

FDS-1 Refined Catalyst Technology of Diesel Oil Hydrogenation

Science & Technology Management Department

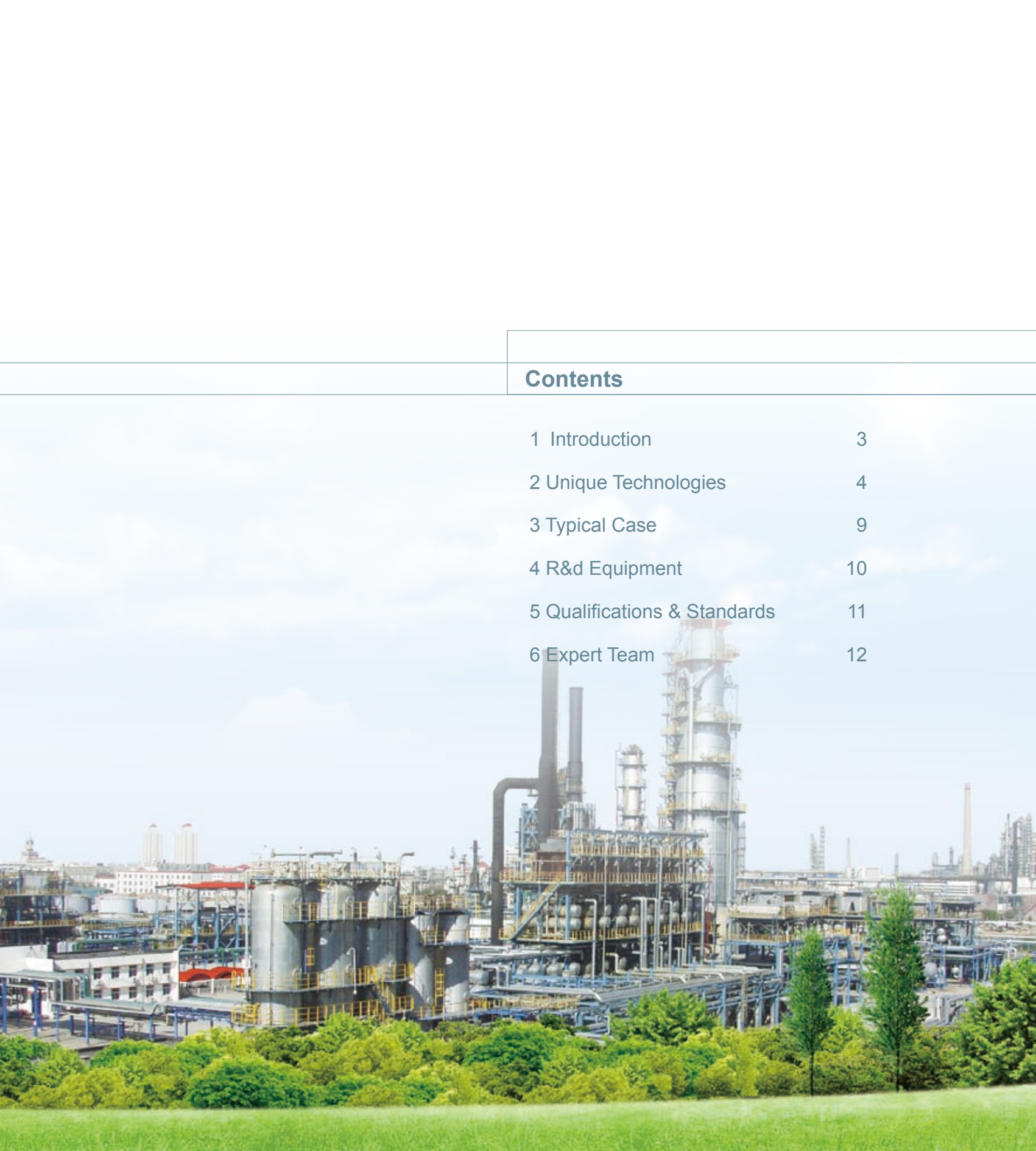
■ 2013



CHINA NATIONAL PETROLEUM CORPORATION

*FDS-1 — The Sharp and Powerful Tools of
Improving Inferior Diesel Oil Quality*





Contents

1	Introduction	3
2	Unique Technologies	4
3	Typical Case	9
4	R&d Equipment	10
5	Qualifications & Standards	11
6	Expert Team	12



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 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.

FDS-1 Refined Catalyst Technology of Diesel Oil Hydrogenation is one of representatives for major innovations of CNPC.

CLEAN ENERGY SUPPLY FOR BETTER ENVIRONMENT

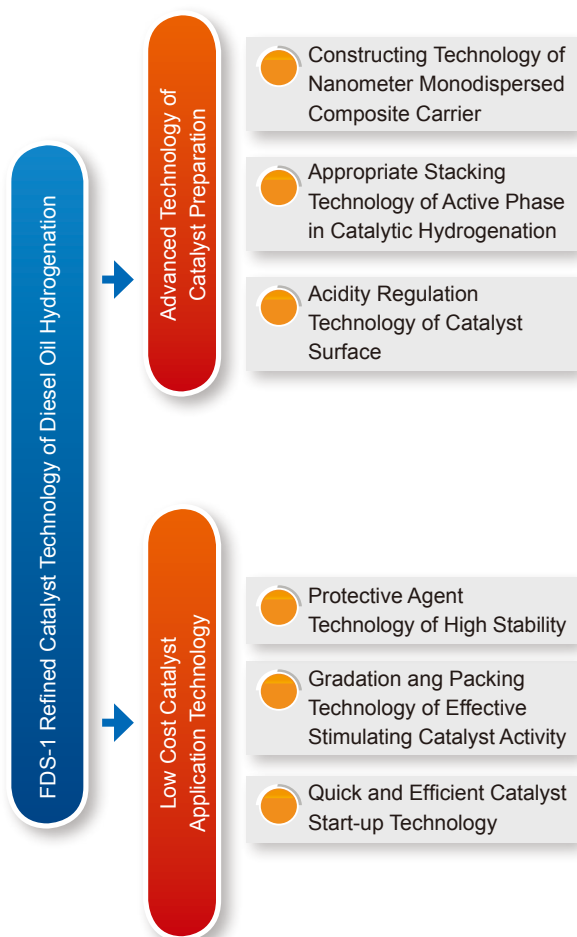
1

INTRODUCTION

CNPC is the pioneer for producing hydrofining catalyst at home. Being the first producer of hydrotreating catalyst in early 1950s, for near 60 years, CNPC has made great contributions to quality upgrading of inferior diesel oil in China.

Started from 2000, in compliance with the trends of global oil refining development and rapid revision on laws and regulations related to clean fuel, CNPC assembled affiliated scientific research institutions for R&D and industrial tests for new inferior diesel oil hydrogenation catalyst.

After years of study and research, important breakthrough was made in preparation of catalyst carrier and catalyst for inferior diesel hydrogenation with success in FDS-1 technology – the deep hydrogenation refined catalyst for inferior diesel oil. Industrial tests were performed in 2009 with final product satisfying National V requirements for clean diesel oil.



2 UNIQUE TECHNOLOGIES

Based on the requirements of fine desulfurization, CNPC succeeded in new generation of inferior diesel oil hydrogenation refined catalyst FDS-1 after years of research and study and breakthrough in catalyst carrier and catalyst preparation technology.

Appearance	Clover Strips
Diameter (mm)	1.2~1.3
Length (mm)	3~8
Edgewise Compressive Strength (N/cm)	160~200
Chemical Composition	
MoO ₃ (%)	22.0~24.0
NiO (%)	4.0~5.0
Pore Volume (cm ³ /g)	0.3~0.4
Specific Surface Area (m ² /g)	180~250
Stacking Density (kg/m ³)	810~850





2.1 Advanced Catalyst Preparation Technology

The performance of catalyst is the key of successful hydrogenation process. Focused on catalyst carrier and technology of preparation, CNPC made breakthrough in improving dispersing performance of metallic constituents on carrier, regulating pore structure of carrier and surface acidity. With the new generation of inferior diesel oil hydrofining catalyst - FDS-1, CNPC provides oil refineries with technical support for low-cost quality improvement of inferior diesel oil.

2.1.1 Constructing Technology of Nanometer Monodispersed Composite Catalyst Carrier

Innovatively proposed and adopted the constructing technology nanometer monodispersed composite carrier which allows homogeneous complex of secondary alumina particles and crystalline particles of nanometer molecular sieve.

To achieve

The composite carrier has larger specific surface area and pore volume, cascaded acid type and acid strength distribution.

2.1.2 Appriat Stacking Technology of Active Phase in Catalytic Hydrogenation

Maximize surface density of II active phase as assuring high dispersion of active phase of NiMoS.

To achieve

- Minimize steric hindrance effect during hydro-desulfurization of most stubborn sulfide (DMDBT), and improve performance of catalyst in deep HDS.
- Improve intrinsic hydrogenation activity of the catalyst, make catalyst be of high hydrogenation capacity to nitrogen-containing compound, and promote fracture response of C-N bond, and finally achieve deep hydrogenation as well as control the inhibitory effect during desulfurization reaction given by organic nitrogen compounds.

2.1.3 Acidity Regulation Technology of Catalyst Surface

Provide “individually characterized” regulation for each catalytic performance during preparation based on composition and molecular structure of target inferior diesel oil, and reaction mechanism of hydrogenation.

To achieve

- Mechanism of simultaneous improvement in performance of deep hydro-desulfurization and hydro-denitrification
- Matching the performance of hydro- dearomatization and selective opening of ring of cyclic hydrocarbon

2.2 Low Cost Catalyst Application Technology

With FDS-1 as core and user application requirements as orientation, CNPC developed quick and easy start-up process. The highly stable protective agent technology significantly restrain increase in catalyst bed pressure drop. The gradation and packing technology maximize performance of catalyst. Specialized package solution in industrial catalyst application is provided to users to prolong normal operation cycle of plants, which significantly reduce catalyst start-up and operation cost, and minimize production cost.



■ Hydrogenation Protective Agent Technology of High Stability

The combination of specialized pore structure and appropriate hydrogenation protection of the protective agent may effectively decrease coking and blockage on catalyst beds.

■ Gradation and Packing Technology of Effective Stimulating Catalyst Activity

This technology provides large operation range for regulation of catalyst temperature at inlet, and delays the deactivation of catalyst at lower bed, and improves the utilization rate of catalyst on reactor beds. Comparing to equivalent diesel oil hydrogenation catalyst in China and abroad, FDS-1 is 10%~15% lower in stacking density, and 10%~15% lower in cost. Heavier and more stubborn

materials can be refined with prolonged operation cycle and catalyst life.

■ Quick and Efficient Catalyst Start-up Technology

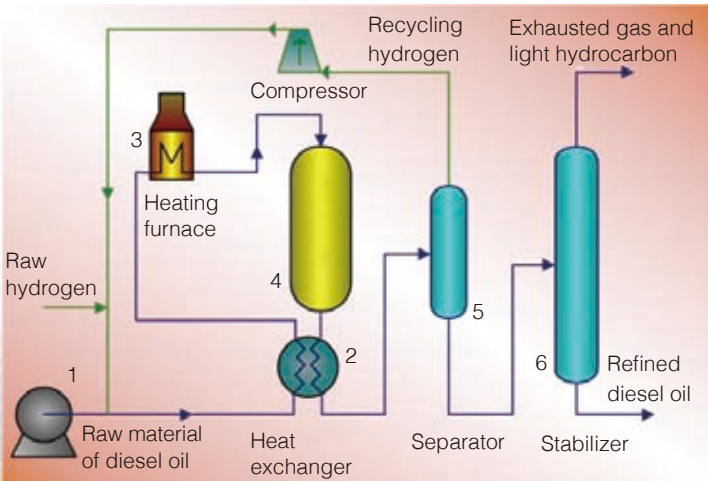
It can significantly reduce risks in start-up and start-up cost.

Application Scope

FDS-1 diesel oil hydrofining catalyst is applicable to deep hydrorefining of diesel oil with medium-low sulfur content, especially deep hydrofining inferior diesel oil (such as naphthenic straight-run diesel oil, coker diesel oil, catalytic cracking diesel oil, or mixture of above). Hydrofined diesel oil can be used as a blending component to National standard V clean diesel oil.

Operating conditions

Reaction Pressure (MPa)	6-8
Volume per hour, h ⁻¹	1.0~2.5
Reaction Temperature (°C)	320~360
Hydrogen-oil Volume Ration	(300~600) : 1



3

TYPICAL CASE

Commercial Application

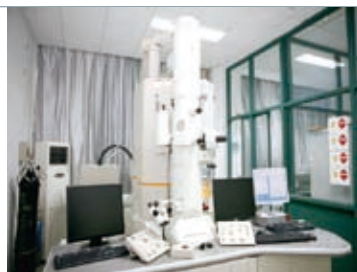
■ The first Industrial application was in 2009 on 500,000 t/y diesel hydrogenation plant at CNPC Dagang Petrochemical with product satisfying National V standard.

■ Following hydrogenation plants are under construction: 800,000 t/y plant at CNPC Changqing Petrochemical, and 1,200,000 t/y plant at Shenghua Refinery of University of Petroleum

Raw materials	Coking+Catalytic Cracked diesel mixture (8:2)
Desulfurization rate (%)	99.4
Denitrification rate (%)	90.4
Cetane number:	51–56
Sulfur content (μg/g)	7
Nitrogen content (μg/g)	132
Achieve to the National V Diesel Standard	



4 R&D EQUIPMENT



The laboratories possess over 30 units of equipments for evaluating performance of catalytic materials, catalyst preparation and hydrofining, which may provide technical support and service for catalyst production plants and users.

CNPC has been granted with over 20 national invention patents in new diesel hydrofining catalyst, with over 200 particularly valuable research paper published, and developed FDS series of hydrofining catalysts for upgrading National Standard V diesel oil.

Catalyst Research Tools

- ① JEM-2100UHR transmission electron microscope by Jeol of Japan
- ② ADVANCE III 400MHz wide cavity solid-state nuclear magnetic resonance spectrometer by Bruker of Swiss

- ③ S4800 field emission scanning electron microscope by Hitachi of Japan
- ④ X'Pert Pro MPD X-ray diffractometer by Panalytical of Netherlands
- ⑤ Multi EA3100 S,N microanalyzer by Jena of Germany
- ⑥ NEXUS in situ reflectance infrared spectrometer by Thermo Nicolet of USA
- ⑦ ASAP2020-M specific surface area analyzer by Micromeritics Instrument of USA
- ⑧ CP3800 refinery gas fast analyzer by Varian of USA
- ⑨ 7890A gas chromatograph (with S,N detector) by Agilent of USA
- ⑩ Pilot test plant for distillate hydrogenation



5 QUALIFICATIONS & STANDARDS

◆ CNPC Possesses following 3 Invention Patents with Proprietary Intellectual Property Rights

- ◎ ZL 03148499.9, A catalyst with molecular sieve for deep hydro-processing of middle distillate and its preparation
- ◎ ZL 03148495.6, A catalyst for deep hydrotreating of distillate and its preparation
- ◎ ZL 03148494.8, A catalyst for deep hydrofining of distillate and its preparation



Developed Enterprise Standard for FDS-1 Diesel Oil Hydro-upgrading Catalyst



ISO 9001 Quality Management System Certification



6

EXPERT TEAM

CNPC is dedicated in research and development of diesel oil hydrofining catalyst with high performance and has a group of specialized talents in R&D, production and after-sale service, various types of advanced equipments for R&D, production and application of catalysts. CNPC provides technical support in diesel oil hydrofining for users.



Liu Chenguang: Professor, expert in hydrogenation. He is currently dean of institute of chemical engineering, University of Petroleum (Huadong), deputy director of CNPC key catalytic laboratory, candidates of first and second elections for “Ten Million Talent Project”. He has been dedicated in R&D of hydrogenation catalysts and catalytic materials with 25 patents of invention granted and over 300 research papers published.

Tel.: 0546-8392280

Email: cgliu1962@sina.com.cn



Fu Xingguo: Professor level senior engineer, senior expert. He has been dedicated in R&D in heavy oil processing and industrial application, R&D in bio-fuel production and industrial production, R&D of clean fuel standards. He has been granted with over 10 Provincial and Ministerial awards for science and technology, over 30 patents of invention in China and abroad, and with over 50 research papers published.

Tel.: 010-52777112

Email: fuxingguo8@petrochina.com.cn



Liu Hualin: Senior engineer. He was granted with Outstanding Contribution Award during reconstruction and expansion of 5,000,000 t/y project at Dagang Petrochemical. He ever participated in and organized work related to a number of plants In catalytic cracking, hydro-cracking, and polypropylene. over 10 research papers published.
Tel.: 022-25979344
Email: liuhualin@petrochina.com.cn



Han Changhong: Senior engineer. She ever participated in design and approval of a number of plants for hydro-cracking, dry hydrogen production, gasoline hydrogenation, catalytic reforming, methanol extract. She organized start-up of plants for catalytic reforming, methanol extract and diesel oil hydrogenation.
Tel.: 022-25968762
Email: hch_tj@petrochina.com.cn



联系人：刁顺 先生
电 话：86-10-5998-6059
Email: sdiao@cnpc.com.cn

Contact: Mr. Diao Shun
Tel: 86-10-5998-6059
Email: sdiao@cnpc.com.cn



