

# **Residue Fluid Catalytic Cracking Technology and Catalysts**

Science & Technology Management Department

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CHINA NATIONAL PETROLEUM CORPORATION

An aerial photograph of a large industrial complex, likely a refinery or chemical plant, situated along a wide river. In the foreground, a suspension bridge spans the river. The industrial facility features numerous tall distillation columns, storage tanks, and processing units. The sky is clear and blue.

*PC would like to provide you with the  
advanced and utility Residue Fluid  
Catalytic Cracking Technology and make  
progress together to promote the worldwide  
residue fluid processing technology!*



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China National Petroleum Corporation (CNPC) is a state-authorized investment agency and a state holding company. As an integrated oil company of cross-regions, cross-industries and cross-countries, it adopts modern enterprise system to realize the integration of upstream and downstream operations, internal and external trade and production and marketing. CNPC has 17 upstream companies, 33 downstream companies and 36 large-scale marketing companies. It is China's largest producer and supplier of oil and gas, and also one of the largest refined oil products and petrochemicals. In 2010 CNPC produced 105 million tons of crude oil and 72.5 billion cubic meters of natural gas, while crude processing volume reached 135 million tons. The total revenue of RMB1,720 billion with a profit of RMB172.7 billion had been achieved the same year. Its profit is among the highest of the domestic enterprises in China.

CNPC was ranked 10th in Fortune Global 500 in

2010 and 5th among global top 50 oil companies.

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.

**Residue Fluid Catalytic Cracking Technology and Catalysts** is one of representatives for major innovations of CNPC.

## CLEAN ENERGY SUPPLY FOR BETTER ENVIRONMENT



# 1

## INTRODUCTION

CNPC, which started R&D in the core technology of catalytic cracking in 1960, is one of the pioneering institutes that engage in the development of catalytic cracking technology and catalyst. CNPC established the first production base for catalyst used in catalytic cracking in Lanzhou in 1964. CNPC's scientific achievements, such as Meta-Y Cracking Catalyst, Moderate Bulk Density LC Catalysts and In-situ Crystallization RFCC Catalyst that were developed successfully for the first time in China, promote China's residue fluid catalytic cracking technology.

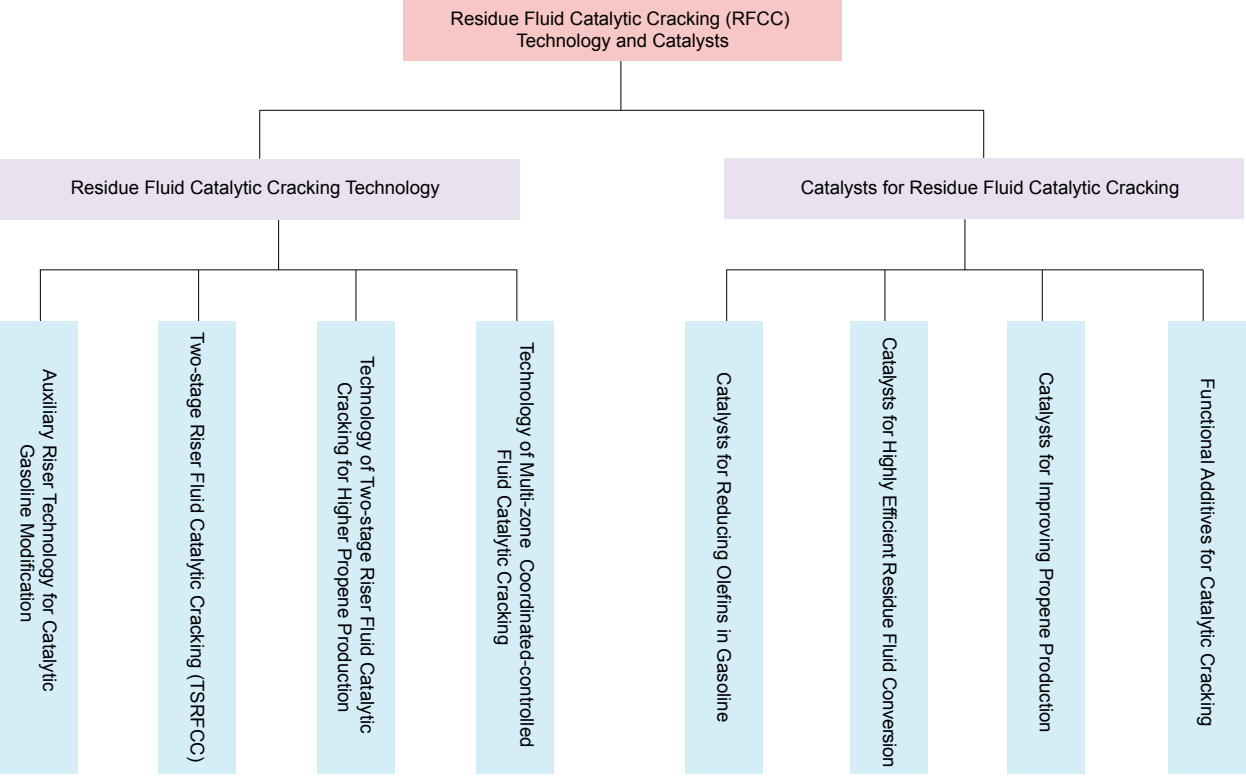
Since 1999, CNPC has been dedicated to R&D and engineering practice of Residue Fluid Catalytic Cracking Technology & Catalysts based on global refining development tendency and domestic refinery demands. Since then, CNPC has developed 26 kinds of unique products and technologies including catalysts for the reduction of olefin in gasoline, highly

efficient residue fluid conversion, higher propene production, catalysts as functional additives in catalytic cracking, Auxiliary Riser Fluid Catalytic Cracking (AFRCC) and Two-stage Riser Fluid Catalytic Cracking (TSRFCC), which cover aspects such as new catalytic material synthesis, catalyst preparation process development, catalyst product technology and catalytic reaction technology.

After years of development, CNPC now possesses a number of talents in R&D, production and after-sales service to provide technical support related to catalytic cracking for customers. The unique technologies and products have been applied in over 40 refining firms at home and abroad. In addition, CNPC owns over 50 patents for invention granted both at home and abroad, the overall technical level of which comes up to that of the internationally advanced.







## 2 UNIQUE TECHNOLOGIES

### 1 Catalyst/Additive Products

Catalysts independently developed by CNPC include products for reducing olefins in gasoline, highly efficient residue fluid conversion and improving propene production as well as functional additives, which satisfy various needs in catalytic cracking of domestic and foreign customers. The specialized technical team can provide pre-sales, sales and after-sales services based on specific requirements and individual refineries to perfectly combine feedstock, operation parameters and catalysts for maximum effectiveness.



Catalyst for Reducing Olefins in Gasoline  
— LBO-12, LBO-16

Development Background

The primary cause for photochemical pollution comes from the olefins in vehicle exhaust. Therefore, it is an important target in the development of catalytic cracking catalysts to reduce olefins in gasoline and satisfy rigorous environmental protection standards.

Introduction

Catalysts (LBO-12, LBO-16) for reducing olefins to produce high-quality gasoline are developed on the basis of advanced CNPC R&D technologies and design platform for catalytic materials and catalysts.

CNPC advises customers to select catalysts for reducing olefins as per specific needs and olefin contents in gasoline.

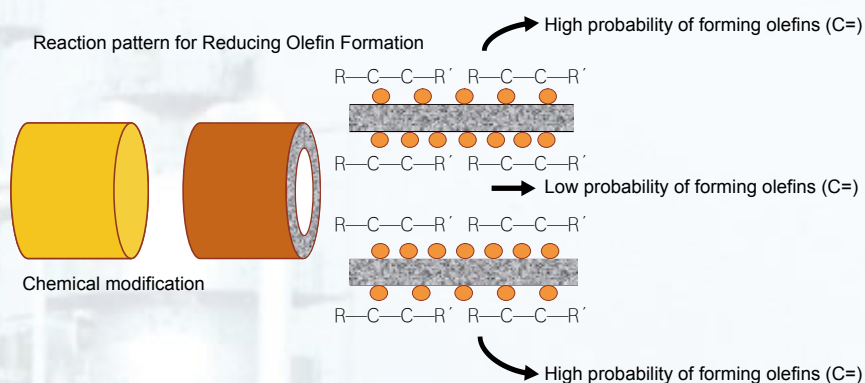


Typical Physical and Chemical Indexes		
	LBO-12 Catalyst	LBO-16 Catalyst
Al <sub>2</sub> O <sub>3</sub> , wt%	≥ 45.0	≥ 45.0
Na <sub>2</sub> O, wt%	≤ 0.35	≤ 0.30
Specific surface area, m <sup>2</sup> /g	≥ 200	≥ 220
Pore volume (droplet method), mL/g	≥ 0.32	≥ 0.34
Micro-activity (800℃ , 4h)	≥ 75	≥ 77



## Unique Technologies

- Olefins in gasoline are controlled at source with the innovative technology platform of “Reaction Pattern for Reducing Olefin Formation in Gasoline” by catalyst which was presented for the first time in China.
- Highly efficient shape-selective molecular sieves of isomerization are used to ensure the improvement of gasoline octane number while effectively reducing olefins in gasoline.



## Major Patents

- (1) ZL 0105235.7 FCC catalyst for reducing olefin content in gasoline and its preparing process
- (2) ZL 02155600.8 Ultrastable Y-type RE molecular sieve active component and its preparation process
- (3) ZL 02155601.6 Olefin cracking catalyst resulting in high diesel oil yield and its preparation

## Scope of Application

LBO-12 Catalyst is applicable to residue fluid catalytic cracking units (RFCCUs) requiring deep olefin reduction.

- Olefins in gasoline reduced by 10%~20% (volume ratio)
- Gasoline octane number unchanged

LBO-16 Catalyst is applicable to catalytic cracking units requiring olefin reduction and increase of diesel oil.

- Olefins in gasoline reduced by 10%~20% (volume ratio)
- Yield of diesel oil improved by over 1.0% (mass ratio)

Commercial Application

LBO-12 Catalyst was put into industrial application in 2000 with the total production of 30,000 tons and has been applied to over 20 catalytic cracking units.

LBO-16 Catalyst was put into industrial application in 2002 with the total production of over 100,000 tons and has been applied to over 40 catalytic cracking units.

LBO-16 Catalyst Applied by CNCP Dalian Petrochemical Company

In 2003, industrial calibration of this catalyst was performed on the 1.4 million t/y residue fluid catalytic cracking unit at Dalian Petrochemical Company. Catalyst for olefin reduction equivalent to that of overseas companies was used for blank calibration.



Item	Catalyst for contrasting	LBO-16	Difference
Diesel oil, wt%	18.4	19.6	+1.2
Slurry oil, wt%	8.2	7.6	-0.6
Yield of total liquid, wt%	79.0	79.4	+0.4
Olefins in gasoline, v%	46.4	40.3	-6.1
Gasoline RON	89.3	89.1	-0.2
Gasoline MON	78.5	79.4	+0.9

## Catalyst for Highly Efficient Residue Fluid Conversion

—LHO-1, LIP-100, LEO-1000

### Development Background

With the increasing scarcity of oil resources, it has become one of the developing directions of oil refining technology to efficiently take use of the existing oil resources, develop deep crude oil processing technology and improve light oil yield.

### Introduction

Catalysts (LHO-1, LIP-100, LEO-1000) for Highly Efficient Residue Fluid Conversion can satisfy the users' requirements for processing different materials to improve the overall liquid yield.

The development of these catalysts is based on the unique CNPC R&D technologies and design platform for catalytic materials and catalysts.

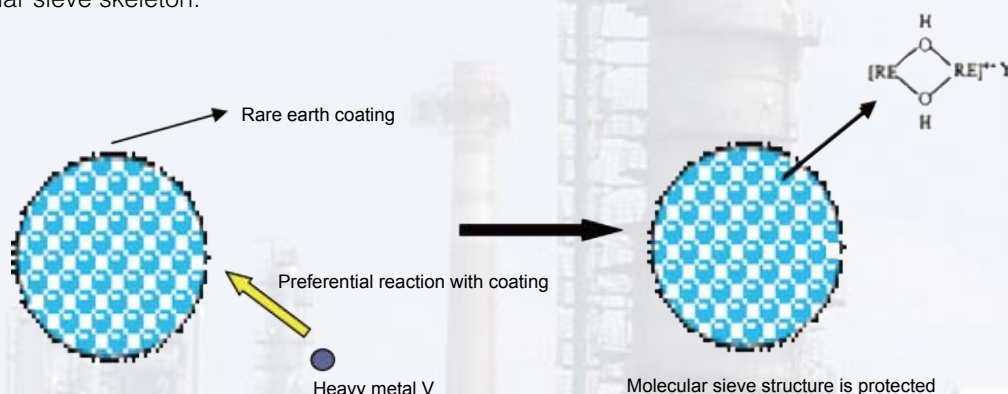


Typical Physical and Chemical Indexes			
	LHO-1 Catalyst	LIP-100 Catalyst	LEO-1000 Catalyst
Al <sub>2</sub> O <sub>3</sub> , wt%	≥ 48.0	≥ 45.0	≥ 45.0
Na <sub>2</sub> O, wt%	≤ 0.30	≤ 0.30	≤ 0.30
Specific surface area, m <sup>2</sup> /g	≥ 240	≥ 220	≥ 220
Pore volume (droplet method), mL/g	≥ 0.35	≥ 0.34	≥ 0.33
Micro-activity (800°C , 4h)	≥ 76	≥ 75	≥ 70

## Unique Technologies

● Special technology for improving the resistance to heavy metal pollution is employed. Inactivation of matrix to nickel and vanadium in the most inferior feedstock is enhanced through the modification on metallic oxides of matrix. In addition, new-type double-aluminum matrix is also used. These can improve the active site accessibility of catalysts and reduce the impact of any change in feedstock properties upon the target product yield.

● Technology for improving the selectivity of catalyst coke is applied. Acid site strength of strong acid is decreased and formation of coke inhibited through adding modified elements to react with aluminum hydroxy in molecular sieve skeleton.



### Major Patents

- |                   |  |
|-------------------|--|
| (1) ZL 98100550.0 | A hydrocarbon cracking zeolite catalyst for capturing vanadium and its preparation |
| (2) ZL 00122003.9 | Heavy metal-resistant new matrix-type cracking catalyst and its preparing process  |
| (3) ZL 02103911.9 | Method of raising the catalytic activity of zeolite molecular sieve                |



## Scope of Application

LHO-1 Catalyst is applicable to RFCCUs for processing the feedstock with high nickel and vanadium contents.

- Content of heavy metals (Ni+V) > 8000ppm
- Iron pollution-resistant
- Olefins in gasoline reduced by over 10% (volume ratio), residue fluid cracking ability improved and overall yield increased by 0.5% (mass ratio)

LIP-100 Catalyst is applicable to RFCCUs for producing clean gasoline with low olefins and high octane number

- While olefins in gasoline reduced, octane number increased by over 1.5
- Overall liquid yield increased by 0.5% (mass ratio)

LEO-1000 is applicable to RFCCUs for processing the feedstock containing high proportion of inferior materials, required to reduce coke yield and with limited carbon-burning load

- Able to be used to process heavy feedstock with Conradson carbon residue (CCR) at 7.0%~9.0%



- Processing capacity improved by over 5% with regeneration temperature in the unit unchanged
- Coke yield reduced by 0.5% (mass ratio)
- Yield of light oils (gasoline, diesel oil) improved by 0.8% (mass ratio)

## Commercial Application

LHO-1 Catalyst was put into industrial application in 2004 and has been applied to over 10 catalytic cracking units in China.

LIP-100 Catalyst was put into industrial application in 2006 and has been applied to 3 catalytic cracking units in China.

LEO-1000 Catalyst was put into industrial application in 2007 and has been applied to 2 catalytic cracking units in China.





### Application of LIP-100 Catalyst at CNPC Jinxi Petrochemical Company

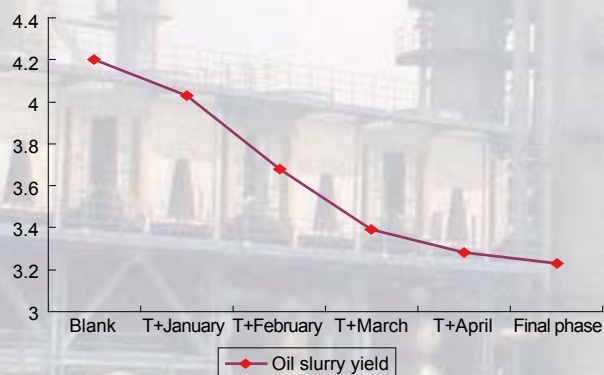
In 2006, industrial calibration for this catalyst was performed on the 1.4 million t/y residue fluid catalytic cracking unit at CNPC Jinxi Petrochemical Company. Residue fluid cracking olefin-reducing catalyst produced by Chinese enterprises was used on vacant calibration unit.

Item	Catalyst for contrasting	LIP-100	Difference
Diesel oil /wt%	23.9	28.4	+4.5
Oil slurry/wt%	3.6	2.7	-0.9
Total liquid yield /wt%	83.7	84.4	+0.7
Propene /wt%	4.3	5.5	+1.2
Gasoline RON	87.5	89.2	+1.7



### Application of LHO-1 Catalyst at CNPC Lanzhou Petrochemical Company

In 2005, industrial calibration for this catalyst was performed on the 3.0 million t/y residue fluid catalytic cracking unit at CNPC Lanzhou Petrochemical Company. Residue fluid cracking olefin-reducing catalyst produced by Chinese enterprises was used on the vacant calibration unit.



## Catalytic Cracking Catalyst for Improving Propene Production

— LIP-200, LIP-200B, LCC-2, LCC-300

### Development Background

Propene is a kind of important basic organic feedstock. Compared with the conventional steam cracking technology, Residue Fluid Catalytic Cracking Technology for Higher Propene Production attracts extensive attention for its abundant feedstock and low cost.

### Introduction

Catalysts for Improving Propene Production (LIP-200, LIP-200B, LCC-2, LCC-300) according to customers' various requirements are developed on the basis of the advanced CNPC R&D technologies and design platform for catalytic materials and catalysts.

CNPC advises customers to select catalysts of specific model for increasing propene production as per specific requirements.



Typical Physical and Chemical Indexes

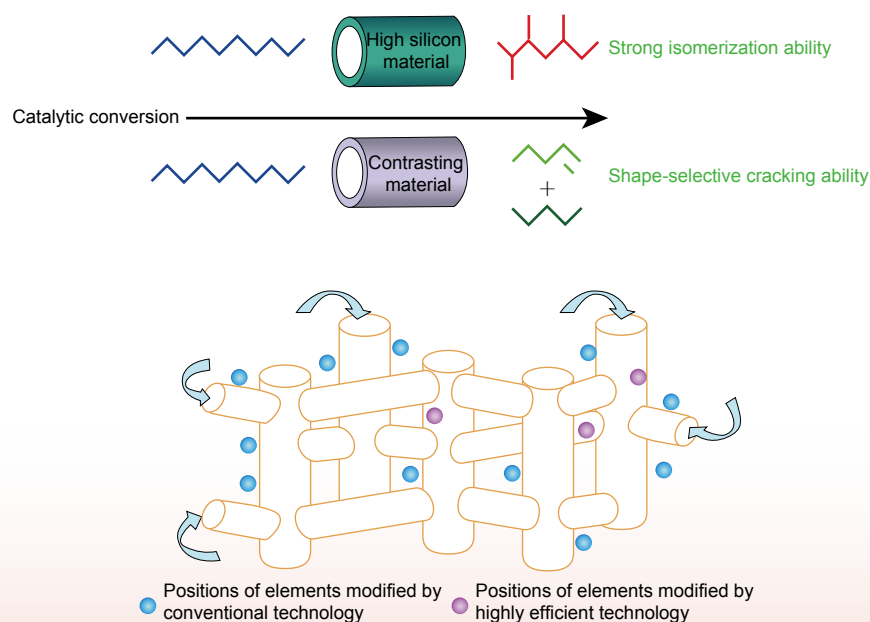
	LIP-200 Catalyst	LIP-200B Catalyst	LCC-2 Catalyst	LCC-300 Catalyst
Al <sub>2</sub> O <sub>3</sub> , wt%	≥ 45.0	≥ 45.0	≥ 45.0	≥ 45.0
Na <sub>2</sub> O, wt%	≤ 0.30	≤ 0.30	≤ 0.30	≤ 0.10
Specific surface area, m <sup>2</sup> /g	≥ 200	≥ 200	≥ 200	≥ 200
Pore volume (droplet method), mL/g	≥ 0.33	≥ 0.34	≥ 0.35	≥ 0.35
Micro-activity (800°C, 4h)	≥ 70	≥ 75	≥ 60	≥ 53

## Unique Technologies

● Technology of Selecting and Controlling ZMS-5 Shape-selective Cracking Components with Different Silicon-aluminium Ratios is applied. It can effectively control the direction and extent of the catalytic secondary reaction to enable the perfect match between isomerization and selective cracking, thereby improving gasoline octane number and propene production.

● Technology of Control on “Short-range Pore Channel Reaction” of Special Shape-selective Molecular Sieve is applied, thus generating the reaction pathway with short residence time and high diffusion rate, controlling the secondary conversion of propene in pore channel and finally improving propene selectivity.

● Technology of “Ion Reverse Migration” is applied, thus preventing the loss of modified elements and improving the activity of shape-selective molecular sieve and selectivity of propene.



## Major Patents

(1) ZL 96114116.6

Catalyst containing modified kaolin for cracking hydrocarbons

(2) ZL 200410088564.1

Hydrocarbon cracking catalyst containing modified faujasite

## Scope of Application

LIP-200 Catalyst is applicable to the catalytic cracking units for producing clean gasoline with low olefin content and high octane number while increasing propene.

- Research octane number (RON) increased by more than 1.5 while olefins in gasoline reduced

- Liquefied gas propene concentration improved and propene yield increased by 0.5% (mass ratio)

LIP-200B Catalyst is applicable to the catalytic cracking units for processing feedstock with high heavy metal content and producing clean gasoline with low olefin in gasoline and high octane number while propene production improved

- Heavy metal content (Ni+V) > 12000ppm

- Research octane number (RON) increased by 0.5 while olefins in gasoline reduced

- Propene production increased by 1.0%

LCC-2 Catalyst is applicable to the catalytic cracking units for significantly improving propene production.

- Applicable to units of wax oil catalyzing, residue fluid catalyzing and units for increasing light olefins

- Propene production under the normal reaction temperature may get to 6%~10wt% according to the properties of feedstock

LCC-300 Catalyst is applicable to the catalytic cracking units that may maximize propene yield.

- Applicable to the catalytic cracking units with the process of improving propene production through two-stage riser or with similar process.

- Propene yield may be over 20wt% under moderate reaction conditions with appropriate process.

- Available to directly produce clean gasoline with octane number over 93.





## Commercial Application

● LIP-200 Catalyst was put into industrial application in 2006 and has been applied to 3 catalytic cracking units in China.

● LIP-200B Catalyst was put into industrial application in 2006 and has been applied to 4 catalytic cracking units in China.

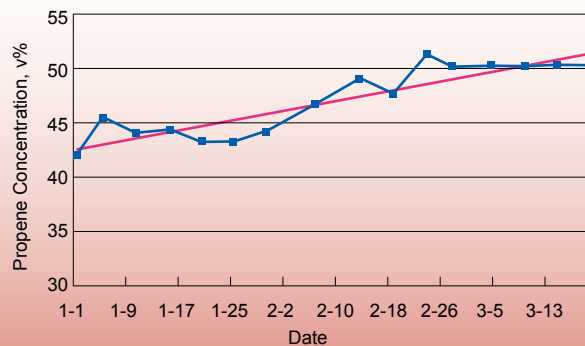
● LCC-2 Catalyst was put into industrial application in 2005 and has been applied to about 10 catalytic cracking units in China.

● LCC-300 Catalyst was put into industrial application in 2008 and has been applied to 1 catalytic cracking unit in China.



## Application of LIP-200B Catalyst at CNPC Lanzhou Petrochemical Company

In 2008, industrial calibration for this catalyst was performed on the 1.4 million t/y RFCC unit at CNPC Lanzhou Petrochemical Company. Residue fluid cracking olefin-reducing catalyst produced by Chinese enterprises was used on vacant calibration unit.





## Functional Additives for Catalytic Cracking —LB-5, LBO-A, LOP-A

### Development Background

It is important to produce customized catalysts with specific properties according to particular requirements for catalysts without changing product distribution.

### Introduction

Functional additives developed on the unique CNPC R&D technologies and design platform for catalytic materials and catalysts can increase gasoline octane number, improve propene production and achieve highly efficient residue fluid conversion, etc.

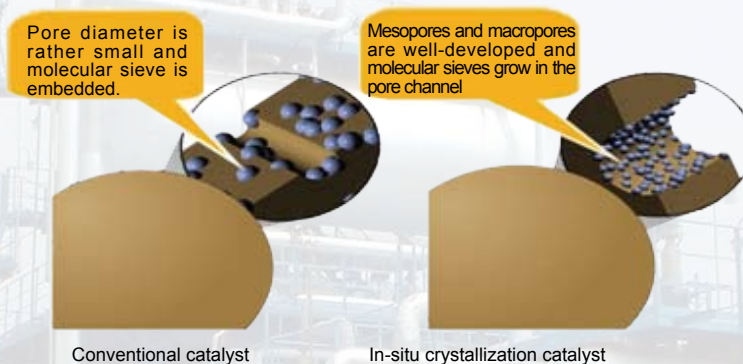
CNPC recommends customers with the above requirements to apply functional additives.



Typical Physical and Chemical Indexes			
	LB-5 Additive	LBO-A Additive	LOP-A Additive
$\text{Al}_2\text{O}_3$ , wt%	$\geq 45.0$	$\geq 45.0$	—
$\text{Na}_2\text{O}$ , wt%	$\leq 0.55$	$\leq 0.30$	$\leq 0.30$
Specific surface area, $\text{m}^2/\text{g}$	$\geq 250$	$\geq 200$	$\geq 180$
Pore volume (droplet method), $\text{mL/g}$	$\geq 0.42$	$\geq 0.33$	$\geq 0.25$

## Unique Technologies

- The proprietary Silica Gel Carrier Technology of  $\text{H}_2\text{SO}_4$ -Waterglass System is applied. The open pore structure ensures product performance. (Apply to LOP-A Additive)
- Technology of Preparing Macroporous Vanadium-resistant Carrier by Kaolin Controlled Thermochemical Modification is applied. The specific surface area and pore volume of catalyst prepared by Special In-situ Crystallization Technology is twice those of the conventional catalyst.
- Zeolite's In-situ Growth and Structure Control Technology in Heterogeneous System is applied to effectively improve the content of active components and accessibility.



## Major Patents

- |                       |  |
|-----------------------|--|
| (1) USP 7390762       | Method for the Preparation of High-content NaY molecular sieves synthesized from kaolin sprayed microspheres |
| (2) ZL 200510069144.3 | Assisted catalyst for catalyzing cracking and preparation process thereof                                    |
| (3) ZL 200510076790.2 | Heavy metal-resistant catalytic cracking adjuvant and process for preparing same                             |

## Scope of Application

LOP-A Additive is applicable to the catalytic cracking units for improving propene production without changing the existing product distribution.

- It can be applied together with other catalysts. Recommended proportion: 2wt%~6wt%.

- Propene yield can be improved by 1.0% and research octane number (RON) of gasoline increased by 0.5 with 5wt% added.

LB-5 Catalyst is applicable to the catalytic cracking units required to improve residue fluid conversion rate and process residue fluid-containing ultra-high heavy metal content.

- It can be applied together with other catalysts. Recommended proportion: 15wt%~25wt%.

- It can be applied after being blended by the manufacturer or by customers themselves.

- Heavy metal-resistant content:  $(\text{Ni}+\text{V}) > 15000\text{ppm}$

- Total liquid yield can be improved by 1.5% (mass ratio) when the adding proportion is 20wt%.

LBO-A Additive is applicable to the catalytic cracking units required to reduce olefins and improve octane number

- It can be applied together with other catalysts. Recommended proportion: 6wt%~10wt%

- Olefins in gasoline can be reduced by 3%~5% (volume ratio) and gasoline research octane number (RON) improved by over 1.0.





Commercial Application

LB-5 Additive was put into industrialization in 2003 and has been applied alone or applied after being blended with other catalysts to 50 catalytic cracking units in China and 2 units abroad.

LBO-A Additive was put into industrialization in 2003 and has been applied alone or applied after being blended with other catalysts to over 20 catalytic cracking units in China.

LOP-A Additive was put into industrialization in 2007 and has been applied alone or applied after being blended with other catalysts to nearly 10 catalytic cracking units in China.



Application of LB-5 Additive at CNPC Lanzhou Petrochemical Company

In 2003, industrial calibration for this catalyst was performed on the 400,000 t/y catalytic cracking unit at CNPC Lanzhou Petrochemical Company. China-made catalyst for high yield of light oil was used as the base component.

Item	Base component	20% LB-5 added	Difference
Equilibrium catalyst			
Ni, ppm	1224	1924	+700
V, ppm	5379	11430	+6051
Consumption, Kg/t	1.81	1.67	-0.14
Light oil yield, wt%	73.05	74.72	+1.67
Total liquid yield, wt%	83.63	84.80	+1.17

## 2 Catalytic Cracking Technology

Unique technologies of CNPC are involved with gasoline modification, increase of total liquid yield, increase of propene production, energy conservation and consumption reduction, which can help you maximize the yield and quality of your target products and achieve the greatest profit efficiency.





## Auxiliary Riser Technology

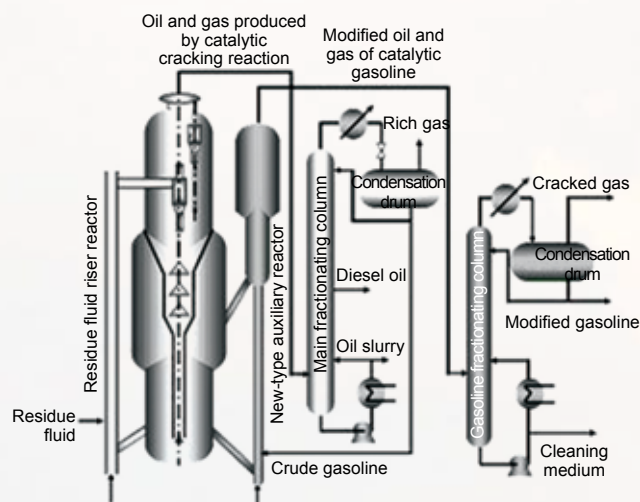
### — Catalytic Cracking Technology for Modifying Catalytic Gasoline and Reducing Olefins

#### Introduction

By using the conventional catalytic cracking catalyst and depending on industry catalytic cracking unit, this technology adds a separate new-type auxiliary reactor to modify catalytic gasoline.

#### Unique Technologies

Technology of “Modification in Different Units” is applied, that is, a separate and exclusive reactor is added for modifying catalytically cracked gasoline and reducing olefins to provide appropriate reaction environment for residue fluid catalytic cracking and gasoline modification & olefin reduction, which not only ensures stable product distribution and quality during the residue fluid catalytic cracking process but also significantly reduces olefins in gasoline.



#### Major Patents

- (1) ZL 02123817.0 Method and system for reducing catalytic cracking gasoline olefine content
- (2) ZL 02146136.8 Method of catalytic gasoline upgrading and lowering olefin hydrocarbon with high light oil yield and its device
- (3) ZL 02146135.X Separation method of catalytic gasoline quality improved oil and gas and its installation
- (4) ZL 02149316.2 Method and device for adjusting and controlling coupling between cracking residue fluid and transnaturing gasoline in high efficiency

## Technical Features

- An auxiliary reactor combining new conveying bed and turbulent bed is equipped on industrial catalytic cracking unit;
- New-type auxiliary reactor for modification may adopt individually optimized technological conditions;
- The intensity of reaction operation and ratio of gasoline modification can be regulated flexibly, yields of liquefied gas and gasoline distillate can be modulated, and propene production can be increased by 3%~6%;

## Technical Indexes

- Olefins in catalytic gasoline can be reduced to less than 20v%, which conforms to the requirements of EU III Emission Standards, with octane number slightly increased.
- The modifying process is with high liquid yield and less gasoline loss which takes less than 1.0wt% of the total feedstock.
- This technological process exerts no negative impact on the residue fluid catalytic cracking process on condition that requirements are satisfied.

## Commercial Application

- This technology is applicable to different types of residue fluid catalytic cracking units.
- It has been applied to 5 residue fluid catalytic cracking units in China with favorable outputs.



## TSRFCC Technology

### —Two-stage Riser Fluid Catalytic Cracking

#### Introduction

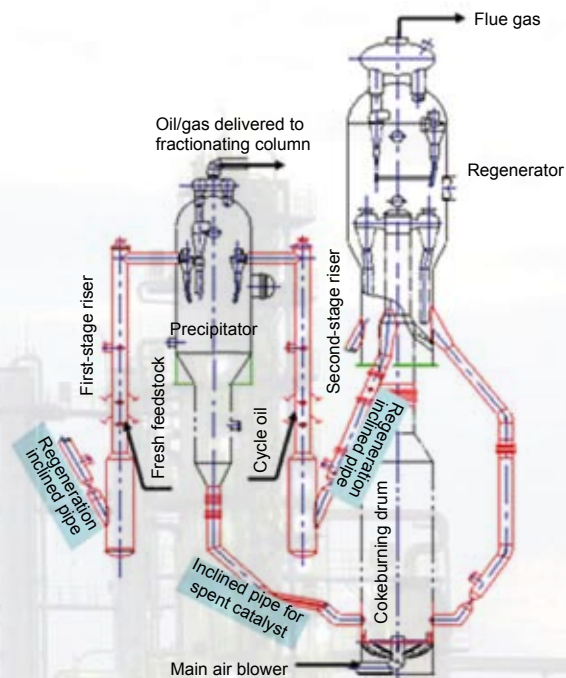
In this technology, two separate riser reactors can effectively prohibit over-cracking, lower coke yield and improve light oil yield and quality.

#### Technical Process

The first stage is for feeding fresh feedstock while the second stage is for the entry of cycle oil, both of which contact with high active regenerant for reaction. This eliminates problems of unfavorable product distribution due to over-long riser and reaction competition between fresh feedstock and cycle oil in the same reactor.

#### Major Patents

- |                       |   |
|-----------------------|---|
| (1) ZL 00134054.9     | Catalytic cracking process with two-stage riser |
| (2) ZL 200410007518.4 | A catalytic cracking method and device thereof  |





## Technical Features

**Staged reaction:** This can prevent reaction competition between fresh feedstock and cycle oil and determine reaction conditions as per the features of individual reactions.

**Catalyst relay:** Catalyst cycles in two paths can improve the overall activity, intensify catalytic reaction and prohibit thermal reaction.

**Short reaction duration:** This can decrease over-cracking of target products, improve product distribution, reduce coke yield and increase light oil yield.

**Operation with high catalyst-oil ratio.** Two-path cycle can form new thermal balance to effectively increase catalyst-oil ratio.

## Technical Indexes

Light oil (gasoline, diesel oil) yield increased by 1.5%~3.0% (mass ratio);

Dry gas and coke yields decreased by 1.5%~2.0% (mass ratio);

Diesel-gasoline ratio can be flexibly adjusted and cetane number in diesel oil can be increased by 3~5.

## Commercial Application

This technology is applicable to process different types of feedstock;

It has been applied to 12 RFCC units in China for long operation cycles.



## TMP Technology

### — Two-stage Riser Catalytic Cracking Technology for Higher Propene Production

#### Introduction

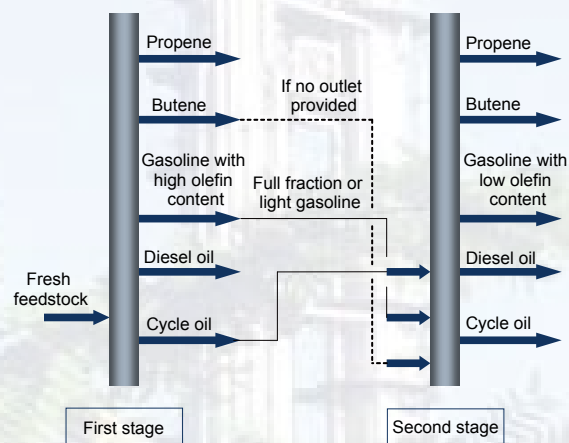
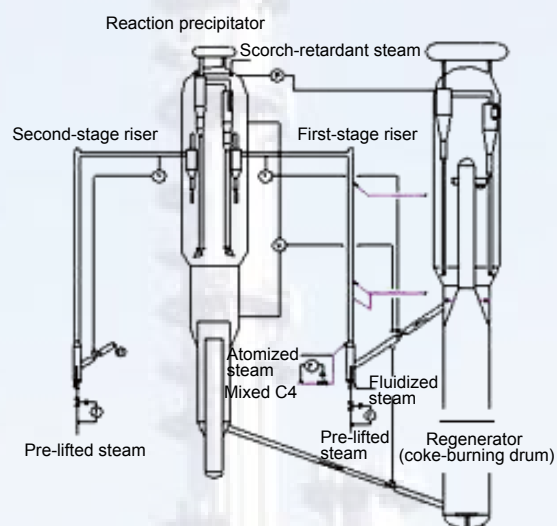
Based on the Two-stage Riser Catalytic Cracking Technology, Residue Fluid Catalytic Cracking Technology for Highly-selective Propene Production and Light Oil Production was developed in view of the demand of higher propene production.

#### Technical Process

New reaction technology with two-stage risers and multiple reaction zones is adopted to achieve the ideal reaction conditions of integrated feedstock delivery, large catalyst-oil ratio under low temperature, appropriate residence time and high catalyst fluidizing density.

#### Major Patents

- (1) ZL 200410096438.0 Selective cracking catalyst for producing low carbon olefin
- (2) ZL 200610080831.X Production of propene and high-quality gasoline and diesel oil by two-stage catalyzed crack





## Technical Features

Low temperature, short reaction duration, high catalyst-oil ratio, prohibition of dry gas formation;

High catalyst fluidizing density

High-density conveying bed reactor

More moderate reaction conditions compared with those of steam cracking

## Technical Indexes

Total yield of coke and dry gas less than 15wt%;

Propene yield no less than 20wt%;

Gasoline research octane number (RON) no less than 93.

## Commercial Application

This technology is applicable to the catalytic cracking units for processing paraffin-based feedstock and maximizing propene production.

It has been applied to a 120,000 t/y industrial demonstration unit for 2 years of long-term operation with the total yield of dry gas and coke at 14.28wt%, gasoline research octane number (RON) 96 and total propene yield at both stages more than 20wt%.



## Industrial Application of TMP Technology at Daqing Refinery

In 2008, industrial calibration for this catalyst was performed on the 120,000 t/y TMP catalytic cracking unit with the matched LCC-300 Catalyst.

Item	Catalyst for contrasting	LCC-300	Difference
Liquefied gas, wt%	39.19	37.34	-1.85
Propene, wt%	17.45	20.38	+2.93
Total liquid yield, wt%	82.47	82.95	0.48

# 3

## R&D AND EQUIPMENT

With catalytic cracking catalysts standing as the core of oil refining industry, CNPC has been dedicated to improvement and innovation in order to promote the technical level and product quality, thereby providing its customers with the most favorable technologies and products.

### Technical Support

CNPC Petrochemical Research Institute

- PetroChina Company Limited is directly subordinate to large comprehensive R&D institute.
- R&D of catalyst was initiated in 1960, which is one of the earliest FCC catalyst development institutes.
- It possesses more than 100 sets of catalyst analysis & evaluation equipment/units including ACE and DCR.
- It possesses internationally advanced and well-equipped pilot test center which can perform different types of pilot tests.
- It possesses a complete technical service system ranging from product research to market technical service and a well-qualified team of professional talents.

### Facility and Equipment

CNPC Lanzhou Petrochemical Company

- Established in 1964, the branch plant for producing catalysts is one of the earliest FCC catalyst manufacturing plants.
- It has created many “firsts” in the history of China’s FCC catalyst production.
- It possesses catalyst production technology with independent intellectual property rights.
- Its main techniques and key facilities and equipment are internationally advanced.
- Its overall annual catalyst production is about 50,000 tons, which, compared with those of the similar Chinese catalysts, takes the lion’s share in the catalyst market.

## CNPC Key Laboratories for Residue Fluid Processing

They initially developed in China Meta-Y Cracking Catalyst, Moderate Bulk Density LC Catalysts, LB Carclazyte Catalysts, etc. which have greatly promoted China's residue fluid catalytic cracking technology.



ACE Reaction Evaluation Unit

More than 70 sets of equipment for analyzing and evaluating different types of catalytic materials, catalysts and catalytic cracking technologies are capable of providing a variety of technical support and services to catalyst manufacturers and customers.

## ACE Reaction Evaluation Unit

Internationally recognized evaluation equipment;  
Rapid catalyst screening;

Capable of successively and automatically evaluating 6 pieces/batches of samples.

DCR Evaluation Unit

Internationally advanced, the only equipment of such kind in China;

Simulating the reaction regeneration successive operation of industrial catalytic units;

Able to conduct the study of catalytic cracking technologies.



DCR Reaction Evaluation Unit



## CNPC Pilot Test Center for Catalytic Cracking Catalysts and Preparation Technologies

The well-equipped pilot test center possesses a complete utility engineering system and over 100 sets of internationally advanced test equipment, with the total value of fixed assets up to RMB 100 million.

The main work at the center covers the synthesis of types of new catalytic materials, modification, FCC catalyst (additive) preparation as well as the pilot test study of process technologies. In addition, FCC catalyst evaluation and catalytic cracking technical study are also carried out.





## Catalyst Plant of CNPC Lanzhou Petrochemical Company

Driven by scientific and technological development, the technical level of main working processes and key equipment of the Catalyst Plant have become internationally advanced, with the overall annual production of mainstream products up to 50,000 tons.

The plant, holding on to the operation objective of “serving more enterprises” and relying on the integration of production, sales and research, has achieved customized serial production as per its customers’ various requirements.



Unit for Molecular Sieve Production and Modification



Advanced Microsphere Production Unit



Proprietary In-situ Crystallization Catalyst Unit

# 4 QUALIFICATION AND STANDARD

CNPC catalytic cracking catalyst manufacturing enterprises have been granted with HSE Certificate.



# 5 DEVELOPMENT HISTORY

- 1960: Research Team for Catalytic Cracking Catalysts was established (Lanzhou).
- 1964: The first unit for producing aluminium silicate pellet catalyst in China (Lanzhou).
- 1965: The first unit for producing microsphere catalyst in China (Lanzhou) and the first fluid catalytic cracking unit were put into operation (Fushun).
- 1970: The first unit for producing 13X molecular sieves in China (Lanzhou).
- 1974: The first riser catalytic cracking unit in China was put into operation (Yumen).
- 1982: The first residue fluid catalytic cracking unit in China was put into operation (Lanzhou).
- 1989: The first in-situ crystallization catalyst unit in China (Lanzhou).
- 2001: LBO Olefin-reducing Catalysts with internationally advanced technology.
- 2002: 3.5 million t/y residue fluid catalytic cracking unit—the largest in China (Dalian).
- 2003: 6,000 t/y ultrastable molecular sieve production unit—the largest in China.
- 2005: LCC Catalysts for Improving Propene Production.
- 2006: Internationally advanced LIP Heavy Oil Catalysts for Improving Propene Production
- 2007: Annual catalyst production and sales volume exceeded 50,000 tons with the largest production and sales capacity per plant in China.
- 2008: Internationally advanced new-type in-situ crystallization heavy oil catalyst.
- 2009: Key heavy oil processing laboratories and pilot test center for catalytic cracking catalysts and its preparation technologies were put into operation.



# 6

## EXPERT TEAM



**Gao Xionghou** CNPC senior technical expert, professor-level senior engineer.

He now assumes the Director of Lanzhou Petrochemical Research Center. He has long been engaged in R&D of refining & petrochemical catalysts and process technologies. He was awarded 2 second-prizes of National Science and Technology Progress Award, granted 35 patents for invention and published over 70 papers. In addition, he was honored Heliang Heli Fund Award for Science and Technology Innovation and the honorable title of "Important Science and Technology Meritorious Master of Gansu Province".

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**Qin Song** Senior engineer, the present Factory Director of the Catalyst Plant of CNPC Lanzhou Petrochemical Company.

He has directed a number of major technological research projects related to the production technology of catalytic cracking catalysts and helped promote CNPC's production technology of catalytic cracking catalysts to the internationally advanced level. He was awarded 3 second-prizes of National Science and Technology Progress Award, made 10 provincial and ministerial-level achievements, applied for 3 patents for invention and published over 20 papers.

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**Mao Xuewen** Professor-level senior engineer, the former Deputy Chief Engineer at Lanzhou Refinery.

He took part in research and production of the first project of silicon aluminium pellet in China which was directed by the academican Min Enze. He directed the establishment and process development of the first unit for producing in-situ crystallization catalyst in China. He was awarded 2 second-prizes of National Science and Technology Progress Award.

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**Liu Conghua** Senior technical expert, professor-level senior engineer, Director of Refining Institute of Lanzhou Petrochemical Research Center.

He is engaged in the development of refining FCC catalysts and relevant technological research. He published over 50 papers domestically and abroad and applied for 23 patents for invention. He won 1 second-prize of National Science and Technology Progress Award, 1 China Patent Excellence Award and made 8 provincial and ministerial-level science and technology achievements.

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**Zhang Zhongdong** Senior technical expert, senior engineer, Director of FCC Pilot Research Institute of Lanzhou Petrochemical Research Center.

He is engaged in refining FCC catalysts and relevant technical development as well as technical production services and marketing promotion. He published over 20 papers in domestic and foreign journals and conferences, applied for 16 patents for invention and won 7 provincial and ministerial-level science and technology progress awards.

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