

# Technical review on flexible processing middle distillate for achieving maximum profit in China

Zhanquan Zhang<sup>1</sup>  · Wei Zhang<sup>1</sup> · Yalin Zhang<sup>1</sup> · Dewei Ji<sup>2</sup> · Haiyan Jin<sup>2</sup> · Gang Wang<sup>3</sup> · Zhihua Zhang<sup>1</sup>

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**Abstract** Currently, refining business is experiencing a transformation from refining to chemical business, or integration of refining and chemical business due to the slow economic growth, and decreased demand of clean fuels, particularly diesel product. Diesel products are over-supplied based on the consumption data in China. Refineries are pursuing technologies that could reduce diesel output, particularly the inferior light cycle oil (LCO) fraction. Herein, this article mainly describes the industrialized technologies for LCO processing such as LCO upgrading, LCO blending into available plants such as fluid catalytic cracking (FCC), and hydro-refining/treating unit, LCO moderate hydrocracking, and LCO to aromatics and gasoline with the integration of selective hydro-refining and optimized FCC. It is figured out that the LCO moderate hydrocracking can provide more gasoline at the expense of high H<sub>2</sub> consumption, while LCO to aromatics and gasoline (LTAG) technology needs more steps for clean fuel production and retrofitting of FCC plant. Based on the analyses of current technologies, it is suggested that implementation of such technologies should consider the configuration of refineries, as well as the benefit of

employed technologies instead of realizing the target for decreasing diesel product unilaterally.

**Keywords** Middle distillate · Processing · Diesel · Transformation · LCO fraction

## Abbreviation List

LCO	Light cycle oil
FCC	Fluid catalytic cracking
LTAG	Light cycle oil to aromatic and gasoline
PX	p-xylene
LPG	Liquefied petroleum gas
SRGO	Straight-run light gas oil
LCGO	Light coke gas oil
HC	Hydrocracking
BTX	Benzene, toluene, and xylene
HCO	Heavy cycle oil
RIPP	Sinopec Research Institute of Petroleum and Processing
FCC-LTG	Fluid catalytic cracking-light light cycle oil to gasoline
VGO	Vacuum gas oil
FRIPP	Fushun Research Institute of Petroleum and Processing
FFI	FCC and FFHT integration technology
SFI	S-RHT and FCC integration technology
MCI	Maximum cetane increase technology
CN	Cetane number
MHUG	Medium pressure hydro-upgrading technology
FD2G	FRIPP diesel to gasoline technology
RLG	RIPP LCO to gasoline technology
FDHC	FRIPP diesel hydrocracking technology
FD2J	FRIPP diesel to jet fuel technology

✉ Zhihua Zhang  
zhangzhihua@petrochina.com.cn

<sup>1</sup> Petrochina Petrochemical Research Institute, Beijing 102200, China

<sup>2</sup> Petrochina Dagang Petrochemical Company, Tianjin 300280, China

<sup>3</sup> Petrochina Petrochemical Research Institute, Daqing Chemical Engineering Research Center, Daqing 163714, China

BHCI	Bureau of mines correlation index
FCA	Fluid catalytic aromaforming
USY	Ultra-stable Y

## Introduction

Regarding the market of traditional fuel and petrochemical product, China's market is strongly relevant to the development of petrochemical industry and also demonstrates a distinctive difference compared with other countries. With the economic growth slowing down, the stagnant consumption of diesel features a negative trend by 5.8%. Other peripheral circumstances also motivate the revolution of China's petrochemical configuration since 2015: (1) the cliff drop of crude oil from 100 to 40 \$/barrel, and this scenario will continue for a long time; this new normal status requires the refinery to explore a new approach to increase its profit by tailoring its configuration without major revamping; (2) the price difference between gasoline and diesel necessitates the adjustment of the ratio between gasoline and diesel, increasing the output of gasoline and decreasing the diesel output, the ratio between diesel to gasoline is projected to be 1.0 in 2020, with a drop from 1.5 in 2015; (3) the growth of jet fuel also motivates the transformation of the refinery, according to the data from National Statistic Bureau: the jet fuel consumption shows an increase by 17.4 and 9.2% in 2015 and 2016, respectively. It is estimated that jet fuel production will increase to 71.27 mega tons; (4) the increasing demand of olefins ( $C_2^=/C_3^=$ ), and aromatics with a high economic benefit accelerate the adjustment from refining-dominant process to chemical business-dominant configuration. The demand of ethylene will be 45.5 mega tons, and the estimated production ability is around 32.3 mega tons in China [1, 2]. In terms of PX demand, China now can only provide 50% of the total demand [3].

To be prepared for the transformation, the direct way is to reduce the production of diesel fraction and increase the production of LPG, gasoline, jet fuel, or ethylene feedstock in addition to the facility optimization. This review mainly summarizes the technical development of middle distillate processing for maximum profit in China.

## Properties of middle distillate/diesel

According to the composition of diesel pool in China, the diesel pool is mainly composed of straight-run light gas oil (SRGO), light coke gas oil (LCGO), and diesel from hydrocracking, light cycle oil (LCO), diesel from residue oil and/or vacuum gas oil hydro-processing plant. The

proportion of each component may vary, depending on quantity of each fraction and product standard (Sino IV, V and VI) [4], management of storage, and transportation section. Table 1 summarizes the proximate properties for each component [5–7] (Fig. 1).

Obviously, HC diesel is a superior clean diesel fuel. SRGO accounts for a large proportion, easing the burden for achieving Sino VI standard for diesel with less hydrogen consumption due to its rich abundance in paraffins and naphthenes. In terms of LCGO fraction, its quality can be improved with hydrogenation unit operated at medium pressure with the removal of sulfur, nitrogen, and polyaromatics. However, light cycle oil produced from FCC unit is a inferior diesel feedstock because of its high aromatics, particularly polycyclic aromatics, and high density, resulting in high difficulty to reduce its aromatic concentration at the cost of excessive  $H_2$  consumption without significant improvement of cetane number (up to 8 ~ 10) [8]. Figure 1 provides an explicit description of group component including saturated and unsaturated hydrocarbons for diesel fraction.

As aforementioned, figuring out an effective and economic way to process the excessive diesel distillate towards the production of valued petrochemicals can bring out high benefit. Accordingly, it is of importance to understand the component for diesel processing since molecular management becomes more dominant in the design of process. SRGO and LCO are employed for comparison. SRGO fraction is richer in paraffin and naphthene than LCO [9–11], while LCO is highly concentrated in mono-aromatics and di-aromatics. According to the analysis of group component, SRGO fraction can be converted to jet-fuel, liquefied petroleum gas providing  $C_3/C_3^=$  and  $C_4/C_4^=$  feedstock, light naphtha as the feedstock of ethylene cracking, and heavy naphtha as the reforming feedstock by using paraffin and naphthene component via a hydro-isomerization or mild hydrocracking pathway. By contrast, due to its characteristic of rich aromatics, LCO can be processed via hydrogenation along with cracking to generate gasoline with high octane number or other lighter components. Since processing LCO and decreasing the quantity of diesel is relatively challenging during the upgrading of Sino V to Sino VI, this review mainly focuses on the invented technologies processing LCO fraction, as well as the technology analysis.

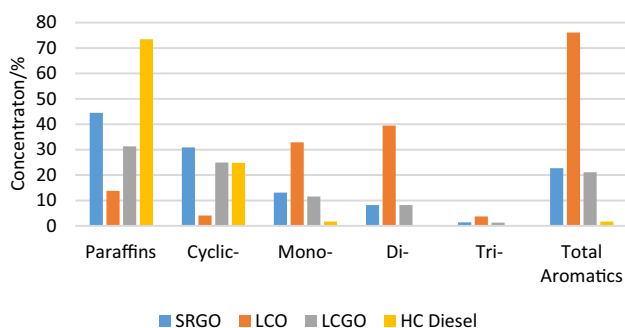
## Diesel blending into current refinery unit

To realize the transformation and adjustment of clean fuel consumption influenced by the economic development from twelfth to thirteenth period, it is not ideal and realistic to rebuild or retrofit more processing units that can

**Table 1** Typical properties of individual component in diesel pool

	SRGO	LCGO	LCO	Diesel from residue unit	HC diesel	Sino VI standard
Proportion, %	58.9	9.73	17.81	1.63	11.92	–
Density, g/cm <sup>3</sup>	0.79 ~ 0.85	0.82 ~ 0.84	0.87 ~ 0.93	0.84 ~ 0.87	0.79 ~ 0.84	0.820 ~ 0.845
Sulfur, µg/g	200 ~ 15,000	1000 ~ 9000	1000 ~ 5000	50 ~ 300	< 10	< 10
Nitrogen, µg/g	20 ~ 800	1000 ~ 4000	600 ~ 3000	40 ~ 300	< 10	
Cetane number	50 ~ 54	48 ~ 51	≠35	45 ~ 47	> 55	≠ 51 <sup>a</sup>
Polycyclic aromatics, %	8 ~ 11	9 ~ 12	40 ~ 50	4 ~ 6	1 ~ 5	≠ 11

<sup>a</sup> This value is cited for 0# diesel

**Fig. 1** Group component analysis for typical diesel distillate

generate more lighter clean fuels such as gasoline or jet fuels with financial investment. The refinery and research institute provide several strategies by employing co-processing or process integration based on the current layout, to adjust the ratio of diesel to gasoline and ease the burden of selling diesel product; of note is the fact that the diesel blending technology can be easily implemented by refineries themselves.

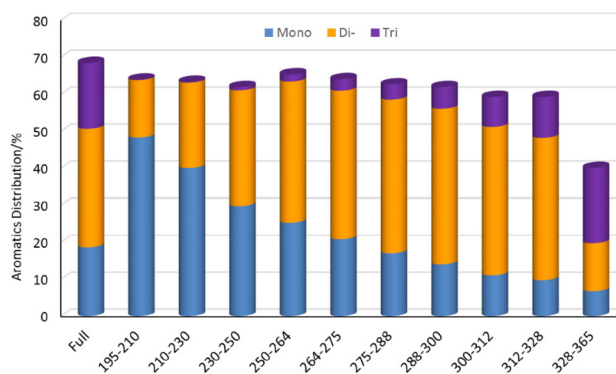
### Diesel direct recycling in FCC unit

Fluid catalytic cracking facilities can process crude atmosphere residue, vacuum residue, as well as vacuum gas oil, accounting for 30% of China's current refining ability, and acting as the main contributor (ca. 70%) of China's gasoline pool. 30 ~ 50 wt% gasoline can be produced in FCC unit. Therefore, utilizing FCC unit to convert diesel fraction to lighter fraction seems a plausible pathway for tailoring the ratio between gasoline and diesel.

Since FCC operation can work with a tailored recycling ratio in which heavy cycle oil (HCO) can be re-cracked via a recycling line with fresh feedstock, FCC diesel (LCO) can also be included by extending the true boiling point (TBP). It is expected to recycle all FCC diesel cut; however, the characteristic of rich di-aromatics, low hydrogen content, high C/H molar ratio, as well as the difficulty in β-scissions of endocyclic carbon–carbon bonds [12], make it

unrealistic due to the low conversion towards gasoline and liquefied gas. By analyzing the group component of FCC diesel in a narrow distillate cut, mono-aromatics that can be cracked into aromatics and C<sub>3</sub>/C<sub>4</sub> are highly concentrated in the lighter fraction (HK to 250 °C), while di-aromatics are mostly dominant in the heavy fraction (260 °C ~ KK) [11] (Fig. 2). With the increasing of TBP, the concentration of mono-aromatic decreases, showing a reverse trend in comparison of di-aromatics. Considering the cracking activity of di-aromatics, RIPP measured the catalytic cracking performance of light LCO cut, heavy LCO cut, and full LCO cut summarized in Table 2 and Fig. 3.

Under identical conditions, the product distribution of three cuts is illustrated in Fig. 3. Compared to traditional catalytic cracking of gas oil with a gasoline yield of 40 ~ 50 wt%, the overall gasoline yield of full cut #3 achieves 22.75% along with a conversion of 42.33%, while cut #1 and cut #2 obtain a gasoline yield of 39.3 and 14.13%, and their conversion of 57.94 and 35.02%, respectively. The discrepancy in product distribution indicates that FCC diesel is less cracked compared with paraffin-rich gas oil, and aromatics is inclined to generate dry gas and heavy oil such as slurry, thus inhibiting the conversion. The higher the di-aromatic concentration, the lower the yield of gasoline. It is reasonable to recycle FCC diesel fraction containing richer mono-aromatics instead of

**Fig. 2** The group component as a function of narrow distillate range

**Table 2** Group component analyses for different distillate ranges of LCO fraction

Items	LCO cut #1	LCO cut #2	LCO cut #3
Density, kg/m <sup>3</sup>	908	975.2	950.9
Group component/wt%			
Paraffins	13.1	10.3	11.1
Naphthene	4.6	4.8	4.0
Total aromatics	82.3	83.9	84.9
Mono-aromatics	42.6	12.2	22.9
Di-aromatics	38.9	59.9	53.9
Distillate range			
HK/50/95%	169/233/277	246/303/368	161/277/363

<sup>a</sup> In the period of implementation of FFI technology, the total processing amount of gas oil was 56, 802 tons, while the treated of FCC diesel equals to 3714 tons accounting for 6.14% of the co-processed feedstock

di-aromatics for achieving high conversion towards gasoline and LPG. RIPP thus developed FCC technology named FCC-LTG in which light LCO cut is recycled with fresh feedstock to achieve high gasoline [14]. A commercial trial with FCC-LTG confirms the processing LCO diesel fraction; compared with blank test, a feedstock with 3.1% light LCO fraction achieved an increase by 1.5% of gasoline yield.

Converting full cut of FCC diesel fraction without any pre-treatment is not practical due to its less pyrolysis ability. To improve its cracking ability, H<sub>2</sub> pre-treatment along with the formation of naphthene is mainly discussed in the following section.

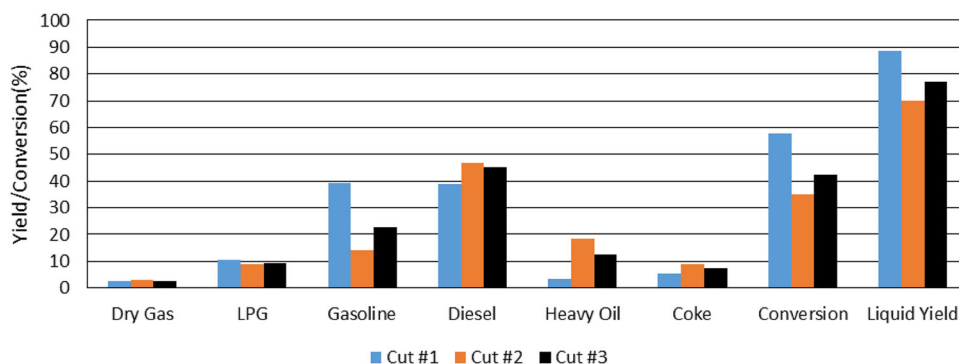
### Diesel blending in gas oil hydrocracking unit

Hydrocracking unit in refineries processes vacuum gas oil with the boiling point less than 550 °C, providing the main products such as light naphtha, heavy naphtha, jet fuel, diesel as well as FCC feedstock, ethylene feedstock, or lubricant feedstock based on the served catalysts including naphtha type, flexible type, middle-distillate, and

unconverted oil type [12]. The catalyst normally serves in active phase with a period of 3 years. During the past twelfth plan, most hydrocracking units were targeted to maximally generate middle distillate; as such, it is probably difficult to purchase new catalysts if not necessary for adjusting the ratio between diesel and gasoline.

To tailor the gasoline and diesel output in addition to process optimization, blending diesel, especially light cycle oil into the current hydrocracking unit can process LCO fraction and generate clean diesel [15, 16]. Considering the naphthalene or its analogue as the main component in LCO, the involved mechanism is simply demonstrated as follows using naphthalene as the molecule model: (1) hydrogenation of naphthalene with the formation of tetralin, as well as decalin at high H<sub>2</sub> partial pressure (< 12 Mpa), (2) cracking of tetralin and decalin into butylbenzene and butylcyclohexane, as well as consecutive cracking with the formation of cyclohexane. Since hydrocracking normally operates at a high pressure, this facilitates the hydrogenation of naphthalene, as well as the hydrogenation of tetralin, correspondingly decreasing the aromatic content in heavy naphtha. Upon blending diesel into the current hydrocracking system, the following suggestions should be taken into consideration: (1) the catalyst type determines the net conversion of LCO diesel, it is not expected to achieve high net conversion on a middle distillate type catalyst (e.g., HC-115/HC-120, UOP); (2) despite the conversion from LCO diesel to light fraction, more than 5 wt% H<sub>2</sub> based on the LCO weight is consumed; therefore, the refinery's H<sub>2</sub> balance and the capacity of H<sub>2</sub> compressor should be optimized or calculated when considering implementation of blending technology; (3) diesel blending into hydrocracking unit needs cooperation of processing parameters, such as the inlet temperature, as well as the fractionating system; (4) due to the rich aromatics, the blending ratio should be optimized to guarantee the quality of products, since the content of aromatic influences smoking point of jet fuels. In addition, the jet fuel regulation restricts that the ratio of secondary processing feedstock should be less than 15%.

**Fig. 3** The product distribution of catalytic cracking of FCC diesel fraction in a pilot scale [13]



One hydrocracking facility introduced LCO components into hydrocracking unit which used to process VGO fraction: after blending 7.8% LCO into VGO fraction and subtracting corresponding amount of VGO, it is found that the middle distillate was reduced by 4.4% and the heavy naphtha and tail oil showed an increase by 0.5 and 4.1%, respectively. In terms of jet fuel and diesel, the smoking point decreased by 1 mm, and the cetane number was reduced by 3 units.

### Diesel blending in gas oil/residue oil hydroprocessing unit

The configuration of hydro-processing of gas oil and residual oil is to improve the properties and qualities of crude oil such as vacuum gas oil, coke gas oil rich in basic nitrogen, sulfur and aromatics, and residue oil with high concentration of Ni, V, sulfur, nitrogen, colloids, and asphalts which can deactivate FCC catalysts and correspondingly decrease catalysts' activity. Normally, gas oil hydro-processing normally operated at high H<sub>2</sub> pressure, depending on the type and properties of gas oil, while residue oil operates at a pressure higher than 14 Mpa with a low space velocity.

By utilizing the available gas oil hydro-processing unit, full LCO cut can be blended with inferior gas oil, followed by H<sub>2</sub> hydrogenation as the FCC feedstock [17]. SINOPEC FRIPP institute developed FFI technology in which FCC LCO was recycled into gas oil hydro-processing unit instead of recycling back into FCC unit, and the generated hydro-treated diesel, including the diesel from FCC diesel and moderate cracking of gas oil, can be totally delivered to FCC unit by removing the fractioning tower. Table 3 summarizes the characteristic of FFI technology developed by SINOPEC FRIPP institute. During the period of implementation of FFI technology in a refinery, 1712 tons of FCC diesel were converted to LPG, gasoline, and coke; it is estimated that the conversion of diesel to other products is 46.1%, and the selectivity towards gasoline and LPG is close to 90%. Apart from the change of product

**Table 3** Production distribution of FFI technology in a refinery

	FFI/tons	FFHT-FCC/tons	Difference/tons
Dry gas	1764	1669	95
LPG	13,235	12,836	399
Gasoline	45,102	43,959	1143
Diesel	18,184	19,896	– 1712
Slurry	1583	1687	– 104
Coke	4642	1224	418
Loss	246	238	8.14

distribution of FCC unit, the energy consumption of gas oil processing unit and FCC unit decreases from 8.04 to 4.36 kg Oil/t, and the energy consumption of FCC unit shows the same trend with a decrease from 53 to 47.55 kg Oil/t.

Identical to gas oil processing, residual oil hydro-processing can also provide atmosphere for hydrogenation [18]. In addition to the hydrogenation of aromatic component, the introduced FCC diesel due to its abundant diaromatics can also dissolve asphalt in residue, preventing the precipitation of asphalt from dissolved phase and decreasing the viscosity that can enhance the hydrogenation ability. As such, the co-processing technology provides a bi-directional benefit. Tables 4 and 5 present SFI condition and production distribution in Jinling Petrochemical Company that co-processed FCC diesel and residue oil. By comparison, the integrated SFI technology demonstrated an increase of gasoline by 2.15%, and diesel with an increase of 1.68%, and correspondingly coke decrease by 2.81%.

Although SFI technology can improve the diesel quality, and realize the conversion from diesel to lighter fraction, SFI seems a comprised approach, in which the conditions required for residue hydrogenation and FCC diesel are not commensurate. In addition, among the hydrogenation involved technologies, FCC diesel is normally treated with other feedstock, and the conditions are not optimized towards less energy consumption, less H<sub>2</sub> consumption, and valued products.

**Table 4** Processing parameters for SFI technology

Items	Without FCC diesel recycling	SFI
FCC diesel flow rate, t/h	0	26.6
Total inlet, t/h	228.9	240.7
First reactor pressure, Mpa	17.9	17.9
Average temperature, °C	397.9	399.1

**Table 5** Production distribution of SFI technology

	Without FCC recycling	SFI	Difference
Production distribution, wt%			
Dry gas	5.22	4.65	– 0.57
LPG	19.47	18.58	– 1.16
Gasoline	41.37	43.52	+ 2.15
Diesel	19.75	21.43	+ 1.68
Slurry	5.03	3.43	– 1.6
Coke	6.96	4.15	– 2.81
Light oil yield, wt%	61.12	64.95	
Liquid oil yield, wt%	80.59	83.53	



## Individual middle distillate processing technology

In this section, technologies that convert individual diesel fraction to lighter fractions in an individual reactor are mainly described, providing an option and database for technology screening.

### Diesel hydro-refining technology

Currently, diesel in China is facing the transition of Sino IV, Sino V, and Sino VI standard. All the refineries in China have finished the upgrade of diesel from Sino IV to Sino V, and some refineries have the ability to produce Sino VI diesel since Beijing started to use Sino VI diesel on 1 Jan 2017, and China will execute Sino VI on 1 Jan 2019 [4].

The hydro-refining technologies of diesel were developed by UOP, LLC, Chevron, Axens, Shell, Haldor–Topsoe, CNPC, and SINOPEC can meet the requirement of Sino VI without significant change in catalyst design and process revamping. The relevant technologies and catalyst development are not discussed here.

### Diesel hydro-upgrading technology

Due to the restriction of cetane number of Sino VI standard (CN < 51 for 0# diesel), it is challenging for di-aromatics hydrogenation at medium pressure ( $\neq 6$  Mpa) due to pressure restriction and thermodynamic equilibrium. Santana et al. figured out the relationship between ring hydrogenation, hydrocracking, and cetane number [19]. During the process of hydro-refining, the process can mainly realize the conversion from naphthalene to tetralin with an increase of CN by 8 ~ 10, in terms of hydro-upgrading technology such as MCI (Maximum Cetane Increase Technology), this technology can increase CN by involving moderate cracking of tetralin and maintain the maximum yield of diesel fraction by preventing secondary cracking. This technology was popular during the past market that requires high consumption of diesel and applied in some refineries with high processing capability of FCC unit [12, 20].

Since the catalyst involved in MCI technology was initially designed for moderate cracking and improving CN value, in spite of the existence of zeolite beta, ultra-stable Y, and silica–alumina as the cracking component, tailoring the processing parameters including temperatures, space velocity probably could not change the selectivity of naphtha fraction significantly. Therefore, MCI technology and application is not recommended during the current period for refineries to resolve the quantity of FCC diesel.

## Medium pressure hydro upgrading technology

Medium-pressure hydro upgrading technology (MHUG) technology developed by RIPP institute is characteristic of its moderate medium pressure (4.5 ~ 12 MPa) [21], its versatility and selectivity on feedstock, and flexibility on products with different operation models towards desired products. Compared with the conventional hydrocracking process, it shows a similarity in catalyst and reactor configuration. The great advantage of MHUG technology for the first application is its saturation ability of multi-cyclic aromatics by interrupting the thermodynamic equilibrium. Additionally, it not only can process diesel fraction, but also can convert mixed fraction including light gas oil, LCO and LCGO, since moderate pressure could not process inferior feedstock with high concentration of poly-cyclic aromatics. One plant employed this technology to convert inferior diesel fraction such as LCO and LCGO from naphthenic-intermediate feedstock, providing the yield of 83.65 and 16.93% for diesel and naphtha product, respectively. The cetane number for diesel is increased by 21 for MHUG [22]. This MHUG technology was later upgraded with MHUG-II technology in which the inferior and superior feedstock were fed into different reactors with different operation conditions and catalysts, resulting in a better improvement of diesel yield and properties since MHUG-II technology can optimize the efficiency of H<sub>2</sub> utilization and avoid the cracking of superior diesel fraction [23]. As aforementioned, MHUG technology features a relatively lower investment compared with high-pressure upgrading process. Notwithstanding, this technology still encounters some technical problem that the smoking point of jet fuel shows a decreasing trend, and could not satisfy the requirement during the long-term running; since the serving catalysts becomes inactive, and the operation of increasing temperature further hinders the saturation of aromatics, as such, the pressure and conditions at end of run are insufficient for jet fuel production. Novel process based on MHUG technology employed a downstream hydro-finishing reactors after fractioning system using liquid-phase hydrogenation technology.

### LCO selective and moderate hydrocracking technology

In order to utilize the aromatic components as the valued products such as BTX, instead of the hydrogenated naphthenes or heavy naphtha fraction as reforming feedstock, novel technologies that can precisely control the hydrogenation degree of multi-ring aromatics were developed to

**Table 6** LCO moderate hydrocracking towards gasoline with high octane number

Items	Properties
Feedstock	
Density, kg/m <sup>3</sup>	941.8
Sulfur, µg/g	2878
Nitrogen, µg/g	678
Paraffins/naphthane/aromatics	16.0/7.3/76.7
Inlet pressure, Mpa	9.3
Average temperature of refining reactor, °C	346.6
Average temperature of cracking reactor, °C	384.7
H <sub>2</sub> consumption (wt %, pure H <sub>2</sub> )	3.55
Production Distribution, wt %	
Dry gas	1.24
LPG	8.16
Light naphtha, C <sub>5</sub> ~ 65 °C	1.62
Heavy naphtha, 65 ~ 165 °C	14.57
Gasoline, 150 ~ 210 °C	18.94
Diesel	58.24

ensure the hydrogen utilization efficiency and the commercial value of petrochemical product. UOP developed LCO-unicracking<sup>TM</sup> technology, and LCO-X<sup>TM</sup> technology based on unicracking technology and aromatic processing unit [8]. Mobil, Akzo Nobel/Nippon Ketjen and The MW Kellogg Company invented MAK-LCO technology [24], while scientists from FRIPP and RIPP SINOPEC formulated FD2G and RLG technologies [20, 25, 26]. Regardless of different names of these technologies, they all convert LCO component to gasoline with high octane number at a moderate pressure.

Relevant to this technology, unique catalysts, processing parameters including temperature, space velocity, H<sub>2</sub> partial pressure, and operation mode (one-through, and recycle mode) all determine the yields and quality of desired products. Table 6 summarizes the industrial result from refinery, demonstrating a typical example including feedstock properties, engineering parameters, product distribution, and operation mode.

It is found that heavy aromatics are available in gasoline fraction, Zheng et al. [27] integrated a downstream unit to convert the fraction ranging from 105 to 240 °C for the production of BTX compounds. In comparison of feedstock and product in the stage, C<sub>10</sub><sup>+</sup> fraction was reduced from 54.04 to 14.31%, while the yield C<sub>6</sub> fraction yield increases from 3.61 to 25.53% with a selectivity of 81.2% in C<sub>6</sub> fraction, and the yield C<sub>8</sub> fraction demonstrates an increase from 16.50 to 27.35%, with a selectivity of 99.3% for xylene.

## LCO hydro-processing and subsequent FCC technology

As stated, the introduction of hydrogen into LCO fraction can enhance the cracking ability on acidic component [28]. In addition to the cracking behavior occurring in RLG/FD2G/LCO-X technology, FCC unit can also convert lighter fraction via a carbenium mechanism. Researchers in RIPP institute developed an integrated process which combined an individual LCO hydro-refining unit and subsequent LCO unit, named as LTAG technology (LCO TO AROMATICS AND GASOLINE) [10, 22, 29–34]. This technology shows a relative flexible and versatile advantage, since single and/or combined LCO hydro-processing and FCC unit can be applied. RIPP organized the commercial trial for LTAG technology in Shijiazhuang Petrochemical Company, using two different systems and facility configuration. System I processes LCO component in hydro-treating and FCC unit, requiring two individual FCC unit and 1 hydro-treating unit. While system II configures 1 FCC unit and 1 hydro-treating unit, in which the hydro-treated LCO diesel fraction was recycled back to the upstream FCC unit, and processed with original FCC feedstock. From the perspective of refineries, it is not practical to introduce a new FCC unit for LTAG implementation, since more investments are required and refineries could not provide large amount of LCO feedstock for processing due to the restriction of refinery processing capability. To increase the octane number of generated gasoline to the maximum and to minimize the hydrogen consumption for LTAG technology, the screening of hydro-processing catalyst, FCC catalyst, and processing parameters should be conducted. Regarding hydro-processing section, the conversion from naphthalene to tetralin should be enhanced and the conversion from tetralin to decalin should be inhibited. The researcher introduced a descriptor, called mono-aromatic selectivity index ( $S_{HDA}$ ), and saturation ratio of di-aromatics to express the effectiveness. The mono-aromatic selectivity index is expressed as the increase of mono-aromatic divided by the decrease of multi-aromatic ( $S_{HDA} = \Delta_{\text{mono-aromatics}}/\Delta_{\text{multi-aromatics}}$ ). Xi et al. figured out that, apart from the optimization of hydro-processing catalyst, the reaction temperature should avoid the thermodynamic effect. With the increasing of reaction temperatures, the saturation degree of di-aromatics demonstrated an volcanic-type curve since low temperature promotes the conversion from di-aromatics to mono-aromatics with a relative lower reaction rate, while high temperatures probably reach the thermodynamic curves of di-aromatics saturation with a higher reaction rate. As for the selectivity for mono-aromatics, relatively lower temperatures are recommended by guaranteeing the relative high saturation degree of di-aromatics

**Table 7** The properties of LCO feedstock and its hydro-treated LCO under different processing parameters [29]

	LCO	HLCO-1	HLCO-2
Density, g/cm <sup>3</sup>	0.9635	0.9062	0.8776
H, wt %	9.55	11.0	12.01
S, µg/g	12,200	150	20
N, µg/g	736	66	1.8
Group component, wt%			
Paraffins	8.6	10.8	15.5
Naphthenes	3.4	13.3	38.8
Total aromatics	88.0	75.9	45.7
Mono-aromatics	28.5	56.1	32.0
Di-aromatics	49.5	17.9	13.6
Tri-aromatics	10.0	1.9	0.1
S <sub>HDA</sub> , %	0	69.2	8.7

[35]. Table 7 states the influence of processing parameters on hydro-treated LCO and its product during cracking.

Using LCO feedstock from Shijiangzhuang petrochemical company, HLCO-1 was obtained under moderate hydro-processing conditions, while HLCO-2 was achieved under severe conditions with more hydrogen content and aromatic saturation. According to the group component, it is obvious that the total aromatic for HLCO-2 fraction decreases by 44.2%, resulting from the over-saturation of di-aromatics and mono-aromatics and resulting in the increase of naphthenes by 25.5 wt%; however, the relative moderate hydrogenation atmosphere provides a slight drop of total aromatics by 12.1%.

From the mechanism of catalytic cracking, more hydrogen in FCC feedstock facilitates the conversion towards gasoline/LPG fractions; however, more saturated FCC feedstock would introduce hydrogen into dry gas and simultaneously decreases RON value of gasoline due to the introduction of cyclo-paraffins. Table 8 confirms the influence of hydrogenation degree on FCC product distribution and the product's properties [29].

The optimization of FCC unit also influences the product distribution and product's properties; alkylation, cracking, hydrogen transfer, and aromatization reactions were involved in FCC system. Regarding hydro-treated LCO component, tetralin component is subject to two reaction pathways including cracking step into lighter fractions, and competitive hydrogen transfer step back to naphthalene fraction which ruins the function of upstream LCO hydro-processing. To enhance the yield of lighter fraction from the hydro-treated LCO catalytic cracking, the possibility of hydrogen transfer should be inhibited by tailoring the properties of FCC catalyst, and optimizing

**Table 8** FCC product comparison of LCO feedstock with different processings

	LCO	HLCO-1	HLCO-2
Product, wt %			
Dry gas	4.44	1.91	1.47
LPG	7.65	14.76	15.63
Gasoline	26.78	48.77	53.83
RON/MON	–	98.4/86.0	95.6/83.4
LCO	43.41	29.32	26.17
Slurry	9.14	1.52	0
Coke	8.58	3.72	2.90
Conversion, %	56.59	70.68	73.83
Light oil yield, %	34.43	63.53	69.46

processing parameters of FCC, along with the promotion of cracking step.

Given that the activation energy of hydrogen transfer (94 ~ 125 kJ/mol) is lower than that of subsequent cracking (184 ~ 205 kJ/mol) [29, 36], hydrogen transfer is preferred in FCC system. To suppress hydrogen transfer, high temperature is recommended since hydrogen transfer is exothermic while catalytic cracking is endothermic. In addition to the optimization of temperature, large cat/oil also facilitates the conversion.

To realize maximum conversion towards gasoline and LPG, LTAG technology introduced two relatively separated reaction zones that process hydro-treated LCO and original FCC feedstock individually under different reaction temperatures and catalyst density. In terms of LTAG technology, it not only can use current hydrogenation unit with appropriate pressure, e.g., gas oil hydro-processing unit [37], and diesel hydro-upgrading unit with minimum investment, but also can utilize FCC with two-stage risers. Gao et al. recently reported that the decrease by 19.68% of diesel was converted to 16.38 wt% gasoline and 2.63 wt% LPG [36].

LTAG technology provides resolution of utilizing LCO fraction based on current layout of refineries, via hydro-processing unit and FCC unit towards the production of superior gasoline with high RON. However, the technology only generates 10 ~ 15 wt% C<sub>6</sub> ~ C<sub>8</sub> when employing hydro-treated LCO as the individual feedstock. Recently, JX Nippon Energy and Oil Company developed fluid catalytic aromaforming process (FCA) to utilize LCO for producing BTX components. In this process, the developer optimized the parameters of FCC including involved catalysts, circulation rate for catalysts, as well as the pre-treatment of LCO fraction. It is figured out that FCA can achieve 35 vol% of BTX. The critical factor is the process



named Z-forming in which LPG, light naphtha can be converted to aromatics by cyclization [38].

### Straight-run diesel cracking technologies

Straight-run diesel featuring with high CN, high paraffin and naphthene, is normally subject to low-medium hydrogenation, as the superior blending fraction in diesel pool. To reduce diesel output, individual technology that only processes SRGO fraction was invented, named as FD2 J or FDHC technology; different in target selectivity [39, 40], these two technologies were developed based on the molecular understanding of naphtha, FCC diesel, unconverted diesel, and jet fuel. Regarding FD2 J or FDHC technologies, the dominant reactions are summarized as follows: (1) the hydrogenation step guarantees the sulfur removal, nitrogen removal, and aromatic saturation, which can influence the quality of jet fuel, such as smoking point that is relevant to the content of aromatics, as well as the cracking ability, such as BMCI value which is strongly related to the content of aromatics. As such, the involved catalyst should render a high hydrogenation ability preferred with Ni–W bi-components. (2) To realize the production of jet fuel and naphtha, the catalysts should have the function of hydro-isomerization of paraffins, and cracking of naphthene to improve jet fuel's smoking point and BMCI value of un-converted tail oil. Therefore, acidic components such as zeolite beta, and Y are recommended for catalyst's design. If the target product is jet fuel, the catalyst with maximum hydro-isomerization activity is preferred.

To reduce the output of diesel, Researchers in FRIPP developed FD2 J technology in which the main product from SRGO feedstock are naphtha, jet fuels, and diesel with lower condensation point by grading hydro-refining catalyst, hydro-upgrading and dewaxing catalyst. The critical factors on product distribution in FD2J technology are studied. When processing narrow diesel, the yields of naphtha and jet fuel are 35.51 and 62.86% under the conditions investigated (Table 9).

According to the results from pilot scale, the potential aromatic content is lower than that obtained from hydrocracking of gas oil. Due to the restriction of low pressure ( $\sim 6$  Mpa), the smoking point of generated jet fuel did not reach the standard ( $\leq 25$  mm); therefore, the jet fuel can be blended with other superior jet fuels. To overcome the issue of low smoking point, FRIPP developed another technology coded as FDHC, in which a supplemental hydrogenation unit before fractioning tower is installed in order to process generated jet fuel and decrease the aromatic content [40, 41]. In a systematic study, the authors selected three different targeted catalysts including FC-50, FC-32, and FC-20 and found that the yield of jet fuel scaled

in the following order: FC-20 > FC-50 > FC-32, and the quality of jet fuel decreased in the following order: FC-50 > FC-32 > FC-20; however, the unconverted tail oil/diesel's BMCI followed the following order: FC-50  $\approx$  FC-32  $\gg$  FC-20. FC  $\sim$  50 catalyst towards middle distillate product was selected. After supplemental hydrogenation with non-nobel catalyst, the aromatic content of jet fuel decreases by 6.7% with a diesel conversion of 56%, and the smoking point increases accordingly.

### Discussion

In this technical review, the possible and potential technologies for processing diesel fraction, as to reduce the production of diesel, are mainly discussed: relying on single technology seems ineffective to conquer the current problem. The employed technologies mainly integrate hydro-treating, cracking in the form of FCC or hydrocracking, extraction, as well as fractioning with different processes and conditions based on the molecular understanding of each component, catalytic behavior of each component, and their inter-influence.

The technologies summarized here have been proved as the accessible and successful, with the strong support of industrial data and pilot results. Before selecting the prospective technology onto the current configuration of certain petrochemical plant, should we consider other aspects related to the consequence of retrofitting, instead of only focusing on the advantage of decreasing diesel production?

- (1) Market regulation and vicinity of local district: The domestic demand of diesel was reduced compared with that for previous years. However, the local demand of diesel probably varies in different petrochemical districts if diesel-employed activities such as real estate construction, transportation business, and industries are relatively prospectus. If inferior diesel fraction after hydro-refining and blending can be supplied for sales in the form of regular diesel, it is not necessary to convert inferior diesel fraction to other fuels (naphtha, gasoline or jet fuels) due to the ostensible advantage of price between gasoline and diesel fraction.
- (2) Analysis of feasibility. First, the most powerful motivation for technology application for refineries is profit. Before applying the technology, the required step is to propose feasibility analysis including financial and technical analyses. For FD2G technology, high H<sub>2</sub> consumption, and processing cost are the critical factors that should be considered, in addition to its products such as gasoline with high octane

**Table 9** Feedstock and product properties relevant to FD2 J technology [38]

Items	Feedstock <sup>a</sup>	Naphtha	Jet fuel	Ffeedstock <sup>b</sup>	Naphtha	Jet fuel	Diesel
Density, g/cm <sup>3</sup>	0.8346	0.7111	0.8077	0.8479	0.7058	0.8110	0.8253
Distillate range							
HK/30%	228/259	48/71	145/193	230/281	40/81	140/178	281/297
50%/70%	266/273	96/103	222/246	295/310	95/104	198/231	304/309
90%/KK	281/294	155/166	267/285	336/358	119/132	255/273	338/348
Yield, wt %	–	35.51	62.86		14.42	52.18	32.25
Potential aromatic/wt %		38%			38.4		
Freezing point, °C	– 18.6		– 49			– 49	
Smoking point, mm	18.6		22.8			22.5	
CN							72.3

<sup>a</sup> Reaction inlet pressure: 6.3 Mpa, H<sub>2</sub>:Oil = 500, space velocity: 1.2 h<sup>-1</sup>, reaction temperature: 365/360 °C

<sup>b</sup> Reaction inlet pressure: 6.8 Mpa, H<sub>2</sub>:Oil = 500, space velocity: 1.2 h<sup>-1</sup>, reaction temperature: 375/370 °C

number and ultra-clean diesel. According to China Coal to hydrogen annual report in 2016 by ASIA-CHEM, hydrogen produced from coal shows a high priority compared with that from methane source. The current refinery giant in China including Zhejiang petrochemical, Hengli petrochemical, and Shenghong petrochemical all select coal to hydrogen strategy. Compared with FD2G technology, LTAG technology seems advantageous since it requires less hydrogen consumption and produce olefins instead of saturated light alkanes in FD2G technology. LTAG is preferred with high price gap between gasoline and diesel, and high net conversion for diesel to other fractions. In terms of FDHC technology, the most attractive feature is its flexibility in converting SRGO fraction to naphtha and jet fuels, but the benefit should be considered since the jet fuel price is lower than that of diesel if the local supply of jet fuel are not necessary.

Second, the configuration of refinery should be considered. (1) When executing FCC involved technology, the capacity of current FCC plant should be considered, as well as the consequence of LCO processing in FCC plant. (2) If a refinery plant introduces FD2G technology, how to process light naphtha is another issue if the refinery does not have ethylene production facility. (3) In the scenario of converting SRGO to jet fuels and naphtha, the influence of extracting good diesel feedstock from diesel pool should be taken into consideration.

## Conclusions

Herein, this review mainly summarizes the potential technologies for processing LCO middle distillates to other fractions such as jet fuel, heavy naphtha, LPG, BTX, as

well as improved diesel fractions including process diagram, mechanism, advantages and disadvantages. The feasibility of each technology for implementation into current plant is also addressed here. The technologies listed can be separated into two categories: (1) LCO blending technology with minor revamping: it is easier for refineries to blend LCO fraction to hydrocracking and hydro-treatment unit towards the production of gasoline; (2) individual LCO processing: most refineries do not have individual facility that are designed for LCO processing; therefore, it is necessary to make feasibility analysis based on the consideration of technology, H<sub>2</sub> price, oil price, product price, and market balance.

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