Reducing hydrogen consumption in diesel hydrotreating

Fractionating a raw diesel stream before hydrotreating reduces consumption of hydrogen to produce high quality diesel

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The demand for clean middle distillates is increasing in India due to stringent environmental specifications. Refineries are focusing on production of Euro V/VI diesel using improved processes and catalysts. Researchers and refiners are working on identification of cost effective processes for production of Euro V/VI diesel with minimum investment. The quality of diesel fuel is improved by treating it with hydrogen in a hydroprocessing reactor where sulphur compounds present in the diesel fraction are removed through hydrodesulphurisation (HDS) reactions in the form of hydrogen sulphide. Along with HDS reactions, hydrodearomatisation (HDA) reactions are also taking place where aromatic rings are saturated with hydrogen and the cetane numbers of the final diesel products are improved. The costliest utility in refinery hydroprocessing units is hydrogen and thus the reduction of hydrogen in the hydrotreating process increases the profitability of the process.

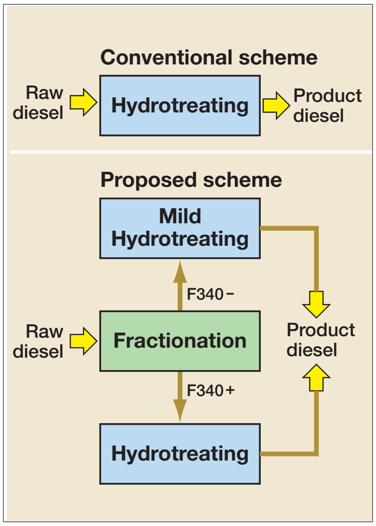

Figure 1 Conventional diesel hydrotreating (top) and a proposed scheme (below) to reduce hydrogen consumption in the refinery

HDA also consumes hydrogen and improves cetane number which is an indicator of fuel combustion efficiency. According to the Euro V specification, diesel fuel should have less than 10 ppm sulphur and 51 cetane number. Sometimes feedstock will already have more cetane. In that case, sulphur removal is the only target. But HDS catalyst will always have some inherent properties for HDA. So it will hydrogenate aromatics which is not required.

Raw diesel oil consists of various types of sulphur compounds, such as thiophenes, dibenzothiophenes (DBT), 4,6-dimethyl dibenzothiophenes (4,6-DMDBT), and so on. For the production of Euro VI diesel with less than 10 ppm of sulphur content, it is mandatory to remove the sterically hindered 4,6-DMDBTs. The removal of 4,6-DMDBTs occurs through a hydrogenation route where one aromatic ring becomes saturated, losing its steric hindrance before the removal of sulphur. Relatively high partial pressures of hydrogen are required for the removal of 4,6-DMDBT through the hydrogenation route. Other aromatic compounds are also saturated under high partial pressures, increasing the hydrogen consumption of the process which actually increases the operating cost.

To tackle this issue, the Research and Development Centre of Hindustan Petroleum Corporation Limited (HPCL) has investigated a process of fractionating diesel in two boil-

Properties of feedstocks

Properties	Raw diesel	F340-	F340+
D86 5	255.0	248.7	338.3
50	298.2	278.8	361.3
95	380.2	341.1	397.4
Density, gm/cc	853.1	842.9	887.9
Cetane number	50	52	45
Aromatics, wt%	27.6	19.14	45.76

Table 1

Sulphur speciation of feedstocks

	Sulphur species, wt%	BT/alkyl BT, wt%*	DBT/alkyl DBT, %*
Raw diesel	1.68	53.3	46.7
F340-	1.4	81.3	18.7
F340+	2.5	0.6	99.4

*BT: Benzothiophenes and DBT: Dibenzothiophenes

Table 2

ing ranges and treating them separately under different process conditions to optimise hydrogen consumption and process conditions (see **Figure 1**). As the boiling point of 4,6-DMDBT is around 364°C, the raw diesel has been fractionated and divided into two fractions: the higher boiling fraction which is comparatively lower in volume but contains almost all of the 4,6-DMDBTs and is hydrotreated under relatively more severe process conditions (for instance, high pressure and high temperature); and the lower boiling range fraction which is comparatively high in volume and contains relatively easily removable sulphur compounds such as thiophenes and benzothiophenes and is hydrotreated under less severe process conditions (for instance, low pressure and low temperature). After hydrotreating both of the fractions in two different reactors under two different sets of process conditions, both the treated streams are mixed further and produce the final product diesel as per specification. In this way, the unnecessary hydrogenation of aromatic compounds present in the lower boiling fractions under the severe process conditions which are necessary for 4,6-DMDBT is avoided. This process actually reduces the overall hydrogen consumption of the process with low severity operation compared to processing the entire raw diesel stream in one reactor with severe process conditions and increases

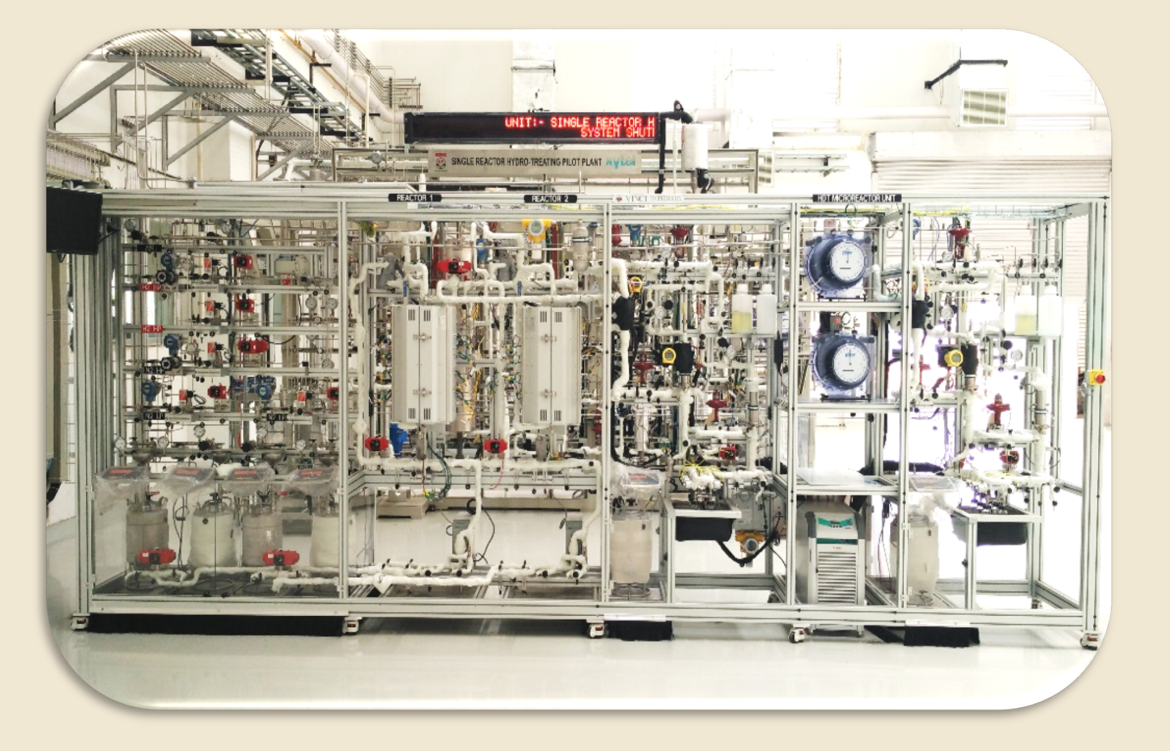

Figure 2 Experimental set-up

Hydrotreated product of raw diesel feedstock

Properties	Products*
Density, gm/cc	830
Sulphur, ppm	13
Cetane	58
H_2 consumption, kg/100 kg feed	0.82
Aromatics, wt%	5.83

*Temperature: 330°C; pressure: 80 barg; H_2/HC: 575 Nm^3/m^3; WHSV: $1Hr^{-1}$

Table 3

Hydrotreated product of F340- feedstock

Properties	Products at different operating pressures, barg*		
	50	60	70
Density, gm/cc	830.8	829.1	827.2
Sulphur, ppm	127	10	9
Cetane number	55	55.6	56
H_2 consumption kg/100 kg feed	0.30	0.37	0.44
Aromatics, wt%	11.13	9.23	7.57

*Temperature: 330°C; H_2/HC: 250 Nm^3/m^3; WHSV: $1Hr^{-1}$

Table 4

Hydrotreated product of F340+ feedstock

Properties	Products at different operating temperatures, °C*		
	330	335	340
Density, gm/cc	854.2	854.3	853.3
Sulphur, ppm	33	23	11
Cetane number	55	55	55
H_2 consumption kg/100 kg feed	1.23	1.24	1.26
Aromatics, wt%	13.06	12.94	12.52

*Pressure: 80 barg; H_2/HC: 575 Nm^3/m^3; WHSV: $1Hr^{-1}$

Table 5

the overall profitability of the refinery.

Laboratory study

The current study has been conducted in a pilot plant set-up shown in **Figure 2**. It is a two reactor system. The design temperature and pressure of the reactors are 550°C and 250 barg. Each reactor was loaded with 25 cc catalyst. Hydrogen flow was maintained through mass flow controllers, and liquid feed flow was maintained through a high pressure pump. Reactor temperatures were maintained through a bronzed line furnace to maintain isothermal temperature inside the catalyst bed. Reaction product gases were measured using a wet gas meter, and the composition of the product gases was measured by a refinery gas analyser (RGA). Liquid product was collected in the product tank. For all of the runs, the material balance of the pilot plant was maintained at ±2%.

Fractionation of raw diesel

Raw diesel (straight run gasoil from the crude distillation unit, see **Table 1**) was fractionated using a TBP-Potstill unit which produced two different feedstocks named F340- and F340+, where F340+ is the portion of raw diesel which has a final boiling point of about 340°C and F340- is the portion of raw diesel which has an initial boiling point below 340°C. The detailed properties of F340- and F340+ are shown in **Table 1**. The yields obtained from the TBP-Potstill unit are 71.5 wt% for F340- and 28.5 wt% for F340+.

Table 2 shows the sulphur speciation of the feedstocks. It was observed that, after fractionation, F340- contains more benzothiophenic sulphur compounds whereas F340+ contains more dibenzothiophenic sulphur compounds. As the boiling point of DBT is 322°C and for 4.6-DMDBT it is 364°C, they become concentrated in the heavier portion of the raw diesel and are produced in F340+ after fractionation.

Hydrotreating

A Ni-Mo type catalyst was used for hydrotreating reactions. Raw diesel was hydrotreated at 330°C (weighted average bed temperature), 80 barg pressure, 1 Hr^{-1} weight hour space velocity, and 575 Nm^3/m^3 hydrogen to oil ratio. The product properties are listed in **Table 3**. The table shows that sulphur content has been reduced to 13 ppm from 1.68 wt%. Eight units of cetane uplift were observed. Total aromatics content has fallen from 27.6 wt% to 5.83 wt%. So almost 21.77 wt% of aromatics has been saturated. Calculated hydrogen consumption is 0.82 kg/100kg of feed.

Table 4 summarises the product properties of hydrotreating F340- feedstocks. Experiments were conducted at different pressures (50 barg, 60 barg, 70 barg), keeping other conditions constant. The product sulphur is low, less than 10 ppm for the 60 barg and 70 barg system pressure. So the optimum pressure can be fixed at 60 barg, for which hydrogen consumption is 0.37 kg/100kg of feed. For these experiments, hydrogen flow was 250 Nm^3/m^3 hydrogen to oil ratio which was low compared to a 575 Nm^3/m^3 hydrogen to oil ratio.

Table 5 shows the product properties of hydrotreating F340+ feedstocks. Experiments were conducted at different temperatures (330°C, 335°C, 340°C), keeping other conditions constant. It was observed that the product sulphur is low, 11 ppm for the 340°C temperature run. So this is the minimum temperature required to obtain the desired level of sulphur in the product. For this arrangement, the cetane uplift is 10 units with a hydrogen consumption of 1.26 kg/100kg of feed.

So the combined product of hydrotreated F340+ (temperature 340°C) and hydrotreated F340- (pressure 60 barg) has a sulphur content of 11 ppm and a cetane number of 55.4. The product sulphur level is equivalent to the hydrotreated product sulphur of raw diesel with an overall cetane uplift of only 5.4 units compared to eight units in the case of the hydrotreated product of raw diesel. The overall hydrogen consumption for hydrotreating fractionated diesel streams is 0.62 kg/100kg. This is low compared to the 0.82kg/100kg of feed which is required for hydrotreating raw diesel. The desired cetane number specification is 52 so, by avoiding unnecessary cetane uplift, this proposed scheme saves almost 0.2 kg/100kg of hydrogen which increases the refinery's profitability. This is happening because almost 71.5 wt% of the feedstock is experiencing less operating severity at 60 barg compared to 80 barg, which is actually reducing the aromatic saturation reactions.

Conclusion

A proposed scheme obtains lower hydrogen consumption to produce high quality diesel by fractionation of the feed diesel streams according to their boiling range and hydrotreating them separately under operating conditions of different severities. The new scheme consumes less hydrogen which increases the profitability of the hydrotreating process. But there is a requirement for a fractionator, additional reactors, a gas compressor, and so on. So the capex of the plant also will increase. A detailed techno-economic feasibility needs to be studied in future for implementation of the scheme.

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