CHEMICAL ENGINEERING TRANSACTIONS
VOL. 114, 2024

A publication of
AIDIC
The Italian Association
of Chemical Engineering
Online at www.cetjournal.it

Guest Editors: Petar S. Varbanov, Min Zeng, Yee Van Fan, Xuechao Wang

ISBN 979-12-81206-12-0; **ISSN** 2283-9216

DOI: 10.3303/CET24114100

The Development Review on Light Cycle Oil Upgrading Technology to Fuels and Petrochemicals

Xia Liu*, Laibin He

Sinopec Shanghai Research Institute of Petrochemical Technology, Shanghai 201208, China
liuxia.sshy@sinopec.com

Light cycle oil (LCO) is a middle distillate produced in the fluidized catalytic cracking (FCC) unit with a high content of aromatics, high sulfur and nitrogen, and low cetane number, which cannot meet the requirements of diesel blending requirement under the China National VI standard regulation. Hydrogenation is an important technology for LCO upgrading and utilization. By combining hydrotreating (HDT) process, desulfurization and denitrification steps are carried out, and the aromatic hydrocarbons with more than two rings are partially converted into cyclo-alkylbenzene. Combined hydrocracking (HYC) steps, cyclohexane undergoes ring opening, cracking, and isomerization reactions, LCO can be upgrading to producing high quality fuels including high-octane gasoline, and chemical products including light aromatic hydrocarbon rich in benzene, toluene, and xylenes. With the development of upgrading technology, integrating heavy oil hydrogenation with selective catalytic cracking, LCO can produce aromatics, ethylene and propylene, which providing an ideal pathway to valuable petrochemicals from LCO. The upgrading utilization of LCO is an important technological choice for refining enterprises to take their own advantages to enhance valuable products and achieve sustainable development.

1. Introduction

Fluid catalytic cracking (FCC) process is one of the important processes of crude oil in the refining industry, which has been widely used in China due to its high gasoline yield and product flexibility. At present, the domestic catalytic cracking processing capacity is about 200 million tons/year in China. In the future, it is expected that the catalytic cracking units in China will increase production capacity by 20-30 %. The widespread application of catalytic cracking technology has resulted in catalytic diesel accounting for over 30 % of China's diesel fuel. The light cycle oil (LCO) is one of the main by-products of fluidized catalytic cracking units. The LCO yield is approximately 15-20 % of the total FCC products (Peng et al., 2016), while the current total LCO production in China is about 50 million tons/year. However, LCO has the characteristics of high density, low cetane number (15–25) (Peng et al., 2016), high aromatic content, and high impurity content such as sulfur (0.2-1.5 wt %) and nitrogen (100-1,000 ug/g) (Stanislaus et al., 2010). The typical commercial LCO properties are shown in Table1 (Dai,2017).

Table 1: LCO typical properties

Item	LCO-1	LCO-2	LCO-3
Cetane number	22.7	27.8	20
elementary composition			
Carbon, wt%	89.3	89.32	90.42
Hydrogen, wt%	9.66	10.68	9.57
Sulfur, wt%	7400	4100	1700
Nitrogen, wt%	1300	700	200

The difficulty for using LCO directly was finished products stems from the LCO physical and chemimcal properties. The mass fraction of aromatics in LCO is generally between 75-90 % (Laredoet al., 2018), and the typical distribution of LCO aromatics is shown in Figure 1. LCO is commonly used as blend stock for heating

Paper Received: 27 April 2024; Revised: 8 August 2024; Accepted: 17 November 2024
Please cite this article as: Liu X., He L., 2024, The Development Review on Light Cycle Oil Upgrading Technology to Fuels and Petrochemicals, Chemical Engineering Transactions, 114, 595-600 DOI:10.3303/CET24114100

oil, industrial fuel oil, and diesel. Nevertheless, with the improvement of environmental protection requirements and continuous improvement of diesel quality standard, the China VI standard legislation on fuel quality has established the maximum polycyclic aromatic hydrocarbon (PAH) content decrease to below 7 % comparing with the previous China V standard legislation value of 11 wt%, the diesel demands for LCO has been reduced.

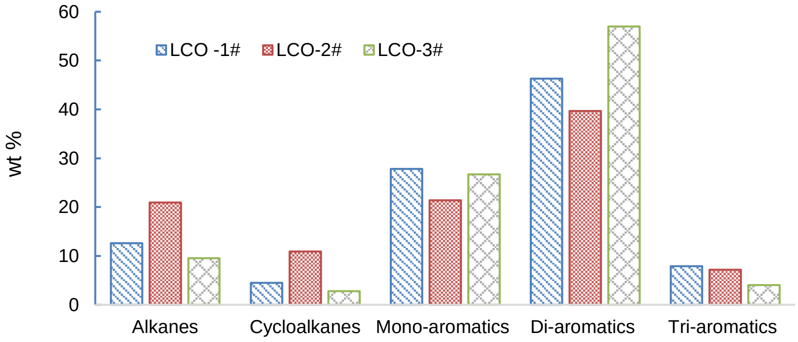

Figure 1: The typical mass fraction distribution of LCO aromatic hydrocarbons

With the proposal of the “Carbon Peak and Carbon Neutrality” goals, China’s energy structure is facing significant adjustment, and the proportion of renewable energy is constantly increasing. Afterwhile, the domestic fuel oil market volume will continue to decline after the peak of the gasoline and diesel in China. Optimizing the utilization of LCO to produce high value-added energy and chemical products is significant for the refining and chemical plants.

Hydrogenation is an important technology to improve the quality of high polycyclic aromatic hydrocarbon (PAH) content LCO. LCO is typically upgraded by hydrotreating units under mild conditions to produce the feed of FCC units, or through severe hydrotreatment to produce high-octane gasoline or ultra-low sulfur diesel (ULSD) contains less than 10 or 15 ppm sulphur (Peng et al., 2016). Combining the hydrotreating and hydrocracking steps, benzene, toluene and xylenes (BTX) are enriched in products fraction (Laredo et al., 2018). With the development of upgrading technology, and integrating heavy oil hydrogenation with selective catalytic cracking, LCO can produce aromatics, ethylene, and propylene. The upgrading utilization of LCO is an important technological choice for refining enterprises to take their own advantages to enhance product value and achieve sustainable development.

2. High quality fuels from LCO

The technologies targeting for producing high-quality fuel using LCO can be divided into two categories: 1) LCO hydrotreating (HDT) and upgrading technology for ultra-low sulfur diesel production, with the target product is diesel. 2) LCO hydrotreating combines hydrocracking (HYC) technology for producing gasoline and ultra-low sulfur diesel, with the target products being gasoline and diesel.

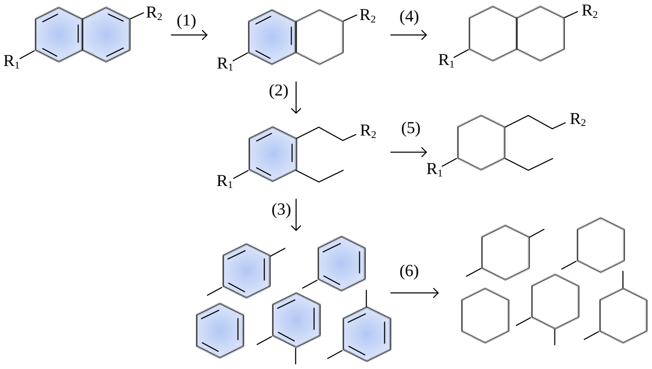

Figure 2: The typical reaction pathways of LCO updating process

The typical reaction pathway of hydrotreaing process is shown in Figure 2, LCO hydrotreating (HDT) pathway: (1)→(2) →(5).

The UOP Unionfining process flow scheme for hydrotreating LCO is typically a once-through process, as shown in Figure 2. The LCO feed is processed over hydrotreating catalysts under hydrogen pressure to affect hydrodesulfurphurization, hydroenitrification and aromatic saturation. Operating conditions conductive for saturating aromatics in LCO are necessary to produce the hydrotreated ultra-low sulfur effluent. The hydrotreating process typically uses an active nickel-molybdenum catalysts with a reactor temperature ranging from 350 to 400 ℃. As a consequence, tremendous saturation reactions occurred during hydrotreating in the reactor.

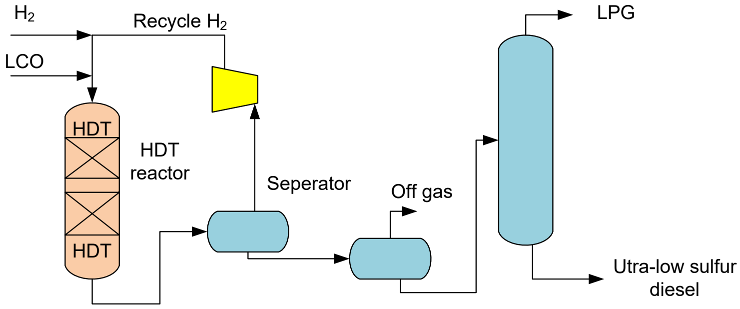

Figure 3: The flowsheet of UOP Unionfining process for LCO targeting utra-low sulphur diesel

MHUG is typical process targeting for producing the diesel using LCO was patented by Sinopec RIPP (Lin, 2019). The feed in MHUG process can be 100 % LCO, or mixture of diesel and LCO. Through hydrotreating and upgrading, polycyclic aromatic hydrocarbons are hydrogenated and saturated, and selective cycloalkane ring opening is carried out to obtained high quality diesel with low aromatic content, high cetane number, and low density.

The LCO hydrotreating combined hydrocracking technology for producing gasoline and diesel is represented by UOP LCO Unicracking (Bisht and Petri, 2014), Sinopec RLG and FD2G technology (Han et al., 2022). The process is applying LCO as the feed, including two-bed catalytic process involving hydrogenation and hydrocracking for producing high-octane gasoline fuel. And relevant reaction pathways are shown in Figure 2, RLG/FD2G pathway: (1)→(2)→(3).

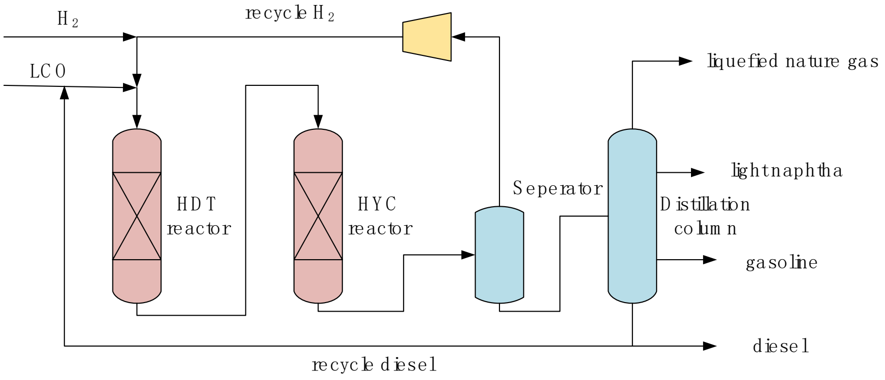

Figure 4: The typical flowsheet of LCO HTD combined HYC process for targeting gasoline and diesel

When LCO is hydrocracked under higher pressure and high conversion into naphtha, the aromatic rings are substantially hydrogenated forming naphtha with a high concentration of naphthenes and a low concentration of aromatics. In addition to reactions that are typical of hydrotreating, hydrocracking also performs alkyl chain cracking and ring opening. The desulphurization, saturation of rings, alkyl chain cracking and ring opening consume larger quantities of ‘make-up’ hydrogen compared to hydrotreating options. And the heat release from these reactions is greater than hydrotreating alone, meanwhile a higher capacity recycle gas compressor are required to manage the catalyst temperature rises.

In the FD2G process, there is a high content of aromatics in the gasoline products, and aromatics can be obtained through aromatics extraction technology. This technology can produce 35-58 % clean diesel with a sulfur content is lower than 10 ppm, a cetane number between 29 and 35, and a cetane index of 36, at the same time, clean gasoline with 92-94 RON can be produced, with the yield of 35-55 %. The typical products distribution in commercial LCO upgrading process is shown in Table 2.

The conventional catalysts required in the hydrotreating step are nickel-molybdenum on alumina ($NiMo/Al_2O_3$) (Fischer et al., 1988) and cobalt/molybdenum on alumina ($CoMo/Al_2O_3$) (Derr et al., 1991). Likewise, ultra-stable zeolite Y (USY) with nickel-tungsten (NiW), NiMo or CoMo, as metal components, were used for the hydrocracking step (Laredo et al., 2018).

Table 2: Products distribution in FD2G process for LCO upgrading (Zheng et al.,2017)

Item	Once-through	Partial recycle	Full recycle
Pressure / Mpa	8.0	8.0	8.0
Temperature /℃	405	415	397
Conversion ratio, %	51	55	50
Gasoline yield, wt%	54.22	53.27	89.65
Diesel yield, wt%	40.81	35.95	-
Aromatics fraction in gasoline	62.01	-	-
Hydrogen consumption, wt%	3.31	3.48	3.99

3. Valuable petrochemicals from LCO

Currently, there is an excess of diesel, however the demand for aromatics and light olefins are increasing year by year. Light aromatics like benzene, toluene and xylene (BTX) are valuable and high demands petrochemicals. Obtaining chemical products from LCO is an ideal way to solve the problem of diesel excess and light aromatics shortage. The production of BTX aromatics from low-quality heavy LCO requires cracking the other aromatic rings while retaining one of the polycyclic aromatic hydrocarbons in the low-quality heavy aromatics, effectively controlling saturation depth and ring opening position, and maximizing the production of light aromatics at lower hydrogen consumption. The LCO hydrotreating combined hydrocracking, or fluidized catalytic cracking (FCC) technology also can targeting for producing valuable petrochemicals, including benzene, toluene and xylene , which is an attractive technology as well.

The technologies targeting for producing light aromatics using LCO also can be divided into three categories:

1) LCO hydrotreating combine hydrocracking technology for producing light aromatics, with the target products being BTX. The product structure of the LCO hydrotreating combine hydrocracking technology process is listed in Table 3. As shown in the table, the yield of high octane gasoline is about 54 %, of which aromatics account for about 60 %, which only requires adaptive modification of the aromatics separation process to be implemented to produce the BTX products.

2) LCO hydrotreating integrated fluidized catalytic cracking technology for producing light aromatics and olefins. LCO is the diesel fraction product of the fluidized catalytic cracking unit, and after hydrogenation pretreatment, LCO is returned to the fluidized catalytic cracking unit, which is a LCO hydrotreating integrated fluidized catalytic cracking conversion. In this conversion scheme, it can reduce the output of low-quality LCO and increase high octane gasoline or aromatics product under low investment.

3) The combination processing scheme of LCO hydrocracking integrated with aromatics maximization targeting for the maximization of BTX. The important step of the scheme is that produced naphtha is sent to the aromatics maximization reaction system and undergoes processes such as cyclohexane dehydrogenation, alkyl transfer, isomerization, xylene separation, and distillation to obtain benzene and xylene products.

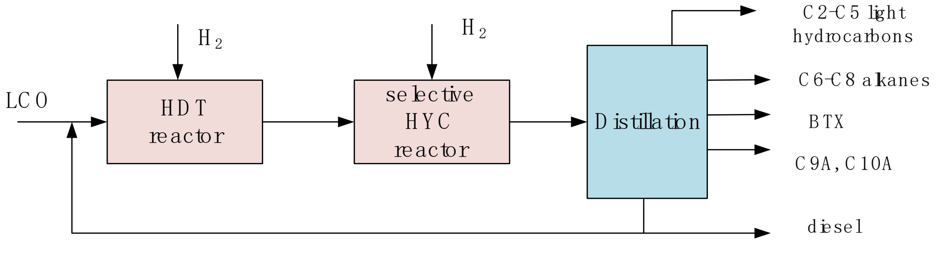

Figure 5: The flowsheet of Sinopec SRIPT LCO HTD combined selective HYC process for chemical materials

Zheng et al. from Sinopec SRIPT patented a process for producing chemical materials from LCO, the flowsheet of the process is shown in Figure 5 (Zheng et al., 2021). The technical solution of the present invention includes hydrotreating and selective hydrocracking technology conversion reaction of LCO feed flow. The selective hydrocracking conversion catalyst includes β zeolite, VIB group metal sulfides, and binders. After separation, the products were sequentially separated into C2-C5 light hydrocarbons, C6-C8 alkanes, benzene, toluene, C8A, C9A, C10A aromatics, and diesel. After the diesel at the bottom of the distillation tower enters hydrotreating reactor. This technology can realize the full fraction conversion of chemical feedstocks from catalytic diesel production has a higher yield of BTX light aromatics, as well as the technical effect of producing chemical feedstocks such as C2-C5 light hydrocarbons and C6-C8 alkanes.

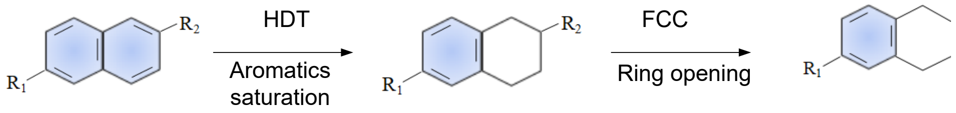

Figure 6: The reaction pathways of LCO HTD combined FCC technology

The LCO hydrotreating combine catalytic cracking reaction pathways are shown in Figure 6. The key of technology is to generated monocyclic aromatic hydrocarbons like tetralin compounds from polycyclic aromatic hydrocarbons in LCO by selective hydrogenation saturated reaction. Then by strengthening hydro-LCO carried on catalytic cracking reaction and inhibiting the hydrogen transfer reaction, hydro-LCO can be converted to high octane number gasoline or light aromatics, ethylene, and propylene (Mao et al., 2020).

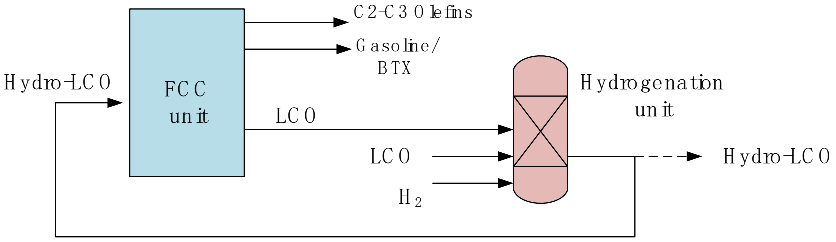

Figure 7: The flowsheet of Sinopec LTAG process for aromatics and gasoline

LTAG (LCO to Aromatics and Gasoline) and LTA (LCO to Aromatics and Gasline) technology is proposed by Sinopec RIPP (Gong et al., 2016). In the LTAG technology the di-aromatics in LCO is selectively hydrotreated in hydrotreating unit to mono-aromatics with tetralin structure. While ring opening reactions are taken place and hydrogen transfer reactions are inhabited in the followed fluidized catalytic cracking (FCC) unit. Applied an optimized combination of two units can achieve maximum production of high octane gasoline or light aromatics. The high octane number gasoline fraction or light aromatics are produced by hydro-LCO individual catalytic cracking. The flowsheet of the LTAG is shown in the Figure 7. The industrial results show that after LCO hydrogenation can achieve full conversion of LCO under full cycle conditions, achieving gasoline yield of 55.87 %, C6-C8 aromatics yield of 16.89 %, and gasoline RON is 96.4 (Gong et al., 2016).

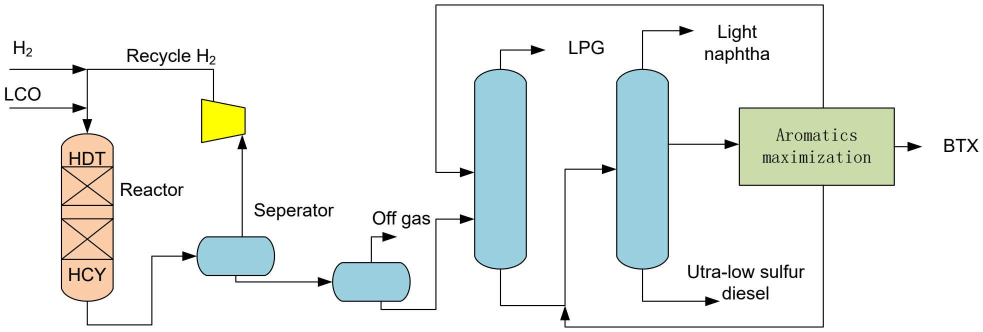

Figure 8: The flowsheet of UOP LCO-X process targeting for the BTX products

UOP company has developed a new process LCO-X for catalytic light cycle oil hydrogenation conversion selective alkyl transfer to produce maximization of xylene and benzene. The principle of LCO-X process is to first refine and remove sulfur and nitrogen impurities from the raw oil, selectively saturate the polycyclic aromatic hydrocarbons, and then enter a series of hydrocracking reactors for selective cracking reaction. The produced naphtha is sent to the aromatics maximization reaction system and undergoes processes such as cyclohexane dehydrogenation, alkyl transfer, isomerization, xylene separation, and distillation to obtain benzene and xylene products. The rest are by-products such as LPG, light naphtha, and utra-low sulfur diesel. Figure 8 shows the process flow diagram of LCO-X technology (Bisht and Petri, 2014). However, this process requires the construction of a series of reaction and the separation units after the hydrocracking reaction, and the whole process is very long.

4. Conclusions

The demand of producing fuels from low-quality diesel will continue to decrease in the future. At the same time, there is a shortage of basic petrochemicals such as benzene, toluene, and xylene (BTX), making it imperative to convert polycyclic aromatic hydrocarbons in LCO into high quality gasoline and light aromatic hydrocarbons to satisfy their increasing demand. Obtaining chemical products from LCO is an ideal way to solve the problem of diesel excess and light aromatics shortage. The production of petrochemicals from low-quality LCO requires cracking the other aromatic rings while retaining one of the polycyclic aromatic hydrocarbons in the low-quality heavy aromatics, effectively controlling saturation depth and ring opening position, and maximizing the production of light aromatics at lower hydrogen consumption. The keys for LCO upgrading are to optimizing the combination of different catalysts and units, maximizing the targeting products, avoiding loss of aromatics. With the development of hydrotreating (HDT) combined fluidized catalytic cracking (FCC) technology, LCO can produce aromatics, ethylene, and propylene, making it a promising choice for refining enterprises.

References

Bisht D., Petri J., 2014, Considerations for Upgrading Light Cycle Oil with hydroprocessing technologies. Indian Chemical Engineer, 56(4), 321-335.

Dai H.L. (Ed), 2017, Aromatic Technology. China Petrochemical Press, Beijing, China (in Chinese).

Derr W.R. Owens P.J. Sarli M.S., 1991, Production of gasoline and distillate fuels from light cycle oil, UA 4, 985,134

Fischer R.H., Huang Y.Y., Lapierre R.B., Varghese P., 1988, Production of high octane gasoline by hydrocracking catalytic cracking products, US 4, 789, 457

Gong J.H., Long J., Mao A.G., Zhang J.X., Jiang D.H., Yang Z., 2016, Development of the LTAG technology for LCO to produce higher RON naphtha and light Aromatics, Acta Petro Science, 32(5), 865-871.

Gong J.H., Mao A.G., Liu X.X., Zhou Q.S., 2016, the Technology of LTAG to produce higher RON naphtha and light Aromatics. Petroleum Processing and Petrochemicals, 47(9), 1-5. (in Chinese)

Han L.N., Chen X.G., Xin J., Yang G.M., Chen Y.F., Fan W.X., Zhang H.H., Zhu Y.B., 2022, Development status and analysis of industrial application technology for value-added and high-value utilization of catalytic diesel oil. Chemical Engineering of Oil & Gas, 51(6), 34-40. (in Chinese).

Laredo F.C., Vega-Merino P.M., Hernandez P.S., 2018, Light cycle oil upgrading to high-quality fuels and petrochemicals: A review. Industrial & Engineering Chemistry Research,57, 7315-7321.

Li D.D., R L., 2022, Development and application of medium pressure hydro-upgrading series technology. Chemical Engineering of Oil & Gas, 51 (5), 1-8.

Lin M.B., 2019, Optimization operation analysis of diesel hydrogenation unit using MHUG technology. Petrochemical Industry Application, 38(8), 115-118 (in Chinese).

Mao A.G., Gong J.H., Tang J.L., Yuan Q.M., 2020, Technical key and practice of producing high octane number gasoline or light aromatics (LTAG) from FCC light cycle oil. Chemical Engineering of Oil & Gas, 49(3), 1-7 (in Chinese).

Peng C., Fang X.C., Zeng R. H., Guo R., Hao W. Y., 2016, Commercial analysis of catalytic hydro-processing technologies in producing diesel and gasoline by light cycle oil. Catalysis Today, 276, 11-18.

Stanislaus A., Marfi A., Rana M.S., 2010, Recent advances in the science and technology of ultra-low sulfur diesel (ULSD) production. Catalytic Today, 153, 1-68.

Zheng J.L., Jiang X.D., Song Q., Li C. Zhou Y.N., 2021, A method and device for efficient production of light hydrocarbons. CN115595175B (in Chinese)

Zheng J.L., Xu X., Qi X.L., Kong D.J., 2017, Low quality heavy aromatic resources and relevant processing technology to produce fundamental petrochemicals. Chemical Industry and Engineering Process, 36(10), 3665-3674 (in Chinese)

Zhou X., Yan W., Zhao H., Liu Y.B., Chen X.B., Yang C.H., 2021, The optimization of two-stage riser fluidized-bed catalytic cracking integrated with LCO deep hydrogenation process. Petroleum processing and Petrochemicals, 52(10), 170-175 (in Chinese).