

High Quality Comonomer Hexene-1 Complete Production Technology

Science & Technology Management Department, CNPC

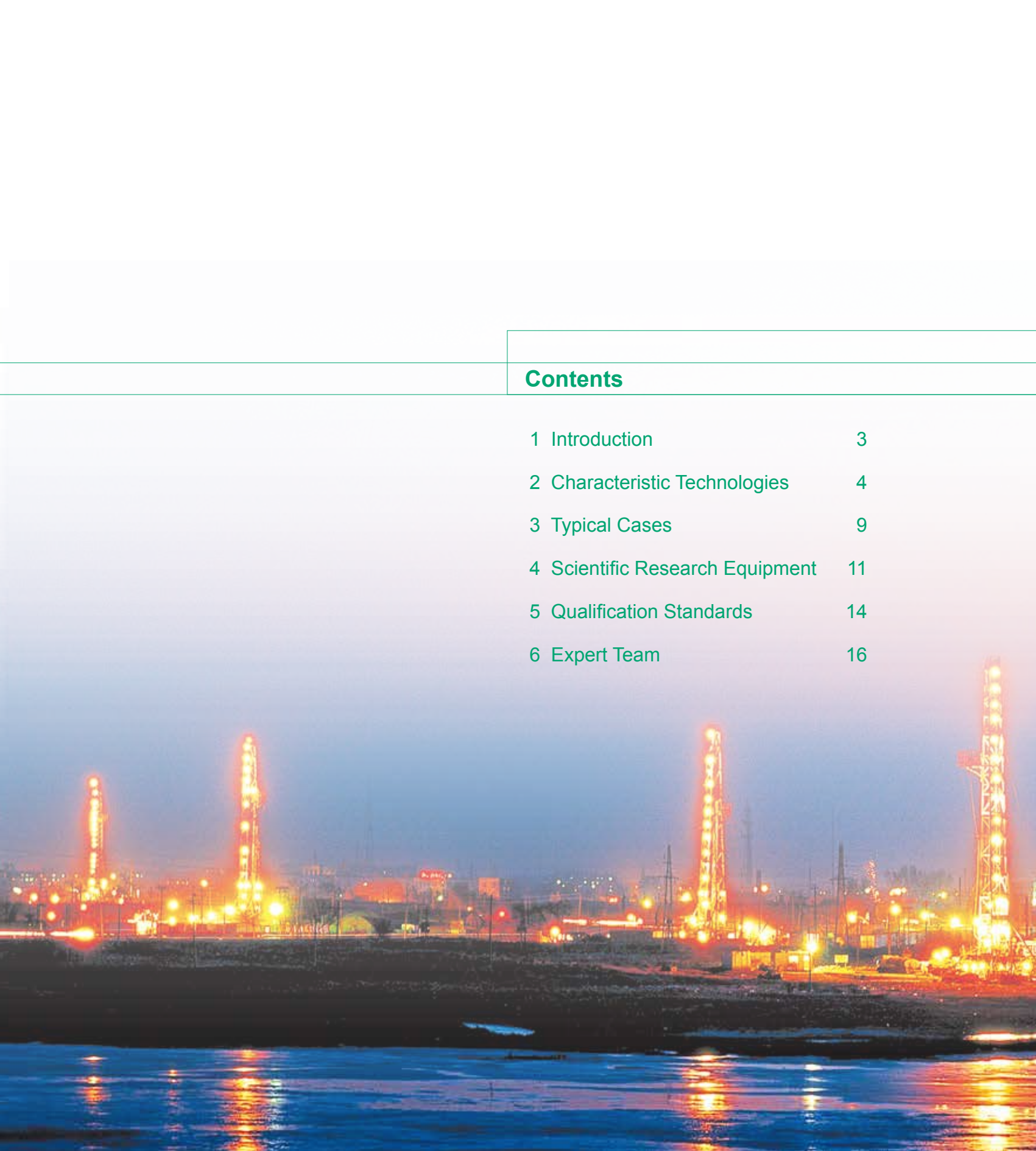
2015



CHINA NATIONAL PETROLEUM CORPORATION

*Hexene-1 to promote olefin
copolymerization all the more!*





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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 reorganized 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 2014 CNPC produced 113.67 million tons of crude oil and 95.46 billion cubic meters of natural gas, while crude processing volume reached 150.2 million tons. The total revenue of RMB 2,730 billion with a profit of RMB173.4 billion had been achieved the same year.

CNPC was ranked 3th among the world's largest 50 oil companies and 4th in Fortune Global 500 in 2014.

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.

The high quality comonomer hexene-1 complete production technology is one of representatives for major innovations of CNPC.

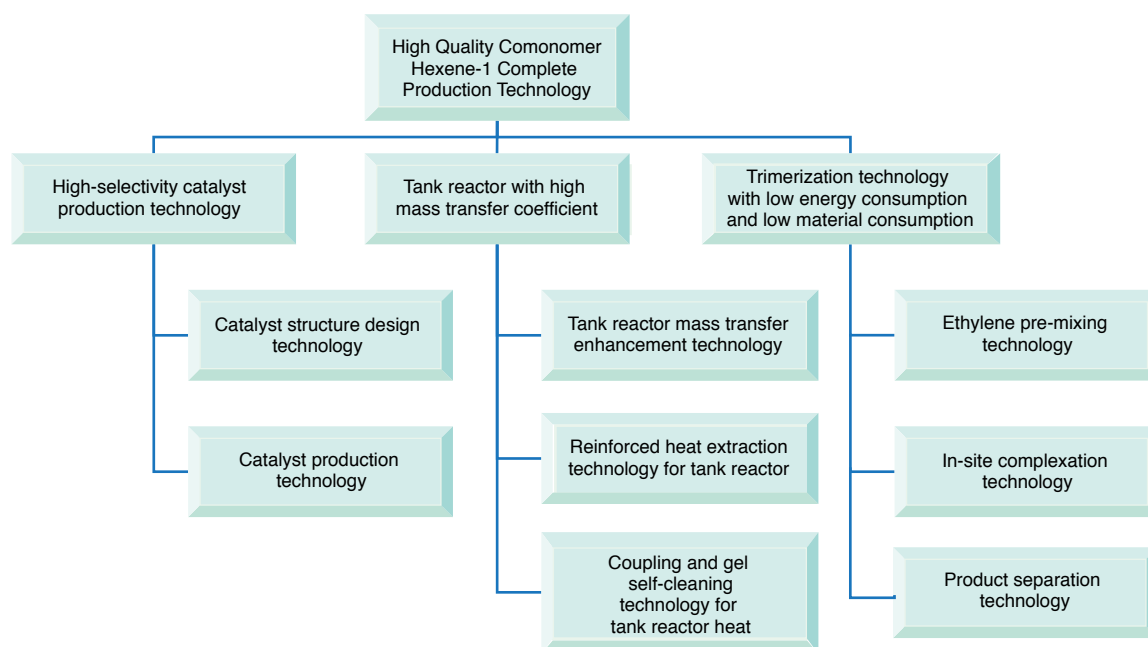
OFFERING ENERGY SOURCES, CREATING HARMONY

1 INTRODUCTION

Hexene-1, an important chemical feedstock, is used mainly to produce high performance LLDPE and HDPE and can remarkably enhance the performance and added value of polyethylene resin. CNPC is devoted to R&D of Hexene-1. Through unremitting efforts, CNPC has completed the conversion from laboratory research to industrialization, made a great technology breakthrough and formed a complete set of technology integrating catalyst, equipment and process. The core technologies reach international advanced level. CNPC has formed a set of “10kt Hexene-1 complete production technology package” with 5.00 million words and complete proprietary intellectual property rights. In addition, 6 China

invention patents and 3 technology secrets have been obtained, and 2 enterprise standards have been formulated.

The developed high quality comonomer Hexene-1 complete production technology has been successfully used in China and the corresponding unit has been successfully started at a time. The produced Hexene-1 product has high quality and it can meets the technical requirements of different series of downstream polyethylene catalysts. The produced copolymerization product has stable performance and has been unanimously approved by customers.



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CHARACTERISTIC TECHNOLOGIES

The independently developed high quality comonomer Hexene-1 technology is a complete set of technology integrating catalyst, process and equipment.

2.1 High-selectivity catalyst production technology

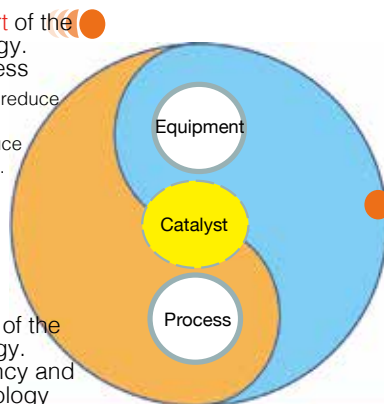
Catalyst is the core of Hexene-1 technology. The developed catalyst has advantages such as high efficiency and temperate catalysis conditions, thus establishing a foundation for reducing unit operation difficulty and equipment investment and shortening separation process flow.

Catalyst is the **heart** of the complete technology.
Core competitiveness

- High selectivity helps reduce single consumption.
- High activity can reduce catalyst consumption.

Process is the **soul** of the complete technology.
Economical efficiency and safety of the technology

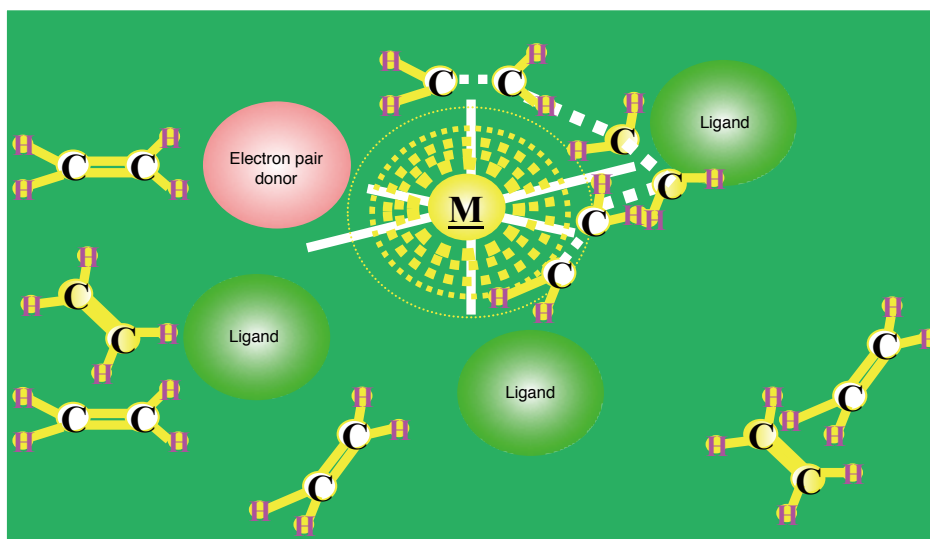
- Low energy consumption process makes for improving economical efficiency.
- Reliable process has stronger competitiveness.



Equipment is the **body** of an industrial unit.
Technology originality

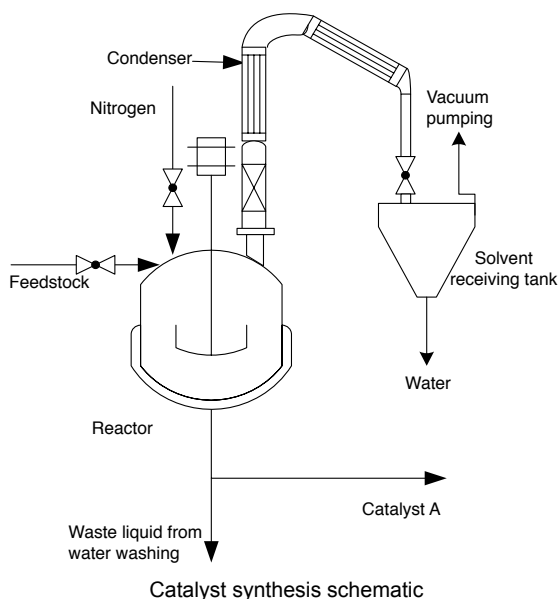
- Core equipment: tank reactor
- Develop catalyst efficiency to the greatest extent possible

Starting from trimerization mechanism, CNPC has proposed and used the “limit-induction” dual-effect



synergy theory and independently developed a high efficiency catalyst. The catalyst includes four components such as main catalyst, ligand, catalyst promoter and electron donor, which enhances catalyst activity and Hexene-1 selectivity, reduce the unit's single consumption and catalyst consumption and improve the unit's economical benefit.

◆ Taking the new concept “dual-function integration optimization design” as guidance, the new N-heterocyclic ligand and electron donor containing halogen have been developed, which thus realizes controllable catalyst steric hindrance and active center electron cloud density and can develop catalyst efficiency to the greatest extent possible.



2.2 Tank reactor with high mass transfer coefficient

Based on the feature “reaction controlled by gas-liquid mass transfer process”, the tank reactor with high mass transfer coefficient and forced heat extraction characteristic has been firstly developed and successfully applied in the process of ethylene

◆ The precipitation and compound decomposition preparation technology for producing catalyst stock solution has been developed, and the catalyst production technology has been innovated. The process is simple, material loss is reduced, and catalyst synthesis yield is increased to 80%.



Catalyst synthesis unit

trimerization and synthesis to Hexene-1. The high gas-liquid mixing capacity and good dispersion effect of the tank reactor increase the mass transfer and heat removal capacity of equipment, develop the efficiency of liquid phase catalyst to the greatest extent possible and ensure the long-period stable running of the unit.

2.3 Tank reactor with high mass transfer coefficient

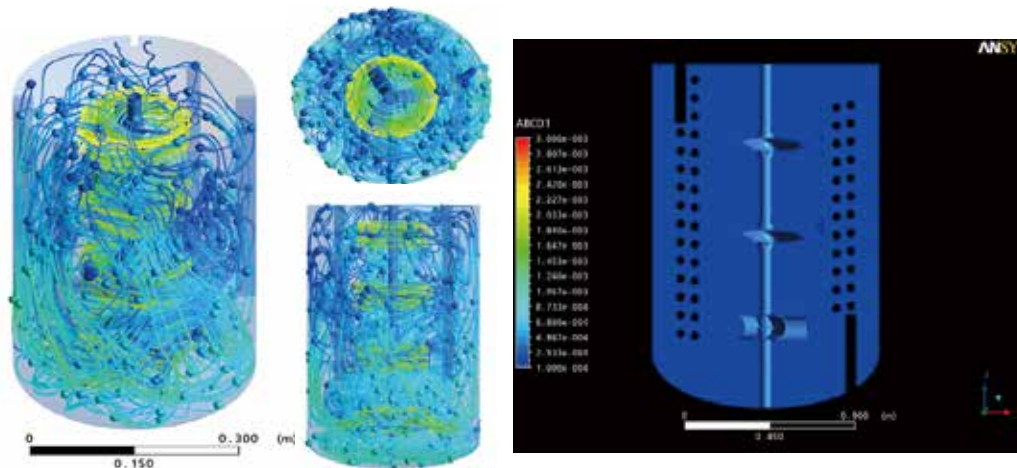
Based on the feature “reaction controlled by gas-liquid mass transfer process”, the tank reactor with high mass transfer coefficient and forced heat extraction characteristic has been firstly developed and successfully applied in the process of ethylene trimerization and synthesis to Hexene-1. The high gas-liquid mixing capacity and good dispersion effect of the tank reactor increase the mass transfer and heat removal capacity of equipment, develop the efficiency of liquid phase catalyst to the greatest extent possible and ensure the long-period stable running of the unit.



◆ Tank reactor mass transfer enhancement technology

Reactor mass transfer enhancement has been realized through optimization design of reactor combination mixing paddle and forced circulation member in the tank reactor development process.

- Increase gas-liquid contact surface area and accelerate catalyst dispersion and the diffusion rate of ethylene in liquid films.
- Increase material mixing rate, eliminate the adverse impact of non-uniform partial concentration on reaction, and effectively increase reaction rate.

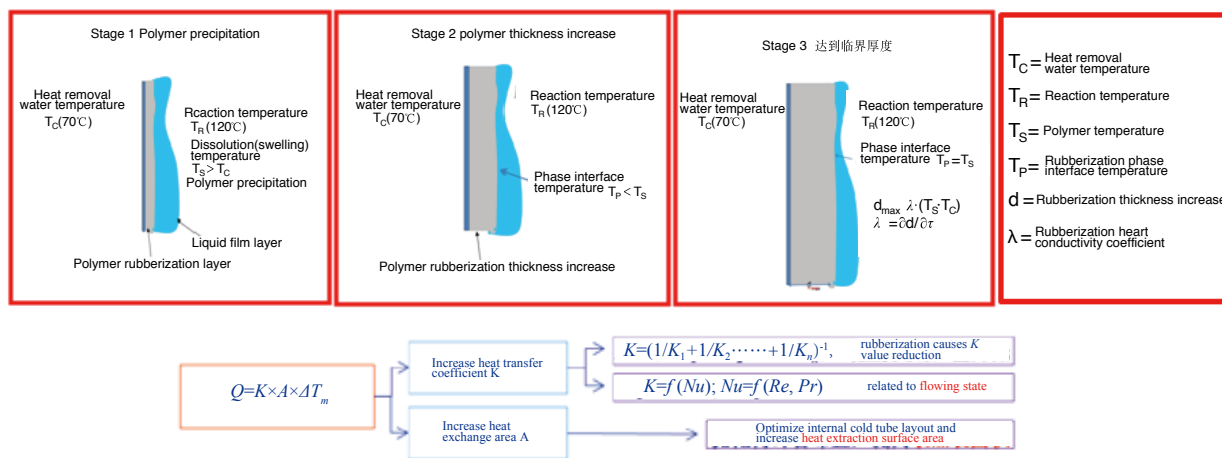


◆ Coupling and gel self-cleaning technology for tank reactor heat exchanger

The physical-mathematical model for cold tube rubberization in the tank reactor has been firstly established and the self-collosol technology has been developed with regard to easy rubberization of

reaction byproducts on heat exchanger surface and reduction of heat removal capacity.

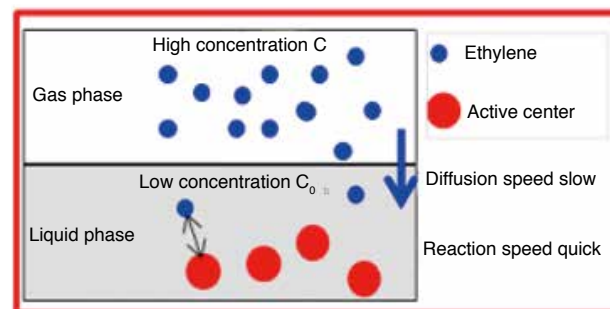
- The problem on impact of polymer rubberization on reactor heat extraction has been solved.
- This ensures “long-period safe and stable” operation of the unit.



2.4 Trimerization technology with low energy consumption and low material consumption

The ethylene premixing technology has been developed in view of the fact that the reaction rate of ethylene trimerization and synthesis to Hexene-1 is affected by ethylene concentration in liquid phase.

- Forcibly increase the ethylene concentration in the liquid phase reaction area and the contact capacity of ethylene with active center.
- Improve catalyst efficiency and reduce unit energy consumption.



Based on the physical and chemical characteristics of each component in coarse trimerization products, the two-stage three-tower separation technology “rough separation—rectification” has been developed using the methods such as simulation, calculation and other ways to optimize process flow separation sequence, capacity

integration and control scheme.

- The process flow is simple, thus greatly reducing high pressure steam consumption and unit's energy consumption.
- The product has high purity and meets the requirements of the downstream polyolefin unit.

Hexene-1 product specifications

Component	Unit	Measured value
Hexene-1	ω %	99.48
Normal α -alkene	ω %	99.68
Internal olefin	ω %	0.42
Peroxide	mg/kg	< 0.6
Benzene	mg/kg	Not detected out
Sulfur	mg/kg	Not detected out
Cl	mg/kg	< 1.0

3 TYPICAL CASES

With the complete technology independently developed by RIPP, the first set of ethylene trimerization and synthesis to Hexene-1 unit based on a tank reactor has been established in Daqing Petrochemical Company. The operation result

indicates that the unit is characterized by easy operation control, long-period smooth and stable running, good product quality and remarkable benefit.



Daqing Petrochemical 5000t/a Hexene-1 unit

With the technology, 20kt/a Hexene-1 production unit is being constructed in Dushanzi Petrochemical Company and will be built up and put into production in 2014 so as to realize 10kt leap of Hexene-1 technology.



Dushanzi Petrochemical 2×10^4 t/a Hexene-1 unit

TYPICAL CASES

The Hexene-1 technology has been successfully applied in downstream full density units. With the technology, multiple trademarks of Ethylene/Hexene-1 copolymerization products have been produced,

including HPR18H10AX, HPR18H20DX, DGDZ-2400, DMDA-8920, DMDA-6200, HF-7042, etc. The copolymerization products have stable performance and have been unanimously approved by customers.



Daqing Petrochemical 25×10^4 t/a polyethylene unit



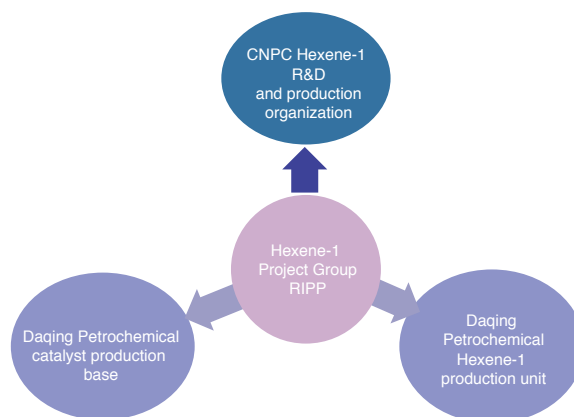
Polyethylene product from Ethylene/
Hexene-1 copolymerization

4 SCIENTIFIC RESEARCH EQUIPMENT

CNPC has catalyst production bases with advanced equipment, key natural gas chemical laboratories, high-level talent doctor mobile stations and scientific research entities integrating scientific research and development, technical service and production operation.

Catalyst synthesis research platform

- Three sets of catalyst synthesis production units
- Catalyst small-scale synthetic reactor (1L)
- Catalyst pilot production unit (50L)
- Catalyst production base (4000L)



Hexene-1 catalyst synthesis unit

Catalyst evaluation and research platform

- A set of Hexene-1 catalyst small-scale evaluation unit (1L, 2L)
- A set of catalyst and process research pilot unit for ethylene trimerization and synthesis to Hexene-1 (300t/a)
- A set of vacuum water-free and oxygen-free operating system and product post-treatment facilities



Hexene-1 small-scale test unit



Water-free and oxygen-free operating system



Hexene-1 pilot unit

Product analysis and test platform

Hexene-1 complete technology: complete facilities, over 10 sets of large analyzers, ICP spectrometers, chromatographic analyzers and nuclear magnetic resonance spectrometers.



HP-6890 gas chromatograph



AVANCE III 400MHz nuclear magnetic
resonance spectrometer



Optima5300DV ICP spectrometer



ANTEK9000VLS sulfur analyzer

5 QUALIFICATION STANDARDS

Standards

Hexene-1 catalyst (DCH-1)(Q/SY SHY 001—2001)

Synthetic 1-Hexene catalyst (DCH-II)(Q/SHY DQ 005—2013)



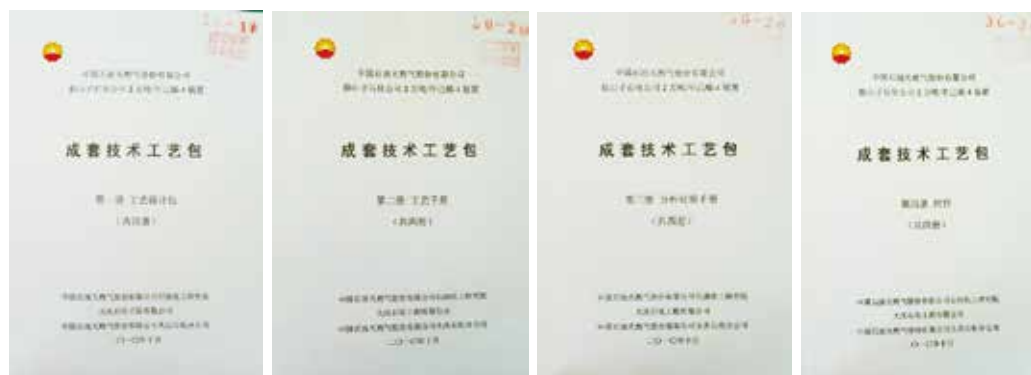
Patents

ZL03153517	A preparation method for 1-Hexene in the presence of ethylene oligomerization catalyst system
ZL03153509	A new preparation method for 1-Hexene in the presence of ethylene oligomerization catalyst system
ZL00107545.4	A catalyst for 1-Hexene preparation in the presence of ethylene oligomerization catalyst system
ZL201120478346.4	A multi-function reactor for preparing Hexene-1 catalyst
ZL200910243233.3	A catalyst for ethylene trimerization and synthesis to Hexene-1 and its application
ZL2012020606140.9	A 1-Hexene synthesis reactor



Process software package

Complete technological process software packaging for 20kt/a Hexene-1 unit of PetroChina Dushanzi Petrochemical Company.



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EXPERT TEAM



Wang Gang

Senior technical expert, professor level senior engineer. He has experience of over 30 years in R&D and production management of polyolefin. He is responsible for coordinating in industrial application and popularization of "Hexene-1 complete technology". 32 papers written by him have been published. He has obtained 34 invention patents and 35 international, provincial and ministerial science and technology advance prizes.

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Wang Sihan

Senior technical expert, professor level senior engineer. He has over 20 years of experience in R&D and production management of polyolefin. He is responsible for completing scientific research and development and industrial application of "Hexene-1 complete technology". He took charge of completing "10kt Hexene-1 complete production technology package". Over 40 papers written by him have been published. He has obtained 35 domestic and foreign invention patents, 1 China excellent patent prize, 1 grade II science and technology advance prize of CNPC, 1 grade III science and technology advance prize of CNPC and 1 innovation achievement prize of Heilongjiang.

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Ling Renzhi

Professor level senior engineer. He has 23 years of field production management experience. He is responsible for providing guidance to the adjustment of the site technical scheme for Hexene-1 industrial application test. He once obtained over 10 provincial and ministerial scientific research achievements. 17 papers written by him have been published. He has obtained 19 domestic and foreign invention patents.

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**Liu Minghui**

Senior technical expert, professor level senior engineer. He has been long engaged in site technical guidance. He is responsible for the construction and manufacturing of Hexene-1 industrial application units and the adjustment of site technical schemes. He once obtained over 20 provincial and ministerial scientific research achievements. 37 papers written by him have been published. He has obtained 36 domestic and foreign invention patents.

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**Zhu Shaopeng**

Engineer. He has over 20 years of field production management experience. He is responsible for comprehensive construction and commencement of Hexene-1 units. He has obtained 9 provincial and ministerial scientific research achievements. 13 papers written by him have been published. He has obtained 12 domestic and foreign invention patents.

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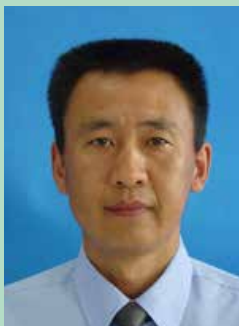
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**Liu Fenlin**

Engineer. He has 18 years of field production management experience. He participated in the construction and commissioning of Hexene-1 units. He has obtained 7 provincial and ministerial scientific research achievements. 17 papers written by him have been published. He has obtained 9 domestic and foreign invention patents.

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**Wu Nanping**

Senior engineer. He has more than 20 years' experience in the engineering design, presided over a number of project designs and developments, and was responsible for completing engineering design and development of « Hexene-1 Technology». And he was served as engineering manager for Petrochina Daqing Petrochemical Company, PetroChina Dushanzi Petrochemical Company, where the whole construction was successfully commissioned by one shot, each indicator has reached the advanced level in domestic country. He has won the First prize 1 of Group Company Technology Progress Awards, and First Prize 1, Second Prize 4 and Third Prize 3 of Provincial Outstanding Design Awards.

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