oxidant is reviewed herein to provide an overview of the explosive growth of its industrial use over the last three decades and of the state of the art in its industrial manufacture, with important details of what determines the viability of the direct production from oxygen and hydrogen compared with the traditional auto-oxidation process.

1. Introduction

Hydrogen peroxide (H_2O_2) is a clear, colorless liquid that is completely miscible with water produced on a massive scale through the anthraquinone auto-oxidation (AO) process developed by Riedl and Pfleiderer in 1939 at I. G. Farbenindustrie.[1] Despite being known since the first synthesis of eau oxygenée in 1818 by Thénard through the acidification of barium peroxide (BaO_2) with nitric acid,[2] its numerous beneficial properties are still being discovered today. For example, unlike many other types of anti-infective drugs or biocides, the general mechanisms of action of H_2O_2 significantly reduce any risk of the development of resistance to the biocide over time,[3] which opens up the possibility of its widespread utilization as an antimicrobial chemical in both developed and developing countries.

Serious environmental concerns (including the formation of dioxins and other deleterious chlorinated products) led, over the course of the second half of the 1990s, to the replacement of chlorine with H_2O_2 as a bleaching agent in paper production.[4] Since 2008, in addition, H_2O_2 started to be extensively used as a terminal oxidant in the newly industrialized synthesis of propene epoxide (PO).[5] In the mid-1990s, the world's global capacity (based on 100% H_2O_2) was around 1.5 million tonnes per annum ($t a^{-1}$) and a world-scale plant had a capacity of around (20 000–40 000) $t a^{-1}$. As of early 2015, the global capacity had reached 5.5 million $t a^{-1}$, with 300 000 $t a^{-1}$ plants built to support PO synthesis. By doing so, H_2O_2 turned from being an expensive specialty chemical into a large-scale commodity, plentiful and affordable, opening up the route to several new uses of this valued substance, which are highly beneficial to the environment. Perhaps unsurprisingly, research into H_2O_2 was reinvigorated, leading to the introduction of interesting new materials and innovative processes based on this valued molecule.

Herein, we review the production and use of H_2O_2 as a green industrial oxidant to provide an overview of the explosive growth of the industrial use of H_2O_2 over the last three decades and of the state of the art in its industrial manufacture, with important details of what determines the viability of direct production from O_2 and H_2 compared with the traditional AO process.

2. Industrial Production

All commercially produced H_2O_2 worldwide is derived from the anthraquinone AO process.[6] Its raw materials are hydrogen, anthraquinone, and air. In a typical plant (Figure 1), hydrogen
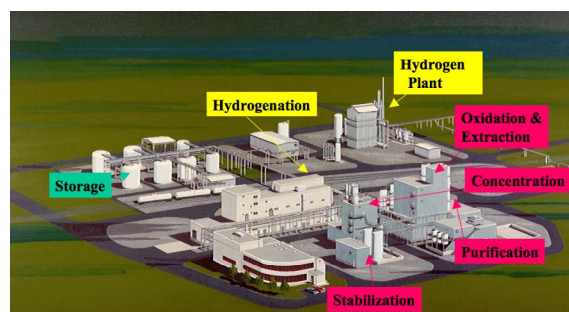
[a] Dr. R. Ciriminna, Dr. M. Pagliaro
Istituto per lo Studio dei Materiali Nanostrutturati, CNR
via Ugo La Malfa 153, 90146 Palermo PA (Italy)
E-mail: mario.pagliaro@cnr.it

[b] Dr. L. Albanese, Dr. F. Meneguzzo
Istituto di Biometeorologia, CNR
via Caproni 8, 50145 Firenze FI (Italy)

Figure 1. H_2O_2 production plant based on the anthraquinone AO process (adapted with permission from Ref. [7]).

is manufactured on site by the steam reforming of methane, whereas air is available for free.

In general, 2-ethylanthraquinone dissolved in a mixture of organic solvents (quinones and hydroquinones have different solubility) is first catalytically hydrogenated to both the alkylanthrahydroquinone and the tetrahydroalkylanthrahydroquinone over a Pd/Al_2O_3 catalyst at temperatures of 45 °C, under H_2 (4 atm; 1 atm = 101325 Pa). Hydrogen is completely consumed in a few minutes, but it is particularly important that the product mixture does not contain leached palladium because even traces later on also catalyze the decomposition of H_2O_2. Hence, rather than old slurry-type hydrogenation reactors equipped with filters, modern technology employs a fixed-bed reactor that avoids the need for filtration; the product mixture is easily separated from the fixed-bed hydrogenation catalyst to be aerated with compressed air in the AO step.

The so-called "working solution", which now contains hydrogenated anthraquinone is then cooled to dissipate heat released during hydrogenation, after which it is safely and non-catalytically oxidized by bubbling air compressed at relatively low pressure (5 bar) at slightly higher than room temperature. After a typical residence time of 40 min in the oxidation reactor, a diluted solution of H_2O_2 at 0.9–1.8 wt% is obtained, along with regenerated anthraquinone. The loss of quinone in the reaction cycle is compensated for by the periodic addition of fresh anthraquinone to the working solution.

To extract H_2O_2 present in the organic phase, demineralized water is added to the top of a tall (> 30 m) liquid–liquid extraction column to ensure maximum contact of water with the working solution. Water flows down the column over perforated trays, while the working solution is pumped up the column. The aqueous crude reaching the bottom of the extractor contains 25–35 wt% (w/w) H_2O_2, while the H_2O_2-free working solution that leaves the top of the extractor is pumped back to the hydrogenator.

H_2O_2 is subsequently purified and concentrated through distillation (with steam, the peroxide does not form azeotropic mixtures with water and can be completely separated by distillation) to different commercial grades, typically up to 70%, after which the concentrated product is stabilized against unwanted decomposition by adding stabilizers, and then pumped to product storage tanks.

It should be noted that the purified crude aqueous extract can be used as such in the large propylene oxide plants, which makes the construction of a H_2O_2 plant next to a propylene oxide plant using H_2O_2 as the oxidant convenient.

Energy consumption in the AO process is not as high as it is often claimed. Neither is the anthraquinone-based technology an "unsustainable production process",[8] in which palladium is "a critical material difficult to extract and expensive to obtain" and benzene "a human carcinogen is used to dissolve the anthraquinone".[8] Indeed, palladium is not consumed in the process, and there is no use of benzene at all.

The major wastes are comprised of slightly contaminated water (ppm levels of peroxide, organic solvent, and quinone residues) from decanted water from cooling tower blowdown and demineralization plant wash water. The pH of both these effluents is adjusted before being pumped to a wastewater treatment plant. Furthermore, in today's ever larger plants, 2-amylanthraquinone is used in place of 2-ethylanthraquinone to increase solubility in the precursor solution, as well as to minimize the over-hydrogenation of the quinone, resulting in the generation of unwanted byproducts that cause water contamination.

According to a leading practitioner of the industry,[9] in 2009 the variable cost of production (raw materials, electricity, and steam consumption) in modern plants was typically $300 t^{-1} H_2O_2 (on 100 wt% product basis), the fixed costs of production around $100 t^{-1} for maintenance and operation, and the capital cost around $300 t^{-1}, with sales price varying from $700 to 1200 t^{-1}, depending on the amount sold.

Stabilization against thermodynamically favored H_2O_2 decomposition makes use of chemical additives, such as sodium pyrophosphate (manufacturers no longer use sodium stannate due to the toxicity of tin salts), that act by complexing with any traces of transition-metal ions present, which would otherwise catalyze the decomposition of H_2O_2 [Eq. (1)] that, regardless of the concentration, continuously decomposes to form water and oxygen with the evolution of heat,[10] as driven by large changes of enthalpy and entropy:

$$H_2O_2 \rightarrow H_2O + \tfrac{1}{2} O_2 + 98.25 \text{ kJ mol}^{-1} \qquad (1)$$

At pH < 3, the disproportionation reaction is slow and, in a stabilized solution, the H_2O_2 concentration may drop by less than 1% after 12 months of storage at about 20 °C. The reaction starts to accelerate when the aqueous solution is exposed to metal impurities, which rapidly mediate catalytic decomposition.

In general, energy released by decomposed H_2O_2 in its aqueous solutions below 70% (w/w) is not enough to vaporize water.[10] For higher grades, if a metal catalyst, such as manganese, is added, steam rapidly evolves along with oxygen; this formed the basis for the first liquid-fueled jet aircraft in 1936, the rocket engine of which used a concentrated 80% solution of H_2O_2 decomposed through the injection of calcium permanganate.[11] The process is so effective that the H_2O_2 decomposition reaction is still used today to propel submarine torpedoes and rockets.[12]

3. Direct Synthesis

In principle, the direct synthesis of H_2O_2 from H_2 and O_2, which would avoid the production of waste (except harmless water) would be highly desirable.[13] Unfortunately, very often in the literature the problems associated with direct synthesis are overlooked and minimized.

Noting in 1999 that no industrial plants had been designed and commissioned based on technologies alternative to the AO process, Clark and Jones argued that "for the conceivable future, the anthraquinone process will continue to dominate",[14] even though the process requires periodic replace-

ment of quinone, as well as of deactivated hydrogenation catalyst.

Plenty of industrial research has been devoted to the development of an industrially viable alternative process based on direct synthesis with noble-metal catalysis.[15] For example, over 100 patents (Table 1) were granted to large chemical companies between 1980 and 1999. In 2006, a one-tonne demonstration plant was built in Germany by a joint venture between a large H_2O_2 manufacturer (Degussa, now Evonik) and a catalyst supplier (Headwaters Technology Innovation). The aim was to collect and evaluate data necessary to design a 200 000 $t\,a^{-1}$ plant and begin commercial production in 2009.[16]

Table 1. Number of patents granted for the direct synthesis of H_2O_2 in the 1980s and 1990s. (Reproduced from Ref. [16].)

Company	Number of patents
Air Products	11
BASF	5
Dow Chemical	1
DuPont	11
ENI	14
Eka Nobel	1
FMC	3
Mitsubishi	21
Shell	1
Solvay	6

The process used a carbon-supported PdPt/C catalyst comprised of uniform 4 nm metal alloy nanoparticles (Figure 2).[17] Prolonged tests of a continuous process at a H_2 gas concentration below 4% in air (far below the flammability limit of H_2 in a mixture of H_2/O_2) afforded yields of H_2O_2 as high as 11 wt%,
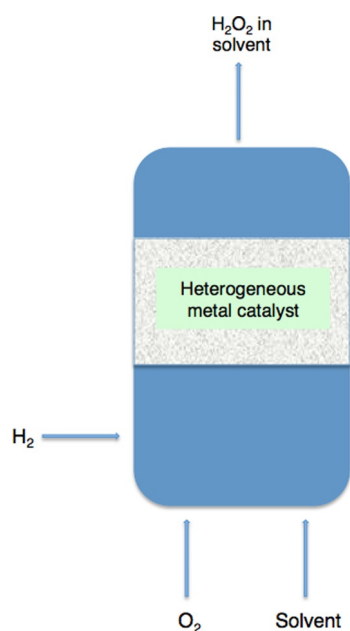

Figure 2. Direct synthesis of H_2O_2 (adapted from Ref. [16]).

and 95% selectivity to H_2O_2, with a long catalyst lifetime (>3 years). Although announced to be commercially available starting from 2009,[18] the process was not commercialized.

One reason might be that direct synthesis is only achievable with costly pure O_2 in excess, but not with freely available air. Furthermore, the reaction pressure is generally much higher than pressures typically employed in the AO process. For example, a state of the art catalyst comprised of alloyed PdSn nanoparticles supported on TiO_2, capable of affording H_2O_2 with >95% selectivity thanks to strong metal–support interactions, works well with H_2 and O_2 in a 1:5 ratio dissolved in MeOH and pressurized at 29 bar.[19]

Two other important points concern the commercial grade of H_2O_2 produced by direct synthesis, in which H_2O_2 is present in methanol at low (<10%) concentration, and thus, requires workup to isolate the product from the aqueous phase and close the material cycles to recover the solvent and oxygen in excess. The product is indeed demanded in an aqueous phase, requiring an extraction step from hydrophilic, expensive methanol, which is costlier than straightforward extraction from the water-immiscible organic phase of the AO process.

Because the price of oxygen is very high ($3.0–3.2 $kmol^{-1}$), one of the two key economic parameters when estimating the competitiveness of the direct synthesis process is the required excess of oxygen to hydrogen, which may vary between 5:1 and 10:1, and largely dictates the operational expenditure (OPEX). The other parameter, which mostly affects the capital expenditure (CAPEX), is the reaction pressure. High pressure requires costly reactors and compressors, for example, which was the reason that made the direct synthesis process announced to be shortly commercialized in Québec by DuPont in 1988 not economically competitive against the AO process.[20] Hence, any reduction in the reaction pressure thanks to the introduction of more active and more selective catalysts will reduce the costs of the reactors and compressors, and thus, improve the economic potential of the process.

In 2007, the company that developed the PdPt/C-based catalytic process claimed that the manufacturing process based on direct synthesis would involve up to 50% lower capital cost and 20% lower H_2O_2 cost.[16] However, such figures were questioned in a subsequent comparative study published in 2013 by the same market research analysis company, which evaluated the Québec direct synthesis mentioned above. According to the latter research, the OPEX and CAPEX for a standalone 98 $kt\,a^{-1}$ direct synthesis plant based on such a catalyst were estimated to be about 25% higher and 33% lower, respectively, compared with a typical anthraquinone-based plant.[21]

4. Market: Drivers and Trends

Driven by sustainability and broad efficacy in different applications, the global demand for H_2O_2 has gone from 0.5 million tonnes in the 1970s to 4.5 million tonnes in 2014,[22] when the market was valued at $3.71 billion (translating into an average price of $825 t^{-1}) with estimated >5% annual growth rate until 2023.[23] The market, historically consolidated by three main producers (Belgium's Solvay, Germany's Evonik, and Fran-
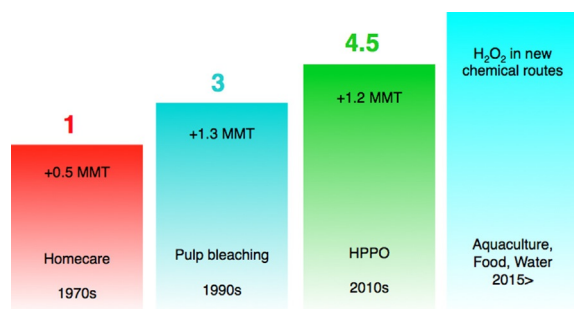
Figure 3. H$_2$O$_2$ market growth (MMT = million metric tonnes) since the 1970s (adapted with permission from Ref. [22]).

ce's Arkema) holding > 50 % of the market, is rapidly expanding with several new applications beyond homecare and pulp and textile bleaching that drove demand until the 1990s (Figure 3).

Similar to any other chemical, the price of H$_2$O$_2$ rapidly increases with increasing purity and scarcity. For example, in late 2014, a manufacturer of high-purity electronic grades of H$_2$O$_2$ based in the Netherlands announced a 31 % rise in price in response to rising demand and limited supply.[24] A few months later, the same manufacturer was purchased by the world's second largest producer.[25] Electronic-grade H$_2$O$_2$, indeed, is in great demand, which may explain why the first global manufacturer in 2015 ended production of sodium percarbonate in one of its plants based in Italy, instead making H$_2$O$_2$ available to feed a new purification reverse osmosis unit to meet the rapidly growing demand from the semiconductor industry.[26] Similar production expansion initiatives are ongoing in Europe with regard to the production of pharmaceutical grades for the synthesis of active pharmaceutical ingredients, as well as disinfection and decontamination agents.[27] In the last case, H$_2$O$_2$ is purified and packed in compliance with good manufacturing process (GMP) conditions.[28]

Today H$_2$O$_2$ is in high demand from companies in well diversified markets. Today's main markets for H$_2$O$_2$ include: HPPO = HP (H$_2$O$_2$) for PO (propylene oxide); textile (bleaching of cotton and wool fabrics); food (aseptic packaging of milk and fruit juice) and aquaculture (antiparasite for salmon farming); mining (detoxification of cyanide tailings, enhanced recovery of metal); water and wastewater treatment (advanced oxidation processes); semiconductors (cleaning silicon wafers in the manufacture of printed circuit boards); chemical industry (reactant); and pulp and paper (bleaching wood pulp).

Thanks to chemical innovation, mostly originating in Sweden, both main technologies used to bleach chemical pulp (elemental chlorine free and total chlorine free) require H$_2$O$_2$ in the bleaching sequence.[4] In 2010, this was the main market for H$_2$O$_2$ (> 50 % of sales volumes) with 85 % for pulp bleaching and 15 % for paper recycling.[29]

The debut, in 2008, of the industrial production of propylene oxide by using H$_2$O$_2$ (the HPPO process) at two commercial plants, one in Belgium and the other in South Korea, was the beginning of the second major expansion of the market. Propylene oxide is mainly (67 %) used for the production of poly-

ether polyols as precursors of polyurethanes, propylene glycol (17 %), and propylene glycol ethers (17 %). Polyurethanes, in particular, are versatile and ubiquitous polymers, the production of which is rapidly growing.[30]

Growth was so rapid that in 2014 the chemical end-user segment of the H$_2$O$_2$ market already approached that of paper and pulp, accounting for about 40 %. In detail, the first HPPO plant (Figure 4) opened in Belgium with a striking capacity of 300 000 t a^{-1}; this was soon after followed by another plant with a capacity of 100 000 t a^{-1} operated by another company in South Korea. In the course of the next 8 years, several other plants were built across the world, with 50 % of new PO capacity installed across the world opting for the HPPO route.
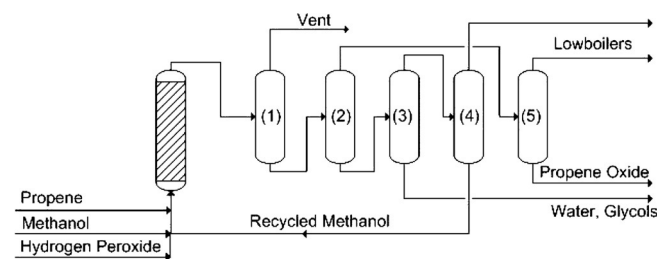

Figure 4. HPPO plant scheme of the DOW/BASF process in which PO is formed in a heat exchanger reactor with a H$_2$O$_2$ conversion of 99.8 %. The purification section is composed by five distillation columns in series, useful to remove first the off-gas (1), then to purify propene oxide (2 and then 5), separate water and glycols (3), and recycle methanol (4). Reproduced with permission from Ref. [31].

A typical propylene oxide facility based on HPPO technology generates 70 % less wastewater, requires 35 % less energy, and has 25 % lower CAPEX when compared with PO produced by the chlorohydrine process with chlorine.[32] The world's largest HPPO plant currently operates in Thailand and has a capacity of 390 000 t a^{-1}. Typically, a plant with a capacity of 250 000 t a^{-1} of propylene oxide requires more than 180 000 t a^{-1} of H$_2$O$_2$ (100 % grade).

All of these HPPO plants rely on advanced versions of the Enichem PO catalytic epoxidation process over titanium silicalite patented in 1983.[33] For example, the BASF/Dow process uses a titanium silicate based catalyst (ZSM-5-type zeolite with 0.5 nm channels) to selectively convert propylene at 40 °C under 5 MPa pressure,[34] whereas the Evonik/ThyssenKrupp process uses a titanium silicalite-1 (TS-1) produced from Evonik.[35] As explained by Teles et al., the process had to wait another 25 years to see the costs of production of H$_2$O$_2$ reach a level at which its use as an oxidant in propylene oxide production became economically attractive.[6] When production of propene oxide by using H$_2$O$_2$ started in 2008, the price of H$_2$O$_2$ (≈ $1500 t^{-1}) was close to that of propene oxide ($2200 t^{-1}),[36] which further explains why early manufacturers opted for the on-site production of H$_2$O$_2$ with direct use of the crude product of the anthraquinone process.

5. Emerging Uses

Falling production costs, due to ramped-up production and improvements in each step of the AO production cycle, opened up the way to the utilization of H_2O_2 in numerous industrial sectors, including wastewater treatment and in the mining industry, for which the peroxide can increase the amount of copper extracted from the ore by around 10%.[37]

In another major advance, in the last two decades Pandit and co-workers in India have been developing wastewater treatment technologies based on controlled hydrodynamic cavitation (CHC).[38] The very large amount of energy released in the microenvironment surrounding the cavitation bubble upon its collapse generates mechanically powerful microjets and shear stress forces that directly inactivate pathogen microorganisms.[39] Furthermore, powerful oxidant hydroxyl radicals (oxidation potential, 2.80 eV) are generated that are capable of oxidizing toxic and non-biodegradable organic pollutants. To improve the amount of hydroxyl radicals, aqueous H_2O_2, which readily dissociates into two $\cdot OH$ radicals under cavitation conditions, is conveniently added. For example, hydrodynamic cavitation in the presence of H_2O_2 can be effectively used for complete removal of methyl parathion,[40] a widely used organophosphorus agricultural insecticide, the biorefractory nature of which results in significant water pollution worldwide. Degradation of the pesticide goes from 44.4% in the absence of H_2O_2 to complete degradation when performing CHC in the presence of 200 mg L^{-1} H_2O_2 (Figure 5).
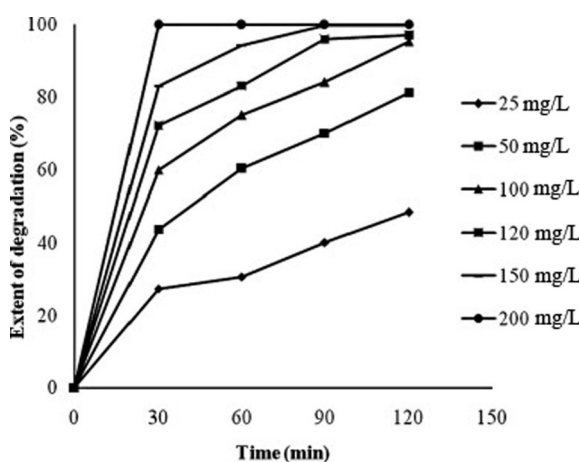

Figure 5. Effect of different concentrations of H_2O_2 on the degradation of methyl parathion (adapted with permission from Ref. [40]).

Although certain metal catalysts, such as Fenton reagents, can sometimes contribute to the overall efficacy, energy-efficient CHC-based processes can successfully achieve their remediation targets, even without assistance from any other chemicals apart from H_2O_2 in low concentration.[41]

The addition of H_2O_2 largely also improves UV disinfection processes. In the UV disinfection of surface water and wastewater from a municipal treatment plant, for instance, the inactivation of *Escherichia coli* bacteria, *Bacillus subtilis* spores, and

MS2 bacteriophage viruses proceeded best when UV irradiation was coupled with optimized doses of H_2O_2 and peroxydisulfate (PDS, $S_2O_8^{2-}$).[42] Although UV-only treatment performed well with regard to *Escherichia coli*, any improvement for H_2O_2 or PDS was marginal, whereas UV/H_2O_2 far outperformed UV/PDS with regard to UV-resistant MS2, and only UV/H_2O_2 succeeded in deactivating *Bacillus subtilis*.

Similar excellent results were obtained in the abatement of antibiotic-resistant genes often hosted in bacteria, such as *Escherichia coli*, by combining UV irradiation with Fenton oxidation (Fe^{2+}/H_2O_2), or with H_2O_2 alone (Figure 6), with the distinct advantage of a drastic reduction of the respective doses and a diminished sensitivity to pH.[43]
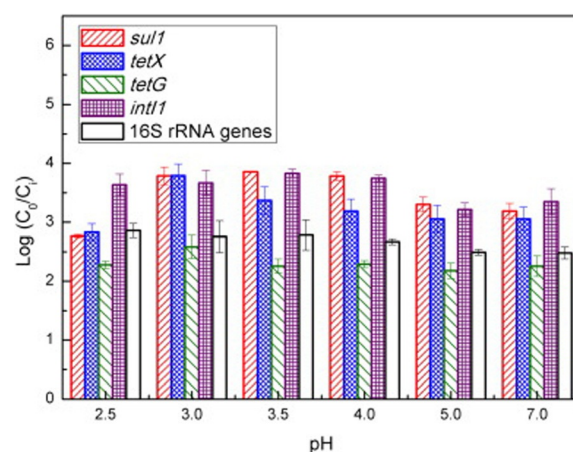

Figure 6. Effect of H_2O_2 concentration on the reduction of target genes (UV irradiation time = 30 min, initial solution pH 3.5). Maximum reduction of all target genes at [H_2O_2] = 0.01 mol L^{-1} (reproduced with permission from Ref. [47]).

Another target-specific, effective H_2O_2-based water remediation process consists of the addition (at about $\delta = 20$ ppm concentration) of wastewater with the TAML (tetraamidomacrocyclic ligand) family of iron complexes, which mimic the action of peroxidase enzymes to boost the oxidative degradation ability of H_2O_2 alone.[44] Successful halving of the concentration of a micropollutant endocrine disrupting synthetic estrogen from municipal wastewater was recently demonstrated,[45] with tests suggesting that 1 kg of the catalyst would be sufficient to treat 20 000–30 000 tonnes of water to eliminate an estrogen that leads to the collapse of fish populations in open water by feminizing male fish, even at concentrations in parts per trillion.

Another important advance that points to the scope and degree of innovation in H_2O_2 science and technology is the recent commercialization, by an Israeli company, of 99.4% H_2O_2 functionalized with (edible) carboxylic acids and catalytic metals, such as zinc, to keep fruits and vegetables fresh and viable for up to 10 weeks.[46] Spraying the formulation solves the issue posed by the use of H_2O_2 as a produce and foodstuff disinfectant, which, as a strong oxidizing agent, also damages surface tissues, coatings, and protective peels of plant matter, making them more vulnerable to pathogen penetration.[47]

The new preservative agent, which is much more efficient than copper sulfate and chlorine fungicides typically applied both pre- and post-harvest to prevent fungi from invading produce, is best applied in the form of ultrasmall drops by an ultrasonic dispensing system that produces a < 10 µm droplet cloud ("dry fog") in the storage room. This fog is highly effective for distributing the H_2O_2-based disinfectant by avoiding the formation of condensed water on produce, while effectively penetrating into small cracks and spaces.

For example, in 2008, the company conducted five concurrent efficacy trials in Ukraine, Germany, and the UK by treating potatoes with its nebulized H_2O_2-based formulation (Figure 7). Stored potatoes showed no quality difference, that is, in frying color, diseases, defects, or dry contents, compared with Chlorpropham-treated potatoes. A few food companies in Israel, the USA, Germany, the UK, Canada, Japan, and Russia were reported to commercialize produce products stabilized with this H_2O_2-based formulation as early as 2013.[49] To understand the relevance of these findings, it is enough to consider that only India[50] and P.R. China,[51] namely, the two most populated countries in the world, due to diseases and lack of correct supply chain, lose as much as 30% of their agricultural produce.

Figure 7. Packed potatoes treated by using Pimi's SpuDefender installation at a Branston farmer site in the UK, October 2008 (reproduced with permission from Ref. [48], with kind permission).

Finally, two domains in which the use of green H_2O_2 as a green and effective oxidant will significantly increase are the fine chemical and healthcare industries. In synthetic organic chemistry, for example, diluted H_2O_2 can replace costly and hazardous oxygen in numerous important oxidations; this eliminates flammability concerns and makes the process inherently safe.[52] For example, diluted H_2O_2 in diethyl ether added to the reaction mixture containing the alcohol substrate, along with a catalytic amount of organosilica-entrapped tetra-n-propylammonium perruthenate (TPAP), leads to the highly selective oxidation of widely different alcohols at room temperature.[53] Slow addition ensures that the decomposition of H_2O_2 catalyzed by ruthenium is minimized (Figure 8), while the alcohol substrate is smoothly oxidized.
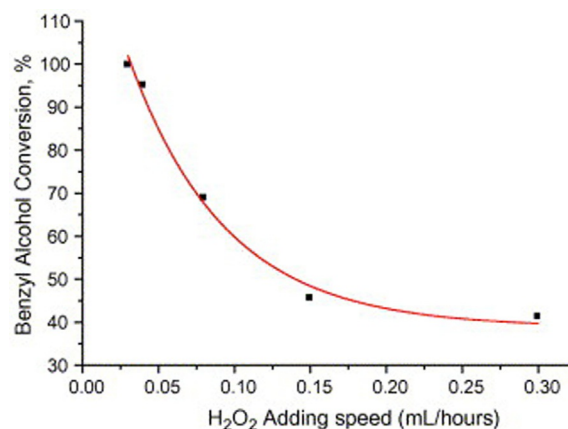

Figure 8. Benzyl alcohol conversion as a function of H_2O_2 addition rate. The oxidation is catalyzed by TPAP encapsulated in an organosilica matrix (reproduced with permission from Ref. [53]).

Finally, once successfully encapsulated and stabilized, practical applications of H_2O_2 will further grow, especially in healthcare. One promising approach was introduced by Żegliński and co-workers in 2007, who described the prolonged antibacterial activity of silica xerogels entrapping 3.8% H_2O_2, which, stored at room temperature, retained 71% of the entrapped peroxide after 63 days;[54] the same composite could be successfully used in place of 30% H_2O_2 in selective oxidation reactions.[55] More recently, Orbey and co-workers sol–gel entrapped again aqueous H_2O_2 in silica xerogels, but this time starting from a much higher concentration (33.2 wt%),[56] and also in hydrogels.[57] More than 70% of H_2O_2 was retained after 40 days of storage at room temperature (Figure 9); this shows that sol–gel encapsulation in silica gels can be used to store high concentrations of H_2O_2 in a stable solid form.
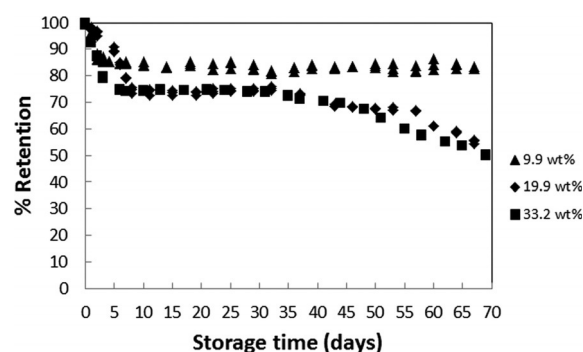

Figure 9. Stability of H_2O_2 entrapped in silica as a function of storage time at various H_2O_2 concentrations (reproduced with permission from Ref. [56]).

6. Summary and Outlook

Driven by the quest for less polluting paper and pulp bleaching, the use of H_2O_2 as an excellent substitute for dioxin-forming chlorine experienced a first significant expansion in the mid to late 1990s. The remarkable success of the propylene oxide synthesis with H_2O_2 as a terminal oxidant debuted in

2008 and further contributed to turning H_2O_2 into a large-scale commodity.

With ever more stringent environmental and health policies being enforced throughout the world, including large and rapidly developing countries such as Russia, P.R. China, and India, the positive trend concerning its utilization will continue, eventually feeding back into higher production levels, system integration and optimization, and lower production costs. Supporting this point, along with many others, from large plants in P.R $>$ China (Jilin; capacity of 230 000 $t\,a^{-1}$)[58] through to medium-sized plants in Russia (Dzerzhinsk)[59] and small units in Africa (Addis Ababa, capacity of 4500 $t\,a^{-1}$),[60] several new H_2O_2 plants started operations in the last two years.

The industrial production route based on the AO process originally conceived in Germany in the late 1930s will remain the technology of choice for large-scale productions for several years to come, until direct synthesis becomes economically viable on a large scale, well beyond the 10 $kt\,a^{-1}$ capacity identified as the ideal plant size by Salmi and co-workers in 2014 when reviewing the engineering of the direct synthesis process.[61] For comparison, the smallest output of the 9 leading companies described therein was (in 2013) 123 $kt\,a^{-1}$; the largest, almost 1000 $kt\,a^{-1}$. Since then, production using the anthraquinone-based process has considerably grown to include mega plants that produce an annual output of 300 $kt\,a^{-1}$.

Along with Teles, we have lately provided arguments for which new catalyst will come into use, leading to the construction of new plants (and to a step change in technology), if the new catalyst enables the development of an entirely new process with different raw materials and breakthrough economics.[62] The high cost of pure oxygen and the numerous technical difficulties of the direct process highlighted herein suggest that, in place of direct synthesis, electrochemical synthesis from water may one day become available,[63] especially now that the ongoing solar photovoltaic boom is lowering the cost of electricity at a fast pace.[64]

Meanwhile, developing environmentally friendly technology based on this eminent green chemical will continue to benefit the environment and human health. Highlighting recent process and providing a critical overview, this Minireview will hopefully contribute to the adoption of H_2O_2 as a central chemical of contemporary sustainable chemistry and green technology.

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