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 focuses 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$_2$O$_2$) 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$_2$O$_2$ production has a concentration range of 30–70% and the areas of application depend on the concentration of H$_2$O$_2$ used. Usually, household, medical/dental, and cosmetic applications need diluted concentrations of Ca. 3–5% H$_2$O$_2$. Higher concentrations of up to 70% are needed for synthesis, wastewater treatment, mining, and bleaching applications. The electronics
industry needs higher H$_2$O$_2$ 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$_2$O$_2$ production in the industry is of utmost importance. The demand for H$_2$O$_2$ is always increasing with recent processes preferring H$_2$O$_2$ as an oxidant. H$_2$O$_2$ 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$_2$O$_2$ Manufacture—A Historical Perspective

To discuss the chronological advancements in industrial H$_2$O$_2$ 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$_2$O$_2$. Yield of 3% H$_2$O$_2$ was 2000 tons/annum (t/a) (Scheme 1a) [9,10] |
| 1853 | H. Meidinger | Electrochemical | Electrolysis of sulphuric acid to yield H$_2$O$_2$ [11] (Scheme 1b) Elucidated the mechanism of sulphuric acid electrolysis. Reported the formation of peroxydisulphuric acid as an intermediate [12] (Scheme 1b) |
| 1878 | M. Berthelot | Electrochemical | Autoxidation of hydroquinones and hydrazobenzenes under alkaline conditions in the presence of molecular oxygen to yield H$_2$O$_2$ [13–15] (Scheme 1e) |
| 1901 | W. Manchot | Chemical | First production plant set up in Wiessenstein, Austria [16,17] |
| 1908 | Degussa-Weissenstein Process | Electrochemical | Developed by Pietzsch and Adolph at the Elektrochemische Werke, Munich. Used potassium peroxydisulphate instead of sulphuric acid to produce H$_2$O$_2$ [16,17] (Scheme 1c) |
| 1910 | Münchner Process or the Pietzsch-Adolph Process | Electrochemical | First account of direct synthesis of hydrogen peroxide using its constituent gases [18] Similar to the Pietzsch-Adolph Process; used ammonium peroxydisulphate to produce H$_2$O$_2$ by electrolysis (Scheme 1d). Yield of 100% H$_2$O$_2$ was 35 kt [16,17] |
| 1914 | Hugo Henkel and Walter Weber | Chemical | Alkaline autoxidation of hydrazobenzenes to form sodium peroxide, later hydrolysed to form H$_2$O$_2$ [20] (Scheme 1f) |
| 1924 | Reidl-Löwenstein Process | Electrochemical | Published their work on the alternate oxidation and reduction of hydrazobenzenes to produce H$_2$O$_2$ [19] (Scheme 1e) |
| 1932 | Walton and Filson | Chemical autoxidation | Anthraquinone autoxidation process (AO) set up in two different cities each with 2000 t capacity [18,21] (Scheme 2a) |
| 1935 | Pfleiderer, Baden Aniline and Soda Factory (BASF) | Chemical autoxidation | Commercial plant setup with based on the Riedl and Pfleiderer process [1,3,8] (Scheme 2a) |
| 1935–1945 | Riedl and Pfleiderer | Chemical autoxidation | Oxidation of 2-propanol to yield H$_2$O$_2$ at a capacity of 15 kt [22] (Scheme 1g) |
Catalysts of H

G. Pfleiderer produces H2O2 in a cyclic manner (Scheme 2).

On an industrial scale, the anthraquinone autoxidation (AO) process described by H.J. Riedl and G. Pfleiderer produces H2O2 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 H2O2 (scheme modified from Campos-Martin et al. [7], reprinted here with the kind permission of John Wiley and Sons).

1.2. State of the Art in the Industrial Production of H2O2

On an industrial scale, the anthraquinone autoxidation (AO) process described by H.J. Riedl and G. Pfleiderer produces H2O2 in a cyclic manner (Scheme 2).
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$_2$O$_2$ and alkyl anthrahydroquinnone, which is then transferred to a second degassing chamber to remove trace oxygen. The degassed solution is then extracted with water to yield H$_2$O$_2$ 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$_2$O$_2$ 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$_2$O$_2$ [26].

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

Currently, the industrial manufacture of H$_2$O$_2$ 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$_2$O$_2$ 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$_2$O$_2$ 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 $1 \times 10^5$ tons per annum producing high concentrations of H$_2$O$_2$, which are diluted prior to use. For a majority of the applications mentioned previously in the introductory section (Section 1), diluted versions of H$_2$O$_2$ (typically 3–8%) is required, in small amounts, and on site. To circumvent the issues mentioned above and promote a green H$_2$O$_2$ production process, the direct synthesis of H$_2$O$_2$ 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$_2$O$_2$; 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$_2$O$_2$, focussing on chemical catalytic methods.

2. The Direct Synthesis Approach to H$_2$O$_2$ Production Using Chemical Catalysis

In 1914, H. Henkel and W. Weber reported the very first process that was capable of producing H$_2$O$_2$ 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$_2$O$_2$ 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$_2$O$_2$, namely water (H$_2$O) |
| 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$_2$O$_2$ | 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$_2$O$_2$. As seen, the reaction produces either water H$_2$O or H$_2$O$_2$ depending on the reaction conditions.

$$
\text{H}_2\text{O} + 0.5 \text{O}_2 \rightleftharpoons \text{H}_2 + \text{O}_2 \longrightarrow \text{H}_2\text{O}_2 \xrightarrow{\text{H}_2} \text{H}_2\text{O} + 0.5 \text{O}_2
$$

Scheme 3. The direct synthesis approach consisting of two parallel reactions (reduction and oxidation) during the production of H$_2$O$_2$. 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$_2$O$_2$

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$_2$O$_2$ synthesis by the reduction of dioxygen [48]. Stahl et al. used a bathocuproine palladium complex in order to catalyse the direct synthesis of H$_2$O$_2$ [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$_2$O$_2$. Subsequently, Pd$^{II}$ is reduced by molecular hydrogen to yield Pd$^0$, thereby completing the catalytic cycle.
2.3. Series of Elementary Steps in H$_2$O$_2$ Synthesis

Several accounts of the possible elementary steps during the direct synthesis of H$_2$O$_2$ 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$_2$O$_2$ and H$_2$O 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$_2$O$_2$ species is unrestricted.

\[
\begin{align*}
(1) & \quad H_2 + 2^* & \quad \xrightarrow{k_1} & \quad 2H^* \\
(2) & \quad H^* & \quad \xrightarrow{k_2} & \quad H^+ + e^- + \cdot \\
(3) & \quad O_2 + ^* & \quad \xrightarrow{k_3} & \quad O_2^* \\
(4) & \quad O_2^* + H^* + e^- & \quad \xrightarrow{k_4} & \quad OOH^* \\
(5) & \quad OOH^* + H^* + e^- & \quad \xrightarrow{k_5} & \quad H_2O_2^* \\
(6) & \quad H_2O_2^* & \quad \xrightarrow{k_6} & \quad H_2O_2 + ^* \\
(7) & \quad O_2^* & \quad \xrightarrow{k_7} & \quad 2O^* \\
(8) & \quad OOH^* & \quad \xrightarrow{k_8} & \quad OH^* + O^* \\
(9) & \quad O^* + H^* & \quad \xrightarrow{k_9} & \quad OH^* + ^* \\
(10) & \quad OH^* + O^* & \quad \xrightarrow{k_{10}} & \quad H_2O^* + ^* \\
(11) & \quad H_2O^* & \quad \xrightarrow{k_{11}} & \quad H_2O + 2OH^* \\
\end{align*}
\]

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$_2$O)$^*$ is an adsorbate bound to a single Pd atom, $X^*$, where $X$ can be $O_2$, OOH, or H$_2$O$_2$, 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 O2 takes place. This initiates Step (4) in Scheme 5, wherein O2** undergoes proton-electron transfer under quasi-equilibration conditions to form OOH** (hydroperoxy radical). Alternatively, O2** 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 H2O2** 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 H2O2 (Step (6), Scheme 5) or H2O (Step (11), Scheme 5) [40,51,52].

2.4. Process Conditions for the Direct Synthesis of H2O2 from H2 and O2

The direct synthesis of H2O2 requires certain operating conditions such as the ratio of H2 and O2, 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 H2O2.

2.4.1. Ratio of the Gaseous Mixture

During direct synthesis, one would expect the reaction of H2 and O2 on a catalytic surface to form only H2O2 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 H2 to H2O instead of H2O2 and the second one is the reduction of the H2O2 produced to H2O (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 H2 and O2 in the reaction mixture directly influences the H2O2 output. Three combinations of H2/O2 are possible for this reaction excess H2, excess O2, and stoichiometric amounts. Using excess H2 would favour the reduction of H2O2, while using stoichiometric amounts would increase H2O2 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 H2 in O2 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% H2 in O2 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 H2 and O2, diluted with inert gases [54]. The most common diluents are helium (He), argon (Ar), nitrogen (N2), or carbon dioxide (CO2) [26]. Most of the recent literature indicates the use of either CO2 [44,58,59] or N2 [39,60,61]. The work of Wilson and Flaherty described the use of N2 and CO2 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 H2O2 using only CO2 as the diluent. However, the combined effect on the overall selectivity was not reported [40]. Using CO2 as a diluent is advantageous as it can expand different solvents during the reaction and increase H2 solubility. Secondly, CO2 dissolves in water to form carbonic acid (HCO3−), which makes the medium acidic. The acidic condition is helpful as it is the most commonly used storage condition for H2O2 [5]. The chemists and engineers in the field have agreed that increasing the solubility of H2 and O2 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 H2O2 [62]. Selinsek et al. recently reported a process design with two separate tanks containing H2 and O2 dissolved in water with a two-fold benefit. First, an explosion is circumvented due to the separate feeding of gases. Second, the H2 to O2 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 H₂O₂ 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 minimize the risk of explosion due to high accuracy of detection [63].

2.4.2. Reaction Medium

As mentioned previously, the direct synthesis of H₂O₂ from H₂ and O₂ 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 H₂O₂ 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 H₂ when compared to pure water as a reaction medium [56,65]. In 2001, Hâncu and Beckmann reported the use of CO₂ as a reaction medium for the direct synthesis of H₂O₂ using a CO₂ soluble ligand-supported Pd catalyst. The researchers worked on the assumption that the H₂O₂ solubility in CO₂ is considerably less than the conventional working solutions of the AO process, i.e. organic solvents. Furthermore, the CO₂ used was liquid under the reaction conditions (298 K, 17 MPa) and the presence of a CO₂-phillic catalyst would minimize the contact time of H₂O₂ on Pd, thereby increasing the selectivity of the process (Figure 1) [28,66].

**Figure 1.** Comparison of direct synthesis of H₂O₂ in conventional (aqueous solutions) and CO₂ with a modified CO₂-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 CO₂ (scCO₂) with methanol (MeOH) water mixture at an operating temperature range of 283 K–318 K and pressure of 16.7 MPa to synthesize H₂O₂ from H₂ and O₂. N₂ 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 H₂O₂ 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 CO₂, more decomposition of H₂O₂ 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 CO₂ as a solvent has not been widely researched. Abate et al., on the other hand, used scCO₂-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 H₂O₂. On doing so, a selectivity of 40% towards H₂O₂ and a productivity of 0.11 mol·H₂O₂·m⁻²·Pd·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 \( \text{H}_2\text{O}_2 \) 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 \( \text{H}_2\text{O}_2 \). In this report, the researchers classified the promoters into two groups:

(i) oxycids such as acetic acid, perchloric acid, phosphoric acid (\( \text{H}_3\text{PO}_4 \)), nitric acid, and sulphuric acid (\( \text{H}_2\text{SO}_4 \))

(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 \( \text{H}_2\text{O}_2 \) conversion in the following order: \( \text{KF} > \text{no halide ions} > \text{KCl} > \text{KBr} \) and selectivity in the following order: \( \text{KBr} > \text{KCl} > \text{no halide ions} > \text{KF} \). 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 (\( \text{H}^+ \)) from mineral acids such as HCl, \( \text{H}_2\text{SO}_4 \), \( \text{H}_3\text{PO}_4 \) and \( \text{HNO}_3 \) aids in reducing molecular oxygen. They also suggested that the corresponding counter ions such as \( \text{Cl}^- \), \( \text{SO}_4^{2-} \), \( \text{PO}_4^{2-} \), and \( \text{NO}_3^- \) 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), \( \text{H}_3\text{PO}_4 \), and \( \text{H}_2\text{SO}_4 \) on the outcome of the direct synthesis of \( \text{H}_2\text{O}_2 \) by varying the concentrations of NaBr and \( \text{H}_3\text{PO}_4 \). The authors conducted the experiments at 288 K, 2.0 MPa, 3 h reaction time, Pd/C, with a gas mixture percent of \( \text{H}_2/\text{O}_2/\text{CO}_2 \) at 4/20/76%. The table (Table 3) below describes the observations of Gallina et al. on testing various combinations of the promoters.

| Serial No. (S/N) | Additive Added | Outcome |
|-----------------|----------------|---------|
|                 | NaBr (M *)     | \( \text{H}_2\text{PO}_4 \) (M) | \( \text{H}_2\text{SO}_4 \) (M) | \( \text{H}_2 \) Conversion (%) | \( \text{H}_2\text{O}_2 \) Selectivity (%) | \( \text{H}_2\text{O}_2 \) Productivity (mol\text{H}_2\text{O}_2·Kg(Pd )^{-1}·h^{-1}) |
| 1               | 0              | 0       | 0     | 100           | 0                      | 0                          |
| 2               | 0              | 0.003   | 0     | 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 (\( \text{H}_3\text{PO}_4 \) or NaBr) led to either (i) a much more prominent water forming reaction than the \( \text{H}_2\text{O}_2 \) forming one or (ii) subsequent reaction of \( \text{H}_2\text{O}_2 \) further to form \( \text{H}_2\text{O} \). The researchers also concluded that NaBr/\( \text{H}_3\text{PO}_4 \) had a combined effect on the leaching of the Pd catalyst and that there was no fixed NaBr to \( \text{H}_3\text{PO}_4 \) ratio to improve the direct synthesis of \( \text{H}_2\text{O}_2 \) [68]. The authors also suggested that a pH of 2.0 in the reaction medium would favour a better selectivity towards \( \text{H}_2\text{O}_2 \) production from \( \text{H}_2 \) and \( \text{O}_2 \) [68].

Another method of acidifying the reaction medium to suit the direct synthesis of \( \text{H}_2\text{O}_2 \) 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 \( \text{H}_2\text{O}_2 \) could be increased and the degradation to \( \text{H}_2\text{O} \) could be decreased [69].
2.4.4. Reactor Design

One of the most important parameters to be discussed for the direct synthesis of H\textsubscript{2}O\textsubscript{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\textsubscript{2}O\textsubscript{2} directly from H\textsubscript{2} and O\textsubscript{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\textsubscript{2}O\textsubscript{2} to H\textsubscript{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\textsubscript{2}O\textsubscript{2} to H\textsubscript{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\textsubscript{2}O\textsubscript{2} in their work [71]. One drawback of using a microreactor for the direct synthesis of H\textsubscript{2}O\textsubscript{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\textsubscript{H\textsubscript{2}O\textsubscript{2}}·kg\textsubscript{cat}\textsuperscript{−1}·h\textsuperscript{−1} with a H\textsubscript{2} conversion of 40% and selectivity of 70% (H\textsubscript{2}/O\textsubscript{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\textsubscript{2}O\textsubscript{2} solutions at a conversion rate of 15% at 42% selectivity (315 K, 2.0 MPa, 0.05 M H\textsubscript{2}SO\textsubscript{4}, 9 parts per million (ppm) NaBr, H\textsubscript{2}/O\textsubscript{2} ratio 20%) [73]. Voloshin et al. elucidated the mass transfer mechanism that occurs in a microreactor during the direct synthesis of H\textsubscript{2}O\textsubscript{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\textsubscript{2}O\textsubscript{2} synthesis [74]. Hirama et al. used 32 parallel microreactors made up of silica and glass to produce H\textsubscript{2}O\textsubscript{2} directly from H\textsubscript{2} and O\textsubscript{2}. The authors were able obtain H\textsubscript{2}O\textsubscript{2} at 10 mass percent at a productivity of 0.5 kg h\textsuperscript{−1}. Inoue et al., on the other hand, used four parallel microreactors to produce four mass percent H\textsubscript{2}O\textsubscript{2} at 0.042 kg h\textsuperscript{−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\textsubscript{2}O\textsubscript{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\textsubscript{2}O\textsubscript{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\textsubscript{2}O\textsubscript{2} [68,76–80], with the maximum being 80% using Pd on a sulfated ceria (CeS) catalyst.
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 H₂O₂ is not thermodynamically favoured. Although promoters such as H₂SO₄, H₃PO₄, 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 H₂O₂ to water (Scheme 3) [4]. On surveying the recent literature in the direct synthesis of H₂O₂, 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

**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 H₂O₂ directly from H₂ and O₂ 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).
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$_2$O$_2$ 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$_2$O$_3$) support, core-shell structures were formed. With the development of the new catalyst, the researchers still faced the problem of H$_2$O$_2$ being reduced to water [82]. The same working group developed a new tin-based Pd alloy to stop the hydrogenation of H$_2$O$_2$. 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]. Ntanjua et al. used ruthenium (Ru) alloyed with Au and Pd to perform the direct synthesis of H$_2$O$_2$. The authors investigated the Ru-Au, Ru-Pd and Ru-Au-Pd catalyst for H$_2$O$_2$ 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$_2$O$_2$ [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$_2$O$_2$ 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$_2$O$_2$ 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$_2$O$_2$ along with the catalyst used.
Table 4. List of operating conditions in literary works involving the direct synthesis of H\textsubscript{2}O\textsubscript{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                            | Pd-Au CeS | Trickle bed reactor with Teflon lining | Methanol | None | No data, 80 | Biasi et al. [75] |
| 298 and 0.1 (ambient)                | Palladium on porous alumina tubing | Membrane reactor | Water | Sulphuric acid (H\textsubscript{2}SO\textsubscript{4}) sodium bromide (NaBr), phosphoric acid (H\textsubscript{3}PO\textsubscript{4}) | No data, 50 | Inoue et al. [91] |
| 283–324 and 4.6–16.7 | Palladium on carbon | Stirred slurry batch reactor | Water + scCO\textsubscript{2} and methanol + scCO\textsubscript{2} | H\textsubscript{3}PO\textsubscript{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\textsubscript{2}SO\textsubscript{4}, KBr | 47 and 0.65 | 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\textsubscript{3}PO\textsubscript{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\textsubscript{2}SO\textsubscript{4}, NaBr | No data and 83 | Pashkova et al. [93] |
| 293 and 4.0                          | Au-Pd on TiO\textsubscript{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\textsubscript{2} | Microreactor | Water | H\textsubscript{2}SO\textsubscript{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\textsubscript{2} | Teflon coated steel reactor | Methanol | H\textsubscript{2}SO\textsubscript{4} | No data and 21 | Abate et al. [65] |
| 263 & 1.0                           | Pd-Au CeS | Trickle bed reactor | Methanol | No data available | No data and 50 | Biasi et al. [95] |
| 278–313 and 2.0                     | Pd-Au on ZS | Teflon coated steel reactor | Methanol | No data available | No data and 60 | Biasi et al. [76] |
| 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\textsubscript{2}SO\textsubscript{4} | No data and 70 | Kilpio 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\textsubscript{2} | Glass stirred tank reactor | Methanol | H\textsubscript{2}SO\textsubscript{4} | No data and 60 | Menegazzo et al. [99] |
| 275 and 4.0                         | Ru-Au-Pd catalyst on TiO\textsubscript{2} support | Stainless steel autoclave | Methanol/water | None added | No data available | Ntanjua et al. [83] |
| 301 and 1.01                        | Palladium on zeolite HZSM-5 | Autoclave reactor | Methanol | H\textsubscript{3}PO\textsubscript{4} | 90 and 16 | Park et al. [100] |
| 294 and 4.0                         | AuPd/C | Stainless steel autoclave | Methanol | 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 | H₃PO₄ and NaBr | No data available | Freakley et al. [103] |
| 278 and 1.0                         | Au-Pd/TiO₂ | Microreactor | Water/Methanol | None | 90 and 25 | Gudarzi et al. [104] |
| 273 and 3.8                         | Pd on activated carbon cloth (ACC) | Stainless steel autoclave | Methanol | None added | No data and 70 | Arrigo et al. [106] |
| 295 and 3.0                         | Pd-Au on carbon nanotube (CNT) | Stainless steel autoclave with Teflon coating | Methanol and sulphuric acid | H₂SO₄ | No conversion values and 15–65 depending on H₂/O₂ flow | Abate et al. [105] |
| 295 and 3.0                         | Pd on nanocarbon | Stainless steel autoclave with Teflon coating | Methanol | H₂SO₄ | 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) | Methanol | NaBr | 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 | Ratchanamureon et al. [108] |
| 278 and 2.0                         | Au-Pd on nanostructured TiO₂ 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/TiO₂ and Au-Pd/TiO₂ | Microreactor with parallel packed beds (1, 8 and 16) | Water | H₂SO₄, H₃PO₄, 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 | Acetonitrile | 15 and 50 | Paunovic et al. [111] |
|                                    |           |              | 1-pentanol | Acetone | 20 and 80 | |
|                                    |           |              | Chloroform | t-butanol | 18 and 38 | |
|                                    |           |              | Hexane | 2-butanol | 20 and 17 | |
|                                    |           |              | Methyl isobutyl ketone | Methanol | 27 and 10 | |
|                                    |           |              | 1-butanol | DMSO | 28 and 60 | |
|                                    |           |              | 2-butanol | Ethanol | 25 and 55 | |
|                                    |           |              | Isopropanol | Dimethyl sulphoxide (DMSO) | 35 and 75 | |
|                                    |           |              | Methanol | Acetonitrile | 45 and 47 | |
|                                    |           |              | Ethanol | Acetone | 50 and 47 | |

1-pentanol: 1-pentanol; Chloroform: Chloroform; Hexane: Hexane; Methyl isobutyl ketone: Methyl isobutyl ketone; 1-butanol: 1-butanol; 2-butanol: 2-butanol; Isopropanol: Isopropanol; Methanol: Methanol; Ethanol: Ethanol; Dimethyl sulphoxide (DMSO): Dimethyl sulphoxide (DMSO); Acetonitrile: Acetonitrile; Acetone: Acetone; t-butanol: t-butanol; H₂SO₄: H₂SO₄; H₃PO₄: H₃PO₄; NaBr: NaBr; NaCl: NaCl; KCl: KCl; KBr: KBr; HCl: HCl; H₂: H₂; O₂: O₂; H₂SO₄: H₂SO₄; H₃PO₄: H₃PO₄; NaBr: NaBr; Acetonitrile: Acetonitrile; Acetone: Acetone; t-butanol: t-butanol; DMSO: DMSO; Ethanol: Ethanol; Concentration: Concentration; Flow rate: Flow rate; Temperature: Temperature; Pressure: Pressure; Catalyst type: Catalyst type; Reactor type: Reactor type; Solvent(s): Solvent(s); Promoters: Promoters; Conversion and Selectivity (%): Conversion and Selectivity (%); Literature Reference: Literature Reference.
Table 4. Cont.

| Temperature and Pressure (K and MPa) | Catalyst | Reactor Type | Solvent(s) | Promoters | Conversion and Selectivity (%) | Literature Reference |
|-------------------------------------|----------|--------------|------------|-----------|--------------------------------|----------------------|
| 313 and 2.0                         | Au-Pd colloidal nanoparticles | Microchannel-Silica capillary reactor | Water | H₂SO₄ and NaBr | 80 and 85 | Paunovic et al. [73] |
| 298 and 2.6                         | Commercial Pd/C | Trickle bed reactor | Water | H₂SO₄, H₃PO₄, and NaBr | No data available | Abejon et al. [81] |
| 333 and 0.1                         | Au-Pd/TiO₂ | Fixed bed reactor | Gas phase synthesis (2% H₂/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/TiO₂ | Stainless steel autoclave | Methanol/water | None added | No data available | Crole et al. [36] |
| 275 and 3.7                         | Pd-8n | 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 | H₂SO₄ | Depended on alloy ratio | Gu et al. [84] |
| 303 and 2.0                         | Porous Pd/SiO₂ | Teflon coated stainless steel autoclave | Methanol | H₂SO₄ | No data and 46 | Sierra-Salazar et al. [115] |
| 273–305 and 0.1–3.0 | Pd/SiO₂ | Packed-bed flow reactor | Methanol/water | HCl, H₂SO₄, and sodium bicarbonate (NaHCO₃) | No data and 31 | Wilson et al. [40] |
| 288 and 2.0                         | Commercial Pd/C | Trickle bed reactor | Water | H₃PO₄, H₂SO₄, and NaBr | 77 and 72 | Gallina et al. [68] |
| 278 and 5.0                         | Pd particles on acidic niobia (Nh)-silica (Si) support | Slurry reactor | Methanol | None added | 38 and 78, 38 and 85 | Gervasoni et al. [43] |
| 278 and 10.0                        | Pd/SiO₂ (sonochemical approach) | Stirred glass reactor | Ethanol/water | KBr and H₃PO₄ | 22 and 85, 12 and 85, 22 and 75, 12 and 80 | Han et al. [116] |
| 293 and 0.1                         | Pd/SiO₂ (incipient wetness approach) | Flow reactor comprising of 8, 16 and 32 parallel micro-packed beds | Water | H₃PO₄, H₂SO₄, and NaBr | 64 and 66 (eight glass beds), 61 and 70 (eight glass + Si beds) | Hirama et al. [117] |
| 300 and 0.95                        | Pd/TiO₂ | Flow reactor comprising of 8, 16 and 32 parallel micro-packed beds | Water | H₂SO₄, NaBr and acetonitrile (MeCN) | 20 and 85 | Kanungo et al. [72] |
| 315 and 2.0                         | Au-Pd nanoparticles | Microreactor | Water | H₂SO₄, NaBr, and acetonitrile (MeCN) | No data available | No data and 80 | Lari et al. [61] |
| 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] |
| 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 | Stirry 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 4.0                        | 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 | Rodriguéz-Gomez et al. [3] |
| 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 \( \text{H}_2\text{O}_2 \) directly from \( \text{H}_2 \) and \( \text{O}_2 \) 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 \( \text{H}_2 \) and \( \text{O}_2 \) 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 \( \text{H}_2/\text{O}_2 \) 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 \( \text{H}_2\text{O}_2 \) selectively from \( \text{H}_2 \) and \( \text{O}_2 \), oxygen is to be used in excess to avoid hydrogenation of \( \text{H}_2\text{O}_2 \). 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 \( \text{NaBr} \), \( \text{H}_3\text{PO}_4 \), \( \text{H}_2\text{SO}_4 \) etc. aid in stabilising the synthesised \( \text{H}_2\text{O}_2 \). 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 \( \text{H}_2\text{O}_2 \) using direct synthesis technology is not that far in the future.

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