

Up-gradation of light cycle oil using solvent extraction route

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Sulphur compounds naturally exist in crude oil and in the oil refinery, various fuel fractions distributed according to their boiling points. Diesel is a significant transportation fuel and made up of various refinery streams like straight run gas oil, light cycle oil, coker gas oil, etc. Light cycle oil (LCO) is rich in aromatics especially polyaromatics, e.g., alkylated naphthenes, etc. as well as refractory sulphur compounds e.g., dibenzothiophene etc. It may not be possible to reduce aromatics through hydrogenation and sulphur compounds through hydrodesulphurization. Both are expensive and releases more greenhouse gasses. Hence, alternative methods are gaining importance among which solvent extraction has attracted worldwide attention due to inherent advantages like mild reaction conditions and low cost.

In this article, LCO has been distilled up to and above 250°C fractions. Extraction of LCO 250°C+ fraction with solvents, aqueous NMP and nitro methane have been carried out using various solvent to feed ratio and achieved polyaromatics reduction from 23.0 % to < 5.0 % and low sulphur < 0.3wt%. Thus process avoids hydro treating step for meeting PAH specifications.

Keywords: Extractive desulfurization, Dearomatization, Liquid-liquid extraction, Light cycle oil, Diesel

Due to environmental concerns, fuel specifications are becoming more and more stringent particularly concerning sulfur⁶ and aromatic content. In India, since 2015 the limit on sulfur content in diesel was fixed to 50 ppm in 50 metro cities and by the end of 2020 expected to be 10 ppm. Diesel fuel is a mixture of some of refinery blendstocks with similar boiling ranges^{1,2}. Blendstock quality depends on the source of the feed stock and process used for its production³. Blendstocks such as light cycle oil (LCO) and coker gas oil are generally high in sulfur, aromatics and low in cetane value (Fig. 1). Thus making poor diesel bottleneck.

Given the above, LCO needs to be upgraded to meet Bharat-VI specifications for diesel.

Hydrotreating has dominated in dearomatization and desulfurization of liquid fuels. LCO being rich in multi-ring aromatics as well as refractory sulfur compounds, it may not be possible to reduce aromatics through hydrogenation^{4,5}. It is well established that reducing the aromatics through hydrogenation requires much higher severity than hydrodesulfurization as it requires high-pressure operation and high hydrogen consumption, particularly for high aromatics feedstocks. High capital and operating cost of hydrotreating and emergence of stringent fuel specifications in future have motivated the development of alternative technologies, such as bio-desulfurization, adsorption⁷, oxidation^{8,9}, extraction¹⁰, etc. Out of these, the extraction based route holds much promise, as it is possible to reduce the aromatics as well as sulfur content making LCO higher in cetane and lower in sulfur content.

This paper contains the experimental data generated on LCO feedstock received from Indian Refinery using NMP and Nitromethane as the solvent to establish the yield and quality of the refined product.

Feed stock and chemicals used

The LCO feedstocks and Hexane (63-69°C) cut were received from an Indian Refinery. NMP of 99.5 % purity was procured from BASF, AG, Germany. Nitro methane (NM) was procured from Merck chemicals AG Germany. The purity of chemicals used in the study was checked by measuring refractive index and density. The purity was found to be 99%.

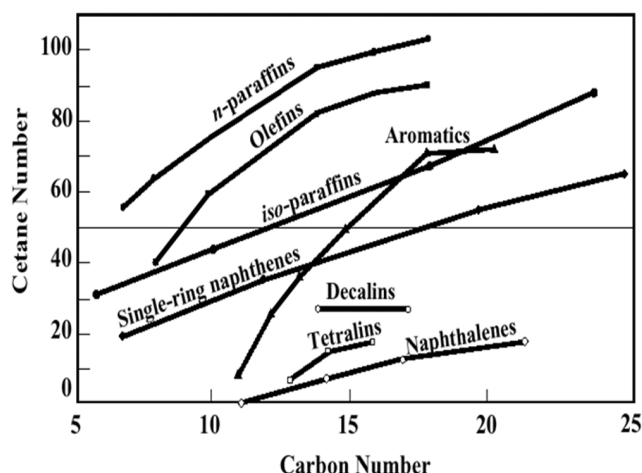


Fig. 1 — Cetane number of distillate hydrocarbon type

Experimental Section

LCO feedstock was distilled to prepare IBP-250°C and 250°C+ cuts. The characteristics of LCO feedstock and LCO 250°C+ cut are given in Table 1. The data shows that this cut contains 6580 ppm of sulfur and about 76 wt% of total aromatics. There is a slight increase in di and poly aromatics as compared to original feedstock.

Continuous counter-current extraction in a packed column

Continuous extraction runs were carried out in a packed glass column with provision of circulating thermo stated water bath maintained at the operating temperature within $\pm 0.5^\circ\text{C}$. The feed and solvent were pumped from separate tanks to the extraction column by metering pumps. The bottom of the column was provided a stop-cock to collect the extract phase at a rate to maintain a constant interphase level in the settling zone. The experiments were carried out at 40°C, and the column was operated with solvent as the dispersed phase. After steady-state was achieved, samples of raffinate and extract phases were collected and analysed.

Continuous counter-current re-extraction of hydrocarbons from extract phase in a packed column

The counter-current re-extraction runs were carried out in the packed column at 40°C using the low paraffinic fraction as secondary solvent. In case of Nitro methane solvent recovery study was carried out in batch mode under vacuum distillation.

Table 1 — Characteristics of LCO feed

Characteristics	LCO Feed LCO feed (250°C ⁺)	
	Value	Value
Density, 20 °C, g/cc	0.93724	0.9441
Refractive Index at 20 °C	1.5421	1.5477
API, deg	27.9	28.8
Sulfur, ppm	6100	6580
ASTM Distillation, D 86, °C		
IBP, °C	191.3	259.0
10% vol.	252.9	269.1
50% vol.	308.2	316.5
90% vol.	364.3	375.0
95% vol.	376.9	388.3
Final boiling point, °C	382.2	391.8
Cetane Index	35.5	27.1
Class type analysis by UV, wt%		
- Alkylated aromatics, Indanes, Tetralenes etc		
- Poly aromatics	17.0	22.8
- Total aromatics	68.2	75.4
- Total saturates	31.8	24.6
Analysis by ASTM 2549		
Aromatics wt %	68.8	76.6
Non Aromatics wt %	31.2	24.4

Analysis of phases

Removal of solvent from the raffinate phase and hexane rich phase

As NMP is highly soluble in water, the raffinate phase was water washed in order to make it solvent free. Analysis of hydrocarbons for aromatic content was carried out by ASTM for aromatic type analysis HPLC / SFC was utilized.

Separation of hydrocarbons from extract phase

The hydrocarbons from the extract phase were recovered by adding sufficient water and distilling the mixture. In the case of Nitromethane solvent being lower boiling (101°C) was distilled from raffinate as well as extract phase as a distillate product. Solvent free hydrocarbons reside in the bottom. Analysis of hydrocarbons for aromatic content was carried out by ASTM for aromatic type analysis HPLC / SFC was utilized.

Results and Discussion

The characteristics of feedstock used in the experiments are given in Table 1. The data shows that the feed contains sulphur 6580 ppm and about 76 wt% of total aromatics respectively. The class type analysis of aromatics is also given in the table.

Counter-current extraction in a packed column

The continuous extraction column runs aqueous NMP and Nitro methane were carried out at 40°C and results are summarized in Tables 2 and 3. The data were generated under different solvent to feed ratios. It is evident from the data that by changing the solvent to feed ratio from 0.5 to 3.0 (w/w), there is a drastic fall in the yield of raffinate, i.e. about 80.01 to 60.65 wt% as expected. It is also clear from the data that on increasing the S/F ratio the selectivity increases and solubility decreases. It is evident from the data that sulfur content has been reduced from 0.66 in the feed to 0.29 and 0.21 wt% and 0.21 and 0.12 wt% in the raffinate at a solvent to feed ratios of 0.6 and 1.0 and 1.0 & 3.0 respectively in both the case. Total aromatic content has been reduced from 76 to 36.7 and 32.8 wt% respectively. The yields of raffinate obtained are 79.5 and 68.0 wt%. The extracts obtained are very rich in aromatics with the BMCI value of 112.5 and 109.8 respectively. It can be revealed from the data that low aromatic and low sulfur LCO can be produced using solvent extraction.

Further reduction in these constituents can be achieved by integrating extraction with additional chemical reaction processes. The data of counter-current extraction in a packed column using NMP+10% water,

Table 2 — Continuous counter current extraction studies

Feed	: LCO (250°C ⁺);	Temperature	: 40°C
Solvent	:	NMP +10% H ₂ O	
Solvent to feed ratio		0.6	1.0
Raffinate hydrocarbons (Solvent free)			
- RI, 20°C		1.4967	1.4873
- Density, g/cc, 20°C		0.8753	0.8628
- yield		80.01	69.7
<i>Class type analysis by HPLC, wt%</i>			
Alkylated aromatics, Indanes, Tetralenes etc.		-	28.8
- Poly aromatics		-	4.2
- Total aromatics		37.9	33.0
- Total saturates		62.1	67.0
<i>Analysis by ASTM 2549</i>			
- Non-aromatics		62.1	66.7
- Aromatics		37.9	33.3
- Total Sulfur, % wt.		0.29	0.21
- Cetane Number		47.53	53.76
Extract (Solvent free)			
- RI, at 20°C		1.6137	1.6085
- Density, g/cc, at 20°C		1.0250	1.0211
- yield		20.0	30.3
<i>Class type analysis; by HPLC, wt%</i>			
Alkylated aromatics, Indanes, Tetralenes etc.		-	28.8
- Poly aromatics		-	37.5
- Total aromatics		-	97.1
- Total saturates		-	2.9
<i>Analysis by ASTM 2549</i>			
- Non-aromatics		18.2	18.7
- Aromatics		81.8	81.2
- Total Sulfur, % wt.		1.12	1.1
- BMCI		120.4	116.10

and Nitromethane at 40°C are presented in Tables 2 and 3. The solvent to feed ratios was kept at 0.6, 1.0 and 3.0 w/w respectively. The results at S/F = 1.0 and 3.0 (for Nitromethane) shows that polyaromatics have been reduced from 22.8 in the feed to 4.2 and 3.1 wt% in raffinate respectively and the sulfur content reduced to 0.21 and 0.12 from 0.6580 in the feed. The yield of raffinate obtained is 69.7 and 60 wt% respectively. The extract contains a high concentration of di and polyaromatics with the BMCI value of 116.1 and 120 respectively. The extract could be a good feedstock for electrode pitches. It is also evident from the data that at S/F = 0.6 the raffinate yield is quite good with the sulfur content of 0.29 wt%. BMCI value of extract obtained is appreciably good, i.e. 120.4.

Conclusion

From the detailed studies above on light cycle oils obtained from Indian refineries, it can be concluded

Table 3 — Continuous counter current Extraction Studies

Feed	: LCO; Temperature		40°C
Solvent	: Nitro methane		
Characteristics			
Solvent to feed ratio		2.9	1.0
Raffinate hydrocarbons (Solvent free)			
- RI, 20°C		1.4789	1.4873
- Density, g/cc, 20°C		--	0.8628
- Yield		60.65	69.7
<i>Class type analysis by UV, wt%</i>			
- Alkylated aromatics, Indanes, Tetralenes etc.		14.3	28.8
- Poly aromatics		3.1	4.2
- Total aromatics		17.2	33.0
- Total saturates		82.8	67.0
<i>Analysis by ASTM 2549</i>			
- Non-aromatics		--	66.7
- Aromatics		--	33.3
- Total Sulfur, % wt.		0.122	0.21
- Cetane Number		49.67	53.76
Extract (Solvent free)			
- RI, at 20°C		1.5919	1.6085
- Density, g/cc, at 20°C		--	1.0211
- yield		39.35	30.3
<i>Class type analysis; by HPLC, wt%</i>			
- Alkylated aromatics, Indanes, Tetralenes etc.		62.1	59.6
- Total saturates		6.6	2.9
- Poly aromatics		31.3	37.5
- Total aromatics		93.4	97.1
<i>Analysis by ASTM 2549</i>			
- Non-aromatics		--	18.7
- Aromatics		--	81.2
- Total Sulfur, % wt.		0.941	1.1
- BMCI		120.4	116.10

that by changing the solvent to feed ratio from 0.6 to 3.0 (w/w) in continuous counter extraction studies it is observed extracts obtained are very rich in aromatics with the BMCI value of 120.4, 116.10, and 109.8 respectively. It can be revealed from the data that low aromatic specially polyaromatics < 5 wt% and low sulfur LCO < 0.3wt% can be produced using solvent extraction with both the solvent: aqueous NMP as well as Nitromethane.

Further reduction in these constituents can be achieved by integrating extraction with additional chemical reaction processes.

Reduction of polyaromatics < 5wt% indicate that the hydrotreating step can be avoided, thereby reduction of hydrogen consumption as well as greenhouse gases. Dearomatized LCO can be blended with diesel before DHDS.

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