Flexible Co-Processing Of Refinery Middle Distillate In FCC To Maximize Gasoline And LPG

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**Nomenclature**

| Abbreviation | Description |
|--------------|-------------|
| FCC          | Fluid Catalytic Cracker |
| LPG          | Liquefied petroleum gas |
| VGO          | Vacuum gas oil |
| LS-LGO       | Low sulphur, light straight-run gas oil |
| HS-LGO       | High sulphur, light straight-run gas oil |
| HS-HGO       | High sulphur, heavy straight run gas oil |
| LS-VD        | Low sulphur, vacuum diesel |
| HS-VD        | High sulphur, vacuum diesel |
| HC-LD        | Hydrocracker light diesel |
| HC-HD        | Hydrocracker heavy diesel |
| FCC-LCO      | Low severity FCC light cycle oil |
| CCU-LCO      | High severity FCC light cycle oil |

**Introduction**

Fluid catalytic crackers (FCC) are one of the most vital conversion units in any modern refinery. With the increasingly stringent regulations on fuel combustion emissions, the utility of heavy oils as an energy source has greatly diminished. On the flip side, the crude oil currently being processed in refineries worldwide is gradually turning contaminated and inferior thereby yielding significant amounts of heavy oil. FCC converts this excessive quantum of heavy oil into high octane gasoline and LPG. It contributes a major volume to the gasoline pool and in a broader sense to the refinery’s profit margin [1, 2].

Yield and selectivity exhibited by any FCC relies on its catalyst properties as well as the feedstock it is processing. Feedstocks which are rich in asphaltenes and organometallic contaminants on cracking produce excess dry gas, reduce the gasoline yield and degrade the catalyst. Modern FCC units and catalysts showcase tremendous flexibility in processing unconventional feeds. Besides the usual straight run and vacuum gas oils (VGO), FCC units have the ability to convert distillation residues, hydrocracker bottoms, coker gas oil, shale oil and crude oil to some extent [3].

There has been an increased impetus towards lowering emissions, reducing carbon footprint and refinery-chemical plant integration. Diesel, gasoline and aviation turbine fuel are the chief sources of energy utilized in transport. Among these, the demand for diesel in the fuel market has been witnessing a downturn. Combustion of diesel releases significant amounts of SOx, NOx and particulate carbon. Gasoline, however exhibits relatively cleaner combustion. In addition to this, the retail price difference between gasoline and diesel further motivates refiners to adjust the ratio at which they supply these fuels [4].

The refining business is slowly morphing into a feedstock supplier to the chemical manufacturing industry. This has reduced the refiner’s interest in manufacturing clean fuels in favor of chemical feedstocks.

There are numerous instances when due to unavailability of gas oils, non-conventional feedstocks are processed in FCC units. Heavy cycle oils and in some extreme cases Light cycle oils are re-cracked in the FCC riser to maximize gasoline production. In an effort to maximize gasoline production, the vast diversity
of middle distillate streams can also be routed towards the FCC complex. Streams from the atmospheric and vacuum distillation towers, hydrocracker, delayed cooker all have diverse chemical compositions and therefore shall demonstrate varying degrees of crackability in the FCC. Refiners can thus promptly adjust their blending variables for the feedstock to process and upgrade their vast stores of middle distillates and respond to the changing market demands as and when required. The volume of middle distillates that can be upgraded is dependent on its crackability, the design and throughput of the FCC in question and the refinery economics [5].

In addition to the aforementioned scenarios, there have been examples where there is excess volume of Diesel product which is left unsold. In some economies Diesel has been oversupplied upon their consumption reports. During the recent worldwide pandemic, the strict restrictions on transport has led to a huge quantum of Diesel fuel left stagnant in refinery storage.

In this work, the cracking performance of nine different middle distillate refinery streams has been systematically studied and compared to the conventionally used vacuum gas oil. The cracking performance is assessed on the basis of up-gradation of the feedstock to gasoline and LPG using plant equilibrated catalysts in an Advanced Catalyst Evaluation (ACE) unit. Subsequently, the benefit from blending middle distillate streams along with the FCC feedstock on the overall conversion of the unit is investigated using a pre-calibrated FCC model in Aspen HYSYS®.

### Experimental Feedstock and Catalyst

The hydrocarbon feedstocks investigated in this work were sourced from the industrial distillation towers, hydrocracker unit and FCC in service at a commercial refinery Subject refinery processes a mix of light sweet and heavy sour crude oil. Their properties are listed in Table 1:

| Feedstock | API | Sulphur wt% | Cetane Index | Distillation ºC | Kwatson |
|-----------|-----|-------------|--------------|-----------------|---------|
| LS-LGO    | 30.45 | 0.07 | 49.9 | 60.2 | 240.6 | 314 | 376.2 | 11.57 |
| HS-LGO    | 38.28 | 0.21 | 57.3 | 61.0 | 200.6 | 283.2 | 341.8 | 11.34 |
| HS-HGO    | 37.63 | 0.57 | 62.6 | 78.6 | 232.2 | 307.8 | 340.8 | 12.00 |
| LS-VD     | 36.09 | 0.12 | 50.2 | 65.0 | 188.4 | 271 | 339 | 11.66 |
| HS-VD     | 31.87 | 0.25 | 53.1 | 84.0 | 232.6 | 312.8 | 353.4 | 11.68 |
| HC-LD     | 39.45 | <0.01 | 54.0 | 118.8 | 181.0 | 254.8 | 335.0 | 11.79 |
| HC-HD     | 37.64 | <0.01 | 76.2 | 130.0 | 260.4 | 361.4 | 412.4 | 12.33 |
| FCC-LCO   | 28.80 | 0.28 | 27.4 | 47.6 | 154.4 | 222.6 | 284.0 | 10.82 |
| CCU-LCO   | 22.76 | 1.54 | 25.9 | 95.6 | 174.4 | 236.2 | 316.6 | 10.53 |

Although the nine feed stocks are in same boiling range, their chemical composition varies drastically. The cracking performance of a hydrocarbon feed can be grossly judged on basis of the Kwatson value. Higher this value, lower the severity required to obtain an optimum yield of products [6]. It is well established that feedstocks rich in aromatics, especially polycyclic aromatics usually have a higher Kwatson value and demonstrate refractory behavior with respect to crackability. Cetane index is a qualitative measure of aromatic content of hydrocarbons.

Cetane index is linked to the cetane number of diesel fuels which signifies the efficacy of its ignition inside a compression ignition engine. Lower the aromatic content of diesel fuel, higher is the cetane index, thereby higher would be the expected crackability [7].

Detailed analysis of the feedstocks was conducted using a M3 Prefrac-Reformulyser (supplied by PAC L.P, Texas). The formulizer identifies groups of hydrocarbons based on their structure as P-Paraffinic, O-Olefinic, N-Naphthene, A-Aromatic (i.e. PONA) in the naphtha boiling ranges of the samples. The results are shown in Figure 1.

![Figure 1: PONA Analysis of Gasoline Fraction of Hydrocarbon Feedstocks](image)

Olefinic hydrocarbons are seldom found in crude oil. This is attributed to the environment within the earth’s crust. They are mostly a result of hydrocarbon cracking; straight run products almost never have olefins. Considerable concentrations of aromatics are observed in CCU-LCO and FCC-LCO along with olefins. This is attributed to the cracking, hydrogen transfer and cyclization reactions that occur in the FCC. A significant amount of naphthene’s are observed in the hydrocracker products (HC-HD and HC-LD). These are formed due to the saturation of ar-
omematics already present in the hydrocracker feed. Paraffins are most pronounced in the straight run products such as LS-HGO, LS-LGO, HS-LGO, LS-VD and HS-VD. As the hydrocarbon streams undergo secondary processing, the concentration of unsaturated hydrocarbons increase. Long-chain paraffins and olefins easily undergo β-scission in the FCC riser. De-cyclisation of naphthene’s into gasoline range molecules occurs at very high severities but dehydrogenation followed by oligomerization into coke may also occur [8, 9].

Two different equilibrated commercial catalysts Cat-1 and Cat-2 were utilized for testing the crackability of the above feedstocks. Their properties are presented in Table 2.

Table 2. Properties of Equilibrium Catalyst

|                      | Cat-1 | Cat-2 |
|----------------------|-------|-------|
| Surface Area (m²/g)  | 153   | 101   |
| Micro pore Area (m²/g)| 52    | 50    |
| Matrix Surface Area (m²/g) | 101   | 51    |
| Micro Pore Volume (cm³/g) | 0.081 | 0.078 |
| Total Pore Volume (cm³/g) | 0.17  | 0.16  |
| UCS (Å)              | 24.92 | 24.45 |
| Strong/Weak acid sites | 0.41  | 0.37  |

Cat-1 was sourced from the inventory of an industrial FCC operating at a higher severity compared to Cat-2. The unit using Cat-1 operates at full combustion mode of regeneration whereas Cat-2 was regenerated at partial combustion mode. The surface area was obtained on the basis N2 physisorption applied to the Brunauer–Emmett–Teller (BET) isotherm. The pore sizes were calculated according to the Barrett–Joyner–Halenda (BJH) method applied to the adsorption branch of the isotherm in accordance with ASTM D3663-99. UCS was determined using X-ray diffraction and acidity was calculated using NH3 desorption spectra. Evidently, Cat-1 is expected to exhibit higher activity owing to its higher surface area and pore volume. This is by virtue of better regeneration and consequently lower CRC (coke on regenerated catalyst). Cat-1 also has higher UCS compared to Cat-2. High UCS corresponds to lower de-alumination of active sites and lower zeolite deactivation. Cat-1 therefore has a greater density of strong acid sites compared to Cat-2.

Experimental Setup

The cracking performance of the nine feedstocks is investigated using the Advanced Cracking Evaluation (ACE R+MM) unit developed by KTI Technology Company, USA. The device is equipped with a single fixed fluidized bed reactor in which reaction, stripping and regeneration processes take place. The device is lab scale, consumes lesser hydrocarbon feed, is fully automated and has a short run length. Figure 2. Schematic Diagram of Advanced Cracking Evaluation (ACE-R+) unit

In this experiment, the weighed catalyst is pneumatically injected into the reactor through the injection system followed by the feedstock through a syringe pump system. The catalyst and feedstock react under a set reaction temperature and cat to oil weight ratio (CTO). The reacted catalyst is stripped with nitrogen while the gasoline, diesel, heavy oil, and other liquid products are collected in a condenser [10]. Dry gas, LPG, and other gas products are collected and weighed in a gravimetric gas collector. The composition analysis is conducted according to ASTM-D7169 method with simulated distillation gas chromatography and ASTM-D7833 with refinery gas analysis gas chromatography, respectively. After stripping, the catalyst in the reactor is regenerated with air, the CO in the regenerating flue gas is converted to CO₂, and eventually, the coke value is tested by in situ IR CO₂ analyzer. According to the weight of each component, the product slates can be calculated and FCC catalyst’s activity and selectivity and its reacting kinetics can be obtained and the feedstock’s cracking performance is evaluated. Only the product slates showing mass balance closure of 100±2% are considered in this work [11].
Results and Discussion

Cracking Performance Of Different Middle Distillates

The nine hydrocarbon feedstocks were catalytically cracked in an ACE microreactor as per the description given in experimental section. The reaction conditions were identical to that of the industrial plants from which the catalysts were sourced. For Cat-1 the cracking temperature is 515°C and for Cat-2 the temperature is 505°C. These temperatures are based on the design and optimum operating conditions devised to crack conventional vacuum gas oil to obtain maximum gasoline. Two sets of runs were conducted; one at CTO 6 w/w and the other at CTO 5 w/w. The liquid crackate was analyzed using simulated distillation. The product yields are defined on basis of distillation cut points i.e. C5-192°C is considered as cracked gasoline, 192°C – 360°C is total cycle oil which is sum of light and heavy cycle oil (TCO = LCO + HCO) and 360°C+ are considered as bottoms or clarified oil (CLO). Ethane, methane, hydrogen and hydrogen sulphone are accounted as dry gas/fuel gas. C3/C4 hydrocarbons are considered as LPG. The conversion obtained after cracking is defined as the sum of product yield that boils at a lower temperature than the feedstock. In our case, conversion is the sum of coke, dry gas, LPG and gasoline yield.

Cracking performance for the middle distillate feedstocks using Cat-1 and Cat-2 in terms of product yield is shown in Figure 3a, 3b, 3c, 3d.

In each case the highest conversion was observed in case of HC-HD followed by HC-LD. Cat-1 demonstrated higher gasoline and LPG yields compared to Cat-2 by owing to its higher surface area and acidity. High concentrations of naphthenes are present in such hydrocracker products due to saturation of aromatic hydrocarbons. Naphthene molecules in FCC feed can either crack into C5-C7 olefins and/or re-condense into lighter aromatics. Both these reactions contribute to production of gasoline range molecules [12].

Straight run streams such as LGO and HGO are characterized by high concentration of paraffinic hydrocarbons. Heavier the paraffinic hydrocarbon, longer the carbon chain and consequently lower is the endothermic energy required for cracking [13, 14]. The cracking performance of HS-HGO, LS-LGO and HS-LGO conforms to this principle. HS-HGO has the highest concentration of heavy paraffinic molecules’ hence it results in higher conversion; higher yield of LPG but slightly lower yield of gasoline compared to LS-LGO and HS-LGO. This can be attributed to further re-cracking of gasoline range molecules into LPG due to high crackability in this case.

Unlike C-C bonds of naphthene rings, the endocyclic bonds in aromatic rings require enormous amount of energy to rupture. CCU-LCO and FCC-LCO fractions contain the richest in aromatic hydrocarbons amongst all the feeds considered in this
study. In a FCC riser, aromatic hydrocarbons undergo de-alkylation of long side alkyl chains which generate light product gasses. They can also go through condensation/polymerization reactions which results in coke formation on the catalyst surface [15]. Consequently lowest conversion and cycle oil yield is observed in the case of CCU-LCO and FCC-LCO. De-alkylation of single ring aromatics followed by cracking does seldom occur in FCC. LCO is an aromatic rich FCC product which is blended into the automotive diesel pool is limited quantities. Since it is already processed through FCC and is characterized by a high concentration of polycyclic aromatics, recycling it into the riser is rarely practiced. Hydrotreatment of LCO is a preferred option if recycling and cracking is to be implemented, but it requires extra capital investment and is followed by a few commercially [16].

HC-HD, HC-LD and HS-HGO demonstrate the highest crackability by virtue of the molecular structure and weights of the hydrocarbons present in them. Blending them with conventional FCC feedstock will increase gasoline and LPG yields. But on the other hand, the octane rating of the gasoline product will be negatively affected. This is attributed to the greater overall paraffinicity and lower olefinicity of the end product [19].

**Cracking performance of VGO and HC-HD Blends**

HC-HD demonstrated the highest crackability and from Figure 4, it is clear that it will have the least negative influence on the product gasoline’s octane number. In order to deduce the optimum blending proportion of HC-HD with conventional FCC feed i.e. VGO, HC-HD was blended with VGO in three proportions viz 10:90, 20:80 and 30:70. The properties of the VGO used in the blending is given in Table 3.

**Table 3: Properties of VGO**

| Property                        | Value          |
|--------------------------------|----------------|
| Density (g/ml) at 15°C          | 0.8929         |
| Kinematic viscosity at 100°C (cst) | 7.05          |
| Total Sulphur (%wt)            | 0.29           |
| Total Nitrogen (ppmw)          | 492            |
| Nickel (ppmw)                  | <1             |
| Vanadium (ppmw)                | <1             |

**Figure 4. PONA Analysis of Gasoline Fraction of Products**

Figure 4 depicts the PONA analysis of the gasoline fraction of the products. Comparing Figure-1 and Figure-4, in almost all cases we can observe a marked conversion of paraffins and naphthenes into olefins and aromatics. Paraffins undergo β-scission and olefins are generated. Naphthenes participate in bimolecular hydrogen transfer reactions with these olefins to generate aromatics. The hydrogen transfer reaction increases the yield of gasoline, but ignition performance of the gasoline i.e. the octane number decreases. This is due to the consumption of olefins in the hydrogen transfer reactions. In case of CCU-LCO and FCC-LCO, the olefinic hydrocarbons were consumed in the hydrogen transfer, hence aromatics slightly increased [17, 18].

**Figure 5: Product Yields at Different HC-HD Blend Ratios**
Figure 5 shows the changes in product yields due to blending HC-HD in VGO. As the volume of HC-HD increases, the coke formation reduces due to lower amount of coke precursors (poly-cyclic aromatics) that will oligomerize into coke [20]. LPG yield increases with blending whereas gasoline yield passes through a maxima. This is due to re-cracking of gasoline range molecules into LPG. TCO yield increases proportionally with blending. This portion is actually the uncracked middle distillate that ends up in the final TCO fraction. In the existing fuel market, Gasoline fetches a better premium compared to LPG, the most optimal blending ratio in terms of maximizing profit would be 20wt% HC-HD with 80wt% VGO.

Simulated Cracking Performance of Blends with VGO

The cracking performance of HC-HD, HC-LD and HS-HGO was superior compared to other middle distillates (Figure 3a & 3b). Cracked gasoline yield was observed to be maximum at 20wt% blending ratio (Figure 5) when processed in the ACE reactor. To further investigate the potential in processing the above mentioned middle distillates in a commercial FCC, a simulation was conducted using a 21 lump kinetic model in ASPEN HYSYS®. The model employed in this simulation is calibrated to closely mimic the operation and product yield provided by the actual industrial unit (details in Table 4).

Table 4. Simulation Details

| Parameter                      | Value |
|--------------------------------|-------|
| Riser outlet temperature (°C)  | 505   |
| Feed charge (MTPD)             | 2500  |
| Feed Preheat (°C)              | 345   |
| Regenerator dense bed (°C)     | 650   |
| Reactor Pressure (kg/cm²)      | 2.3   |

The middle distillates were blended in 20wt% ratio and preheated with the same VGO as mentioned in Table 4. The mixed feed was injected into a single elevation point in the bottom portion of the riser but the commercial operation varies in this regard. In the commercial unit, the middle distillate feed shall be injected via a separate nozzle downstream from the VGO injection nozzle at a higher elevation. The simulated shifts in product yields due to blending of HC-HD, HC-LD and HS-HGO are shown in Figure 6.

The feed streams were defined in the simulation using their TBP assay and macroscopic properties (Density, viscosity, sulphur content, CCR). The reactor product was fractionated in the similar cut points as defined in section 3.1. Since lighter hydrocarbons are blended into VGO, coke production has reduced in all three cases. LPG yields increased in case of HC-HD and HS-HGO blends by virtue of their heavy molecular weight and high paraffinity. In case of HC-LD the LPG yield was lower than that of conventional VGO cracking and TCO yield was higher that both HC-HD and HS-HGO. This suggests that a considerable amount of feed was left unconverted on account of low molecular weight of HC-LD hydrocarbons and some portion cracked into gasoline. Gasoline yields improved in all three cases with HS-HGO producing the highest amount. This is contrary to what the laboratory results suggested where HC-HD produced higher gasoline and HS-HGO produced higher LPG. This disparity can be attributed to the changes due scale up and the assumptions used in the simulation.

Case Study: Benefit in Blending HC-HD in Industrial FCC

During the 2020 pandemic, the demand for automotive diesel declined on account of restriction in movement of goods and transportation. However the market requirement for motor gasoline and LPG persisted since they are supplied as petrochemical feedstocks and domestic fuel respectively. Since it was not profitable to supply automotive diesel, a commercial trial was planned to process middle distillate in FCC and upgrade it to naphtha or LPG. Based on above results, HC-HD was deemed optimal since it displayed the highest crackability
and at the same time contained negligible impurities. This implies that the catalyst activity would remain unaffected. 400 MT of HC-HD was routed from the hydrocracker unit to the FCC plant per day. The results of the commercial trial is shown below in Table 5.

Table 5. Commercial Trial Result

|                      | Case-1  | Case-2  |
|----------------------|---------|---------|
| Total FCC throughput (MTPD) | 1809    | 2209    |
| HC-HD addition (MTPD)            | 0       | 400     |
| Gasoline yield (MTPD)            | 668     | 872     |
| LPG yield (MTPD)                | 251     | 357     |
| Extra Reprocessing costs ( million /year) | 0       | 42.8    |
| Estimated Revenue ( million /year) | 3006    | 4023    |

Case-1 is the default operating condition of the FCC in question. In Case-2 400 MT/day HC-HD was blended in FCC feedstock VGO. The properties of VGO and HC-HD are in Table 3 and Table 1 respectively. Approximately 18 wt% HC-HD led to 22% increase in the unit’s throughput. Blending did not alter the heat balance and catalyst circulation rate by to a noticeable degree. The 400 MTPD HC-HD contributed to 204 MTPD of additional gasoline and 106 MTPD of additional LPG yield. The remaining portion ended up as cycle oil. Due to higher unit capacity additional 24 TMT of crude throughput is estimated, a net value increment of ₹1017 million/year can be expected.

Conclusion

In this work, the benefit of reprocessing middle distillate streams and products into the FCC to maximize motor gasoline and LPG yields was investigated. The oil market witnesses vast periods of uncertainty and disorder. In course of such events, the shortage of FCC feedstock or sudden decline in automotive diesel’s demand can put tremendous pressure on a refiner’s margin. For such scenarios, processing middle distillates into the FCC can be a quick remedy. With the increasingly stringent environmental norms on automotive diesel, there are considerable constraints in blending LCO into the diesel product pool on account of its high sulphur and aromatic content. Refiners are looking into means to hydro treating LCO into naphthalene analogues and further crack them into gasoline using FCC. Commissioning LCO hydrotreatment facilities would incur heavy capital expenses, but since the fuel market is on a steady decline and refiners are more inclined to manufacture chemical feedstock, cracking LCO into naphtha and light olefins is a viable alternative in the long run.

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