Hydroprocessing For Fuels And Lubes Production

A.Meenakshisundaram
R&D Centre
Chennai Petroleum Corporation Limited
Manali, Chennai 600 068

Abstract

The increased demand for improved quality fuels and lubes, stringent specifications adopted worldwide and deteriorating crude quality requires new processing options for fuels and lubes production. Hydroprocessing offers flexiblity for processing difficult feeds and also the quality of products vastly improved mainly due to removal of sulfur and nitrogen compounds and reduction in aromatics content. The increase in hydrogen content also increases yields of products which makes hydroprocessing option economically viable process.

Introduction:

The ever increasing demand for transportation fuels and increasing pressures on the environment has made the Governments world over to regulate quality and composition of transport fuels especially gasoline and diesel. Over 90% of transportation fuels and lubes are obtained from petroleum and hence refineries demand technologies designed for meeting stringent product quality specifications and environmental regulations. In India, there is a considerable shift towards fuel quality issues in the last decade, unlike the demand and supply considerations, which dictated product specifications earlier. With greater accent on environmental policies, Indian refiners are adopting innovative catalytic technologies which have more flexibility and adaptability for complying with new product and process regulations. Hydroprocessing is considered as an important option for refiners for production of quality fuels and lubes complying the quality standards and environmental regulations. The sale of hydroprocessing catalysts has surpassed in value many of the refining process catalysts including FCC which has been the main workhorse of refinery. The present paper discusses research programs summarises some of our efforts in developing hydroprocessing options for improving fuels and lubes quality.

The quality of fuels is continuously changing and especially the sulfur content has been decreasing in both gasoline and diesel. The specifications of gasoline and diesel adopted in India are given in Table 1 and 2. The sulfur levels which are currently at 500 ppm will be reduced further to less than 30 ppm and also the benzene content has to be lowered to less than 1 Wt%. These changes in fuel quality would require new processing options depending on the process objectives, secondary processing units available and crude slate processed and hence refinery specific. The FCC Naphtha forms the major pool for Motor spirit in many refineries and also contributes to the sulfur levels in Gasoline. The sulfur in FCC naphtha varies between 600 -1200 ppm depending on the type of crude processed and processes for reducing sulfur in FCC gasoline will enable to meet the sulfur requirements in gasoline. The sulfur reduction in products can be achieved either by pretreating the FCC feed or post treating the products.

Table 1. Gasoline Specifications

S.No.	Characterstics	Unit	Bharat Stage II Equivalent	Requirements for Euro III Equivalent	Euro IV
1	Density @15 C	kg/m^3	710-770	720 - 775	720 - 775
2	Distillation Recovery upto 180 C Min.	Vol%	90	75	75
3	RON min		88	91	91
4	Sulfur Total Max.	%Mass	0.05	0.015	0.005
5	Benzene Content Max	%Vol	3.0(Metro)	1.0	1.0
6	Olefins max.	%vol		21	18
7	RVP Max	kPa	35-60	60	60

Table 2. Diesel Specifications

S.No	Characterstics	Unit	Bharat Stage II Equivalent	Requirements for Euro III Equivalent	Euro IV
1	Density at 288K	kg/m^3	820-860	820-845	820-845
2	Distillation 95% Vol Recovery	@ $^{\circ}C$ Max		360	360
3	Cetane Number min		48	51	51
4	Sulphur Total Max	% mass	0.05	0.035	0.005
5	PAH Max	% mass		11	11
6	Flash Point(Abel) Min	^{o}C	35	35	35
7	Lubricity, corrected Wear scar dia (wsd 1.4)@60C, max	μ	460	460	460

Table 3. Effect of FCC Feed Hydrotreating

Feed Characterstics	Escravos Untreated	HVGO Hydrotreated	Upper Zakkum Untreated	HVGO Hydrotreated
Density @15 C g/ml	0.9187	0.91356	0.9187	0.9001
. Viscosity @100 C cst	7.51	7.85	6.34	5.93
Sulphur wt%	0.28	0.08	2.02	0.64
. Nitrogen wt%	0.15	0.12	0.07	0.05
Saturates Wt%	59.7	61.1	51.5	54.5
Aromatics wt%	40.3	38.9	48.5	45.5
MAT Yields Wt%(Cost. Conversion)				
Light Gases	5.3	6.3	5.6	6.1
LPG	17.2	18.8	18.3	19.1
Gasoline(C5-150C)	19.5	20.8	24.8	25.4
Diesel	37.0	38.0	34.9	35.3
Residue	15.5	11.7	11.1	9.5
Coke	5.5	4.4	5.3	6.2
Propylene	5.0	5.9	5.4	6.2

FCC feed pretreating: Hydrotreating of FCC feed is increasingly considered though it is investment intensive due to potential benefits in increased yields and improved product quality. The FCC feed pretreating has many potential benefits which include

- Reduction of sulfur in distillates
- Improved FCC yields
- Reduction in Sox emissions
- Potential for processing residue

Besides the pretreatment of FCC feed also leads to reduction of Nitrogen content which reduces FCC catalyst acid site poisoning and improves stripper operation in FCC unit as chemisorbed nitrogen compounds are reduced. The hydrotreating of FCC feed was studied in hydrotreating pilot plant using Co/Mo/ Al2O3 catalyst system. The effects of hydrotreating FCC feed, Escravos and Upper Zakkum HVGO and a comparison of FCC yields before and after hydrotreating are given in Table 3. The hydrotreating results in large reduction in sulfur in the feed and aromatics reduction and these improvements in FCC feed quality leads to increased FCC yields and product quality.

Post treating of FCC Gasoline: The typical gasoline pool in Indian refineries consists of the following:

- FCC Gasoline
- Reformate
- Light Straight Run Naphtha
- Full range Naphtha

The FCC gasoline is typically about 60-70 wt% in the overall gasoline pool and has about 600 - 1200 ppm sulfur and about 30% olefins and the reformate contributes the bulk of benzene and aromatics . The proposed specifications of MS limits all these constituents and processes for reduction of the above will also lead to following possible consequences:

Hydrodesulfurisation for removal of sulfur will lead to large reduction of olefins and can cause a loss of octane and octane barrels.

Removal of Benzene and Aromatics can lead to loss of Octane and Octane barrels.

The processing options under these constraints will have a combination of processes to reduce the loss in product value.
Reformate splitter with Benzene saturation and Isomerisation.
FCC gasoline fractionation with extractive removal of Mercaptan sulfur from the light fraction and selective HDS of heavier fraction followed by Isomerisation.

The studies on FCC gasoline desulfurisation were carried out using commercially available HDS catalysts followed by isomerisation using catalyst developed in collaboration with IIP, Dehradun. The results obtained for FCC gasoline desulfurisation followed by isomerisation are given in Table 4. The octane loss is about 10 -12 units during desulfurisation and isomerisation of the heavy fraction improves octane although not to the original level but the overall objective of reduction in sulfur and olefins in Gasoline pool can be achieved.

Hydrodesulphurisation of Diesel for production of Ultra Low Sulfur Diesel: The sulfur content in Diesel is progressively reducing over the years and worldwide there will be a shift to ultra low sulfur diesel 10 - 50 ppm from the year 2005. The desulfurisation of diesel to less than 50 ppm is difficult due to the presence of sterically hindered S-compounds . The development of HDS catalyst for production of Ultra Low Sulfur Diesel is in progress with the collaboration of NCL,Pune and this mainly involves increasing the availability of the active Co-Mo-S phase in the catalyst. The results obtained in our pilot plant using the catalyst
developed is given in Table 5. The sulfur compounds present in Diesel before and after HDS are analysed using GC-PFPD unit and these are given in Fig.1. The results show that the catalyst is active for removal of refractory substituted Dibenzothiophene compounds, which is achieved by increasing the active phase in the catalyst.

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Table 4. Sulfur Reduction in FCC Gasoline

FCC Gasoline is fractionated into Light Gasoline (IBP- 65C) and Heavy Gasoline.
Light Gasoline is treated using Merox Catalyst
Heavy Gasoline is Desulphurised using commercial catalyst and isomerised using developed catalyst. The final product is blended with merox treated light gasoine.

Properties	Feed	Product (Blended Product)
Sulfur ppm	854	<30
RON (GC)	92	87
Olefins Vol%	30	15

Operating Conditions (Isomerisation)
Temperature C : 500 , Pressure : 7 bar
Yields (Overall) : Liquid yield - 90 Wt% LPG+Gases : 10 wt%

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Hydroprocessing for Lube Oil Production

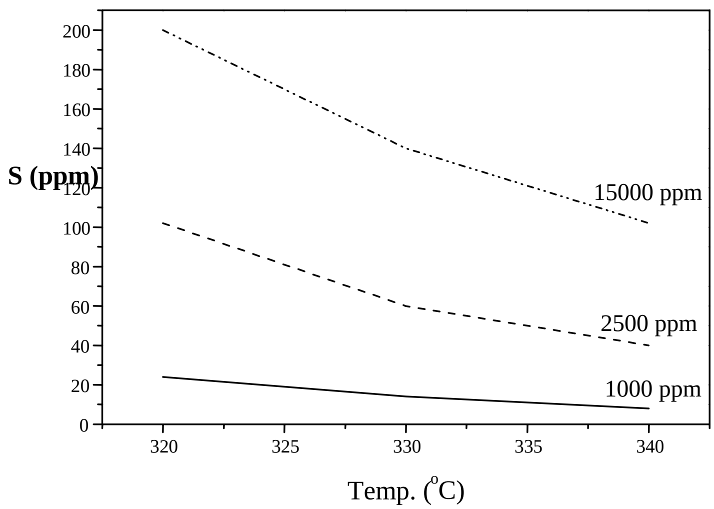
The specifications of the lubricating oils have changed considerably owing to improved engine designs, changing environmental legislation and increasing competitive pressure.

The demands for improving the automotive fuel and oil quality has heightened the need for manufacturing lower viscosity , high VI multi grade oils with reduced volatility and lower pour points. Also the availability of good lube bearing crudes have become scarcer which has necessitated the introduction of new technologies based on hydroprocessing.The API classification of the base oils is given in Table 6. The increase in demand for Group II base oil has made increase the hydroprocessing route for base oil production. The hydroprocessing although expensive offers several advantages over the conventional solvent extraction and dewaxing route.

The hydroprocessing offers greater flexibility in the choice of crude as conventional processing is based on separation of unwanted components. Thus an hydrocracker will result in

Table 5. Effect of Hydrodesulfurisation of Diesel using Novel Catalysts

Performance of catalyst prepared by new procedure: Studies on three different diesel feed-stocks



15,000 ppm, SRGO;
2,500 ppm, after HDS;
1,000 ppm, after HDS

WHSV (h^{-1}); Press = 40 bars;
H_2/oil (v/v) = 300

<u>Typical distribution of product (S in feed = 2500 ppm)</u>
(320°C/1h^{-1}/40bars/300v/v)
Total S = 102 ppm; < DMDBT = 8 ppm; 4,6 DMDBT = 36 ppm; >Alk. DBT = 58 ppm

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Table 6. API Base Oil Classification

Group	Sulfur ppm	Saturates Wt%	VI
I	>300 and/or	<90	80 -120
II	≤300 and	≥90	80 -120
III	≤300 and	≥90	>120

IV All Polyalphaolefins (PAOs) Synthetic Lubricants

higher yields and high VI base oil and can be used for processing any type of crude.
Hydroprocessing route can result in products having superior properties such as ultra high VI, very low pour point and base oils with much better oxidation stability and color compared to conventional process.
Hydroprocessing results in higher product yields unlike the conventional extraction process where the base oil yield is limited by the optimum recovery of lube components naturally occurring

in the feed stock. Also the byproducts obtained in hydroprocessing route are primarily high quality fuels.

Development of Hydro -processing Routes for improved lube quality:

The work carried out by CPCL in collaboration with NCL,Pune in lubes area include Development of catalyst for catalytic dewaxing for production of low pour oils and isomerisation process for production of high VI lube base oils.

Catalytic Dewaxing: The catalytic dewaxing process uses a shape selective catalyst which selectively cracks n-paraffins in base oils resulting in low pour point. Thus catalytic dewaxing offers very low pour point which is not attainable with conventional solvent dewaxing process and also results in higher base oil yields especially for heavier grades.

The typical yields obtained in solvent dewaxing and catalytic dewaxing and properties of lube base oil is given in Table 7. The byproducts of dewaxing are mainly LPG which has a greater demand in India. However, catalytic dewaxing suffers from one disadvantage as the paraffin wax , which is a valuable product obtained in the conventional route is cracked to fuels.

Isomerisation process for high VI lube base stocks: The isomerisation process aims at converting high VI and high pour point n- paraffins to iso paraffins which retains high VI but with low pour point. A comparison of dewaxing processes is given in Table 8. Isodewaxing offers improved product quality and also increases yields of Lube oil Base stocks. Typically, the isodewaxing process employs noble metal catalyst with mildly acidic shape selective sieves as support and hence has a stringent requirements on sulfur content of the feed (less than 10 -20 ppm). This constraint makes it suitable for processing only hydroprocessed feeds such as hydrocracker bottom. The results obtained in our pilot plant with hydrocracker bottom as feed and the yields obtained by conventional solvent dewaxing are given in Table 9. Iso dewaxing leads to increased yields of Lube Oil Base Stocks with high VI.

Table 7. Comparison of Solvent and Catalytic Dewaxing Typical Yields And Quality Of LOBS

	Light SDW	Neutral CDW	Heavy SDW	Neutral CDW	Bright SDW	Stock CDW
Yield Vol%	80	75	84	82	86	91
Visc.(cst)@40 C	31	35	119	131	538	533
VI	96	90	94	93	94	93
Pour Point C	-6	-6	-3	-3	-3	-3

Table 8. Comparison of Dewaxing Processes

	Solvent	Catalytic Dewaxing	Isodewaxing
Feed	Raffinate	Raffinate	Typically Hydroprocessed
Wax Removal	Physical Separation	Shape selective Cracking of wax	Isomerisation of paraffins
DWO P.Pt (C)	-10 to -15 C	-10 to -50 C	-10 to -50 C
VI of DWO	Base	Less or equal to Base	Higher than Base
Main By Products	Wax	LPG, Naphtha	Middle distillates
Operating Costs	100%	50 - 60%	55 - 65%

Table 9:.Comparison of Isodewaxing And Solvent Dewaxing

Feed : Hydrocracker Bottom (400 - 440 C fraction)

	Isodewaxing	Solvent Dewaxing
Yield of DWO (wt% on total HC bottom)	50.0	30.2
Viscosity @ 40 C cst	13.7	16.6
Viscosity @ 100 C cst	3.3	3.7
Viscosity Index	112	104
Pour Point C	12	12

CONDITIONS USED IN THE STUDY

ISO DEWAXING: CATALYST 0.5% Pt/SAPO-11

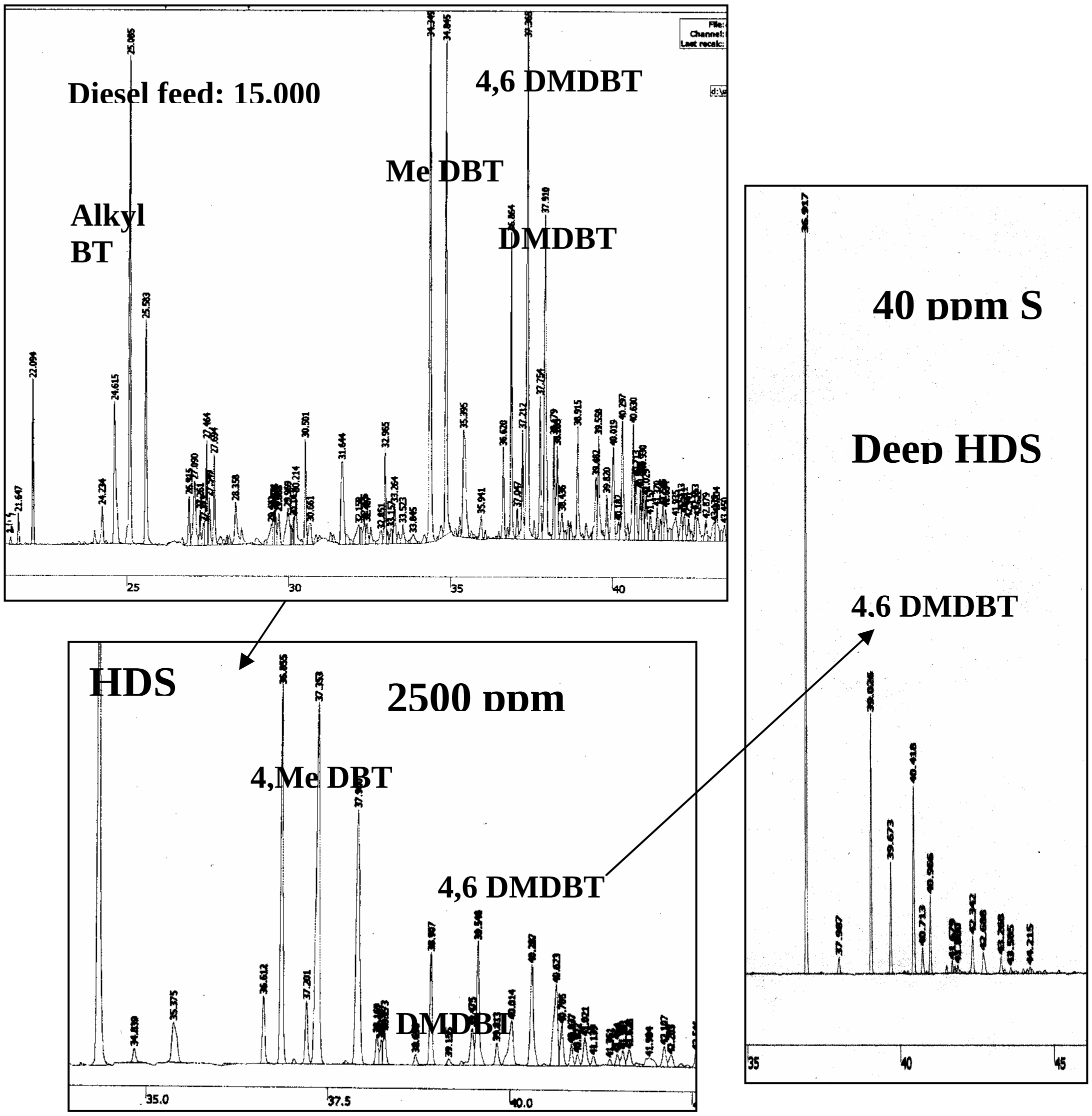
Temparature: 340 C H2/HC : 400; WHSV : 1.0

SOLVENT DEWAXING: Solvent : Commercial solvent (MEK:TOLUENE 50:50)

Total Dilution Ratio 4:1

Dewaxing Temparature: -17 C; Filter Cloth : NS-3 Nylon

Fig. 1 PFPD analysis of S compounds in Diesel before and after hydrodesulfurisation



Conclusions:

Thus hydroprocessing route offer greater flexibility in terms of feed and results in improved product quality and yields. The higher operating costs due to hydrogen requirement is often compensated by the improved product quality and yields. The challenges ahead lie in the development of new catalysts and refinements in the existing catalyst systems particularly with resistant to sulfur and nitrogen poisoning. If the catalyst designed has more sulfur and nitrogen tolerance, hydro-processing will offer wider flexibility to handle all types of feedstocks making it more acceptable.