

## Impact of Crude Selection on Light and Middle distillates product Specification

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### ABSTRACT

The present investigation deals with the impact of crude selection on Kerosine, Aviation Turbine Fuel, Gasoline and Diesel product specification. To carry out this, four different crude oils are selected on random basis from four different regions namely Middle East, North America, West Africa and Europe. Based on the product specifications given by Indian Standard, how the properties of kerosine cut, naphtha cut and diesel cut from crude oil assay are affecting the product specifications and operating costs of a petroleum refinery is elaborated.

**Keywords:** Crude Oil, Refinery Configurations, Research Octane Number, Cetane Index, Smoke Point, Mercaptan Sulphur, Total Acid Number, Hydrotreating, Caustic Treatment, Catalytic Reforming.

### INTRODUCTION

Crude oil is a naturally occurring mixture of liquid hydrocarbons. In its natural state, crude oil has few direct uses. However, when it is processed in an oil refinery, it is transformed into a variety of highly valued petroleum products such as gasoline and diesel. The value of these products comes from their high energy density and liquid state, which makes them ideal as transportation fuels.

Many types of crude oil are produced around the world. The market value of an individual crude stream reflects its quality characteristics. Two most important quality characteristics of crude oil are density and sulphur content. Density ranges from light to heavy, while sulphur content is characterized as sweet or sour. Crude oils that are light (higher degrees of API gravity, or lower density) and sweet (low sulphur content) are usually priced higher than heavy, sour crude oils.

### Types of Refinery Configurations

#### Topping Refineries

Topping refineries are crude oil fractionation units that produce oil fractions and these oil fractions are sold either domestically or exported to the oil refining and petrochemical companies that have the necessary production facilities to process the oil fractions to increase the profitability. Products of topping

refineries typically consist of refinery fuel gas, liquefied petroleum gas, light and heavy naphtha, distillate, atmospheric gas oil, atmospheric residual oil. Some of the topping refineries also has a small-scale asphalt production.

#### Hydro skimming Refineries

A Hydro skimming refinery has crude distillation unit, a vacuum distillation unit, a catalytic reformer, and hydrotreating units for treating the naphtha, distillate, and vacuum gas oil fractions. It is little more complex than a topping refinery.

#### Cracking Refineries

In Cracking Refineries, either fluid catalytic crackers or possibly vacuum gas oil hydrotreaters and alkylation units have been added to the hydro skimming refinery configuration. Cracking refinery configurations are also known as medium conversion refineries.

#### Cooking Refineries

Major portion of the refiner's margin comes from the higher value "light products" such as gasoline, diesel, Aviation Turbine Fuel that it makes. Delayed coking, fluid coking, and hydrocracking units are added today in revamps of existing refineries and in grassroots refineries that are used in the conversion of vacuum residual oil to produce greater percentages of lighter transportation fuels from crude oils relative to cracking

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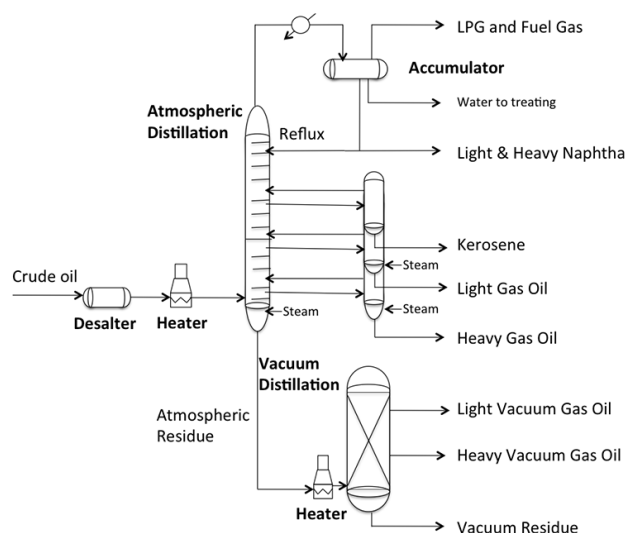
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configuration refineries.. Solvent deasphalting units such as residual oil solvent extraction (ROSE) units are sometimes used with coking units to enhance the refinery's crude oil bottom upgrading capabilities.

In all the refinery configurations, Crude Distillation Unit (CDU) (often referred to as the Atmospheric Distillation Unit) is usually the first **processing equipment** through which crude oil is fed. In the CDU, crude oil is distilled into various products like naphtha, kerosene, and diesel which are then treated in secondary processing units before being sold as finished products.

First the crude oil is heated to a temperature between 120°C to 150°C and then it enters the Desalter and this allows salts, which can be harmful to some equipment, to be removed. The desalted crude continues through the system into the heater where it is further heated to a temperature between 330°C and 385°C depending on the crude composition. Next, it is fed into the atmospheric column where the vapours and liquids separate. Residues are stripped out at the bottom of the column. The products (naphtha, kerosene, diesel and gas oil) are taken from the side of the column and moved through the refinery for further processing.



The atmospheric residue is reheated in a fired furnace to 380°C to 415°C before introduction into the vacuum distillation unit (VDU). This is common in all the refinery configurations except topping refinery which does not have VDU. Furnace outlet temperature is selected depending on the coking property of crude oil and the desired level of separation in the column. Steam ejectors, or, more recently, vacuum pumps, are used to create vacuum for evaporation of the light vacuum gas oil and heavy vacuum gas oil fractions. To minimize the pressure difference between the bottom and top of the column, some special packing materials are used instead of trays for providing contact between liquid and vapour streams to improve fractionation. The heavy distillates (light vacuum gas oil and heavy vacuum gas oil) separated in VDU are further processed in secondary processing units to produce light and middle distillates. The residue from vacuum distillation (VDR) can be upgraded into marketable products and fuels using processes such as visbreaking, deasphalting, and coking.

**Typical boiling range of various hydrocarbon fractions from crude and vacuum distillation unit are:**

- Butane and Lighter (IBP to 15 °C)
- Light Naphtha (C5 to 75 °C)
- Heavy Naphtha (75°C to 165°C)
- Kerosine (165°C to 250°C)
- Diesel (250°C to 343 °C)
- Vacuum Gas Oil (343°C to 538 °C)
- Vacuum Residue (538°C+)

Butane and Lighters, Naphtha, Kerosine are commonly called as Lighter distillates while Kerosine, ATF, Diesel are known as middle distillates. Depending on the type of crude oil, the properties of the above mentioned hydrocarbon fractions vary widely. How this varying nature of crude oil is impacting the final product specification is discussed in this paper.

### Impact of Crude Selection on Kerosine product specification

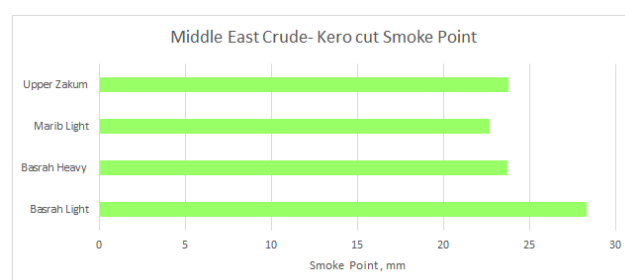
The kero cut from crude oil with boiling range 165 °C to 250 °C is normally sold as SKO (Superior Kerosine Oil) and ATF (Aviation Turbine Fuel). Further SKO can be sold as Low Sulphur Kerosine or normal Kerosine depending on the total sulphur content (wt %) in the finished Kerosine. Kerosine with total sulphur content < 0.10 wt% is sold as Low Sulphur Kerosine and sulphur content above 0.10 wt% and < 0.20% is sold as normal kerosine. Kerosine is used as domestic fuel. Kerosine is mainly used for cooking and lighting. The most important product specification that determines the burning characteristics of Kerosine is smoke point. Smoke point is the maximum flame height in mm at which the fuel will burn without smoking when determined in a smoke point apparatus under specified conditions. The tendency of kerosine to smoke mainly depends on the type of hydrocarbon present. Higher the amount of aromatics in the kerosine, the tendency of smoking will be higher. The smoking tendency of various hydrocarbons are mentioned below

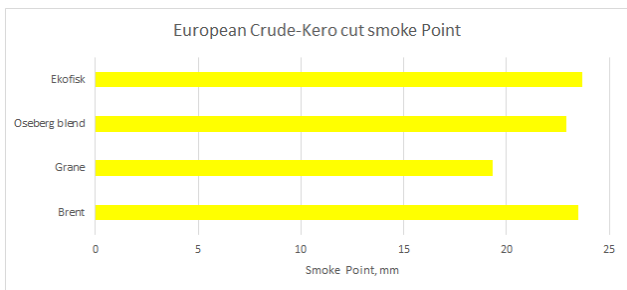
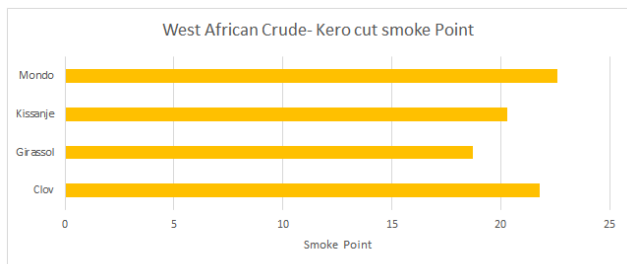
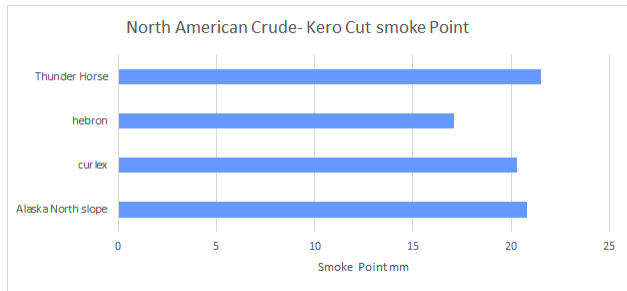
Aromatics > Naphthenes > Isoparaffins > Paraffins

Smoking tendency of paraffins increases with increase in molecular weight. In case of Naphthenes and aromatics, smoking tendency decreases with increase in molecular weight.

As per IS Specification 1459 for Kerosine, smoke point in finished kerosine product should be minimum 18 mm.

Kero cut smoke points of various crude oil are plotted in the graph below.





From the above plot it is inferred that all the crude except Hebron meets the smoke point specification of Kerosine. As the aromatic contents of Hebron crude kero cut is 30.5 vol%, this aromatic contents in kerosine must be reduced to improve the smoke point. One way of improving the smoke point is hydrotreating process where the aromatics content are converted into Naphthenes thereby improving the smoke point of the finished product. This is very popular in refineries that normally process sour crude oils. Another way of removing the aromatics content in the kero cut is Edeleanu process. In Edeleanu process, the straight run kerosine is treated with liquid SO<sub>2</sub>, where all the aromatics and unsaturated hydrocarbons becomes miscible with liquid SO<sub>2</sub> except paraffins and Naphthenes. Some amount of cyclic sulphur and nitrogen compounds are also removed from the straight run kerosine and hence this process reduces the sulphur content in straight run kerosine. As liquid SO<sub>2</sub> is toxic and causes air pollution, no new plants employing Edeleanu process have been built since the late 1950s. Now-a-days the most commonly used process in petroleum refinery for smoke point improvement in Kerosine cut is hydrotreating. The sulphur content of kero cut in various crude oils are given in the table below

**Middle East Crude- Kero cut Properties**

Parameters	Basrah Light	Basrah Heavy	Marib Light	Upper Zakum
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Sulphur wt %	0.279	0.394	0.016	0.244
Smoke point, mm	28.3	23.7	22.7	23.8
Meeting IS 1459 Spec for smoke point and sulphur	No	No	Yes	No
Requirement for Hydrotreating	Yes for reducing the sulphur	Yes for reducing the sulphur	No	Yes for reducing the sulphur

**Table1: Middle East Crude- Kero cut Properties**

**North American Crude- Kero cut Properties**

Parameters	Alaska North slope	Curlex	Hebron	Thunder Horse
Sulphur wt %	0.07	0.017	0.032	0.097
Smoke point, mm	20.8	20.3	17.1	21.5
Meeting IS 1459 Spec for smoke point and sulphur	Yes	Yes	No	Yes
Requirement for Hydrotreating	No	No	Yes for increasing the smoke point	No

**Table2: North American Crude- Kero cut Properties**

**West African Crude- Kero cut Properties**

Parameters	Clov	Girassol	Kissanje	Mondo
Sulphur wt %	0.029	0.08	0.038	0.058
Smoke point, mm	21.8	18.7	20.3	22.6
Meeting IS 1459 Spec for smoke point and sulphur	Yes	Yes	Yes	Yes
Requirement for	No	No	No	No

Hydrotreating
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Table3: West African Crude- Kero cut Properties

European Crude- Kero cut Properties				
Parameters	Brent	Grane	Oseberg blend	Ekofisk
Sulphur wt %	0.014	0.034	0.01	0.015
Smoke point, mm	23.5	19.3	22.9	23.7
Meeting IS 1459 Spec for smoke point and sulphur	Yes	Yes	Yes	Yes
Requirement for Hydrotreating	No	No	No	No

Table4: European Crude- Kero cut Properties

Therefore, those crude oil whose kero cut is inherently meeting the IS 1459 product specification doesnot require additional hydrotreatment or Edeleanu process and this reduces the operating cost when compared to crude oils whose kero cut requires hydrotreatment.

### Impact of Crude Selection on Aviation Turbine Fuel (ATF) product specification

Jet fuel is a colorless, combustible, straight-run petroleum distillate liquid. Its principal uses are as jet engine fuel. The most common jet fuel worldwide is a kerosine-based fuel classified as JET A-1. For JET A-1, the governing specification in India is IS 1571. Among all the hydrocarbon based fuels, ATF have the most extensive specifications since this is used in gas turbine engines in jets. Among the various JET A-1 specifications, few are very important which include Total Acid Number (TAN) in mgKOH/g of oil, Aromatics vol%, total sulphur wt%, Mercaptan sulphur ppm, freezing point (°C), Smoke point in mm. Important properties of Kerosine cut from various crude oils are mentioned in the table below.

Middle East Crude- Kero cut Properties					
Parameters	IS 1571 Spec	Basrah Light	Basrah Heavy	Marib Light	Upper Zakum
Density kg/m3	775-840	793	797	808	802

Smoke Point in mm, min	25	28.3	23.7	22.7	23.8
Smoke point in mm, min & Naphthalenes vol% Max	18	28.3	23.7	22.7	23.8
Total Aromatics vol %, Max	3	0.9	0.9	1	1.7
Total Sulphur wt%	26.5	15.1	18.1	19.3	23.5
Mercaptan Sulphur ppm	30	42.1	95.4	5.8	1.8
TAN mgKOH/g	0.3	0.279	0.394	0.016	0.244
Freezing Point, °C	0.015	0.092	0.097	0.029	0.054
	47	43.33	44.88	38.2	44.3

Table5: Middle East Crude- Kero cut Properties

North American Crude- Kero cut Properties					
Parameters	IS 1571 Spec	Alaska North slope	Curlex	Hebron	Thunder Horse
Density kg/m3	775-840	819	813	851	802
Smoke Point in mm, min	25	20.8	20.3	17.1	21.5
Smoke point in mm, min & Naphthalenes vol% Max	18	20.8	20.3	17.1	21.5
Total Aromatics vol %, Max	3	1.8	4.8	7	1.4
	26.5	21.9	23.8	30.5	15.7

Total Sulphur wt%	0.3	0.07	0.017	0.032	0.097
Mercaptan Sulphur ppm	30	5.1	0.9	1.0	8.6
TAN mgKOH/g	0.015	0.02	0.20	0.384	0.039
Freezing Point, °C	-47	-45.3	-40.38	-71.2	-46.55

Table6: North American Crude- Kero cut Properties

West African Crude- Kero cut Properties					
Parameters	IS 1571 Spec	Clov	Girassol	Kissanje	Mondo
Density kg/m <sup>3</sup>	775-840	826	827	818	822
Smoke Point in mm, min	25	21.8	18.7	20.3	22.6
Smoke point in mm, min & Naphthalenes vol% Max	18 3	21.8 1.9	18.7 3.8	20.3 1.8	22.6 1.9
Total Aromatics vol %, Max	26.5	18.1	22.7	25.3	22.2
Total Sulphur wt%	0.3	0.029	0.08	0.038	0.058
Mercaptan Sulphur ppm	30	9.1	12.3	1.0	0.1
TAN mgKOH/g	0.015	0.394	0.186	0.557	0.374
Freezing Point, °C	-47	-59	-56.67	-52.83	-52.8

Table 7: West African Crude- Kero cut Properties

European Crude- Kero cut Properties					
Parameters	IS 1571 Spec	Brent	Grane	Oseberg blend	Ekofisk
Density kg/m <sup>3</sup>	775-840	812	822	804	804
Smoke Point in mm, min	25	23.5	19.3	22.9	23.7
Smoke point in mm, min & Naphthalenes vol% Max	18 3	23.5 3.2	19.3 2.6	22.9 1.8	23.7 2.3
Total Aromatics vol %, Max	26.5	16.2	26.3	18.3	18.3
Total Sulphur wt%	0.3	0.014	0.034	0.01	0.015
Mercaptan Sulphur ppm	30	0.6	2.3	0.3	3.4
TAN mgKOH/g	0.015	0.053	0.029	0.025	0.035
Freezing Point, °C	-47	-50.6	-50.2	-47.17	-42.38

Table8: European Crude- Kero cut Properties

Among the various crude oil kero cuts in the table above, it is observed that TAN in Kerosine cut is very high in all crude oils, mercaptan sulphur is higher in Basrah Light and Basrah Heavy. Total sulphur is higher than 0.3 wt% in Basrah Heavy. Freezing point specification is not meet by any of the Middle East crudes, Alaska North Slope, Curlex and Thunderhorse. Total Aromatics in Hebron crude is greater than 26.5 vol%.. As per IS 1571 Spec, there are two options to meet the smoke point specification. One is to have smoke point greater than 25 mm in Aviation Turbine Fuel. If this could not be meet, then the smoke point should be greater than 18 mm and Naphthalenes upto 3 vol% max. From the table above, it is observed smoke point characteristics is not meet by Brent, Curlex, Hebron, Girrasol crudes. As the specification of ATF is very stringent, all the above mentioned constraints has to be addressed at refinery level to meet the desired product specification. Options for



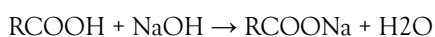
addressing the various specification constraints are mentioned below:

#### Freezing Point

It is generally observed from the crude assay data that the freezing point of heavy naphtha is always lower than that of kerosine. By decreasing the IBP and 5% temperature of Kerosine i.e. by dropping heavy naphtha into kerosine cut, the freezing point of Kerosine can be adjusted and dropping of heavy naphtha into kerosine is permitted till the temperature at 10 vol% recovery in ASTM distillation does not exceed 205 °C as per IS 1571 Specification. Thus by adjusting the column operating conditions, freezing point specification can be achieved.

#### Total Acid Number (TAN)

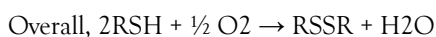
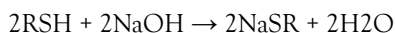
Higher TAN in Kerosine cut is mainly because of Naphthenic acid ( a type of carboxylic acid ) and other acid compounds. Reducing the TAN number in Kero cut is not possible just by varying the column operating conditions. The most commonly used method to reduce TAN number in kerosine cut is by extracting the acidic compounds from Kerosine by using caustic solution. Naphthenic acids (RCOOH) will react with sodium hydroxide (NaOH) and form sodium naphthenates and water according to the following reaction:



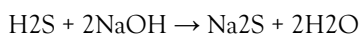
Thus for reducing the TAN number of Kerosine cut, refinery complex requires Kerosine caustic treatment unit.

#### Mercaptan Sulphur

Caustic solution (NaOH) is also suitable for removing mercaptan sulphur in kerosine cut. When kerosine is contacted with caustic solution, mercaptans are extracted from the hydrocarbon into the caustic solution to form sodium mercaptides (NaSR). Sodium mercaptides are then oxidised to form aqueous-insoluble disulphide oil (RSSR) which diffuses back into kerosine. Cobalt phthalocyanine catalyst is used to promote this sweetening reaction. However this process does not change the total sulphur content in Kerosine. The reactions that are involved in this process are mentioned below.



Any hydrogen sulphide (H<sub>2</sub>S) present in kerosine will react rapidly upon contact with caustic and form sodium sulphide and water according to the following reaction:



Thus for reducing mercaptan sulphur in Kerosine cut, refinery complex requires Kerosine caustic treatment unit. All refineries in general are designed for certain crude oil. Based on that crude assay data all secondary units are designed and similarly kerosine caustic treatment unit will also be designed based on the design crude assay kerosine cut. But because of various reasons such as profitability maximization, change in product pattern based on market demand, design crude oil will not be

processed always. Whenever crude oil other than design is processed, it is very important to check whether the crude oil selected will cause any constraints in secondary units. Kerosine treatment unit will be designed for certain feed TAN, Mercaptan sulphur and H<sub>2</sub>S. If feed TAN, Mercaptan sulphur and H<sub>2</sub>S exceeds beyond the design values, then Kerosine caustic treatment unit could not produce the desired ATF Specifications.

#### Total Sulphur

Since, caustic treatment of Kerosine does not bring any change in total sulphur wt%, the only method for meeting the total sulphur specification is hydrotreating of Kerosine.

#### Smoke point and Total Aromatics

Hydrotreating of kerosine reduces the total aromatics vol % in kerosine thereby improving the smoke point of kerosine.

Thus depending on the kerosine cut, Caustic treatment and/or Hydrotreating will help in meeting the desired ATF Product specification.

### Impact of Crude Selection on Gasoline product specification

Those refineries that doesn't have Natural Gas facility, Light Naphtha from crude oil with boiling range C<sub>5</sub> to 75°C is normally used as fuel in Gas Turbines in Captive Power Plant and also steam reformed for producing Hydrogen after hydrotreating. Heavy Naphtha from crude oil with boiling range 75°C to 165 °C along with naphtha from various secondary processing units are hydro treated and feed into Catalytic Reforming unit to produce high Octane C<sub>5</sub>+ Reformate. As the benzene content in the C<sub>5</sub>+ Reformate is more than 1 vol%, they are often blended with various naphtha streams of low octane number and benzene content in addition to alkylate and/or isomerate depending on the refinery configuration to meet the desired MS BS VI specifications.

For a hydro skimming refinery, light naphtha isomerization units can be used to saturate benzene in C<sub>5</sub>+ reformat from Catalytic reformer to aid in meeting gasoline benzene quality. However for a cracking refinery and coking refinery ( also called as deep or maximum conversion refinery), butenes from the Fluid Catalytic Cracker is feed to the alkylation unit where the butenes react with isobutanes from the various LPG streams to form isooctane which is blended with C<sub>5</sub>+ reformat from Catalytic reformer to meet the BS VI gasoline specifications.

Heavy naphtha from crude oil is hydrotreated in Naphtha hydrotreater to decompose the organic sulphur, nitrogen compounds in the hydrocarbon fractions. Hydrotreating removes organo- metallic compounds and also saturates the olefinic compounds in the feed naphtha. The hydrotreated naphtha is then feed to the Platforming unit (Catalytic Reforming Unit) to produce high Octane C<sub>5</sub>+ Reformate. Catalytic Reformer also produces Hydrogen, Refinery Fuel Gas and LPG. Hydrogen from Catalytic Reformer is used in the hydrotreating units. But the key objective of Catalytic Reforming process is to increase the octane number of low octane naphtha

by 25 to 50 units. The actual octane improvement depends on the reforming severity, activity state of the reforming catalyst and the starting octane of the naphtha feed. Thus selection of crude oil will have an impact on the C5+ Reformate Octane number.

A good correlative factor has been developed that provides a measure of the quality of naphtha and the relative ease of processing or reforming of naphtha. The relative quality factor of a naphtha is defined in terms of the composition of the naphtha. N+2A factor is determined and used. N is the vol % of Naphthenes and A is the vol % of Aromatics in the Naphtha. N +2A factor for various crude oils are listed in the table below.

Middle East Crude- Heavy Naphtha cut Properties

Parameters	Basrah Light	Basrah Heavy	Marib Light	Upper Zakum
Naphthenes Vol%	23.8	21.5	29.6	20.3
Aromatics Vol%	11.5	12.6	14.7	14.4
N+2A	46.8	46.7	59	49.1

Table 9: Middle East Crude- Heavy Naphtha cut Properties

North American Crude- Heavy Naphtha cut Properties

Parameters	Alaska North slope	Curlex	Hebron	Thunder Horse
Naphthenes Vol%	42.8	43.8	70.8	34
Aromatics Vol%	16.7	15.8	5.4	15.7
N+2A	76.2	75.4	81.6	65.4

Table 10: North American Crude- Heavy Naphtha cut Properties

West African Crude- Heavy Naphtha cut Properties

Parameters	Clov	Girassol	Kissanje	Mondo
Naphthenes Vol%	35.1	50.6	54.6	49.6
Aromatics Vol%	9.6	7.8	10	10.9
N+2A	54.3	66.2	74.6	71.4

Table 11: West African Crude- Heavy Naphtha cut Properties

European Crude- Heavy Naphtha cut Properties

Parameters	Brent	Grane	Oseberg blend	Ekofisk
Naphthenes Vol%	36.8	47.7	26.1	35.8
Aromatics Vol%	17.1	10.3	15.3	14.4
N+2A	71	68.3	56.7	64.6

Table 12: European Crude- Heavy Naphtha cut Properties

Catalytic reforming data base compiled by Maples (1993) were correlated using multiple regression. Yield correlations for the reformer were developed as given below:

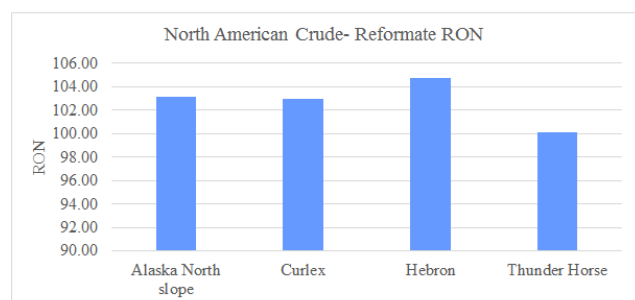
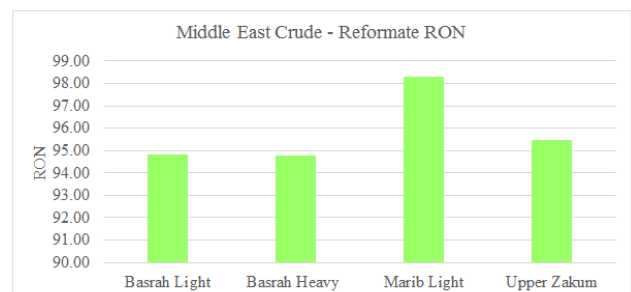
$$C5+Volume \% = 142.7914 - 0.77033 \times RONR + 0.219122 \times (N + 2A)F$$

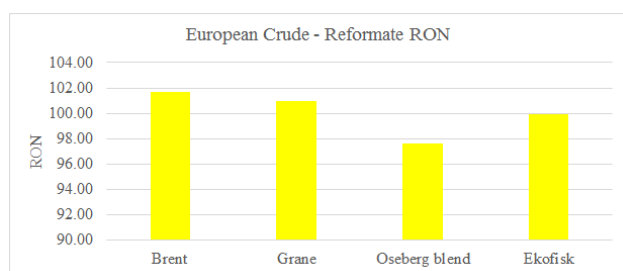
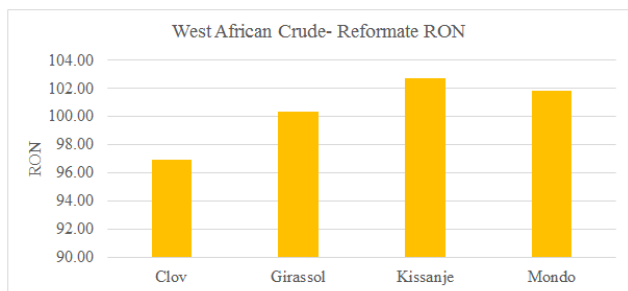
C5+Volume % is the volume percentage of reformate yield.

RONR is the Research Octane Number of Reformate.

(N+2A)F is the feed naphtha N+2A factor.

Thus for a fixed C5+ Volume % of 80, RONR will vary depending on the N+2A factor of heavy naphtha feed. Research Octane Number (RON) of the reformate that will be produced by processing the heavy naphtha of above mentioned crude oils in Catalytic Reformer is calculated based on the above correlation with fixed C5+ Volume % of 80 and the same is plotted in the graph below.





From the graph plotted above, it is inferred that among the four Middle East crude, Marib Light crude is capable of producing high RON Reformate. All the North American crudes plotted above can produce reformate of 100 and above and the same is the case in West African crudes except Clov. Among the European crudes plotted above, Brent crude has the potential of producing high Octane Reformate. Thus crude oil with higher N+2A heavy Naphtha cut should be selected to produce higher RON reformate for the same severity. Crudes with lower RON Reformate potential should be maintained at lower percentages in crude assay so that the gasoline produced in the refinery complex is capable of meeting the BS VI specifications after proper blending of reformate, alkylate, isomerate, naphtha streams depending on the refinery configuration.

### Impact of Crude Selection on Diesel product specification

In a coking refinery, Atmospheric gas oil, Diesel from the Vacuum distillation unit, Light coker gas oil from Delayed coker unit, diesel cut from Fluid Catalytic cracking and VGO Hydrocracking units are blended and processed in diesel Hydrotreater. In a hydrotreating process, sulphur compounds in the hydrocarbon feed are removed as Hydrogen Sulphide H<sub>2</sub>S. The main purpose of a diesel hydrotreater is to remove sulphur but other properties such as cetane number, density and aromatic contents are improved. In a hydrotreater the feedstock is contacted with hydrogen rich gas in the presence of a catalyst at higher temperature and pressure. Aromatics, Polyaromatics, Olefins that are present in the feedstock are hydrogenated in the diesel hydrotreater for improving the cetane number.

Diesel produced in the refinery is mainly used in diesel engines for automotive purposes in buses, Lorries, diesel locomotives. Ignition quality is important in high speed automotive diesel engines. The most universally accepted measure of the ignition quality of diesel fuels is cetane number. Cetane index which provides a measure of the ignition quality very close to cetane number, is also commonly used. It is calculated based on 10%,

50%, 90% distillation temperatures and specific gravity. The relationship is given by the following equation:

$$CCI = 45.2 + 0.0892 T_{10N} + (0.131 + 0.901B)T_{50N} + (0.0523 - 0.42B)T_{90N} + 0.00049((T_{10N}^2 - T_{90N}^2) + 107B + 60B^2)$$

Where:

CCI = Calculated Cetane Index by Four Variable Equation,

D = Density at 15°C, g/mL determined by Test Methods D1298 or D4052,

$$DN = D - 0.85,$$

$$B = [e^{-(3.5)(DN)}] - 1,$$

T<sub>10</sub> = 10 % recovery temperature, °C, determined by Test Method D86 and corrected to standard barometric pressure,

$$T_{10N} = T_{10} - 215,$$

T<sub>50</sub> = 50 % recovery temperature, °C, determined by Test Method D86 and corrected to standard barometric pressure,

$$T_{50N} = T_{50} - 260,$$

T<sub>90</sub> = 90 % recovery temperature, °C, determined by Test Method D86 and corrected to standard barometric pressure, and

$$T_{90N} = T_{90} - 310.$$

Diesel of poor ignition quality i.e., lower cetane number can lead to extended ignition delay and this result in the phenomenon of “diesel Knock”. This will result in reduction in efficiency, smoky exhaust, crankcase oil dilution and carbonaceous deposits in the piston ring grooves. High molecular weight normal alkanes have higher cetane number. As per IS 1460 specification for Automotive Diesel Fuel (BS VI), the cetane index should be minimum 46. Diesel component with boiling range 250°C to 345°C in crude oil shows varying range of cetane index, Sulphur, Aromatics content. These three parameters of the diesel component in crude oil mainly affect the finished diesel specifications. For those crude oil with lower cetane index in diesel cut requires higher severity operation or addition of cetane improves in the finished product to meet the BS VI Automotive Diesel Fuel specifications. Similarly, higher sulphur content and higher aromatics content in the diesel cut require higher amount of hydrogen which in turn increases the operating cost of the diesel hydrotreater. Thus diesel cut from crude oil with higher cetane index, lower sulphur content and lower aromatic content will result in lower operating cost of the diesel hydrotreater. Diesel cut sulphur content, Aromatics vol% in the crude oil selected for the study is given in the table below.

Middle East Crude- Diesel Cut properties

Parameters	Basrah Light	Basrah Heavy	Marib Light	Upper Zakum
Sulphur wt %	1.786	2.054	0.088	0.687
Aromatics Vol%	25.7	28.3	19.4	27



Hydrogen Requirement	Very High	Very High	Less	Very High
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Table 12: Middle East Crude- Diesel Cut properties

North American Crude- Diesel Cut properties				
Parameters	Alaska North slope	Curlex	Hebron	Thunder Horse
Sulphur wt %	0.546	0.135	0.222	0.628
Aromatics Vol%	30.8	23.3	29.8	25.4
Hydrogen Requirement	Very High	Less	High	High

Table 13: North American Crude- Diesel Cut properties

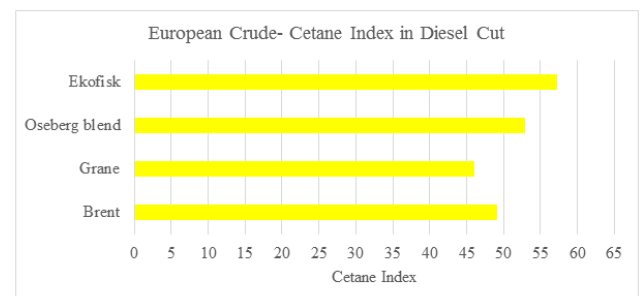
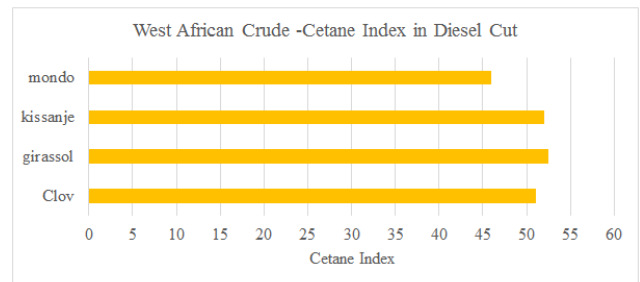
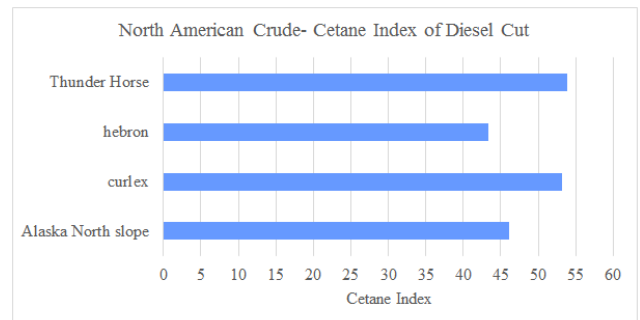
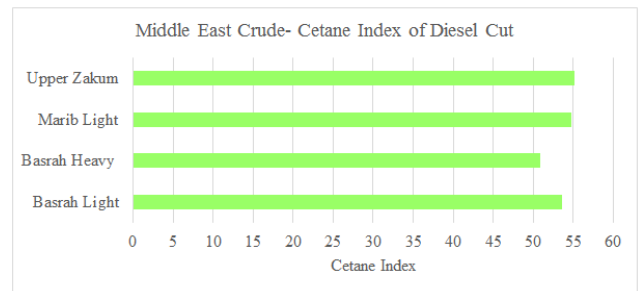
West African Crude- Diesel Cut properties				
Parameters	Clov	Girassol	Kissanje	Mondo
Sulphur wt %	0.15	0.19	0.162	0.232
Aromatics Vol%	22.7	22.2	21.9	29.8
Hydrogen Requirement	Less	Less	Less	Very High

Table 14: West African Crude- Diesel Cut properties

European Crude- Diesel Cut properties				
Parameters	Brent	Grane	Oseberg blend	Ekofisk
Sulphur wt %	0.207	0.272	0.117	0.108
Aromatics Vol%	21.1	26.6	20.2	20.7
Hydrogen Requirement	Low	High	Less	Less

Table 15: European Crude- Diesel Cut properties

The cetane index of the diesel cut are plotted in the graph below.



From the above plot, it is inferred that all the Middle East crude selected for this study has diesel cut with cetane index more than 50. Diesel cut of Hebron crude has cetane index less than 45. when the diesel components of such crudes from Crude and Vacuum distillation unit is mixed with diesel components from Fluid Catalytic cracker whose cetane index ranges from 10 to 20, overall cetane number of the diesel feed to hydrotreater becomes very low and the cetane index of the hydrotreated diesel cannot reach 46 even after increasing the severity of the operation. In such scenarios, the only option to increase the cetane index is by adding Cetane Improver to the finished diesel product. 2-Ethyl Hexyl Nitrate (EHN) is the most commonly used Cetane Improver. EHN decomposes rapidly in the high temperatures of the combustion chamber, yielding products that help initiate combustion and shorten the ignition delay period. EHN is typically added in the concentration range of 0.05-0.4 mass percent. The effect on cetane increases with a higher cetane base

blend. Typical improvement is 3-10 cetane numbers. A drawback of EHN is that it can decrease thermal stability, requiring the use of a stability additive.

Based on practical experience, those crude oil with cetane index of 45 and above in diesel cut results in higher cetane index of finished diesel product for the same severity of operation.

## CONCLUSION

The following are the conclusions of this study

- For those crude oil kerosine cuts with low smoke point and higher sulphur content requires hydrotreating for removing sulphur and improving the smoke point by saturating the aromatics content and the refinery should ensure the availability of Kerosine hydrotreating unit for such kerosine cut.
- In order to meet the stringent Aviation Turbine Fuel Specifications, Kerosine caustic treatment unit is required for removing Naphthenic acids, Mercaptan sulphur and Hydrogen sulphide. In addition to the above, hydrotreating might be required for sulphur removal and smoke point improvement depending on kerosine quality from the crude distillation unit. Freezing point in kerosine can be improved

by a adjusting the operating conditions of the crude distillation unit.

- Higher N+2A heavy Naphtha cut in crude oil should be selected to produce higher RON reformate. Otherwise the severity of Catalytic Reformer has to be increased which in turn increases the operating cost of the refinery.
- Those crude oil with diesel cut cetane index less than 45 requires addition of cetane improver like 2- Ethyl Hexyl Nitrate in finished diesel. Hydrogen requirement in diesel hydrotreater depends on feed sulphur, bromine number and aromatics vol %.

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