Front. Chem. Sci. Eng. 2018, 12(1): 124–131
https://doi.org/10.1007/s11705-017-1676-5

REVIEW ARTICLE

Advances in the slurry reactor technology of the anthraquinone process for H_2O_2 production

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Abstract This paper overviews the development of the anthraquinone auto-oxidation (AO) process for the production of hydrogen peroxide in China and abroad. The characteristics and differences between the fixed-bed and fluidized-bed reactors for the AO process are presented. The detailed comparison indicates that the production of hydrogen peroxide with the fluidized-bed reactor has many advantages, such as lower operation cost and catalyst consumption, less anthraquinone degradation, higher catalyst utilization efficiency, and higher hydrogenation efficiency. The key characters of the production technology of hydrogen peroxide based on the fluidized-bed reactor developed by the Research Institute of Petroleum Processing, Sinopec are also disclosed. It is apparent that substituting the fluidized-bed reactor for the fixed-bed reactor is a major direction of breakthrough for the production technology of hydrogen peroxide in China.

Keywords anthraquinone process, fixed-bed reactor, slurry-bed reactor, hydrogen peroxide

1 Introduction

Hydrogen peroxide is widely used in almost all industrial areas, particularly in chemical industry and environmental protection. Hydrogen peroxide is a versatile oxidant with a high oxidation potential and effectiveness in a wide range of pH. Owing to the high active oxygen content (47.1% w/w), hydrogen peroxide is a more efficient oxidant than other ones [1]. The demand of hydrogen peroxide is growing dramatically due to its "green" character: the only byproduct from it is water. It has played an important role in the environmentally friendly processes in chemical industry. Currently, the main markets for hydrogen peroxide include H_2O_2 for propylene oxide (HPPO), textile (bleaching of cotton and wool fabrics), food (aseptic packaging of milk and fruit juice) and aquaculture (antiparasite for salmon farming), mining (detoxification of cyanide tailings, enhanced recovery of metal), water and wastewater treatment (advanced oxidation processes), semiconductors (cleaning silicon wafers in the manufacture of printed circuit boards), chemical industry (reactant), and pulp and paper (bleaching wood pulp) [2].

The consumption of hydrogen peroxide (based on 100% H_2O_2) in China has boosted from 0.25 million tons per year in 2000 to 1.15 million tons per year in 2009. The annual growth percentage of the consumption in this decade is approximately 20% [3]. The domestic capacity (based on 100% H_2O_2) had reached 3.07 million tons per year in 2016, which accounted for half of the global capacity of hydrogen peroxide. It is estimated that the rapid growth of the capacity will continue, eventually feeding back into higher production scales, system integration and optimization, and lower production costs.

Several commercial processes have been developed for the production of hydrogen peroxide, such as the anthraquinone auto-oxidation (AO), primary and secondary alcohol oxidation [4,5], and electrochemical process [6]. New synthesis processes for hydrogen peroxide are still being explored, e.g., the direct synthesis from hydrogen and oxygen in the presence of a catalyst [7–11], photocatalytic reactions over semiconductor oxides [12], and synthesis from $CO/O_2/H_2O$ mixtures in the presence of metal complexes [13]. However, these processes are plagued by high explosion risk and/or low concentration of the resulting hydrogen peroxide. Owing to the mild reaction temperatures, lower production costs and energy consumption, and larger production scales, the AO process has supplanted all its commercial competitors. The share of the AO process in the production of H_2O_2 is above 95% in the world and above 99% in domestic.

The first commercial AO process (one ton H_2O_2 per day)

Received April 28, 2017; accepted July 29, 2017

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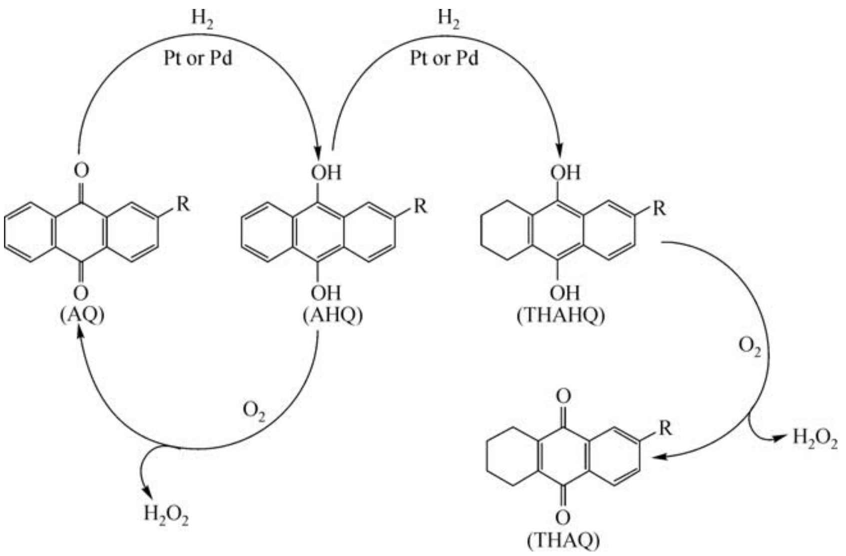

Fig. 1 The production routes of the AO process

was developed by IG Farbenindustrie in Germany in the 1940s. All the plants based on the AO process follow the original concept composed of four major steps: hydrogenation, oxidation, hydrogen peroxide extraction, and treatment of the working solution. The working solution refers to the organic solution dissolving anthraquinone during the AO process. A simplified production route of this process is showed in Fig. 1.

In general, 2-alkylanthraquinone (AQ; usually, 2-ethylantraquinone) dissolved in a mixture of organic solvents (including nonpolar and polar solvents) is first catalytically hydrogenated to the corresponding anthrahydroquinone (AHQ) over a Pd/Al_2O_3 catalyst at temperature of 40–70 °C and under H_2 pressure of 4 atm. The resulting solution of AHQ is sent to an oxidation reactor, where AHQ is oxidized with air to the original AQ and an equimolar hydrogen peroxide is simultaneously produced with a concentration of 0.6–1.8 wt-% [14,15]. The produced hydrogen peroxide is extracted by demineralized water in an extraction column to produce a hydrogen peroxide solution of usually 27.5% by weight. The mixture of organic solvent and AQ is recycled. Hydrogen peroxide is subsequently purified and concentrated through distillation (with steam, the peroxide does not form a azeotropic mixture with water and can be completely separated by distillation) to different commercial grades, typically up to 70%. The concentrated hydrogen peroxide is stabilized against decomposition by adding stabilizers and then pumped into product storage tanks.

The AO process has advantages such as the very high yield of hydrogen peroxide per cycle and remarkable economic benefits. However, it still has some drawbacks. Both the working solution and hydrogenation catalyst need to be regenerated because of side reactions in the hydrogenation step. Furthermore, the produced hydrogen peroxide usually contains trace organic impurities, which require to be further purified [16]. Therefore, it is still highly desirable to improve the efficiency of the AO process.

In this paper, we reviews the progresses on the research and development of the AO process in China and abroad. The main focus is the characteristics and differences of the hydrogenation reactors for the AO process. The trend for the further development of the AO process in China is also suggested.

2 The development of the AO process in China

In China, the research on the technology to produce hydrogen peroxide via the AO process developed by IG Farbenindustrie in Germany can be traced back to the year of 1958. Due to the limitation of the research conditions, a batchwise operation was adopted and did not afford satisfactory results. Another bench test was carried out and succeeded in 1961. The parameters such as the temperature, pressure, residence time, operation method, analytical method, and catalyst preparation method were investigated. However, the road from the bench test to a large-scale implementation is long. A pilot plant with a scale of 7 tons per year was established in 1964. It took three years to obtain the satisfactory result in the pilot test. The first plant with an industrial scale of 300 tons per year was established in Beijing in 1971. Then, another eight similar factories had been set up since 1976, indicating the success of this technology in industrial application in China. The largest unit located in Zunyi could produce 2000 tons H_2O_2 per year [3].

The technology used in the above plants is regarded as the first generation technology of hydrogen peroxide production in China, and is characterized by the Raney Ni catalyst and the slurry stirring tank reactor used in the AQ hydrogenation. Although this technology is the earliest one studied, and several demonstration plants have been established with the capacities of several thousand tons per year, it was displaced due to its obvious drawbacks listed in Table 1 [17] and the difficulty in scaling up.

The substitution technology, which is regarded as the second generation technology, is also based on the AO process. A schematic diagram of the second generation AO process is illustrated in Fig. 2 [18], and a comparison of the first generation technology with the second generation technology is shown in Table 1. For the second generation technology, a fixed-bed reactor (trickle-bed reactor) and the Pd/Al_2O_3 catalyst are selected, which renders a larger production scale, higher selectivity, improved system safety, and lower production cost. Liming Research Institute of Chemical Industry of China (LRICI) has been engaged in developing the AO process for over 30 years. The first unit using the fixed-bed reactor and the Pd/Al_2O_3 catalyst was established in the 1990s. Then over 40 plants have been constructed and successfully started up in domestic and abroad with the capacities ranging from several thousand tons per year to over 40000 tons per year [19].

Although the second generation technology for hydrogen peroxide production has been widely used, the large volume of the units hinders the further expansion of the capacity. The AQ hydrogenation efficiency in domestic plants is 6–7 g/L, whereas it is usually $\geqslant$10 g/L abroad. To enhance the hydrogenation efficiency, both the activity and selectivity of the catalyst should be improved. The catalytic performance are affected by the properties of the support (surface area, pore structure and physical strength) and the dispersion of the active component. LRICI focused on the development of a suitable Al_2O_3 support and a proper method to impregnate palladium on the support [17]. Compared with other catalysts, the newly developed palladium catalyst had several distinct advantages: 50%–60% higher in productivity, 20%–30% lower in bulk density, 10%–20% less in palladium content, and 15%–20% smaller in diameter. For a similar selectivity, its hydrogenation activity was about 30%–40% higher. The consumption of this catalyst was only half of that of the previous one. Such significant improvements made this Pd/Al_2O_3 hydrogenation catalyst highly competitive in the industrialization of the AO process.

Process intensification by optimizing engineering design is another way to improve the production efficiency of the unit. The hydrogen peroxide unit of Sinopec with the capacity of 120000 tons per year (27.5%, mass fraction)

Table 1 Highlights of the characteristics of the hydrogenation steps in the first generation technology and second generation technology for the production of hydrogen peroxide via the AO process

Item	First generation technology	Second generation technology
Reactor	Slurry stirring tank reactor	Trickle-bed reactor
Catalyst	Raney Ni leached from 30–50 mesh of Ni-Al alloy; easy to prepare; self-ignition	0.3±0.02% Pd/Al_2O_3; 3 mm in diameter extrudate
Hydrogenation activity	$\geqslant$9 g H_2O_2/L of working solution	6–7 g H_2O_2/L of working solution
Selectivity	Acceptable	High
Filtration	Inside back-washable primary filters; outside safety filter	Safety filter
Structure	Complicated; carefully designed mechanical stirrer and seal	Simple; gas and liquid distributors

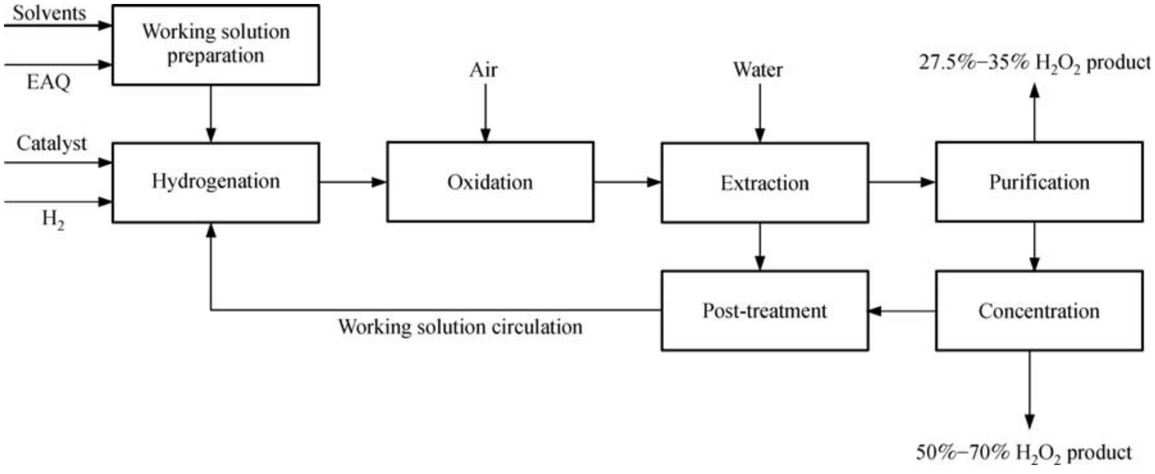

Fig. 2 Block diagram of the AO process for the production of hydrogen peroxide

has several problems such as low product concentration of hydrogen peroxide, high residual content of hydrogen peroxide in the extraction raffinate, and high alkali consumption. Fushun Research Institute of Petroleum and Petrochemicals (FRIPP), Sinopec, focused on optimizing the key units and internals in the steps of hydrogenation, oxidation, extraction, and alkali treatment [20]. After the optimization, the product mass fraction of hydrogen peroxide increased from the range of 20%–23% to more than 27.5%, the residual content of hydrogen peroxide in the extraction raffinate decreased to less than 0.15 g/L from higher than 0.30 g/L, and the alkali consumption decreased to 3.4 t/h from 4.0 t/h. Both the economic benefit of the enterprise and the unit operation safety were improved after the optimization. Researchers also focused on enhancing interphase mass transfer in the hydrogenation and oxidation reactors to make the contact between the reactant and the surface of catalyst more homogeneous. A gas distributor was recommended to install in the hydrogenation and oxidation reactors as reported in the patents, CN102009960A [21] and CN102009961A [22]. The gas distributor should be composed of a microporous membrane or sieve plate so that the microbubbles with dimensions of 10 to 1000 μm could be produced. Compared with a conventional reactor, the dispersion in these reactors is more homogeneous. As a result, the hydrogenation and oxidation reactions are more effective and the cost is more economical. However, these technologies have not been industrialized yet.

Conventionally, AQ is dissolved in a mixture of C_9-C_{10} aromatics (AR) and trioctylphosphate (TOP) as the working solution. It is known that the components of the solvent and solute system affect noticeably the performance (viscosity, density, partition coefficient of hydrogen peroxide) of the working solution, the hydrogenation activity of the Pd catalyst, and the extraction process. To increase the solubility of AQ, some researchers have evaluated the performance of different solvent systems. For example, researchers at LRICI substituted tetrabutyl urea (TBU) for TOP, and found that TBU is better than TOP because it could increase the hydrogen peroxide throughput and content in the extract and decrease the hydrogen peroxide content in the extraction raffinate [23]. Other solvent systems have been also studied, such as the conventional solvent (AR + TOP) with addition of 2-methylcyclohexyl acetate (2-MCHA) or 2,6-dimethyl-4-heptanol (DIBC) [24,25], and a mixed solvent of 1,3,5-trimethylbenzene (TMB) and DIBC [26,27]. The results indicated that both the solubility of AQ and hydrogenation efficiency increased in these systems. Another way is to discover new solutes. Jia et al. have tried to use 2-amylanthraquinone (AAQ) instead of 2-ethylanthraquinone (EAQ) as the solvent, and found that the solubility of AAQ was 2–3 times greater than that of EAQ in a mixed solvent of AAQ, TMB and DIBC as the work solution. So it was benefit to select AAQ as the new solute [27].

FRIPP, cooperating with Hunan Xing Peng Chemical Technology Co., Ltd. and Shanghai Chemical Industry Co., Ltd. [3], developed a new technology for the production of hydrogen peroxide via the AO process on a fixed-bed reactor. The merits of this technology include the implementation of a vacuum dehydration system in the step of alkali working solution treatment and the adoption of a Pd-based catalyst with high activity and selectivity. Moreover, AAQ was used and its influence on the working solution was investigated. Process intensifications, such as the feeding of hydrogen in stages to the hydrogenation reactor and optimization of the internals in the oxidation reactor and extraction column, were also studied. Based on this technology, a plant was built in Guangxi with a production capacity of 40000 tons per year for 40% H_2O_2. Calibration results in 72 h on stream showed that the mass solubility of AAQ in the working solution was 180 g/L. The efficiency of hydrogenation was 10 g/L. The concentration of hydrogen peroxide without being concentrated was 42%. And the residual content of hydrogen peroxide in the extraction raffinate was 0.14 g/L. The concentration of hydrogen peroxide before being concentrated was 7% higher than those of other plants. The amount of catalyst was reduced to 1/3. And the investment of the catalyst was only half that of the existing plants. Due to the higher solubility of AAQ in the working solution, higher extraction efficiency, shorter oxidation time, and lower energy consumption, the cost per ton production (based on 27.5% H_2O_2) is reduced by 50 Yuan. At the same flow rate of the working solution, detailed comparisons between this plant and other plants in China indicated that the capacity of the new plant was increased by 30%.

3 The AO process developed abroad

The hydrogenation of AQ is the key step to affect the yield of hydrogen peroxide and the consumption of AQ [28]. Because the fixed-bed reactor is simple in structure and easy to operate, it is widely used in the production of hydrogen peroxide via the AO process in China. However, the fixed-bed reactor suffers from high pressure drop, low catalyst utilization, and insufficient heat removal. For example, the catalyst dimension should be in the range of 1 and 3 mm on the fixed-bed reactor, so the influence of internal mass and heat transfer resistances are not negligible, leading to a decrease in the utilization of catalyst and the formation of hot spot. Furthermore, the degradation of the active anthraquinones tends to occur. That is why in a fixed-bed reactor with an anthraquinone solubility of 120 g/L, the efficiency of hydrogenation is controlled at 5–8 g/L, through the theoretical value is as high as 17 g/L.

It is an appropriate substitution to employ a slurry bubble column (fluidized bed) as the hydrogenation reactor. In this reactor, catalyst powders with diameters of 20 to 300 μm are selected. As a result, the influence of internal mass transfer resistance is minimized, and optimal activity and selectivity can be achieved. Heat transfer is significantly enhanced in the fluidized-bed reactor, which allows for a nearly isothermal operation. Even though the catalyst fraction is lower than that in the fixed-bed reactor, the hydrogenation efficiency in the fluidized-bed reactor is higher on account of the higher catalyst productivity. Other advantages of the fluidized-bed reactor over the fixed-bed reactor are the lower catalyst consumption per ton of hydrogen peroxide and the easiness in on-line removal/addition of catalyst, which prolongs operating period of the reactor.

DuPont, Solvay, Akzo Nobel, MGC, FMC, Total, Degussa, and BASF have developed the technology using the fluidized-bed reactor and palladium catalyst for the production of hydrogen peroxide for several decades. Degussa employs a meandering tube system as the reaction space, in which the hydrogenation is carried out in a loop reactor made of tubes with the same nominal diameter; these tubes are arranged either vertically or horizontally and connected by curving tubes (tube elbows) [29]. The flow velocities in the tubes are greater than 3 m/s. Catalytic hydrogenation is carried out with hydrogen or a hydrogen containing gas and palladium black suspended in the working solution at a temperature up to 100 °C and a pressure up to 15 bar absolute in this reactor. The mixture of the product stream and catalyst must be rigorously separated with the aid of a filter system. The efficiency of hydrogenation was reported as 12 g/L.

BASF introduced a special bubble column or a special multi-tube reactor with an internal fitting having openings or channels [30]. The fitting should be the packings having a hydraulic diameter significantly smaller than that of the comparable internal fittings in the field of distillation or extraction technology. Compared with conventional reactors for suspension hydrogenation of AQ, mass transfer was greatly enhanced and higher space-time yields were obtained in this reactor. However, this reactor still has some shortcomings, such as a more significant loss of the working solution and a shorter lifetime of the catalyst.

The detailed comparisons of the technological parameters of the main companies in domestic and abroad and the consumption of the processes using the fluidized- or fixed-bed reactor are summarized in Tables 2 and 3, respectively [31]. The separation of the powdered catalyst

Table 2 The comparison of the technological parameters of main companies

Item		Domestic companies	FMC	MGC	Solvay	Degussa	Arkema
Working solution	Solvent 1	AR	AR	AR	AR	AR	AR
	Solvent 2	TOP	TOP			TOP	
	Solvent 3			TBU	TBU		2-MCHA
	AQ	EAQ	EAQ	AAQ	EAQ	EAQ	EAQ
	Solubility of AQ /($g\cdot L^{-1}$)	125–140	160–180	250–300	160–180	160–180	160–180
	Pd mass fraction /%	0.3	0.3	1–2	1–2	1–2	1–2
Hydrogenation	Reactor	Fixed bed	Fixed bed	Fluidized bed	Fluidized bed	Fluidized bed	Fluidized bed
	Hydrogenation efficiency/ ($g\cdot L^{-1}$)	7–8	10–12	15–18	12–15	11–15	11–14
Extraction	H_2O_2 /%	27.5–35	27.5–35	45–48	43–46	40–45	40–45

Table 3 The consumption of the processes using the fluidized- or fixed-bed reactor

Item		Fluidized-bed reactor (a foreign company)	Fixed-bed reactor (China)	Fixed-bed reactor (China) optimized
Main material	EAQ /($kg\cdot tH_2O_2^{-1}$)	0.7	1.8	1.1
	AR /($kg\cdot tH_2O_2^{-1}$)	0.8	10.9	9
	TOP /($kg\cdot tH_2O_2^{-1}$)	0.8 (TBU)	1.3	0.54
	H_2 /($Nm^3\cdot tH_2O_2^{-1}$)	720	737	720
	H_3PO_4/($kg\cdot tH_2O_2^{-1}$)	0.6	0.9	0.8
	Al_2O_3 /($kg\cdot tH_2O_2^{-1}$)	3.5	12.8	9
	Pd-based catalyst /($kg\cdot tH_2O_2^{-1}$)	0.02 (Pd 2%)	0.4 (Pd 0.3%)	0.252 (Pd 0.3%)
Utilities	Cooling water /($t\cdot tH_2O_2^{-1}$)		228	
	Electricity /($kWh\cdot tH_2O_2^{-1}$)	700	742	
	Steam /($t\cdot tH_2O_2^{-1}$)		1.6	
	Capacity/($t\cdot a^{-1}$)	30000	22000	30000

from the liquid product and the scale-up of this reactor are major technical challenges for industrial application. However, as far as the higher efficiency of hydrogenation, better quality of the product, lower production costs, and less AQ degradation are concerned, the production of hydrogen peroxide with the fluidized-bed reactor has become the trend of the AO process.

4 The technology using the fluidized-bed reactor developed by Sinopec

Although the technology of hydrogen peroxide production based on the fluidized-bed reactor has been widely used abroad for more than 30 years, the domestic companies have not succeeded in developing their own technology yet. Several domestic plants adopting the fluidized-bed reactor process have been or will be established, but all the technologies are introduced from companies abroad. For example, the largest plant located in Jilin with a capacity of 230000 tons per year (based on 100% H_2O_2) was designed by Evonik. Another two joint ventures located in Shanghai and Jiangsu were set up by Total and MGC, respectively.

In China, a pilot test with the slurry bubble column as the hydrogenation reactor was firstly conducted by LRICI in 1997 [32]. A Pd/Al_2O_3-SiO_2 powder catalyst and the outside back-washable primary filters were used. It was successfully operated with average hydrogenation efficiency of above 9 g/L for more than one year, but further research on its application in an industrial scale was not continued.

Sinopec has developed its proprietary technologies of the integrated HPPO process and caprolactam production process, in which hydrogen peroxide is used as the oxidant. The commercialization and expansion of these processes stimulate a large growth in the proportion of hydrogen peroxide used in chemical syntheses. The current hydrogen peroxide plants all use a fixed bed as the hydrogenation reactor. Due to the difficulties in scaling up, the largest capacity of the unit with the fixed-bed reactor is only 75000 tons per year (based on 100% H_2O_2), whereas the capacity of the largest unit with the fluidized-bed reactor is 330000 tons per year (based on 100% H_2O_2). The fact that the capacity cannot match the demand of hydrogen peroxide in a continuously expanding market prompted Sinopec to develop its own production technology using the fluidized-bed reactor.

RIPP has been engaged in developing the AQ hydrogenation catalyst for several years [33–38]. Based on these endeavors, a reactor of pilot scale was established by RIPP in Shijiazhuang in 2013 (Fig. 3). A series of new technologies, such as the slurry bubble column, a powdered Pd-based catalyst, new outside back-washable primary filters, and a mixed work solution of EAQ and AAQ, had been applied in the pilot test. On this pilot plant, the efficiency of hydrogenation was 12–13 g/L, with a maximum of 14.3 g/L being detected. The efficiency of oxidation was 10–12 g/L. And the residual content of hydrogen peroxide in the extraction raffinate was less than 0.3 g/L. In the case of catalyst leakage, hydrogen peroxide will be sharply decomposed in oxidation reactor, which is prone to the production accident. Hence, detailed tests focusing on the hydrogenation system, especially on the back-washable filtration system and the mechanical strength of the powder catalyst had been carried out. The turbidity of the hydrogenated working solution was checked. It was demonstrated that the filtration system and the mechanical strength of the catalyst were reliable. The unit ran stably with a high selectivity, and the degradation of the active anthraquinones remained at a low level. Thus, the consumption of the regeneration agent in the treatment step of the working solution could be reduced, leading to a lower operation cost. Another advantage was that the new working solution employed AAQ mixed with EAQ as the solutes, which could cut down the cost in expanding the capacity of the current units.

Fig. 3 Pilot plant of hydrogen peroxide production in Shijiazhuang

Encouraged by the results of the pilot test, Sinopec is planning to set up a plant with a capacity of 20000 tons per year (based on 100% H_2O_2) in Yueyang this year using the fluidized-bed reactor.

The current slurry-bed reactor usually contains outside primary filters, a back-washable system and a recycle gas pressurization system, leading to the complication of the process. RIPP cooperating with Hebei Topun Petrochemical Engineering Co. Ltd developed a slurry stirring tank integrating with inside primary filter as the hydrogenation reactor [39]. The hydrogenated AQ working solution and the Pd-based catalyst powder were separated by the inside primary filter without any back-washable system. The material of the filter should be filter cloth or wire mesh having a filament diameter from 0.015 to 0.085 mm. It is important to select a suitable catalyst particle size, filter pore size, and stirring intensity, so that the catalyst powders could be homogeneously suspended in the reactor. Compared to the slurry bubble column reactor, the volume of the slurry stirring tank reactor without any back-washable system would be smaller, which could lead to a reduction of approximately 50% in the consumption of the working solution and the catalyst.

5 Conclusions

Hydrogen peroxide is a key reagent for green chemistry, as water is the only by-product in oxidation reactions. The industrial production route based on the AO process originally conceived in Germany in the late 1930s will remain the technology of choice for large-scale production in the future. There are more than 100 hydrogen peroxide units in China, with an average capacity of approximately 30000 tons per year (based on 100% H_2O_2). In contrast, the smallest output of the main leading companies abroad in 2013 was 123000 tons per year (based on 100% H_2O_2). The production technology of hydrogen peroxide in China is lagged far behind that abroad. Although much more work is needed to expand the scale of production of hydrogen peroxide, replacing the fixed-bed reactor with the fluidized-bed reactor is undoubtedly the trend and the major direction of breakthrough for the production technology of hydrogen peroxide via the AO process in China. Sinopec will continue to develop its own fluidized bed technology and slurry stirring tank technology in the production of hydrogen peroxide. Further work will be focused on the exploration of the Pd-based bimetallic supported catalyst, the multi-component working solution system, the degradation mechanism of active anthraquinones, and the regeneration method of the working solution, with the aim to establish an industrial scale plant with a capacity of 200000 tons per year (based on 100% H_2O_2).

Acknowledgements This project is supported by the National Key Research and Development Program of China (2016YFB0301600).

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