

“VALUE ADDITION OF DIESEL STREAM TO PRODUCE NAPHTHALENE”

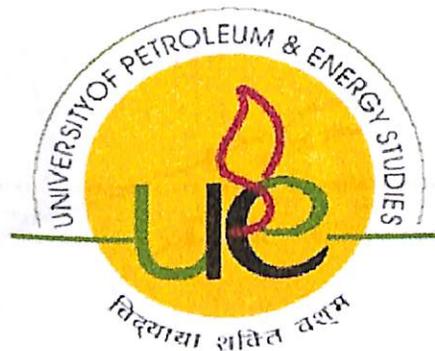
A Thesis Submitted in Partial Fulfillment of the Requirement for the degree of

**BACHELOR OF TECHNOLOGY
(APPLIED PETROLEUM ENGINEERING)**

By

**AKSHAY SINGHAL (R240207006)
KARTIKAY SHARMA (R240207027)
SAURABH MISHRA (R240207050)**

**Under the Guidance of
Dr. R.P. BADONI
(Distinguished Professor)**



College of Engineering

University of Petroleum and Energy Studies

Dehradun

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(Distinguished Professor, Chemical Engg. Department)
UPES, Dehra Dun.**

Approved

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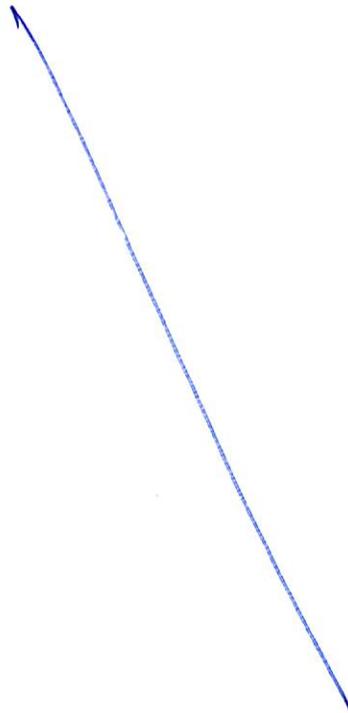
Dehradun

May, 2011

CERTIFICATE

This is to certify that Akshay Singhal, Kartikay Sharma, Saurabh Mishra have done their major project at University of Petroleum & Energy Studies during the fourth year of their academics.

The thesis titled “**VALUE ADDITION OF DIESEL STREAM TO PRODUCE NAPHTHALENE**” is original work and has been carried out under supervision and has not been submitted elsewhere for a degree .



Handwritten signature of Dr. R.P. Badoni in blue ink.

Dr. R.P. BADONI
Distinguished Professor,
Chemical Engg. Department
UPES, Dehra Dun.

ACKNOWLEDGEMENT

Major Project in the final year is an indispensable part of any engineering curriculum. It provides the students with an opportunity to gain experience on the practical application of their technical knowledge and to study the various theoretical aspects as well.

We would like to thank our Project Guide **Dr. R.P. BADONI**, Professor, Chemical Engg. Department, UPES, Dehra Dun for giving us this opportunity to work under his guidance on this project and for also providing us with all the necessary information. His technical help and goal oriented approach has been unique and a stepping stone towards the successful completion of the project.

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Date-18 May, 2011

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ABSTRACT

Petro diesel, is produced from the fractional distillation of crude oil between 200 °C (392 °F) and 350 °C (662 °F) at atmospheric pressure, resulting in a mixture of carbon chains that typically contain between 8 and 21 carbon atoms per molecule. Diesel is generally simpler to refine from petroleum than gasoline and contains hydrocarbons having a boiling point in the range of 180-360°C (360-680°F). The density of diesel is about 0.832 kg/l (6.943 lb/US gal), about 12% more than ethanol free petrol (gasoline), which has a density of about 0.745 kg/l (6.217 lb/US gal). About 86.1% of the fuel mass is carbon and when burned, it offers a net heating value of 43.1 MJ/kg as opposed to 43.2 MJ/kg for gasoline.

Naphthalene, also known as naphthalin, is a crystalline, aromatic, white, solid hydrocarbon with formula $C_{10}H_8$ and the structure of two fused benzene rings. It is volatile, forming a flammable vapour, and readily sublimates at room temperature, producing a characteristic odour that is detectable at concentrations as low as 0.08 ppm by mass. Naphthalene is a starting material for the production of chemicals such as dyes, surfactants, tanning agents, lube oil additives, fumigants, etc.

Diesel in India has a consumption of 45 MMTPA, that is around 6 times that of petrol. It has considerable amount of naphthalene in it. Naphthalene in India has a huge supply demand imbalance. Hence our objective is to recover Naphthalene from diesel by suitable aromatic extraction.

This will lead to twin benefits that are we shall get valuable petrochemical in form of naphthalene which is short in supply in the country and after removal of it from diesel the cetane number of diesel shall significantly increase.

Petroleum derived diesel is a mixture of straight run product (150 °C and 350 °C) with varying amount of selected cracked distillates and is composed of saturated hydrocarbons (primarily paraffin including n, iso, and cycloparaffins), and aromatic hydrocarbons (including naphthalenes and alkylbenzenes).

Diesel in India has a consumption of 45 MMTPA, that is around 6 times that of petrol. It has considerable amount of naphthalene in it. Naphthalene in India has a huge supply demand imbalance.

Similarly gas derived diesel oil also is a mixture of straight run products composing mainly of paraffins, aromatic hydrocarbon along with some dissolved organic compounds containing N,S,O compounds.

The composition of naphthalene in Diesel is in the range of 14-15% by weight. Now the aim is to reduce this percentage to as low as possible, by extraction process, which will be discussed later. Reduction in the amount of naphthalene from diesel will improve the cetane number of diesel as well as color is improved. Also the emissions resulting from diesel will be much more cleaner and environment friendly. Naphthalene extracted from diesel can then be used as a precursor for various petrochemicals.

Diesel

Diesel is used in diesel engines, a type of internal combustion engine. Rudolf Diesel originally designed the diesel engine to use coal dust as a fuel, but oil proved more effective. Diesel engines are used in cars, motorcycles, boats and locomotives. Automotive diesel fuel serves to power trains, buses, trucks, and automobiles, to run construction, petroleum drilling and other off-road equipment and to be the prime mover in a wide range of power generation & pumping applications. The diesel engine is high compression, self-ignition engine. Fuel is ignited by the heat of high compression and no spark plug is used.

The Indian Standard governing the properties of diesel fuels is IS 1460:2005 (5th Rev). Important characteristics are ignition characteristics, handling at low temperature, flash point.

Diesel fuel often contains higher quantities of sulphur. In India, emission standards (equivalent to Euro II, Euro III, Euro IV) have necessitated oil refineries to dramatically reduce the level of sulphur in diesel in view of the auto fuel policy brought in force by Govt. of India.

Diesel (HSD), largely a transport fuel, forms the biggest chunk (35 per cent) of total petroleum product consumption in India. Diesel is mainly used in the road transport, rail transport, and agriculture and power generation sectors. Road transport and agriculture

account for 73-75 per cent of total diesel consumption. The balance is accounted for by the railways 4-5 per cent, the manufacturing industry (captive power generation) and power utilities 13-14 per cent and other end-users. The transport fuel demand was met with by considerable imports just six years back. However, the scenario has changed and India has recently emerged as net exporter of diesel.

	HVO, such as renewable diesel	EN 590 diesel fuel (summer)	GTL	FAME (from rapeseed oil)
Density +15°C, kg/m ³	775–785	≈ 835	770–785	≈ 885
Viscosity +40°C, mm ² /s	2.9–3.5	≈ 3.5	3.2–4.5	≈ 4.5
Cetane number	≈ 80–99	≈ 53	≈ 73–81	≈ 51
Distillation range, °C	≈ 190–320	≈ 180–360	≈ 190–330	≈ 350–370
Cloud point, °C	–5 — –25	≈ –5	–0 — –25	≈ –5
Heating value, MJ/kg	≈ 44	≈ 42.7	≈ 43	≈ 37.5
Heating value, MJ/l	≈ 34.4	≈ 35.7	≈ 34	≈ 33.2
Total aromatics, wt%	0	≈ 30	0	0
Polyaromatics, wt% ¹	0	≈ 4	0	0
Oxygen content, wt%	0	0	0	≈ 11
Sulfur content, mg/kg	<10	<10	<10	<10
Lubricity HFRR +60°C, μm	<460 ²	<460 ²	<460 ²	< 460
Storage stability	Good	Good	Good	Very challenging

Table 1. Properties of various types of Diesel

Naphthalene

Naphthalene is a crystalline, aromatic, white, solid hydrocarbon with formula $C_{10}H_8$ and the structure of two fused benzene rings. It is best known as the traditional, primary ingredient of mothballs. It is volatile, forming a flammable vapor, and readily sublimates at room temperature, producing a characteristic odor that is detectable at concentrations as low as 0.08 ppm by mass.

PROPERTIES OF NAPHTHALENE

Molecular formula	$C_{10}H_8$
Molar mass	128.17052 g/mol
Appearance	White solid crystals/flakes, strong odor of coal tar
Density	1.14 g/cm ³
Melting point	80.26 °C, 353 K, 176 °F
Boiling point	218 °C, 491 K, 424 °F
Solubility in water	Approximately 30 mg/L

Table 2. Properties of Naphthalene

Indian Scenario

With high economic growth rates and over 15 percent of the world’s population, India is a significant consumer of energy resources. In 2009, India was the fourth largest oil consumer in the world, after the United States, China, and Japan. Despite the global financial crisis, India’s energy demand continues to rise. In terms of end-use, energy demand in the transport sector is expected to be particularly high, as vehicle ownership, particularly of four-wheel vehicles, is forecast to increase rapidly in the years ahead. India lacks sufficient domestic energy resources and imports much of its growing energy requirements. In addition to pursuing domestic oil and gas exploration and production projects, India is also stepping up its natural gas imports, particularly through imports of liquefied natural gas.

According to the International Energy Agency (IEA), coal/peat account for nearly 40 percent of India’s total energy consumption, followed by nearly 27 percent for combustible renewables and waste. Oil accounts for nearly 24 percent of total energy consumption, natural gas six percent, hydroelectric power almost 2 percent, nuclear nearly 1 percent, and other renewables less than 0.5 percent. Although nuclear power comprises a very small percentage of total energy consumption at this time, it is expected to increase in light of international civil nuclear energy cooperation deals. According to the Indian government, nearly 30 percent of India’s total energy needs are met through imports.

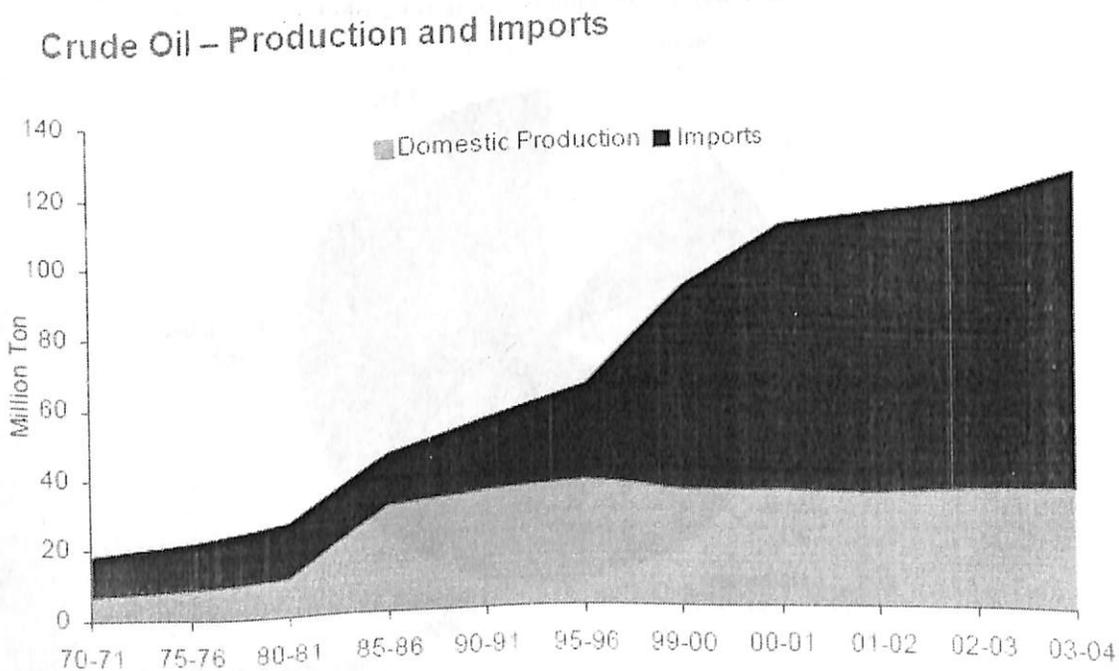


Fig 1. Crude Oil Production & Import in India

Energy plays a critical role in the socio-economic development of a country. The Indian economy has been on a the long-term growth trend since the decade of 80s when it breached the average GDP growth rate of 3.5% a year (“Hindu rate of growth”) to move to an average of 6% in the 90s. Over the last 5 years, the GDP has grown at an average of 5.6 per cent. Global experience proves that the energy market needs to keep pace with growth of economy. In fact, the sustained handholding by energy availability is one of the important requirements for growth. India, over the last 5 years, has prominently shown this trend. The requirement of energy in the form of power, natural gas and refined fuel products has increased steadily. Towards the end of 20th century, a wide gap existed between the demand for crude, natural gas as well as refined products and their domestic supply. Both crude and refined products were heavily imported to bridge this gap. The trend changed substantially after a sudden increase in domestic refining capacity just before the 21st century dawned. In almost all refined products, the dependence on imports is now reduced and as we move towards 2004, India has surplus refining capacity. Regarding crude oil, the gap between domestic supply and demand has been increasing. The import burden has increased because of the increase in refining capacity and no growth in domestic production. There has been a wide gap in the potential demand and supply gap of natural gas. The limited availability of natural gas was due to a lack of domestic discoveries and non availability of import facilities . The recent construction of 2 LNG import terminals is aimed at improving the availability of natural gas in India. A major gas discovery in 2002 in KG basin on Eastern coast, when commercialized, would bring relief to the gas starved situation but would not be sufficient to bridge the demand supply gap.

Crude Oil production has increased at a CAGR 7 per cent from 1970-71 to 1995-96 and is declining at a CAGR 0.6 per cent from 1995-96. Domestic crude oil production has been stagnant around 32 MMT during 1999-2000 to 2003-04. India imports around 73 per cent of its total crude oil requirements.

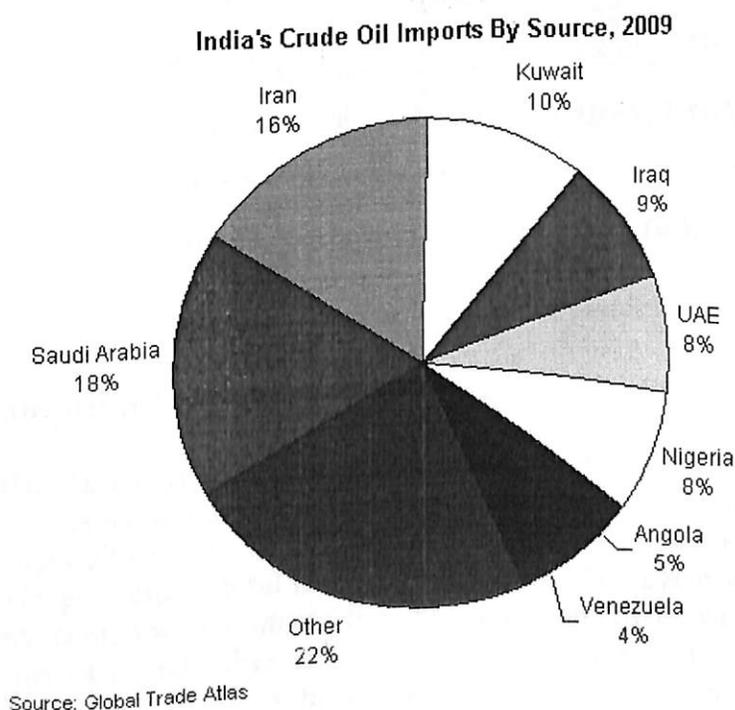


Fig 2. India's Crude Oil Imports

State-Wise & Company-Wise HSD (PSU) Sale during 2005-06										
STATE	AOD	BPC	KRL	BRPL	HPCL	IOC	IBP	CPCL	(Figs. in MTs)	
									OTHS	TOTAL
ANDHRA PRADESH	0	815784	0	0	717727	1410571	287923	400	20	3232424
ANDMAN & NIKOBAR	0	0	0	0	0	73571	0	0	0	73571
ARUNACHAL PRAD.	22229	924	0	0	0	21101	425	0	3	44682
ASSAM	173372	15494	0	0	47539	183083	16108	0	11364	446960
BIHAR	2279	235353	0	0	157582	374350	151819	0	10	921393
CHANDIGARH	0	11356	0	0	10793	37797	3631	0	0	63578
CHHATTISGARH	0	171537	0	0	149228	267857	21675	0	0	610297
DADRA&NAGARHAV.	0	12178	0	0	18200	30025	0	0	0	60403
DAMAN & DIU	0	17548	0	0	10722	17051	6734	0	0	52055
DELHI	0	278902	0	0	293508	452471	138712	0	0	1163193
GOA	0	80684	0	0	75638	111418	4795	0	0	272535
GUJARAT	0	454897	0	0	357455	1009322	235472	0	0	2056948
HARYANA	50221	465841	0	0	380566	1106189	293522	0	10598	2306747
HIMACHAL PRADESH	1036	67976	0	0	59649	160183	17992	0	0	306835
JAMMU & KASHMIR	0	72446	0	0	48881	238243	6207	0	0	365778
JHARKHAND	208	217796	0	0	179983	428616	62520	0	0	889122
KARNATAKA	0	544577	0	0	350452	1306333	126906	0	59499	2387767
KERALA	0	306800	0	0	283346	593939	145850	0	3940	1333875
LAKSHADEEP	0	893	0	0	0	3430	0	0	0	4323
MADHYA PRADESH	0	348121	0	0	270461	705448	58501	0	0	1380531
MAHARASHTRA	0	905954	0	0	787378	1397905	151121	0	103413	3345770
MANIPUR	11427	0	0	0	0	16797	3199	0	518	31939
MEGHALAYA	45295	5757	0	0	17111	68875	13977	0	14078	185090
MIZORAM	17909	0	0	0	0	7916	0	0	0	25825
NAGALAND	12640	10	0	0	697	12637	1051	0	10	27045
ORISSA	2056	267020	0	0	187382	471056	59308	0	0	966823
PONDICHERRY	0	37773	0	0	71363	90013	58771	0	0	257920
PUNJAB	0	440475	0	0	466718	848201	355553	0	0	2110946
RAJASTHAN	2404	611827	0	0	615603	1084525	97875	0	678	2412911
SIKKIM	0	5326	0	0	2194	23334	2440	0	0	33293
TAMILNADU	0	778478	0	0	589809	1434888	171372	0	6563	2981109
TRIPURA	31105	0	0	0	0	10579	1258	0	0	42941
UTTAR PRADESH	0	966816	0	0	626920	2078203	343018	0	25	4014981
UTTARANCHAL	0	73767	0	0	64940	180649	24720	0	10	324086
WEST BENGAL	5004	320882	0	0	334963	755902	177215	0	31	1593997
ALL INDIA HSD										
TOTAL	377185	8530389	0	0	7156804	16892488	3039670	400	210754	36307689

Table 3. State Wise Diesel Sale in India

Diesel Consumption Pattern

Diesel (HSD), largely a transport fuel, forms the biggest chunk (35 per cent) of total petroleum product consumption in India. Diesel is mainly used in the road transport, rail transport, and agriculture and power generation sectors. Road transport and agriculture account for 73-75 per cent of total diesel consumption. The balance is accounted for by the railways 4-5 per cent, the manufacturing industry (captive power generation) and power utilities 13-14 per cent and other end-users. The transport fuel demand was met with by considerable imports just six years back. However, the scenario has changed and India has

recently emerged as net exporter of diesel. Diesel consumption did not rise noticeably from 1998 to 2004 (HSD growth was negative in the first half of 2003-04).

HSD - Trend Analysis

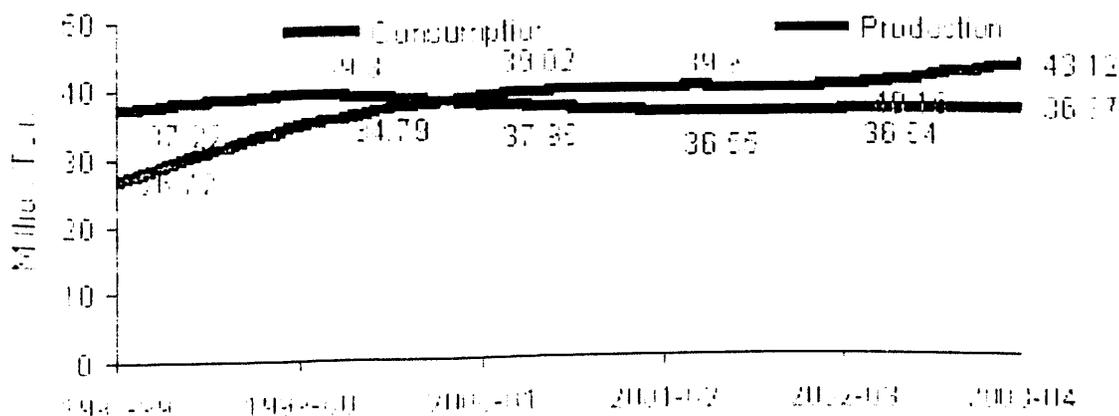


Fig 3. Diesel Production & Consumption Trend

Indian Downstream Industry

India had 2.8 million bbl/d of crude oil refining capacity at 18 facilities as of January 1, 2010. India has the fifth largest refinery capacity in the world. In 2009, privately-owned Reliance Industries added another refinery to its Jamnagar complex to raise the entire complex's refining capacity from 660,000 bbl/d to 1.24 million bbl/d. The Jamnagar complex is the largest oil refinery complex in the world. Other key upcoming refinery projects include Essar Oil's Vadinar refinery expansion of 110,000 bbl/d in 2011, 120,000 bbl/d greenfield refinery in Bina in 2011 by a joint venture between Bharat Petroleum Corporation Limited and Oman Oil Company Limited, a 180,000 bbl/d grassroots refinery in Bhatinda in 2014 by Hindustan Petroleum Corporation Limited, and IOC's grassroots Paradeep refinery of 300,000 bbl/d in 2015. India is slated to add 840 thousand bbl/d of refining capacity through 2015 based on currently proposed projects. Due to expectations of higher demand for petroleum products in the region, further investment in the Indian refining sector is likely. As part of the country's 11th Five Year Plan from 2007 to 2012, the government would like to promote India as a competitive refining destination, and industry experts expect the country to be an exporter of refined products to Asia in the near future.

Refined Fuel Subsidies

The Market Determined Price Mechanism is notionally benchmarked to international oil prices, but the Indian government heavily subsidizes domestic prices of oil products such as diesel, gasoline, kerosene, and LPG. At the same time, taxes on crude and petroleum products imposed by different layers of Indian government often exceed the subsidies. According to industry analysts, though originally an attempt to protect economically disadvantaged Indian consumers, fuel subsidies distort India's domestic market by forcing

India's state owned oil companies to accept under-recoveries (i.e. losses) and encouraging India's private companies to orient their product sales internationally. With diesel prices significantly lower than other fuels, particularly gasoline, diesel consumption rose by nearly 20 percent from 2007 through 2009. The International Energy Agency reports that losses from fuel price subsidies for the 2010-11 fiscal year are expected to exceed \$23 billion.

Sulphur Content In Diesel

Diesel fuel often contains higher quantities of sulphur. In India, emission standards (equivalent to Euro II, Euro III, Euro IV) have necessitated oil refineries to dramatically reduce the level of sulphur in diesel in view of the auto fuel policy brought in force by Govt. of India.

Table
Diesel Fuel Quality in India

Date	Particulars
1995	Cetane number: 45; Sulfur: 1%
1996	Sulfur: 0.5% (Delhi + selected cities)
1998	Sulfur: 0.25% (Delhi)
1999	Sulfur: 0.05% (Delhi, limited supply)
2000	Cetane number: 48; Sulfur: 0.25% (Nationwide)
2001	Sulfur: 0.05% (Delhi + selected cities)
2005	Sulfur: 350 ppm (Euro 3; selected areas)
2010	Sulfur: 350 ppm (Euro 3; nationwide)
2010	Sulfur: 50 ppm (Euro 4; selected areas)

Table 4. Diesel Fuel Quality in India Since 1995

Indian Economy

According to IMF, global GDP growth in 2004 is expected to be higher than the performance recorded over the past 3 decades. China and India are among the star performers. However, the momentum of global growth, including India's, is now being threatened inter alia by fluctuating oil prices. In 2003-04, India registered an overall GDP growth rate of 8.1%. This is a record performance in the new millennium and a substantial improvement over 2002-03. This growth was accompanied by stable inflationary conditions and was backed by favourable balance of payments situation. The fuels for this growth were the buoyancy in the services sector, a resurgence in agricultural growth and a stable manufacturing sector. Even in coming years, India is expected to remain among the faster growing economies in the world. The petroleum sector not only needs to gear up for the desired growth but also fuel the economy more efficaciously.

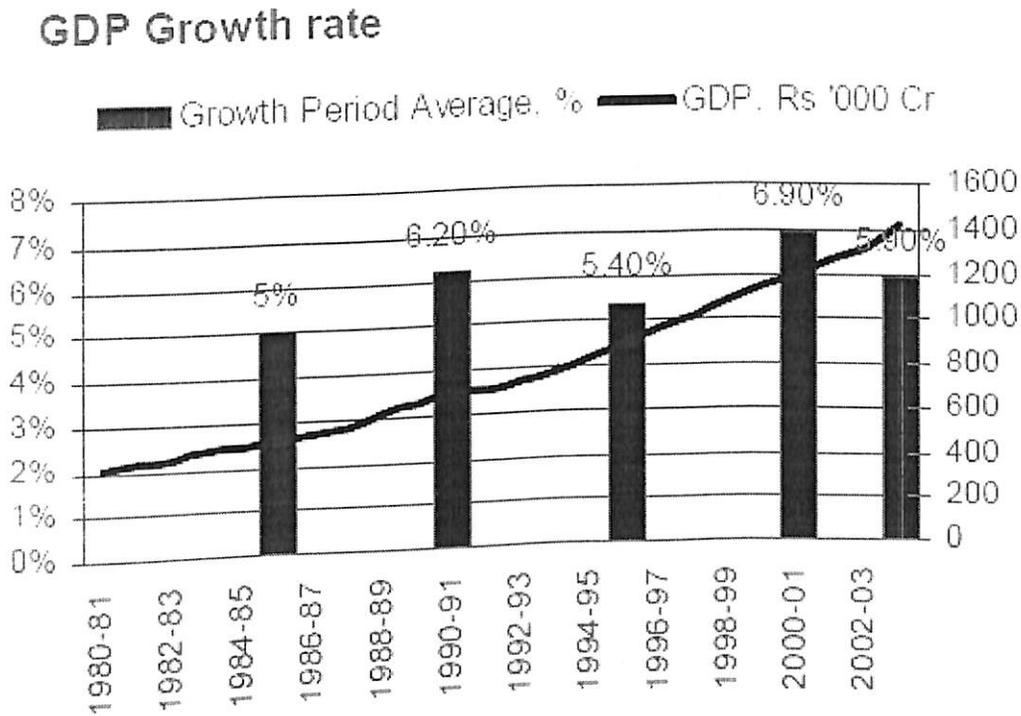


Fig 4. GDP Growth Rate

Specification	India Year 2000	EU Year 2000	Fuel Charter
Cetane Number	48 (min)	51 (min)	55 (min)
Cetane Index		N.A.	52 (min)
Density @ 15°C, g/cm ³	0.82 - 0.87	0.845 (max)	0.840 (max)
Distillation			
85% Boiling Point, °C	350 (max)	N.A.	320 (max)
90% Boiling Point, °C		360 (max)	340 (max)
95% Boiling Point, °C	370 (max)	N.A.	350 (max)
Final Boiling Point, °C		11 (max)	2.0 (max)
Poly-aromatic Hydrocarbons, wt%		N.A.	15 (max)
Total Aromatics Content, wt%			
Flash Point, °C	35 (min)		
Sulphur Content, wppm	2500 (max)	350 * (max)	30 (max)

Table 5. Comparison Of Indian And European Standards

Factors Impacting Energy Demand

Growth in energy consumption is intrinsically linked to growth in the economy. The planners and policymakers of the Indian economy have envisaged a faster rate of growth of the economy. Most economists and planners expect India to record a real GDP growth rate anywhere between 5 percent and 8 per cent. In fact, the Government of India in its Vision 2020 has targeted an annual GDP growth rate of 8.5 to 9 per cent over the next 20 years. This would result in quadrupled per capita income in real terms and almost eliminate poverty. This confidence in the Indian economy is shared by many international agencies. The recent trends as indicated in the figure below have borne out this optimism.

The high rate of economic growth is likely to be accompanied by increasing per capita income and changes in lifestyles. Besides, in view of the rising awareness about environmental protection and conservation, future growth in the energy sector has to be environmentally benign. At the same time, the overall energy intensity of the economy is expected to continue to decline on account of progressive substitution of primary non-commercial energy sources by more efficient commercial energy sources and adoption of more efficient technologies. As discussed in the report, the GDP intensity of use for individual petroleum products do not always follow the same pattern.

In addition to the above, other factors that affect energy demand are:

- a. the price of oil products
- b. environmental considerations
- c. increase in efficiency of use
- d. higher contribution of the service sector in the GDP
- e. impact of information technology, telecommunication and e-commerce

These factors also increase the room for substitution by other products such as natural gas, nonconventional and other renewable sources of energy. Oil security is a matter of key concern to policymakers because India is heavily import-dependent. Global oil prices are especially volatile as they are sensitive to various global factors. The impact of such volatility on India is aggravated by its current inability to respond by increasing crude production.

Approach For Demand Projections Of Refined Products

The econometric model used for projections of demands of fuels demanded time series data for modeling. Similarly, in order to estimate the domestic supply of these fuels in 2011-12, information has been used as regards the availability of capacities of production, expected infrastructure developments and transport facilities. This information, including time series data, has been sourced from Ministry of Petroleum & Natural Gas (MoPNG), Directorate General of Hydrocarbons (DGH), Centre for Monitoring Indian Economy (CMIE) and CRIS Infac.

Future Diesel Fuel Quality Requirements In India

Future diesel fuel quality in India would be governed by requirement for compliance with stringent vehicle emission regulations. The Indian scenario is different from that of U.S. and Europe in terms of fuel consumption pattern, vehicle composition and road conditions, which calls for unique solutions. Consumption of diesel fuel is almost 6 times that of gasoline fuel on national average basis but in the major Indian cities, consumption of diesel may be less than that of gasoline. On national average basis, about 95 per cent of the total NO_x and particulate matter generated by the vehicles is contributed by diesel vehicles.

Emission norms equivalent to Euro-I are currently applicable throughout India for diesel vehicles and additionally, emission norms equivalent to Euro-II are being enforced in metropolitan cities. Time schedule for applicability of Euro-II and Euro-IV emission norms is also in active discussion. These norms are putting severe demands on the oil industry for improving diesel fuel quality.

Emission Norms Beyond 2005

It is seen that India 2000 norms applicable in India from 2000 and Euro-I norms applicable in Europe from 1992 are similar. However, this gap of 8 years would reduce in future and beyond year 2005, the emission norms would show trend of convergence. It is also seen that large reductions have been effected over the years. To meet these standards, advanced engine technologies like turbochargers with inter-cooling, ultra high injection pressures of 1500 bar or more, electronic fuel injection, multi-valve technology and in some cases, exhaust catalytic converters or particulate traps would be employed. Apart from advanced engine technology, improvement in fuel quality is also required.

The desirable diesel fuel characteristics that can control engine exhaust emissions are:

- Low sulphur content to reduce SO₂ emissions and formation of sulphates contributing to particulates in the exhaust.
- Low density to reduce particulates, smoke, CO and HC
- High cetane number to reduce CO, HC and particulates
- Low aromatics content for reduction of smoke, particulates and hydrocarbons
- Low 95 per cent distillation temperature to reduce particulates
- Presence of deposit control additives, lubricity additives and oxygenates

Sulphur content was the first fuel property to be controlled as a means of limiting harmful diesel exhaust emissions. Sulphur is present to a greater or lesser extent in all crude oils and, as a result of the distillation process, some sulphur compounds which boil in the same range are present in the streams used for diesel fuel blending. During combustion, they burn to form acidic by-products (SO₂ and SO₃), together with other gases and also solid compounds, such as sulphates.

After low sulphur, low density is another effective means to reduce particulate emissions. The density of diesel fuel has an impact on combustion and emissions because the

injectors in diesel engines inject a constant volume of fuel into a fixed volume of air. Because all diesel engines operate with excess air, the fuel air mixture becomes leaner and less polluting in terms of CO, HC and particulates when a lower density fuel is used. However, power output decreases with lower density fuels. If diesel engines are returned to adjust their power output, the beneficial effect of lower density on emissions is reduced. According to a report 14 per cent reduction in particulates for direct injection engine and 10 per cent reduction in particulates for indirect injection engine for a reduction in diesel fuel density from 863 to 841 kg/m³ alongwith beneficial effect on CO and HC emissions. A marginal reduction in NOx was also observed for reduction in density from 863 to 841 kg/m³.

A high diesel cetane number reduces engine cranking time for cold start and thus, the HC emissions. Improved quality of combustion is also expected to result in lower emissions of smoke, CO and NOx. However, the beneficial effect is more pronounced when cetane number is increased from low values and gets narrowed down with further increase.

The aromatics on combustion are expected to increase combustion temperatures and thus, the formation of NOx. Engine evaluations suggest that while total aromatics may have no influence on particulate emissions, a more significant role may be played by polycyclic (di-and-tri) aromatics. Low polyaromatic content also reduces smoke, hydrocarbons and biological activity of the exhaust gases.

To maximise diesel production, refineries resort to extension of the boiling range to include heavier fractions. Effect of heavy- ends in diesel fuel has been perceived to increase particulate emissions.

Addition of deposit control additives in the diesel fuel would help to prevent fouling of injectors due to fuel coking leading to deposit formation. Diesel fuels may also require lubricity additives to protect injection equipment when sulphur content is reduced to very low levels. Incorporation of oxygen in the diesel fuels by adding glycol ethers, diglymes, methyl soyate etc. reduce particulate emissions. A slight increase in NOx is observed when oxygen is added. Oxygen contained in ethers is found to be more effective than alcohols blended in diesel fuel.

Isolating the impact of any one particular fuel characteristics on engine emissions is difficult because the physical characteristics of diesel fuel, such as density, distillation characteristics, cetane index and aromatics content, are closely interrelated. However, the European Program on Emissions, Fuels and Engine Technologies (EPEFE) research work with diesel fuels was designed to overcome this difficulty and to provide definitive results for a wide range of engine types.

Light-duty and heavy-duty vehicles respond differently to changing diesel fuel characteristics. On an average, diesel fuel characteristics have little impact (less than 5 per cent) on the emissions of NOx from either type of diesel vehicle. However, the PM₁₀ (particulate matter smaller than 10 microns) emissions can be reduced significantly by reducing the density of diesel used in light-duty vehicles and the sulphur content of diesel used in heavy-duty vehicles. A further reduction of PM₁₀ emissions from both light-duty and heavy-duty vehicles can be obtained by reducing the polycyclic aromatic hydrocarbons in diesel fuel. Reduction of T₉₅ from 370 to 325°C reduced PM₁₀ by 6.9 per cent in light-duty vehicles but no effect was observed in heavy-duty vehicles. Increase in cetane number from

50 to 58 is seen to have no effect on PM₁₀ in heavy-duty vehicles and adverse effect on light-duty vehicles. However, increase in cetane number reduces the CO and HC emissions considerably in both, light-duty and heavy-duty vehicles.

The sulphur content of diesel fuel has been closely correlated with the emissions of SO₂ and PM₁₀. As a result, the reduction of diesel fuel sulphur to a maximum of 0.05 wt-% has become a worldwide trend in the late 1990s. It is felt that fuel refining and automotive industries should work hand in hand in formulating the future emission norms and the fuel quality requirements and systematic research work should be continuously carried out for study of their effect on the air quality in India.

Auto Fuel Policy

The strides that the refineries have taken can be gauged from the fact that the oil sector today is the largest merchandised exporter of the country, ahead of even gems and jewellery. This may be surprising to many but the oil sector has steadily overtaken every other commodity in terms of exports. During April-July 2006 gross oil exports exceeded \$ 6.5 billion as compared to about \$4.8 billion for gems and jewellery, the next largest export of the country. This is 15% of total expenditure further, with the slated expansions in the sector in the next five years the oil sector will maintain its number one position by a large margin.. In the global market, India is likely to emerge as a major exporter of quality fuels.

In terms of vehicle technologies, as per the notified schedule Bharat Stage III vehicles are already available with fuels BS-III quality in 11 cities. The rest of the country has BS-II fuels and corresponding vehicle technology. India in comparison to other developing nations is ahead so far as emission norms are concerned. China for instance will introduce Euro III standards from July 2007, except for Beijing where the standards have been introduced earlier.

Policy Objectives

This policy aims to promote integrated, phased, enduring and self-sustained growth of the Indian automotive industry. The objectives are to:-

- Exalt the sector as a lever of industrial growth and employment and to achieve a high degree of value addition in the country.
- Promote a globally competitive automotive industry and emerge as a global source for auto components.
- Establish an international hub for manufacturing small, affordable passenger cars and a key center for manufacturing Tractors and Two-wheelers in the world.
- Ensure a balanced transition to open trade at a minimal risk to the Indian economy and local industry.
- Conduce incessant modernization of the industry and facilitate indigenous design, research and development.
- Steer India's software industry into automotive technology.

- Assist development of vehicles propelled by alternate energy sources.
- Development of domestic safety and environmental standards at par with international standards.

The Auto Policy has spelt out the direction of growth for the auto sector in India and addresses most concerns of the automobile sector, including-

- Promotion of R&D in the automotive sector to ensure continuous technology upgradation, building better designing capacities to remain competitive.
- Impetus to Alternative Fuel Vehicles through appropriate long term fiscal structure to facilitate their acceptance.
- Emphasis on low emission fuel auto technologies and availability of appropriate auto fuels and encouragement to construction of safer bus/truck bodies - subjecting unorganised sector also to 16% excise duty on body building activity as in case of OEMs

The policy has rightly recognised the need for modernising the parc profile of vehicles to arrest degradation of air quality. The terminal life policy for commercial vehicles and move toward international taxing policies linked to age of vehicles, are steps in the right direction.

The report has estimated that the existing domestic oil refineries, in addition to the investment of Rs. 10,000 crore already made to achieve Euro-I auto fuel specifications, would need to incur an additional investment of around Rs. 18,000 crore by the year 2005. Further investment of around Rs. 12,000 crore will need to be made during the period 2005-2010. The investment requirement of the automobile industry is estimated at around Rs. 25,000 crore over this period.

Shri Naik said that in view of a number of Public Interest Litigations had been filed in the various Courts of the country seeking for issuance of directions for controlling vehicular pollution in Delhi, Mumbai, Kolkata, etc. In order to take a holistic view of the diverse aspects of auto emissions, auto technologies and auto fuel quality on the one hand and the social costs and security of fuel supply on the other, it was decided at a meeting chaired by the Prime Minister on 30.8.2001 to set up a Committee of Experts of national repute headed by Dr. R.A. Mashelkar, Director General, Council of Scientific & Industrial Research (CSIR), to make recommendations to the Government on an appropriate Auto Fuel Policy for the country. Accordingly, this Ministry constituted an Expert Committee on 13.9.2001 to suggest an Auto Fuel Policy for India, along with a roadmap for its implementation as also suitable auto fuels, automobile technologies, fiscal measures, etc., to attain the desired objectives.

Reduction of pollution from in-use vehicles: For reduction of pollution from in-use vehicles, the following measures are suggested:

- New improved Pollution Under Control (PUC) checking system for vehicles.
- Inspection & maintenance (I&M) system for vehicles.
- Performance checking system of catalytic converter and conversion kits for CNG/LPG.
- Augmentation of city public transport system.

- Compliance of emission norms by city public service vehicles and inter State vehicles.

Road Map for New Vehicles

Coverage	Passenger Cars, light commercial vehicles & heavy duty diesel vehicles	2 / 3 wheelers
Entire country	Bharat Stage II - 1.4.2005 Euro III equivalent - 1.4.2010	Bharat Stage II - 1.4.2005 Bharat Stage III* - Preferably from 1.4.2008 but not later than 1.4.2010
11 major cities (Delhi / NCR, Mumbai, Kolkata, Chennai, Bangalore, Hyderabad, Ahmedabad, Pune, Surat, Kanpur & Agra)	Bharat Stage II - 1.4.2003 Euro III equivalent - 1.4.2005 Euro IV equivalent* - 1.4.2010	

Table 6. Road Maps for Vehicles

Indian diesel specifications required to meet *Bharat Stage II* emission norms

Sl. no.	Characteristics	Unit	Requirements
1	Acidity, inorganic		Nil
2	Acidity, total, mg of KOH/g, max	mg of KOH/g	0.2
3	Ash, max	% mass	0.01
4	Carbon residue (Ramsbottom) on 10 % residue, max	% mass	0.3
5	Cetane number (CN), min OR Cetane index (CI), min		without additives 48* 46*
6	Pour point, max, as per OCC Directive		
	a) Winter (Nov-Feb), max	°C	3
	b) Summer, max	°C	15
7	Copper strip corrosion for 3 hrs @ 100 °C, max		Not worse than No. 1
8	Distillation :		
	a) at 350 °C, min recovery	% volume	85
	b) at 370 °C, min recovery	% volume	95
9	Flash point		
	a) Abel, min	°C	35
10	Kinematic viscosity @ 40 °C	cm ²	2.0-5.0
11	Sediment, max	% mass	0.05
12	Density @ 15 °C,	kg/m ³	820-860(820-870)
13	Total Sulphur, max	% mass	0.05
14	Water content, max	% volume	0.05
15	Cold filter plugging point (CFPP)		
	a) Winter (Nov-Feb), max	°C	6
	b) Summer, max	°C	18
16	Total sediments, max	mg/100ml	1.6
17	Lubricity, corrected wear scar diameter (wcd 1.4) @ 60 °C, max	µm, (micron)	460

* For diesel processed from Ashm crude, either CN of 45 min or CI of 43 min and density of 820-870 shall be applicable

Table 7. Indian Diesel Specifications required to meet Bharat Stage II emission norms

**Indian diesel specifications required
to meet Euro III equivalent emission norms**

Sl no.	Characteristics	Unit	Requirements
1	Ash, max	% mass	0.01
2	Carbon residue (Ramsbottom) on 10 % residue, max	% mass	0.3 without additives
3	Cetane number(CN), min		51
4	Cetane Index(CI), min		46
5	Distillation : 95 % vol. recovery at °C, max	°C	360
6	Flash point : a) Abel, min	°C	35
7	Kinematic viscosity @ 40 °C	cst	2.0-4.5
8	Density @ 15 °C,	kg/m ³	820-845
9	Total sulphur, max	mg/kg	350
10	Water content, max	mg/kg	200
11	Cold filter plugging point (CFPP) a) Summer, max b) Winter, max	°C °C	18 6
12	Total contaminations, max	mg/kg	24
13	Oxidation stability, max	g/m ³	25
14	Polycyclic Aromatic Hydrocarbon (PAH), max	% mass	11
15	Lubricity, corrected wear scar diameter (wsd 1,4) @ 60 °C, max	µm (microns)	460
16	Copper strip corrosion for 3 hrs @ 50 °C, max	rating	class-1

Table 8. Indian Diesel Specifications required to meet Bharat Stage III emission norms

**EURO IV/BHARAT STAGE IV EMISSION NORMS COMPLIANT — SPECIFICATION FOR
AUTOMOTIVE DIESEL FUEL**

<i>Sl No</i>	<i>Characteristics</i>	<i>Requirements</i>	<i>Test Method [P:] of IS 1448/ISO/ASTM</i>
(1)	(2)	(3)	(4)
i)	Acidity, inorganic	Nil	[P : 2]
ii)	Acidity, total, mg of KOH/g, <i>Max</i>	To report	[P : 2]
iii)	Ash, percent by mass, <i>Max</i>	0.01	[P : 4]/ISO 6245
iv)	Carbon residue (Ramsbottom) on 10 percent residue ¹ , percent by mass, <i>Max</i>	0.30	[P : 8]/ISO 10370
v)	Cetane number, <i>Min</i>	51 ²	[P : 9]/ISO 5165
vi)	Cetane index, <i>Min</i>	46 ²	D 4737/ISO 4264
vii)	Pour point ³ , <i>Max</i> :		[P : 10]/D 5949 or D 5950 or D 5985
	a) Winter	3°C	
	b) Summer	15°C	
viii)	Copper strip corrosion for 3 h at 50°C	Not worse than No. 1	[P : 15]/ISO 2160
ix)	Distillation, percent v/v, recovered at 360°C, <i>Min</i>	95	[P : 18]/ISO 3405
x)	Flash point ⁴ :		
	a) Abel, °C, <i>Min</i>	35	[P : 20]
	b) Pensky Martens closed cup ⁴ , °C, <i>Min</i>	66	[P : 21]
xi)	Kinematic viscosity, cSt, at 40°C	2.0 to 4.5	[P : 25]/ISO 3104
xii)	Sediment, percent by mass, <i>Max</i>	—	[P : 30]
xiii)	Total contamination, mg/kg, <i>Max</i>	24	EN 12662
xiv)	Density at 15°C ⁵ , kg/m ³	820-845	[P : 16] or [P : 32] ⁶ /D 4062/ ISO 3675 or ISO 12185
xv)	Total sulphur ⁷ , mg/kg, <i>Max</i>	50	ISO 20846 or ISO 20847 or ISO 20884/ [P : 83]/D 5453/ D 2622/D 4294/[P : 34] ⁸
xvi)	Water content, mg/kg, <i>Max</i>	200	ISO 12937
xvii)	Cold Filter Plugging Point (CFPP) ³ , <i>Max</i> :		[P : 110]/D 6371
	a) Winter	6°C	
	b) Summer	18°C	
xviii)	Oxidation stability ⁹ , g/m ³ , <i>Max</i>	25	ISO 12205 or ASTM D 2274 ⁹
xix)	Polycyclic Aromatic Hydrocarbon (PAH), percent by mass, <i>Max</i>	11	IP 391 or EN 12916
xx)	Lubricity corrected wear scar diameter (wsd 1.4) at 60°C, microns,	460	ISO 12156-1/Cor 1

Table 9. Indian Diesel Specifications required to meet Bharat Stage IV emission norms

Chemical Composition

Petroleum derived diesel is composed of about 75% saturated hydrocarbons (primarily paraffins including n, iso, and cycloparaffins), and 25% aromatic hydrocarbons (including naphthalenes and alkylbenzenes).

Diesel typically weighs about 7.1 pounds (lb) per US gallon (gal) (850 grams per liter (g/l)), whereas gasoline weighs about 6.0 lb per US gal (720 g/l), or about 15% less. When burnt diesel typically releases about 147,000 British thermal units (BTU) per US gal (40.9 megajoules (MJ) per liter), whereas gasoline releases 125,000 BTUs per US gal (34.8 MJ/l), also about 15% less. Diesel is generally simpler to refine than gasoline and often costs less (although price fluctuations often mean that the inverse is true; for example, the cost of diesel traditionally rises during colder months as demand for heating oil, which is refined much the same way, rises).

Diesel fuel, however, often contains higher quantities of sulfur. In Europe, emission standards and preferential taxation have both forced oil refineries to dramatically reduce the level of sulfur in diesel fuels. In contrast, the United States has long had "dirtier" diesel, although more stringent emission standards have been adopted with the transition to ultra-low sulfur diesel (ULSD) occurring in 2006. U.S. diesel fuel typically also has a lower cetane number (a measure of ignition quality) than European diesel, resulting in worse cold weather performance and some increase in emissions.

High levels of sulfur in diesel are harmful for the environment. It prevents the use of catalytic diesel particulate filters to control diesel particulate emissions, as well as more advanced technologies, such as nitrogen oxide (NO_x) adsorbers (still under development), to reduce emissions. However, lowering sulfur also reduces the lubricity of the fuel, meaning that additives must be put into the fuel to help lubricate engines. Biodiesel is an effective lubricity additive.

Diesel contains approximately 18% more energy per unit of volume than gasoline, which, along with the greater efficiency of diesel engines, contributes to fuel economy (distance traveled per volume of fuel consumed).

In the maritime field various grades of diesel fuel are used.

HYDROCARBON TYPE	HEAVY REFORMATE	DIESEL	STEAM CRACKING BYPRODUCT
Total Aromatics	90 - 95	45 - 65	70 - 95
Alkyl Benzene	20	25	20
Indane & Tetralines	15	25	10
Alkyl Indanes	2	7	18
Alkyl Naphthalene	55	35	45
Biphenyls and Acenaphthalenes	6	6	5
Tricylics	2	2	2

Table 10. Chemical Composition of Diesel

PRODUCT	Wt %
Naphthalene	1.5
Methylnaphthalene	6.82
Dimethyl naphthalene	10.65
Trimethyl naphthalene	8.06
Tetramethyl naphthalene	3.72

Table 11. Naphthalene composition in Diesel

Sources of Diesel

Diesel oil is fuel specifically produced to power diesel engines. Most diesel oils are derived from petroleum, but some are produced using gases, plants and other biological material. Somewhat denser than regular gasoline, diesel is categorized according to qualities including heaviness, purity and source. Each type has different properties and performs differently in engines.

1. Conventional and Low-Sulfur Diesel

Diesel fuel, while allowing diesel engines to get greater fuel economy than regular gasoline engines, also results in a higher production of nitrogen oxide and soot, mainly due to its higher sulfur content. In order to meet environmental requirements in many countries, some of this sulfur must be removed before the diesel can be used as a fuel in car engines. Conventional diesel has approximately 500 parts per million of sulfur.

2. Ultra-Low-Sulfur Diesel

Since 2006, the United States has required that all diesel engines burn ultra-low-sulfur diesel, which contains no more than 15 parts per million of sulfur. This change allowed diesel engines to use their catalytic converters and traps to significantly reduce the emission of nitrogen oxide and soot. The device couldn't be used before without being clogged by the relatively high sulfur content of available diesel fuel.

3. Grades No. 1D and No. 2D

Diesel fuels have varying densities, which affect how the fuel is combusted within an engine. Diesel comes in two main grades: 1D and 2D. Grade 1D, the lighter of the two, allows the engine to start more easily in cold weather, while 2D is preferred for high-speed engines.

4. Biodiesel

In the wake of recent spikes in the price of oil, there has been increased interest in the production of fuels derived from sources other than petroleum, including biodiesel, which is produced from biological matter, commonly vegetable oil and animal fats. The performance of biodiesel in engines is comparable to that of petroleum-derived diesel, and biodiesel has been shown to produce fewer emissions.

5. Gas-To-Liquid Diesel

Gas-to-liquid (GTL) diesels are produced using the Fischer-Tropsch process of converting gases into liquid fuels. The gas used can be natural gas, or it can be derived from certain types of coal and biomass. GTL diesel has been shown to produce lower tailpipe emissions than regular diesel. GTL fuels typically suffer from a slight loss of fuel economy, but diesel engines are already significantly more efficient than engines that burn gasoline.

6. Blended Diesel

Diesel fuel is often composed of a blend of different types of diesel fuel. Recently, biodiesel has begun to be regularly blended in with regular, petroleum-derived diesel. One fuel, called B-20, is composed of 20 percent biodiesel and 80 percent regular diesel.

7. Diesel from Fischer Tropsch Process

The Fischer–Tropsch process (or Fischer–Tropsch Synthesis) is a set of chemical reactions that convert a mixture of carbon monoxide and hydrogen into liquid hydrocarbons. The process, a key component of gas to liquids technology, produces a petroleum substitute, typically from coal, natural gas, or biomass for use as synthetic lubrication oil and as synthetic fuel. The F-T process has received intermittent attention as a source of low-sulfur diesel fuel and to address the supply or cost of petroleum-derived hydrocarbons.

The Fischer–Tropsch process involves a series of chemical reactions that lead to a variety of hydrocarbons. Useful reactions give alkanes:



Fischer Tropsch Process

Chemical mechanisms

The conversion of CO to alkanes involves net hydrogenation of CO, the hydrogenolysis of C-O bonds, and the formation of C-C bonds. Such reactions are assumed to proceed via initial formation of surface-bound metal carbonyls. The CO ligand is speculated to undergo dissociation, possibly into oxide and carbide ligands. Other potential intermediates are various C-1 fragments including formyl (CHO), hydroxycarbene (HCOH), hydroxymethyl (CH₂OH), methyl (CH₃), methylene (CH₂), methylidyne (CH), and hydroxymethylidyne (COH). Furthermore, and critical to the production of liquid fuels, are reactions that form C-C bonds, such as migratory insertion. Many related stoichiometric reactions have been simulated on discrete metal clusters, but homogeneous F-T catalysts are poorly developed and of no commercial importance.

Process conditions

Generally, the Fischer–Tropsch process is operated in the temperature range of 150–300 °C (302–572 °F). Higher temperatures lead to faster reactions and higher conversion rates but also tend to favor methane production. As a result, the temperature is usually maintained at the low to middle part of the range. Increasing the pressure leads to higher conversion rates and also favors formation of long-chained alkanes both of which are desirable. Typical pressures range from one to several tens of atmospheres. Even higher pressures would be favorable, but the benefits may not justify the additional costs of high-pressure equipment.

A variety of synthesis gas compositions can be used. For cobalt-based catalysts the optimal $H_2:CO$ ratio is around 1.8-2.1. Iron-based catalysts promote the water-gas-shift reaction and thus can tolerate significantly lower ratios. This reactivity can be important for synthesis gas derived from coal or biomass, which tend to have relatively low $H_2:CO$ ratios (<1).

A good diesel fuel should meet certain specified requirements. One of the most well known is the cetane index. The cetane index of a diesel fuel is a measure for the ignition quality of a diesel. In general, high cetane fuels eliminate engine roughness or diesel knock, permit an engine to be started at lower air temperatures, provide faster engine warm-up without misfiring or producing white smoke, and reduce the formation of coke deposits. Cetane, which has a high ignition quality represents 100 on the cetane index scale. The cetane index of a fuel depends mainly on its hydrocarbon composition. In general, paraffins have a high cetane index, followed by olefins and cycloparaffins, while aromatics have the lowest cetane index. Another parameter which is of importance for a diesel fuel is its API gravity, which is a measure for the density of fuel. Diesel fuel is sold by volume. The greater the volume swell (density decrease), the greater the increase in product value.

Process Description (ADU)

The ADU (Atmospheric Distillation Unit) separates most of the lighter end products such as gas, gasoline, naphtha, kerosene and gas oil gas, gasoline from the crude oil. The bottoms of the ADU is then sent to the VDU

Crude oil is preheated by the bottoms feed exchanger, further preheated and partially vaporized in the feed furnace and passed into the atmospheric tower where it is separated into off gas, gasoline, naphtha, kerosene, gas oil, and bottoms.

This tower contains 20 fractionation trays, is equipped with one top pump around, an overhead reflux system, and three side strippers (for naphtha, kerosene, and gas oil products).

The liquid from the feed furnace enters the tower bottoms, where it is collected and sent for further processing to the VDU. Steam is injected into the base of the tower to reduce the hydrocarbon partial pressure by stripping some light boiling components from the bottoms liquid. The vapors from the feed heater enter the tower below tray 20.

At tray 19, a draw pan is located from which gas oil product is drawn. The gas oil product flows by gravity to the top of the gas oil stripper. Stripping steam is used to remove the light ends, improving the flash point. The stripped gas oil product is pumped to storage.

The next product draw is located at tray 12, where the kerosene product is drawn. The kerosene product flows by gravity to the top of the kerosene stripper. Stripping steam is used to remove the light ends, improving the flash point. The stripped kerosene product is pumped to storage.

The last product side draw is located at tray 5, where the naphtha product is drawn. The naphtha product flows by gravity to the top of the naphtha stripper. Stripping steam is used to remove the light ends, improving the flash point. The stripped naphtha product is pumped to storage.

A pump around liquid stream is drawn from tray 6, cooled and returned to tray 3.

The condensed gasoline and water are separated by gravity in the reflux drum. Part of the gasoline is pumped back to the tower as reflux, with the rest going to storage. The water is drained to disposal and the vapor from the ADU overhead is passed to an untreated fuel gas system.

The VDU (Vacuum Distillation Unit) takes the residuum from the ADU (Atmospheric Distillation Unit) and separates the heavier end products such as vacuum gas oil, vacuum distillate, slop wax, and residue. Heavy crude oil is preheated by the bottoms feed exchanger, further preheated and partially vaporized in the feed furnace, and passed into the vacuum tower where it is separated into slop oil, vacuum gas oil, vacuum distillate, slop wax, and bottoms residue.

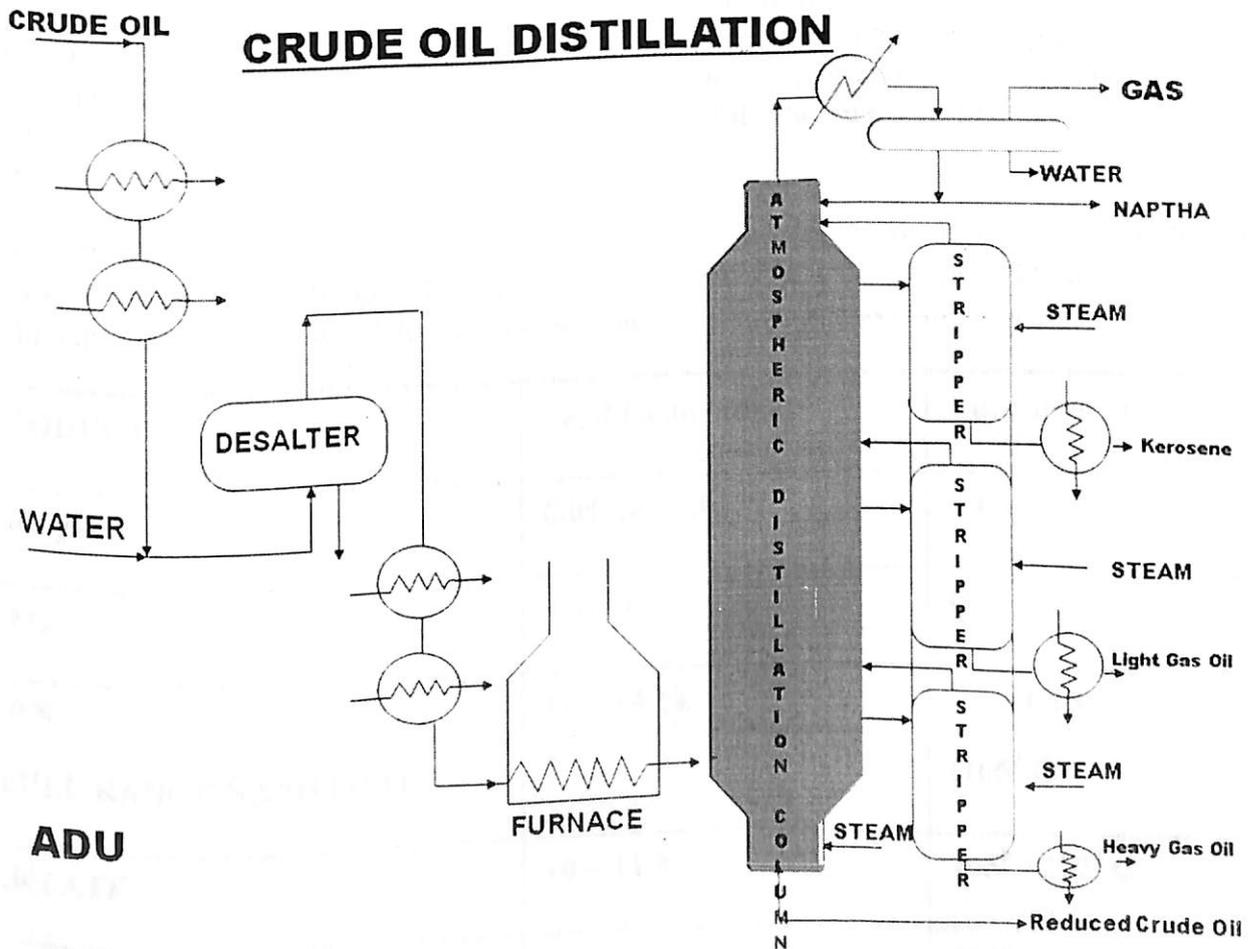


Fig 5. PFD of Crude Distillation Unit

This tower contains a combination of 14 fractionation trays and beds. It is equipped with three side draws and pump around sections for vacuum gas oil, vacuum distillate, and slop wax products.

The liquid from the feed furnace enters the tower bottoms, where it is collected and sent for further processing. Steam is injected into the base of the tower to reduce the hydrocarbon partial pressure by stripping some light boiling components from the bottoms liquid. The vapors from the feed heater enter the tower below tray 14.

At tray 14, a draw pan is located from which slop wax product is drawn. The slop wax product and pump around are cooled, with the slop wax product going to storage, while the pump around is returned to the tower at tray 11.

The next product draw is located at tray 8, where the draw for vacuum distillate product is located. The vacuum distillate draw tray is a total draw tray, where the reflux from the tray is pumped under flow control to the tray below. The product and pump around are cooled, with the vacuum distillate product going to storage, while the pump around is returned to the tower at tray 7.

The last product draw is located at tray 4, where the draw for vacuum gas oil product is located. The vacuum gas oil draw tray is also a total draw tray, where the reflux from the tray is pumped under flow control to the tray below. The product and pump around are cooled with the vacuum gas oil product going to storage, while the pump around is returned to the tower at tray 1.

The overhead from the VDU is condensed and combined with the vacuum steam. The slop oil and water are separated by gravity in the vacuum drum. The water is drained to disposal, while the slop oil is accumulated and occasionally drained to slop collection.

PRODUCT	% of Crude input	Cut range ° C
Fuel gas	0.01 % - 0.03 %	< C ₂₅
LPG	1.0 - 1.5 %	C ₃ - C ₄
FRN (FULL RANGE NAPHTHA)	11 - 14 %	C ₅ - C ₁₆ (165° C)
LK / ATF	10 - 11 %	165° - 227° C
HK	6 - 7 %	227° - 270° C
Diesel	16 - 17 %	270° - 370° C

HAGO	2.5 – 3.0 %	370 ⁰ - 392 ⁰ C
R.C.O (Atm. Residue)		< 392 ⁰ C
LVGO	2.5 – 3.5 %	
HVGO	21 – 22 %	
V.R.	23 – 26 %	

Table 12. Composition of Product in Feed Stream with Cut range

Properties Of High Speed Diesel Obtained At Hazira Plant:

The source of following data is:

Test report No: ONGC/HZR/CHEM/HSD/963/2010

Sample source: Tank- A/09

Date and Time of collection: 28/06/10, 1145 Hrs

S. NO	CHARACTERSTICS	LIMIT	TEST METHOD P: OF IS1448	RESULTS
1	APPEARANCE	FREE FROM W/S		CLEAR
2	ACIDITY INORGANIC	NIL	P:2	NIL
3	TOT. ACIDITY mg/KOH/g, MAX	0.20	P:2	0.08
4	ASH, % BY MASS, MAX	0.01	P:4	0.009
5	CARBON RESIDUE (RAMSBOTTOM) ON 10% RESIDUE, % BY MASS, MAX	0.30	P:8	0.21
6	CETANE INDEX, MIN	46	ASTM D4737	47.82
7	POUR POINT, MAX A)WINTER B)SUMMER	3 ⁰ C 15 ⁰ C	P:10	-12
8	COPPER STRIP CORROSION	NOT WORSE	P:15	1(a)

	3H/100°C	THAN 1		
9	DISTILLATION, % v/v RECOVERED A) AT 350°C, MIN B) AT 370°C, MIN	85 95	P:18	FBP 337
10	FLASH POINT ABEL °C, MIN	35	P:20	70
11	KINEMATIC VISCOSITY @ 40° C	2 TO 5	P:25	2.06
12	SEDIMENT, % BY MASS, MAX	0.05	P:30	0.008
13	DENSITY @15°C, kg/m ³	820-860	P:16/32	825.9
14	TOT. SULFUR, % BY MASS, MAX	0.25	P:33, IP:336	0.035
15	WATER CONTENT, % BY vol, MAX	0.05	P:40	<0.05
16	COLD FILTER PLUGGING POINT, MAX A)WINTER B)SUMMER	6° C 18° C	P:10	-11
17	TOT. SEDIMENTS, mg/100ml, MAX	1.5	ASTM D2274	1.40

Table 13. Properties of HSD at Hazira Plant

Cetane is an **un-branched** open chain alkane molecule that ignites very easily under compression, so it was assigned a cetane number of 100, while alpha-methyl naphthalene was assigned a cetane number of 0. All other hydrocarbons in diesel fuel are indexed to cetane as to how well they ignite under compression. The cetane number therefore measures how quickly the fuel starts to burn (auto-ignites) under diesel engine conditions. Since there are hundreds of components in diesel fuel, with each having a different cetane quality, the overall cetane number of the diesel is the average cetane quality of all the components.



Fig 6. Cetane, or n-hexadecane ($C_{16}H_{34}$), typical of diesel fuel

What is Cetane Number?

- Cetane Number is a measure of the ignition quality of a diesel fuel. It is often mistaken as a measure of fuel quality. Cetane number is actually a measure of a fuel's ignition delay. This is the time period between the start of injection and start of combustion (ignition) for the fuel. In a particular diesel engine, higher cetane fuels will have shorter ignition delay periods than lower cetane fuels.
- Cetane number should not be considered alone when evaluating diesel fuel quality. API gravity, BTU content, distillation range, sulfur content, stability and flash point are also very important. In colder weather, cloud point and low temperature filter plugging point may be critical factors.

Determining Cetane Number

- The optical method for determining cetane number is ASTM test D-613. This method requires the use of an industry standard test engine equipped with accepted instrumentation and operated under specific conditions. In this test, the engine compression ratio is varied for the test sample and reference fuels of known cetane number to obtain a fixed ignition delay. The compression ratio of the sample is bracketed by those of two reference fuels. The cetane number of the sample fuel is determined by estimating between the two reference fuel points.
- Because the ASTM D-613 test is time consuming and expensive, calculated cetane index is derived from the fuel's density and boiling range. While useful for estimating the cetane number of distilled fuels, this technique can not be applied to fuels

containing conditioners that raise cetane number. These conditioners do not change the fuel density or distillation profile, so they do not alter the calculated cetane index.

How Does Cetane Number Affect Engine Operation?

- There is no benefit to using a higher cetane number fuel than is specified by the engine's manufacturer. The ASTM Standard Specification for Diesel Fuel Oils (D-975) states, "The cetane number requirements depend on engine design, size, nature of speed and load variations, and on starting and atmospheric conditions. Increase in cetane number over values actually required does not materially improve engine performance. Accordingly, the cetane number specified should be as low as possible to ensure maximum fuel availability." This quote underscores the importance of matching engine cetane requirements with fuel cetane number.
- Diesel fuels with cetane number lower than minimum engine requirements can cause rough engine operation. They are more difficult to start, especially in cold weather or at high altitudes. They accelerate lube oil sludge formation. Many low cetane fuels increase engine deposits resulting in more smoke, increased exhaust emissions and greater engine wear.
- Using fuels which meet engine operating requirements will improve cold starting, reduce smoke during start-up, improve fuel economy, reduce exhaust emissions, improve engine durability and reduce noise and vibration. These engine fuel requirements are published in the operating manual for each specific engine or vehicle.
- Overall fuel quality and performance depend on the ratio of paraffinic and aromatic hydrocarbons, the presence of sulfur, water, bacteria, and other contaminants, and the fuel's resistance to oxidation. The most important measures of fuel quality include API gravity, heat value (BTU content), distillation range and viscosity. Cleanliness and corrosion resistance are also important. For use in cold weather, cloud point and low temperature filter plugging point must receive serious consideration. Cetane number does not measure any of these characteristics.

Cetane Improvers / Ignition Accelerators

- US diesel fuels are blends of distillate fuels and cracked petroleum hydrocarbons. The cracked hydrocarbons are low cetane compounds, largely due to their aromatic content. To meet the cetane number demands of most diesel engines, cetane improvers must be added to these blends. The lower cetane cracked compounds are less responsive to these cetane improvers than the higher cetane paraffinic fuels.
- Cetane improvers modify combustion in the engine. They encourage early and uniform ignition of the fuel. They discourage premature combustion and excessive rate of pressure increase in the combustion cycle. Depending on the amount of high versus low cetane components in the base fuel, typical alkyl nitrate conditioner treatments can increase cetane by about 3 to 5 numbers (1:1000 ratio). With high natural cetane premium base fuels (containing a high percentage of paraffins) and a 1:500 treatment ratio, cetane may increase up to a maximum of about 7 numbers.
- Most cetane improvers contain alkyl nitrates which break down readily to provide additional oxygen for better combustion. They also break down and oxidize fuel in

storage. This generates organic particulates, water, and sludge - all of which degrade fuel quality. The result is often a fuel which no longer meets even minimum requirements. Because of these drawbacks, nitrate cetane improvers are not used in DurAlt fuel conditioners.

- DurAlt conditioners are blended to improve oxidation stability, while providing a cetane number increase of 2 to 3 numbers. DurAlt products are designed to improved combustion while reducing oxidation and particulate formation, increasing storage stability, and enhancing fuel quality.

Specifying Diesel Fuel

Cetane number is an important measure of ignition quality, or cold-starting ability. API gravity is an excellent indicator of heat value which translates into fuel economy and power. The distillation curve reflects the molecular weight distribution, with higher boiling fractions providing better lubrication, higher cetane - and more deposits. Sulfur content is directly related to corrosion; this needs to be as low as possible. Oxidation stability, water, and sediment content affect the storage life of the oil. For winter use, low cloud point and low temperature filter plugging point are critical to uninterrupted operation. To ensure the best quality fuel for your diesel engines, follow the engine manufacturer's specifications for all these characteristics.

Typical Values

Generally, diesel engines run well with a CN from 40 to 55. Fuels with higher cetane number which have shorter ignition delays provide more time for the fuel combustion process to be completed. Hence, higher speed diesels operate more effectively with higher cetane number fuels. There is no performance or emission advantage when the CN is raised past approximately 55; after this point, the fuel's performance hits a plateau.

In Europe, diesel cetane numbers were set at a minimum of 38 in 1994 and 40 in 2000. The current standard for diesel sold in European Union, Iceland, Norway and Switzerland is set in EN 590, with a minimum cetane index of 46 and a minimum cetane number of 51. Premium diesel fuel can have a cetane number as high as 60.

In North America, most states adopt ASTM D975 as their diesel fuel standard and the minimum cetane number is set at 40, with typical values in the 42-45 range. Premium diesels may or may not have higher cetane, depending on the supplier. Premium diesel often use additives to improve CN and lubricity, detergents to clean the fuel injectors and minimize carbon deposits, water dispersants, and other additives depending on geographical and seasonal needs.

Dimethyl ether may prove advantageous as a future diesel fuel as it has a high cetane rating (55) and can be produced as a biofuel.

Alkyl nitrates (principally 2-ethyl hexyl nitrate) and di-tert-butyl peroxide are used as additives to raise the cetane number.

Biodiesel from vegetable oil sources have been recorded as having a cetane number range of 46 to 52, and animal-fat based biodiesels cetane numbers range from 56 to 60.

Cetane index

It is another method that fuel-users control quality is by using the Cetane index (CI), which is a calculated number based on the density and distillation range of the fuel. There are various versions of this, depending on whether you use metric or Imperial units, and how many distillation points are used. These days most oil companies use the '4-point method', ASTM D4737, based on density, 10% 50% and 90% recovery temperatures. The '2-point method' is defined in ASTM D976, and uses just density and the 50% recovery temperature. This 2-point method tends to over-estimate cetane index and is not recommended. Cetane index calculations cannot account for cetane improver additives and therefore do not measure total cetane number for additized diesel fuels. Diesel engine operation is primarily related to the actual cetane number and the cetane index is simply an estimation of the base (unadditized) cetane number.

Introduction

Naphthalene is a white, crystalline solid which is flammable, and has an aromatic odour of mothballs. Naphthalene is the most abundant component of coal tar, which is the liquid byproduct of the distillation of coal into coke for use as a smokeless fuel. Naphthalene is also produced upon the burning of organic material, such as fossil fuels, wood and tobacco, and is present in exhaust emissions and cigarette smoke.

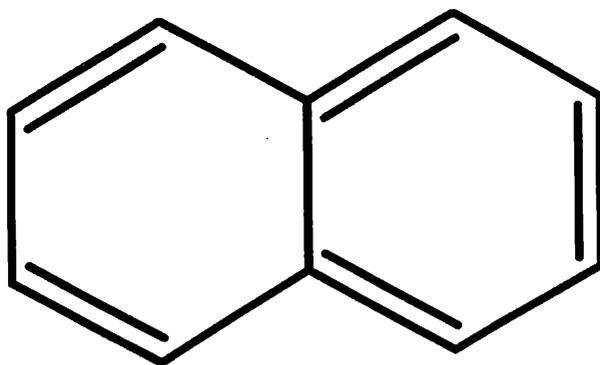


Fig 7. Structure of Naphthalene

The primary use of naphthalene is as a raw material in the production of phthalic anhydride, which is commonly used in the production of dyes, plasticizers, insecticides and some pharmaceutical products. In the past, naphthalene has been used as a fumigant for repelling moths, for which it is popularly known as mothballs. Another classical use of naphthalene was as a fumigant for soil. Such uses are now discontinued.

Exposure to naphthalene is most likely to occur in an occupational setting. However, the general public may be exposed if they burn fossil fuels or other organic materials. Its use in household preparations such as mothballs has been replaced and therefore, such exposure in the home is now less common.

Naphthalene is toxic by all routes of exposure, whether it is ingested, inhaled or comes into contact with skin and eyes. Breathing fumes containing naphthalene, drinking solutions or swallowing solid naphthalene can cause nausea, vomiting, pain in the abdomen, diarrhoea, confusion, sweating, fever, fast heart rate, rapid breathing and may lead to convulsions, coma and possibly death. Approximately 3-5 days after an exposure to naphthalene, blood may be present in the urine and may be dark brown in colour, caused by breakdown of the red blood cells, leading to kidney failure. Skin contact with naphthalene can cause skin irritation and could possibly cause inflammation of the skin, with redness, swelling, pain and itching. Exposure of the eyes to naphthalene may result in irritation, damage to the cornea and may lead to the formation of cataracts.

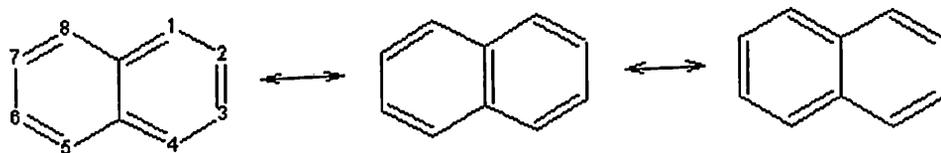
Children exposed to naphthalene are expected to show similar effects to those seen in exposed adults although the effects may be more severe. Exposure during pregnancy is not likely to cause damage to the unborn child at doses where the mother appears unaffected.

Naphthalene has been classified by the International Agency for Research on Cancer as being possibly carcinogenic in humans.

Structure and reactivity

A naphthalene molecule is derived by the fusion of a pair of benzene rings. (In organic chemistry, rings are fused if they share two or more atoms.) Accordingly, naphthalene is classified as a benzenoid polycyclic aromatic hydrocarbon (PAH). There are two sets of equivalent hydrogen atoms: the alpha positions are positions 1, 4, 5, and 8 on the drawing below, and the beta positions are positions 2, 3, 6, and 7.

Unlike benzene, the carbon-carbon bonds in naphthalene are not of the same length. The bonds C1–C2, C3–C4, C5–C6 and C7–C8 are about 1.36 Å (136 pm) in length, whereas the other carbon-carbon bonds are about 1.42 Å (142 pm) long. This difference, which was established by x-ray diffraction, is consistent with the valence bond model of bonding in naphthalene that involves three resonance structures; whereas the bonds C1–C2, C3–C4, C5–C6 and C7–C8 are double in two of the three structures, the others are double in only one.



Like benzene, naphthalene can undergo electrophilic aromatic substitution. For many electrophilic aromatic substitution reactions, naphthalene reacts under milder conditions than does benzene. For example, whereas both benzene and naphthalene react with chlorine in the presence of a ferric chloride or aluminium chloride catalyst, naphthalene and chlorine can react to form 1-chloronaphthalene even without a catalyst. Similarly, whereas both benzene and naphthalene can be alkylated using Friedel-Crafts reactions, naphthalene can also be alkylated by reaction with alkenes or alcohols, with sulfuric or phosphoric acid as the catalyst.

Specifications for Naphthalene (Crude)

Parameter	Value
Molecular Formula	C ₁₀ H ₈
Mol Wt	128.17
CAS #	[91-20-3]
Description	White to almost white crystals, tablets or flakes
Purity (%)	97 min
Melting point in deg cel	79 - 83

Specifications for Naphthalene (Refined)

Parameter	Value
Molecular Formula	C ₁₀ H ₈
Mol Wt	128.17
CAS #	[91-20-3]
Description	White crystalline powder or crystals
Purity (%)	99 min
Melting point in deg cel	80 - 82

Uses

Industry	Application
Process and Manufacturing	In mfr of phthalic and anthranilic acid In mfr of naphthols and aminonaphthalenes In mfr of tetralins and decalins
Polymer	In mfr of synthetic resins and celluloids
Public Hygiene	In mfr of naphthalene tablets used as sterilizing deodorants

Table 14. Specification of Naphthalene & its Uses

Applications

- FUMIGANTS (MOTHBALLS – household fumigants)**
Naphthalene is known as the traditional, primary ingredient of mothballs. It kills moths and moth larvae with the vapor.
Other fumigant uses of naphthalene include use in soil as a fumigant pesticide, in attic spaces to repel animals and insects, and in museum storage-drawers and cupboards to protect the contents from attack by insect pests. Such uses are now limited.

2. CHEMICAL INTERMEDIATES

Naphthalene is mainly used as a precursor to other chemicals. Some naphthalene-derived chemicals are listed below:

WETTING AGENTS/SURFACTANTS

Alkyl naphthalene sulfonates (ANS) are used as nondetergent wetting agents that effectively disperse colloidal systems in aqueous media which are used in paints and coatings and in a variety of pesticides and cleaner formulations. Textile and fabric industry utilize the wetting and defoaming properties of ANS for bleaching and dyeing operations.

PLASTICIZERS

Naphthalene sulfonate polymer plasticizers are used to produce concrete and plasterboard (wallboard or drywall), also as dispersants in synthetic and natural rubbers, and as tanning agents in leather industries, in agricultural formulations (dispersants for pesticides), dyes and as dispersants in lead-acid battery plates.

INSECTICIDES

1-naphthyl-N-methylcarbamate (carbaryl) is used as a general-purpose, broad-spectrum insecticide.

DYES

Naphthalenes substituted with combinations of strongly electron-donating functional groups, such as alcohols and amines, and strongly electron-withdrawing groups, especially sulfonic acids are used as dyes.

LUBRICANTS AND MOTOR FUELS (LOW-VOLATILITY SOLVENTS)

The hydrogenated naphthalenes tetrahydronaphthalene (tetralin) and decahydronaphthalene (decalin) are solvents in lubricants and in motor fuels.

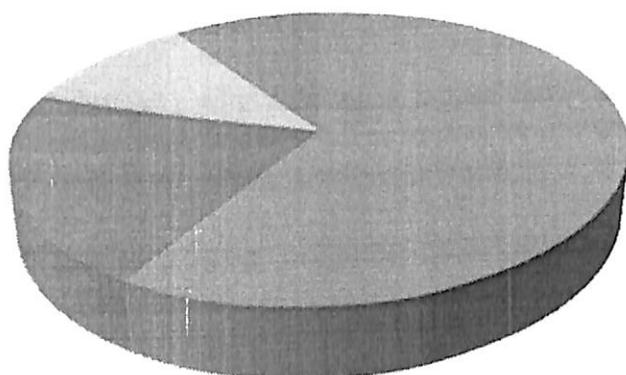
2-naphthol

That is a precursor for various dyestuffs, pigments, rubber processing chemicals and other miscellaneous chemicals and pharmaceuticals.

3. Other uses include:

- Pyrotechnic special effects such as the generation of black smoke and simulated explosions.
- Engineering, to study heat transfer using mass sublimation.
- Production of phthalic anhydride (used in the production of dyes, polyvinyl chloride plasticizers, insecticides, some pharmaceutical products), polyethylene naphthalene (for making plastic beer bottles).
- Creating artificial pores in the manufacture of high-porosity grinding wheels.
- Paint and fuel additive products (e.g. HITEC 4110 for diesel fuels).
- Component of coal tar creosote (it was used as a wood preservative, however, in the EU its use has since been banned for amateur and unlicensed professional applications due to the health effects of many other toxic constituent compounds)

Percentage Uses of Naphthalene



- Phthalic Anhydride
- Naphthalene Sulphonate based surfactants
- 1-naphthyl N-methyl carbamate insecticide
- Miscellaneous including mothballs

Fig8. Percentage Uses of Naphthalene

<u>COMPOUND</u>	<u>BOILING POINT AT 760,^oC</u>	<u>NAPHTHALENE WEIGHT%</u>
Benzoic acid	217.7	95
1,2-benzenedion (catechol)	216.3	98.8
4-chlorophenol	216.3	63.5
2-nitrophenol	215.75	40
1,3,5-triethylbenzene	215.0	15
Benzyl acetate	214.65	28
Benzyl alcohol	204.1	40
m-cresol	202.08	97.2
Acetamide	199.55	72.8
Ethylene glycol	183.9	49

Table 15. Naphthalene Composition in Various Compounds

Health Effects Of Naphthalene

1. Skin contact : Naphthalene causes skin irritation and in the case of a sensitized person, severe dermatitis. Lesions clear spontaneously when the exposure is terminated. Percutaneous absorption is apparently inadequate to produce acute systemic reactions except in newborns.
2. Eye contact : Cataracts and ocular irritation have been produced experimentally in rabbits and have been described in man.
3. Inhalation : On inhalation naphthalene causes headache, confusion, excitement, nausea, vomiting and sweating. There may be dysuria, haematuria and an acute haemolytic reaction. Rarely optic neuritis is encountered.
4. Ingestion : After ingestion naphthalene causes abdominal cramps with nausea, vomiting and diarrhoea.
5. Patients may have headache, profuse sweating, listlessness and confusion. In severe poisoning there is coma with or without convulsions.
6. Irritation of the urinary bladder causes urgency, dysuria and the passage of a brown or black urine with or without albumin and casts.
7. Acute intravascular haemolysis is the most characteristic sign, particularly in persons with red cell glucose-6-phosphate dehydrogenase deficiency; it is accompanied by anaemia, leucocytosis, fever, haemoglobinuria, jaundice, renal insufficiency and sometimes disturbances in liver function.
8. In the absence of adequate supportive treatment, death may result from acute renal failure in adults or kernicterus in young infants.

Symptoms

Stomach problems may occur a day after exposure to the poison. They include:

Abdominal pain

Nausea

Vomiting

Diarrhea

The patient may also have a fever. Over time, the following additional symptoms may occur:

Coma

Confusion

Convulsions

Drowsiness

Headache

Increased heart rate (tachycardia)

Low blood pressure

Low urine output (may stop completely)

Pain when urinating (may be blood in the urine)

Shortness of breath

Yellowing of skin (jaundice)

Growth In India

1989 to 1998 : 0.5%

Future per year through 2010 : 1.5%

In India, naphthalene is produced from coal tar available from steel plants. The present installed capacity is around 10,000 TPA and new LIO approved capacity is 6,000 TPA. The demand supply scenario indicated that there will be a deficit of 37,000 tonnes by the year 1999-2000. The import of naphthalene in the year 1992-1993 from various countries was around 14,000 tonnes.

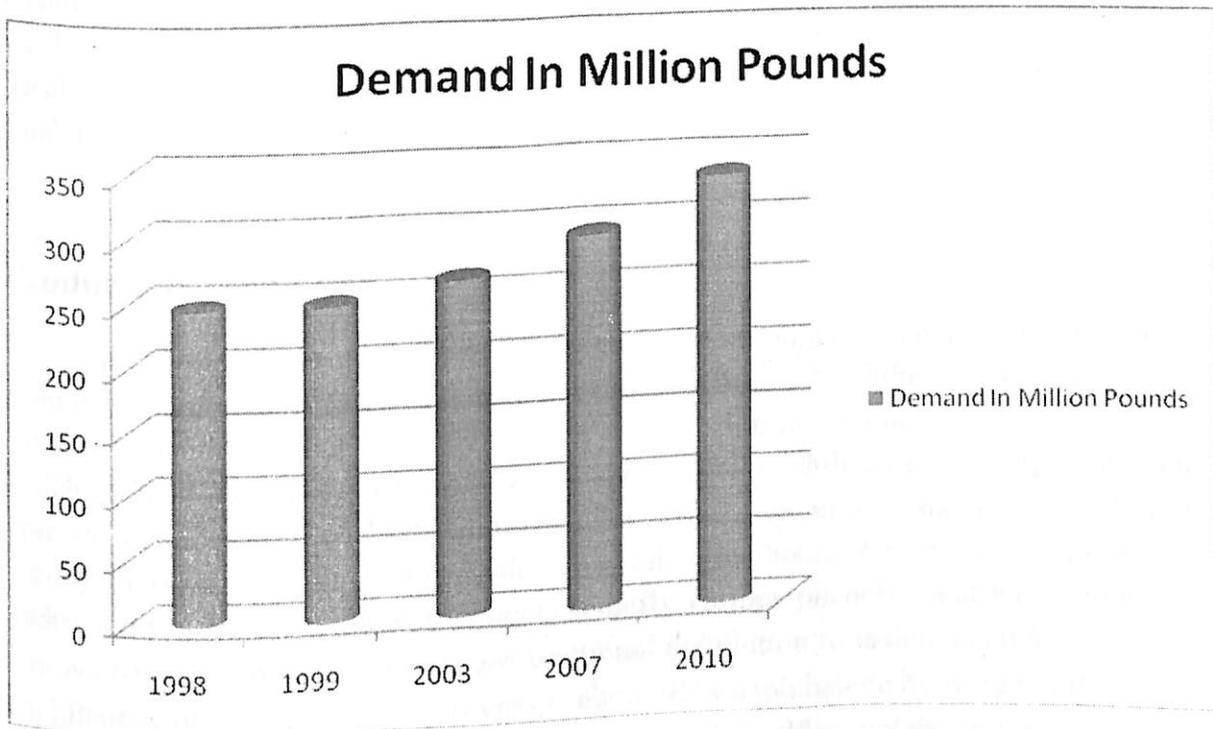


Fig 9. Demand of Naphthalene in recent Years

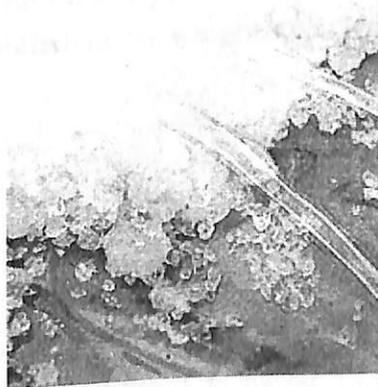


Fig 10. Naphthalene Crystals

Substituted derivatives

Two isomers are possible for mono-substituted naphthalenes, corresponding to substitution at an alpha or beta position. Usually, electrophiles attack at the alpha position. The selectivity for alpha over beta substitution can be rationalized in terms of the resonance structures of the intermediate: for the alpha substitution intermediate, seven resonance structures can be drawn, of which four preserve an aromatic ring. For beta substitution, the intermediate has only six resonance structures, and only two of these are aromatic. Sulfonation, however, gives a mixture of the "alpha" product 1-naphthalenesulfonic acid and the "beta" product 2-naphthalenesulfonic acid, with the ratio dependent on reaction conditions. The 1-isomer forms predominantly at 25 °C, and the 2-isomer at 160 °C.

Naphthalene can be hydrogenated under high pressure in the presence metal catalysts to give 1,2,3,4-tetrahydronaphthalene or tetralin ($C_{10}H_{12}$). Further hydrogenation yields decahydronaphthalene or decalin ($C_{10}H_{18}$). Oxidation with chromate or permanganate, or catalytic oxidation with O_2 and a vanadium catalyst, gives phthalic acid.

Production Technique

From the 1960s until the 1990s, significant amounts of naphthalene were produced from heavy petroleum fractions during petroleum refining, Naphthalene is the most abundant single component of coal tar. Although the composition of coal tar varies with the coal from which it is produced, typical coal tar is about 10% naphthalene by weight. In industrial practice, distillation of coal tar yields an oil containing about 50% naphthalene, along with a variety of other aromatic compounds. This oil, after being washed with aqueous sodium hydroxide to remove acidic components (chiefly various phenols), and with sulfuric acid to remove basic components, undergoes fractional distillation to isolate naphthalene. The crude naphthalene resulting from this process is about 95% naphthalene by weight, often referred to as 78°C (melting point). The chief impurities are the sulfur-containing aromatic compound benzothiophene (<2%), indane (0.2%), indene (<2%), and methylnaphthalene (<2%). Petroleum-derived naphthalene is usually purer than that derived from coal tar. Where required, crude naphthalene can be further purified by recrystallization from any of a variety of solvents, resulting in 99% naphthalene by weight, referred to as 80 °C (melting point).

Technology Status

In India, naphthalene is entirely produced from coal tar available from steel plants. The main limitation of this technology is that production of high purity naphthalene of 80 °C freezing point with low sulphur content is quite difficult. The feedstock for naphthalene production are either coal tar based or petroleum based. In USA both coal tar and petroleum feedstock contribute to naphthalene production. There are several petroleum based oil

fraction which have relatively high concentration of naphthalene and its precursors such as alkyl naphthalene, tetralin, decalin and Indanes. These are :

- Heavy reformat
- LCO from catalytic/thermal cracking
- Aromatic rich kerosene
- Heavy aromatic extract from kerosene treating units
- Naphtha cracker bottom
- Coker distillates and clarified oil

Each feedstock has its own limitation in terms of its availability, naphthalene precursors and techno-economic viability.

The refined grade petronaphthalene having a melting point of around 80 C and the product is almost free from sulphur, nitrogen and oxygen compounds. Hydrodealkylation of alkyl naphthalene to naphthalene is the basis of all the process for the commercial production of naphthalene from petroleum sources. Hydrogenative cleavage of alkyl side chains i.e. hydrodealkylation is generally applied for the manufacture of naphthalene from methyl and dimethyl homologues. The hydrodealkylation is either conducted purely thermally at 550-800 °C and 30-100 bar or catalytically at somewhat lower temperatures and pressures. The catalyst generally used are Cr_2O_3 , Mo_2O_3 or CoO on supports. The conversions and selectivities are markedly higher and the catalyst cost can thus be compensated in this way. The high working temperatures result in relatively strong coking so that reaction is usually conducted alternatively in two parallel reactors, one for reaction and the other for regeneration of the catalyst. An account of the high amount of resulting CH_4 , special measures become necessary to remove it from the recycle gas. One of the method practiced commercially is the low temperature separation of CH_4 from the CH_4/H_2 mixture.

There are various commercial processes available for the production of petrobased naphthalene. The major process licensors are Hydeal, Unidak, Sunoil, Montanso and Atlantic Refining company.

Apart from 7.0 MMTPA installed capacity in 2003, additional FCC capacity is likely to come in big way. Out of the various product streams of FCC, cycle oil is generally the largest product in India, where all FCCU's are geared towards the maximization of middle distillates production. These cycle oil contain significant quantities of alkyl benzenes, naphthalenes, alkylnaphthalenes and other higher aromatic compounds along with saturates as shown in Table.

GROUP TYPES	CYCLE OIL FRACTION (IBP-280 °C), wt%
Paraffin	33.0
Non condensed cycloparaffins + monoolefins	17.5
Condensed cycloparaffins	0.6
Alkyl benzenes	24.2
Indane & Tetralins + Styrenes	9.8
Fluorenes + Acenaphthanes	0.0
Benzothiophenes	0.1
Alkynaphthalenes	14.8
▪ C ₁₀ Naphthalenes	1.6
▪ C ₁₁ Naphthalenes	4.8
▪ C ₁₂ Naphthalenes	8.4
▪ C ₁₃ Naphthalenes	0.0
▪ C ₁₄ Naphthalenes	0.0

Table 16. Diesel Fraction from an FCC Unit

The typical reaction in catalytic cracking which gives naphthalene are:

- Cracking of aromatics with large alkyl groups.
- Dehydrogenation of polycyclo paraffins.
- Dehydrogenation of aromatic cycloparaffin.

Presently all cycle oil is blended into diesel fuels i.e. HSD and LDO inspite of its low cetane rating. A select portion of cycle oil can be used for the production of naphthalene and the balance quantity with improved cetane number may be advantageously blended in the diesel pool.

Typical fluidized bed catalytic cracker of low severity operation may contain 31 % naphthalene and its precursors. The concentration of naphthalene in LCO increases with increasing severity of cracking. A 230-290 °C cut contains maximum naphthalene concentration. Heavy cycle oil (HCO) generally contains only small quantities of naphthalenes.

VAPOR PRESSURE TEMPERATURE RELATIONSHIP FOR NAPHTHALENE:

<u>TEMPERATURE, °C</u>	<u>PRESSURE, KPa</u>
0	0.0008
10	0.003
20	0.007
40	0.043
87.6	1.33
119.1	5.33
166.3	26.66
191.3	53.33
214.3	93.33
218.0	101.33
230.5	133.32
250.6	199.98

VISCOSITY - TEMPERATURE RELATIONSHIP FOR LIQUID NAPHTHALENE:

<u>TEMPERATURE, °C</u>	<u>VISCOSITY, mPa.s</u>
80.3	0.960
90	0.846
100	0.754
110	0.678
120	0.616
150	0.482
180	0.394
220	0.320

Table 17. Variation of Pressure & Viscosity of Naphthalene with Temperature

Process Description

1. Objective:

A method of purifying an ultralow sulfur diesel fuel containing polycyclic aromatic color bodies, which comprises contacting the ultralow sulfur diesel fuel in the liquid phase with a coal-based activated carbon adsorbent having a surface area ranging from 800 to 1500 m²/g and containing pores having pore size greater than 20 Å, and recovering a purified diesel product having a decreased polycyclic aromatic color bodies content.

The presence of sulfur compounds in diesel fuel is undesirable as they result in a serious pollution problem. Combustion of diesel fuel containing these sulfur impurities results in the release of sulfur oxides which are noxious and corrosive. Federal legislation, has imposed increasingly more stringent requirements to reduce the amount of sulfur released to the atmosphere. As a result, the United States Environmental Protection Agency lowered the sulfur standard for diesel fuel to 15 parts per million by weight (ppmw), effective in 2006.

Numerous methods for removing various impurities in diesel streams, such as process for decolorizing and removing some trace impurities such as indanes, naphthalenes, phenanthrenes, pyrene, and alkylbenzenes from diesel streams. The process comprises contacting the fuel stream with a coal-based activated decolorizing carbon. In this process the selective removal of polynuclear aromatic hydrocarbons containing 2 or more aromatic rings from feed (ULSD). Wood and peat based carbons are significantly more effective in the removal of these polynuclear aromatic hydrocarbons and also the use of promoted carbon adsorbents, which may include various metals or other promoters, for the purification and decolorization of hydrocarbon fuel. Activated carbon useful in purification and decolorization of hydrocarbon fuel, which includes within its pore structure a polymerized phosphate.

2. Detailed description :

Ultralow sulfur diesel fuel (diesel fuel having less than 15 ppm sulfur, by weight, and preferably less than 10 ppm sulfur) is typically produced by a hydrodesulfurization method to remove sulfur from diesel fuel. The diesel fuel is reacted with hydrogen gas at elevated temperature and high pressure in the presence of a catalyst. Typical hydrodesulfurization catalysts include supported cobalt-molybdenum or nickel-molybdenum catalysts.

Ultralow sulfur diesel fuel (ULSD), as produced commercially, contains significant amounts of polycyclic aromatic hydrocarbons such as naphthalene, acenaphthalene, fluorene, anthracene, phenanthrene, pyrene, and the like (e.g., 10-30, and usually 15-20, weight percent polycyclic aromatic hydrocarbons based on the total amount of ULSD). The amount of polycyclic aromatic hydrocarbons in ULSD is large. The polycyclic aromatic color bodies which are the major components of fluorescence color in desulfurized diesel are anthracene, fluoranthene, and their alkylated derivatives. These color bodies are first excited by UV light in the 320-400 nm range and then emit visible light in the 400-550 nm range.

We have found that a color problem associated with these color bodies is related to catalyst deactivation and polycyclic aromatic hydrocarbon-type color bodies in the feed to the ULSD hydrotreater. As the hydrodesulfurization catalyst deactivates with time onstream, the average bed temperature needs to be increased to maintain desulfurization activity. As the bed temperature reaches about 376° C. or above, the color of the diesel fuel increases and approaches 2.5-3 or greater. The maximum specification for ULSD is 2.5. Ultimately, the ULSD reactor run ends when the ULSD fuel fails to meet the color specification, even though the catalyst is still performing well in terms of desulfurization.

In order to reduce the level of polycyclic aromatic color bodies in the ultralow sulfur fuel. The impure ultralow sulfur diesel fuel is contacted in the liquid phase with a carbon adsorbent whereby polycyclic aromatic color bodies are retained on the carbon adsorbent and a purified ultralow sulfur diesel product reduced in polycyclic aromatic color bodies content is conveniently separated.

The carbon adsorbent used in the process is a coal-based activated carbon adsorbent having a surface area ranging from 800 to 1500 m²/g. The coal-based activated carbon adsorbent also contains pores having a pore size greater than 20 Å (Angstrom). Preferably, at least 10 percent of the total pore volume of the coal-based activated carbon is from pores having a pore size greater than 20 Å. More preferably at least 30 percent, even more preferably at least 50 percent, and most preferably at least 90 percent, of the total pore volume is from pores having a pore size greater than 20 Å. Molasses number is another often used method to measure the total pore volume from pores having a pore size greater than 20 Å. A high molasses number (e.g., a molasses number greater than about 200) is typically indicative of a substantial amount of pores having a pore size greater than 20 Å.

The coal-based carbon adsorbent may be in granular, pelleted, or powdered form. Adsorption is preferably carried out by passing the impure ultralow sulfur diesel fuel through a bed of granular carbon adsorbent or pelleted carbon adsorbent. Alternatively, powdered carbon

adsorbent can be slurred in the impure ultralow sulfur diesel fuel and separated by filtration. Granular carbon adsorbent is particularly preferred.

The process is carried out in a continuous or batch-wise fashion. Continuous operation is preferred, as is the use of a plurality of adsorbent contact zones. When a plurality of adsorbent contact zones is used, one zone may be in use while adsorbent in a second zone is regenerated or changed out. The use of three contact zones is particularly preferred, with two zones in use at the same time, one a lead contact zone and the second a polishing zone, while the third zone is regenerated or changed out.

The adsorptive contact is preferably carried out at moderate temperatures. Suitable temperatures are in the range of about 0° C to 100° C, preferably 10° C to 60° C. Flow rates of about 0.005 to 50 volumes of ultralow sulfur diesel fuel per volume of adsorbent per hour are preferred, more preferably about 0.01-0.6. In general, slower feed flow rate reduces product impurity at a given bed-volume. Therefore, flow rate may be optimized depending on the volume of adsorbent utilized in the method.

The carbon adsorbent retains the impurities adsorbed thereon and purified diesel fuel product can be separated. Initially, there can be substantially complete removal of the polycyclic aromatic color bodies and the recovered ultralow sulfur diesel fuel is of exceptional color purity. Over the course of time, the contact solids gradually become less effective for the removal of these impurities.

Thus, when the separation efficiency of the carbon adsorbent has fallen below a desired point, for instance as demonstrated by a color level greater than 2.5, the carbon adsorbent contact materials are preferably regenerated, as by contact with a heated vapor stream such as nitrogen, steam, or air at a temperature of at least 200° C or by wash with a solvent such as mixed xylenes, methanol, acetone or water. It is advantageous to employ a plurality of parallel contact zones such that while one zone is being regenerated, the feed is passed through another zone containing fresh or regenerated adsorbent so that optimum impurities removal can be achieved.

Following the purification method, a purified diesel fuel product having a decreased polycyclic aromatic carbon bodies content is recovered. Preferably, the purified diesel fuel product has an equilibrium color in solution of less than 2.5, according to ASTM D 6045.

The experiment also includes a process for extending the life of a supported hydrodesulfurization catalyst used in the production of an ultralow sulfur diesel fuel. This

process comprises first hydrodesulfurizing a diesel fuel stream in the presence of the supported hydrodesulfurization catalyst until the ultralow sulfur diesel fuel produced has a color greater than 2.5 as measured by ASTM D 6045, thus above the maximum specification. The ULSD having a color greater than 2.5 is then contacted with a coal-based activated carbon adsorbent having a surface area ranging from 800 to 1500 m²/g and pores having a pore size greater than 20 Å to reduce color, and recovering an ultralow sulfur diesel product having a color less than 2.5 as measured by ASTM D 6045 in the procedure detailed above. The supported hydrodesulfurization catalyst is preferably a supported cobalt-molybdenum or nickel-molybdenum catalyst.

3. **Example** (Adsorption Runs with Coal - Based Activated Carbon Compared to Wood-Based Carbon)

a. ULSD (56-58 g) having a color in solution of 2.9, as measured by ASTM D 6045, is placed in a 250-mL beaker. A coal-based carbon adsorbent (Calgon CAL® 12×40 granulated activated carbon, having surface area between 800 to 1500 m²/g, and a molasses number of 230 min.) or a wood-based carbon adsorbent (NORIT® Darco G 60/80), in varying amounts for each adsorption run, is placed in the beaker and the mixture is stirred overnight. The adsorbent is filtered (with a Buchner funnel, 3 micron filter paper) and the final equilibrium color is measured according to ASTM D 6045.

b. ULSD (58 g) having a color in solution of 4.5-5.1, as measured by ASTM D 6045, is placed in a 250-mL beaker. Adsorbent (1.16 g), in an amount equivalent to 2 weight percent based on the amount of ULSD, is placed in the beaker and the mixture is stirred overnight. The adsorbent is filtered (with a Buchner funnel, 3 micron filter paper) and the final equilibrium color is measured according to ASTM D 6045.

c. The procedure of Example (b) is repeated with a ULSD having a color in solution of 3.1 and with a variety of adsorbents, in amounts equivalent to 10 weight percent based on the amount of ULSD.

The results show that coal-based carbon adsorbents are much more effective than wood-based carbon adsorbents (and other adsorbents) at removing color bodies from ULSD. The results also show that it is important that the adsorbent contains pores having a pore size greater than 20 Å to be effective at removing color bodies. This indicates that too small a porosity is ineffective when trying to adsorb large (tri- and tetracyclic) color bodies.

Possible Solvents For Extraction

1. A mixture of methyl- and ethyl-carbamates is an effective solvent for the extraction of the bicyclic, aromatic hydrocarbons from the kerosene-gas oil fractions of petroleum products by the method of liquid extraction,
2. The conditions were determined for the liquid extraction of the light gas oil from catalytic cracking with alkylcarbamate to obtain an aromatized extract which contains 95% aromatic hydrocarbons including 54,5% bicyclic hydrocarbons. The extract yield is 27.5% calculated on the gas oil. A 70% dearomatized raffinate is obtained which is a high-quality component for diesel fuel.
3. In the extraction separation of the light gas oil from catalytic cracking of a low-sulfur vacuum-distillate with the alkylcarbamate and hydrogenation of the extract the following are obtained (calculated on the gas oil): 10% naphthalene, 7% high-octane component of gasoline, and 70% of the diesel fuel component.

Chemical Required

- Coal-based Granulated Activated Carbon Adsorbent

Required amount 2% by weight of fuel sample (Diesel)

Sample taken	:100 ml
Required need of granulated activated carbon	:2% by wt. of 100 ml
	:2 gram
Market price of granulated activated carbon	: \$1500 - \$2000 / tonne
	: Rs. 68 – 90 / kg
2 gram of granulated activated carbon costs	: Rs. 0.14

- Diesel (fuel Sample)

Required amount	: 100 ml
Cost of 1 litre diesel	: Rs. 40 / litre
Cost of 100 ml	: Rs 4

- Naphthalene

Cost of naphthalene in market	: \$1800 - \$2200 / tonne
	: Rs. 81 – 99 / kg
Extracted naphthalene	: 4% of fuel sample
	: 4 gram
Cost of 4 gram naphthalene	: Rs. 0.40

Recovered diesel : $(100 - 4) = 96$ ml

Cost of 96 ml @ Rs. 43/litre : Rs 4.12

(increased price of diesel due to improved quality and cetane number)

Approximate Profit Calculation

$\text{Rs. } 4.12 + 0.40 - (4 + 0.14) = \text{Rs. } 0.38 / 100 \text{ ml}$

Hence, profit / tonne of diesel : Rs 3800

Conclusion

Extracting naphthalene from the diesel stream will provide us with various benefits. The diesel from which naphthalene has been extracted will have a higher cetane number, improved colour and lower emissions which will prevent the poisonous naphthalene to contaminate our environment, as naphthalene highly toxic for plants, animals as well as human beings. At the same time this extracted naphthalene is a valuable feedstock for various chemicals such as dyes, surfactants, dispersion agents, tanning agents etc.

REFERENCES

1. Modern Petroleum Technology, **Alan G. Lucas**, co authors P. Ellis James, J.F. Davies, V. Ilori Pg 5-100.
2. W.L. Nelson 1958 Petroleum Refinery Engineering, 5th Edition, New York : McGraw-Hill , Pg 10-78.
3. Petroleum Refining Technology and Economics, Fourth Edition, **James H. Gary and Golden**, 2001, New York
4. American Conference of Governmental Industrial Hygienists Inc. Documentation of the Threshold Limit Values and Biological Exposure Indices (1986) Cincinnati, Ohio, p.420.
5. Anziulewicz JA, Herman JD and Chiarulli EE (1959) Transplacental naphthalene poisoning. American Journal of Obstetrics and Gynaecology, 78:519-521.
6. Chun T, Perrone J, Osterhoudt K, Ugur S, Henretig F (1998) Mothball blues: confusion in naphthalene toxicities and treatment. Clin Toxicol, 36: 465
7. http://www.sbioinformatics.com/design_thesis/Naphthalene/Naphthalene_Properties&uses.pdf
8. <http://www.biopetroclean.com/search/tag/activated-carbon-price-in-india/>
9. http://www.alibaba.com/trade/search?Test_2010_no&albag=list_no_naphthalene_product&albmt=phrase&albst=search&albom=IN_none_20110408