Recent Advances in the Direct Synthesis of Hydrogen Peroxide Using Chemical Catalysis—A Review

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Abstract: Hydrogen peroxide is an important chemical of increasing demand in today's world. Currently, the anthraquinone autoxidation process dominates the industrial production of hydrogen peroxide. Herein, hydrogen and oxygen are reacted indirectly in the presence of quinones to yield hydrogen peroxide. Owing to the complexity and multi-step nature of the process, it is advantageous to replace the process with an easier and straightforward one. The direct synthesis of hydrogen peroxide from its constituent reagents is an effective and clean route to achieve this goal. Factors such as water formation due to thermodynamics, explosion risk, and the stability of the hydrogen peroxide produced hinder the applicability of this process at an industrial level. Currently, the catalysis for the direct synthesis reaction is palladium based and the research into finding an effective and active catalyst has been ongoing for more than a century now. Palladium in its pure form, or alloyed with certain metals, are some of the new generation of catalysts that are extensively researched. Additionally, to prevent the decomposition of hydrogen peroxide to water, the process is stabilized by adding certain promoters such as mineral acids and halides. A major part of today's research in this field focusses on the reactor and the mode of operation required for synthesizing hydrogen peroxide. The emergence of microreactor technology has helped in setting up this synthesis in a continuous mode, which could possibly replace the anthraquinone process in the near future. This review will focus on the recent findings of the scientific community in terms of reaction engineering, catalyst and reactor design in the direct synthesis of hydrogen peroxide.

Keywords: catalyst; direct synthesis; hydrogen peroxide; Pd based catalyst; reactor engineering; microreactor

1. Introduction

Hydrogen peroxide (H_2O_2) is a colorless, odorless, and slightly acidic liquid used mainly as an oxidant in chemical synthesis [1–3]. It is an atom efficient, benign, and eco-friendly oxidant that produces water or oxygen as a degradation product, depending on the catalyst used [4,5]. Commercial H_2O_2 production has a concentration range of 30–70% and the areas of application depend on the concentration of H_2O_2 used. Usually, household, medical/dental, and cosmetic applications need diluted concentrations of Ca. 3–5% H_2O_2. Higher concentrations of up to 70% are needed for synthesis, wastewater treatment, mining, and bleaching applications. The electronics
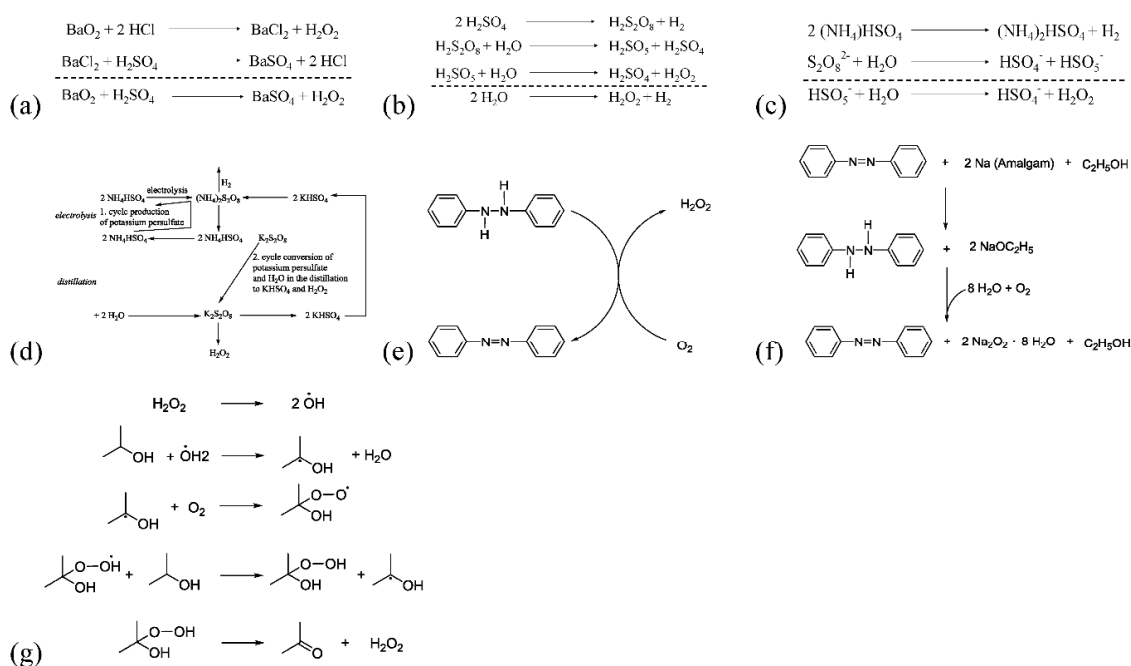
industry needs higher H_2O_2 concentrations (ranging from 70–90%) for cleaning and anti-corrosion purposes. Finally, the concentrated versions of 90–98% are used for military and aerospace purposes [6]. Given its wide range of applications in almost every aspect of human life, the method of H_2O_2 production in the industry is of utmost importance. The demand for H_2O_2 is always increasing with recent processes preferring H_2O_2 as an oxidant. H_2O_2 production can be done using chemical, electrochemical, enzymatic, or photocatalytic means. Of these routes, only the chemical processes are capable of industrial production [3,7] in an economical manner and only these will be discussed in detail in this work.

1.1. Industrial H_2O_2 Manufacture—A Historical Perspective

To discuss the chronological advancements in industrial H_2O_2 production, one has to split the progress into electrochemical and chemical methods. A detailed description of the processes has been summarized in the works of Goor [1,3] and Jones [8] (Table 1) and the reaction schemes are depicted in Scheme 1.

Table 1. Historical development in the industrial manufacture of hydrogen peroxide.
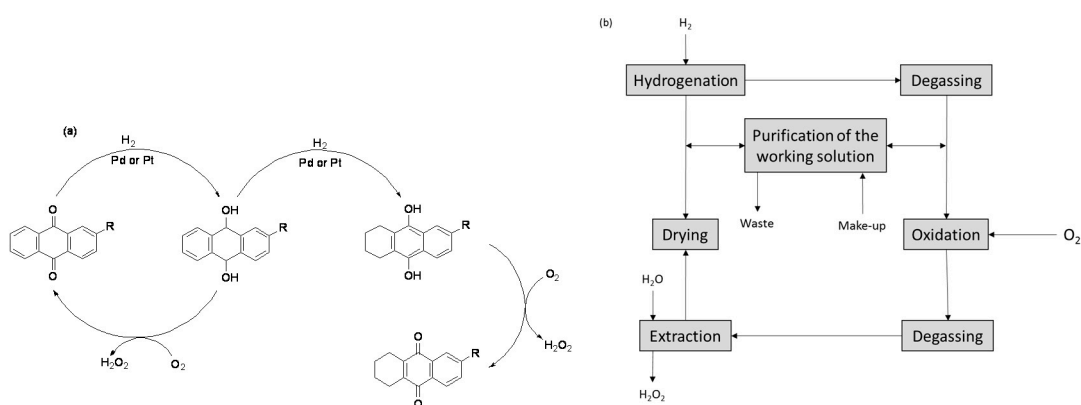
Year	Inventor	Catalysis Type	Details
1818	L.J. Thenard	Chemical	Barium peroxide reacts with hydrochloric acid to form barium chloride and H_2O_2. Yield of 3% H_2O_2 was 2000 tons/annum (t/a) (Scheme 1a) [9,10]
1853	H. Meidinger	Electrochemical	Electrolysis of sulphuric acid to yield H_2O_2 [11] (Scheme 1b)
1878	M. Berthelot	Electrochemical	Elucidated the mechanism of sulphuric acid electrolysis. Reported the formation of peroxodisulphuric acid as an intermediate [12] (Scheme 1b)
1901	W. Manchot	Chemical	Autoxidation of hydroquinones and hydrazobenezenes under alkaline conditions in the presence of molecular oxygen to yield H_2O_2 [13–15] (Scheme 1e)
1908	Degussa-Weissenstein Process	Electrochemical	First production plant set up in Wiessenstein, Austria [16,17]
1910	Münchner Process or the Pietzsch-Adolph Process	Electrochemical	Developed by Pietzsch and Adolph at the Elektrochemische Werke, Munich. Used potassium peroxodisulphate instead of sulphuric acid to produce H_2O_2 [16,17] (Scheme 1c)
1914	Hugo Henkel and Walter Weber	Chemical	First account of direct synthesis of hydrogen peroxide using its constituent gases [18]
1924	Reidl-Löwenstein Process	Electrochemical	Similar to the Pietzsch-Adolph Process; used ammonium peroxodisulphate to produce H_2O_2 by electrolysis (Scheme 1d). Yield of 100% H_2O_2 was 35 kt [16,17]
1932	Walton and Filson	Chemical autoxidation	Published their work on the alternate oxidation and reduction of hydrazobenzenes to produce H_2O_2 [19] (Scheme 1e)
1935	Pfleiderer, Baden Aniline and Soda Factory (BASF)	Chemical autoxidation	Alkaline autoxidation of hydrazobenzenes to form sodium peroxide, later hydrolysed to form H_2O_2 [20] (Scheme 1f)
1935–1945	Riedl and Pfleiderer	Chemical autoxidation	Anthraquinone autoxidation process (AO) set up in two different cities each with 2000 t capacity [16,21] (Scheme 2a)
1953	E.I. du Pont de Nemors	Chemical autoxidation	Commercial plant setup with based on the Riedl and Pfleiderer process [1,3,8] (Scheme 2a)
1957–1980	Shell process	Chemical autoxidation	Oxidation of 2-propanol to yield H_2O_2 at a capacity of 15 kt [22] (Scheme 1g)

(a)
$$BaO_2 + 2\,HCl \longrightarrow BaCl_2 + H_2O_2$$
$$BaCl_2 + H_2SO_4 \longrightarrow BaSO_4 + 2\,HCl$$

$$BaO_2 + H_2SO_4 \longrightarrow BaSO_4 + H_2O_2$$

(b)
$$2\,H_2SO_4 \longrightarrow H_2S_2O_8 + H_2$$
$$H_2S_2O_8 + H_2O \longrightarrow H_2SO_5 + H_2SO_4$$
$$H_2SO_5 + H_2O \longrightarrow H_2SO_4 + H_2O_2$$

$$2\,H_2O \longrightarrow H_2O_2 + H_2$$

(c)
$$2\,(NH_4)HSO_4 \longrightarrow (NH_4)_2HSO_4 + H_2$$
$$S_2O_8^{2-} + H_2O \longrightarrow HSO_4^- + HSO_5^-$$

$$HSO_5^- + H_2O \longrightarrow HSO_4^- + H_2O_2$$

(d)

(e)

(f)

(g)

Scheme 1. (**a**) L.J. Thénard method of H_2O_2 production from BaO_2. (**b**) Electrolysis of sulphuric acid to produce hydrogen peroxide according H. Meidinger and M. Berthelot. (**c**) Münchner Process to produce H_2O_2 (**d**) Riedel-Löwenstein Process [3,8,23]. (Image taken from Berl [23], reproduced here with the kind permission of the Journal of the Electrochemical Society) (**e**) Hydrazobenzene oxidation to produce H_2O_2 (scheme modified from Walton and Filson [19], copyright 1932, American Chemical Society). (**f**) Georg Pfleiderer Process of producing H_2O_2, an adaptation of the Walton and Filson Process [20] (**g**) Shell 2-propanol Process to produce acetone/H_2O_2 [3] (Scheme taken from [3], reproduced here with the kind permission of John Wiley and Sons)

1.2. State of the Art in the Industrial Production of H_2O_2

On an industrial scale, the anthraquinone autoxidation (AO) process described by H.J. Riedl and G. Pfleiderer produces H_2O_2 in a cyclic manner (Scheme 2).

Scheme 2. (**a**) Mechanism of the autoxidation (AO) process developed by Riedl-Pfleiderer [21,24] (Image taken from Li et al. [24], 2017, reprinted here with the kind permission of Springer Nature) and (**b**) block diagram of the AO process steps to synthesise H_2O_2 (scheme modified from Campos-Martin et al. [7], reprinted here with the kind permission of John Wiley and Sons).

Scheme 2a shows the reaction mechanism of the AO process and Scheme 2b depicts the practice of H_2O_2 manufacture in the industry. The hydrogenation chamber is usually a slurry reactor consisting

of the alkylated anthraquinone dissolved in a so-called "working solution" along with a catalyst. Hydrogen gas is initially fed through the reactor for hydrogenation to alkyl anthrahydroquinol. After this, the contents of the hydrogenation chamber are degassed in a separate chamber to remove traces of hydrogen. Following this step, the alkyl anthrahydroquinol is transferred to the oxygenation chamber. Here, oxygen or air is used to produce H_2O_2 and alkyl anthrahydroquninone, which is then transferred to a second degassing chamber to remove trace oxygen. The degassed solution is then extracted with water to yield H_2O_2 and the working solution is transferred to the hydrogenation chamber to complete the synthetic cycle. In the mid-1990s, the world capacity of 100% H_2O_2 was approximately 1.5 million tons with an average plant capacity of around 20 kt–40 kt per annum. By 2015, the capacity was 5.5 million tons with a plant capacity of 300 kt per annum [25]. Solvay (30%), Evonik (20%), and Arkema (13%) represented the global contributors of H_2O_2 [26].

1.3. Why Is There an Increased Interest in the Direct Synthesis of Hydrogen Peroxide?

Currently, the industrial manufacture of H_2O_2 is based on the work of Riedl and Pfleiderer, also known as the AO process [21] (Scheme 2) [24] using polynuclear hydroquinones [1]. Although this process is capable of meeting the world's H_2O_2 demand, it does have certain drawbacks such as:

- excessive use of solvents for the process
- a negative environmental impact owing to the production of unwanted waste
- complex and multi-step process
- mass transfer limitations and low efficiency
- transport limitations of reactants between reactors
- organic contamination of H_2O_2 stemming from organic solvents or hydroquinones/hydroquinols during liquid-liquid extraction [27,28].

Considering environmental issues and resource conservation aspects, academia and the industry have set out to design benign and non-polluting processes. The principles of green chemistry helps in achieving this goal. The principles outlined in the 1990s clearly state that it is necessary to design and execute industrial processes that are clean, benign, non-polluting, and safe [29–32]. Two important terms, atom utilization and E-factor, are important in assessing the greenness of a process. Atom utilization, atom efficiency or atom selectivity (AE) maybe defined as the actual mass of reactants that actually end up in the final desired product, the rest of which is termed as "waste". AE helps in assessing the amount of wastes generated by a certain process, which in turn, will determine the E-factor. The E-factor is the ratio of the amount of waste produced to the amount of desired product [33–35]. Considering the AO process, the amount of solvents and the alkylated hydroquinones used in the process are waste products, as the reaction is not atom efficient [1,3,7,8]. This brings up an important question: why is the AO process still practiced at an industrial level if it is not sustainable? The answer: operating the AO process is economically feasible at a scale of 1×10^5 tons per annum producing high concentrations of H_2O_2, which are diluted prior to use. For a majority of the applications mentioned previously in the introductory section (Section 1), diluted versions of H_2O_2 (typically 3–8%) is required, in small amounts, and on site. To circumvent the issues mentioned above and promote a green H_2O_2 production process, the direct synthesis of H_2O_2 from H_2 and O_2 was researched, but only at the laboratory scale. Theoretically, it is clear that the direct synthesis approach is the simplest way to synthesise H_2O_2; however, issues with respect to practicality limit the industrialization of this process [36,37]. This review will address the challenges and developments in the field of direct synthesis of H_2O_2, focussing on chemical catalytic methods.

2. The Direct Synthesis Approach to H_2O_2 Production Using Chemical Catalysis

In 1914, H. Henkel and W. Weber reported the very first process that was capable of producing H_2O_2 from hydrogen (H_2) and oxygen (O_2). The patent described the reaction of two gaseous mixtures: an oxygen species (free and bound) and hydrogen in a pressurised vessel along with water.

An important aspect of the patent was the use of noble metals capable of fixing hydrogen as catalysts; e.g., palladium (Pd), platinum (Pt), nickel (Ni), etc. [18].
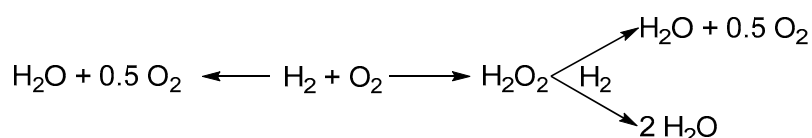
2.1. Pros and Cons of the Direct Synthesis Approach to H_2O_2 Synthesis

The direct synthesis approach has not been industrially practiced due to several technological and scientific barriers [38] and Table 2 lists the advantages and disadvantages of this approach.

Table 2. Analysis of the advantages/disadvantages of the direct synthesis approach [27,39–42].

Advantages	Disadvantages
Absence of organic substrates such as anthraquinones or organic solvents	Unselective reactions leading to simultaneous side products other than H_2O_2, namely water (H_2O)
Usage of green solvents like water, methanol, or ethanol	Complex process with mass transfer limitations involving three phases: gas (H_2/O_2), liquid (reaction medium), and solid (catalyst)
Economical because of fewer downstream operations to produce H_2O_2	Safety: explosive nature of the H_2 and O_2 mixture over a wide range of concentrations (4 mol %–94 mol %)
The whole process can be accomplished with a single reactor system	Presence of chloride and/or bromide ions in the reaction medium

Scheme 3 depicts the direct synthesis of H_2O_2. As seen, the reaction produces either water H_2O or H_2O_2 depending on the reaction conditions.

$$H_2O + 0.5\ O_2 \longleftarrow H_2 + O_2 \longrightarrow H_2O_2 \underset{H_2}{\overset{H_2O + 0.5\ O_2}{\diagup\diagdown}} 2\ H_2O$$
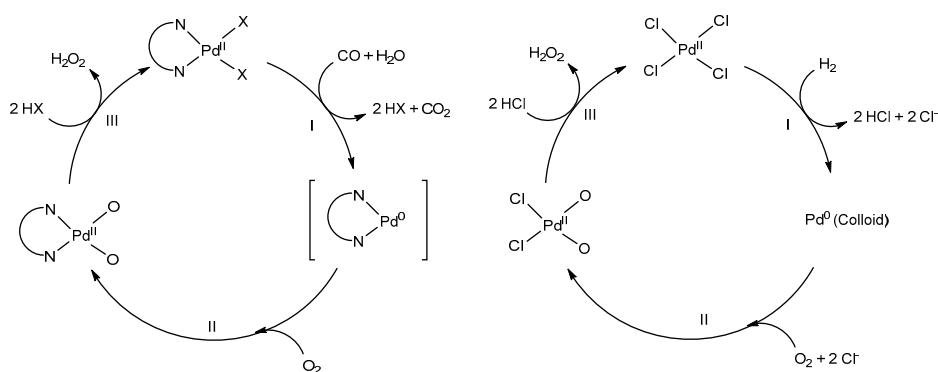
Scheme 3. The direct synthesis approach consisting of two parallel reactions (reduction and oxidation) during the production of H_2O_2. Scheme taken from Gervasini et al. [43], reprinted here with the kind permission of the American Chemical Society, Copyright 2017, Khan et al. [44], and Seo et al. [45].

2.2. Mechanism of the Direct Synthesis of H_2O_2

The mechanism of hydrogen peroxide synthesis using H_2 and O_2 is shown in Scheme 4. A possible mechanism of such a synthesis was proposed by Bianchi et al. in 1999 [46], based on the 1980 report published by Zudin et al. [47]. While Zudin et al. used palladium triphenylphosphane in a biphasic system, Bianchi et al. found out that 2,9-dimethyl-4,7-diphenyl-1,10-phenantroline ligand was the best among other ligands tested. Based on these findings, Werner published the proposed mechanism of H_2O_2 synthesis by the reduction of dioxygen [48]. Stahl et al. used a bathocuproine palladium complex in order to catalyse the direct synthesis of H_2O_2 [49]. All three processes utilised acid halides such as hydrochloric acid or hydrogen bromide to facilitate efficient catalysis [46,47,49]. However, the actual mechanism was reported in 2001 by Stahl et al. [49] Scheme 4(i), which was confirmed by Chinta and Lunsford in 2004 using tetrachloropalladate ($PdCl_4^{2-}$) prepared prior to use (Scheme 4(ii)) by replacing nitrogen ligands with chloride [50].

The mechanism follows these steps: initially, Pd^0 reduces molecular oxygen in the presence of the nitrogen ligands (Scheme 4(i))/halide ions (Scheme 4(ii)) to form the respective Pd^{II} complex that contains a peroxo-species. This is replaced by halides yielding H_2O_2. Subsequently, Pd^{II} is reduced by molecular hydrogen to yield Pd^0, thereby completing the catalytic cycle.
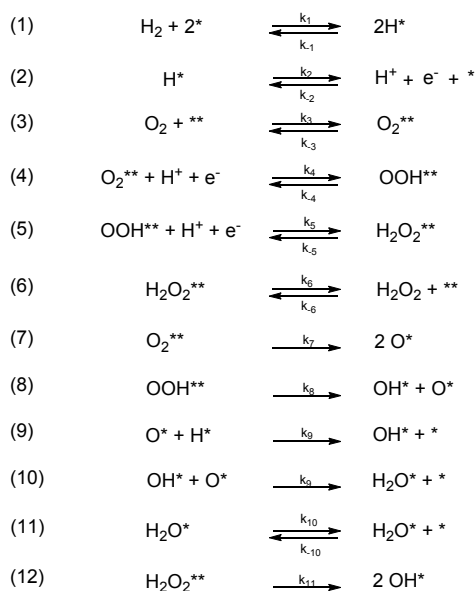
Scheme 4. (**i**) Mechanism of H_2O_2 formation in water with CO and O_2 in the presence of palladium catalyst complexed with nitrogen ligands (scheme from Werner et al. [48], and reprinted here with the kind permission of John Wiley and Sons, copyright 1999). (**ii**) The catalytic cycle of H_2O_2 manufacture using palladium catalysts complexed with chloride ions (Chinta and Lunsford [50], and reprinted here with the kind permission of Elsevier, copyright 2004).

2.3. Series of Elementary Steps in H_2O_2 Synthesis

Several accounts of the possible elementary steps during the direct synthesis of H_2O_2 have been described in literature by Wilson and Flaherty [40], Plauck et al. [51] and Yi et al. [52], to name a few. Scheme 5 depicts the series of steps that lead to the synthesis of H_2O_2 and H_2O during the direct synthesis approach using Pd catalysts in liquid solvents. In each of the steps in the process, bimolecular reactions exist between the H^+ and chemically adsorbed intermediates on the catalyst surface. The elementary steps are based on the following assumptions:

- Free energies of H_2 and O_2 adsorption are negligible under saturation conditions
- The adsorption and desorption of the H_2O_2 species is unrestricted

$$
\begin{array}{lll}
(1) & H_2 + 2* \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} & 2H* \\
(2) & H* \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} & H^+ + e^- + * \\
(3) & O_2 + ** \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} & O_2** \\
(4) & O_2** + H^+ + e^- \underset{k_{-4}}{\overset{k_4}{\rightleftarrows}} & OOH** \\
(5) & OOH** + H^+ + e^- \underset{k_{-5}}{\overset{k_5}{\rightleftarrows}} & H_2O_2** \\
(6) & H_2O_2** \underset{k_{-6}}{\overset{k_6}{\rightleftarrows}} & H_2O_2 + ** \\
(7) & O_2** \overset{k_7}{\rightarrow} & 2\,O* \\
(8) & OOH** \overset{k_8}{\rightarrow} & OH* + O* \\
(9) & O* + H* \overset{k_9}{\rightarrow} & OH* + * \\
(10) & OH* + O* \overset{k_9}{\rightarrow} & H_2O* + * \\
(11) & H_2O* \underset{k_{-10}}{\overset{k_{10}}{\rightleftarrows}} & H_2O* + * \\
(12) & H_2O_2** \overset{k_{11}}{\rightarrow} & 2\,OH*
\end{array}
$$

Scheme 5. Plausible series of elementary steps for hydrogen peroxide and water formation during the direct synthesis approach on Pd catalyst (* is an empty site on the catalyst surface, X (H, O, OH, H_2O)* is an adsorbate bound to a single Pd atom, X**, where X can be O_2, OOH, or H_2O_2, is an intermediate adsorbed. All reversible arrows represent a quasi-equilibrate step. It is to be noted that each of the steps has its own rate constants) [40]. Scheme taken from Wilson & Flaherty, 2016 https://pubs.acs.org/doi/abs/10.1021/jacs.5b10669.

Based on these assumptions, the first step is that the hydrogen adsorbs dissociatively on to the catalyst surface (Step (1) in Scheme 5) yielding H* and is subsequently oxidized (Step (2) in Scheme 5). In Step (3) of Scheme 5, the molecular adsorption of O_2 takes place. This initiates Step (4) in Scheme 5, wherein O_2** undergoes proton-electron transfer under quasi-equilibration conditions to form OOH** (hydroperoxy radical). Alternatively, O_2** cleaves the O-O bond irreversibly to form O*, also known as chemi-absorbed oxygen atoms (Step (7) Scheme 5). The OOH** is then adsorbed, which then reacts further to form either H_2O_2** by proton-electron transfer, as shown in Step (5) of Scheme 5, or dissociates itself (Step (8) of Scheme 5). This finally leads to the release of H_2O_2 (Step (6), Scheme 5) or H_2O (Step (11), Scheme 5) [40,51,52].

2.4. Process Conditions for the Direct Synthesis of H_2O_2 from H_2 and O_2

The direct synthesis of H_2O_2 requires certain operating conditions such as the ratio of H_2 and O_2, reaction medium for the synthesis, the reactor used, additives and/or promoters, a catalyst, and its supporting material [53–55]. The following sections explain the influence of each of these parameters on the conversion and yield of the direct synthesis of H_2O_2.

2.4.1. Ratio of the Gaseous Mixture

During direct synthesis, one would expect the reaction of H_2 and O_2 on a catalytic surface to form only H_2O_2 as the product. However, unwanted side reactions also occur that reduce the productivity of this otherwise green process. The first side reaction is the oxidation of H_2 to H_2O instead of H_2O_2 and the second one is the reduction of the H_2O_2 produced to H_2O (Scheme 3). One can influence the selectivity of the process by optimising the parameters mentioned previously, but it is self-explanatory that the amount of H_2 and O_2 in the reaction mixture directly influences the H_2O_2 output. Three combinations of H_2/O_2 are possible for this reaction excess H_2, excess O_2, and stoichiometric amounts. Using excess H_2 would favour the reduction of H_2O_2, while using stoichiometric amounts would increase H_2O_2 concentration during synthesis. However, an excess of oxygen, up to three times compared to hydrogen, would also increase the selectivity and yield of the direct synthesis approach [56]. It is worth mentioning that the flammable and explosive nature of these two gases over a wide concentration range at 25 °C and 0.1 (MPa) (1 atmospheric pressure) is a point of great concern. The flammability limit for H_2 in O_2 is 4% (lower flammability limit) to 94% (upper flammability limit), while the detonation limit is at 15% to 95%, with an increased risk of explosion with increasing pressure [42,54,57]. DuPont faced frequent explosions in their pilot plant by feeding 10% H_2 in O_2 to their process, which led to the discontinuation of the pilot plant studies [27,54].

In order to minimise the explosion risk, it is suitable to perform the reaction at lowered feed rates of H_2 and O_2, diluted with inert gases [54]. The most common diluents are helium (He), argon (Ar), nitrogen (N_2), or carbon dioxide (CO_2) [26]. Most of the recent literature indicates the use of either CO_2 [44,58,59] or N_2 [39,60,61]. The work of Wilson and Flaherty described the use of N_2 and CO_2 as the diluents during synthesis using palladium catalysts (Pd) supported on silica (Si). By doing so, the researchers reported an overall selectivity of 31% towards H_2O_2 using only CO_2 as the diluent. However, the combined effect on the overall selectivity was not reported [40]. Using CO_2 as a diluent is advantageous as it can expand different solvents during the reaction and increase H_2 solubility. Secondly, CO_2 dissolves in water to form carbonic acid (HCO_3^-), which makes the medium acidic. The acidic condition is helpful as it is the most commonly used storage condition for H_2O_2 [5]. The chemists and engineers in the field have agreed that increasing the solubility of H_2 and O_2 in the reaction medium would also lead to a better adsorption of the gases on to the catalytic surface. This, in turn, would lead to a better yield of H_2O_2 [62]. Selinsek et al. recently reported a process design with two separate tanks containing H_2 and O_2 dissolved in water with a two-fold benefit. First, an explosion is circumvented due to the separate feeding of gases. Second, the H_2 to O_2 ratio in the reaction cell can be easily controlled by varying the flow rate of the pump, ensuring that at any given point in time, the process operates in a safe manner [4]. The recent work of Urban et al. describes

the use of an electrochemical sensor system to detect the hydrogen and oxygen amounts present in the system during direct synthesis. Additionally, the sensor is capable of monitoring the H_2O_2 levels in the reactor as well. This sensor is capable of performing under high analyte concentrations and high pressures. The authors also claim that the usage of this novel electrochemical sensor could minimise the risk of explosion due to high accuracy of detection [63].

2.4.2. Reaction Medium

As mentioned previously, the direct synthesis of H_2O_2 from H_2 and O_2 in the gaseous state without any reaction medium is highly dangerous. This is because the gases form an explosive mixture over a wide range of concentrations [64]. Hence, performing the synthesis of H_2O_2 at lowered temperatures in highly pressurised environments, in an appropriate reaction medium, prevents explosions and produces high yields [27]. Therefore, the choice of the reaction medium is crucial to the success of the process. Most of the existing literature uses water as the reaction solvent, with some exceptions where pure methanol or ethanol is used. Additionally, using water with co-solvents such as methanol or ethanol favours a higher dissolution of H_2 when compared to pure water as a reaction medium [56,65]. In 2001, Hâncu and Beckmann reported the use of CO_2 as a reaction medium for the direct synthesis of H_2O_2 using a CO_2 soluble ligand-supported Pd catalyst. The researchers worked on the assumption that the H_2O_2 solubility in CO_2 is considerably less than the conventional working solutions of the AO process, i.e. organic solvents. Furthermore, the CO_2 used was liquid under the reaction conditions (298 K, 17 MPa) and the presence of a CO_2-phillic catalyst would minimize the contact time of H_2O_2 on Pd, thereby increasing the selectivity of the process (Figure 1) [28,66].
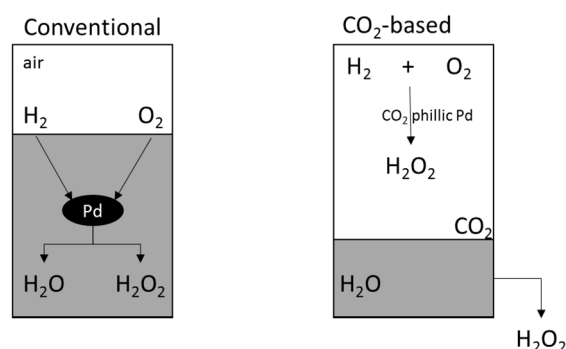

Figure 1. Comparison of direct synthesis of H_2O_2 in conventional (aqueous solutions) and CO_2 with a modified CO_2-phillic Pd catalyst (Figure taken from Hâncu and Beckmann [28]). Reprinted here with the kind permission of the Royal Society of Chemistry.

Moreno et al. reported the use of a supercritical CO_2 (scCO_2) with methanol (MeOH) water mixture at an operating temperature range of 283 K–318 K and pressure of 16.7 MPa to synthesize H_2O_2 from H_2 and O_2. N_2 was used as a diluent in this reaction to achieve a yield between 11.6% and 45.9% [42]. Except for these works, almost every direct synthesis of H_2O_2 using chemical catalysis is documented in water, alcohol, or a defined ratio of both. Landon et al. reported that at 31.1 °C, which is the critical temperature of CO_2, more decomposition of H_2O_2 was observed than formation. The researchers suggested that the synthesis was performed at a temperature just below the critical temperature [67]. This could be one of the many reasons as to why the use of CO_2 as a solvent has not been widely researched. Abate et al., on the other hand, used scCO_2-expanded methanol (a solution operating below the triple point in the presence of a solvent to form a two-phase fluid system) as the solvent in the presence of a Pd catalyst supported on mesoporous silica for the direct synthesis of H_2O_2. On doing so, a selectivity of 40% towards H_2O_2 and a productivity of 0.11 $mol_{H2O2}m^{-2} \cdot Pd \cdot h^{-1}$ at the end of 3 h [65].

2.4.3. Additives/Promoters

Along with the reaction medium, special additives termed "promoters" are often used to stabilize H_2O_2 production and to increase the process yield. The most commonly used promoters are acids or halides. Edwards et al. published the effect of acids and halides on the outcome of the direct synthesis of H_2O_2. In this report, the researchers classified the promoters into two groups:

(i)　oxyacids such as acetic acid, perchloric acid, phosphoric acid (H_3PO_4), nitric acid, and sulphuric acid (H_2SO_4)

(ii)　halide acids such as hydrochloric acid (HCl), hydrobromic acid (HBr), and hydroiodic acid (HI).

The authors reported that the reactions could accept potassium and sodium salts of halide acids as well. The presence of halide ions in the reaction could influence the H_2O_2 conversion in the following order: KF > no halide ions > KCl > KBr and selectivity in the following order: KBr > KCl > no halide ions > KF. The report also claimed that the presence of iodide ions eventually poisoned the catalyst [55]. The next pioneering work in the field was that of Wilson and Flaherty, pointing out that the presence of protons (H^+) from mineral acids such as HCl, H_2SO_4, H_3PO_4 and HNO_3 aids in reducing molecular oxygen. They also suggested that the corresponding counter ions such as Cl^-, SO_4^{2-}, PO_4^{2-}, and NO_3^- modify the structure of the metal catalyst. By adding halide groups to the Pd catalyst and performing the synthesis in ethanol at an acidic pH, the selectivity would eventually increase from 60% to 80% [40]. The recent report of Gallina et al. compared the roles of sodium bromide (NaBr), H_3PO_4, and H_2SO_4 on the outcome of the direct synthesis of H_2O_2 by varying the concentrations of NaBr and H_3PO_4. The authors conducted the experiments at 288 K, 2.0 MPa, 3 h reaction time, Pd/C, with a gas mixture percent of $H_2/O_2/CO_2$ at 4/20/76%. The table (Table 3) below describes the observations of Gallina et al. on testing various combinations of the promoters.

Table 3. Effect of different promoters on H_2 conversion, H_2O_2 selectivity, H_2O_2 productivity as reported by Gallina et al. [68].

Serial No. (S/N)	Additive Added			Outcome		
	NaBr (M *)	H_3PO_4 (M)	H_2SO_4 (M)	H_2 Conversion (%)	H_2O_2 Selectivity (%)	H_2O_2 Productivity ($mol_{H2O2} \cdot Kg(Pd)^{-1} \cdot h^{-1}$)
1	0	0	0	100	0	0
2	0	0.003		100	0	0
3	0.0005	0	0	92	50	740.1
4	0.0005	0.003	0	85	61	891
5	0.0005	0.005	0.025	79	65	830

* mole (mol)/litre (L); molar.

The researchers formulated that the absence of promoters (H_3PO_4 or NaBr) led to either (i) a much more prominent water forming reaction than the H_2O_2 forming one or (ii) subsequent reaction of H_2O_2 further to form H_2O. The researchers also concluded that NaBr/H_3PO_4 had a combined effect on the leaching of the Pd catalyst and that there was no fixed NaBr to H_3PO_4 ratio to improve the direct synthesis of H_2O_2 [68]. The authors also suggested that a pH of 2.0 in the reaction medium would favour a better selectivity towards H_2O_2 production from H_2 and O_2 [68].

Another method of acidifying the reaction medium to suit the direct synthesis of H_2O_2 is to use solid acid catalysts (SAC) as reported by the publication of Lewis et al. [57]. The problem of the acidic additives and halide salts being soluble in aqueous medium making the recovery of these a tedious downstream operation was addressed in this work. By using a SAC such as caesium substituted phosphotungstic acid (HPA) in the presence of a Pd or Au-Pd alloyed catalyst, the productivity of H_2O_2 could be increased and the degradation to H_2O could be decreased [69].

2.4.4. Reactor Design

One of the most important parameters to be discussed for the direct synthesis of H_2O_2 is the type of reactor used for the reaction. Until today, slurry reactors, plugged flow reactors, microreactors or trickle bed reactors are often used to synthesise H_2O_2 directly from H_2 and O_2. One of the major requirements when choosing a reactor is that the vessel should withstand high pressure. It is known that the prolonged exposure of H_2O_2 to H_2 in the presence of a Pd catalyst would lead to the formation of water (Scheme 3). One possible way to overcome this phenomenon is to limit the exposure of H_2O_2 to H_2 on the catalytic surface.

Microreactors present a unique way to operate this process in a continuous manner, with defined flow characteristics, large surface area to volume ratio, promising heat and mass transfer rates, and excellent process safety. A microreactor is "a device that contains micro structured features with a sub millimetre dimension, in which chemical reactions are performed in a continuous manner." The microreactors are constructed from silicon, quartz, glass, metals, polymers, and ceramics, to name a few [70]. The work of Shang and Hessel describes the operational- and reaction-based benefits of using microreactors for the direct synthesis of H_2O_2 in their work [71]. One drawback of using a microreactor for the direct synthesis of H_2O_2 is the incorporation of the metal catalyst within the capillaries of such a reactor [72]. Kanungo et al. described a technique to incorporate an Au-Pd alloy on to the walls of a silica coated capillary microreactor. The innovation in the design lies in the fact that the catalytic particles were formed in situ on the walls of the microreactor by a layer-by-layer self-assembly creating a multi-layer catalyst. By using this approach, the researchers were able to produce 210 $mol_{H2O2} \cdot kg_{cat}^{-1} \cdot h^{-1}$ with a H_2 conversion of 40% and selectivity of 70% (H_2/O_2–1:1, 315 K, 2.0 MPa, 5 h) (Figure 2a) [72]. Paunovic et al. reported a production process using the same catalysts in a microchannel reactor. The researchers were able to obtain five mass percent H_2O_2 solutions at a conversion rate of 15% at 42% selectivity (315 K, 2.0 MPa, 0.05 M H_2SO_4, 9 parts per million (ppm) NaBr, H_2/O_2 ratio 20%) [73]. Voloshin et al. elucidated the mass transfer mechanism that occurs in a microreactor during the direct synthesis of H_2O_2 (Figure 2b). In their work, the researchers claimed that flow of the fluids through the microreactor was slug-flow like. In other words, the liquid flow pattern is interrupted by catalytic particles and the pattern resembles that of a liquid slug being broken down. Using a set of assumptions, the researchers came up with a kinetic model that would explain the behaviour of a packed bed microreactor during direct H_2O_2 synthesis [74]. Hirama et al. used 32 parallel microreactors made up of silica and glass to produce H_2O_2 directly from H_2 and O_2. The authors were able obtain H_2O_2 at 10 mass percent at a productivity of 0.5 kg h^{-1}. Inoue et al., on the other hand, used four parallel microreactors to produce four mass percent H_2O_2 at 0.042 kg h^{-1}. Ng et al. reported the use of palladium nanoparticles immobilised on to polystyrene based polymer supports in a capillary microreactor, enabling a continuous production of 1.1 mass percent H_2O_2 over 11 days [75]. The reviews of Kolehmainen et al. [56] and Dittmeyer et al. [53] summarize the innovations in the field of catalyst design and reactor engineering in a detailed manner.

Another technique to overcome H_2O_2 decomposition by reactor engineering is the use of a trickle bed reactor or a plugged flow reactor. Almost all works of Biasi et al. uses trickle bed reactors (Figure 3) to improve the selectivity towards H_2O_2 [68,76–80], with the maximum being 80% using Pd on a sulfated ceria (CeS) catalyst.
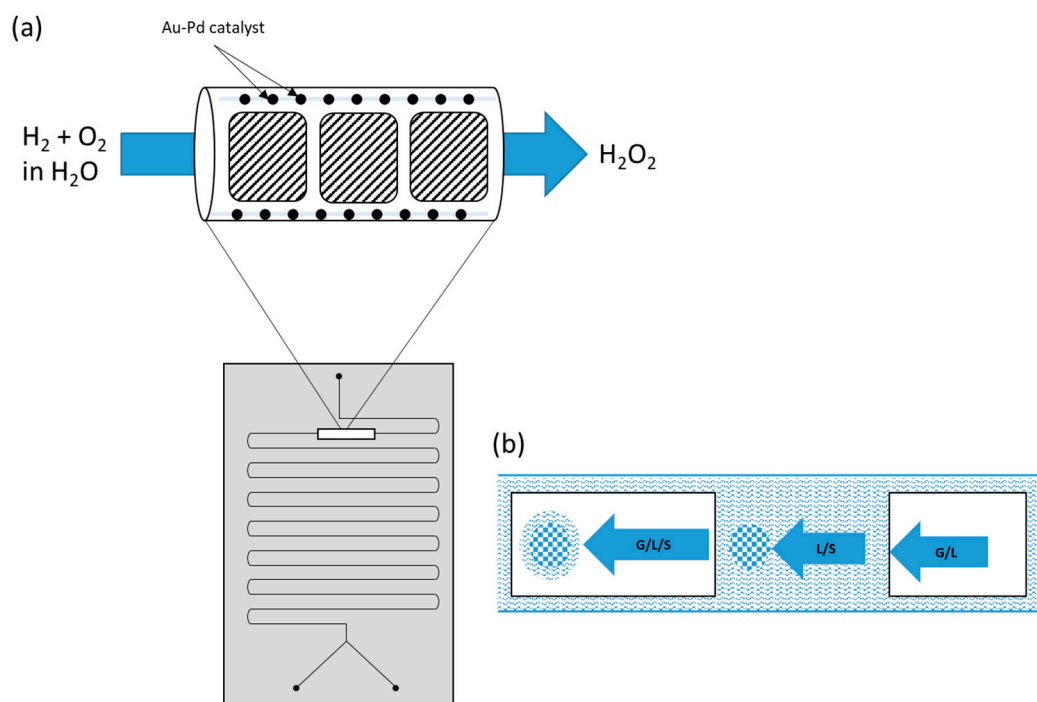
Figure 2. (**a**) A general microreactor design adapted by Kanungo et al. with a magnified view of the Au-Pd packing in the capillaries of the channel (scheme adopted from Kanungo et al. [72], https://pubs.acs.org/doi/abs/10.1021/acs.nanolett.7b03589). (**b**) Mass transfer scheme in a packed bed microreactor (G-gas, L-liquid, S-Solid) (scheme taken from Voloshin et al. [74], reprinted here with the kind permission of Elsevier publishing group).
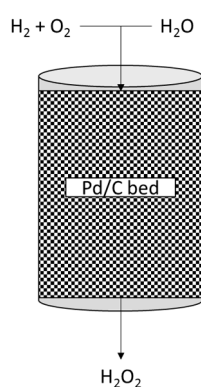

Figure 3. Trickle bed reactor used by Gallina et al. [68] to produce H_2O_2 directly from H_2 and O_2 in water in the presence of a commercial Pd/C catalyst (Scheme modified from Gallina et al. [68], 2017, copyright 2017. Reprinted here with the kind permission of the American Chemical Society).

2.4.5. Influence of the Catalytic Material

A major hindrance in the direct synthesis approach is the process' low selectivity, as the formation of H_2O_2 is not thermodynamically favoured. Although promoters such as H_2SO_4, H_3PO_4, NaBr, and KBr help enhance the selectivity of the process, one might consider the catalyst and its supporting material to be the most influencing parameter [81]. Furthermore, the presence of noble metals or noble metal alloys as catalysts aid in the hydrogenation and subsequent decomposition of H_2O_2 to water (Scheme 3) [4]. On surveying the recent literature in the direct synthesis of H_2O_2, it is certain that the majority of scientists in the field are dedicated towards developing new, robust and stable catalysts. Existent catalysts and the newly developed versions of noble metal catalysts are

characterized based on two criteria: conversion and selectivity. Pd catalysts are almost exclusively used for such reactions either as obtained or alloyed with other metals and/or supports to enhance the selectivity of the process.

Edwards et al. published the importance of alloying Pd with other metals to increase the efficiency of H_2O_2 production. Their observation stemmed from the highly reactive nature (25 times more active) of an Au-Pd catalyst that was capable of oxidising alcohols better than the corresponding monometallic catalysts. They also reported that when Au-Pd alloys were attached to a titanium dioxide (TiO_2) or alumina (Al_2O_3) support, core-shell structures were formed. With the development of the new catalyst, the researchers still faced the problem of H_2O_2 being reduced to water [82]. The same working group developed a new tin-based Pd alloy to stop the hydrogenation of H_2O_2. With the new alloyed catalyst accompanied by a heat treatment cycle, the hydrogenation reactions were prevented and selectivities of more than 95% were reported [37]. Ntainjua et al. used ruthenium (Ru) alloyed with Au and Pd to perform the direct synthesis of H_2O_2. The authors investigated the Ru-Au, Ru-Pd and Ru-Au-Pd catalyst for H_2O_2 synthesis. The amount of Ru added to the alloy, along with the calcination conditions, had an effect on the catalyst activity and reusability. So far, this report is the only one using an Ru catalyst for the direct synthesis of H_2O_2 [83]. Besides Au, only silver [44,84], tellurium [85], tin [37], and zinc [86] are described as possible metals for alloying with Pd. Xu et al. reported the possible increase of H_2O_2 production by using different metals such as tungsten (W), lead (Pd), molybdenum, etc. and validated their results with density functional theory (DFT). The researchers suggested that all these metals were superior to platinum (Pt) as a promoter. The research was a computational model and experimental evidence to substantiate this fact is needed [87].

Tian et al. reported that by increasing the amount of Pd in the system, the H_2 conversion increases as well, which is self-explanatory. However, the selectivity and productivity increases with decreasing Pd content. From these results, they were able to conclude that having a Pd particle size in the range of 2.5 nm to 1.4 nm would yield a selectivity of approximately 94% with 0.5% Pd loading [88]. Most recently, Howe et al. used microwaves to prepare an Au-Pd alloy supported on TiO_2 for synthesizing H_2O_2 from H_2 and O_2. The authors claim that the catalysts were capable of maintaining their activity for four reaction cycles. Compared to other alloyed Pd particles, these particles have a core-shell structure and can be prepared in 0.25 h [89]. The recent 2017 patent of Desmedt et al. used metallic catalysts supported on sulphate and phosphate to reduce the amount of inorganic acid content in the reaction medium. The inventors varied the metal content between 0.001 mass % and 10 mass % (0.62 to 2 wt % Pd) to obtain conversions ranging between 26.9% and 46% and selectivities between 19.9% and 74% [90].

Table 4 below summarises the reaction conditions and the catalysts for the direct synthesis of H_2O_2 along with the catalyst used.

Table 4. List of operating conditions in literary works involving the direct synthesis of H_2O_2 between 2010 and 2018.

Temperature and Pressure (K and MPa)	Catalyst	Reactor Type	Solvent(s)	Promoters	Conversion and Selectivity (%)	Literature Reference
263 and 2	Palladium-CeS	Trickle bed reactor with Teflon lining	Methanol	None	No data, 80	Biasi et al. [76]
298 and 0.1 (ambient)	Palladium on porous alumina tubing	Membrane reactor	Water	Sulphuric acid (H_2SO_4) sodium bromide (NaBr), phosphoric acid (H_3PO_4)	No data, 50	Inoue et al. [91]
283–324 and 4.6–16.7	Palladium on carbon	Stirred slurry batch reactor	Water + scCO$_2$ and methanol + scCO$_2$	H_3PO_4 and NaBr	No data available	Moreno et al. [42]
298 and 0.1 (ambient)	Pd nanoparticles immobilized on polystyrene based polymer	Capillary microreactor	Methanol	No additive H_2SO_4, KBr	47 and 0.65 3.9 and 77	Fei Ng et al. [75]
301 and 1.01	Insoluble heteropoly acid supported on Pd immobilized on mesostructured foam (MCF) silica	Autoclave reactor	Methanol	H_3PO_4 and NaBr	85 and 35	Park et al. [92]
298 and 4.5	Metallic Pd deposited on ceramic tubes	Porous tubular membrane reactor	Methanol	H_2SO_4, NaBr	No data and 83	Pashkova et al. [93]
293 and 4.0	Au-Pd on TiO$_2$ on carbon	Stainless steel autoclave	Methanol/water	No data available	No data available	Pritchard et al. [94]
315 and 2.06	Pd on SiO$_2$.	Microreactor	Water	H_2SO_4, NaBr	No data and 85	Voloshin et al. [74]
263 and 1.0	Bimetallic Pd-Au catalyst on CeS and sulphated zirconia	Trickle-bed reactor	Methanol	No data available	90	Biasi et al. [77]
293 and 0.65	Pd on SiO$_2$ Pd on mesoprous silica (SBA-15)	Teflon coated steel reactor	Methanol	H_2SO_4	No data and 21 No data and 58	Abate et al. [65]
263 & 1.0	Pd-Au CeS Pd-Au on ZS	Trickle bed reactor	Methanol	No data available	No data and 50 No data and 60	Biasi et al. [95]
278–313 and 2.0	Pd/C	Batch reactor	Methanol	H_2SO_4	100 and 35	Biasi et al. [78]
298 and 2.4	Commercial 5% Pd/C	Batch slurry reactor	Methanol	None added	No data available	Gemo et al. [96]
263 and 2.0	Pd on CeS	Packed bed reactor	Methanol	H_2SO_4	No data and 70	Kilpiö et al. [97]
303 and 5	Pd nanoparticles immobilized on a functionalised resin	Fixed bed reactor	Methanol	None added	No data and 73	Kim et al. [98]
293 and 0.1	Pd on SiO$_2$	Glass stirred tank reactor	Methanol	H_2SO_4	No data and 60	Menegazzo et al. [99]
275 and 4.0	Ru-Au-Pd catalyst on TiO$_2$ support	Stainless steel autoclave	Methanol/water	None added	No data available	Ntainjua et al. [83]
301 and 1.01	Palladium on zeolite HZSM-5	Autoclave reactor	Methanol	H_3PO_4	90 and 16	Park et al. [100]
294 and 4.0	AuPd/C	Stainless steel autoclave	Methanol/water	None added	No data available	Piccinini et al. [101]
298 and 2.3	Pd on sulfated zirconia and Pd on alumina	Batch autoclave reactor	Methanol	None added	No data available	Rossi et al. [102]
278–308 and 2.8	Commercial Pd/C	Trickle bed reactor	Water	NaBr	No data and 90	Biasi et al. [79]
298 and 2.4	Commercial Pd/C	Stainless steel batch autoclave	Methanol	None added	No data and 33	Biasi et al. [80]

Table 4. *Cont.*

Temperature and Pressure (K and MPa)	Catalyst	Reactor Type	Solvent(s)	Promoters	Conversion and Selectivity (%)	Literature Reference
278 and no data	Commercial Pd/C	Trickle bed reactor	Water	H_3PO_4 and NaBr	No data available	
278 and 1.0	Au-Pd/TiO_2	Microreactor	Water/Methanol	None	90 and 25	Freakley et al. [103]
273 and 3.8	Pd on activated carbon cloth (ACC)	Stainless steel autoclave	Methanol	None added	No data and 70	Gudarzi et al. [104]
295 and 3.0	Pd-Au on carbon nanotube (CNT)	Stainless steel autoclave with Teflon coating	Methanol and sulphuric acid	H_2SO_4	No conversion values and 15–65 depending on H_2/O_2 flow	Abate et al. [105]
295 and 3.0	Pd on nanocarbon	Stainless steel autoclave with Teflon coating	Methanol	H_2SO_4	No data and 25	Arrigo et al. [106]
293 and 0.1	Pd nanocubes on silica	Similar to the work of Lee et al. (2011)			10 and 25	Kim et al. [107]
273 and 2.0	Pd on activated carbon cloth (ACC)	Stainless steel microreactor	Methanol	None added	No data and 23	Ratchananusorn et al. [108]
278 and 2.0	Au-Pd on nanostructured TiO_2 nanotube support	Stainless steel autoclave	Methanol	HCl	No data available	Torrente-Murciano et al. [109]
275 and 2.0	Pd/C treated with NaBr	Custom made stainless steel batch reactor	Methanol	NaBr	95 and 1	Biasi et al. [58]
293 and 2.0	Pd supported metal organic framework (MOF)	Autoclave reactor	Methanol	None added	No data and 26	Chung et al. [60]
296 and 1.0	Combination of Pd/TiO_2 and Au-Pd/TiO_2	Microreactor with parallel packed beds (1, 8 and 16)	Water	H_2SO_4, H_3PO_4, and NaBr	Varied depending on number of channels and the flow rate	Inoue et al. [110]
303 and 2.0	Supported Au, Pd and Au-Pd	Autoclave reactor	Water 1-pentanol Chloroform Hexane Methyl isobutyl ketone 1-butanol 2-butanol Isopropanol Methanol Ethanol Dimethyl sulphoxide (DMSO) Acetonitrile Acetone t-butanol	NaBr	15 and 50 20 and 80 18 and 38 20 and 17 27 and 10 28 and 60 25 and 55 35 and 75 45 and 47 50 and 47 25 and 87 32 and 100 35 and 95 40 and 70	Paunovic et al. [111]

Table 4. *Cont.*

Temperature and Pressure (K and MPa)	Catalyst	Reactor Type	Solvent(s)	Promoters	Conversion and Selectivity (%)	Literature Reference
313 and 2.0 323 and 2.0					10 and no data 30 and no data	
313 and 2.0	Au-Pd colloidal nanoparticles	Microchannel-Silica capillary reactor	Water	H_2SO_4 and NaBr	80 and 85	Paunovic et al. [73]
298 and 2.6	Commercial Pd/C	Trickle bed reactor	Water	H_2SO_4, H_3PO_4, and NaBr	No data available	Abejón et al. [81]
333 and 0.1	Au-Pd/TiO$_2$	Fixed bed reactor	Gas phase synthesis (2% H_2/air)	None	No data available	Akram et al. [113]
313 and 9.5	Pd loaded on a sulfonic acid resin	High pressure stirred reactor	Methanol	Three compounds tested: 2-bromo-2-methyl propane, 2-bromopropane, bromobenzene compared to NaBr	No conversion data; selectivity for NaBr was 80 and 75 for the rest	Blanco-Brieva et al. [114]
298 and 0.5	Au-Pd/TiO$_2$	Stainless steel autoclave	Methanol/water	None added	No data available	Crole et al. [36]
275 and 3.7	Pd-Sn	Stainless steel autoclave	Methanol/water	None added	9 and 96	Freakley et al. [37]
275 and 3.0	Pd-Ag (varying amounts)	Teflon coated stainless steel autoclave	Methanol	H_2SO_4	Depended on alloy ratio	Gu et al. [84]
303 and 2.0	Porous Pd/SiO$_2$	Teflon coated stainless steel autoclave	Methanol	H_2SO_4	No data and 46	Sierra-Salazar et al. [115]
273–305 and 0.1–3.0	Pd/SiO$_2$	Packed-bed flow reactor	Methanol/water	HCl, H_2SO_4, and sodium bicarbonate (NaHCO$_3$)	No data and 31	Wilson et al. [40]
288 and 2.0	Commercial Pd/C	Trickle bed reactor	Water	H_3PO_4, H_2SO_4, and NaBr	77 and 72	Gallina et al. [68]
278 and 5.0 278 and 10.0	Pd particles on acidic niobia (Nb)-silica (Si) support	Slurry reactor	Methanol Water	None added	38 and 78 38 and 85	Gervasini et al. [43]
293 and 0.1	Pd/SiO$_2$ (sonochemical approach) Pd/SiO$_2$ (incipient wetness approach) Pd/TiO$_2$ (sonochemical approach) Pd/TiO$_2$ (incipient wetness approach)	Stirred glass reactor	Ethanol/water	KBr and H_3PO_4	22 and 85 12 and 85 22 and 75 12 and 80	Han et al. [116]
300 and 0.95	Pd/TiO$_2$	Flow reactor comprising of 8, 16 and 32 parallel micro-packed beds	Water	H_3PO_4, H_2SO_4, and NaBr	64 and 66 (eight glass beds) 61 and 70 (eight glass + Si beds)	Hirama et al. [117]
315 and 2.0	Au-Pd nanoparticles	Microreactor	Water	H_2SO_4, NaBr and acetonitrile (MeCN)	20 and 85	Kanungo et al. [72]
273 and 4.0	Pd on a hexadecyl-2-hydroxyethyl-dimethyl ammonium dihydrogen phosphate (HHDMA)	Stirred reactor	Methanol/water	No data available	No data and 80	Lari et al. [61]

Table 4. *Cont*.

Temperature and Pressure (K and MPa)	Catalyst	Reactor Type	Solvent(s)	Promoters	Conversion and Selectivity (%)	Literature Reference
275 and 4.0	Au-Pd nanoparticles supported on cesium substituted phosphotungstic acid (HPA)	Stainless steel autoclave	Methanol/water	No data available	69 and 86	Lewis et al. [69]
293 and 0.1	Pd/SiO$_2$	Glass stirred reactor	Ethanol/water	KBr	30 and 27	Seo et al. [45]
283 and 0.1	Pd on hydroxyapatite	Slurry reactor	Ethanol	H$_2$SO$_4$	2 and 94	Tian et al. [88]
283 and 0.1	Pd-Tellerium (Te)/TiO$_2$	Micro triphase reactor	Ethanol	H$_2$SO$_4$	6 and 100	Tian et al. [85]
283 and 0.1	Pd on mesoporous anatase TiO$_2$	Glass triphase reactor	Water	H$_2$SO$_4$	40 and 40	Tu et al. [118]
275 and 3.0	Pd-zinc (Zn) on alumina (Al$_2$O$_3$)	Stainless steel autoclave	Methanol	H$_2$SO$_4$	57 and 78.5	Wang et al. [86]
278 and 3.0	Au-Pd supported on carbon	Stainless steel autoclave	Methanol/water	None added	65 and 60	Yook et al. [119]
275 and 4.0	Au-Pd/TiO$_2$	Stainless steel autoclave	Methanol/water	None added	No data available	Howe et al. [89]
No data and 4.0	Ag-Pd/TiO$_2$	Stainless steel autoclave	Methanol/water	None added	No data available	Khan et al. [44]
275 and 4.0	Au-Pd/mesoporous silica (SBA-15)	Autoclave	Methanol/water	None added	No data available	Rodrigéz-Goméz et al. [5]
298 and 1.1	Pd/TiO$_2$	Teflon coated reaction cell	Water	NaBr	No data available	Selinsek et al. [4]
273–337 and 0.1–3.1	Au-Pd alloy	Plugged flow reactor	Methanol/water	None added	32 and 40	Wilson et al. [39]

3. Summary, Conclusions and Future Perspectives

More than a century has passed since the first documented work of Henkel and Weber in 1914 producing H_2O_2 directly from H_2 and O_2 using Pd catalysts, and the direct synthesis has only reached to pilot plant scale of production. This is because the synthesis needs to be operated beyond the explosive range of H_2 and O_2 ratios and the thermodynamic favoring of water formation over hydrogen peroxide formation. The conversion and selectivity of the process depends on several parameters such as the H_2/O_2 ratio, the diluent used in the process, the reaction medium used to prevent explosion, the catalyst and its supporting material, reactor design, and the operating temperature and pressure, to name a few. From recent literature, it is understood that it is an advantage to perform the synthesis at reduced temperatures (263 K to 283 K) and pressures (most commonly 2.0 MPa to 4.0 MPa). To synthesise H_2O_2 selectively from H_2 and O_2, oxygen is to be used in excess to avoid hydrogenation of H_2O_2. With the new developments in microreactor technology, great advancements are being achieved in increasing the selectivity of the process. Moreover, robust and stable catalysts have been the research focus of the scientific community ever since this reaction was reported. The use of Pd in its pure form or as an alloy presents an opportunity towards industrializing this process. Additionally, additives such as NaBr, H_3PO_4, H_2SO_4 etc. aid in stabilising the synthesised H_2O_2. Finally, with the scientific community focusing on green and sustainable processes, ably supported by the advancements in the field of direct synthesis, the first commercial plant producing H_2O_2 using direct synthesis technology is not that far in the future.

Conflicts of Interest: The authors declare no conflicts of interest.

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