

Various Ways for Increasing Production of Middle Distillate

Dr. Shailesh N. Gadhvi

Sardar Patel University, Gujarat, India

*Corresponding author

Dr. Shailesh N. Gadhvi, Sardar Patel University, Gujarat, India.
Email: sgadhavi1710@gmail.com

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Abstract

Currently, refiners are experiencing a big challenge due to the slow economic growth, over diesel production and decreased demand of it. Refineries are searching for technologies that could reduce diesel output, particularly the inferior light cycle oil (LCO) fraction. Here in, this article mainly we will 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 some aromatic rich stream and also with gasoline with the integration of selective hydro-refining and resulting optimized FCC unit. It is analyzed that the LCO moderate hydrocracking can provide more gasoline at the expense of high H_2 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 end users.

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

Introduction

Regarding the market of traditional fuel and petrochemical product, market is strongly relevant to the development of petrochemical industry and also indicates a distinctive difference among different countries. The cliff drop of crude oil from 100 to 40 \$/barrel, and if this scenario will continue for a long time; refiner to explore a new approach to increase its profit by tailoring its configuration without major revamping; the price difference between gasoline and diesel required 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 2024, with a drop from 1.5 in 2015; the growth of jet fuel also motivates the transformation of the refinery, according to the data from National Statistical Bureau: the jet fuel consumption shows an increase so it is estimated that jet fuel production must be increase to complies market needs. The increasing demand of olefins ($C=2/C=3$), and aromatics with a high economic benefit.

In order to meet this one of the 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 refinery business.

Chemistry of Middle Distillate/Diesel

According to the composition of diesel pool, the diesel fuel is mainly composed of various stream like straight-run light gas oil (SRGO), light coke gas oil (LCGO), Diesel from vacuum gas oil hydro-processing plant(VGOHT), and Diesel from hydrocracking units, light cycle oil (LCO). The proportion of each component may vary, depending on quantity and quality of diesel demanded by market.

Obviously, SRGO is composed in diesel with a large proportion due to its easing production and less hydrogen consumption due to its rich abundance in Paraffins and Naphthenes by treating LCGO with hydrogen we can remove sulfur, nitrogen, and poly aromatics and resulting LCGO quality can be improved. On other hand LCO obtained from FCCU unit is considered as very inferior diesel fuel additive due to presence of high aromatic specially poly aromatic not only that it is difficult to reduce its aromatic concentration with comparative cost of H_2 consumption without getting any significant improvement in cetane number (up to $8 * 10$).

As discussed above it is big challenge to figuring out an effective and economic way to process the excessive middle distillate for production of quality diesel which can have high economic and environmental benefit. If we compare SRGO and LCO, SRGO fraction has higher proportion of paraffin and naphthene than LCO,

while LCO is rich in mono-aromatics and di-aromatics. According to the group component study, SRGO fraction can be converted to jet-fuel, liquefied petroleum gas which providing C₃/C=3 and C₄/C=4 feedstock, light naphtha which provide the feedstock of ethylene cracking, and heavy naphtha which provide feed stock of reformate production in CCR unit. In contrast, LCO due to characteristic of rich aromatics, can be processed via hydrogenation along with cracking to generate gasoline with high octane number or other lighter components. Hence processing LCO to enhance production of gasoline and decreasing the quantity of diesel is relatively challenging.

Table 1: Typical properties of individual component in diesel pool

	SRGO	SRGO	LCO	Diesel from residue unit	HC diesel
Proportion, %	58.9	9.73	17.81	1.63	11.92
Density, g/cm ³	0.79 to 0.85	0.82 to 0.84	0.87 to 0.93	0.84 to 0.87	0.79 to 0.84
Sulfur, lg/g	200 to 15,000	1000 to 9000	1000 to 5000	50 to 300	10
Nitrogen, lg/g	20 to 800	1000 to 4000	600 to 3000	40 to 300	10
Cetane number	50 to 54	48 to 51	35	45 to 47	55
Polycyclic aromatics, %	8 to 11	9 to 12	40 to 50	4 to 6	1 to 5

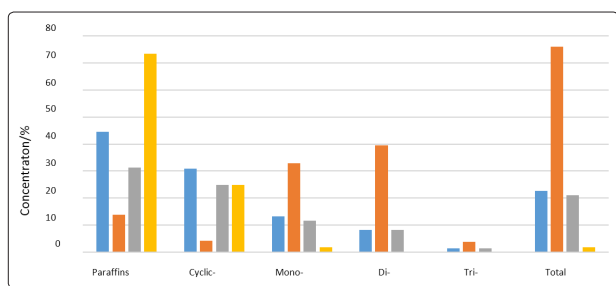


Figure 1: Group Component Analysis for Typical Diesel Distillate

The refinery and various refinery technologist explain various strategies to adjust the ratio of diesel to gasoline and ease the burden of selling diesel product.

Diesel Direct Feeding in FCC Unit

Fluid catalytic cracking facilities can process crude atmosphere residue received from CDU unit, vacuum residue received from VDU, as well as vacuum gas oil received from VGO unit, accounting for 30% of current refining ability. About 30 to 50 wt% gasoline can be produced in FCC unit. Therefore, using FCC unit to convert diesel fraction to lighter fraction that can blend for gasoline seems a plausible pathway for adjusting the ratio between gasoline and diesel.

In FCC unit heavy cycle oil (HCO) can be re-cracked by blending it with recycling line of fresh feedstock, FCC diesel (LCO) can also be included in this stream by extending the true boiling point (TBP). It is favorable if it make feasible to recycle all FCC diesel cut; however certain characteristics like rich di-aromatics, high C/H molar ratio, low hydrogen content, as well as the difficulty in breaking carbon-carbon bonds, make it unrealistic and resulting there is low conversion towards gasoline and liquefied gas. By analyzing the group component of FCC diesel in a narrow distillate cut, it is found that mono-aromatics highly concentrated in the lighter fraction (HK to 250 C), while di-aromatics are mostly dominant in the heavy fraction (260 C) (Fig. 2). As the TBP increases, the concentration of mono-aromatic decreases, while as the TBP decreases di-aromatics decreases.

Under identical conditions, the product distribution of three cuts is illustrated in Fig. 3. The discrepancy in product distribution indicates that FCC diesel is less cracked compared with paraffin-rich gas oil, and aromatics is transformed to generate dry gas and heavy oil such as slurry, resulting inhibiting the conversion. As the

di-aromatic concentration increases it gives lower yield of gasoline. So it is favorable to recycle FCC diesel fraction with richer mono-aromatics instead of di-aromatics for achieving high conversion towards gasoline and LPG. On account of this it is essential to recycled LCO cut with fresh feedstock to achieve high gasoline volume. Experimental study shows that, feedstock with 3.1% light LCO fraction achieved an increase by 1.5% of gasoline yield.

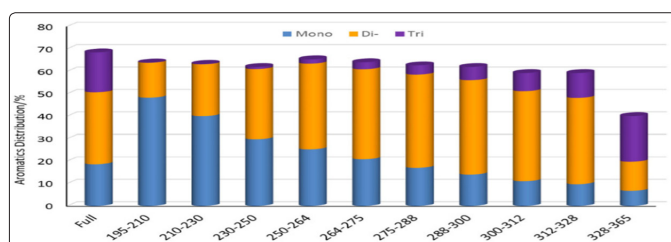


Figure 2: The Group Component as a Function of Narrow Distillate Range

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 ³ Group component/wt %	908	975.2	950.9
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

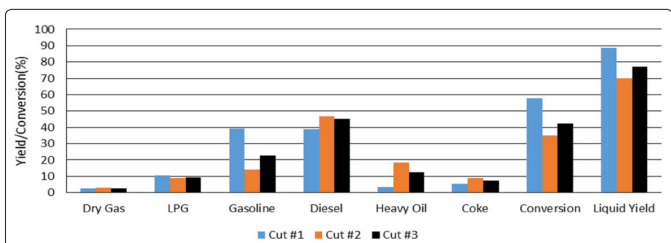


Figure 3: The Product Distribution of Catalytic Cracking of FCC Diesel Fraction In A Pilot Scale

Converting full cut of FCC diesel is not a practical way because it has pyrolysis ability thus it required some pretreatment. This cracking tendency can be improved by doing pretreatment of FCC diesel cut by hydrogen it is discussed below.

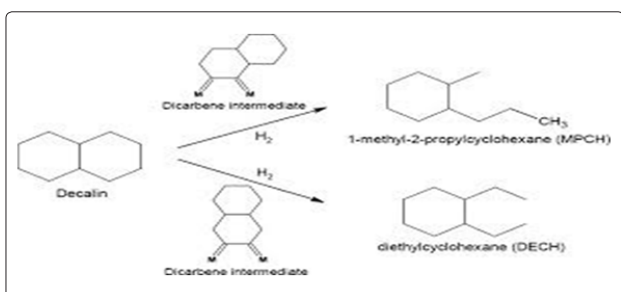
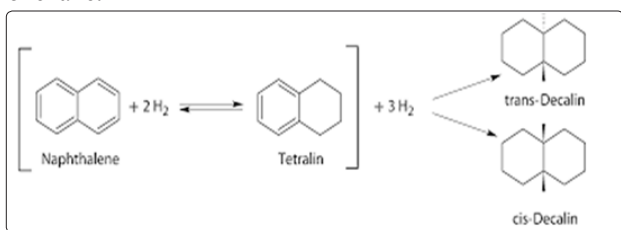
Diesel Blending in Middle Distillate Hydrocracking Unit

Various type of hydrocracking unit in refineries giving distillate 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 technical characteristics of catalysts. The catalyst normally work in active phase for a period of 3 years. It is not preferable to purchase new catalysts if not necessary for adjusting the ratio between diesel and gasoline.

To increase gasoline and diesel output in addition to process optimization, blending diesel, especially light cycle oil (LCO) into the current hydrocracking unit with its feed can process LCO fraction and generate clean diesel. In order to understand hydrogenation of LCO let us take naphthalene or its analogue as the main component in LCO, the involved mechanism can be simply demonstrated as given bellowing.

In first step hydrogenation of naphthalene gives intermediate product as Tetralin,

In second step this intermediate product undergo further hydrogenation at high H₂ partial pressure, produced Decalin, similarly cracking of Decalin gives 1-methyl-2-propyl cyclohexane(MPCH) and Diethyl (DECH).as well as consecutive cracking leads to the formation of cyclohexane.



Such hydrocracking required to operates at a high pressure, this facilitates correspondingly decreasing the aromatic content in refinery aromatic reach stream like LCO, heavy naphtha. For blending diesel into the current hydrocracking system, the following suggestions should be taken into consideration: (1) The middle distillate type catalyst does not give higher net conversion of LCO so proper catalyst must be employed in process (2) During conversion from LCO diesel to light fraction, approximately 5 wt% H₂ on the LCO weight based is consumed; hence the refinery's H₂ compressor capacity must be modified before blending LCO to main stream (3) Diesel blending into hydrocracking unit needs suitability of

processing parameters, such as the inlet temperature, flow rate of through put as well as the fractionating system(4) Rich aromatics content in the blending ratio should be optimized in a way that it complies with the quality of products, since the aromatic content of fuel influences some specification like smoking point of jet fuels.

Result obtain by introducing 7.8% LCO component in hydrocracking facility of VGO unit and subtracting corresponding amount of VGO, it is found that the middle distillate was reduced by 5.0% and the heavy naphtha and tail oil showed an increase by 0.5 and 4.0%, respectively. In terms of jet fuel and diesel, the smoking point decreased by 1 mm, and the Cetane number was reduced by 3 to 4 units.

Diesel cut Feeding in Hydro Processing Unit

Residual oil gain from the bottom of the vacuum column is rich in basic nitrogen, sulfur and aromatics, and residue oil with high concentration of Ni, V, sulfur, nitrogen, colloids, and asphalts which causes for deactivating and poisoning of FCC catalysts and correspondingly decrease catalysts' activity hence it is essential to undergo hydro processing of this vacuumed gas oil. Based on various property and chemistry of vacuum gas oil it undergo hydro processing at high H₂ pressure.

By using the available gas oil hydro-processing unit facility, FCC LCO has been 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 LCO and moderate cracking of gas oil, can be totally delivered to FCC unit by removing the fractioning tower. During the process FCC diesel (LCO) were converted to lighter product like LPG, gasoline, and coke; it is calculated that the conversion of diesel to other products is 45%, and the selectivity towards gasoline and LPG is close to 90%. Apart from the change of product.

By such a distribution of FCC unit, we can minimize the energy consumption of gas oil processing unit and FCC unit from 8.0 to 4.0 kg Oil/t, and the energy consumption of FCC unit shows the same trend with a decrease from 55 to 48 kg Oil/t.

Same as to vacuum gas oil processing, residual oil hydro-processing unit can also provide atmosphere for hydrogenation of LCO. In addition to the hydrogenation of aromatic component, blending of FCC diesel (LCO) because its rich di aromatics it help to dissolve asphalt in residue, preventing the precipitation of asphalt from dissolved its dissolve state and decreasing the viscosity further that can enhance the hydrogenation ability.

Hydro-Upgrading Technology for Middle Distillate

Due to the strict specification of Cetane number of diesel, it is challenging for di-aromatics hydrogenation at medium pressure due to pressure restriction and thermodynamic equilibrium. During the process of hydro-refining of stream mainly there is conversion from naphthalene to Tetralin which can increase of CN by 8 to 10, one most adopted cetane number improving technology such as MCI (Maximum Cetane Increase Technology), this technology can help us to increase CN by moderate cracking of Tetralin and also preventing secondary cracking so maximum diesel yield gain. This technology is popular during high demand of diesel in market and applied in some refineries having high processing capability of FCC unit.

Since the catalyst used in MCI do moderate cracking and improving CN value, in spite of the existence of this catalyst some processing parameters including temperatures, space velocity does not work to change the selectivity of naphtha fraction significantly. Due to this reason, MCI technology and application is not recommended during the current period for refineries to resolve the quantity of FCC diesel.

Hydro Upgrading Technology with Moderate Pressure

Compare to our conventional hydrocracking process in a medium pressure hydro up grading, it has similar catalyst and reactor configuration. Even if measure advantage of this technology is its saturation ability for multi-cyclic aromatics by creating the thermodynamic equilibrium. In addition to this it is not only can process diesel fraction, but also having ability to convert mixed fraction including LGO from atmospheric column, LCO from FCC and LCGO from coker plant, since moderate pressure does not help to process inferior feedstock having high concentration of poly-cyclic aromatics. Experimental result of this technology for converting inferior diesel fraction such as LCO from FCC and LCGO from Coker unit produced from naphthenic-intermediate feedstock, providing the yield of 85 and 17 % for diesel and naphtha product, respectively. The Cetane number for diesel is increased by 21. This technology was then after upgraded in which the inferior and superior feedstock were processed into different reactors with different operational conditions and different catalysts, resulting it gives better diesel yield and its quality As aforementioned, this technology required a comparative lower investment compared to high-pressure upgrading process. This technology still having some technical problem like smoking point of jet fuel shows a lowering trend, and not able to full fill the requirement during the long-term running; because the serving catalysts becomes inactive, and increasing temperature further hinders the saturation of aromatics.

Hydrocracking Technologies for Atmospheric Pressure Middle Distillate

Straight-run diesel with high paraffin and Naphthenic having resulting high Cetane number, is generally required low-medium hydrogenation, it is 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; these two technologies were developed based on the molecular chemistry of naphtha, FCC diesel, unconverted diesel, and jet fuel. In both the technologies, the dominant reactions are summarized as follows: (1) the hydrogenation step guarantees the sulfur removal, nitrogen removal, and aromatic saturation, catalyst involved in this must have higher hydrogenation capability that can be carried out with Ni-W bi-components. (2) To increase the quality production of jet fuel and naphtha, the catalysts should have the ability of hydro-isomerization of paraffin's, and cracking of naphthene to improve jet fuel's smoking point value of un-converted tail oil. Therefore, acidic components such as zeolite beta, and Y are recommended for catalyst's design. To aim jet fuel, the catalyst with maximum hydro-isomerization activity is preferred.

To reduce the output of diesel, Researchers developed FD2 J technology according to which the main product from SRGO feedstock are naphtha, jet fuels, and diesel with lower condensation point treated by grading hydro-refining catalyst, hydro-upgrading and de waxing catalyst.

As per the results obtained from pilot scale, proportion of aromatic content is lower than that obtained from hydrocracking of gas oil.

This is due to the restriction of low pressure, the smoking point of produced jet fuel did not reach the standard specification value; therefore, the jet fuel can be blended with other superior jet fuels.

Conclusions

Here in, this review mainly summarizes the potential technologies for processing LCO middle distillates to other fractions such as jet fuel, heavy naphtha, LPG, 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, H₂ price, oil price, product price, and market balance.

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