Efficient and robust hydrogen peroxide propylene oxide (HPPO) process

Special Focus: Petrochemicals Technology

Propylene oxide (PO) is an important organic building block in industry and is used to manufacture polyether polyols, unsaturated resins, nonionic surfactants and carbonates.1,2,3

Propylene oxide (PO) is an important organic building block in industry and is used to manufacture polyether polyols, unsaturated resins, nonionic surfactants and carbonates.[1,2,3] In 2020, the global PO market was more than 10 MMt—China's consumption was estimated at 3.5 MMt. However, more than 50% of PO in China is still prepared by the classic chlorohydrin method, which produces serious environmental pollution (with wastewater and waste residues of 40 t/t–80 t/t PO and 2 t /t PO, respectively) and equipment corrosion problems due to the use of hazard chlorine (Cl_2) and solid base as raw materials.[4,5,6]

Although co-oxidation processes (including PO/SM, PO/TBA and PO/CHP processes) eliminate the generation of wastes, they still generally suffer from complex processing, high investment cost, restriction by the co-product market and a stringent technology monopoly by international companies.[7,8] Comparatively, the direct epoxidation of propylene with hydrogen peroxide (the authors' company's HPPO process) catalyzed by TS-1 zeolite under mild conditions shows promising and positive advantages—with high atomic efficiency and almost without hazardous waste formation—and is attracting attention in various countries.[9]

However, this process is rather difficult at large scale due to the high reactivity of the PO product and the poor mass diffusion property of epoxidation catalysts, causing serious byproduct formation and rapid coke deposition inside confined zeolite micropores during HPPO processing, therefore limiting the commercial application process. As a result, before 2010, only two international companies (BASF/Dow and Evonik/Uhde) held this novel and efficient HPPO technology at industrial scale.

Consequently, to master this technology, the authors' company began to develop its HPPO process and corresponding catalysts on a small scale in 2000, and constructed the first Chinese 100,000-tpy industrial HPPO unit at the Changling branch in 2014. This novel HPPO process features a long catalyst lifetime, excellent catalytic performance and low material and energy cost,[10] providing a green alternative pathway to produce PO in China to meet strong downstream market demand while supporting environmental protection and carbon neutralization. This article details the development evolution and characteristics of the HPPO catalyst, fixed-bed reactor design, and novel process and combined technologies, while demonstrating the technology's advantages.

Overview of the HPPO process

In this industrial HPPO approach, two independent processes are involved—a 150,000-tpy hydrogen peroxide (H_2O_2) (50% concentration in an aqueous solution) synthesis process and a 100,000-tpy HPPO process—due to the short transport radius and explosion risk of the aqueous H_2O_2 solution.[11] H_2O_2 is generally synthesized from hydrogen (H_2) and oxygen (O_2) over Pd-based catalysts via a conventional anthraquinone oxidation (AO) method within fixed-bed reactors.[12]

Six main systems are involved with the HPPO process: a propylene epoxidation system, a propylene separation system, a propylene purification system, a PO separation system, a PO refining system, and a methanol separation/purification system, as shown in **FIG. 1.** The propylene epoxidation system serves as the heart of the HPPO process, in which propylene directly reacts with H_2O_2 to create PO under the effects of framework Ti sites of TS-1 zeolite and

methanol solvent at relative low temperatures (around 20°C–50°C). After separation and purification, both methanol and propylene are reinjected into the propylene epoxidation reactor, while PO is collected as a high value-added product. Additionally, the effluent is removed from the bottom of the methanol distillation column and further treated by combined treatment methods.
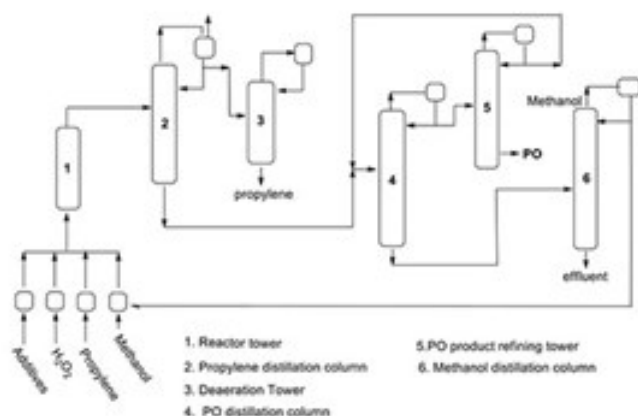

FIG. 1. A flow chart of the authors' company's HPPO process.

For more than 20 yr, the authors' company has focused on catalyst development, as well as the small-scale, pilot-scale, side-line and industrial demonstration tests of the HPPO process, as illustrated in **FIG. 2.** From 2010–2012, to optimize reaction parameters and investigate the stability of the HPPO catalyst, a 1,000-tpy HPPO process pilot plant was constructed and evaluated at the company's Changling Branch—this pilot plant has run smoothly for more than 6,000 hr without any decrease in H_2O_2 conversion and PO selectivity. Following this achievement, the first Chinese 100,000-tpy industrial HPPO industrial plant was built and run successfully for first time at the end of 2014. After that, to meet the high PO product demand dictated by the Chinese national standard published in 2015 (GB/T 14491-2015) and to improve process efficiency, the HPPO technology was updated by intensifying the inhibition and distillation removal of low-molecular side products, resulting in a final PO purity of > 99.97% and wide applications in many areas. In April 2018, this device completed 72 hr of full load operation calibration, and the key parameters were superior to design values and reference technologies.
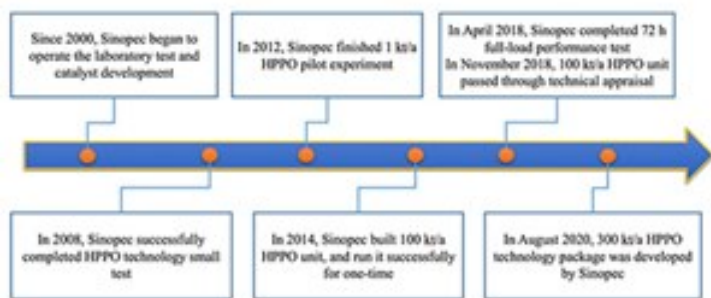
FIG. 2. The development evolution of the HPPO process.

In November 2018, the HPPO process passed its technical appraisal, meaning the successful commercialization of the technology. In 2020, the first Chinese self-created 300,000-tpy HPPO technology package was developed and approved. To date, four sets of 300,000-tpy commercial HPPO processes have been licensed in China, while five HPPO technology transfers are under negotiation and will be licensed in the near future. These units are anticipated to begin operations in 2024, promoting environmentally-friendly and sustainable bulk PO production in China and, to some extent, globally. To continue technological advantages, the second-generation HPPO technology at the authors' company, based on the catalyst design and reaction processing innovation, is under development with the goal of a 1,000-tpy pilot to be built at the end of 2023.

The HPPO catalyst

Catalyst plays a vital role in the industrial HPPO process—not unlike a chip within a computer operating system—because high catalytic activity, PO selectivity and catalyst stability, and a long running time are required to achieve optimum economic and operational benefits.[13] However, both H_2O_2 and PO product are highly reactive, so side reactions like H_2O_2 decomposition, deep oxidation, PO ring opening and polymerization can easily occur within confined catalyst channels, decreasing catalytic activity, selectivity and lifetime.[14]

To overcome these problems, researchers at the authors' company have explored active component TS-1 zeolite synthesis and catalyst shaping technologies since 2000. It was determined that both high

mass transfer performance and inhibiting H_2O_2 decomposition are vital for promising HPPO performance. Consequently, a novel surface silicon-rich hollow titanium silicate (SR-HTS) zeolite and the corresponding shaped catalyst (referred to as the proprietary catalyst[a]) with sufficient mechanical strength and catalytic activity were initially developed, exhibiting improved mass diffusion and catalytic performance than reference catalysts and, therefore, supporting the industrialization and smooth extended operation of the integrated 100,000-tpy HPPO process.

Synthesis of SR-HTS zeolite as an active component

The classic TS-1 zeolite synthesized by the EniChem method is a poor framework for Ti incorporation and mass diffusion property, leading to low H_2O_2 utilization efficiency, high byproduct selectivity and fast coke deposition in the microporous channels during the HPPO process.

To enhance the accessibility and intrinsic activity of active sites, SR-HTS zeolite was initially synthesized by combining controlled hydrothermal crystallization and post synthesis methods developed by researchers from the authors' company.[15,16] In the first step, surface silicon-rich TS-1 (SR-TS-1) zeolite was prepared by slowing down the hydrolysis and crystallization rate of Si precursors in the presence of organic template [tetrapropylammonium hydroxide (TPAOH)] at high temperatures under hydrothermal conditions.

Then, the calcined SR-TS-1 was post treated through an in-situ dissolution-recrystallization process in the presence of an aqueous TPAOH solution under hydrothermal conditions, thus with the formation of SR-HTS zeolite. It is confirmed that abundant hollow cavities (intracrystalline mesopores and/or macropores) are highly dispersed within SR-HTS zeolite particles, as shown in **FIG. 3**; therefore, the diffusion coefficient of SR-HTS ($9.41 \pm 0.20 \times 10^{-10}$ m^2s^{-1}) is far higher than that of SR-TS-1 zeolite ($8.04 \pm 0.16 \times 10^{-10}$ m^2s^{-1}), using rigid cyclohexane as a probe molecule.
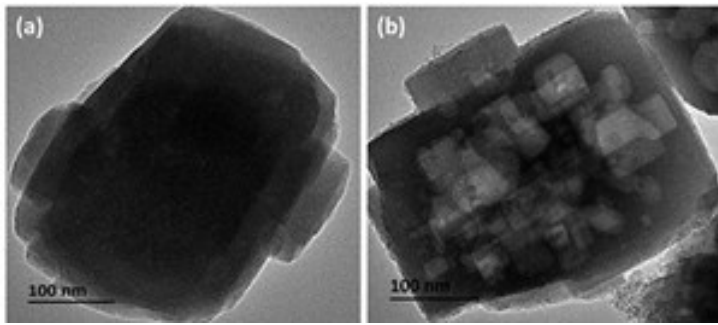
FIG. 3. TEM images of SR-TS-1 and SR-HTS zeolites: (a, left) SR-TS-1 zeolite and (b, right) SR-HTS zeolite.

It has been confirmed that hollow cavities can significantly shorten the residence time within zeolite particles and so favor the mass transfer of reactant and product molecules (**FIG. 4**). It is useful to restrict the etherification and polymerization of PO to propylene glycol ether, propylene glycol and polymers, thus concurrently improving PO selectivity and catalyst lifetime. In addition, much more tetrahedral framework Ti species are generated by intensifying the condensation of Ti-OH and Si-OH groups during post treatment. More importantly, the ratio of Ti and Si of bulk SR-HTS zeolite is higher than that of the zeolite's external surface, which means it reduces the direct contact of H_2O_2 molecules and the framework Ti species, thus increasing H_2O_2 utilization efficiency. Consequently, SR-HTS shows far better catalytic performance than TS-1 in both laboratory and industrial tests, as shown in **FIG. 5**. The SR-HTS zeolite active component was commercially manufactured by using industrial 12-m^3 autoclaves by the authors' company. **TABLE 1** shows the pore volume, surface area and self-diffusion coefficients for SR-TS-1 and SR-HTS.

FIG. 4. The main epoxidation reaction and side reactions, including H2O2 decomposition, ring-opening and polymerization of PO product in the HPPO process.
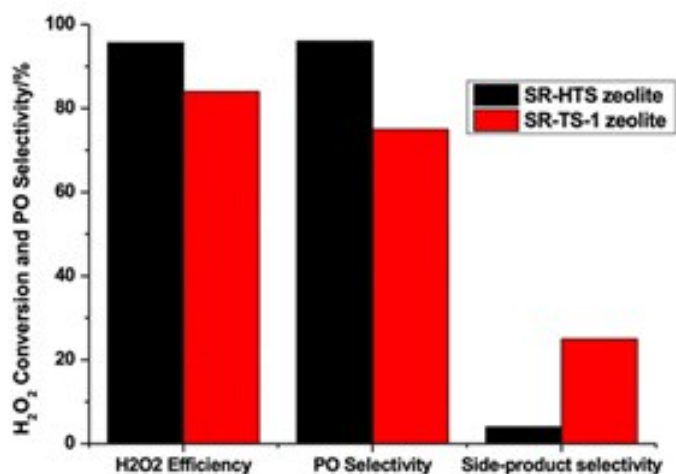
FIG. 5. Catalytic evaluation of SR-TS-1 and SR-HTS tablet catalysts in the HPPO process at the same conditions in small scale, with a catalyst weight of 20 g in the micro-reactor, a reaction temperature of 35°C, and a propylene pressure of 2.0 MPa.

TABLE 1. Pore volume, surface area and self-diffusion coefficients of SR-TS-1 and SR-HTS

Sample	S_{BET}/ ($m^2 \times g^{-1}$)	S_m/ ($m^2 \times g^{-1}$)	V_{tot}/ ($m^2 \times g^{-1}$)	V_{meso}/ ($ml \times g^{-1}$)	Self-diffusion coefficient of cyclohexane/(10^{-10} m/s^{-1})^a
SR-TS-1	433	64	0.248	0.082	9.41±0.20
SR-HTS	441	72	0.279	0.125	8.04± 0.16

^{a}Confirmed by pulsed-field gradient (PFG) NMR diffusion measurements using cyclohexane as probe self-diffusion molecules within zeolite particles, carried out by researchers from the University of Cambridge, UK.

Manufacture of proprietary catalyst^a

The HPPO process is normally operated in a fixed-bed reactor due to the strong exothermic properties of the propylene epoxidation reaction, with a reaction heat of ~210 KJ/mol PO formation.[17] Therefore, SR-HTS zeolite must be shaped by mixing with binders, carriers and modification agents under the effect of mechanical force, with the generation of industrial epoxidation catalyst, which is referred to as the proprietary catalyst^a (**FIG. 6**). This catalyst possesses controllable morphology and size, excellent mechanical strength and good coke formation resistance. As shown in **FIG. 7**, through a low-temperature nitrogen adsorption-desorption method, it is confirmed that two hysteresis loops are in the P/P_0 range of 0.45–0.8 and 0.8–1, respectively. These loops are attributed to hollow cavities within zeolite particles and intercrystalline mesopores of 10 nm–30 nm in size, respectively, suggesting excellent mass diffusion performance. Additionally, to inhibit the influence of extra acidic centers from binders and carriers on PO

selectivity, specific auxiliaries were added during catalyst molding processing, thus only few weak acid and base sites, originated from tetrahedral framework Ti centers, are discovered in the proprietary catalyst[a].
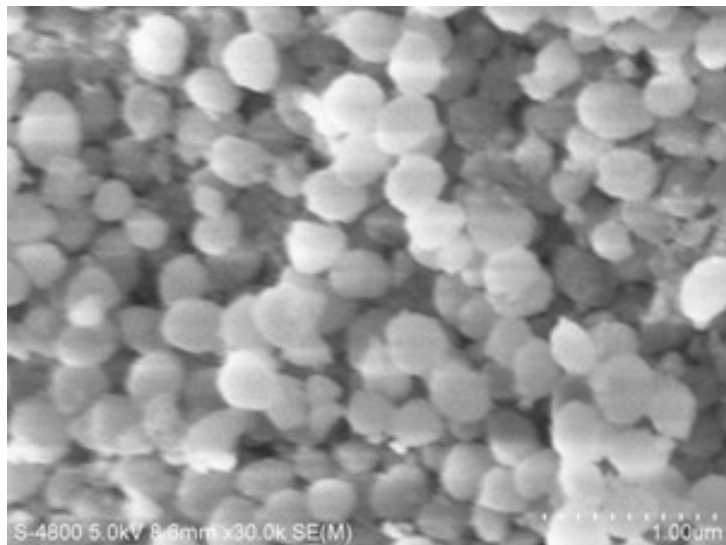

FIG. 6. An image of aggregated zeolite morphology and intercrystalline mesopores of the proprietary catalyst[a] at high magnification.
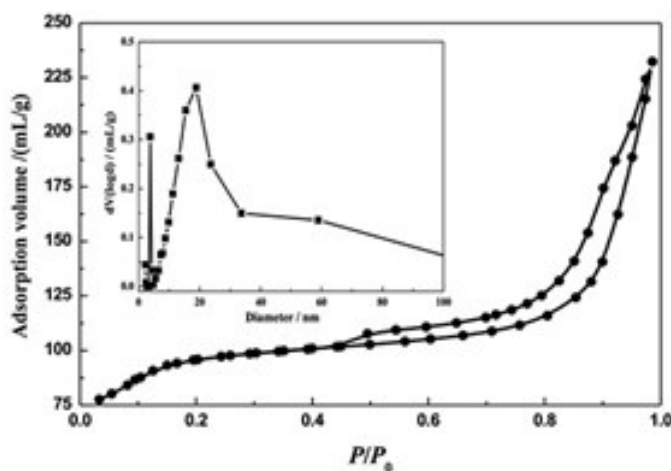

FIG. 7. Low-temperature N2 adsorption-desorption curves and pore size distribution (inserted image) of the proprietary catalyst[a].

The HPPO reactor and process

The authors' company's HPPO process consists of catalyst application and regeneration systems, an epoxidation reactor and corresponding controlling system, a reaction operation process, separation and refining technologies, and safety, environmental protection and energy-saving technologies.

The propylene epoxidation reactor and reaction engineering system play an ultra-important role in an industrial plant—the heart of the entire industrial process. In principle, from the viewpoint of reaction engineering, propylene epoxidation can be carried out in both a fixed-bed reactor and a slurry-bed reactor. The advantages of a slurry-bed reactor are in the great flexibility of catalyst regeneration and high heat removal efficiency; however, the PO selectivity is difficult to maintain at a high level due to the strong backmixing effect and non-uniform residence time distribution of mixed flow operation.[1,2,4]

Therefore, it is optimal to carry out the HPPO reaction by using a fixed-bed reactor because plug flow benefits from high catalyst activity and PO selectivity at the same time, owing to the low back-mixing effect. The major challenges of a fixed-bed reactor involve quick heat removal, high reactants distribution and intrinsic safety, as a high-concentration H_2O_2 solution is a dangerous chemical regent and sensitive to temperature for fast decomposition and even explosion.

A novel domestic epoxidation reactor of a unique inner structure and feed controlling system was developed and manufactured by the authors' company. In this reactor, all reactants can be homogenously mixed in a short time and uniformly injected into every reaction tube through a specific feed unit structure under optimal flow parameters, avoiding the existence of hot spots in the reaction zone and reducing side reactions. Conversely, the reaction heat can be quickly removed by a specific heat exchange system, ensuring the propylene epoxidation reaction is precisely carried out at low temperature, and with low energy cost and high safety.

Moreover, based on pilot-test experimental results, increasing the reaction pressure and solvent amount enhances the reaction rate and PO selectivity due to the increase of propylene solubility in methanol—this does cause high energy consumption on methanol solvent distillation separation and purification for recycling. Due to an activation energy of propylene epoxidation that is less than the side reaction, rising reaction temperature favors high H_2O_2 conversion but has a negative impact on PO selectivity. Additionally, a short contact time of reactants and catalyst helps

high PO selectivity when high H_2O_2 conversion must be maintained.

It is vital to flexibly alter the reaction parameters and catalyst feature, as the apparent performance of catalyst is influenced by coking and pore blocking by large organic polymers. In the end, the optimized reaction parameters and controlling methods were achieved via numerous experimental tests at pilot scale by using the proprietary catalyst[a], a reaction temperature of 40°C–50°C, and a turnover frequency of 30.9 $mmol.g^{-1}h^{-1}$–32.2 $mmol.g^{-1}h^{-1}$.[10]

Other key practical factors, such as capital investment, machining feasibility and reactor bed pressure drop were also considered and investigated. Consequently, a novel and advanced multi-tube, fixed-bed reactor of 100,000-tpy PO production scale with optimized structure parameters to remove epoxidation reaction heat rapidly by cool intermediates was developed and evaluated by the authors' company to ensure the intrinsic safety of the HPPO reactor during industrial processing.

Notably, in the interest of best industrial practices and in addition to catalytic performance, energy consumption, safety and environmental protection issues of the process were also considered—they are all closely correlated to the sustainability, technical economy and market competitiveness of this HPPO process.

A novel comprehensive heat utilization technology was developed with high-energy cascade utilization efficiency. For example, the distillation of methanol from water requires high energy consumption at high temperatures, so the outlet evaporator (usually > 100°C) serves as the heat source to drive other low-temperature unit operations, such as propylene separation and PO purification. To further enhance process efficiency, the wastewater treatment system cooperates with the fluid catalytic cracking unit (FCCU)—the most important part of a petroleum refinery—using chlorine-free effluent of high-chemical oxygen demand (COD) value as the FCC process terminator.

Notably, these organic byproducts in wastewater (i.e., polyether polyol, propylene glycol, propylene glycol ether) can be transformed into valuable chemical intermediates, such as ethylene

and propylene, under the thermal effects at high temperature. Conversely, these organic byproducts can also be converted to methane via an anaerobic fermentation approach. Obviously, these waste effluents can not only be treated easily and efficiently, but can also produce useful products, thus further improving the technical economy of this process.

At the end of 2014, based on the reactor and processes mentioned here, the first set of Chinese independently-developed 100,000-tpy HPPO industrial plant using the proprietary catalyst[a] was built and successfully operated for the first time by the authors' company at Changling Branch in Yueyang, Human province (**FIG. 8**).

FIG. 8. The first Chinese-created 100,000-tpy HPPO industrial demonstration unit began operations in 2014.

The plant boasts H_2O_2 conversion and PO selectivity of 97.6% and 97.8%, respectively, based on a 72-hr continuous full-load calibration test in 2018—this exceeds the referenced HPPO processes and achieves the initially designed goals. Additionally, compared to reference technologies, the propylene consumption and energy cost of this process are also reduced by 2.1% and 11.9%, respectively, showing the desired economic advantages as a result of the relatively high price of propylene and H_2O_2 in the market.

The general PO product purity is > 99.97% (and even higher to 99.99% when dictated by the market), which is much greater than the China national standard of premium grade PO product (purity ≥ 99.95%, GB/T 14491-2015). The content of aldehydes and water impurities are < 0.003 wt% and < 0.015 wt%, respectively, which are far lower than those of the national standard level, as shown in **TABLE 2**.

TABLE 2. Comparison between the proprietary HPPO technology and reference HPPO technology

	Premium grade, Chinese national standard of PO GB/T 14491-2015	Proprietary HPPO technology
PO purification, wt%	≥ 99.95	≥ 99.97
Chroma, Hazen, Pt-Co standard method	≤ 5	≤ 5
Acidity (taken as acetic acid), wt%	≤ 0.003	≤ 0.003
Aldehydes content, wt%	≤ 0.005	≤ 0.003
Water content, wt%	≤ 0.020	≤ 0.015

The final PO product has been used in many PO downstream areas, such as polyether polyols, surfactants, oilfield demulsifiers and other products. In particular, when it is used in polyether polyols and the polyurethane industry, the final products are colorless and present only a slight odor, making them more popular. As shown in **FIG. 9**, to date, the proprietary catalyst[a] in the 100,000-tpy HPPO unit has run smoothly for > 38,000 hr while showing almost the same excellent catalytic performance as that of fresh catalyst in the initial stage.
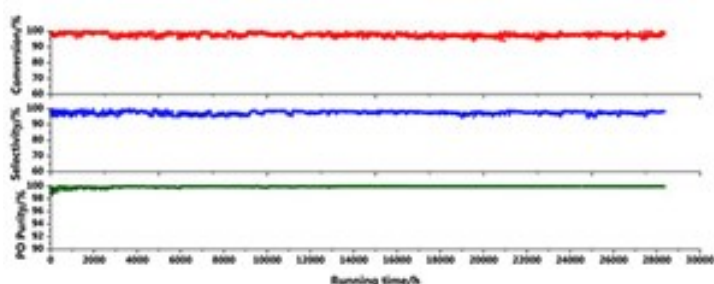
FIG. 9. The running characteristics of the industrial 100,000-tpy HPPO plant.

Although a variety of harsh reaction conditions have been experienced, there is no difference in texture properties and Ti coordination between the fresh and used proprietary catalyst[a] in accordance with multiple characterization methods.

In August 2020, the first Chinese self-developed 300,000-tpy HPPO technology package, with several process innovations, was developed by the authors' company. Owing to the significant economic and technological advantages of this scale, four sets of the 300,000-tpy HPPO process have been commercially licensed; five additional HPPO technology transfers are predicted to be completed by the end of 2023. To further optimize and update HPPO processes, the second-generation HPPO technology, which involves both catalyst and process route sustainable innovations, is being designed—a pilot test at 1,000-tpy scale will be constructed and put into operation at the end of 2023.

Takeaways

To provide an efficient alternative PO synthesis method to overcome the drawbacks of a traditional chlorohydrin route, the first Chinese self-developed 100,000-tpy HPPO integrated technology has been developed by researchers at the authors' company combining several innovations, including a SR-HTS zeolite active component, a proprietary catalyst[a] and corresponding shaping technology, an epoxidation reactor and process design and safety investigation, a heat integration technology, and wastewater treatment in collaboration with the refinery FCCU. This HPPO process exhibits superior advantages in high catalytic performance, catalyst lifetime, raw material and energy consumption, product purity, and economic and social benefits.

Based on further comprehensive innovations, a 300,000-tpy HPPO technology package and the second generation of the HPPO process have been developed—the 300,000-tpy HPPO technology has been licensed to four commercial units, and will be licensed to more than three in the near future. **HP**

NOTES

[a] Sinopec's HPO-1 catalyst and

LITERATURE CITED

1. Russo, V., R. Tesser, E. Santacesaria and M. Di Serio, "Chemical and technical aspects of propene oxide

production via hydrogen peroxide (HPPO process)," *Industrial & Engineering Chemistry Research*, 2013.

2. Nijhuis, T. A., M. Makkee, J. A. Moulijn and B. M. Weckhuysen, "The production of propene oxide: Catalytic processes and recent developments," *Industrial & Engineering Chemistry Research*, 2006.

3. Blanco-Brieva, G., M. C. Capel-Sanchez, M. P. de Frutos, *et al.*, "Direct synthesis of hydrogen peroxide without the use of acids or halide promoters in dissolution," *Industrial & Engineering Chemistry Research*, 2008.

4. Baer, H., M. Bergamo, A. Forlin, *et al.*, "Propylene oxide," *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA, 2012.

5. Clerici, M. G., "The activity of titanium silicalite-1 (TS-1): Some considerations on its origin," *Kinetics and Catalysis*, July 2015.

6. E. Kertalli, E., L.S. van Rijnsoever, V. Paunovic and M. F. Neira D'Angelo, "Propylene epoxidation with hydrogen peroxide in acidic conditions," *Chemical Engineering Science*, September 2016.

7. Buijink, J. K. F., J. J. M. van Vlaanderen, M. Crocker and F. G. M. Niele, "Propylene epoxidation over titanium-on-silica catalyst—the heart of the SMPO process," *Catalysis Today*, September 2004.

8. R. Martos Calvente, R., J. M. Campos-Martin and J. L. G. Fierro, "Effective homogeneous molybdenum catalyst for linear terminal alkenes epoxidation with organic hydroperoxide," *Catalysis Communications*, June 2002.

9. Ghanta, M., D. R. Fahey, D. H. Busch and B. Subramaniam, "Comparative economic and environmental assessments of H_2O_2-based and tertiary butyl hydroperoxide-based propylene oxide technologies," *ACS Sustainable Chemistry & Engineering,* 2013.

10. Lin, M., C. Xia, B. Zhu, H. Li and X. Shu, "Green and efficient epoxidation of propylene with hydrogen peroxide (HPPO process) catalyzed by hollow TS-1 zeolite: A 1.0 kt/a pilot-scale study," *Chemical Engineering Journal*, July 2016.

11. Wang, T.-S., S.-H. Liu, Y.-C. Lin, Y.-C. Chen and C.-M. Shu, "Green process of propylene oxide reaction for thermal hazard assessment by differential scanning calorimetry

and simulation," *Chemical Engineering Technology*, February 2015.

12. Lewis, R. J. and G. J. Hutchings, "Recent advances in the direct synthesis of H_2O_2," *ChemCatChem*, October 2018.

13. Signorile., M., V. Crocellà, A. Damin, B. Rossi, C. Lamberti, F. Bonino and S. Bordiga, "Effect of Ti speciation on catalytic performance of TS-1 in the hydrogen peroxide to propylene oxide reaction," *The Journal of Physical Chemistry C*, 2018.

14. Schmidt, F., M. Bernhard, H. Morell and M. Pascaly, "HPPO process technology: A novel route to propylene oxide without coproducts," *Chimica Oggi*, 2014.

15. Xia, C., B. Zhu, M. Lin, X. Peng, X. Shu and C. Shi, "Titanium silicalite molecular sieve and its synthesis," U.S. Patent 9896343B2, 2018.

16. Xia, C., M. Lin, B. Zhu, *et al.*, "A kind of titanium sieve molecular sieve and its synthetic method," China Patent 104556111B, 2018.

17. F. Cavani, F. and J. Henrique Teles, "Sustainability in catalytic oxidation: An alternative approach or a structural evolution?" *ChemSusChem*, 2009.

Sinopec VAM Process to Maximize Carbon Efficiency

2023-06-21

能源至净　生活至美
Cleaner Energy　Better Life

中石化上海工程有限公司
SINOPEC SHANGHAI ENGINEERING CO.,LTD

Contents

- **Background**

- **VAM Catalyst and Critical Equipment**

- **Process and Optimization**

- **Economics**

- **Technical Service**

Background-VAM applications

Vinyl acetate monomer (VAM) is a significant intermediate used in the production of a wide range of resins and polymers for paints & coatings, adhesives, elastomers, textile finishes, paper coatings, binders, films, and a myriad of other industrial and consumer applications

Global Vinyl Acetate Resin Applications by End-Use Industry, 2019 (wt.%)

- Packaging & Films — 27%
- Adhesives & Sealants — 24%
- Paint & Coatings — 19%
- Construction & Cements — 11%
- Textiles & Paper — 10%
- Others — 9%

https://www.gantrade.com/blog/vinyl-acetate-monomer-vam-a-highly-versatile-polymerization-intermediate
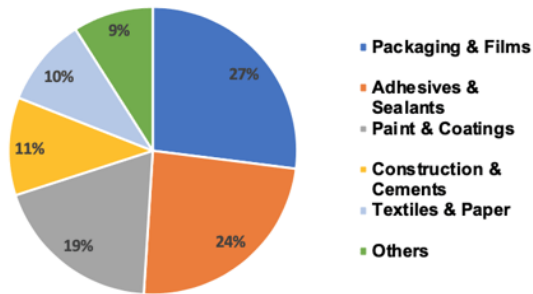
Adhesives

paints & coatings
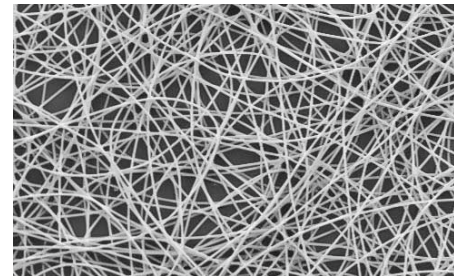
textile finishes
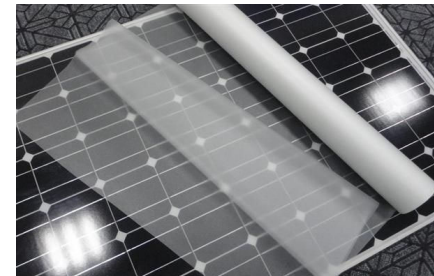
film

Background - VAM forecast in China

➤ A fast-growing use of VAM is the manufacture of EVA used in solar modules
➤ Rapid growth of photovoltaics worldwide
➤ Rapid growth of EVA capacity in China

Worldwide growth of photovoltaics

2021 EVA demand in China

- Film 36%
- Foam 30%
- Wire/Cable 16%
- Adhesives 7%
- Coatings 7%
- Others 4%
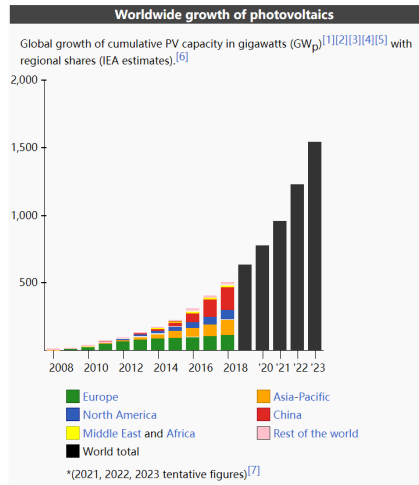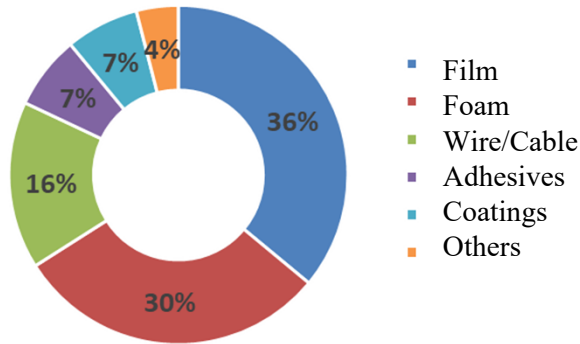
2018-2025E EVA Production (-0000-t)
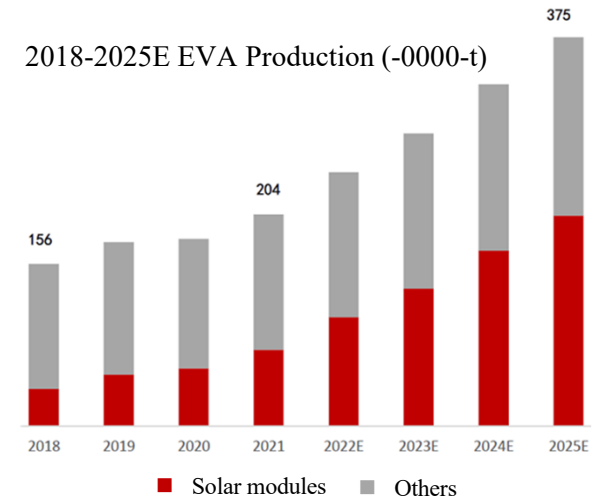
Background – VAM Capacity

➤ **The key regions for global vinyl acetate monomer capacity are Asia-Pacific, Middle East, North America, South America, and Europe;**

➤ **Global Market size 2020: 8million t/a**

➤ **VAM capacity in China: 3million t/a**

➤ **Sinopec production: 1.25million t/a**

➤ **Sinopec Technology licensed 400 kta in total**

Background - VAM forecast in China

Company	Annual Capacity (-000-metric tons)	Location	Remarks
Jiangsu Eastern Shenghong Co.,Ltd.	300	Jiangsu	2023 Start up
Zhejiang Petroleum&chemical Co., Ltd	200	Zhejiang	2023 Start up
Fujian Meizhouwan Chlor-Alkali Chemical Industry Co.,Ltd	200	Fujian	2024 Start up
Levima	100	Shandong	2024 Start up
Shanghai Huayi Group Corporation Limited	300	Guangxi	2024 Start up
Sinopec Zhenhai Refinning & Chemical Company	300	Zhejiang	Planning
Fujian Petrochemical Co.,Ltd	300	Fujian	Planning
Daqing Petrochemical Company	200	Hei Longjiang	Planning
Sinopec Shanghai Petrochemical Company Limited	300	Jiangsu	Planning
Shandong Yulong Petrochemical Company	300	Shandong	Planning
Zhongtianhechuang Ordos Chemical Coal	200	Anhui	Planning
Shaanxi Yanchang Petroleum	300	Shaanxi	Planning
Fujian Billion Industrial holding Ltd.	200	Fujian	Planning
More than 3 million tons per year			

Background

Sinopec catalyst application

- Sinopec takes 40% VAM market share within China

- 30% in total are ethylene process

- Sinopec VAM catalyst has been applied to 5 plants
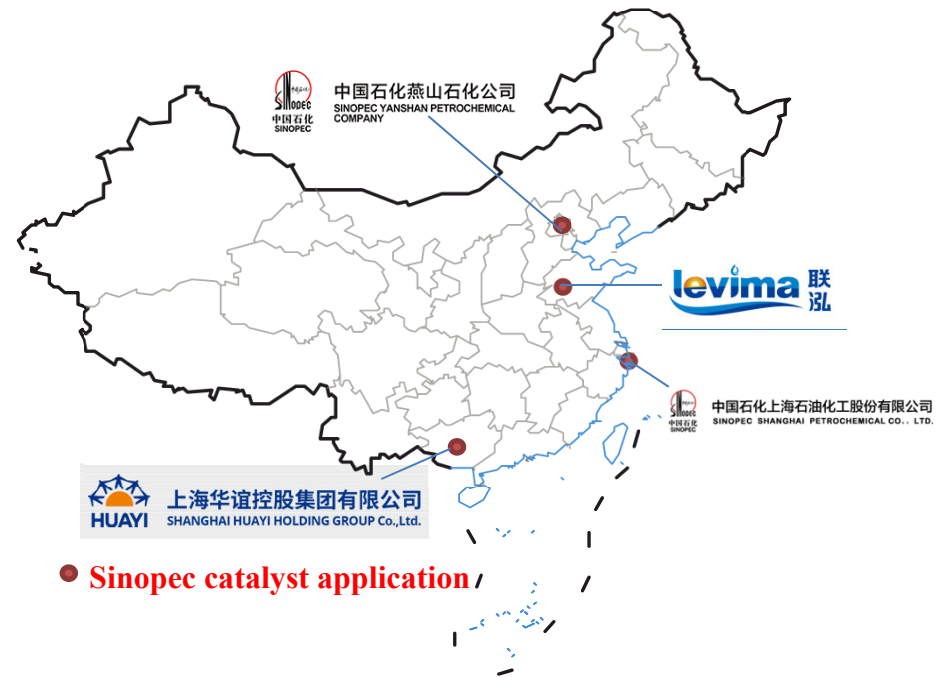
中国石化燕山石化公司
SINOPEC YANSHAN PETROCHEMICAL COMPANY

中国石化
SINOPEC

levima 联泓

中国石化上海石油化工股份有限公司
SINOPEC SHANGHAI PETROCHEMICAL CO., LTD.

HUAYI 上海华谊控股集团有限公司
SHANGHAI HUAYI HOLDING GROUP Co.,Ltd.

● **Sinopec catalyst application**

Contents

- **Background**

- **VAM Catalyst and Critical Equipment**

- **Process and Optimization**

- **Economics**

- **Technical Service**

Sinopec catalyst introduction

The reaction occurs over palladium and gold catalyst.

Water, CO_2 and small quantities of ethyl acetate, ethylidene diacetate and glycol acetates are the main byproducts.

Main Rout:

$C_2H_4 + HOAc + 1/2O_2$ -- Palladium Catalyst--> $VAM + H_2O + Q1$

Side Reaction:

$C_2H_4 + 3O_2$ ---> $2CO_2 + 2H_2O + Q2$

$1/2HOAc + O_2$ ---> $CO_2 + H_2O$
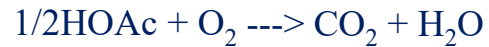
Catalyst selectivity:

Ethylene: 93 – 94%

Acetic acid: 98 – 99%
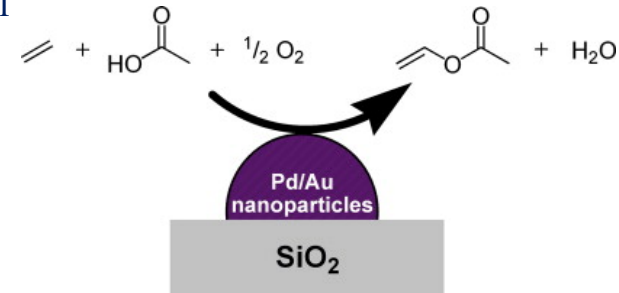
VAM technology typical process

1. Vaporizer
2. Oxidation reactor
3. Pre-dehydration column
4. Crude VAM tank
5. Scrubber
6. Water wash
7. CO_2 removal
8. Azeotropic column
9. Wastewater column
10. Light-ends column
11. Pure VAM column
12. Steam boiler
13. Cooling tower

ST Steam
CW Cooling water
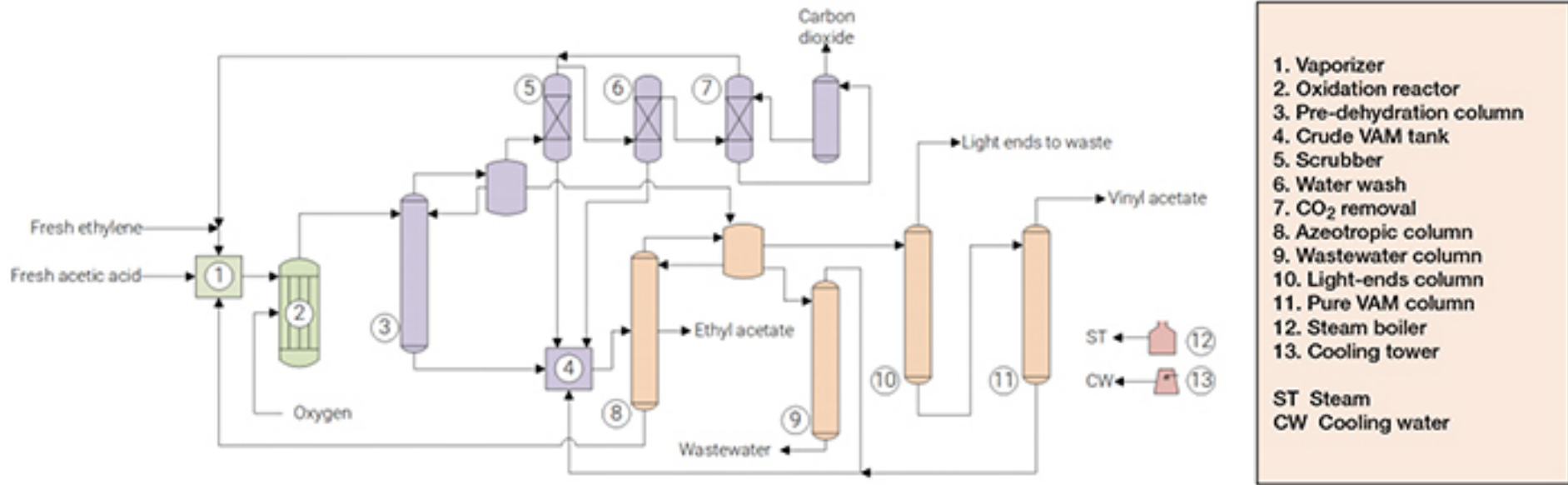
The process for manufacturing vinyl acetate monomer from acetic acid and ethylene
Site: www.chemengonline.com/technology-profile-production-of-vinyl-acetate/

Raw Material Specification

Ethylene

Component	Specification (Vol)
Ethylene	min 99,9%
Ethane	max 500 ppm
Propylene	max 50 ppm
Acetylene	max 0.5 ppm
Carbon monoxide	max 0.5 ppm
Ammonia	max 0,3 ppm
Methanol	max 0.5 ppm
Sulfur compounds in terms of sulfur	max 0.2 ppm

Oxygen purity ≥ 99.7% .

Acetic acid

Component	Specification
Acetic acid	min 99.5%
Formic acid	max 0.05%
Acetic aldehyde	max 0.004%
Propionic acid	30-500 ppm
Chlorides	max 0.0004%
Heavy metals deposited by H_2S	max 0.0004%
Sulfates	max 0.0003%
Iodine and methyl iodide in terms of methyl iodide	max 0.04 ppm

O_2 content in N_2 ≤ 0.02% .

Impurities

Poisons and impurities in raw materials	Impact	Specification
water (ppm)	Temporary	
Total organic nitrogen / phosphorus	Temporary	
CO	Temporary	
S (ppm)	Permanent	≤5
As (ppb)	Permanent	≤5
Pb (ppb)	Permanent	≤5
Hg (ppb)	Permanent	≤5
I (ppb)	Permanent	≤10

Iodide effect to catalyst
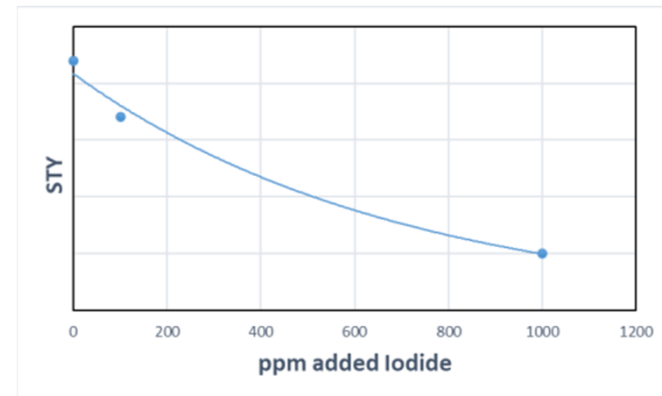
- Main catalyst poison: As、Pb、I
- The Iodine content in acetic acid is preferably ≤5ppb

Molecular insights into VCM catalyst
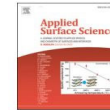
Full Length Article

Molecular insights into the vinyl acetate synthesis on Pd/Au (1 1 1) Surface: Effects of potassium ion

Haoyang Sun [a,1], Pengyuan Qiu [a,*,1], Yunxin Yang [a], Junxiao Liu [a], Libin Zhang [a], Zhen Liu [b,*]

[a] State Key Laboratory of Green Chemical Engineering and Industrial Catalysis, Shanghai Research Institute of Petrochemical Technology, SINOPEC, Shanghai 201208, China
[b] State Key Labor...
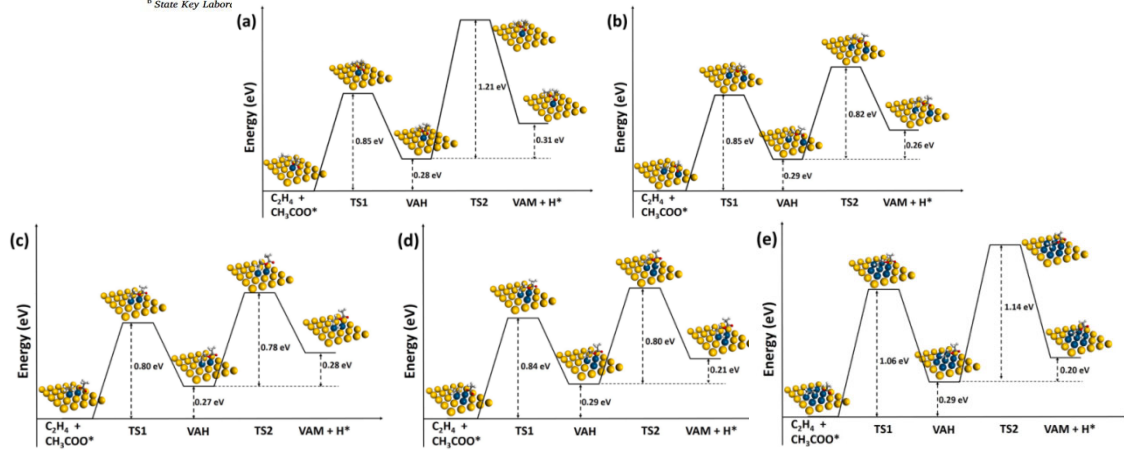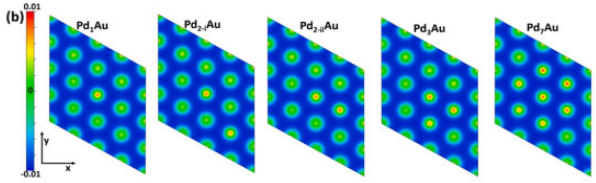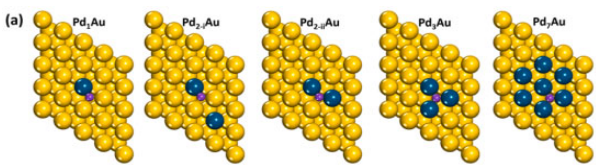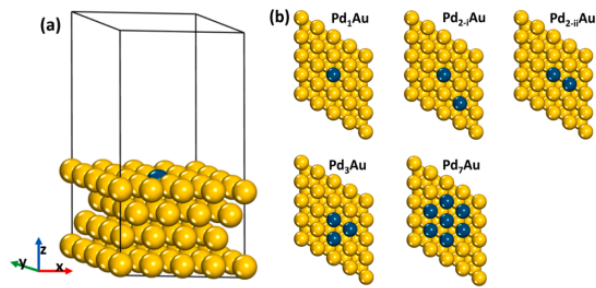
Application of CTV series catalyst

➢ CTV-III、CTV-IV and CTV-VI catalysts applications

Catalysts	CTV-III	CTV-IV	CTV-VI
Operating Temp. °C	140-175	140-175	140-175
Operating Press. MPa	0.80	0.80	0.80
GHSV, h^{-1}	≧ 1930	≧ 1930	≧ 3000
STY, t/(m^3·d)	8.7	9.3	14.5
Sel, %	≥93	≥93	≥93
Industrial Application，kt/a	90	300	20
Catalyst service life, years	≥2	≥2	≥2

Application of CTV series catalyst

➢ CTV-III、CTV-IV and CTV-VI running data

➢ CTV-IV running for 46 months continuously

CTV-III

CTV-IV

CTV-VI
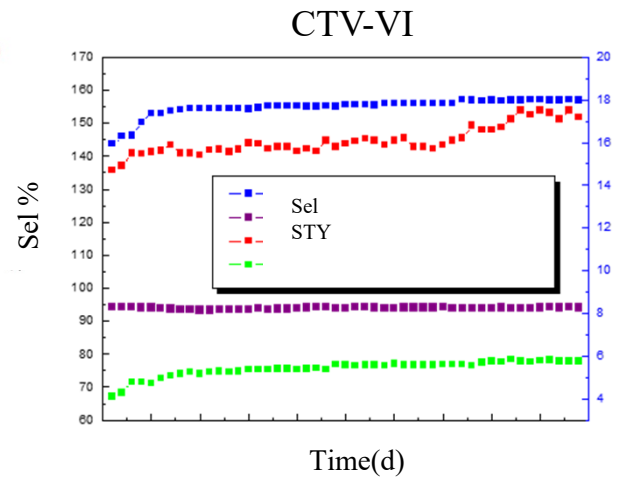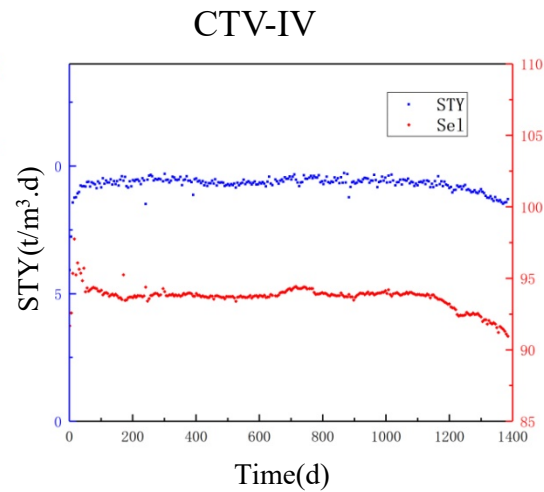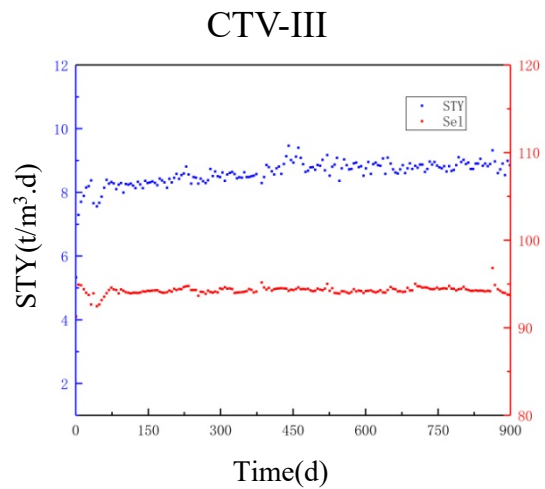
Test Bench and CFD modeling

- ➢ **Reactor internal simulation**

- ➢ **Reactor feed gas inlet distributor design**

- ➢ **Reactor shell side inlet and outlet distributors design**

Reactor Scale up

– Reactor scale up based on CT-IV and CV-VI catalyst

Scale Up

Industrial applied

100 kta reactor

Tube reactor scale up principle

150 kta reactor

Tube reactor scale up principle

300 kta reactor

Tube side：

- Gas phase
- Turbulence
- Porous

Shell side：

- liquid/gas two phases
- Turbulence
- Euler-Euler model
- Phase change
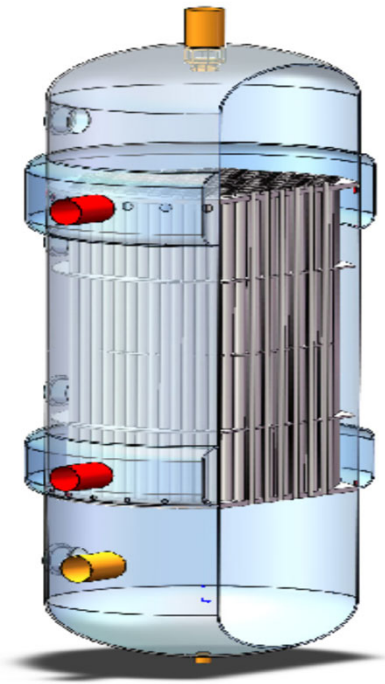
Reactor CFD modeling

Shell side study: reaction heat removal with water latent heat

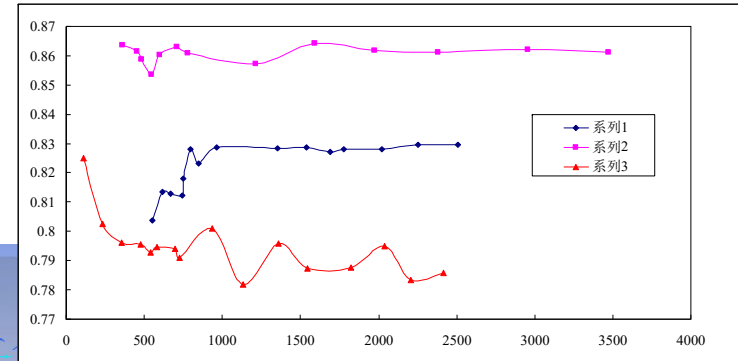- ➢ Vapor escape

- ➢ Less pressure loss

Shell side study: water inlet distributor
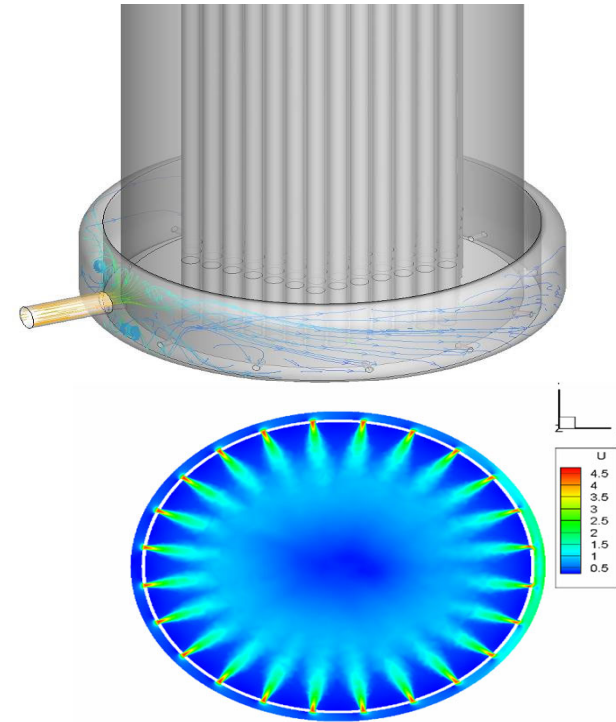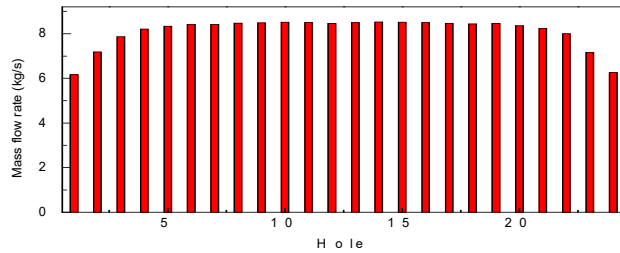
Reactor CFD modeling

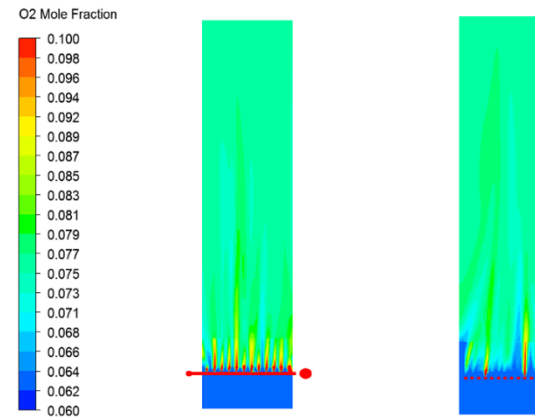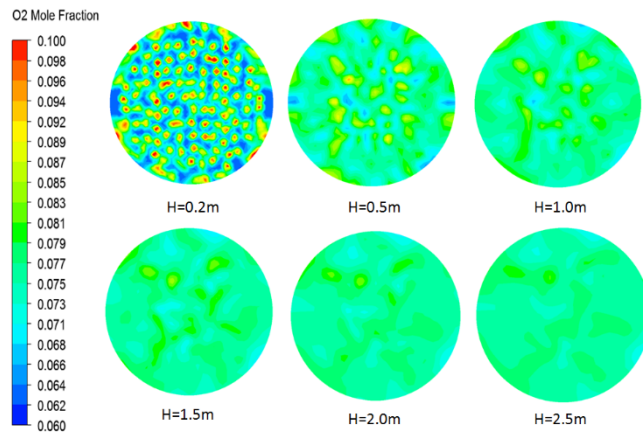## Tube side study: gas inlet

➢ Distributor with sieve holes

Oxygen Mixer

- Key
  - O2 concentration in the reaction mixture should be kept below 8%
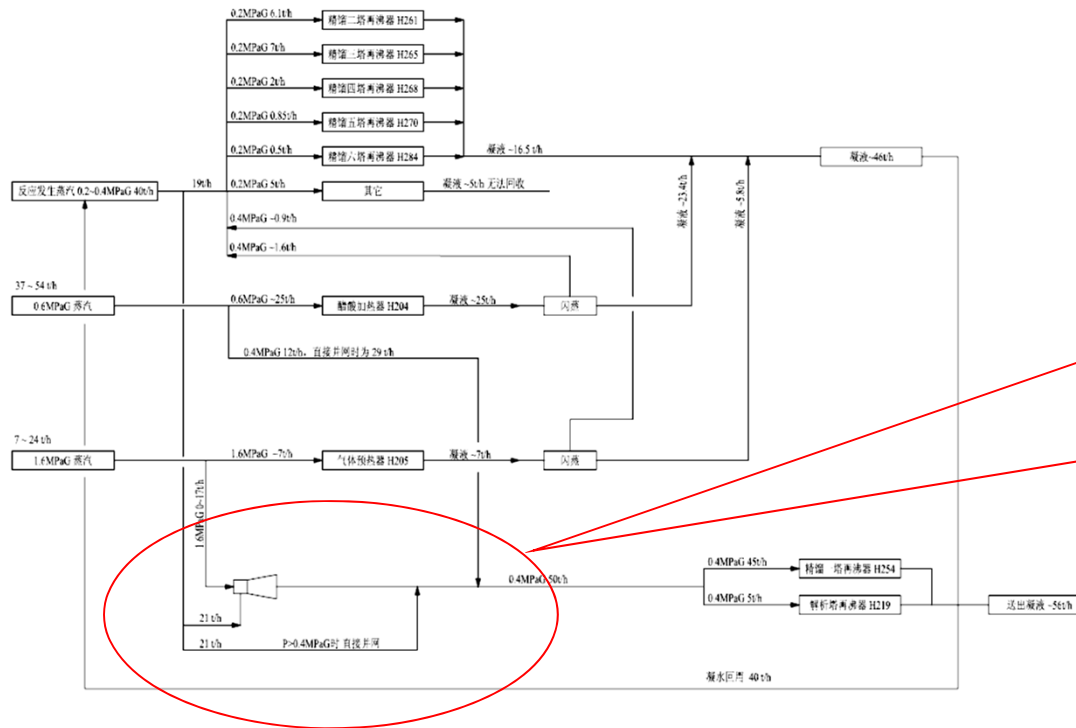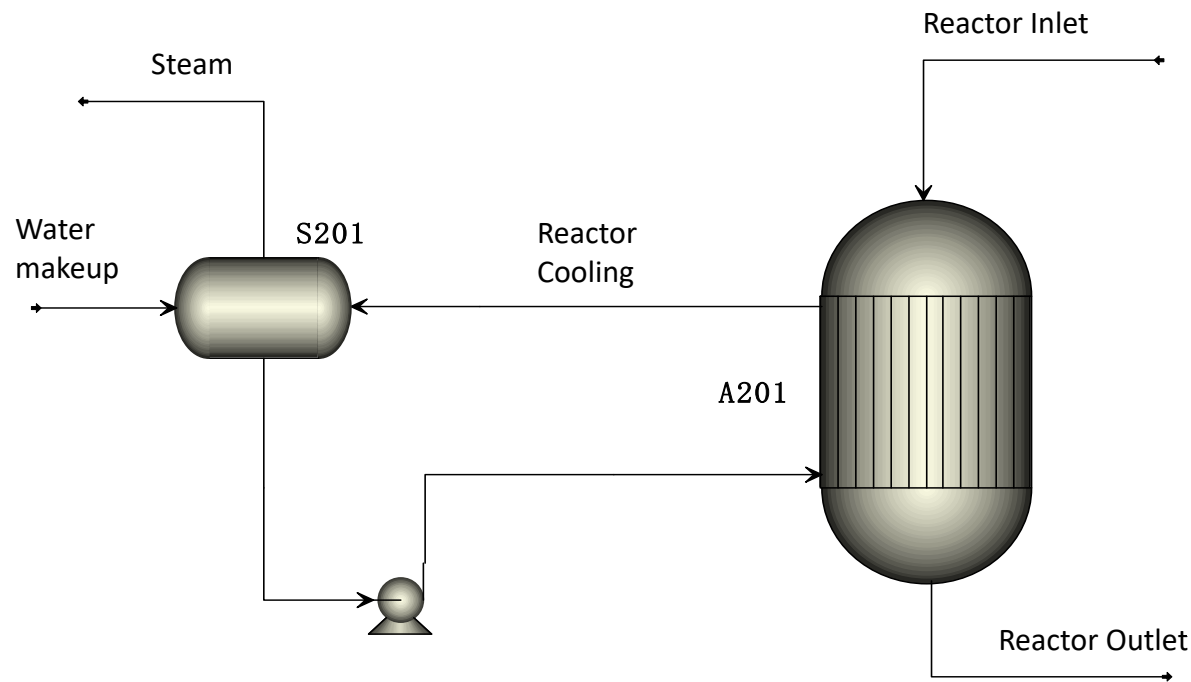 - Shorten Mixing length

Testing Oxygen Mixer

Contents

- **Background**

- **VAM Catalyst and Critical Equipment**

- **Process and Optimization**

- **Economics**

- **Technical Service**

When the steam pressure is lower than 0.4 MPag, the steam injection boost is started;
when it is higher than 0.4 MPag, it is directly connected to the grid

Optimization

Reactor Inlet

Steam

Water makeup

S201

Reactor Cooling

A201

Reactor Outlet

Reactor heat removal by water evaporation.
The vaporization rate increase from 1.3% to 2% with catalyst improving and reactor design.
To decrease water circulation rate power consumption.

Thermosiphon design could decrease more power consumption

Contents

- **Background**

- **VAM Catalyst and Critical Equipment**

- **Process and Optimization**

- **Economics**

- **Technical Service**

Sinopec VAM Technology Economics

- ➢ Raw material consumption

  - ➢ Ethylene < 0.362 t/t VAM

  - ➢ Acetic acid < 0.72 t/t VAM

  - ➢ O_2 < 200 Nm^3/t VAM

- ➢ Utility consumption < 240 kg ce/t VAM

- ➢ Catalyst STY ≥ 9.3 $t/(m^3 \cdot d)$

- ➢ Selectivity (ethylene to VAM) ≥ 93%

Sinopec VAM Technology Economics

- ➢ Advanced catalyst

- ➢ Multitubular Fixed-Bed Catalytic Reactor

- ➢ Safety oxygen mixing technology

- ➢ High efficiency separation technology

Raw Material	Unit	Comparison 1	Comparison 2	Sinopec Technology
Ethylene	t/t VAM	0.378	0.360	0.355
Acetic acid	t/t VAM	0.704	0.721	0.715
Energy consumption	kg ce/t VAM	268	235	232

Contents

- **Background**

- **VAM Catalyst and Critical Equipment**

- **Process and Optimization**

- **Economics**

- **Technical Service**

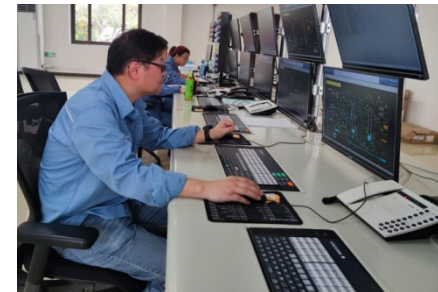# Technical Service

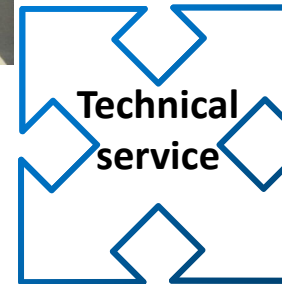**Technical Service Team**

- Engineering
- Catalyst
- Operation

Project entire life cycle services

- Project execution
- Catalyst loading, etc
- Start up and trouble shooting

Remote technical service

- Fast response
- 24 hr * 7 d

Technical service

Technical Service

- ➢ **>30 years of catalyst R&D team with industrialization experience**

- ➢ **Specialized team for VAM reactors and other critical equipment development**

- ➢ **Engineering team with experience of 100-300 kt/ VAM PDP design and engineering working along with catalyst R&D team**

- ➢ **Operation experts with more than 30 years working on VAM plants**

THANK YOU