

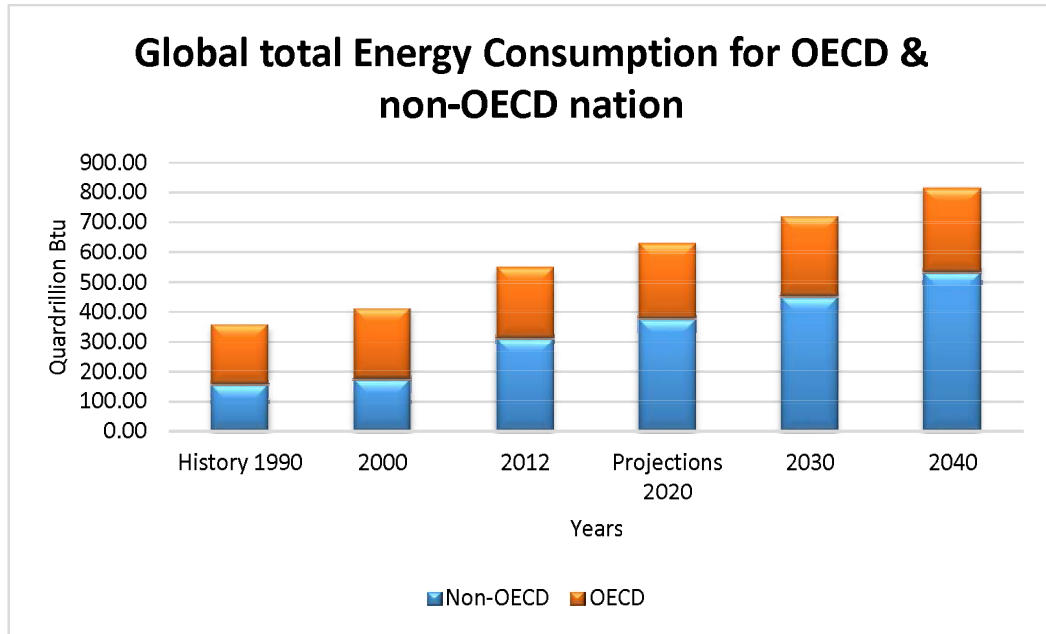
# CHAPTER 1

## INTRODUCTION

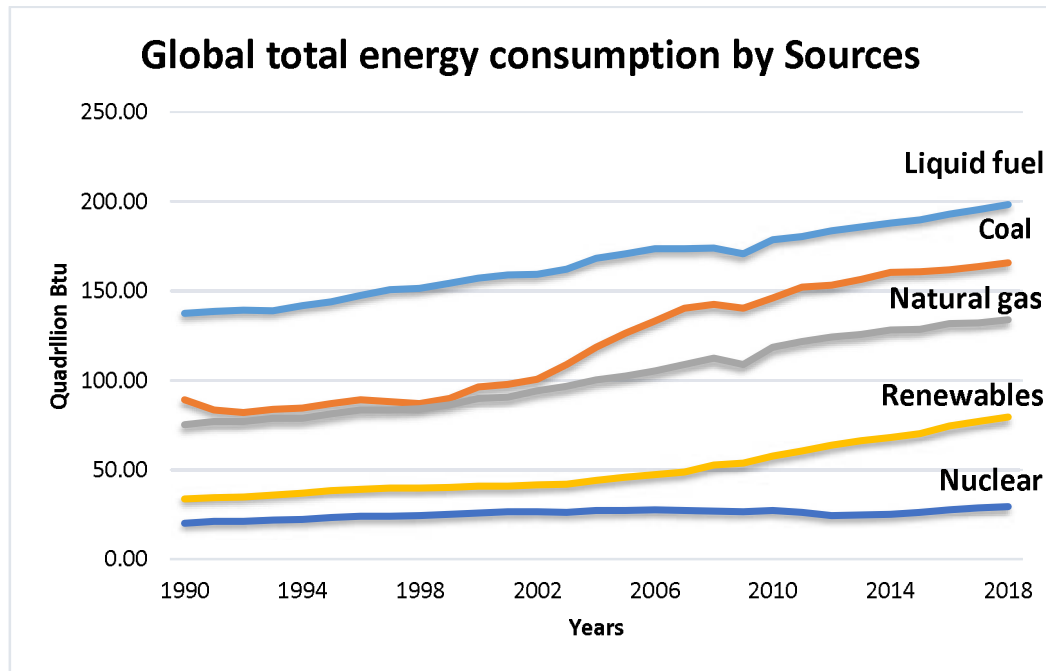
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### 1.1 GLOBAL ENERGY SCENARIO

Globally total energy consumption is likely to grow from present 549 quadrillion to 629 quadrillion Btu in 2020 and 815 quadrillion Btu in next two decades. Very high growth of nearly 48% increase by any standard. It is found that the maximum world's energy growth occur in the non-Organization for Economic Co-operation and Development (OECD) countries. Non-OECD countries energy demand rises by 71% from 2012 to 2040, while only 18 % growth is occurred in OECD countries. Combined energy used for non-OECD countries first crossed that of OECD in 2007 and by 2012, around 57% of total world energy consumption consumed by the non-OECD countries. It is predicted that almost two-thirds of the world primary energy would be consumed in the non-OECD countries by 2040. **[International Energy Outlook 2016]**. Fig. 1.1 shows the global total energy consumption for OECD and non-OECD countries and Fig 1.2 shows the global energy consumption based on the type of fuel source. The conventional fuel coal and oil will continue to be used in larger proportion globally as well as in India. However, natural gas demand is likely to increase substantially reason for this is if the natural gas continued to be used as present rate and likely future projection it may last more than for 100 years. There for the share of natural gas in the primary energy mix will continue to grow over the years.



**Figure 1.1 Global Total Energy Consumption**



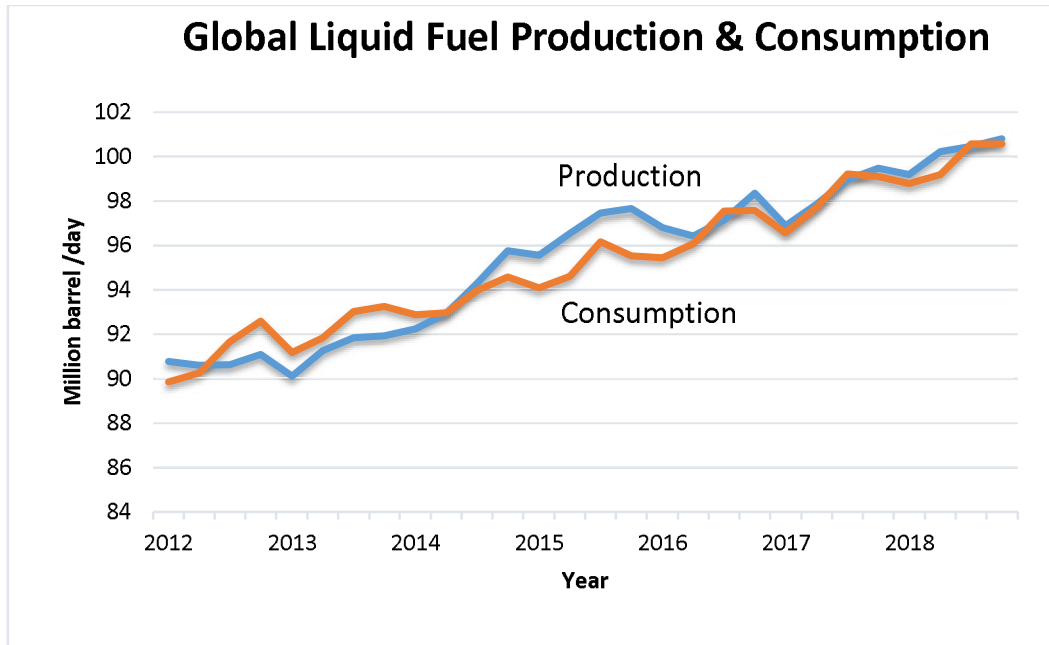
**Figure 1. 2 Global Total Energy Consumption for each fuel type**

## **1.2 GLOBAL LIQUID FUEL SCENARIO**

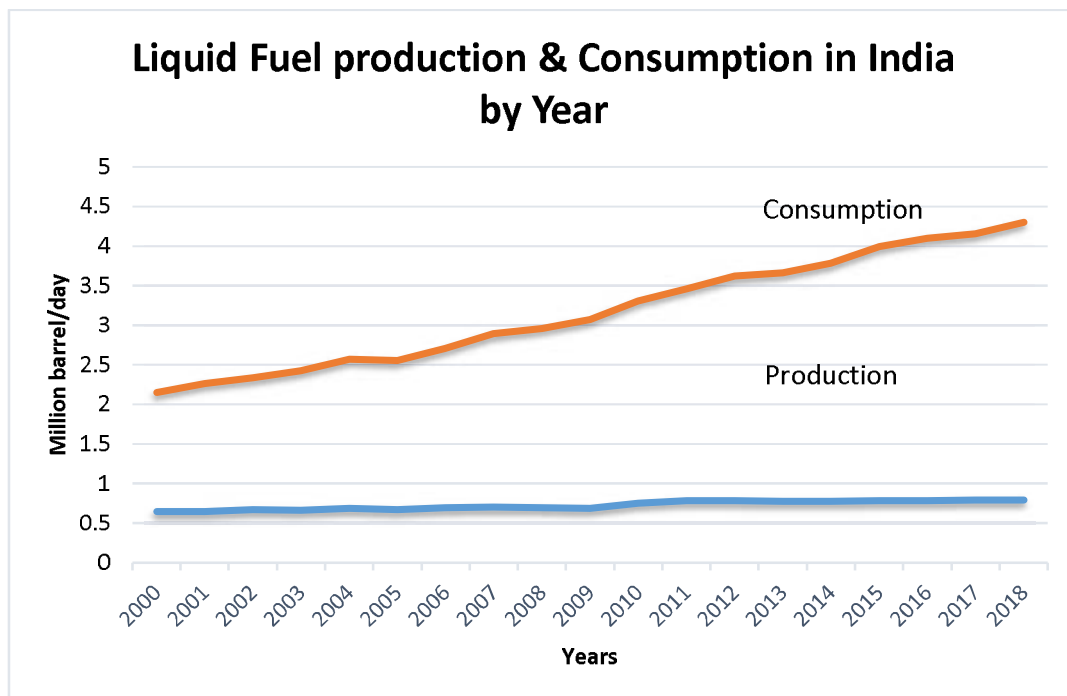
Crude oil is the largest and most widely used source of energy in the world, although it is limited, non-renewable and also the volume left is not exactly known. World liquid fuel demand will grow by 100 million barrel/day (mb/d) in 2020 compared to 90 mb/d in 2012 and will further grow to 121 mb/d in 2040. Fig. 1.3 shows globally liquid fuel production and consumption [IEO, 2017]. According to the United State Energy Information Administration (EIA), global liquid fuel demand 95.64 mb/d in 2016 to grow 1.4 mb/d from 2015. Consumption growth is expected to be around 1.6 mb/d in 2017 and 1.5mb/d in 2018, with 1.2 mb/d growth in both the years. Projection growth in the consumption of hydrocarbon gas liquids (HGL) is an important driver of whole global liquid fuel consumption growth [US Energy Information Administration, Short Term Energy Outlook, Jan 2017].

## **1.3 LIQUID FUEL SCENARIO IN INDIA**

After the China, United States and Japan, India was the fourth highest net consumer and importer of crude oil and petroleum products in the world in 2013. Mostly, India depends on imported crude oil, especially from the Middle East. The gap between India's oil consumption and supply is enlarging, as consumption has reached nearly 4 mb/d in 2016 compared to total liquid fuels production of nearly 1 mb/d. The Energy Information Administration (EIA) projects that India's oil consumption would be grow more than double around 8.2 mb/d by next two decades, while internal production will remain comparatively same, i.e. around 1 mb/d. Fig. 1.4 shows the liquid fuel production and consumption in India.



**Figure 1. 3 Global Liquid Fuel Production & Consumption**



**Figure 1. 4 Liquid Fuel Production & Consumption in India**

## 1.4 GASOLINE

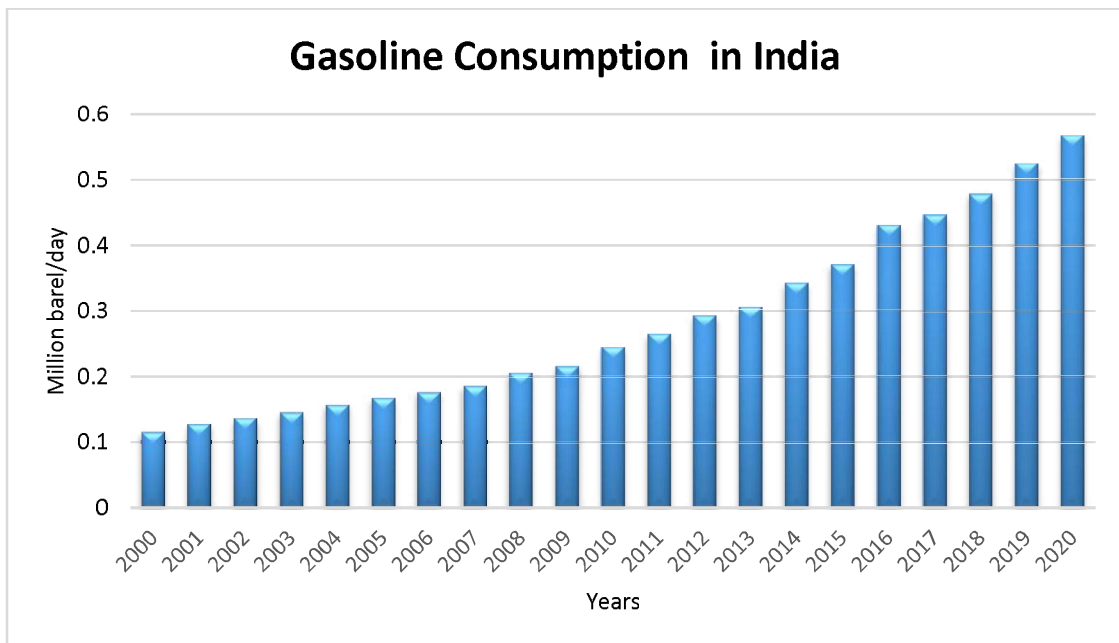
Gasoline (petrol) is a transparent petroleum derivative liquid fuel used in internal combustion engine (ICE). It is obtained by fractional distillation of petroleum improved by the addition of various fuel additives and mostly it contain hydrocarbon. Natural gasoline contains  $C_5$ - $C_{12}$  alkanes and cycloalkanes (naphthenes) with boiling range about 40–200°C. Being associated with many limitations, it cannot be used directly, and therefore requires processing before commercial application. Some important limitation associate with the gasoline obtained by fractional distillation of crude oil includes lead content, nitrogen, sulphur, oxygen, certain metals and octane number etc. Octane number of gasoline is recorded by the knocking extent of the sample. It is a measurement of how fast the gasoline burns and is used to signify the resistance of a motor fuel to knock. Knocking of internal combustion engines (ICEs) is a common problem and it depends upon the quality of gasoline. It is a pinging sound coming from engine, which is caused by the un-timed combustion of the air-fuel mixture in the cylinder. This decreases the efficiency of the engine and increases the risk of engine injury. Normal gasoline burns very fast in the cylinder and causes explosion.

India has its own fuel quality specification for gasoline named as Bharat stages I-IV (Table 1.2). Among various parameters, anti-knocking index (AKI), represented, as octane number in the table is a key property reflecting the efficiency of gasoline. To achieve this, various catalytic processes and fuel additives (as octane booster; TEL, MTBE, aromatics and alcohols), are used to enhance the octane number of the gasoline and enhance its efficacy.

Gasoline with high-octane number is one of the most demanding fuel in transportation sector, especially to run the spark ignition engine. Crude oil on fractional distillation under control condition produces various streams of gasoline, which vary in their properties. These are straight run gasoline, hydrocracked gasoline, FCC gasoline, thermally cracked gasoline, reformate gasoline, alkylate gasoline, polymer gasoline and isomerase gasoline. Straight run gasoline also known as naphtha is obtained by the direct distillation of crude oil. It has low aromatic content, contains some naphthenes, low olefins and possess low octane rating. Being associated with low octane rating, its contribution is very small in gasoline pool (only up to 20%). Its octane number can be improved by the addition of anti-knocking agents; however, isomerization and reforming are the chemical processes useful for improving its chemical properties. Hydrocracked gasoline is produced by hydrocracker and contains low aromatic level and low octane rating. It is obtained by the catalytic cracking of heavy hydrocarbons into lighter unsaturated hydrocarbons inside the hydrocracker. FCC gas or naphtha is obtained by catalytic cracking, it contains moderate aromatic level, high olefin and possesses moderate octane number. Thermally cracked gasoline is obtained by thermally cracked operation at mild condition, in this the long chain molecule is broken into short chain molecules in heavy feedstocks, as a result the thermally cracked gasoline with low viscosity will form. Reformate gasoline contains relatively low olefins and is obtained by catalytic reformer with high aromatic and possess high octane rating. It is one of the important blending component of gasoline.

In the current scenario, three main types gasoline are used i.e. alkylate gasoline, polymer gasoline, isomerase gasoline. Alkylate gasoline does not contain any aromatic and alkenes. Alkylate gasoline is obtained in an alkylation unit by the reaction of branched iso-alkane

and olefin in the presence of an acidic catalyst and possess high MON. It is an excellent high-octane blending component for motor gasoline, and is well accepted in the market. Polymer gasoline is obtained by catalytic polymerization of the propylene, propane and butylene fractions of gases obtained from petroleum cracking and reforming. This gasoline contains 20-90% unsaturated hydrocarbon, with a low content of paraffin, naphthene, and in particular, aromatic hydrocarbons. Isomerate gasoline is obtained by isomerization of low octane straight run gasoline to iso-paraffins. It has medium MON and RON but have no olefins and aromatics. Gasoline consumption in India is shown in Fig 1.5.



**Figure 1.5 Gasoline consumption scenario in India [Petroleum Planning and analysis cell, Ministry of petroleum and natural gas may, 2016]**

### 1.5 LEGISLATION REQUIREMENTS

Gasoline is a mixture of lower hydrocarbons ( $C_5$ - $C_{12}$  alkanes), cycloalkanes (naphthenes) with some impurities, including certain metals, nitrogen, Sulphur and oxygen. The four

main component groups of gasoline are aromatics, olefins, naphthenes and paraffins. Untreated gasoline has many disadvantages. The most important characteristics of gasoline are vapor pressure, density, distillation range, chemical composition and octane rating. It must have (a) antiknock resistance (b) desirable volatility (c) minimal deposition on engine component surfaces (d) good fuel economy (e) low pollutant emissions and complete combustion [Chigier, 1981]. According to clean air act (CAA) there are some limitations in using gasoline i.e. level of aromatics content, sulphur and some fuel additives.

Aromatics and oxygenates have been discontinued to form toxic peroxyacetyl nitrate (from ethanol) or formaldehyde (from methanol). Olefin and aromatic react with NO<sub>x</sub> emitted to form ozone, which is responsible for smog formation and causes carcinogenicity [Mills et al., 1953]. On the other hand, the limitation of vapor pressure, reduction of sulphur content and aromatics has a bad effect on the octane rating of the gasoline, which is responsible for the resistance of gasoline to early ignition in the combustion chamber of an ICE. Such type ignitions causes reduction in the engine performance and potentially harm the engine. It is expected that, an increased share of isomerate needs to be added for maintaining the octane rating of gasoline in the gasoline pool [Kimura, 2003].

Vapor pressure, when applied to gasoline, has tendency to change the liquid into vapor at relevant temperature. The volatility of gasoline affects ease of starting, length of warm up period, and engine performance during ordinary action. The rate of vaporization rises as the temperature rises and as the pressure is reduced. The volatility of gasoline must be controlled carefully, so that it convert into volatile and enough to deliver suitable cold climate starting, yet not be so volatile that it is matter to vapor lock during ordinary action. Refiners mixed some additives into gasoline to control volatility according to regional



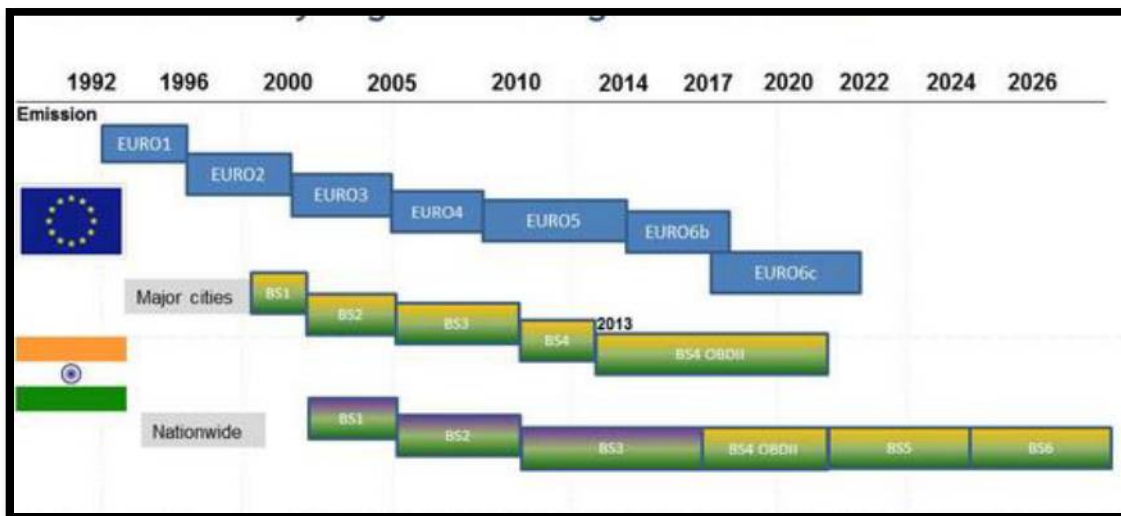
climates and seasons. Keeping in mind the environmental concern and health issues, the government have set the limit of all component of the gasoline.

Lighter branched alkanes are promising for the production of environmentally friendly gasoline. The content of branched alkanes is very low in naphtha fraction of crude oil. The fact that they have high octane numbers than straight chain alkanes, offers the possibility of increasing the quality of gasoline through isomerization reaction. In 1970s when the tetraethyl lead is phased out due to the Clean Air Act Amendments (CAAA), the isomerization process was developed [Weisz, 1962]. In Europe (1992) and in the US (1995), oxygenates (ETBE RON-112; MTBE RON-110; ethanol RON-115), methanol and some aromatics (Benzene, toluene, xylene) were used as octane boosters in premium gasoline up to 10 vol. %. According to the European Program on Emission Fuel and Engine Technologies (EPEFE), the amount of olefin, aromatic, oxygen, and sulphur should be reduce in the gasoline for the protection of environment.

### **1.5.1 Emission Norms in India [SIMA, 2017]**

According to the report of Society of Indian Automobile Manufacturers [SIAM], the first stage emission norms were implemented in 1991 for gasoline engine and in 1992 for diesel engine. Catalytic conversion was brought as a mandatory process for maintaining the important parameters of fuel along with unleaded petrol (ULP) in four metro cities viz. Delhi, Kolkata, Mumbai and Chennai with effect from April 1995. The availability of ULP was further extended to 42 major cities and now it is implemented all over the country. Figure 1.6 shows the journey of emission norms in India. The commercial vehicles and passenger cars met Euro I equal to Bharat Stage (BS-I, India 2000) norms in the year 2000. In 2001, the BS-II norms were implemented in Chennai, Delhi, Kolkata and Mumbai. In

August 2002, the first Auto Fuel Policy was launched which, covered all the Emission norms and Fuel roadmap up to 2010. According to the roadmap, four wheeled vehicles from April 2005 in the 13 metro cities were moved to BS-III norms and remaining cities moved to BS-II norms. BS-IV was implemented in April 2010 for 13 metro cities, when rest of the country moved to BS-III norms. Another 20 cities were added in BS-IV norms in October 2014, which has been implemented throughout the country with effect from April 2017. According to the report of SIAM, BS-VI is proposed to be introduced in 2020 skipping BS-V [Society of Indian Automobile Manufacture (SIAM)]. At present, India is behind the Euro norms by few years, however, emission norms are being align with Euro standard and vehicular technology being accordingly improved. Vehicles Company are also working towards connecting the gap between Euro standards and Indian norms.



**Figure 1.6 Journey of Emission Standards in India**

The fuel specifications (gasoline and diesel) is shown in table 1.1 as per various BS norms in India. The main regulation in India has decreased the sulphur content to gasoline from

current maximum of 150 ppm to 50 ppm and the reduction in diesel sulphur content from current 350 ppm to 50 ppm. Among various parameters, sulphur and octane specification along with reduction in aromatic content is most critical and challenging issues for refinery **[Auto fuel policy, 2017, R.K. Malhotra].**

**Table 1. 1 Fuel quality specifications for gasoline and diesel in India**

Standard	Gasoline					Diesel				
	Lead (ppm)	Benzene (%)	Sulphur (ppm)	Density (kg/m <sup>3</sup> )	Octane Number	Sulphur (ppm)	Cetane Number	Density (kg/m <sup>3</sup> )		
<b>India 2000</b>	130	3 (Metro)	1000	710-770	88	2500	48	820-860		
		5 (Rest of India)								
<b>Bharat-Stage-II</b>	130	1 (Metro)	500	710-770	88	500	48	820-860		
		3 (Rest of India)								
<b>Bharat-Stage-III</b>	50	1 (Metro)	150	720-775	91	350	51	820-845		
<b>Bharat-Stage-IV</b>	50	1 (Metro)	50	720-770	91	50	51	820-845		

## 1.6 ISOMERIZATION

Isomerization is an important catalytic reaction used in petroleum industry for the production of clean and high-octane fuel. The branch isomers of C<sub>5</sub> and C<sub>6</sub> have high octane numbers as compared to straight chain hydrocarbon, consequently valuable blending component of the gasoline pool and these are main components of light naphtha. It is generally recognized that isomerization reaction needs a bi-functional catalyst consisting of protonating acid function and the hydrogenation/dehydrogenation metal function. As an example, the difference in octane numbers for hydrocarbons and the branched isomers is shown in Table 1.2 [Mendes et al., 2012].

Various catalysts have been used to carry out isomerization of alkanes, owned by different licensors; however, paraffin isomerization technology is dominated by UOP namely Penex<sup>TM</sup> (C<sub>5</sub>/C<sub>6</sub>). Butamer<sup>TM</sup> (C<sub>4</sub>) Zeolites promoted by platinum, e.g. HYSOPAR<sup>®</sup> from Sud-Chemie and HS-10<sup>TM</sup> from UOP, are used in the Penex<sup>TM</sup> process [Zhang et al., 2008; Nieminen et al., 2005; Essayem et al., 2003]. Zeolite, zirconia [Vartuli et al., 1999] based catalysts, sulfated zirconia [Fogash et al., 1998; Ahmad et al., 2003], chlorinated platinum/alumina [Ono, 2003; Weyda and Kohler, 2003] and tungsten carbide [Ribeiro et al., 1991] are widely used catalysts for isomerization reaction. Each of these classes is associated with its own merits and demerits.

Although, these catalysts have shown a yield up to 86%, but they possess some major drawbacks, such as high cost, poisoning by impurities as sulphur and water (10 ppm), sensitive to coke deposition, etc. therefore the development of catalyst which can overcome these limitations and give better yield under mild conditions [Delporte et al., 1997].

**Table 1. 2 Octane numbers (RON) of the hydrocarbons**

	Hydrocarbons	RON	MON
	n-butane	93	89
	n-pentane	62	62
	2-methylbutane	92	90
	2,2-dimethylpropane	85	80
	n-hexane	25	26
	3-methyl pentane	75	76
Paraffin's	2-methyl pentane	73	75
	2,3 dimethyl butane	105	104
	2,2 dimethyl butane	93	96
	n-heptane	0	0
	2,2-dimethyl pentane	92	93
	2,2,3-trimethyl pentane	100	100
	1-pentene	91	77
Olefin's	2-methyl-2-butene	97	85
	Benzene	Above 100	Above 100
Aromatics	Toluene	Above 100	Above 100

### 1.7 VARIOUS CATALYSTS USED FOR ISOMERIZATION PROCESS

In the last four decades around three hundreds solid acids/bases catalysts have been developed for isomerization processes viz. Pt/zeolites, chlorinated-Pt/alumina, zirconia, mixed oxide etc. [Tanabe et al., 1999]. In particular, zeolite and metal oxides are most important for industrial application. However, in case of acid/base bi-functional catalysts, only limited commercial catalyst have been developed for isomerization [Feller et al.,

2004; Mukhrjee et al., 2006]. Combination of Weak acid and weak base sites on the solid surface is responsible for high activity, selectivity and lifetime of the catalyst, and expected this type of catalysts more important for industrial application [Tanabe et al., 1999]. Earlier catalysts used for the isomerization processes in the industries for lighter alkanes are Friedel-Crafts catalysts such as  $\text{AlCl}_3$  with additives,  $\text{SbCl}_3$  and  $\text{HCl}$  [George et al., 1962]. These catalysts are highly acidic and highly active even at 300–390 K. Equilibrium point of view low temperature activity is very favorable to branched isomers. The processes due to the corrosion of the reactor and the disposal issue of the used catalysts do not exit any more [Galadima et al., 2009].

Alumina with acid and platinum metal is most widely used catalyst for isomerization of lighter alkanes at low temperature with high conversion rate (approximately 86% yield). But the main drawback of  $\text{Pt}/\text{Al}_2\text{O}_3$  is that, it needs continuous addition of chloride to maintain its activity [Kimura, 2003]. The use of chlorides has corrosion problems to the reactor and environmental hazards. In addition to that,  $\text{Pt}/\text{Al}_2\text{O}_3$  is very sensitive to impurities in the feed like ammonia and water act as permanent poisons to the active sites. Platinum promoted zeolite is an alternate for isomerization of alkanes and has been replaced chlorinated  $\text{Pt}/\text{alumina}$  catalysts to some extent. This catalyst is less active than  $\text{Pt}/\text{chlorinated alumina}$  but has more resistance to sulphur and water in the feed, thus requires higher reaction temperature. From a thermodynamic point of view, the formation of high octane branched isomer is favored at low temperature. Hence, the best isomerization catalysts will be strong acidic catalysts able to work at the lowest possible temperature [Kimura, 2003].

Sulphated zirconia has attracted great attention due to its strong acidity and activity in the catalyst for lighter alkanes isomerization at relatively milder condition [Hino and Arata, 1979; Reddy, 2009]. One such class that seems to be promising is sulfated zirconia and heteropoly acids (HPAs), such as tungstophosphoric acid (TPA), molybdophosphoric acid (MPA) tungstosilicic acid (TSA) etc. having discrete ionic structure [Galadima et al., 2009]. Heteropoly acids behave as bi-functional catalysts and participate in dehydrogenation and isomerization step at the same time. The metal present in the HPAs can exist in variable valences, thereby supports dehydrogenation of alkane while it is reduced to lower oxidation state. At the same time, owing to its super acidic nature and presence of Bronsted acidity, it can easily provides proton to form the carbocation, which can be easily isomerized to form more stable carbocation and reacts with a second molecule of alkane to form branched alkanes [Nikita, 2014]. Typical operating conditions for conventional isomerization catalysts are summarized in Table 1.3 [Kimura, 2003, Nikita, 2013].

Because of various drawbacks and environmental concern associated with the conventional processes, an intense effort is required to develop solid acid catalysts which can be utilized and replace these expensive catalysts. Based upon the higher acidity and stability of sulphated zirconia in combination with heteropoly acids (HPAs) can behave as an efficient catalytic system to transform lighter straight alkanes to branched one. The formation of these acids two or more than two kinds of oxo-anions are condensed and are known as polyoxometalates [Coronado et al., 1998; Gouzerh et al., 1988]. The formation of weak acid sites by the amphoteric metals of Groups 5 (Nb, V, Ta) and 6 (Mo, Cr, W) in the +5 and +6 oxidation states respectively which easily condense and form anions containing



some acid anhydride molecules. The structures of heteropolyanion are classified into numerous structure according to the structure and composition, such as Keggin type  $\text{XM}_{12}\text{O}_{40}^{n-}$ , Dawson type  $\text{X}_2\text{M}_{18}\text{O}_{62}^{n-}$ , and Anderson type  $\text{XM}_6\text{O}_{24}^n$ , where X known as heteroatom and M is molybdenum or tungsten for catalytic application and can be used directly as heterogeneous catalysts in their solid form. The catalytic properties of Keggin type heteropoly acids have been studied broadly. The catalytic activity of these acids are estimated by the polyanions (primary structure), three-dimensional arrangement of polyanions, water of crystallization, counter cations, etc. (secondary structure), or the tertiary structure (pore structure, particle size, etc.) [Lee et al., 1997; Misono, 1988; Olaf et al., 2009]. The polar molecules that gets easily absorbed to the solid due to the flexibility of HPAs. These acids formed oxidizing and acidic function, therefor they are very useful for acid and redox reaction. Thermal stability order of several heteropoly acids follow as,  $\text{H}_3\text{PW}_{12}\text{O}_{40} > \text{H}_4\text{SiW}_{12}\text{O}_{40} > \text{H}_3\text{PMo}_{12}\text{O}_{40} > \text{H}_4\text{SiMo}_{12}\text{O}_{40}$  [Lee et al., 1997; Misino, 1988]. It could be enhance by the development of suitable salts [Moffat, 2001]. Because of their multifunctionality, these acids could catalyze various type of reactions including dehydration, hydration, isomerization, condensation, reduction, oxidation etc. with Keggin type anions of W, Mo [Moffat, 2001; Okuhara et al., 1994]. Many of researchers have been used HPA for the isomerization of alkanes [Wang et al., 2009; Chen et al., 2007].

**Table 1. 3 Operating conditions and feed limitations for the current conventional isomerization Catalysts**

<b>Operating condition</b>	<b>Pt/Al<sub>2</sub>O<sub>3</sub></b>	<b>Pt/zeolite</b>	<b>Pt/SO<sub>4</sub>-ZrO<sub>2</sub></b>
<b>Temperature</b>	120-160°C	220-300°C	130-180
<b>Pressure</b>	30 bar	30 bar	30 bar
<b>Feed limitation</b>	Sensitive to water and low Sulphur resistance, require continuous addition of chlorine	Resistance to water and Sulphur in feed	Resistance to water and Sulphur in feed Sensitive to C <sub>7+</sub>
<b>RON Yield</b>	82-84%	76-78%	83-85%