Milliontons PTA Technology Package

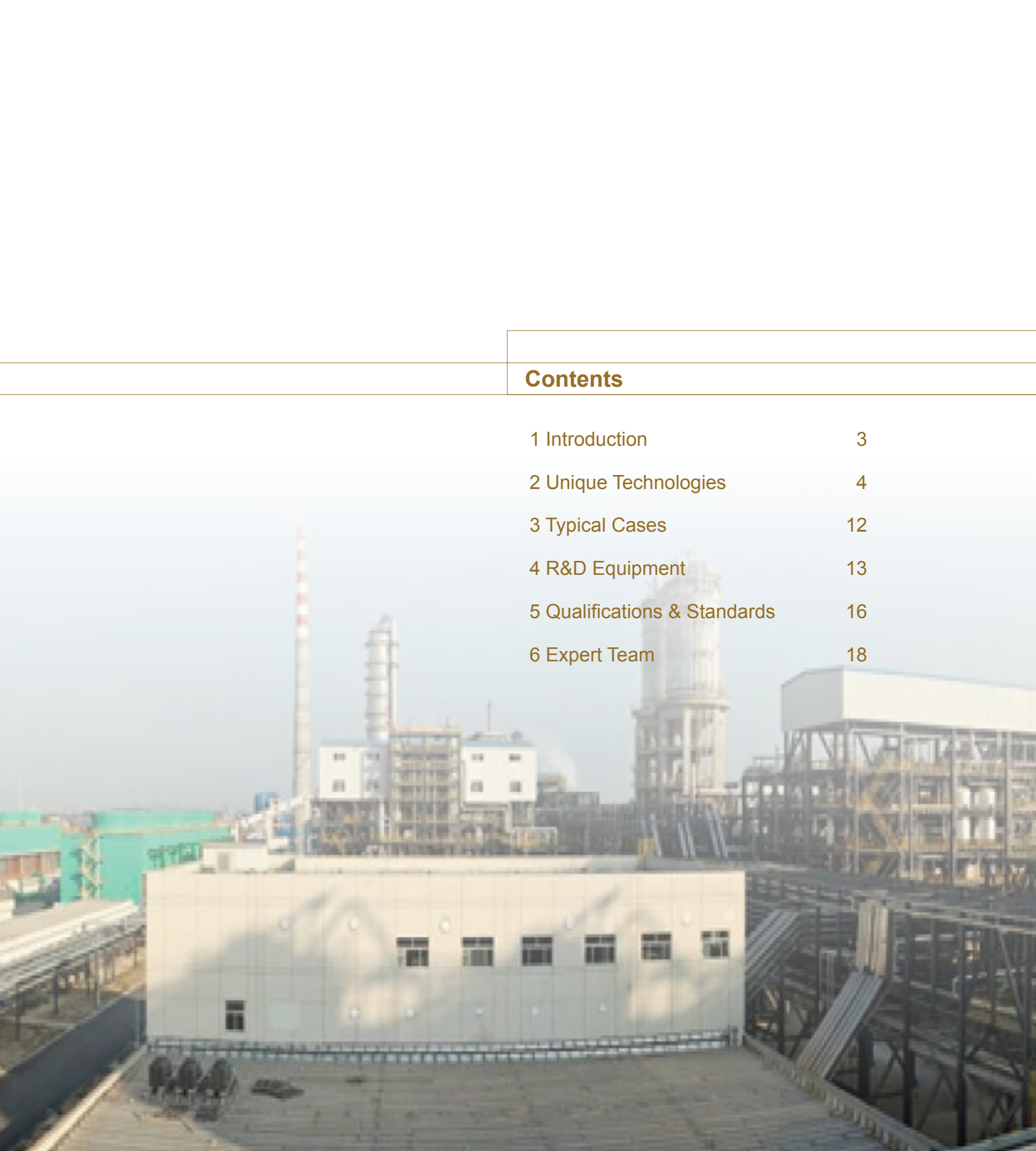
Science & Technology Management Department

2013

CHINA NATIONAL PETROLEUM CORPORATION

Advanced and Practical PTA Technology from CNPC!

Contents



China National Petroleum Corporation (CNPC) is a state-authorized investment agency and a state holding company. On July 1998, with the implementation of the Institutional reform of the State Council, CNPC was reorgnized to become an integrated oil company of cross-regions, cross-industries and cross-countries, it adopts modern enterprise system to realize the integrations of upstream and downstream operations, internal and external trade, production and marketing. CNPC's business covers six main sectors: oil and gas operations, petroleum engineering service, petroleum engineering construction, petroleum equipment manufacturing, financial services and new energy development. In 2012 CNPC produced 110 million tons of crude oil and 79.82 billion cubic meters of natural gas, while crude processing volume reached 191 million tons. The total revenue of RMB 2,690 billion with a profit of RMB139.1 billion had been achieved the same year.

CNPC was ranked 4th among the world's largest 50 oil companies and 6th in Fortune Global 500 in 2012.

CNPC strictly follows by the combined strategies of increasing resource capacity, expanding market shares and consolidating the international role, and persists in regarding technical innovation as a key framework to advance technological progress. To develop its core businesses, focuses will be placed on the solutions of key bottleneck technologies and key proprietary technologies. Thanks to continuously improving of the technical innovation system, optimizing the configuration of technological resources and strengthening the construction of strong talent teams, CNPC's technological creativity has been considerably upgraded. Consequently, a large number of technologies have been developed independently, with its own intellectual property.

Milliontons PTA Technology Package is one of representatives for major innovations of CNPC.

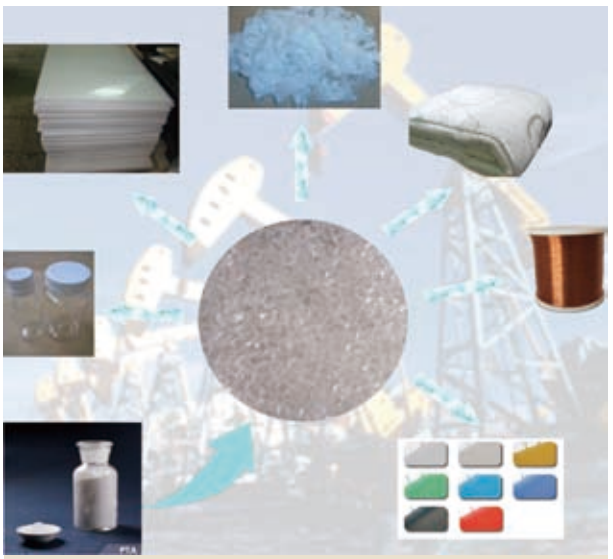
CLEAN ENERGY SUPPLY FOR BETTER ENVIRONMENT

1 INTRODUCTION

PTA (purified terephthalic acid), one of the major bulk chemical raw materials, is mainly used for producing polyester products (e.g. fiber, thin film, bottle), which is widely applied in national economy (e.g. chemical fiber, light industry, electronics, architecture) and closely associated with people's living.

Committed to PTA R&D, CNPC has made breakthroughs in key PTA technologies after constant exploration and improvement—Milliontons PTA Technology Package and Equipment that have reached a domestically leading level and internationally advanced level. With independent intellectual property rights, CNPC has won 22 patents for the Technology Package, including 4 international patents.

CNPC's Milliontons PTA Technology Package has been applied in many Chinese enterprises and included in the project service plans of both domestic and foreign enterprises. The number of PTA projects that CNPC has conducted or is conducting reaches up to 6 with a total capacity of almost 8 million tons/year.

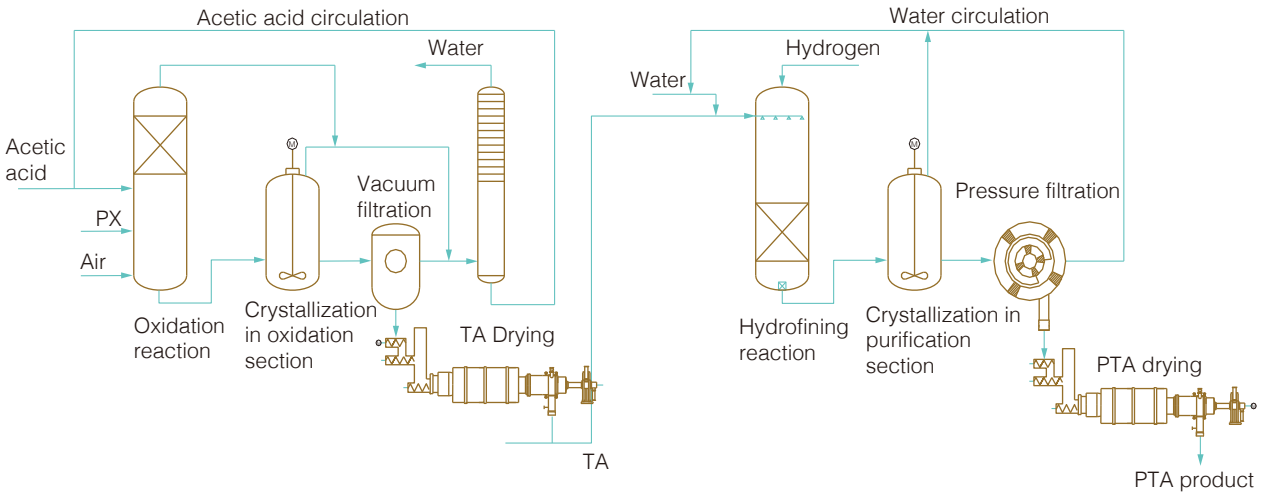


PTA Product Usage

Responsible for PTA R&D and engineering, China Kunlun Contracting & Engineering Corporation under CNPC is state-owned and technology-based backbone engineering and construction enterprise, as well as an international engineering enterprise capable of technological R&D, engineering design, consulting, technical service, project management and EPC. It boasts the National Engineering Design Qualification Class-A, Petrochemical and Chemical Fiber Project EPC Qualification and an overwhelming expert team, which can offer customers with economical, secure, reliable, reasonable and internationally standardized engineering design, as well as top-class services.

2 UNIQUE TECHNOLOGIES

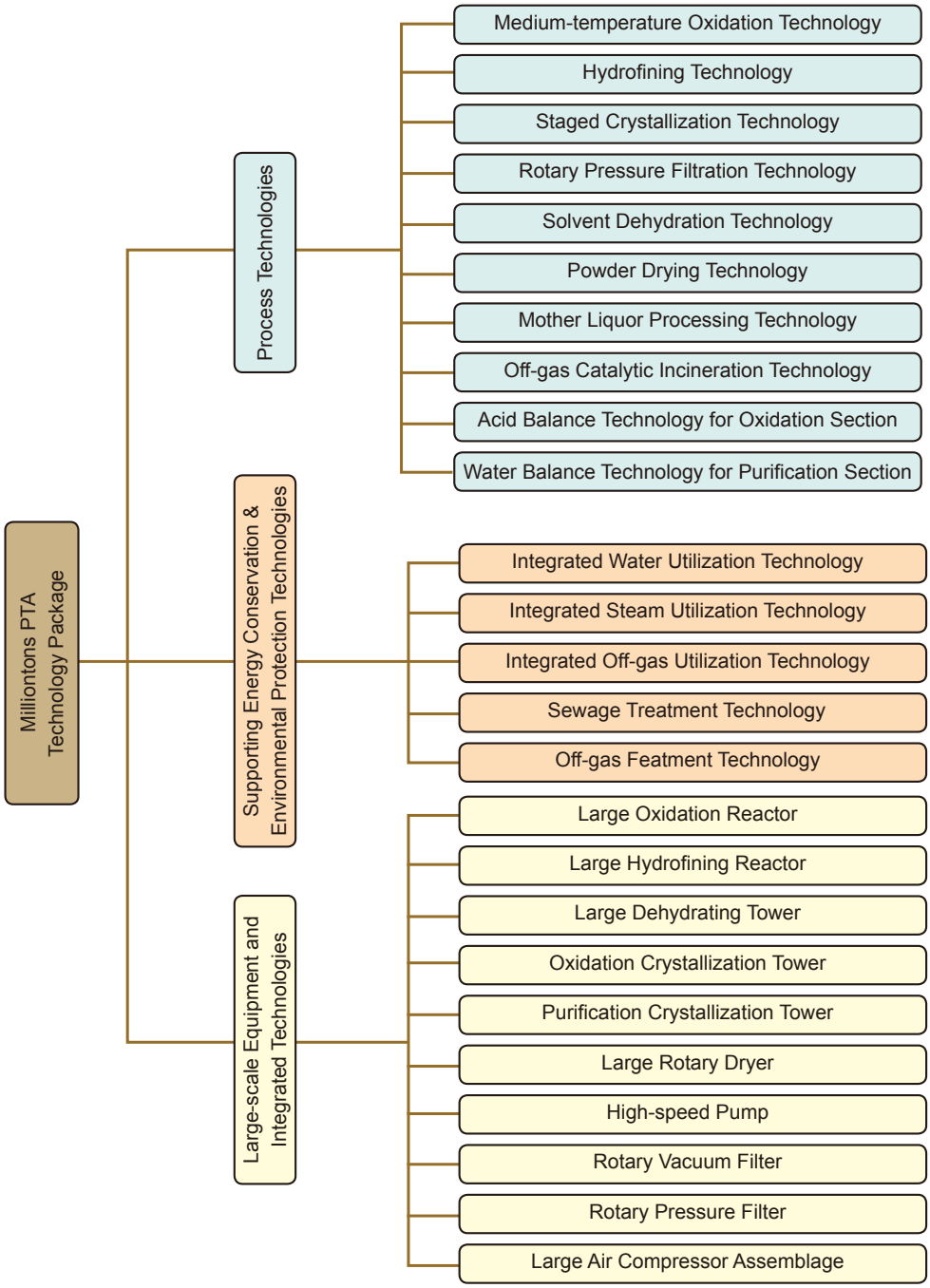
The PTA technology takes PX as the raw material, cobalt acetate and manganese acetate as catalysts and hydrobromic acid as the accelerant, and produces crude TA at medium temperature and pressure and transforms crude TA into PTA through hydrofining.



Schematic Diagram of PTA Technical Process

The Milliontons PTA Technology Package has distinctive technical features in oxidation process, crystallization, solvent recovery, integrated utilization of off-gas and byproduct steam, wastewater treatment, catalyst recovery, etc.

The PTA Technology Package includes 28 unique technologies of three series, i.e. production technologies, supporting energy conservation and environmental protection technologies, and equipment. Each single technology is applicable not just to PTA projects but also to similar projects.



PTA Technology Package

CNPC's Milliontons PTA Technology Package takes your PTA products to premium quality, with the following specification:

PTA Product Specification Table

No.	Item	Indicator
1	Appearance	White Powder
2	Acid Value (mg-KOH/g)	675±2
3	Ash Content (μg/g)	⩽ 9
4	Total Heavy Metal (Mo, Cr, Ni, Co, Ti, Mn, Fe) (μg/g)	⩽ 4
5	4-CBA (μg/g)	⩽ 25
6	PT Acid (μg/g)	⩽ 150
7	Water (%)	⩽ 0.2
8	Chroma (APHA)	⩽ 10
9	B Value	⩽ 1.2
10	Average Particle Size of Model Product (μm)	110±20

The PTA Technology Package effectively reduces production cost by optimizing the technical process and strictly controlling the consumption of PX, acetic acid, catalysts and other raw materials.

2.1 Medium-temperature Oxidation Technology

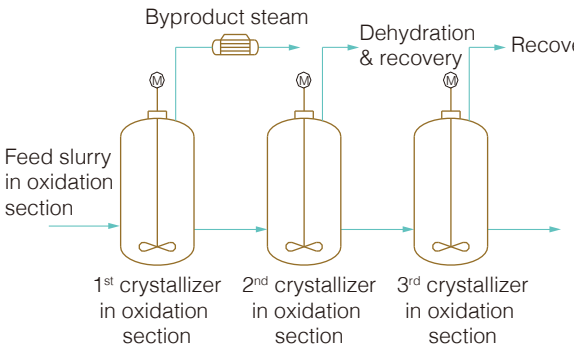
The world's major PTA production technologies fall into three categories, i.e. high-temperature, medium-temperature and low-temperature, each of which has its own features. CNPC's PTA Technologies exploit each technology's strengths and avoid weaknesses, with oxidation going on at medium temperature and pressure, thus possessing great advantages—avoiding such weaknesses as large investment in compressor and reactor and high HAc consumption required by high-temperature production, while averting complicated mother liquor processing and catalyst recovery procedures in low-temperature production.

Compared with other production technologies, CNPC's PTA Technology Package features mild operating conditions, high product quality, low consumption of raw materials (e.g. PX), low energy consumption, etc., with the integrated technical level up to the global advanced level.

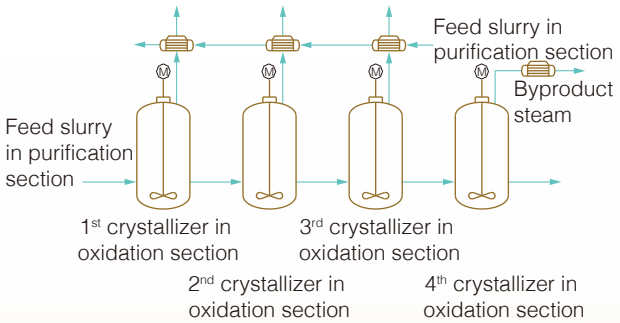
Oxidation Reactor

2.2 Staged Crystallization Technology

Crystallization in oxidation section adopts three-stage flash evaporation while crystallization in purification section applies four-stage flash evaporation. Through adjustment of temperature, pressure, retention time and other parameters, the grain size of finished crystals is controlled and the steam gained through flash evaporation is recovered and utilized, thus effectively reducing the plant's energy consumption.



Crystallization Process in Oxidation Section

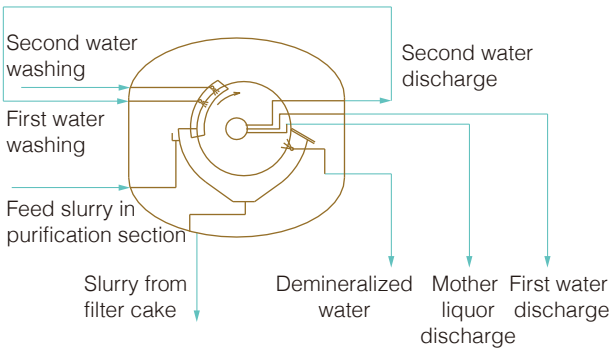


Crystallization Process in Purification Section

The Purification-section Crystallization Technology adopts a four-stage process, which features shorter flow, less equipment investment, easier operation and less operating cost compared with the five-stage process.

2.3 Rotary Pressure Filter Technology

PTA feed slurry adopts the Rotary Pressure Filter Technology, which realizes separation of solid and liquid feed slurry as well as separated collection of mother liquor and washing liquor through multi-step washing, dehumidification, blow-off, etc.



Rotary Pressure Filter System

CNPC's Rotary Pressure Filter Technology has won the national patent for invention and been applied in processing feed slurry in purification section, which can also be used in processing feed slurry in oxidation section.

2.4 Powder Drying Technology

The Rotary Drying Technology heats powder evenly by indirect steam heating and dryer rotation, so that acetic acid or moisture can be taken out with inert gases.

Based on experiment study, operating conditions are adjusted: the material of oxidation dryer is changed from dual-phase steel to 316L, thus saving equipment investment substantially.

Rotary Dryer

2.5 Mother Liquor Processing Technology

The Mother Liquor Processing Technology involves mother liquor processing in oxidation section and purification section.

95% of mother liquor in oxidation section is directly recovered while 5% is condensed through filtration and steam stripping to separate most acetic acid, water and nonvolatile components. The condensed mother liquor is vaporized by the film evaporator for solvent recovery. The residual liquor at the bottom is separated to get residues which are then sent out for uniform disposal, while the catalyst concentration and recovery is done in liquid phase.

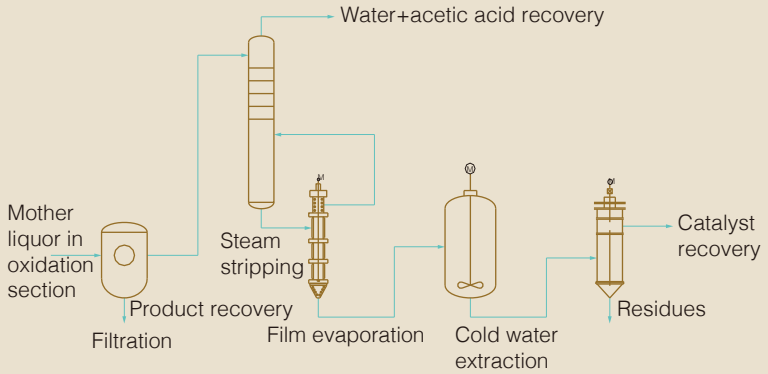


Diagram for Mother Liquor Processing in Oxidation Section

Through flash evaporation, concentration and ultrafiltration, mother liquor in purification section produces intermediate product, which then undergoes ion exchange to remove iron and nickel ions while cobalt and manganese ions are recovered selectively. The water from ion exchange is directly recycled while the rest is recycled after COD is reduced through the reverse osmosis system.

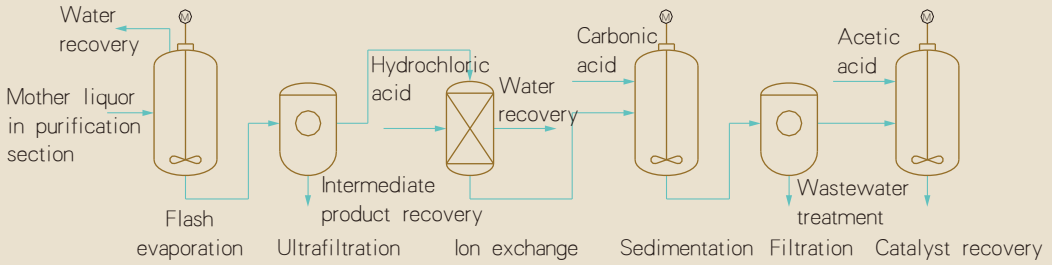


Diagram for Mother Liquor Processing in Purification Section

The processing of mother liquor in oxidation and purification sections realizes separated recovery of different useful substances like acid, water and catalyst, with the recovery rate of acid solvent up to 95%-plus, that of water up to 50%~70% and that of catalyst up to 80%~90%. Meanwhile, the solid and liquid wastes are disposed and discharged after reaching standards, thus reducing the production cost and protecting the environment.

2.6 Integrated Water Utilization Technology

The water generated from oxidation reaction is mainly used to spray the blow-down tower, and the spray liquid is purified by wastewater treatment and then recycled, with the recovery rate up to 98%. The condensate liquor from flash evaporation for crystallization in purification section undergoes a series of steps, such as heating of feed slurry in purification section, spray washing and adjustment of feed slurry concentration, thus realizing water self-circulation in the system.

The Integrated Water Utilization Technology, plus the advanced Purified Mother Liquor Processing Technology, greatly reduces water consumption in the plant, with the unit consumption of each ton of demineralized water controlled at 1.2~1.6t/t.

2.7 Integrated Steam Utilization Technology

The steam required in the plant is processed by pressure-grading and volume-grading techniques according to heat source quality and user demands in order to produce steam of different grades. The redundant steam is used for driving the air compressor unit and generator unit to act and generate electric power so as to balance energy utilization in the system.

Part of oxidized off-gas obtained through oxidation and burning is dried to serve as inert gas in the plant, while the redundant off-gas is sent to off-gas expansion turbine to drive the compressor to act, in a bid to realize energy recovery.

Through integrated energy utilization, the PTA plant with capacity of 1.4 million tons/year generates 18,000kW·h electric power, which does not only balance electricity consumption in the master plant but also sends net electricity of 35kW·h/t-PTA outside, thus saving energy significantly.

Large-scale Air Compressor Unit

2.8 Wastewater Treatment Technology

The wastewater generated in the production process undergoes integrated treatment, such as sedimentation, pH adjustment, anaerobic disposal, aerobiotic disposal, membrane separation, reverse osmosis. The wastewater after treated returns to the plant to serve as circulating cooling water, with the water recovery rate up to more than 70%, so that the demand of fresh water is reduced and cost saved.

Wastewater Treatment Station

2.9 Tail-gas Disposal Technology

The exhaust gases in the plant contain acid, solid particles, organic matter and other elements, so different methods (e.g. acid, demineralized water, alkali) are used for spray washing. Meanwhile, according to different pressures of exhaust gases, differentiated disposal is applied by use of high-pressure absorption column, medium-pressure absorption column and normal-pressure absorption column, in order to make the exhaust gases meet environmental protection requirements and maximize the recovery of useful products.

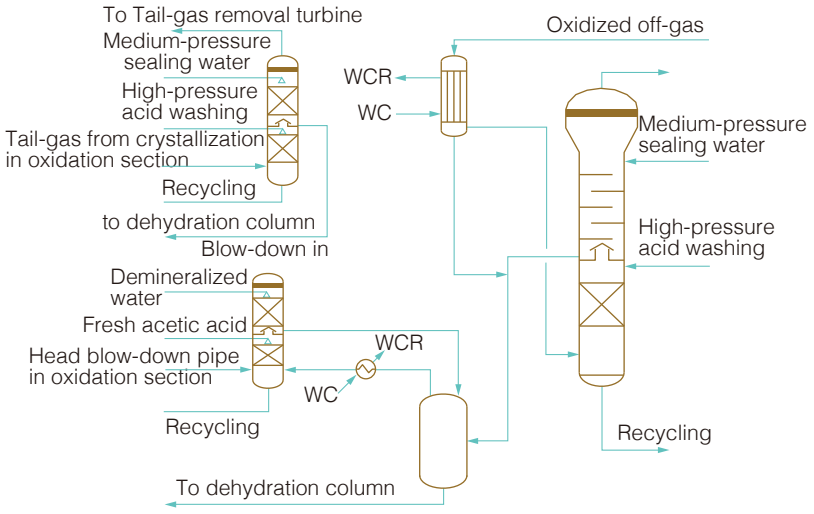


Diagram for tail-gas Disposal

3 TYPICAL CASES

CNPC's Milliontons PTA Technology Package has been applied by a number of Chinese enterprises and technical negotiation is under way with many Chinese and foreign enterprises, so its application continues to expand.

3.1 Chongqing Pengwei Petrochemical Co., Ltd.: PTA Project with 900,000 tons/year

The PTA plant with capacity of 900,000 tons/year of was put into production in Chongqing Pengwei Petrochemical Co., Ltd. in November 2009, with product quality, material consumption and energy consumption up to the internationally advanced level. It is of milestone significance as China's first PTA plant that uses the domestic proprietary technology package.

CNPC's PTA research team overcame many difficulties (e.g. no domestic technology for reference, very difficult engineering design and construction) and finally put the PTA plant into smooth production after making independent innovations and tackling critical problems. This marks the great success of CNPC's PTA technology R&D.

3.2 Shaoxing Far Eastern Petrochemical Co., Ltd.: PTA Project with 1.4 million tons/year

The PTA plant with capacity of 1.4 million tons/year was put into production in Shaoxing Far Eastern Petrochemical Co., Ltd. in May 2012. As the third plant that uses CNPC's proprietary PTA Technology Package, it only took 25 months from construction to official production, setting a record in terms of the shortest construction period of PTA plant in China.

Based on the in-service plant, the process design is continuously optimized to further reduce material and energy consumption, with the total energy consumption 8% lower than the industry average. This signals that CNPC's PTA Technology Package has become mature, realized capacity diversification and joined the world-leading ranks.

4 R&D EQUIPMENT

4.1 Complete Engineering R&D Software

With kinds of process simulation software (e.g. Aspen plus, Hysis, Prot II, HTRI), CNPC is able to conduct analysis and simulation of key equipment, section process and whole process of the plant, thus providing a solid foundation for engineering R&D and design. Furthermore, the analysis of integrated energy utilization is made to develop measures for further energy conservation and consumption reduction in the PTA plant.

4.2 Key Scientific Breakthroughs

In collaboration with famous universities home and abroad, CNPC conducted R&D on key engineering technologies to maintain its technologically leading position.

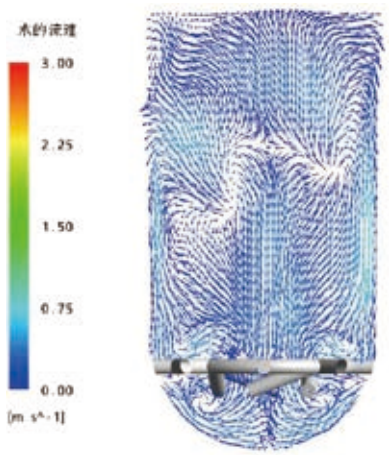
(1) In cooperation with Zhejiang University, CNPC conducted research on oxidation reaction and established a reliable gas-liquid reaction kinetic model through thermal simulation experiment. Through cold-state simulation experiment, CNPC made research on mixture/solid suspension, gas holdup, gas-liquid mass transfer rate and influences of internal and external components, defined the speed control steps of the process, learned the hydraulic performance of gas distributor, external circulating pipe and dehydration section, and presented process design parameters of the bubble column reactor in the PTA plant.

Thermal Simulation Experiment Facility

Cold-state Simulation Experiment Facility

(2) In cooperation with Tianjin University, CNPC conducted experiment research on thermodynamics of crystallization and got data of solubility of TA in oxidation reaction solution and metastable zone width for crystallization. It conducted experiment research on crystallization kinetics and obtained the equation for crystallization kinetics of TA in oxidation reaction solution. Based on such experiment research, CNPC built the mathematic model for TA crystallization through multi-stage depressurization and evaporation, finished the simulation of TA crystallization through continuous multi-stage depressurization and evaporation and presented process design parameters of TA crystallizer.

(3) In collaboration with Beijing University of Chemical Technology, CNPC conducted the cold-state simulation experiment on oxidation reactor and further verified process design parameters.



Cold-state Simulation Experiment on Oxidation Reactor

4.3 Equipment R&D

CNPC has the capability of developing and designing large-scale special material equipment for chemical engineering, and jointly developed key equipment for

Medium-temperature Oxidation Reactor

PTA Lab Dryer

Large Air Compressor Unit

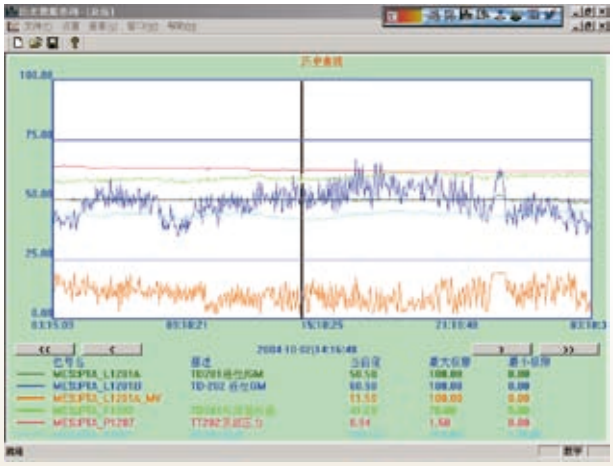
PTA plant with a number of domestic professional equipment manufacturers. CNPC developed titanium equipment such as oxidation reactor in collaboration with Nanjing Baose Co., Ltd., PTA/TA dryer with AVIC Liming Jinxi Chemical Machinery (Group) Co., Ltd., purification reactor and crystallizer with Sinopec Nanjing Chemical Industrial Co., Ltd. - Chemical Machinery Works, large air compressor unit with Shaanxi Blower (Group) Co., Ltd. and Shenyang Blower Works Group Corporation, etc.

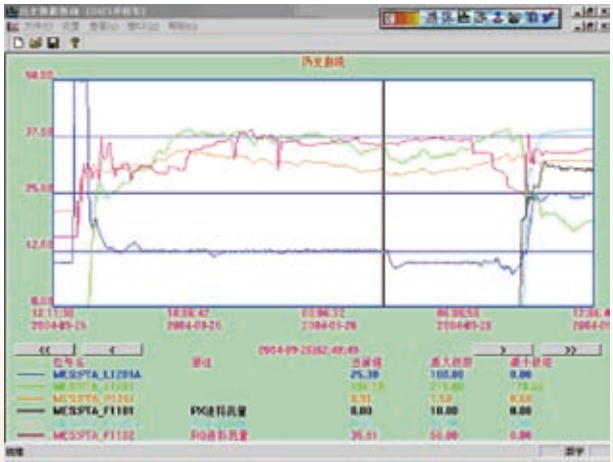
4.4 Pilot Plant Experiment

Based on the process simulation, key experiment research and bench-scale plant experiment, CNPC actively conducted pilot plant experiment and verified the acquired operating parameters and control schemes.

In 2004 and 2005, with the PTA plant (capacity of 75,000 tons/year) of Ji'nan Zhenghao Advanced Fiber Co., Ltd. as the pilot plant, CNPC conducted an array of industrial tests for medium-temperature oxidation, purification and crystallization technologies and gained ground-breaking test results and valuable data, which effectively verified the fundamental experiment results and computational simulation level, as well as CNPC's proprietary PTA Technology Package.

PTA Plant in Ji'nan Zhenghao Advanced Fiber Co., Ltd.





5 QUALIFICATIONS & STANDARDS

(1) National licenses for engineering consulting, engineering investigation, engineering design, engineering supervision and EPC.

(2) QMS and HSE-MS certifications.

(3) 22 patents for PTA technologies and equipment, including 4 international patents.

(4) PTA technologies and equipment were granted the first prizes for science and technology progress granted by China National Petroleum Corporation (CNPC) and China National Textile and Apparel Council.

(5) CNPC referred to international (e.g. the U.S., Europe) and China's national standards, and developed technical standards for PTA engineering.

No.	Patent Code	Name of Patent	Type of Patent
1	ZL03142246.2	An Oxidation Device of Airlift External Circulation Bubble Column for Terephthalic Acid Production	Invention
2	ZL03209727.1	An Oxidation Device of Airlift External Circulation Bubble Column for Terephthalic Acid Production	Utility model
3	200710108238.6	A Method and Device of Terephthalic Acid Separation and Purification	Invention
4	200719110271.2	A New Method of Separating and Purifying Terephthalic Acid	Invention
5	200810057722.5	Catalytic Oxidation Processing of Reaction Tail-gas in PTA Plant and Total Energy Utilization System	Invention
6	ZL200810103270.X	A Method and System of Purified Mother Liquor Recovery in PTA Plant	Invention
7	200810238996.4	An Easy Method and System of Efficient Recovery and Utilization of Mother Liquor in Purification Section of PTA Plant	Invention
8	ZL200910076703.1	PX Oxidation Reactor of Terephthalic Acid Production	Invention
9	200920106089.4	A System of Mother Liquor Recovery in Purification Section of PTA Plant	Utility model
10	200920106088.X	An Easy System of Efficient Recovery and Utilization of Mother Liquor in Purification Section of PTA Plant	Utility model
11	200920106087.5	PX Oxidation Reactor of Terephthalic Acid Production	Utility model
12	200910090509.9	A Method and System of TA Separation and Filtration in PTA Preparation	Invention
13	200910090510.1	A Method and Device of Hydrogen Recovery in Purification Section of PTA Plant	Invention
14	200920173002.5	A Device of Hydrogen Recovery in Purification Section of PTA Plant	Utility model
15	200920173004.4	Organic Acid Wastewater Processing Method and System	Utility model
16	200920173001.0	A System of TA Separation and Filtration in PTA Preparation	Utility model
17	201010160611.4	A Device of P-xylene Oxidation and Crystallization	Invention
18	201020176237.2	A Device of P-xylene Oxidation and Crystallization	Utility model
19	PCT/CN2009/075363	A Method and System of TA Separation and Filtration in PTA Plant	Invention
20	PCT/CN2009/075352	An Easy Method and System of Efficient Recovery and Utilization of Mother Liquor in Purification Section of PTA Plant	Invention
21	PCT/CN2009/075361	A Method and Device of Hydrogen Recovery in Purification Section of PTA Plant	Invention
22	PCT/CN2009/075384	PX Oxidation Reactor for Terephthalic Acid Production	Invention

6 EXPERT TEAM

Luo Wende National engineering designer. Engaged in chemical, chemical fiber engineering design, technological R&D and technological management, he has presided over R&D of four-kettle polyester production technology and equipment, a series of China-made polyester plants, PTA Technology Package and other projects. He was granted the second prize of National Science & Technology Progress Award, gold prize of National Excellent Engineering Design Award, etc.

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Kan Xuecheng Professor-level senior engineer and expert with special government allowance. Engaged in R&D of petrochemical technologies, he won the second prize of National Science & Technology Award and the first prize of CNPC Science & Technology Award.

Li Lijun Professor-level senior engineer. Engaged in petrochemical and chemical fiber engineering design as well as technological R&D, he has participated in R&D of polyester technologies and equipment, PTA Technology Package and other research projects. Furthermore, he assumed the manager of China's first proprietary PTA demonstration project and won multiple ministerial and provincial-level awards.

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Yao Ruikui Professor-level senior engineer and expert with special government allowance. Engaged in chemical engineering design and technological R&D, he has played a major role in R&D of PTA Technology Package, and won multiple ministerial and provincial-level awards.
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Zhang Chun Professor-level senior engineer and expert with special government allowance. Engaged in chemical equipment R&D, he has participated in R&D of key equipment for PTA Technology Package, and won the second prize of National Science & Technology Progress Award and multiple ministerial and provincial-level awards.
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Wan Wangsheng Professor-level senior engineer, national approval officer for pressure vessel design and national registered mechanical engineer. Engaged in R&D of polyester, PTA and other chemical equipment, he won the second prize of National Science & Technology Progress Award, as well as multiple ministerial and provincial-level awards.
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Qiu Huayun Professor-level senior engineer and expert with special government allowance. Engaged in petrochemical and chemical fiber engineering design as well as technological R&D for over 30 years, he has participated in systematic research on a viscose project with capacity of 45,000 tons/year, as well as R&D of PTA Technology Package and other research projects. He won the first prize of National Science & Technology Progress Award, as well as multiple ministerial and provincial-level awards.

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Zheng Baoshan Senior engineer and national approval officer for pressure vessel design. Engaged in R&D of polyester, PTA and other chemical equipment, he headed Chongqing Pengwei and Jiangsu Hailun projects, coordinated and presided over professional equipment R&D, design, manufacture and on-site installation. He won multiple ministerial and provincial-level awards.

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Xu Jianming Professor-level senior engineer with U.S. PMP Certificate and national senior project manager. Engaged in engineering project management, he has managed 10-plus large PTA and polyester plant projects, and won multiple ministerial and provincial-level awards.

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Wang Yingzhi Professor-level senior engineer and member of National Pressure Piping Technology Committee. Engaged in R&D of chemical process and technologies, engineering consulting and design, she has participated in R&D of PTA Technology Package and won multiple ministerial and provincial-level awards.
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Liu Feng Senior engineer, registered ASE and TÜV functional safety engineer. Engaged in automatic control design for chemical fiber and raw material production technologies as well as relevant control technology R&D, she has participated in R&D and design of automatic control technologies for large-capacity polyester, PTA plant and other projects, and won multiple ministerial and provincial-level awards.
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