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# METHANOL AND Di Methyl Ether UTILISATION ISSUES



TIFAC, DST, GOVT. OF INDIA

AUGUST-2016

## **METHANOL AND DME UTILISATION,**

## **REPORT**

### August 2016

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FOREWORD

### **FOREWORD**

### Methanol & DME Economy – Utilization Issues

In the current high growth trajectory phase, India has sharply increasing energy requirements. Currently our country consumes around 29 billion L (22 MMT) of petrol and 90 billion L (74.6 MMT) of diesel and 20 million tonnes of LPG, per year, for which we are heavily dependent on imports costing around 74,000 Million dollars. In view of this, there are vigorous efforts going on for tapping renewable energy resources such as solar, wind and biomass.

In such scenario, a promising and potential approach to meet our energy requirements is through methanol and Dimethyl Ether (DME), both of which have potential to replace fossil fuels for energy storage and transportation. Besides, these would reduce CO2 emission.

Methanol, a bulk commercial chemical is commonly made from natural gas worldwide. However, in the last one decade China has significantly gone into higher capacity production through coal. China has also become the largest producer of methanol, much beyond the production capacity individually from the rest of the world.

According to new IHS research 2015, Global Methanol demand is set to rise significantly – from 64.5 MMT in 2013 to more than 100 MMT in 2020 – with an annual average growth rate of 6% with China a major driver. China's methanol consumption is expected to be more than doubled from 40 million tons from 2015 to 83 million tons in 2020. China's imports are projected to go up by six fold from more than 4 million tons in 2013 to almost 25 million tons in 2023.

At the same time North American Methanol market – riding the wave of low cost US shalederived feedstocks - is undergoing a renaissance as new projects deliver significant capacity additions.

Natural gas is the most economical and widely used feedstock for methanol production. However, in India's context, production via natural gas is not viable at current prices. There are other feedstocks which can be used as well to produce syngas via steam reforming. In China, coal is the dominant feedstock. Technologies are also available for biomass gasification to syngas – which has attained industrial maturity -, besides being produced from carbon dioxide by catalytic hydrogenation.

Methanol can be used in today's internal combustion engines, while Dimethyl ether (DME), a colourless, odourless gas can be an excellent substitute for diesel and can used as a transportation fuel, LPG blending, aerosol propellant be also be burned in, besides being used in common household stoves and water heaters and numerous applications in the chemical and petrochemical industries. DME can also be generated from various raw materials such as coal, natural gas, methanol and biomass.

Worldwide DME market size in terms of volume is estimated to be 3,740.46 KT in 2014 and expected to register a CAGR of 15.67% in between 2015 and 2020 with the largest market being Asia-Pacific, registering a significant share of 95.66% of the total market in 2014. Again in this too, China is leading country in terms of volume & value.

The transition from oil and gas to methanol is also likely to be easier than a transition to the Hydrogen Economy or to electric vehicles. Thus the Methanol Economy could therefore, in principle, be a relatively feasible and affordable path towards replacing oil.

In Indian context, however, the real success will be considered when Methanol will be produced by using low grade high ash coal or utilizing the high concentrated CO2 stream coming out of factories or plants e.g. large power plant, steel plant etc.

Sensing the need for evaluating technologies, prioritizing R&D, nucleating and pursuing scaling up efforts, NITI Aayog has constituted a core team to work on all aspects of Methanol Economy and three different groups to focus of issues related to R&D, Production and Utilization of Methanol and DME and come up with a road map.

This survey report broadly consists of collation of information on the following:

International and National status on utilization of methanol & DME in three segments viz transport, chemicals and fuel cells etc.

Largest user/importers of methanol & DME in India

Issues on quality ,txicity, human exposer & vehicle performance, Emissions with use of methanol & DME

Issues relating to Storage, Transportation and Distribution

Suggested areas for improvement and R&D prioritization

The survey report has culled out information available in literature, public domain besides inputs from experts and organizations like- Methanol Institute and International DME Association.

The preparation was guided by the experts Group constituted for the purpose. This report will serve as a reference/base document for the Group to further discuss and deliberate with national and international experts to evolve recommendations for a Methanol and DME Road Map for our Country.

N. R Raje

Chairman-Expert Group

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CP Consultants Pvt. Ltd. (CPC) acknowledges the support provided by members of the Expert Committee on "Utilisation issues of Methanol and DME" during different stages of preparation of this report. CPC is thankful to Sh. Niranjan Raje and other members of committee for their observations and valuable guidance.

CPC acknowledge the active involvement of Sh. Rohit Vedhara of Aum Energy, Dr. Greg Dolan of Methanol Institute, Sh. G.K. Archarya, IOCL, Mr. Vijay Kumar, GNFC and Dr. SS Thipse, ARAI for their invaluable assistance in editing, providing technical information as well as suggestions on the flow and content of the report.

CPC thanks Shri Sanjay Singh (TIFAC) and Ms. Nirmala Kaushik (TIFAC) for their coordination and networking support at every stage of the project.

#### **EXECUTIVE SUMMARY**

The present survey report is on the Utilization of Methanol & Dimethyl Ether (DME). DME is a downstream product of Methanol. Methanol drew the World's attention towards it following the oil crisis in 1970 and subsequent years, when the crude oil price shot up to \$100 per Barrel. Countries started looking for alternative fuels like Methanol, Ethanol and Bio-diesel to chalk out their energy strategy. India has limited oil & gas reserves and 80% of the energy needs are being met by imports. India is presently importing 202 million tonnes of crude oil and 16 million tonnes of Natural Gas with a big foreign exchange outgo. With better standard of living and purchasing power, the Automobile industry is enjoying a 9% growth rate with consequent increase in demand for gasoline. Government is looking for a solution to cut import bill and at the same time keep the economic development sustained. The advantage of Methanol is that alternative raw materials are available for it in the country in the form of coal, bio-mass and municipal solid wastes. The technology is mature; however it is desirable to examine global experience in the utilization of Methanol & DME.

#### **Resource status**

India has proven Oil reserves of 5.7 billion barrels, Gas reserves of 1.4 trillion cubic meters and Coal reserves of 125 billion tonnes. As per IBEF analysis the energy demand of India will double from 775 mtoe in 2013 to 1440 mtoe by 2030.

#### Indian Status

## There are six major producers of Methanol in India with a total installed capacity of 0.66 million TPA.

Imports constitute around 70% of total consumption. In 2014 – 15 the production was 0.2098 million tonnes (30% capacity utilization) & imports was 1.8019 million tonnes. DME is not currently manufactured in the organized sector in India.

In India, Formaldehyde, Acetic Acid and Pharmaceuticals (bulk Drugs & Intermediates) are the three important end-use segments, which together account for 55% of the total Methanol consumed in the country.

#### **Global Status**

There are more than 100 plants operating worldwide which produce 110 million tonnes of Methanol annually. China, Saudi Arabia, Trinidad and Tobago, Iran and Russia are the top five methanol producing countries in the world. Global methanol demand is around 62-65 million tonnes excluding integrated methanol to olefins demand.

Methanol is an important feedstock for chemical Industry. Globally, Natural Gas is the most popular feedstock for Methanol due to reasonable cost and good operational factors. China derives its Methanol mainly from coal.

Methanol is also utilised as transportation fuel, both in-land and marine sector as well as in fuel cells especially for remote use as in military applications. It has been tested as boiler fuel in Israel.

Globally, 60% of Methanol is consumed in traditional Chemical Sectors (Acetic Acid, Formaldehyde, while 40% is consumed in Energy related applications (Biodiesel, MTO, Fuel Blending, DME & MTBE). The global methanol installed capacity is 105 million tonnes per annum, while production is between 80 to 100 million tonnes.



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#### Methanol & DME Utilization

Traditionally, Methanol is utilized as a raw material for production of Formaldehyde, Acetic Acid & Acetic Anhydride etc.

Methanol use in the transportation sector as a blended fuel is established since 1980.

DME has shown encouraging results when utilized as a blend for diesel substitution as well as with LPG for domestic fuel purpose.

#### Formaldehyde

Presently in India, there are about 25 formaldehyde plants having total installed capacity of about 413,000 tonnes per annum with production of 275,000 tonnes. The global consumption of formaldehyde in 2014 has been reported to be around 20.5 million tonnes.

#### **Acetic Acid**

Gujarat Narmada Valley Fertilizers Corporation (GNFC) is the only unit producing acetic acid. In 2014, India produced 159.61 thousand tonnes of Acetic Acid and imported 712.38 thousand tonnes. The global acetic acid market was estimated 12.9 million tonnes in 2014 with following utilization break-up: VAM 32%, PTA 20%, Acetic Anhydride 13%, Ethyl & Butyl Acetate 20%.

#### MTO (Methanol to Olefins)

Methanol is used as a feedstock for the production of polyethylene and propylene. This process is confined to China only at present (2016).

#### Methanol as Transportation Fuel

Methanol was introduced commercially in the 1980s following crude price variations in 1970. In 1990s, several car manufacturers came out with Flexible Fuel vehicles which could run with M15 blends.

Compared to gasoline, methanol emits less nitrogen oxides, zero sulfur emissions and lesser volatile harmful organic compounds that form smog or ozone when burned as fuel.

Lower level methanol-blends (M5, M10, and M15) can be directly used in most existing vehicles with little to no modification, as industry experience confirms.

#### **Bio-Diesel**

In the process of making biodiesel fuel, methanol is used as a key component in a process called transesterification. Currently, India has 5-6 large capacity plants (10,000 to 250,000 MT per year) currently utilizing 28 percent of the installed capacity to produce <u>125-140 million liters of biodiesel</u> from multiple feed-stocks such as inedible vegetable oils, unusable edible oil waste (used-once) and others.

#### Methanol as Marine Fuel

According to Methanol Institute, globally there are an estimated 90,000 marine vessels with a consumption of 370 million tonnes of bunker fuel. The use of methanol/methanol-diesel dual-fuel system has been found to be cost effective, competitive and environment friendly. Methanol's use in marine application is mainly due to MARPOL sulfur emissions restrictions.

#### Technology

Methanol ships have been powered by diesel concept engines which have been modified to run on both methanol and marine diesel. Sweden's Stena Line launched the world's first methanol-fuelled ferry in March 2015. Seven 50,000 dead weight tonnes vessels based on MAN B&W ME-LGI 2-stroke dual fuel engines that can run on methanol, fuel oil, marine diesel oil, or gas oil have also been commissioned in





2016. Dual fuel technology is used, with methanol as the main fuel, but with the option to use Marine Gas Oil (MGO) as backup.

#### Fuel Cell

Methanol fuel cells have been reported for use in forklifts in combination of normal batteries. These DMFC have reported to improve the working time, reduce operating costs and reduce GHG emissions by up to 66% (specific model: Oorja Model 3).

#### Policy in India

India's policy on fuel cells and financial support is driven largely by four agencies, viz. Ministry of New and Renewable Energy (MNRE), Department of Science and Technology (DST), Department of Atomic Energy (DAE) and Council of Scientific and Industrial Research (CSIR).

#### **Dimethyl Ether (DME)**

DME is being currently utilized as a cooking fuel in China. The possibility of using it as a transport fuel is being currently pursued in many countries. Due to DME's physical and chemical properties, (it can be liquefied at low pressures, 5 bars), it has been established as a diesel substitute.

The emission – related benefits of DME as shown by Volvo Trucks certainly point to zero particulates, lower NOx and 10% lower CO<sub>2</sub> emissions but with equivalent fuel efficiency against a diesel engine.

#### **Environment & Safety**

Methanol is not a persistent chemical and is broken down in the environment. Methanol fires can be easily managed by alcohol-resistant foam. The IDLH of methanol has been reported by NIOSH as 6000 ppm. Various toxicity studies has confirmed that exposure up to 6000 ppm of methanol vapours in animals (Monkeys & Rats) didn't result in any exposure related adverse effects. Human toxicity values in terms of half-lives methanol in body are roughly 2.5 to 3 hours at doses less than 100 mg/kg bw. Methanol's GHG emissions are 7.6% less than diesel and 5.3% less than Ethanol.

The Indian standard, IS7444 (1974) provide storage guidelines for methanol, both for small and large storage facilities including packaging and labeling. There are no Indian standards for DME. The storage, handling, distribution and safety aspects of DME are very similar to those of LPG. JIS standard K2180, ISO 16861:2015 and ASTM D7901 - 14b are relevant standards for DME.

#### Observations

Presently many European countries have allowed blending methanol with gasoline upto 3% of methanol with no concerns on environmental and technological issues. Similarly, DME has also been researched for use in trucks & cars (which are running on diesel fuel) with change in fuel system and additives. If Government changes fuel policy & allows 3% to 5% Methanol blending with gasoline in place of Ethanol then it will ease pressure on alcohol based industry.

For DME, as per Government's desire to supply LPG cylinder to poor people, the new demand for LPG can be met by blending 5% to 9% of DME with LPG. The present domestic demand is 16 million tonnes. The requirement of DME at 7% - 9% blending will be about 1 to 2 million tonnes.

#### Utilization of Coal

India has good reserves of Coal in the country. It is observed that India's coal reserves are spread mainly in seven states. The non-coking varieties are spread over Chhattisgarh, Jharkhand, Orissa and West Bengal.





It may be an appropriate opportunity for these states to make an effort to establish coal based chemical industry starting with methanol along with DME and other basic chemicals. This will give a much needed impetus for utilization of methanol and DME in India.

#### **Demand Projection**

The present demand of methanol in the country is limited to traditional chemicals like formaldehyde, acetic acid and in pharmaceuticals sector. The present consumption is of the order of 1.8 million tonnes. It is observed that the demand in the sector is growing at the rate of 6% per annum. It is estimated that the demand will grow to 3.0 million tonnes by 2025.

The automobile industry in the country is growing at the rate of 9% (excluding two and three wheelers, SIAM) and alongside gasoline demand.

It is observed throughout the world that many countries are planning to blend methanol at 5% per liter. With blend of 5% methanol and 5% ethanol as co-solvent, India will be in comfortable position. The demand of gasoline presently is 23 million tonnes per annum with 11% growth rate. The methanol demand for fuel blending would be 2.0 million tonnes by 2025.

India with 1.33 billion people consumes 20 million tonnes of oil. The used cooking oil and other inedible oil and animal tallow can be utilised for biodiesel production.

Government in the last 15 months (2014-2016) gave more than 40 million LPG connections to rural poor people. Presently, the demand of LPG is 21 million tonnes. With additional connections, the demand of DME could be more than 2.5 million tonnes requiring 3.0 million tonnes of methanol.

The domestic demand of methanol by 2025 will be about 10.50 million tonnes along with the demand for DME as a blend for LPG requiring 3.00 million metric tonnes.



#### LIST OF ABBREVIATIONS

- 1. AEGL: Acute Exposure Guideline Levels
- 2. AFDC: Alternate Fuels Development Centre, US
- 3. API: American Petroleum Institute
- 4. ASTM: American Society for Testing and Materials
- 5. BP: British Petroleum
- 6. BTEX: Benzene, Toluene, Ethylbenzene and Xylene
- 7. CV: Calorific Value
- 8. DME: Dimethyl Ether
- 9. DMFC: Direct Methanol Fuel Cell
- 10. DOT: Department of Transportation, US Government
- 11. EN: European Norm (Standard)
- 12. EPRG: Emergency Planning Response Guide, 3 levels
- 13. EU: European Union
- 14. EUR/t: Euro per tonne
- 15. FAME: Fatty Acids of Methyl Esters
- 16. FFV: flexible fuel vehicle
- 17. FTP: Federal Test Procedure
- 18. GHG: Green House Gas
- 19. GWP: Global Warming Potential
- 20. IDA: International DME Association
- 21. IDLH: Immediate Dangerous Level to Health
- 22. IEA: International Energy Agency
- 23. IIP: Indian Institute of Petroleum
- 24. IMO: International Maritime Organisation
- 25. IS: Indian Standard
- 26. ISO: International Standard Organisation
- 27. Kb/d: kilo barrels per day
- 28. Kta: kilo tonnes per annum
- 29. LNG: Liquefied Natural Gas
- 30. LPG: Liquefied Petroleum Gas
- 31. MDO: Marine Diesel Oil
- 32. mg/cu.m: milli gram per cubic meter
- 33. MMSCM: Million Metric Standard Cubic Meters
- 34. MMT: million metric tonnes
- 35. MON: Motor Octane Number
- 36. MRO: Marine Residual Oil
- 37. MTBE: methyl tertiary butyl ether

- 38. MTO: methanol to olefins
- 39. Mtoe: million tonnes oil equivalent
- 40. MX: methanol percentage in gasoline; X denotes number from 1-100
- 41. NFPA: National Fire Protection Agency, US
- 42. NIOSH: National Institute of Occupational Safety and Health, US
- 43. NLM: National Library of Medicines, US
- 44. OECD: Organisation of Economic Cooperation and Development
- 45. OSHA: Occupational Safety and Health Administration, US
- 46. PEL: Permissible Exposure Limit
- 47. PNGRB: Petroleum and Natural Gas Regulations Board
- 48. ppm: parts per million
- 49. pS/m: picosiemens per meter
- 50. RON: Research Octane Number
- 51. SIDS: Screening Information Datasets
- 52. SMFT: Swedish Motor Fuel Technology
- 53. TAME: tertiary amyl methyl ether
- 54. TEEL: Temporary Emergency Exposure Limit
- 55. TLV: Threshold Value
- 56. TPA: tonnes per annum
- 57. TWA: Time Weighted Average
- 58. ULP: unleaded petrol
- 59. w/w: weight by weight basis
- 60. WISER: Wireless Information System for Emergency Responders, NLM

### CHAPTER-1 FEEDSTOCKS

The present study is on the Utilization issues of Methanol & Dimethyl Ether (DME), a downstream product of Methanol.

Methanol drew the World's attention towards it following the oil crisis in 1970 and subsequent years, when the crude oil price shot up to \$100 per Barrel. Countries started looking for alternative fuels like Methanol, Ethanol and Bio-diesel to chalk out their energy strategy.

India has limited oil & gas reserves and 80% of the energy needs are being met by imports. India is presently importing 202 million tonnes of crude oil and 16 million tonnes of Natural Gas with a big foreign exchange outgo. With better standard of living and purchasing power, the Automobile industry is enjoying a 9% growth rate with consequent increase in demand for gasoline. Government is looking for a solution to cut import bill and at the same time keep the economic development sustained.

The advantage of Methanol is that the alternative raw materials are available for it in the Country in the form of coal, bio-mass and municipal solid waste. The technology is mature; however it is desirable to examine global experience in the utilization of Methanol & DME.

This chapter provides overview of feedstocks for Methanol including that of coal, coal bed methane and natural gas. The gas hydrate exploration has been featured as it could be a possible future feedstock. LPG and Auto LPG scenario have also been outlined. The crude oil production and import scenario has been provided to provide an essence of the volume in terms of quantity and value currently managed by the country.

#### 1.1 INDIA ENERGY OUTLOOK

As per IEA India energy outlook 2015, India consumes 6% of the global energy [1]. As per IBEF analysis [3], India became the 3<sup>rd</sup> largest energy consumer with the energy demand expected to double from 775 million tonnes oil equivalent (Mtoe) in 2013 to 1,440 Mtoe by 2030. IEA estimate the energy consumption to be 1900 Mtoe by 2040. The global energy consumption as compared to China and India is provided in Figure 1.1



India, with **125** Billion Tonnes of proven **Coal** reserves and **500** million tones of **Biomass** generated every year, has a huge potential for ensuring energy security based on alternate feedstock and fuels. The energy share in terms of oil and coal in India has been provided by different sources:

- 1. IEA (2013): Oil- 23%, Coal- 44%
- Ministry of Statistics and Programme Implementation (2014-15) [10] : Oil- 30.14%, Coal- 65.69%
- 3. Statista (2015) [11]: Oil-37.91%, Coal-58.12%

The future energy scenario has been provided in Table 1.1.

Table 1.1: India Energy Scenario, IEA, 2040

	Unit	2000	2013	2020	2030	2040	Change	CAAGR*
Oil	Mtoe	37	43	35	31	31	-12	-1.2%
	kb/d	771	917	734	678	725	-192	-0.9%
Natural gas	Mtoe	23	29	32	46	75	46	3.6%
	bcm	28	35	38	55	89	55	3.6%
Coal	Mtoe	131	238	298	443	648	410	3.8%
	Mtce	187	340	425	632	926	586	3.8%
Nuclear	Mtoe	4	9	17	43	70	61	7.9%
Renewables	Mtoe	155	204	237	274	297	93	1.4%
Hydropower	Mtoe	6	12	15	22	29	16	3.2%

Bioenergy	Mtoe	149	188	209	217	209	20	0.4%
Other renewables	Mtoe	0	4	13	35	60	56	11.0%
Total production	Mtoe	351	523	619	836	1 121	598	2.9%
Total demand	Mtoe	441	775	1 018	1 440	1 908	1 133	3.4%
Share of imports	%	20%	32%	39%	42%	41%	n.a.	n.a.

\* CAAGR = compound average annual growth rate. Notes: kb/d = thousand barrels per day; bcm = billion cubic metres; Mtce = million tonnes of coal equivalent.

Source: IEA

#### 1.2 INDIA CHEMICALS SECTOR

According to a Press Information Bureau (PIB), Government of India, release in 2016, [2] by the Ministry of Chemical and Fertilizers, the growth rate of Chemicals & Petrochemicals industries, in the country is around 11 - 12 % (2015-16) with output worth \$200 billion annually. Further, as per the above ministry, the sector contributes 3.8% to Indian GDP and 9.4% to exports; the per capita consumption of the products is low and hence, there is immense potential to grow.

India has become an **import destination** for host of **Organic Chemicals** like **Methanol** & **Acetic Acid** etc., due to shortage of raw materials viz. **Naphtha & Natural Gas** in the Country.

China, has forged ahead and has become the hub of **World Supply Centre** for all these Organic Chemicals and energy self sufficiency because of its pragmatic policy & desire to make/build their country sustainable in the **Chemicals & Energy Sector** by shifting their attention from **Oil imports** to indigenous **Coal** with having World's second largest proven Coal Deposits (**130** Billion Tonnes) in their Country which is just next to **USA**.

**Methanol and Di-methyl ether** (DME) are two chemicals, which can be embedded in our energy and fuel policies as these are flexible for use as a feedstock for several chemicals, olefins as well as can be utilized as blending components in petrol (gasoline) and Liquefied Petroleum Gas (LPG) respectively.

#### 1.3 INDIA RESOURCE STATUS

India has proven oil reserves of 5.7 billion barrels, and gas reserves of 1.4 trillion cubic meters. In 2014, imports accounted for more than 80% of the country's total oil demand and 25% of the total gas demand. As per the BP statistical Review of World Energy, 2015, the present natural gas share in the country's fuel basket is 6.5% vis-à-vis, the world average of 23.8%.

	Initial In-Place (MMT)			Ultima	Ultimate Reserves (MMT)			Balance Recoverable			
								Reserves (MMT)			
	Oil	Gas	O+OEG	Oil	Gas	O+OEG	Oil	Gas	O+OEG		
ONGC	5229	2415	7644	1493	1297	2790	454	541	995		
OIL	798	357	1155	247	198	445	83	115	198		
Pvt/JV	975	1460	2435	215	767	982	98	597	695		
Total	7002	4232	11234	1955	2262	4217	635	1253	1888		

Table 1.2: Ir	າdia's Oil a	ind Gas	reserve
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At present (2015-16), the country is having about 15,000 km of natural gas pipeline infrastructure and an additional 15,000 km of pipeline is required for completion of National Gas Grid. Out of this additional 15,000 km, PNGRB/Government of India has authorized entities for laying of about 11,900 km of pipelines [4]. The ensuing sections explore the present scenario of crude oil, coal, petrol, diesel, natural gas, bio-mass and gas hydrates, which are relevant to the scope of study. The productions of oil, coal and natural gas in 2016 (updated June 2016) are provided in Table 1.3:

Commodity	Unit	Jan	Feb	Mar	Apr	Мау	June
Crude Oil	Million tonnes	3.037	2.896	3.062	2.956	3.078	2.966
Natural Gas	MMSCM	2447.38	2565.01	2539.65	2488.07	2656.09	2598.41
Coal	Million tonnes	52.97	53.69	60.25	44.45	49.05	46.00

Table 1.3: India Energy Commodity Production in 2016

Source: Annual Report, Ministry of Petroleum and Natural Gas and Ministry of Coal

An All India Study [5] conducted by M/s Nielsen (India) Pvt Ltd for Petroleum Planning and Analysis Cell (PPAC) of Petroleum Ministry (2013-14) provide the following outcomes:

- 1. Diesel constitutes about 44% of total consumption of petroleum products in India, petrol accounts for about 10%.
- 2. 70% of diesel and 99.6% petrol is consumed in the transport sector
- 3. The agriculture sector is a major consumer of Diesel with about 13% of the total consumption

#### 1.3.1 Crude Oil

Crude oil imports during the past three years are provided in Table 1.4. The annual average import bill is around INR 8 lakh crores (5 year period). Import of Crude Oil during 2015 was 202 million tonnes valued which marked an increase of 5.05% in quantity terms and 41.37% decrease in value terms over the same period of last year. Cumulative crude oil production during April, 2015-March, 2016 was 36.95 million metric tonnes which is 0.26% lower than target for the period and 1.36% lower than the production during corresponding period of last year. CAGR of crude oil as per various estimates over 2008-16 is around 3.3%

#### Table 1.4: Crude Oil Imports

#### (Qty = million metric tonnes, Value in Rupees Crores)

2	012	20	2013 2014 2015		2014		)15
Qty	Value	Qty	Value	Qty	Value	Qty	Value
184.17	784652	189.20	864875	189	7,986,37	202	

Source: Annual Report, Ministry of Petroleum and Natural Gas and Ministry of Coal

The crude oil production by various companies is provided in Table 1.5. In 2015-16, the production was 36.949 million metric tonnes against a target of 37.045 million metric tonnes. The production in 2014-15 was 37.461 million metric tonnes.

Oil Company	Target	April-March (Cumulative)					
	2015-16	2015-16		2014-15	% over last		
	(Apr-Mar)	Target Prod.		Prod.	year		
ONGC	22732.00	22732.00	22367.94	22263.69	100.47		
OIL	3595.00	3595.00	3226.04	3412.10	94.55		
PSC Fields	10718.74	10718.74	11356.01	11785.21	96.36		
Total	37045.74	37045.74	36949.99	37461.00	98.64		

Table 1.5: Crude Oil Production (000 MT)

Source: Annual Report, Ministry of Petroleum and Natural Gas and Ministry of Coal

A comparative analysis of crude oil production for the years 2014-15 and 2015-16 is provided in Figure 1.2



Figure 1.2: Crude oil Production in India Source: Annual Report, Ministry of Petroleum and Natural Gas and Ministry of Coal

#### 1.3.2 Coal

#### 1.3.2.1 Coal Reserves

A total of 3,06,595.56 million tonnes (306.595 billion tonnes) of geological resources of coal have so far ( as on 2015) been estimated in India, upto the maximum depth of 1200 m. Out of the total resources, the Gondwana coalfields account for 305102.92 Mt (99.5%), while the Tertiary coalfields of Himalayan region contribute 1492.64 Mt (0.5%) of coal resources

STATE	PROVED	INDICATED	INFERRED	TOTAL
WEST BENGAL	13518	13010	4907	31435
JHARKHAND	41463	33026	6559	81049
BIHAR	00000	00000	0160	00160
MADHYA PRADESH	10411	12784	3341	26536
CHHATTISGARH	18237	34390	2285	54912
UTTAR PRADESH	00884	00178	0000	01062
MAHARASHTRA	05953	03190	2110	11253
ODISHA	30747	36545	8507	75799
ANDHRA PRADESH	00000	1149	0432	01581
TELANGANA	09807	8808	2597	21211
ASSAM	00465	0047	0003	00515
SIKKIM	00000	0058	0043	00101
ARUNACHAL PRADESH	00031	0040	0019	00090
MEGHALAYA	00089	0017	0471	00576
NAGALAND	00009	0000	0307	00315
GRAND TOTAL	131614	143241	31740	306596

Table 1.6 <sup>-</sup> India Coal Reserves as on 2015 (	(in Million Tonnes)

Source: Annual Report, Ministry of Coal, 2015-16

#### 1.3.2.2 Coal Production

In the year 2014-15, the total production of raw coal in India increased by 8.25%, (from 565.765 MT in 2013- 14 to 612.435 MT in 2014-15) whereas the corresponding decrease in the production of lignite was 9.00 % (from 44.271 MT in 2013-14 to 48.257 MT in 2014-15).

During 2014-15, despatch of indigenous raw coal was 607.630 MT against 572.06 MT during 2013-14 (increase of 6.22% over 2013-14). Consumption / actual supply of coal (including import) increased from 713.39 MT in 2012-13 to 820.32 MT in 2014-15.

All India Coal Demand of various consuming sectors including power utility and steel plants has been assessed to be 787.03 MT against which supplies from indigenous sources has been planned at 643.75 MT.

The Government as on 25<sup>th</sup> July, 2016 has allocated 75 coal mines for specified end uses (31 Coal mines through e-auction & 44 coal mines through allotment) under the provisions of the Coal Mines (Special Provisions) Act, 2015 and the Rules made thereunder.

	Sector	2012-13	2013-14	2014-15	2015-16	2015-16
		Actual	Actual	Actual	Est	Actual
				(P)	Demand	(AprDec.15)
I	Coking Coal					
1.	Steel/Coke Oven & Cookeries	16.90	15.49	22.28	-	10.68
	(Indigenous)					
2.	Steel(Import)	35.56	36.87	43.72	-	26.79
	Sub Total	52.46	52.36	66.00	77.00	37.47
	Non Coking Coal					
3.	Power (Utilities)	457.43	438.83	418.50	604.00	347.71
4.	Power (Captive)	55.05	54.42	51.23	69.00	009.04
5.	Cement	22.39	11.94	11.36	38.00	006.16
6.	Sponge Iron/CDI	20.90	18.49	14.68	34.00	000.19
7.	BRK & Others including	107.95	163.31	258.55	88.00	174.00
	Fertilizer and colliery					
	consumption					
	Sub Total	662.94	686.99	754.32	833.00	537.10
	Total Raw Coal	713.39	739.35	820.32	910.00	574.57

Table 1.7: Coal Consumption and Demand (Thousand Tonnes)

Source: Ministry of Coal

The Coal gasification scenario in India has changed recently. Two projects: one operational since July, 2014 at Jindal Steel (Angul, Odissa) for Sponge Iron production; and the other one for Large Petroleum Coke (petcoke) gasification project now under implementation at Reliance Industries Ltd., for Power and later for Chemical production. The Government has opted for Coal Gasification route for Talcher Fertilizer plant and is also laying gas pipelines to make available gas in the Eastern part of the country.

#### 1.3.3 LPG

The production of LPG from all sources in 2014-15 was 9.84 million tonnes. LPG imports were of 8.3 million tonnes. LPG to the tune of 0.23 million tonnes were exported to other countries. There are more than 16,000 distributors of LPG in India. There are more than 18 million domestic LPG consumers. Auto LPG consumption was 1.63 million tonnes in 2014-15. The consumption of LPG in the country was 18.00 million metric tonnes. The Average Annual Compound Growth Rate has been estimated to be 10% in 2016 with CAGR of 6.90% for 2012-17 five year plans. The average demand of LPG has been estimated to be 21.83 million metric tonnes per annum in 2016-17 with domestic production of 13 million metric tonnes per annum.

#### 1.3.4 Petrol (Motor Spirit/ Gasoline)

The production of Motor Spirit (MS) was 32 million metric tonnes, while the domestic consumption was 19 million metric tonnes in 2014-15. The growth rate of consumption was 11% over previous year. The imports of MS was 0.23 million metric tonnes. The exports were to the tune of 15.8 million metric tonnes. The average demand for Petrol has been estimated to be 23 million metric tonnes per annum with domestic production of 38 million metric tonnes per annum in 2016-17. The growth rate for production during 2012-17 has been estimated to be 8.5%.

#### 1.3.5 Natural Gas

India had 1.4 trillion cubic meters of proven natural gas reserves at the beginning of 2014 (3). Approximately 34% of total reserves are located onshore, while 66% are offshore. The natural gas production 2013-14 was 35.41 billion cubic meters with provisional Figures for 2014-15 as 33.66 billion cubic meters [7]. Natural gas share in the country's fuel basket is 6.5% vis-a-vis the world average of 23.8% [8]. The production of natural gas is provided below in Table 1.8. Some of the main industries that use natural gas are pulp and paper, metals, chemicals, glass, plastic and food processing apart from fertilizer & power plant.

Natural Gas Production	2008	2009-	2010-	2011-	2012	2013-	2014
(MMSCM)	-09	10	11	12	-13	14	-15*
(I) Onshore:							
Gujarat	2605	2444	2262	2173	2032	1657	1526
Assam	2573	2703	2680	2905	2910	2868	2958
Arunachal Pradesh	30	40	44	40	41	41	34
Tripura	553	564	610	644	647	822	1140
Tamil Nadu	1242	1178	1119	1285	1206	1304.020	1191.565
Andhra Pradesh	1524	1479	1384	1364	1249	4171	541
Rajasthan	216	239	432	590	685	982	1178
West Bengal(CBM)	20	38	41	79	101	156	224
Madhya Pradesh (CBM)	0	0	0	2	3	6	2
Jharkhand(CBM)	0	0	0	4	3	3	2
Total(a)	8763	8685	8574	9084	8877	9012	8796
Of which							
OIL	2268	2416	2350	2633	2639	2626	2722
ONGC	5753	5634	5504	5751	5447	5316	4750
JVC/Private	742	635	720	699	791	1069	1323
(II) Offshore:							
ONGC	16733	17462	17591	17565	18102	17968	17272
JVC/Private	7348	21350	26054	20910	13700	8428	7589
Total (b)	24082	38811	43645	38475	31802	26395	24861
Grand Total (a+b)	32845	47496	52219	47559	40679	35407	33656

	Table	1.8:	Natural	Gas	Production
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Source: Annual Report, Ministry of Petroleum and Natural Gas

During 2013-14, 32.56 % of the natural gas consumed in the country was used by the fertilizer industry and 31.02 % by the power generation sector

Oil Company	Target	April-March (Cumulative)				
	2015-16 (Apr-	2015-16		2014-15	% over last	
	Mar)	Target	Prod.	Prod.	year	
ONGC	23908.00	23908.00	21176.64	22022.12	96.16	
OIL	3009.97	3009.97	2837.94	2722.21	104.25	
PSC Fields	8361.91	8361.91	8234.63	8911.94	92.40	
Total	35279.88	35279.88	32249.21	33656.27	95.82	

Table 1.9: Natural Gas Production (MMSCM)

Source: Annual Report, Ministry of Petroleum and Natural Gas and Ministry of Coal

The natural gas production for 2014-15 and 2015-16 is provided in Figure 1.3. Production for the last two years follows a very close overlapping trend with a marginal fall in January 2016 and March 2016.



#### Figure 1.3: Natural Gas Production

Source: Annual Report, Ministry of Petroleum and Natural Gas and Ministry of Coal

The country's natural gas pipeline network amounted to over 17,421 km in 2015 and a proposed expansion of 30,000 km is envisaged by 2018-19.

#### 1.3.6 Coal Bed Methane

As per the statistics [7] available from Ministry of Petroleum and Natural Gas, the estimated Coal Bed Methane (CBM) resources are of the order of 2600 Billion Cubic Metres (BCM) or 91.8 Trillion cubic feet (TCF) spread over in 11 states in the country. Jharkhand has the highest of the reserve accounting for 27.7% of the total reserves followed by Rajasthan and Gujarat with 13.83% and 13.50% respectively. Around, 280.3 BCM (9.90 TCF) of recoverable CBM reserves have been established by different operators as on 01.04.2015. 30 blocks have been allocated to various parties as on 2015. As per ministry sources [9], coal bed methane would contribute to around 5% of the total gas production in the country by 2017.

#### 1.3.7 Gas Hydrate

The National Gas Hydrate Programme (NGHP) is also of national strategic importance for the exploration and development of gas hydrates reserves in India. Gas Hydrates are ice-like crystalline compound, consisting of natural gas (mainly methane) and water. Gas hydrates are formed under high pressure and low temperature conditions, and occur in sedimentary deposits in permafrost regions and beneath the sea in outer-continental margins. One cubic meter of gas hydrate contains 164 cubic meter of natural gas. Gas hydrate resources in India are estimated at 1894 trillion cubic meter and these deposits occur in Western, Eastern

and Andaman offshore areas. Hydrate Energy International has estimated resource potential of gas hydrate in India at 933 trillion cubic feet.

Year	Event Description
1997	Initiation, Steering Committee and a Technical Committee, DGH is the coordinator of the programme, two centre, one on East Cost and one on West Coast are Model Laboratory Areas
2000	Ministry of Petroleum and Natural Gas (MoPNG) formulated the NGHP
2006	NGHP identified four offshsore areas for gas hydrate coring/drilling operations
2006	Operations carried out in these areas during April, 2006 to August, 2006 through a consortium consisting of Overseas Drilling Limited, Fugro, McClelland Marine Geosciences, Geo-TeK Limited, Lamont, Doherthy, Earth Observatory and scientists from numerous universities and national laboratories.
2008	Research completed with several findings including
	<ul> <li>Discovery of one of the thickest and deepest gas hydrate occurrences yet known which revealed gas-hydrate-bearing volcanic ash layers as deep as 600 meters below the seafloor;</li> </ul>
	<ul> <li>Existence of a fully developed gas hydrate system in the Mahanadi basin of the Bay of Bengal;</li> </ul>
2014	Memorandum of Understanding (MoU) between India and the United States for cooperation in gas hydrates for a period of five years.
	Planned NGHP Expedition-02 and 03 in deep water areas of the Eastern, Western and Andaman Sea
2016	Indian National Gas Hydrate Programme Expedition 02
	Completed 42 wells in 147 days against target of 40 wells in 150 days
	Huge reserves in Krishna Godavari (KG) deep off shore areas

Table 1.10: Timeline of NGHP

Source: Ministry of Petroleum and Natural Gas and Ministry of Coal

The project objectives and outcomes of NGHP-02 are provided at a glance

#### **Project Objectives of NGHP 02**

- Identification of sites/areas with high saturation of gas hydrates in sand facies.
- Interpret and collect the data to identify a suiTable site for pilot production testing in NGHP Expedition-03.

#### Outcome of NGHP-02

- Producible gas hydrates have been discovered in KG deep offshore areas in sand reservoirs.
- Two types of gas hydrate accumulation have been discovered. One is ~ 20 to 100 m thick, layer-type unit developed in sand-rich layers at depths of a few 100 mbsf
(meter below sea floor) and another is fracture-type unit of variable thickness at shallow levels.

- The occurrence and texture of hydrates have been extensively examined by X-ray CT scanning and IR images. These demonstrate high concentration in some particular cores from layer-types and fracture types in different areas
- Based on the expedition and post expedition results, 3 sites near Visakhapatnam and 2 sites near Kakinada have been found suiTable sites for pilot production testing.

#### 1.3.8 Biomass

India generates approximately 500-600 million tonnes of agro-based biomass. 150-200 million tones of biomass is surplus after meeting local requirement like fuel, fodder, etc. which could be processed to produce alcohol. There is enormous biomass availability in terms of agro-residues such as rice straw, wheat straw and sugarcane bagasse, etc. A study by TIFAC in 2009 provides the generation and surplus lignocellulosic biomass as shown in Table 1.12.

Biomass	Generation(MMT)	Surplus(MMT)
Rice Straw	112.0	8.5
Rice Husk	22.4	0.4
Wheat Straw	109.9	9.1
Sugarcane Tops	97.8	79.5
Sugarcane Bagasse	101.3	6.4
Maize Stover	22.7	1.1
Maize Cob	4.2	1.7
Maize Husk	2.7	1.1
Sorghum Stover	15.6	1.6
Bajra Stalk	12.2	1.2
Cotton Stalk	18.9	11.4
Chillies Stalk	0.6	0.5
Ragi Stalk	4.6	0.5
Pulse Waste	18.9	5.7
Oilseed Waste	57.7	17.3
Bamboo(Tops, Roots, Leaves)	5.4	3.3
Pine Needles	1.6	1.2
Water Hyacinth(Whole)	15.0	14.0
Total	623.4	164.5
I	Source: TIFAC Report 2009	

Table 1.12: Generation and Surplus Ligno-cellulosic Waste Biomass\*

\*excluding the forest residues;

# 1.4 **REPORT STRUCTURE**

Keeping in the view the scope of work & objectives of the study the report is covered in the following six chapters:

- 1. Feedstock
- 2. Status of Methanol & DME
- 3. Methanol & DME Utilization
- 4. Enviornment, Health & Safety
- 5. Demand Forecast
- 6. Conclusion & Recommendation

The First Chapter discussed the feedstock scenario for Methanol.

The Second chapter provides status of Methanol and DME both nationally & globally

The Third chapter discusses the utilization of Methanol & DME, which are used for producing organic chemicals such as formaldehyde and acetic acid. Methanol and DME are also utilised as a blending option with petrol (gasoline) and diesel respectively. These aspects have been covered in this chapter. The global experience of DME as a blending fuel in LPG for residential applications has been explored. The use of Methanol in fuel cells has been discussed. The chapter further examines the experience of utilizing Methanol & DME as Marine Fuel in place of heavy fuel oil which is creating enormous environmental damage.

The Fourth Chapter focuses on safety, health and environmental aspects of Methanol and DME.

The fifth chapter provides the observations and recommendations based on survey report

The Sixth Chapter outlines a demand forecast of Methanol and DME

# CHAPTER-2 STATUS OF METHANOL & DI METHYL ETHER

## 2.1 INTRODUCTION

Methanol (methyl alcohol or referred to wood alcohol) is a versatile chemical. It finds application in several sectors. The methanol industry is spread all over the globe. There are more than 100 plants operating worldwide which produce an estimated 113 million tonnes of methanol annually [1]. Methanol is produced in Asia, North and South America, Europe, Africa and the Middle East.

#### 2.1.1 Product Pathways

Methanol is an important feedstock for the chemical industry (refer Figure 2.1). It has been often labeled as a future feedstock or building block for replacing conventional oil to chemical routes. Several projects in China produce Methanol to Olefins (MTO), which forms a base for chemicals earlier derived from petroleum crude. Methanol can be produced from any carbon source, viz. natural gas, coal & biomass. Natural Gas is however the most popular feedstock to produce methanol due to cost and operational factors.





#### 2.1.2 Properties

The important properties of methanol are provided in Table 2.1 as obtained from IS 7444

S.No	Property	Value
a)	Colour	Colourless, water white
b)	Boiling point	64·5°C at 760 mmHg
c)	Density (g/ml)	0·791 3 at 20°C
d)	Hygroscopicity	None
e)	Odour	Pure material has a slight alcoholic odour. Other grades may have a pungent oily odour
f)	Flash point:	
	Open cup	16°C
	Close cup	12°C
g)	Reactivity	Not dangerously reactive
h)	Solubility	Miscible in all proportions with water
j)	Corrosivity	Slightly corrosive to metals especially in presence of moisture. Exceptions—lead and aluminium
k)	Freezing point	–97·6°C
m)	Vapour density (air = 1)	1.11
n)	Flammable limits, percent by volume in air at STP	7·3 to 36
p)	Vapour pressure	at 0°C—52 mmHg
		at 20°C—96 mmHg
		at 40°C—253 mmHg
q)	Auto-ignition Temperature	470°C
r)	Refractive index at 20°C	1.331 2
s)	Latent heat of vaporization	262·8 cal/g at 64·7°C
t)	Latent heat of fusion	16·4 cal/g at –97°C

Source: Indian Standard 7444

The ensuing sections cover the Indian as well as global Methanol scenario.

# 2.2 METHANOL- NATIONAL STATUS

There are six major producers of methanol in India with a total installed capacity of **0.66 million TPA.** Gujarat Narmada Fertilizer Company (GNFC) in Bharuch (Gujarat) is the biggest player with 51% of the total capacity, followed by Deepak Fertilizers & Petrochemicals Ltd. (DFPCL) with 21% and Assam Petrochemicals Ltd. (APL) with 7%.

#### 2.2.1 Manufacturers of Methanol

The major players of Methanol in India are as follows:

#### 2.2.1.1 GNFC, Bharuch (Gujarat)

**GNFC** produces approximately 132,000 tonnes of Methanol and is the largest producer in the country. The **installed capacity is 238,100 tonnes per annum**. The company gets its required gas from GAIL. Due to lack of availability of gas the company is now running at a lesser production rate of 300 to 450 tonnes per day only. Of the total methanol produced by the company, 40% is used for producing Formaldehyde and 10% is used for producing Acetic acid.

#### Capacity utilisation of GNFC in 2015-16 was around 54%

The production and sales volume of methanol are provided in Table 2.2 for GNFC as obtained from annual reports

Plant	Installed Capacity	Technical Collaborator					
Methanol-I	50,000 TPA	ICI, UK & Linde AG, Germany					
Methanol-II	1,88,100 TPA	ICI, UK & Toyo Engg., Japan					
	Source: Annual Reports						

Table 2.2: GNFC Plants Installed capacity and Technology Collaborations

The production and sales for three years beginning 2013-14 is provided in Table 2.3 and Table 2.4 respecitively. Overall capacity utilization improved in 2015-16 due to a substantial increment in Methanol-1 plant.

Table 2.3:	GNFC	Production
------------	------	------------

PLANTS	ACTUAL (MT)			CAPACITY UTILIZATION (%		
	2013-14	2014-15	2015-16	2013-14	2014-15	2015-16
Methanol-I	18,224	3,743	25,208	36.45	7.49	50.42
Methanol-II	1,45,347	1,00,970	1,07,241	77.27	55.68	57.01

Source: Annual Reports

Table 2.4: GNFC Dispatch / Sale (MT)

	2013-14	2014-15	2015-2016
Methanol	65,043	26,782	43,687
Acetic Acid	1,23,050	1,27,905	124,165

Source: Annual Reports

#### 2.2.1.2 Deepak Fertilizers & Petrochemicals (DFP), Raigarh

The Company has a **manufacturing capacity of 100,000 MT of Methanol**. Due to nonavailability of competitively priced raw material and unfavourable market conditions, the capacity remained unutilised during the year. New environment friendly process for producing dimethyl carbonate (DMC) from Urea and Methanol is being developed in collaboration with NCL, Pune and IIT, Mumbai under the aegis of CSIR (NMITLI project).

**Capacity utilisation of Deepak Fertilizers and Petrochemicals in FY2015 was 8.5%.** The production and sales of DFP for past five years are provided in Table 2.5 and 2.6 respectively.

	Units	FY2015	FY2014	FY2013	FY2012	FY2011	
Methanol	MT	8,578	34,172	13,431	63,733	81,888	
Source: Annual Reports							

Table 2.6: DFP Sales (MT)

	Units	FY2015	FY2014	FY2013	FY2012	FY2011		
Methanol	MT	9,419	32,830	14,933	62,266	81,708		
	Occurrent Annual Bananta							

Source: Annual Reports

#### 2.2.1.3 Rashtriya Chemicals and Fertilizers Limted (RCF), Mumbai

Methanol plant was put up in 1966 which was known as "Trombay – II" diversification. **RCF** has 85,000 tonnes per annum installed capacity. Capacity utilisation for methanol in RCF was 80%

The production and sales of RCF for past five years are provided in Table 2.7 and 2.8 respectively.

Table 2.7: RCF Methanol Production (MT)

	Units	2014-15	2013-14	2012-13	2011-12	2010-11
Methanol	MT	64,443	77,660	76,830	78,317	68,700

Source: Annual Reports

Table 2.8: RCF Methanol Sales (MT)

	Units	2014-15	2013-14	2012-13	2011-12	2010-11
Methanol	MT	41,015	54,862	52,994	50,669	41,264
		0	waa. Awaaaal F			

Source: Annual Reports

## 2.2.1.4 National Fertilizers Limited (NFL), Nangal (Punjab)

The **Methanol Augmentation** Scheme at Nangal Unit was commissioned in October 1998 with an **installed capacity of 23,000 tonnes per annum** for internal requirement of Methanol as a solvent for gas cleaning. As of 2015, in case of Nangal unit, following plants were identified as economically impaired cash generating units during the year as they are not in operation:-

- 1. Naphtha Modernization Phase-I (NMP) Hydrogen Plant
- 2. Methanol Plant

EIL had also carried out study to find alternate utilization of the old Nangal Methanol Plant (NMP) I plant at Nangal using Petcoke for production of Methanol/ alternate industrial chemicals for which detailed feasibility is being undertaken.

## 2.2.1.5 Assam Petrochemicals Limited (APL)

**APL's Methanol plant has an installed capacity of 41,250 TPA** (increased from 100 TPD to 125 TPD) with Natural Gas as feedstock.

The company achieved 78% capacity utilization in 2014-15 for Methanol production.

Year	Production	Sales
2014-15	32,168	12,645.82
2013-14	28,822	8,028
2012-13	33,546	13,648
2011-12	26,994	11,500
2010-11	17,982	6,618
2009-10	33,759	15,040

Table 2.9: APL Production and Sales (tonnes)

Source: Annual Reports

The methanol distribution by region (only from APL sales) as obtained from APL website is provided in Table 2.10. It can be derived from the Table that 49% of the sales are obtained from Northern India, while West region accounts for 26% of the sales volume.

		, .
Methanol (in MT)	FY 2014-15	FY 2013 – 14
North East Region	1,177.360	973.940
West Region	3,265.980	1,923.430

6,145.200

2,057.280

12,645.820

Source: Annual Reports

Table 2.10: Methanol sales from APL by region

North India

Nepal & Bangladesh

Total

3,865.140

1,265.614

8,028.12

#### 2.2.1.6 Gujarat State Fertilizer Corporation (GSFC)

#### GSFC has production capacity of 525 TPD of Methanol

The Company had taken up conversion of Ammonia-I plant for production of Methanol based on technology for M/s.Haldar Topsoe, Denmark. M/s.Projects & Development India Ltd. was appointed as Consultant for carrying out Detail Engineering work for the project. The mechanical completion of the project was achieved on 28.12.12 and trial production was achieved on 2nd March, 2013. This Plant was commissioned during 2nd quarter of F.Y.2013-14 and could achieve the guaranteed quality product at full load. **Methanol sales reported during FY2013-14 were 57037 MT** 

#### 2.2.2 India-Imports and Exports

Due to the local demand exceeding supply and raw material pricing issues, India has to depend on imports to meet its requirements. Imports, in fact, constitute around 70% of total consumption.

Imports have grown from 527,000 tonnes in 2006-07 to 16, 41,624-tonnes in 2014-15. More than 95% of the imports are being sourced from two countries: Saudi Arab & Iran. Small quantities of methanol are also exported from India.

Exports are in the region of 40,000-tonnes to 45,000-tonnes, constituting only around 3-3.5% of total consumption. The import, export, production and consumption as obtained from Ministry of Chemicals are provided in Table 2.11.

Year	Import	Export
	Million	tonnes
2007-2008	0.7888	0.0317
2008-2009	1.0588	0.0326
2009-2010	0.8222	0.0459
2010-2011	0.8134	0.0435
2011-2012	1.1996	0.1204
2012-2013	1.3989	0.1846
2013-2014	1.3104	0.0819
2014-2015	1.6416	0.0494

Table 2.11: Import and Export statistics of Methanol for India

Source: Ministry of Chemicals and Petrochemicals

## 2.2.3 Domestic Consumption and End Use Pattern

## 2.2.3.1 Consumption

Consumption of methanol in India increased from 0.5 million tonnes in 2006-07 to 1.81 million tonnes in 2014-15 with an average annual consumption of 1.37 million tonnes between 2007 and 2014 (7 years). The production and consumption statistics for methanol is provided in table 2.12.

The average growth rate of consumption over 2007 to 2014 is 7%, with 17% in 2014-15 over the last fiscal.

Year	Production	Consumption	Year Growth
	Millio	Rate (%)	
2008-2009	0.2371	1.2927	16.59
2009-2010	0.3308	1.1071	-14.35
2010-2011	0.3745	1.1443	3.36
2011-2012	0.3599	1.4391	25.76
2012-2013	0.2549	1.4692	2.09
2013-2014	0.3072	1.5357	4.53
2014-2015	0.2098	1.8019	17.33

Table 2.12: Production & Consumption statistics of Methanol for India

Source: Ministry of Chemicals and Petrochemicals, Govt. of India

## 2.2.3.2 End Use Pattern

Formaldehyde and pharmaceuticals (bulk drugs and intermediates) are the two important end-use segments, which together account for 55% of the total methanol consumed in the country. While formaldehyde alone accounts for 38%, the pharmaceutical sector accounts for 17%. The balance is shared between oxygenates, alkylamines, acetic acid, chloromethane and other uses as shown in Table 2.13.

TADIE 2. 13. DUTTESTIC METHATIOT CONSUMPTION DATENT AND MALKET SHALE, 2013-10	Table 2.13: Domestic Methanol	consumption p	pattern and Market	Share, 2015-16
---	-------------------------------	---------------	--------------------	----------------

S. No.	Sector/Zones	Total ( Qty. in MT)	Market Share (%) 2015
1.	Formaldehyde/Plywood/Laminates	702180	37.60
2.	Pharmaceuticals(solvents)	323620	17.33
3.	Pesticides Sector	104520	5.60
4.	Glacial Acetic Acid	84000	4.50
5.	Methyl Amines	42000	2.25
6.	Methyl Tertiary Butyl Ether (MTBE) (fuel)	22800	1.22

7.	Dyes & Intermediates	47040	2.52
8.	Dimethyl Sulfide (DMS)	24000	1.29
9.	Choloro Methanes	39600	2.12
10.	Tert Amyl Methyl Ether (TAME) (fuel)	168000	9.00
11.	Thinner/Paint	116760	6.25
12.	Purified Terephthatic Acid (PTA)	1800	0.10
13.	Others	191040	10.23
	Total	1867360	100

Source: GNFC, 2015-16

# 2.2.4 Future demand forecast of India

Demand forecast for methanol by 2025 is projected to grow to 10.5 million tonnes, at an average growth rate of 6% per annum. The demand takes into account the potential demand that may arise from the biodiesel and fuel blending sectors.

Methanol is also utilized as a trans-esterification agent for biodiesel manufacturing. The Ministry of Road Transport & Highways has notified the Mass emission standards for biodiesel for B100 in April 2016, which could enhance methanol consumption by 2020 in biodiesel production.

The estimated demand for methanol has been provided in Chapter-6 across end use sectors in India.

In the case of methanol blending with gasoline, there is no policy focused on methanol on the horizon, and the focus, as pointed out earlier, is on ethanol blending. However, a potential methanol demand based on blending in gasoline in future upto 5% of methanol could be around 1.0 million tonnes annually.

# 2.3 INTERNATIONAL STATUS

## 2.3.1 Production

Globally, by 2014, 60% of the methanol was consumed in traditional chemical sectors (acetic acid, formaldehyde, silicone, methyl methacrylate), while 40% was consumed in Energy related applications (Biodiesel, MTO, Fuel Blending, DME, MTBE) [2]. The global methanol installed capacity as per GlobalData report [28] was 117.5 million tonnes per annum in 2015 while the global production for past five years is provided in Table 2.14 from different sources.

Voor	Quantity <sup>1</sup>	Quantity <sup>2</sup>	Quantity <sup>3</sup>
Tear	(million tonnes)	(million tonnes)	(million tonnes)
2012	60.0	55.0	59.0
2013	65.0	60.0	62.2
2014	75.0	68.0	66.7
2015	85.0	74.0	69.5
2016	100.0	78.0	

Table 2.14: Global Methanol Production (Million tonnes)

1. Argus—Dewitt report,

2. Methanol Institute

3. Methanex annual report 2015

As per Argus media estimates, the **global methanol production** [5] is estimated to grow at 14% to 120 million tonnes by 2018 as shown below.



Million tonnes

The top global producers (companies) along with their market share in 2015 are provided below in Figure 2.5 and Table 2.15





The top five major producers in 2015 were Methanex, SCC, Sabic, MGC and Zagros. The share of top producers fell by average 1% over 2014.

Company	Share	Share
Company	2014	2015
Methanex Corp.	15%	14%
SCC / Helm (MHTL)	8%	7%
Sabic	7%	6.2%
Zagros	3.6%	2.8%
MGC	3.5%	3.9%
Mitsubishi (MSK)	2.4%	2.2%
Petronas	2.2%	0.8%
Mitsui	1%	0.5%
Other Companies in China & ROW	57.3	62.6

Table 2.15: Top Producers of Methanol

Source: Methanex Investor presentation, 2016

Methanex is the leading producer and supplier of methanol to the major international markets in Asia Pacific, North America, Europe and South America. The 2015 sales volume of 8.5 million tonnes of methanol represented approximately 14% of global methanol demand.

CEL is the 2<sup>nd</sup> largest producer of methanol in the world with 4.1 million tonnes per annum of installed capacity through its 100% subsidiary Methanol (Holding) Trinidad Limited ("MHTL"). MHTL is the largest methanol exporter to North America and significant producer of fertilizer products. CEL further owns strategic minority stakes via Oman Methanol Company LLC ("OMC"), in world scale methanol plant in Sohar, Oman [26].

The global methanol demand category wise for chemicals, fuels in one category and Methanol to olefins separately, are given in table 2.16.

S.No.	Category	2012	2013	2014	2015
1	Chemicals, fuels	51, 470	54, 283	58, 200	61, 000
2	ΜΤΟ	7, 459	7, 991	8, 504	8, 471

Table 2.16: World Production of Methanol

Source: Methanex annual report, 2015 (Excluding demand from integrated MTO facilities)

## 2.3.2 Future Methanol Capacity

As per IHS, **Globally coal based Methanol constitutes around 35% of the installed capacity [3].** The largest producing region/country today is China, and it will continue to have the largest production capacity and be the largest producer in future too. Methanol proposed capacity additions and changes are provided in Table 2.17.

Considering present scenario, 4.24 million tonnes of methanol capacity have been projected with top three capacity additions from China, US and Iran by 2020. GlobalData [4] reports that **by 2020, methanol capacity would rise to 184.4 million metric tonnes per annum**. The largest capacity addition would come from Mozambique based GigaMethanol B.V. with 5.3 million metric tonnes capacity addition by 2020.

Country	2015	2016	2017	2018	2019	2020
Canada	20	20				
China	4,550	2,775	2,600	150		
India		165				
Iran			1,150	1,150	1,650	
Nigeria						990
Other CIS & Baltic States	400					300
Qatar	80					
Russia	50	240		450		865
Trinidad					833	167

Table 2.17: World Methanol capacity additions proposed (000 tonnes)

United States	1,355	2,193	875	2,075	1,900	1,922
WORLD	6,455	5,393	4,625	3,825	4,383	4,244
0						

Source: IHS

# 2.3.3 Global Imports and Exports [6]

The total value of trade in 2014 for methanol was 10.8 Billion USD. The major exporting nations were Trinidad and Tobago (15%), Saudi Arabia (14%) and Iran (9.2%), while the top three importing countries were United States (15%), China (14%) and Germany (6.7%). China's exports were 1.7%, while India's import constituted 4.7% of the world's trade. Methanol is a globally traded commodity with transparent pricing. Methanol generally trades at a discount to oil on an energy basis making methanol blended fuels potentially lower cost of energy to consumers.

In terms of value in 2015, the top exporters of Methyl alcohol are Trinidad and Tobago (\$1.65B), Saudi Arabia (\$1.53B), Iran (\$996M), Oman (\$708M) and New Zealand (\$681M).

The top importers, in terms of value are the United States (\$1.59B), China (\$1.48B), Germany (\$726M), Japan (\$715M) and the Netherlands (\$672M).

The exports and imports of methanol in 2014 are depicted in Figure 2.4 and 2.5 as reproduced from the observatory for economic complexities (OEC):

Saudi Arabia	Oman	Malays	ia	Netherlands	Germany	Norway		Equatorial Guinea	New Zealand
				5.6%	2.2%	2.0%	1.9%	3.6%	
4.40/	6.5%	3.79	%	Russia 5.0%	Finland	Spain	1.0 %	Egypt	
14%	Brunel 2.0%	Bahrain ini		Trinidad and	Tok	bago	)	3.0%	6.3%
II dII	<b>Qatar</b> 2.0%	1.5% 1.						Venezuela	. **
9.2%	China 175			15%	0			4.7%	ARG

Figure 2.4: Country Exports of Methanol (2014) by percentage Source: Observatory of Economic Complexities

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China	South	Ind	ia	Germany	Nether	lands	22		United States
	5.4%	4.	7%	6 7%	6.2%				
	Thailand	Turkey	Other	0.1 /0	0.2	- /0	3.	1%	
14%	2.6%		Asia	France	Finland	Sector	Antis	-	15%
1-170	Singapore	2.0%	1.9%	2.5%	1.8%				1070
Japan	2.5%	Indonesia	PHIL.	kdy	Poland	Remarks	CZE	HUN	Canada Mexico
	Malavala	4 7%			1,4%	Participat			Brazil
6.6%	2.1%	Vetrum		2.0%	United	Greece			3.4% 🛥



In terms of Asian scenario, the total trade was worth 4.92 Billion Dollars. The top five import destinations were China (30%), Japan (15%), South Korea (12%), India (10%) and Thailand (5.7%).

The exports for Asia were Saudi Arabia (32%), Iran (21%), Oman (15%), Malaysia (8.4) and China (4%). The imports and exports for Asian countries are provided in Figure 2.6 and Figure 2.7 in value terms.

China	South	Ind	ia	Germany	Nether	ands	2	,	United States
	5.4%	4.	7%	6 70/	6 2	)0/			
	Thailand	Turkey	Other	0.170	0.2	. 70	3.	1%	
1/1%	2.6%		Asia	France	Finland	. Banders	Antis	-	15%
1-1/0	Singapore	2.0%	1.9%	2.5%	1.8%				1070
Japan	2.6%	Indonceia	PHI.	kaly	Poland	Renaria	CZE	HEN	Canada Mexico
	Helevela	4.7%			1.65	-			Brazil
6.6%	2.1%	Vietnam		5pain 2.0%	United	Greece			3.4% 🛥

Figure 2.6: Asian Country Imports of Methanol (2014) Source: Observatory of Economic Complexities

## TIFAC, DST, Govt. of India | Utilisation issues of Methanol and DME

Saudi Arabia	Iran		Malaysia	Brunei	Qatar
	21	%	8.4%	4.6%	4.5%
	Oman		China	Indone	sia deces
			4.0%	3.0%	6 1.2%
220/	15	0/	Bahrain	5x6. *	AZE
3270	19	70	3.4%	India 9	(pros

Figure 2.7: Asian country Exports of Methanol (2014) Source: Observatory of Economic Complexities

Asia constituted 44% of the global exports, followed by Europe 20% and North America 17%. In terms of imports, Asia led with a commanding share of 46%, followed by Europe with 33% and North America, 16%.

# 2.4 GLOBAL SUPPLY AND DEMAND

The global supply and demand trends are discussed in this section. Past trends along with future projection as obtained from various market research organisations, manufacturer's annual reports, methanol institute as well as methanol and DME associations have been analyzed in this section.

## 2.4.1 Historical Trend

The following Table 2.18 shows world historical supply and demand of methanol from 2011 to 2015.

	2011	2012	2013	2014	2015	2016E	11-16E
Supply							CAGR%
Nameplate Capacity	86,727	95,264	100,868	110,471	122,162	126,503	7.8
Total Capacity	86,727	95,264	100,868	110,471	122,162	126,503	7.8
Macro Operating Rate	63.0%	63.5%	63.9%	65.7%	64.3%	67.9%	1.5
Production	54,635	60,479	64,482	72,607	78,512	85,911	9.5
Imports	24,344	23,860	24,425	24,194	24,220	25,796	1.2
	2011	2012	2013	2014	2015	2016E	11-16E
Total Supply	54,635	60,479	64,482	72,607	78,512	85,911	9.5

Table 2.18: Historical Global Methanol Supply and Demand (000 Tonnes)

## TIFAC, DST, Govt. of India | Utilisation issues of Methanol and DME

Demand	2011	2012	2013	2014	2015	2016E	11-16E
Formaldehyde	17,569	18,410	19,387	20,488	21,017	21,828	4.4
Acetic Acid	5,189	5,307	5,714	6,020	5,994	6,105	3.3
Methyl tert-Butyl Ether(MTBE)	7,558	8,060	8,844	9,641	9,748	10,124	6.0
Methyl Methacrylate	1,462	1,507	1,549	1,634	1,648	1,706	3.1
Dimethyl terephthalate(DMT)	457	458	468	472	467	473	0.7
Methanethiol (Methyl Mercaptan)	444	461	478	493	503	513	2.9
Methylamines	1,360	1,401	1,441	1,482	1,522	1,559	2.8
Methyl Chloride (Chloromethane)	1,857	1,916	1,985	2,107	2,099	2,166	3.1
Alternative Fuels							
Gasoline Blending & Combustion	7,143	8,311	8,926	11,093	11,323	12,168	11.2
Biodiesel	1,156	1,210	1,175	1,173	1,146	1,220	1.1
DME	4,297	4,557	4,734	4,853	3,844	3,932	-1.8
Fuel Cells	6	7	7	7	8	8	5.4
Methanol to Olefins	2,479	4,908	5,767	9,108	15,150	19,848	51.6
Others	3,584	3,872	4,067	4,027	4,077	4,259	3.5
Total	54,562	60,382	64,539	72,597	78,546	85,911	9.5
Exports	24,344	23,860	24,425	24,194	24,220	25,796	1.2
Total Country Demand	54,562	60,382	64,539	72,597	78,546	85,911	9.5

Source: MMSA

As per absolute reports [7], value wise, the methanol market size is projected to reach USD 54.16 billion by 2021, registering a CAGR of 12.4% between 2016 and 2021.

## As per Methanex, 30% of global demand comes from top 20 consumers.

As per Methanol Institute, global methanol demand in 2015 was 70 million metric tons with China's share at 40%. Further, China consumed 7 million metric tonnes of methanol as transportation fuel in 2015.

## 2.4.2 Demand Projections

The global methanol demand as predicted by Argus media is provided in Figure 2.8. China is stated to hold 69% of the total global demand by 2018.



# Figure 2.8: Global Methanol Demand by Argus Media

As per the Argus reports, Global methanol consumption grew at a CAGR of 6.3% from 2000 to 2015 and 10.3% from 2009-2014



The global production and demand as projected by MMSA, is provided in Figure 2.9

Figure 2.9: Projected Methanol Global Production and Demand by MMSA

Similar percentage for worldwide capacity and demand as provided by IHS <u>region wise</u> is depicted in Figure 2.10. North east region commands more than 55% in capacity and 62% in Demand. <u>India's share is 1% of the total global capacity and 2% of the total global demand.</u> IHS further states that the installed capacity for methanol will increase from 112 in 2015 to 140 million metric ton in 2020.



Figure 2.10: IHS, Methanol Demand by end use, 2015

The global methanol demand by IHS is provided in Figure 2.11:



Figure 2.11: Global Methanol Demand by IHS

The global demand for methanol from Argus, MMSA and IHS projections are 120 million tonnes, 100 million tonnes and 90 million tonnes by 2018 and respectively. The demand by 2020 as estimated by MMSA would be around 117 million tonnes, while IHS provides a Figure of around 100 million tonnes

Overall, world demand for methanol is projected to grow at an average annual rate at 7-8% from 2016 to 2025. Further, China constituted 43% of the demand followed by Asia pacific at 21%. Europe consumed 20% of the total demand.

#### 2.4.3 Demand by End Use Sector

The end use sector wise worldwide demand as obtained from various sources is provided below in Table. Methanol demand in 2013 was around 63-65 million metric tonnes, which rose to 62-70 million metric tonnes in 2015. The demand for Formaldehyde, Acetic Acid and MTBE has been steady, while that of DME on account of it being utilized as LPG alternate and fuel has risen from 6% in 2014 to 10% in 2015. The demand for MTO, which was negligible 5-6 years back, has 10% of the market share. This is predominantly due to Chinese plans of a self reliant economy based on methanol based derivatives. The demand for biodiesel sector has been 3-4% over the last 5 years. This sector has the potential for good growth. However, the regulations as well as a strong bio-diesel based policy worldwide are a challenge.

Worldwide, Formaldehyde production is the largest consumer of Methanol with more than 27% of world methanol production at present. Demand is driven by the construction industry since Formaldehyde is used primarily to produce adhesive for the manufacture of various construction board products.

As per IHS (2014), Gasoline blending is the second largest single end-use for methanol, accounting for 14% of global demand in 2014, followed by DME with 8% share. The use of methanol for gasoline blending is also expected to rise by 12.5% in the next five years from 2014, growing from a market share of 11% in 2013 to about 14% in 2018 [29].

The demand by end use sector as per Argus Media is provided in Figure 2.12:



Figure 2.12: Global Methanol Demand by End Use Application

The end use consumption by derivative as provided by Methanex is provided in Figure 2.13



Figure 2.13: Methanol consumption by end use segment, 2015 Source: Methanex

The world methanol demand by end use sector by MMSA is provided in figure 2.14:



The methanol demand from end use sectors retrieved from various sources are provided in Table 2.19

S. No.	End Use Sector	2013	2014 <sup>(1)</sup>	2014 <sup>(2)</sup>	2015 <sup>(3)</sup>
1	Formaldehyde	32%	31%	30%	29%
2	Acetic Acid	11%	10%	10%	9%
3	МТВЕ	10%	13%	12%	10%
4	DME	11%	7%	6%	10%
5	Fuel Blending	11%	13%	12%	10%
6	МТО	2%	7%	5%	10%
7	Biodiesel	4%	3%	4%	4%
8	Others	19%	16%	2%	18%

Table 2.19: Global Methanol demand Sector wise

1. Tecnon Orbichem,

2. Methanex Corporation

3. IHS Chemical

The global demand of methanol based products by 2020 has been estimated by IHS group has been provided in Table 2.20:

S.No	End Use Application	Demand, %
1.	Formaldehyde	27
2.	МТО	18
3.	Acetic Acid	09
4.	MTBE/TAME	08
5.	MMA	02
6.	Gasoline Blending	09
7.	Biodiesel	03
8.	DME	08
9.	Methylamines	03
10.	Chloromethanes	02
11.	Solvents	04
12.	Others	07
	Source: IHS	

Table 2.20: Global Demand of Methanol by end use sector, 2020

The share of chemicals would be more than 60%, while the MTO will see substantial rise to command 18% of the market share.

Lurgi has also provided demand Figures based on ICIS, IHS and AL Intelligence for 2020. The Figure 2.15 indicates the gasoline and gasoline blend as separate entity with 13% market share. The share of olefins has been predicted as 22%.



Figure 2.15: Demand by end use, 2020, Lurgi Source: Lurgi

#### 2.5 COUNTRY SCENARIO

# 2.5.1 China

China accounts for more than half of the methanol which is produced globally. The production distribution by region is provided in Table 2.21. The share of China rose by 11% in 2015, while that of Europe decreased by 10% over the same period. The rest of Asia pacific produced similar quantities in 2014 and 2015. In 2014-15, the installed capacity in China was 62 million tonnes out of world capacity of 105 million tonnes with consumption of 40 million tonnes.

S.No	Region	2014	2015
1	Latin America	4%	4%
2	China	43%	54%
3	Asia Pacific	21%	21%
4	North America	12%	11%
5	Europe	20%	10%

Table 2.21: Region wise distribution

At present China's 65% Methanol production is based on Coal Gasification and another 15% on Refining Residue Gasification and balance 20% on Natural Gas. As per Argus Media [11], coal-based methanol will account for 80% of China's total methanol capacity by 2018. In 2015, China's methanol production capacity reached 74.54 million tons, an average annual growth rate of 13.3% over 2010. The actual production recorded in 2015 was 47.2

million tonnes with an average annual growth rate of 22.4%. The installed capacity and production of methanol in China is presented below:



Source: Derived Data, CNFIA, Methanol Institute

China's methanol consumption pattern by sector is presented in Table 2.22. The share of olefins in 2010 was only 1%, which grew to 31% in 2015. Formaldehyde share fell by 14% in 5 years, while methanol fuel consumption grew by 3% over the same five year period (2010-15)

End use	2010 (%)	2015 (%)
Formaldehyde	35	21
Methanol Fuel	16	19
Olefins	01	31
Dimethyl Ether	17	12
Acetic Acid	8	4
MTBE	6	4
DMF	14	2
Others	13	7

Table 2.22: China methanol end use sector consumption pattern

Source: CNFIA, Argus Media

The import and export of methanol is provided below in Table 2.23 for China

000 tonnes	2010	2011	2012	2013	2014	2015
Import	519.0	573.2	500.1	485.9	433.2	554
Export	1.2	4.4	6.7	77.3	74.9	16.3

Table 2.23: Import and Export of Methanol, China

Source: CNFIA (9), MMSA (13), Enerdata (14)

China's demand for methanol has been estimated to be at 86 million tonnes by 2020, while the production capacity would reach 92 million tonnes.

Table 2.24: China's Consumption and Demand of Chemicals from Methanol

S.No	Demand	2015	2020	Growth Rate
		Million	Crowin Rate	
1.	Formaldehyde	10.89	14.00	5%
2.	Methanol Fuel	10.03	18.00	12%
3.	Olefins	16.06	38.00	19%
4.	DME	6.56	6.50	
5.	Acetic acid	2.35	2.50	1%
6.	MTBE	2.00	2.50	5%
7.	DMF	0.94	1.00	1%
8.	Others	3.75	3.50	-1%
	Total	52.58	86.00	10%

Source: CNFIA [9], CPCIA [10], Argus Media [11]

Demand projections for China have also been estimated by Argus Media [11]. These are reproduced in Figure 2.17



In China, MTO capacities are to the tune of the 8 million tonnes. Among new additions, the China Coal Yulin Project involves a capacity of 3.6 million/ year tons of methanol to 120 million/ year tons of olefin. The Phase I project includes methanol (1800kta) unit, DMTO unit (600kta), and recovery unit with PE (300kta), PP (300kta), MTBE and OCU.

# 2.5.2 USA

In 2016, three methanol plants are expected to come online in the Gulf of Mexico area, with a combined capacity of almost 0.4 Billion cubic feet per day

Company	Location	Capacity	Cost, US\$ MM	Completion date
		Million tonnes per annum		
Methanex—Geismar I	Geismar, LA	1	550	Completed 2015
Methanex—Geismar II	Geismar, LA	1	550	Completed 2016
Valero	Norco, LA	1.6	700	2018
OCI (Natgasoline)	Beaumont, TX	1.75	1,000	4Q 2016
NWIW—Port of Kalama	Port of Kalama, WA	1.825	1,000	2018
NWIW—Port Westward	Port Westward, OR	1.825	1,000	2018
South Louisiana	St. James	1.825	1,300	2Q 2017

Table 2.25: US Methanol Capacities (Existing and Proposed) [27]

Methanol	Parish, LA			
Celanese/Mitsui	Clear Lake, TX	1.3	800	Completed 4Q 2015
Celanese	Bishop, TX	1.3	700-800	2018
CCI	Braithwaite, LA	1.825	1,200	2019
Yuhuang Chemical (Plant 1)	St. James Parish, LA	1.5	925	2018
Yuhuang Chemical (Plant 2)	St. James Parish, LA	1.5	925	2020
Connell Group- Chemical Inv. Corp. JV	Shoal Point, TX	7.2	4,500	2020
Total				

Source: Hydrocarbon processing, Active Methanol Projects



Figure 2.18: US Methanol Plants, 2015 Source: EIA [12]

Although most of the proposed new methanol plants are on the Gulf Coast, Northwest Innovation Works, a multinational company, is planning two methanol facilities for 2018 on the Columbia River in Washington and Oregon. The company plans to export methanol produced in the United States to a plant in Dalian, China, where it would be converted to olefins and used in manufacturing.

The methanol status regarding production and operating rates for North America reproduced from IHS is provided below in Figure 2.21. It can be observed that the domestic demand is around 5-6 million metric tonnes per annum



Figure 2.19: North America Methanol Status, Source: IHS

Similar projections are also obtained from OCI NV investor presentation, which is provided in Figure 2.20:





As per OCI NV, the U.S. imported approximately 4.8 million metric tons of Methanol in 2014.

# 2.5.3 Iran

Iran, which accounts for about 5% of the global capacity for methanol (from four plants), has plans to ramp up production using its vast natural gas reserves. Much of this additional output will find its way to export markets, including to India. The methanol capacities in Iran (planned) are provided below as given by IHS. Iran hopes to raise its methanol production capacity to 25 million tons per year in the next five years and establish itself as the biggest supplier of the product.

Kaveh Methanol Co	New Facility	2,300	Medium Term		
Marjan PC	New Facility	1,650	Medium Term		
Fanavaran PC	Expansion	1,650	Long Term		
Kharg	Expansion	1,400	Long Term		
Sabalan PC	New Facility	1,650	Long Term		
Siraf Energy Invest.	New Facility	1,650	Long Term		
Source: IHS					

Table 2.26: Methanol Capacities in Iran (000 tonnes)

The export of methanol from Iran is shown in Table 2.27. Exports to China account for 60% of the Iranian production, while that to India for 29%. Iran's current production of methanol is 6 million tonnes per annum with production capacity of 60 million tonnes in 2013.

Country	Exports (%) , 2015
China	60
India	29
Turkey	11
Italy	6
Taiwan	5
Rest of the World	5
Total	100

## Table 2.27: Iran's methanol exports, 2015

Source: Mobasherin International Middle East Co., Ltd.

# 2.6 METHANOL IN THE EUROPEAN UNION

Competitive Methanol derived from natural gas has been produced in Europe since early 1990s before China became a hub in early 2000s using cheap coal. Dominant uses of methanol in the EU are related to production of:

- 1. Formaldehyde
- 2. MTBE (Methyl t-butyl ether)
- 3. DMT (Dimethyl Terephthalate)
- 4. Methylamines
- 5. Gasoline Blending & Combustion
- 6. DME (Dimethyl ether)
- 7. Acetic Acid
- 8. Methyl Methacrylate
- 9. Methanethiol
- 10. Methyl Chloride
- 11. Biodiesel
- 12. Fuel cells

Platts provides that the total European methanol demand is more than 9 million metric tonnes per annum (2015). Current MTBE capacity in Europe totals 5.8 million metric tonnes per year.

Table 2.28: Market Share of Methanol in Europe by Region

Agency	Region	Market share of Methanol
IHS	West Europe	22%
Business wire	UK	4%

Source: IHS and Business Wire

As per OCI NV, Netherlands, Methanol consumption in Western Europe is currently more than 7 million tonnes per annum, of which more than 5 million tonnes per annum is imported. This deficit is expected to continue to increase for foreseeable future.

As per Denmark Methanol Association, in the Danish market 1.8 million m<sup>3</sup> of gasoline is consumed annually. 3% - blends corresponds to a domestic market of 54 million liters of methanol. The European market is a hundred times greater, equivalent to 5 billion liters of methanol.

The total average costs in Europe in 2013 amounted to 337 EUR/t for ammonia and 408 EUR/t for methanol.





According to a recent paper [16] published by European Commission, Joint Research Centre, Institute for Energy and Transport, (2016) costs of electricity play an important role in the European methanol industry, about 90% of the European methanol industry is located in Germany, which had the second most expensive electricity in the EU in 2013. The article further states that the European methanol industry faces stiff price competition. Therefore, there are several capacity additions and switching to bio-methanol segment.

Regulatory document	How methanol is regulated		
	- There are 33 pieces of legislation dealing with		
	methanol in wines -but they all seem only to		
33 pieces of legislation	mention methanol as a dilutant used in testing		
	methods.		

Table2.29: EU Regulations for Methanol [17]

A statement from the Economic and Social Committee on 'Research needs for a safe and sustainable energy". 2002/C 241/03. Regulation No. 231 of 9. March 2012 on specifications for food additives	<ul> <li>Examples of possible themes for future development include 'production techniques for alternative fuels (such as methanol).</li> <li>Methanol is allowed as solvent in the production of certain colorants.</li> </ul>
Regulation No. 10 of 14. January 2011 on "plastic materials and – objects destined for contact with food".	- Substances used for manufacturing of plastic materials must comply with requirements listed in Table 1. Here it is stated that methanol must not be used as additive or polymerizing agent and that migration results of methanol cannot be corrected by use of a fat-consumption-reduction-factor.
Regulation No. 110 of 15. January 2008 on "definition, description, presentation, labeling and protection of geographic indications of spirits"	<ul> <li>Wine, spirits and brandy must not exceed a maximum content of methanol of 200 g/hl alcohol (100%). Fruit spirits similar but with a limit value of 1000 g/hl alcohol (100%). Vodka similar but with a limit value of 10 g/hl alcohol (100%). Further different limit values for other types of spirits.</li> </ul>
Regulation (EC) No 1907/2006 of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH)	<ul> <li>According to REACH import into the EU or production of methanol must be registered within the REACH system – either June 1 2013 (&gt;100 tonne) or June 1 2018 (&gt; 1 tonne) depending on the tonnage of the individual companies</li> </ul>
Regulation (EC) No 1272/2008 of 16 December 2008 on classification, labeling and packaging of substances and mixtures (CLP)	<ul> <li>Describes the EU requirements for classification and labeling of methanol and chemical mixtures containing methanol.</li> <li>Annex VI describes the harmonized classification of methanol.</li> </ul>

# 2.7 GLOBAL DME MARKET

Markets and Markets [18], estimate that the global dimethyl ether market size in terms of volume to be 3,740.46 Thousand tonnes in 2014, registering a CAGR of 15.67% in between 2015 and 2020.

In terms of value, as per markets and markets report, Dimethyl Ether Market is projected to reach USD 9.7 Million in terms of value by 2020, signifying firm annualized growth of 19.65% between 2015 and 2020.

The DME global market derived from various sources is projected in Table 2.30.

Source	DME C (millio tor	Capacity n metric ines)	DME Production (million metric tonnes)		acityDME ProductionGlobal DMEnetric(million metricDemands)tonnes)		DME and	DME blend with LPG
	2007	2015	2013	2015	China	80%		
CCF Group/Aum Energy	3	14	-	-	Asia- Pacific	15%	20%	
International DME Association	-	-	3	4	Others	5%	-	

Table 2.30: DME Global Market

Source: Derived Data

Asia-Pacific is the largest market of DME, registering a significant share of 95.66% of the total market in 2014 [18]. A number of key companies operating in the DME market are based in China and these companies collectively account for a massive 85% of the global market. China accounts for 80% of the demand for DME, for LPG blending. Jiutai Energy Group (China) and China Energy Limited (Singapore) are the leading players in the Asia-Pacific market. The market patterns of DME and its various raw materials used for manufacturing are continuously witnessing an upward trend which is mainly due to the increase in the usage of DME in various applications such as LPG blending, aerosol propellant, transportation fuel and other applications. China is the leading country in Asia-Pacific and across the globe in terms of volume and value.

## 2.7.1 DME in China

DME is produced in China from methanol (coal based) via the catalytic dehydration process. In 2010, DME production capacity was around 9 million tonnes. Installed capacity of DME has been estimated to be 18 million tonnes in 2014-15. APIC 2015, estimates that in 2013, domestic demand for DME in China was 5 to 7 million metric tonnes. **The China Association of Alcohol & Ether Fuel and Automobiles [19]** estimate that in 2013, about 6.7 million tons of Methanol was used to product DME as an alternative to LPG. There are more than 60 DME manufacturing plants in operation across China.

According to Argus media, Chinese DME plants ran at 30-35% in 2014 on 13 million tonnes capacity amid weak demand and squeezed margins.

Argus media estimated that 50% of all methanol produced in China went into DME and 90% of all DME produced went into LPG blending in 2014-15. However, transparency market states that around 80% of DME went for blending in 2015 [31]. Its blend ratio in residential LPG was around 20-25% in 2013-14

In 2011, China's National Development and Reform Commission called for 20 million tonnes of DME production capacity by 2020 [30]. MMSA estimates that China's DME production would be about 8.9 million tonnes by 2020 [20]. CCF Group [21] provides the DME capacity and production in China. As per this article, DME installed capacity could be nearly 14 million tonnes in 2015 in China.





China Energy is believed to be China's largest producer of Dimethyl Ether ("DME") based on current production capacity. Using a patented proprietary DME production technology, DME production capacity is currently 900,000 metric tonnes per annum (MTPA).

The group also produces Methanol, which is used as a feedstock for in-house DME production. At present, production capacity of Methanol is 250,000 MTPA.

The various operating rates for DME plants for 2012 in China are provided in table 2.31: Table 2.31: Operating rates of DME plants in China

Local Region	Number of Plants	Capacity	Operation Rate
South China	10	1520	45%
East China	16	2200	43%
Areas around Yangtze river	14	3700	32%
Northwest	13	7230	30%
Southwest	14	2900	35%
Total	81	19650	35%

Source: Jovo Chemical Co., China; 16<sup>th</sup> IMPCA 2013 Asian Methanol Corporation

An EU report (January 2016), on alternate fuels [22] states that currently in China, a **market for DME** for vehicles has been developed, and production capacity of 13 million tons achieved. In Shanghai, a field test of 10 city buses in a commercial bus line that are running on DME is being conducted now.



Figure 2.23: DME as a fuel blend, global position Green = commercial/new commercial; Blue = Assessment Stage

## 2.7.2 Major Players in the World

Some of the major players in the world [23, 24] for DME are in China are Guangdong JOVO Group Co., Ltd, Kaiyue, Jiutai Group, Lanhua Sci-tech, Biocause Pharmaceutical, Shenhua Ningxia Coal, Yuhuang Chemical, Henan Kaixiang, Chemours (DuPont) and Grillo-Werke AG. Jiutai Energy Group (China) and China Energy Limited (Singapore) are the leading players in the Asia-Pacific market.

Other Global players are Akzo Nobel N.V. (The Netherlands), Royal Dutch Shell Plc. (The Netherlands), The Chemours Company (U.S.), China Energy Limited (Singapore), Mitsubishi Corporation (Japan), Ferrostal GmbH (Germany), Grillo Werke AG (Germany), Oberon fuels (U.S.), and Zagros Petrochemical Company (Iran).
## **CHAPTER-3**

# **METHANOL & DME UTILIZATION**

Traditionally, Methanol was utilized as raw materials for production of Formaldehyde, Acetic Acid & Acetic Anhydride etc. Methanol use in the transportation sector as a blended fuel with Gasoline has come up as an emerging sector. The conversion to Dimethyl Ether (DME) has also been reported as promising. DME has shown encouraging results when utilized as a blend for diesel substitution as well as with LPG for domestic fuel purpose.

In recent developments, methanol has found its way into Fuel Cell Technology and research work is being conducted in this respect. Methanol to "Olefins" is the latest trend in Petro-Chemical sector for the production of Polyethylene & Polypropylene.

The following sections describe the various end use sectors derived from Methanol and DME. The sections (3.1 to 3.8) describe the end use of Methanol including as a transportation fuel both on road and as marine fuel. The fuel cells based applications of Methanol with commercial success as well as Research & Development in various countries are provided. The subsequent sections provide findings of the secondary research for DME end use sectors such as those as transportation blending with diesel and use of DME as a domestic fuel.

## 3.1 CHEMICALS FROM METHANOL

Methanol is utilized for deriving several chemicals, which find applications in daily lives. At present, Methanol is majorly (60%) converted into formaldehyde, acetic acid and olefins (*Olefins (or alkenes) are mainly used in the production of polymers*) all basic chemical building blocks for a number of common products. There are a number of products that are developed from these materials. The major uses for methanol are presented in the Table 3.1. The Table presents the commercially relevant chemicals which have significant global demand at present. The versatility of methanol and its derivatives from this list indicates that many commercial pathways leading to modern-day consumer goods rely on Methanol.

Primary Derivative	Secondary Derivative	Tertiary Derivative	Quaternary
Acetic Acid	Vinyl Acetate Acetic Anhydride	Polyvinyl Acetate	Polyvinyl
(CH3COOH)	Terephthalic Acid	Cellulose Acetate(filter	Alcohol EVA
		tow) Polyesters (PET)	
Formaldehyde	Phenol Formaldehyde Resins	Polyester (PBT)	
	Urea Formaldehyde Resins	Rubber	
	Melamine Resins	(Polyisoprene)	
	Polyoxymethylene (POM or Polyacetal)		
	Polyols Butanediol		
	MDI		
	Isoprene		
	Paraformaldehyde Hexamine		
Methyl Tert-Butyl			
ether (MTBE)			
Methyl Methacrylate	Polymethylmethacrilate (PMMMA)	Chloroform (CHC13)	Carbon Tetra
	Methacrylate/Acrylate Co Polymers		chloride
Methylamines	Caffeine (stimulant diruretic)		
Monomethyamine	Sevin/Carbary//Insecticide /		
Monomethyamine	Pesticide/Herbicide Water Gel		
	Explosives Photographic Dovelopers		
	Antispasmociics		

Table 3.1: Major Uses of Methanol

Source: Lurgi Technical Brochure

**Formaldehyde** is used mainly to make amino and phenolic resins which are employed in the manufacture of wood-based products such as panels, flooring and furniture.

The main use reported for **MTBE** is as an octane booster and oxygenate in gasoline. However, it has been phased out in the US following its contamination of underground water supplies and the removal of the oxygenate mandate and liability protection.

According to market research firms, MTBE will continue to be vital for fuel quality and cleaner emissions. MTBE could make significant contribution to improve fuel quality as environmental regulations call for reducing sulphur emissions. However, the demand for MTBE would primarily from Asian countries.

The various uses of methanol and its derivates as adapted from ICIS [1] and Methanol Institute [2] are provided below:

- Methanol is used as a solvent as a component of windscreen wash antifreeze. It can also be used to extract, wash, dry and crystallise pharmaceutical and agricultural chemicals.
- Methanol has also been described (Methanol Institute) for use in waste water treatment especially denitrification. In India, this consumption sector is not yet present due to absence of regulatory mechanisms for relevant processes.
- Acetic acid is primarily utilized for manufacturing vinyl acetate monomer (VAM) and purified terephthalic acid (PTA).
- Methylamines are used as intermediates in a range of speciality chemicals with applications in water treatment chemicals, shampoos, liquid detergents and animal feeds.
- Methyl methacrylate (MMA) is employed in the production of acrylic polymers.
- Dimethyl terephthalate (DMT) is used to make polyesters although PTA is the preferred feedstock.
- Methanol and sodium chlorate are used to produce chlorine dioxide, a bleaching agent for the pulp and paper industry.
- Glycol ethers are solvents used in acrylic coatings and newer high-solids and waterborne coatings.
- Methyl mercaptan is used an intermediate in the production of DL-methionine, an amino acid supplement in animal feeds.

## 3.1.1 Methanol specification

Methanol specification for use in chemical industry is provided in Table 3.2:

ITEM	LIMIT	ANALYSIS METHOD
CAS No.	67-56-1	
U.N.No.	1230	
Appearance	Clear and free of suspended matter	IMPCA 003-98
Purity % W/T on dry basis	min. 99.85	IMPCA 001-02
Colour Pt-Co	max. 5	ASTM D 1209-05
Water % W/W	max. 0.1	ASTM E 1064-05
Distillation range at 760 mm Hg	max. $1.0^{\circ}$ C to include $64.6^{\circ}$ C ± $0.1^{\circ}$ C	ASTM D 1078-05
Specific Gravity 20°C / 20°C	0.791 - 0.793	ASTM D 4052-02
Potassium Permanganate time test 15°C minutes	min. 60	ASTM D 1363-06

Table 3.2: Methanol Specifications

Carbonizable substances (Sulphuric Acid Wash Test), Pt-Co scale	max. 30	ASTM E 346-03
Ethanol mg/kg	max. 50	IMPCA 001-02
Chloride as CI mg/kg	max. 0.5	IMPCA 002-98
Sulphur mg/kg	max. 0.5	ASTM D 3961-98
Hydrocarbons	pass test	ASTM D 1722-04
Carbonilic Compound as Acetone mg/kg	max. 30	ASTM E 346-94
Acidity as Acetic Acid mg/kg	max. 30	ASTM D 1613-06
Total Iron mg/kg	max. 0.1	ASTM E 394-04
Non volatile matter mg/1,000 ml	max. 8	ASTM D 1353-03

Source: GNFC: Product specification

Market scenario of Formaldehyde and Acetic Acid are discussed in sections 3.2 and 3.3 respectively.

## 3.2 FORMALDEHYDE

Formaldehyde applications [3, 4] include direct use, manufacture of resins and as intermediate for synthesizing other chemicals as provided below.

- As Resins: Phenol Formaldehyde (PF), Urea Formaldehyde (UF) and Melamine Formaldehyde (MF) which finds applications in laminates, plywood, MDF, particle board and hard boards.
- As an Intermediate: Formaldehyde is also used for synthesizing chemicals like: Pentaerythritol, Hexamine, Para formaldehyde, 1,4-Butanediol, etc.
- Direct Use: Formaldehyde is also used directly for the following:
  - Mirror finishing and electroplating
  - Preservation and disinfection
  - Film development in photography industry



Fig 3.1: End use share for Formaldehyde, 2015 [5]

## 3.2.1 Technology

Though, there are several routes to manufacture formaldehyde, only routes based on catalytic oxidation of methanol are being employed today. Today, all of the world's commercial formaldehyde is manufactured from methanol and air using either a silver catalyst or a metal oxide catalyst. Silver catalyst process combines dehydrogenation and oxidation to obtain formaldehyde, while metal oxide process employs an oxide catalyst for a direct oxidation route to formaldehyde.

## 3.2.2 Indian Scenario

The formaldehyde industry started in India in early 1960s. Presently, there are about 25 formaldehyde plants having total installed capacity of about 413,000 tonnes per annum.

Table 3.3: Production, Consumption, Import and Export of Formaldehyde (000'MT)

a. Product-wise Installed Capacity & Production of Formaldehyde (in Thousand MT)

2014-15
255.95

Source: Ministry of Chemicals and Petroleum, Statistics, 2015

b.	Consumption of	Formaldehyde	(Product-wise)	) during 200 <sup>-</sup>	7-08 to 2014-15
----	----------------	--------------	----------------	---------------------------	-----------------

Year	2007-08	2008-09	2009-10	2010-11	2011-12	2012-13	2013-14	2014-15
Quantity	237.49	229.13	258.01	262.94	259.94	270.66	262.35	248.89

Source: Ministry of Chemicals and Petroleum, Statistics, 2015

Year	2007-08	2008-09	2009-10	2010-11	2011-12	2012-13	2013-14	2014-15
Imports	0.439	0.545	0.713	0.605	0.614	0.342	0.433	0.412
Exports	5.710	3.256	3.995	4.275	4.474	5.041	6.369	7.467

~	Importo and Ex	norte of Cormoldob	vda during 2007 0	0 to 2014 15
<b>.</b>	mpons and Ex	יאטונא טו רטווומועפוו	yue uuring 2007-0	0 10 20 14-15

Source: Ministry of Chemicals and Petroleum, Statistic, 2015

At present silver process is predominant in the Indian formaldehyde industry. About 72% of the total capacity is based on silver process. Metal oxide process has been introduced in the country by mid- 1980s and is found to be gaining acceptance.

Growth rate of the formaldehyde industry is found to be about 5% to 6% per year. The major producers of Formaldehyde are M/s. Kanoria Chemicals, Ankleshwar and M/s. Simalin Chemicals, Vadodara. The present consumption of Methanol in Formaldehyde & Plywood Industry is nearly around 700,000 tonnes. The specification of Formaldehyde available in the Country is as under:

S. No.	Property	Value
1	Colour	Clear
2	Appearance	Liquid
3	Purity	37% (+/-0.5%)
4	Specific Gravity	1.098 - 1.114
5	Methanol	2.0% to 3.0%
6	Acidity	0.05% (Max)
7	Iron	10 PPM (Max)
8	PH (AQUEOUS SOLN)	2.8 TO 4.0
9	Ash Content	0.01% (Max)
10	Flammability	Combustible
11	Molecular Weight	30.03

Table 3.4: Specification for Formaldehyde (37%)

Source: GNFC: Product specification

## 3.2.4 Projected Demand

This sector has seen negative growth, four times since 2008-09. The consumption of formaldehyde in the country has been declining for the past two years (2014 and 2013) due to a slump in the construction industry. The import too declined by a little under 5% in 2014-15. However, the exports trend portrays positive growth of an average 18% over past three years since 2012-13.

	2008-09	2009-10	2010-11	2011-12	2012-13	2013-14	2014-15
consumption	-3.52	12.60	1.91	-1.14	4.12	-3.07	-5.13
import	24.15	30.83	-15.15	1.49	-44.30	26.61	-4.85
export	-42.98	22.70	7.01	4.65	12.67	26.34	17.24

Table 3.5: Growth Rate of Formaldehyde in India

Source: Derived from Annual Report and Chemical Statistics, Ministry of Chemicals and Petrochemicals

The demand of formaldehyde in the country assuming 1% growth rate for the next 10 years is provided in Table 3.6 based on present consumption. The estimated demand by 2025 of formaldehyde should be 275,000 metric tonnes per annum. Alternately, the sector could also grow at 5% due to the revival of the construction industry in the next few years. The demand considering high growth rate has been estimated to be 405,000 tonnes in 2025.

Table 3.6: Estimated Future Demand of Formaldehyde in India

Year	2015-16	2016-17	2017-18	2018-19	2019-20	2020-21	2021-22	2022-23	2023-24	2024-25	
Quantity	251.38	253.89	256.43	259.00	261.59	264.20	266.84	269.51	272.21	274.93	
	Source: derived from Annual Benert, Ministry of Chamicale and Betrachemicals										

#### Source: derived from Annual Report, Ministry of Chemicals and Petrochemicals

## 3.2.3 International Scenario

The global consumption of Formaldehyde in 2014 has been reported to be around 20.5 million tonnes [6]. Global production in 2014 was around 45 million tonnes, while installed capacity was around 50 million tonnes.

According to Formox [7], Global formaldehyde growth is projected to exceed 4% annually and demand is expected to grow from 46 to 58 million tons by the end of 2020.

Urea-, phenol-, and melamine-formaldehyde resins (UF, PF, and MF resins) account for approximately 70% of world demand for formaldehyde in 2015 [8].

The wood segment is expected to grow and the global formaldehyde demand within the segment will rise from 25 million tons to more than 30 million by the end of 2020.

Technavio's [9] market research analysts have estimated the global formaldehyde market to grow steadily at a moderate CAGR of more than 5% over 2016-2020.

The construction segment has led the global formaldehyde market and is expected to reach more than 32 million tons by 2020.

According to IHS market [10], Northeast Asia, especially China, continues to add capacity for formaldehyde, reigning as the largest producer globally. China has been stated to be the single-largest market for formaldehyde, accounting for 42% of world demand in 2015.

According to Technavio's market research, currently (2015), the APAC region accounts for around 62% of the overall market share and dominate the global formaldehyde market.

In the EU approximately 10 million tonnes are produced per year, worldwide around 47 million tonnes. By 2017 it is expected that the global annual production will reach 52 million tonnes [11].



Source: (5)

Between 2010 and 2015, world capacity for 37% formaldehyde grew at an average annual rate of about 3%, slightly behind world consumption, which grew at an average annual rate of 4.4% during the same period.



Source: [5]

It can be observed from the above Table that Asia and North America constitutes 90% of the global consumption of Formaldehyde in the world.

## 3.3 ACETIC ACID

Acetic Acid among organic compound is familiar to mankind since it has been used as vinegar for a long time. Over the years Acetic acid has become an important chemical with application in several downstream industries like Textiles & Packaging Industry, Paints, Adhesives & Pharmaceuticals etc.

## 3.3.1 Status of Indian Industry

Prior to globalization, there were around two-dozen units in the country engaged in the production of acetic acid. Of these, except one, all were making acetic acid from the ethanol oxidation route. The total installed capacity in 1995-96 was 2.10 lakhs tonnes.

Gujarat was leading, with a share of 37% in total capacity, followed by Maharashtra (33%) and Uttar Pradesh (24%). However, after globalization and the entry of methanol based acetic acid by Gujarat Narmada Valley Fertilizers Corporation (GNFC) in September 1995, with technical know-how from BP Chemicals (UK), a number of units had to close down as they were not able to compete imports and methanol based production. GNFC, to date, is the only unit in India making methanol based acetic acid, and was the largest producer with capacity of 50,000 TPA, constituting 24% of the total installed capacity, during 1998-99. GNFC has further expanded its capacity to 100,000 TPA and its production has reached 150,000 TPA at present.

The installed capacity of acetic acid was 177.43 thousand tonnes in 2014-15. The demand growth has happened mainly due to increase usage by manufacturers of PTA and organic esters such as RIL and Vinyl chemicals. New PTA capacities added by Indian Organic Chemicals (IOC) (0.55 million tonnes per annum) and RIL (0.53 million tonnes per annum) in the recent past have spurred demand growth further.

Table 3.7a: Production, Consumption, Import and Export of Acetic Acid (000'MT)

	Installed Capacity					Productior	1	
Year	2012-13	2013-14	2014-15	2010-11	2011-12	2012-13	2013-14	2014-15
Quantity	192.28	192.28	177.43	156.48	160.73	160.56	157.17	159.61

Installed Capacity & Production of Acetic Acid (in Thousand MT)

\*(Sources: Annual Report 2014-15, Ministry of Chemicals & Petrochemicals; Ministry of Commerce Import Export Databank) b. Consumption of Acetic Acid (Product-wise) during 2007-08 to 2014-15

Year	2008-09	2009-10	2010-11	2011-12	2012-13	2013-14	2014-15
Quantity	486.49	523.07	614.21	704.88	800.68	814.63	865.50
Growth rate %	5.03	7.52	17.42	14.76	13.59	1.74	6.24

c. Import of Acetic Acid during 2007-08 to 2014-15

Year	2008-09	2009-10	2010-11	2011-12	2012-13	2013-14	2014-15
Quantity	285.037	389.65	466.097	570.04	646.738	664.797	712.384
Growth rate %	108.94	36.70	19.62	22.30	13.45	2.79	7.16

#### d. Exports of Acetic Acid during 2007-08 to 2014-15

Year	2008-09	2009-10	2010-11	2011-12	2012-13	2013-14	2014-15
Quantity	12.589	13.022	8.368	25.887	6.617	7.338	6.489
Growth rate %	-16.30	3.44	-35.74	209.36	-74.44	10.90	-11.57

\*(Sources: Annual Report 2014-15, Ministry of Chemicals & Petrochemicals; Ministry of Commerce Import Export Databank)

## 3.3.2 Current Domestic Demand

Acetic acid finds application in wide spectrum of end-uses. However, major applications in India are:

- Acetic anhydride;
- Vinyl acetate monomer;
- Purified terephthalic acid;
- Organic esters such as ethyl and butyl acetate;
- Diketene derivatives;
- Monochloroacetic acid;
- Camphor;
- Pharmaceuticals;
- Textiles;
- Others including rubber, pigments, pesticides, paper, leather, photographic chemicals etc.

As can be observed from following Table 3.7c, imports of acetic acid have been increasing since 2005-06. They increased from over 43,119 tonnes in 2005-06 to nearly 705,890 tonnes in 2014-15. Majority of it has been coming from the US, UK, France, South Korea and Singapore. The import jumped by nearly 6 times.

#### 3.3.3 Domestic Projected Demand

As far as future demand for acetic acid is concerned, the major factor influencing the demand would be the development in the Purified Terephthalic Acid (PTA) industry, which in turn depends on the polyester industry.

Reliance, Mitsubishi (MCCPTA India) and IOC are the only producers of PTA with combined capacity of 3.07-mtpa. However, considering the prospects of the polyester industry in Indian and the global scenario of PTA, further expansion in capacities is likely to take place here in India.

RIL has a total PTA capacity of 4.2 million tonnes per year. In India, the current total PTA capacity, including that of RIL, is 6 million tonnes. Another 1.2 million tonnes of PTA capacity will be added in the current year (2016) itself. However, the total PTA demand in India is around 5 million tonnes (2015-16).

The other major drivers for acetic acid demand would be growth in the organic esters, particularly ethyl acetate and pharmaceuticals segment that are enjoying good growth. The other segments like MCA, VAM, etc. are mature and not much growth is expected from these areas. Ethyl acetate is used in a variety of coating formulations such as epoxies, urethanes, cellulosic's, acrylics and vinyls. Applications for these coatings are numerous, including wood furniture and fixtures, agricultural, construction and mining equipment, auto refinishing, and maintenance and marine uses.

	2008-09	2009-10	2010-11	2011-12	2012-13	2013-14	2014-15
Consumption	5.03	7.52	17.42	14.76	13.59	1.74	6.24
Imports	108.94	36.70	19.62	22.30	13.45	2.79	7.16
Exports	-16.30	3.44	-35.74	209.36	-74.44	10.90	-11.57

Table 3.8: Growth Rate of Acetic Acid (during 2007-08 to 2014-15)

Source: Derived from Annual report, Ministry of Chemicals and Petrochemicals

The acetic acid exports in 2014-15 saw a decline of 11.57% over 2013-14, while the consumption and imports grew at 6.24% and 7.16% respectively over the same period. The consumption has seen a CAGR of 10.75% over 5 year's period. The consumption has risen on an average of 10% over the past 7 years.

Ethyl acetate is also used as a solvent in inks for flexographic and rotogravure printing, where its main function is to dissolve the resin, controls the viscosity and modifies the drying

rate. It is also used as an extraction solvent in the production of pharmaceuticals and food, and as a carrier solvent for herbicides. High purity product can be used as a viscosity reducer for resins used in photo resist formulations in the electronics industry.

Paint, inks and adhesives together constitute 31% of the total consumption; flexible packaging and aluminum foils together constitute 34% and pharmaceuticals industry 18% and the balance 17% is shared between chemical intermediates, electronics and miscellaneous uses. While the paint industry in India is expected to grow at around 8 to 10% in the next few years, flexible packaging industry is expected to grow at over 15% per annum.

Table 3.9: Demand of Acetic Acid (000 MT)

865.5 952.05 1047.26 1151.98 1267.18 1393.90 1533.29 1686.61 1855.28 2040.8	2014-15	2015-16	2016-17	2017-18	2018-19	2019-20	2020-21	2021-22	2022-23	2023-24	2024-25
	865.5	952.05	1047.26	1151.98	1267.18	1393.90	1533.29	1686.61	1855.28	2040.80	2244.88

Source: Derived from Annual report, Ministry of Chemicals and Petrochemicals

The overall demand for acetic acid is expected to grow at around 10% per annum in the next 10 years. Accordingly, the demand is projected to be around 2.2 million tonnes by the year 2025. Looking at the tremendous scope in this field, Assam Petrochemicals Ltd. is setting up a 200 TPD Acetic Acid plant in Namrup district of Assam. Indian Oil Corporation is planning to set up a 1 million tonnes per annum Acetic Acid plant at its Vadodara Refinery under 50:50 joint venture with B. P. Chemicals, UK.

## 3.3.4 Acetic Acid-International Scenario

The global Acetic Acid market was estimated 12.9 million tonnes in 2014 with following break-up.

End Use of Acetic Acid	Consumption (%)
VAM (Vinyl Acetate Monomer)	32%
PTA (Purified Terephthalic Acid)	20%
Acetic Anhydride	13%
Ethyl Acetate	13%
Butyl Acetate	7%
MCAA (Monochloroacetic Acid)	6%
Others	9%

Table 3.10: World Acetic Acid Consumption by end use in 2014

Source: Techno Orbichem

Acetic acid is the main feedstock to manufacture vinyl acetate monomer, which was at the forefront in terms of volumetric consumption.

It is mainly driven by the growing demand of polyvinyl acetates and vinyl alcohols, which in turn are accelerating the demand for acetic acid. The demand from PTA manufacturing segment is estimated to grow at a very high pace, next only to Ester Solvents, which is the strongest growth segment of Acetic Acid. According to markets and markets research [12], The growing Textile & Packaging Industry is the key driver behind strong growth of PTA; while budding coatings consumption is pushing the demand of Ester Solvents at a noTable pace.

In addition, polyester is also being increasingly employed for manufacturing textiles owing to its lightweight, breathability and durability. Acetate esters applications are expected to witness above average growth over the forecast period. Increasing demand for low-cost solvents and diluents in food & beverage industry is expected to drive acetate esters demand.

Vinyl acetate monomer (VAM) was the largest application segment of the market accounting for over 25% of the market volume share in 2014 [13]. Increasing demand for VAM is expected to drive global acetic acid industry over the next seven years. However, PTA is projected to witness the fastest growth due to an increasing demand for polyethylene terephthalate (PET) in bottle and textile applications. Increasing demand for PET bottles owing to their light weight, recyclability, ability to mold them into different shapes and sizes and excellent aesthetics is expected to drive PTA demand.

Vinyl acetate monomer (VAM) is the largest end use for acetic acid in China, the United States, Western Europe and Japan. VAM is used in Polymer manufacture for Adhesives & Coatings. Approximately 32% for VAM, 20% for PTA, 13% Ethyl Acetate, 13% Anhydride, 7% Butyl Acetate & 9% others are the Global statistics.

China is the largest producer of acetic acid holding a production share of over 40% in terms of volume [13]. China acetic acid market was largest in the same year with limited exports of the organic compound from the country owing to high domestic demand. The presence of a robust manufacturing base on a large scale has resulted in high demand for the chemical. China is anticipated to dominate the global demand over the forecast period owing to rapid industrialization in the country over the next several years.

North America and Europe are expected to witness below average growth for the compound owing to the high trend among manufacturers to shift their production bases to low-cost economies of Asia Pacific. Latin America and MEA are the average growth market with numerous countries in the region primarily exporting the compound.

China, United States with rest of Asia & Europe account for the majority of the Acetic Acid market. Of total Global acetic acid capacity 43% is in China, followed by 23% in rest of Asia, 22% in United States, 6% Western Europe, 2% Eastern Europe and 4% in Africa.

The Asia – Pacific region is the most promising chemical market and is expected to be the same in the near future too. Asia-Pacific is the World's largest market of Acetic acid, which consumes more than half of the total global demand in 2012, and also for most of its applications that include Vinyl Acetate Monomer, Purified Terephthalic Acid (PTA), Acetic Anhydride, Ester Solvents – Ethyl Acetate & Butyl Acetate. The demand for acetic acid in the region is anticipated to grow at a CAGR of about 5.01% from 2013 to 2018. It is estimated that China & Taiwan are the biggest consumers of acetic acid in the region, followed by Japan in 2012.

COUNTRY	PRODUCTION (%)	CONSUMPTION (%)
CHINA	43%	42%
USA	22%	19%
NE - ASIA	15%	13%
S & SE ASIA	8%	12%
WESTERN EUROPE	6%	10%
EASTERN EUROPE	2%	1%
AFRICA	4%	3%

Table 3.11: World Acetic Acid Consumption by country/region in 2014

Source: Techno Orbichem

Asia-Pacific was the second-largest market for acetic acid, with India and Japan dominating the regional market. The acetic acid market in Asia is projected to grow at a CAGR of over 10 percent over the forecast period and is estimated to reach a value of over \$3.0 billion by 2022.

PTA is expected to be the fastest-growing application segment within the global acetic acid market, owing to the increasing demand for polyester from the textile and packaging end-use industries. Global acetic acid demand for PTA exceeded 2,500 kilo tons in 2014 [14] and is expected to be over 3,800 kilo tons by 2020, growing at a CAGR of over 5 percent from 2015 and 2022.

## 3.4 METHANOL TO OLEFINS

Methanol is used as a feedstock for the production of polyethylene and propylene. This segment is called Methanol to Olefins (MTO). MTO is an alternative process to Naptha cracking for olefins production (plastics).



Figure 3.4: Methanol to Olefins Route

As per OCI NV [15], there are a total of twelve completed MTO/MTP plants with a consumption of 6.5 million metric tons of methanol in China. An additional four MTO Plants are planned to be completed in 2016 which are expected to add an additional 6.5 million metric tons of methanol demand. Methanex (16) provides that there are thirteen plants with 12.6 million tonnes capacity which are completed and four plants with a capacity of 6.6 million tonnes are in pipeline as on 2016. As per Methanex, methanol demand from MTO is poised to grow upon olefin price recovery.

Table 3.12: MTO	plants in China
-----------------	-----------------

	Number of plants	Capacity (million tonnes)			
Completed	13	12.6			
2016	4	6.6			
Total	17	19.2			
Source: Methanex					

MTO (methanol-to-olefins) in China is a strong driver of demand growth and it accounted for almost 18% of demand in 2015

## 3.5 METHANOL AS TRANSPORTATION FUEL

Methanol was introduced commercially in the 1980s following crude price variations in 1970. The carbureted fuel systems, prevalent in the vehicle fleets on the road at that time, had limited ability to handle high oxygen levels in the fuel. Hence, methanol blends limited to 3 to 5 volume percent of the gasoline blend. However, with today's modern pressurized fuel injector systems with computerized feedback control loops, current experience shows that methanol blends as high as 15 volume percent (M15) of the gasoline can now be successfully used in the more modern vehicles that are on the road today.

AFDC, US [16] states that Methanol was marketed in the 1990s as an alternative fuel for compatible vehicles. The report states that 6 million gasoline gallon equivalents of 100% methanol and 85% methanol/15% gasoline blends were used annually in alternative fuel vehicles in the United States during the peak years.

According to Methanol Institute, out of the ~64 million metric tons (80 billion liters) of methanol sold globally in 2014, energy and fuel uses represent ~40% of total demand in the following end use sectors.

• MTBE • TAME • Low blends • High blends • Biodiesel • DME • MTG/MTO • Diesel blends • Fuel cells

From 2009-2014, direct methanol fuel blending has increased at an annual rate of nearly 23%. In 2014, China used ~7 million metric tonnes of methanol in existing vehicle fleets (i.e., M15).

A research in MIT Energy Initiative [17], concluded that Methanol a viable transportation fuel. The team did extensive testing with a four-cylinder engine completely powered by pure methanol – M100. The research was undertaken for one year with the following conclusions:

- Lower combustion temperatures
- Faster flame speeds
- Higher Octane

Demand of Methanol is transportation fuels world wide as provided by Methanol Institute are provided below:

- Blended (3% to 100%) 8 million tonnes
- DME 4.7 million tonnes
- Biodiesel 1.3 million tonnes
- <u>Total Demand 14 million tonnes</u>

Higher blends containing 85 vol-% methanol and 15 vol-% gasoline (M85), can be used only in special Flexible Fuel Vehicles (FFVs), which were actually first developed for methanol and later on optimized for ethanol.

## **3.5.1 Fuel Properties**

The fuel properties of methanol are provided in Table 3.12, compared to ethanol and gasoline. Methanol has the highest oxygen content with the lowest air to fuel ratio.

	METHANOL	ETHANOL	GASOLINE
Molecular Formula	СНЗОН	C2H5OH	C4 - C12
Molecular Weight	32	46	95 - 120
Oxygen Content (%)	50%	34.80%	0
Density (kg/m3)	792	785	740
LHV (MJ/kg)	20	26.9	44.3
Octane number	111	108	> 90
Auto-ignition temp. (*C)	465	425	228 - 470
Stoichiometric A/F ratio	6.47	9	14.8
Latent heat of vapour. (kJ/kg)	1103	840	305
Boiling point (*C)	64	78	38 - 204

Table 3.13: Fuel Properties of Methanol

## 3.5.2 Methanol as Alternate Fuel:

The timeline for methanol as an inland transportation fuel in the United States of America, European Union and China are provided in Table 3.14 [18]. It can be observed from the Table that Germany had also introduced methanol blend as early as 1960s

Time Frame	Methanol Fuel Intervention				
	118				
	0.0.				
1980-1990	California experimental program 85% methanol with 15% additives of choice (M85)				
1993	Over 12 million gallons of methanol were used as a transportation fuel.				
1997	M85 FFV vehicles, 21,000 in number 15,000 in California, 100 public and private refueling stations.				
2005	Ethanol displaced methanol in the U.S. California stopped the use of methanol after 25 years and 200,000,000 miles of operation.				

Table 3.14: Methanol Fuel Timeline in US, EU and China

2007	First time Methanol blended with Ethanol in 2007. From 1996-2006 pure methanol
	was used by the IRL.
	European Union
1960-1970	First introduced in the Federal Republic of Germany in the late 60's, with
	composition slightly lower than those allowed in the US by the EPA (4% methanol
	and cosolvent, vs. 5.5% in the US), but reaching general use by the late 70's.
1980	The use of light methanol blends spread through Europe during the 1980s and
	through much of the 1990s
1980-82	In Sweden, a large M15 fuel testing project was done with 1000 vehicles at 19 fuel
	stations and 11 car makes with 20 million km of driving. As neat fuel M100 was
	tested 1984-86 by SAAB-Scania and Volvo with 20 vehicles.
1988	An agreement was reached to set minimum allowable methanol concentration in
	gasoline in 1988 through member countries of the European Economic Community
	(which eventually became the European Union), along with a maximum level of
	methanol blends,
2004	In 2004 a European standard increases the amount of methanol in gasoline to
	comparable levels of those by the US EPA, 3% methanol, to be mixed with a
	cosolvent.
2007	In 2007, a proposal was introduced for the increased use of biofuels to decrease
	the green house emissions of transportation fuels by 1% per year from 2011 to
	2020.
2008	The amendment approved in 2008 replaces the BioFuel Directive with a Directive
	on the promotion of Renewable Energy Sources. The new Directive requires that
	the emissions of green house gases decrease by 10% by 2020.
	CHINA
2003	M15 introduction in 2003 was limited to four cities.
2007	By 2007 it had spread to all 11 cities across the province 130,000 tons (40 million
	gallons) of methanol used officially as fuels, mostly as M15 blends. Natural gas
	contributed about 15% of the methanol production in China
2007	In 2007 there were 40 regional standards in 5 provinces, with 17 of these in
	practice, including low methanol blends
2007	There were more than 770 methanol refill stations, 17 with M85, mostly not
	associated with the two top oil companies.
2007	In 2007, official consumption rate of M15 was 530,000 tons (180 million gallons),

	with over 40 million refueling operations.
	There were over 2000 taxis in Shanxi operating on M100 from a limited number of private refueling stations.
	In addition to light duty vehicles, by 2007 there were 260 buses, with 100 running on M100
2008	Additional 4 Regional Standards were published in Shanxi province alone in 2008.
2009	The Central Government finally acted in late 2009, publishing a National Standard for the use high blends (M85) of methanol.
2010	China is in the final stages of reviewing a national standard for M15 (October 2010). This work included a 70,000 kilometer road test on M15 blends.
2010	The 2010 estimated amounts of methanol consumption in China transportation sector are very large, between 4.5 and 7 million tons of methanol (about 1.5-2 billion gallons).
2010	The development plan for coal chemical in China projects that in 2010 coal would be the feedstock of choice for methanol production, with an estimated 80% market share, expected to grow to 90% by 2015.

## 3.5.3 Salient Features:

The salient features and outcomes of various projects [18] which ran methanol as a fuel in cars in the respective regions during the above timelines are as follows:

## U.S.A:

- 1. There were ten automobile manufacturers, 16 different models, 900 vehicles (light to heavy vehicles). DOE operated 40 Nos. vehicles from 1986-91
- 1. The fuel economy was lower because of the lower energy density of methanol.
- 2. The fuel efficiency of the vehicles was comparable to that of the baseline gasoline vehicles.
- 3. Increased aging of the performance of the emission catalyst in those vehicles operating in M85.
- 4. Methanol emissions are less reactive in terms of ozone formation potential. Acceleration from 0 to 100 km/hr was 1 second faster than the original vehicle.
- 5. The failure of methanol in US as transportation fuel due to no economic incentive at that period.
- 6. Little advocacy for that as a pathway towards replacing petroleum fuel with renewable.

7. FFVs have demonstrated that it is a viable fuel and technology exists for both vehicle application and fuel distribution.

## **European Union:**

- 1. Methanol first introduced in the Federal Republic of Germany in the late 60's, with composition slightly lower than those allowed in the US by the EPA (4% methanol and co-solvent, vs. 5.5% in the US),
- 2. One of the countries that allowed the use of the higher methanol blends was France,
- 3. In Sweden there was an oxygenate requirement that specified a maximum blending of methanol of 2%. (SMFT).
- 4. The Main results obtained from Swedish runs were the methanol cars provided the same or better performance than for petrol in terms of engine performance, fuel handling and distribution [106, 107].
- 5. The European interest in Alternative Fuels is driven mostly by desire to curtail CO2 emissions.
- 6. In 2007, a proposal was introduced for the increased use of biofuels to decrease the green house emissions of transportation fuels by 1% per year from 2011 to 2020.
- The new Directive requires that the emissions of green house gases decrease by 10% by 2020.
- At present European Community is having discussion on issues of Indirect Land Use Change (ILUC), and its contribution to green house gases, as the reduction in greenhouse gases is determined by life-cycle analysis.
- 9. Substantial efforts in Scandinavia for the production of biofuels.
- 10. In Sweden, Värmlands Metanol AB is building a biomass-to-methanol plant, with an annual production of 100,000 tons (30 million gallons) of fuel-grade methanol from forest-residue biomass.

Overall, U.S. manufacturers (General Motors, Ford and Chrysler), Asian companies Honda, Toyota, Nissan, Mazda, Mitsubishi, Subaru, Suzuki (Japan) and Hyundai (Korea), and European companies Audi, Volkswagen, Mercedes-Benz, Porsche (Germany), SAAB and Volvo (Sweden) all developed and tested methanol based vehicles during 1990s [103].

A survey released by the National Association for Fleet Administrators Inc. (NAFA) revealed that out of the 79 responding fleet managers who were responsible for about 85 percent of methanol-powered FFVs that were on the road in California at the end of 1992, a total of 73 percent of the fleet managers were "equally satisfied" with methanol FFVs when compared

to gasoline-only vehicles, and a total of seven percent said they were "more satisfied" with FFVs. Only 20 percent were "less satisfied" with FFVs compared to gasoline vehicles [104].

The major modifications [105] carried out for running methanol gasoline blend vehicle were

- 1. Larger gas tank and corrosion resistant (stainless steel) fuel system components
- Capacitive sensor which detected the type and mix of fuels being fed to the cylinders. The engine computer then adjusted ignition and injection programs to optimize combustion.
- 3. Tin and nickel plating of fuel lines,
- 4. Installation of methanol-resistant rubber and plastics,
- 5. Use of steel alloys for valves and seats, and installation of high-volume injectors.
- 6. Modified injectors for increased fuel flow, and a methanol percentage gauge
- 7. Special methanol compatible motor oil is also used.

#### China:

- 1. China is currently the largest user of methanol for transportation vehicles in the world.
- 2. In 2007 natural gas contributed about 15% of the methanol production in China.
- 3. In 2010 coal would be the feedstock of choice for methanol production, with an estimated 80% market share, expected to grow to 90% by 2015.
- 4. Several companies have set up methanol gasoline blending centers, with a total capacity of 600,000 tons/yr (200 million gallons).
- 5. As retail pricing controlled by the central government, there is a significant incentive for private retailers to identify lower costs wholesale fuel additives.
- 6. The methanol gasoline is very popular among taxi drivers, as the drivers can save about Yuan 600 per month on the price differential between M15 and gasoline.
- 7. In 2007, official consumption rate of M15 was 530,000 tons (180 million gallons), with over 40 million refueling operations.
- 8. Most of the methanol used in China is illegal blended with gasoline based simply on methanol's favorable economics.
- China is carrying out a larger uncontrolled study of methanol use in transportation. Estimated amounts of methanol consumption in China transportation sector on 2010 were very large, between 4.5 and 7 million tons (about 1.5-2 billion gallons).

As per the China Association of Alcohol & Ether Clean Fuel and Automobiles (CAAEFA), in China [19] the research, test and demonstration of methanol fuel for vehicle was carried out from 1981 to 2005 with Sino-US and Sino-German co-operations. The process was basically consistent with foreign countries and included the following:

- R & D of low proportion methanol blending technology,
- R & D of high proportion methanol fuel engine and vehicle technology
- Researches on related objects.
- Demonstration operation.

As per Chinese research outcomes, low proportion methanol use in vehicle can fit well and there is no need to change the car. In this case, M15 is most commonly used. High proportion of methanol fuel is used on special vehicle. The car should adapt to fuel. The advantages are better economy, stronger adaptability, better efficiency and improved emissions.

The Chinese experiences with methanol also provide the following solutions for existing challenges dealing with methanol as a fuel for cars and trucks.

Challenges	Prospective Solution
lubrication, corrosion, swelling, cleaning, safety	additives
cold start, combustion control, emission control, swelling and	developing of engine and
corrosion	vehicle
water control, using alcohol-resistant materials, quality and safety	Infrastructure improvement
On the Design OAAFEA OA	*

Table 3.15: Challenges & Prospective Solution

Source: Derived Data from CAAEFA, China

Utilizing various blends of methanol, more than 800 trucks and more than 1500 intercity bus have been put into operation in China.

In China as per several industry sources, there are 12 automobile enterprises which have carried out the methanol engine and vehicle development. The M100 and M85 blends are used as methanol utility vehicles, Flexible fuel utility vehicles, Methanol / diesel dual fuel commercial vehicle, M100 gasoline engine commercial vehicle and M100 diesel engine commercial vehicle with 36 standards promulgated in 16 provinces and municipalities.

The IEA, Advanced Motor Fuel Division [20] reports that in China, methanol is used as a motor fuel in various blends ranging from 5% methanol in gasoline (M5) to 100% methanol (M100). Methanol accounts for 7-8% of China's transportation fuel pool.

Methanol-blended fuels are explored also by other countries, such us Israel, Australia, Sweden, Poland, United Kingdom, Iceland, Netherlands, Trinidad and Tobago, Iran, Pakistan, Vietnam, Azerbaijan, and Uzbekistan. In some markets, the focus is on blends of gasoline, ethanol and methanol (GEM). In this concept, ethanol is serving as a co-solvent for methanol.

Volvo has carried out successful tests with DME as a trucking fuel. In Sweden, 10 trucks were run with an average run of 380,000 km per truck on Bio-DME produced from biomass.

## 3.5.4 VEHICLE EMISSIONS

Recently Ashraf Elfasakhany [21] conducted a study on the effects of Ethanol-Methanol-Gasoline Blend in a spark ignition engine and it was observed that ethanol + methanol +gasoline blend (EM) burnt cleaner than both Methanol-Gasoline Blend (E) & the neat Gasoline Fuel (G). However, in methanol + gasoline blend (M) confirmed the lowest emission of CO & UHC (Unburnt Hydrocarbon) among all test fuel. Blended fuels are recommended to be used at all engine speed but especially at high vehicle speed (more than 3000 RPM). Results are tabulated in Table-3.17.

The results demonstrated that if we intend to get fewer emissions of CO & UHC and higher volumetric efficiency and output torque from SI engine, we should use methanol as fuel.

Compared to gasoline, methanol emits less nitrogen oxides and other volatile, harmful organic compounds that form smog or ozone when burned as fuel. This is due to the fact that methanol is much less reactive than gasoline in the atmosphere, with the only toxic component of the emissions being formaldehyde, as compared to dozens of carcinogenic components of gasoline emissions including formaldehyde.

The use of heated catalytic converters has shown that methanol-fueled auto emissions meet and exceed California's stringent Ultra Low Emission Vehicle (ULEV) emission targets for formaldehyde. Methanol fuel also does not contain the toxic BTEX (benzene, toluene, ethylbenzene, and xylenes) additives found in gasoline.

These compounds are highly carcinogenic, do not readily biodegrade in the environment, and are capable of contaminating groundwater supplies. The following 'Tables' (3.15 & 3.16) compares the air toxic exhaust emissions and ozone-forming potential between gasoline and two different methanol-fuel-blends; they show that the fuel blend with higher

methanol concentrations emits less toxic exhaust (except for formaldehyde) and possesses lower ozone-forming potential, thus proving the superiority of methanol.

# Table 3.16: Average Air Toxic Exhaust Emission(RFG indicates reformed gasoline, FFV indicates flexible fuel vehicle, STD indicatesstandard vehicle)

Vehicle-Fuel	1,3-Butadiene		Benzene		Formalde	hyde	Acetaldehyde	
	Avg (mg/mi)	CV	Avg (mg/mi)	CV	Avg (mg/mi)	CV	Avg (mg/mi)	CV
FFV-RFG	0.83	0.15	4.50	0.11	1.48	0.37	0.43	0.37
FFV-M50	0.37	0.13	2.96	0.15	6.23	0.32	0.41	0.31
FFV-M85	0.10	0.00	1.39	0.23	12.31	0.36	0.25	0.47
STD-RFG	0.30	0.19	2.15	0.29	1.09	0.31	0.30	0.43

Source: SAE Technical Paper Series [22]

## Table 3.17: Ozone Forming Potential and Specific Reactivity

Test Fuel	Vehicle Type	Ozone Forming Potential (mg O3/mile)	Specific Reactivity (mg O3/mg NMOG)
RFG	FFV	546.7	3.7
M50	FFV	359.5	3
M85	FFV	265.7	1.8
RFG	STD	388	4.4

Source: Methanex [23]

									**********			
	G	E3	E7	E10	M3	M7	M10	EM3	EM7	EM10		N r/min
CO	3.9	3.2	2.9	2	3.6	1.5	1.4	3.6	2.5	1.9		
CO <sub>2</sub>	12.2	12.5	12.6	13.2	12.4	13.6	13.2	12.4	13	13.2		
UHC	242	218	200	190	210	215	205	210	205	197		3450
BP	2.12	2.32	2.35	2.38	2.34	2.24	2.29	2.33	2.34	2.34	~	
Ta	4.45	4.43	4.48	4.57	4.47	4.44	4.51	4.28	4.3	4.36		
VE	0.27	0.28	0.28	0.45	0.28	0.405	0.4	0.403	0.406	0.407	J	
CO	4.5	3.8	3.1	2.6	37	2.2	2	3.7	2.9	2.4	5	
co.	11.8	12.3	12.8	13	12.3	13.3	13	12.3	12.9	13	1	
UHC	280	220	240	220	225	225	207	250	227	215		2400
DD	280	270	240	220	225	235	207	250	237	215	$\geq$	3400
BP	2.23	2.57	2.44	2.45	2.59	4.5	2.55	-	2.54	2.31	1	
Iq	4.56	4.54	4.65	4.68	4.57	4.5	4.62	-	4.5	4.6		
VE	0.275	0.277	0.276	0.411	0.277	-	0.405	-	0.4	0.405	$\leq$	
CO	4.9	4.4	4.2	3.8	4.3	3.3	3.7	4.6	3.9	3.7		
$CO_2$	11.3	11.8	11.9	12.1	11.7	12.4	11.7	11.7	11.9	11.9		
UHC	319	310	291	268	226	250	217	280	270	230	5	3300
BP	2.345	2.427	2.473	2.501	2.42	2.38	2.44	2.37	2.40	2.42	ſ	
Tq	4.63	4.65	4.72	4.78	4.63	4.6	-	4.55	4.54	4.64		
VE	0.268	0.282	0.275	0.408	0.278	0.404	<u> </u>	0.408	0.405	0.407	2	
CO	5.5	5.4	5	4.3	4.6	4.3	4.5	5.4	4.7	4.4		
CO2	11.1	11.2	11.4	11.8	10.8	11.7	11.3	10.8	11.5	11.6		
UHC	322	315	300	280	230	270	235	290	280	250		3200
RP	2 44	2 455	2 511	2 537	2.47	2 453	2.46	2.45	2.49	25		5200
Ta	4.66	4.71	4.9	4.84	4.72	4.68	4.7	4.47	4.54	176		
VE	0.27	0.281	0.27	0.414	0.276	0.414	0.425	0.400	0.407	0.407		
CO	5.0	5.9	57	5.2	5	4.7	4.7	6.409	5.2	6.407	-	
CO	3.9	5.0	5.7	5.2	3	4.7	4.7	5.6	5.5			
$CO_2$	10.8	10.9	10.9	11	10.5	11.5	10.9	10.5	11	11.2		
UHC	325	321	315	295	224	265	232	300	285	260	5	3100
BP	2.455	2.499	2.513	2.529	2.51	2.473	2.51	2.46	2.46	2.47	ſ	
Tq	4.69	4.77	4.82	4.85	4.8	4.69	4.74	4.62	4.59	4.75		
VE	0.272	0.279	0.269	0.418	0.274	0.428	0.446	0.408	0.405	0.404	_	
VE CO	0.272 6.6	0.279 6.9	0.269 6.5	0.418 5.7	0.274 5.6	0.428 5.1	0.446 5.5	0.408 6.7	0.405 6	0.404 5.6	2	
VE CO CO <sub>2</sub>	0.272 6.6 10.2	0.279 6.9 10.4	0.269 6.5 10.5	0.418 5.7 10.6	0.274 5.6 10.3	0.428 5.1 11.2	0.446 5.5 10.6	0.408 6.7 10.3	0.405 6 10.6	0.404 5.6 10.6	7	
VE CO CO <sub>2</sub> UHC	0.272 6.6 10.2 341	0.279 6.9 10.4 339	0.269 6.5 10.5 325	0.418 5.7 10.6 310	0.274 5.6 10.3 240	0.428 5.1 11.2 301	0.446 5.5 10.6 268	0.408 6.7 10.3 325	0.405 6 10.6 315	0.404 5.6 10.6 285		3000
VE CO CO <sub>2</sub> UHC BP	0.272 6.6 10.2 341 2.453	0.279 6.9 10.4 339 2.506	0.269 6.5 10.5 325 2.522	0.418 5.7 10.6 310 2.545	0.274 5.6 10.3 240 2.5	0.428 5.1 11.2 301 2.491	0.446 5.5 10.6 268 2.53	0.408 6.7 10.3 325 2.42	0.405 6 10.6 315 2.44	0.404 5.6 10.6 285 2.43	}	3000
VE CO CO <sub>2</sub> UHC BP To	0.272 6.6 10.2 341 2.453 4.68	0.279 6.9 10.4 339 2.506 4 79	0.269 6.5 10.5 325 2.522 4.81	0.418 5.7 10.6 310 2.545 4.86	0.274 5.6 10.3 240 2.5 4.77	0.428 5.1 11.2 301 2.491 4.64	0.446 5.5 10.6 268 2.53	0.408 6.7 10.3 325 2.42 4.63	0.405 6 10.6 315 2.44 4.69	0.404 5.6 10.6 285 2.43 4.73	}	3000
VE CO CO <sub>2</sub> UHC BP Tq VE	0.272 6.6 10.2 341 2.453 4.68 0.27	0.279 6.9 10.4 339 2.506 4.79 0.267	0.269 6.5 10.5 325 2.522 4.81 0.268	0.418 5.7 10.6 310 2.545 4.86 0.438	0.274 5.6 10.3 240 2.5 4.77 0.27	0.428 5.1 11.2 301 2.491 4.64 0.445	0.446 5.5 10.6 268 2.53	0.408 6.7 10.3 325 2.42 4.63 0.412	0.405 6 10.6 315 2.44 4.69 0.425	0.404 5.6 10.6 285 2.43 4.73 0.415	}	3000
VE CO UHC BP Tq VE CO	0.272 6.6 10.2 341 2.453 4.68 0.27 7.5	0.279 6.9 10.4 339 2.506 4.79 0.267 7.2	0.269 6.5 10.5 325 2.522 4.81 0.268 6.8	0.418 5.7 10.6 310 2.545 4.86 0.438 6.2	0.274 5.6 10.3 240 2.5 4.77 0.27 6.4	0.428 5.1 11.2 301 2.491 4.64 0.445 6.3	0.446 5.5 10.6 268 2.53 - 0.467 6.2	0.408 6.7 10.3 325 2.42 4.63 0.412 7.3	0.405 6 10.6 315 2.44 4.69 0.425 6 5	0.404 5.6 10.6 285 2.43 4.73 0.415 6.2	}	3000
VE CO CO <sub>2</sub> UHC BP Tq VE CO	0.272 6.6 10.2 341 2.453 4.68 0.27 7.5	0.279 6.9 10.4 339 2.506 4.79 0.267 7.2	0.269 6.5 10.5 325 2.522 4.81 0.268 6.8 9.9	0.418 5.7 10.6 310 2.545 4.86 0.438 6.2	0.274 5.6 10.3 240 2.5 4.77 0.27 6.4	0.428 5.1 11.2 301 2.491 4.64 0.445 6.3	0.446 5.5 10.6 268 2.53 - 0.467 6.2	0.408 6.7 10.3 325 2.42 4.63 0.412 7.3	0.405 6 10.6 315 2.44 4.69 0.425 6.5	0.404 5.6 10.6 285 2.43 4.73 0.415 6.2	}	3000
VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub>	0.272 6.6 10.2 341 2.453 4.68 0.27 7.5 9.8	0.279 6.9 10.4 339 2.506 4.79 0.267 7.2 9.9	0.269 6.5 10.5 325 2.522 4.81 0.268 6.8 9.9	0.418 5.7 10.6 310 2.545 4.86 0.438 6.2 10.2 221	0.274 5.6 10.3 240 2.5 4.77 0.27 6.4 10.1	0.428 5.1 11.2 301 2.491 4.64 0.445 6.3 10.6	0.446 5.5 10.6 268 2.53 - 0.467 6.2 10.7	0.408 6.7 10.3 325 2.42 4.63 0.412 7.3 10.1	0.405 6 10.6 315 2.44 4.69 0.425 6.5 10.3	0.404 5.6 10.6 285 2.43 4.73 0.415 6.2 10.5		3000
VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC	0.272 6.6 10.2 341 2.453 4.68 0.27 7.5 9.8 343 2.422	0.279 6.9 10.4 339 2.506 4.79 0.267 7.2 9.9 341 2.479	0.269 6.5 10.5 325 2.522 4.81 0.268 6.8 9.9 334 2.491	0.418 5.7 10.6 310 2.545 4.86 0.438 6.2 10.2 331	0.274 5.6 10.3 240 2.5 4.77 0.27 6.4 10.1 293 2.4	0.428 5.1 11.2 301 2.491 4.64 0.445 6.3 10.6 314	0.446 5.5 10.6 268 2.53 - 0.467 6.2 10.7 290	0.408 6.7 10.3 325 2.42 4.63 0.412 7.3 10.1 330 2.20	0.405 6 10.6 315 2.44 4.69 0.425 6.5 10.3 325	0.404 5.6 10.6 285 2.43 4.73 0.415 6.2 10.5 320		3000 2900
VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC BP	0.272 6.6 10.2 341 2.453 4.68 0.27 7.5 9.8 343 2.422	0.279 6.9 10.4 339 2.506 4.79 0.267 7.2 9.9 341 2.478	0.269 6.5 10.5 325 2.522 4.81 0.268 6.8 9.9 334 2.481	0.418 5.7 10.6 310 2.545 4.86 0.438 6.2 10.2 331 2.517	0.274 5.6 10.3 240 2.5 4.77 0.27 6.4 10.1 293 2.46	0.428 5.1 11.2 301 2.491 4.64 0.445 6.3 10.6 314 2.494	0.446 5.5 10.6 268 2.53 - 0.467 6.2 10.7 290 2.49 2.49	0.408 6.7 10.3 325 2.42 4.63 0.412 7.3 10.1 330 2.39	0.405 6 10.6 315 2.44 4.69 0.425 6.5 10.3 325 2.4	0.404 5.6 10.6 285 2.43 4.73 0.415 6.2 10.5 320 2.43	}	3000 2900
VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC BP Tq Tq	0.272 6.6 10.2 341 2.453 4.68 0.27 7.5 9.8 343 2.422 4.62 2.422	0.279 6.9 10.4 339 2.506 4.79 0.267 7.2 9.9 341 2.478 4.76 4.262	0.269 6.5 10.5 325 2.522 4.81 0.268 6.8 9.9 334 2.481 4.78 4.78	0.418 5.7 10.6 310 2.545 4.86 0.438 6.2 10.2 331 2.517 4.81	0.274 5.6 10.3 240 2.5 4.77 0.27 6.4 10.1 293 2.46 4.7	0.428 5.1 11.2 301 2.491 4.64 0.445 6.3 10.6 314 2.494 4.62 0.456	0.446 5.5 10.6 268 2.53 - 0.467 6.2 10.7 290 2.49 4.69	0.408 6.7 10.3 325 2.42 4.63 0.412 7.3 10.1 330 2.39 4.57 6.42	0.405 6 10.6 315 2.44 4.69 0.425 6.5 10.3 325 2.4 4.67 0.417	0.404 5.6 10.6 285 2.43 4.73 0.415 6.2 10.5 320 2.43 4.71 2.43	}	3000 2900
VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC BP Tq VE	0.272 6.6 10.2 341 2.453 4.68 0.27 7.5 9.8 343 2.422 4.62 0.265	0.279 6.9 10.4 339 2.506 4.79 0.267 7.2 9.9 341 2.478 4.76 0.262	0.269 6.5 10.5 325 2.522 4.81 0.268 6.8 9.9 334 2.481 4.78 0.265	0.418 5.7 10.6 310 2.545 4.86 0.438 6.2 10.2 331 2.517 4.81	0.274 5.6 10.3 240 2.5 4.77 0.27 6.4 10.1 293 2.46 4.7 0.266	0.428 5.1 11.2 301 2.491 4.64 0.445 6.3 10.6 314 2.494 4.62 0.456	0.446 5.5 10.6 268 2.53 - 0.467 6.2 10.7 290 2.49 4.69 0.46	0.408 6.7 10.3 325 2.42 4.63 0.412 7.3 10.1 330 2.39 4.57 0.421	0.405 6 10.6 315 2.44 4.69 0.425 6.5 10.3 325 2.4 4.67 0.417	0.404 5.6 10.6 285 2.43 4.73 0.415 6.2 10.5 320 2.43 4.71 0.418		3000 2900
VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC BP Tq VE CO CO 2 CO 2 UHC CO 2 CO 2 CO 2 CO 2 CO 2 UHC BP Tq CO 2 CO 2 UHC BP Tq CO 2 CO 2 UHC BP Tq CO 2 CO 2 CO 2 UHC BP Tq CO 2 CO 2 CO 2 CO 2 CO 2 CO 2 CO 2 CO	$\begin{array}{c} 0.272 \\ 6.6 \\ 10.2 \\ 341 \\ 2.453 \\ 4.68 \\ 0.27 \\ 7.5 \\ 9.8 \\ 343 \\ 2.422 \\ 4.62 \\ 0.265 \\ 8.2 \end{array}$	0.279 6.9 10.4 339 2.506 4.79 0.267 7.2 9.9 341 2.478 4.76 0.262 8.1	0.269 6.5 10.5 325 2.522 4.81 0.268 6.8 9.9 334 2.481 4.78 0.265 7.3	0.418 5.7 10.6 310 2.545 4.86 0.438 6.2 10.2 331 2.517 4.81 - 7	0.274 5.6 10.3 240 2.5 4.77 0.27 6.4 10.1 293 2.46 4.7 0.266 7.2	$\begin{array}{c} 0.428\\ 5.1\\ 11.2\\ 301\\ 2.491\\ 4.64\\ 0.445\\ 6.3\\ 10.6\\ 314\\ 2.494\\ 4.62\\ 0.456\\ 6.8 \end{array}$	0.446 5.5 10.6 268 2.53 - 0.467 6.2 10.7 290 2.49 4.69 0.46 6.7	0.408 6.7 10.3 325 2.42 4.63 0.412 7.3 10.1 330 2.39 4.57 0.421 8.1	0.405 6 10.6 315 2.44 4.69 0.425 6.5 10.3 325 2.4 4.67 0.417 7	0.404 5.6 10.6 285 2.43 4.73 0.415 6.2 10.5 320 2.43 4.71 0.418 6.8		3000 2900
VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub>	0.272 6.6 10.2 341 2.453 4.68 0.27 7.5 9.8 343 2.422 4.62 0.265 8.2 9.3	$\begin{array}{c} 0.279\\ 6.9\\ 10.4\\ 339\\ 2.506\\ 4.79\\ 0.267\\ 7.2\\ 9.9\\ 341\\ 2.478\\ 4.76\\ 0.262\\ 8.1\\ 9.3 \end{array}$	0.269 6.5 10.5 325 2.522 4.81 0.268 6.8 9.9 334 2.481 4.78 0.265 7.3 9.5	0.418 5.7 10.6 310 2.545 4.86 0.438 6.2 10.2 331 2.517 4.81 - 7 9.7	0.274 5.6 10.3 240 2.5 4.77 0.27 6.4 10.1 293 2.46 4.7 0.266 7.2 10	0.428 5.1 11.2 301 2.491 4.64 0.445 6.3 10.6 314 2.494 4.62 0.456 6.8 10.3	0.446 5.5 10.6 268 2.53 - 0.467 6.2 10.7 290 2.49 4.69 0.46 6.7 10.3	0.408 6.7 10.3 325 2.42 4.63 0.412 7.3 10.1 330 2.39 4.57 0.421 8.1 10	0.405 6 10.6 315 2.44 4.69 0.425 6.5 10.3 325 2.4 4.67 0.417 7 9.8	0.404 5.6 10.6 285 2.43 4.73 0.415 6.2 10.5 320 2.43 4.71 0.418 6.8 10		3000 2900
VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC	0.272 6.6 10.2 341 2.453 4.68 0.27 7.5 9.8 343 2.422 4.62 0.265 8.2 9.3 357	$\begin{array}{c} 0.279\\ 6.9\\ 10.4\\ 339\\ 2.506\\ 4.79\\ 0.267\\ 7.2\\ 9.9\\ 341\\ 2.478\\ 4.76\\ 0.262\\ 8.1\\ 9.3\\ 350 \end{array}$	0.269 6.5 10.5 325 2.522 4.81 0.268 6.8 9.9 334 2.481 4.78 0.265 7.3 9.5 344	0.418 5.7 10.6 310 2.545 4.86 0.438 6.2 10.2 331 2.517 4.81 - 7 9.7 340	0.274 5.6 10.3 240 2.5 4.77 0.27 6.4 10.1 293 2.46 4.7 0.266 7.2 10 300	0.428 5.1 11.2 301 2.491 4.64 0.445 6.3 10.6 314 2.494 4.62 0.456 6.8 10.3 320	0.446 5.5 10.6 268 2.53 - 0.467 6.2 10.7 290 2.49 4.69 0.46 6.7 10.3 310	0.408 6.7 10.3 325 2.42 4.63 0.412 7.3 10.1 330 2.39 4.57 0.421 8.1 10 340	0.405 6 10.6 315 2.44 4.69 0.425 6.5 10.3 325 2.4 4.67 0.417 7 9.8 335	0.404 5.6 10.6 285 2.43 4.73 0.415 6.2 10.5 320 2.43 4.71 0.418 6.8 10 330		3000 2900 2800
VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC BP	0.272 6.6 10.2 341 2.453 4.68 0.27 7.5 9.8 343 2.422 4.62 0.265 8.2 9.3 357 2.399	$\begin{array}{c} 0.279\\ 6.9\\ 10.4\\ 339\\ 2.506\\ 4.79\\ 0.267\\ 7.2\\ 9.9\\ 341\\ 2.478\\ 4.76\\ 0.262\\ 8.1\\ 9.3\\ 350\\ 2.432\\ \end{array}$	0.269 6.5 10.5 325 2.522 4.81 0.268 6.8 9.9 334 2.481 4.78 0.265 7.3 9.5 344 2.465	0.418 5.7 10.6 310 2.545 4.86 0.438 6.2 10.2 331 2.517 4.81 - 7 9.7 340 2.503	0.274 5.6 10.3 240 2.5 4.77 0.27 6.4 10.1 293 2.46 4.7 0.266 7.2 10 300 2.42	0.428 5.1 11.2 301 2.491 4.64 0.445 6.3 10.6 314 2.494 4.62 0.456 6.8 10.3 320 2.458	0.446 5.5 10.6 268 2.53 - 0.467 6.2 10.7 290 2.49 4.69 0.46 6.7 10.3 310 2.49	0.408 6.7 10.3 325 2.42 4.63 0.412 7.3 10.1 330 2.39 4.57 0.421 8.1 10 340 2.35	0.405 6 10.6 315 2.44 4.69 0.425 6.5 10.3 325 2.4 4.67 0.417 7 9.8 335 2.4	0.404 5.6 10.6 285 2.43 4.73 0.415 6.2 10.5 320 2.43 4.71 0.418 6.8 10 330 2.45		3000 2900 2800
VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC BP Tq	0.272 6.6 10.2 341 2.453 4.68 0.27 7.5 9.8 343 2.422 4.62 0.265 8.2 9.3 357 2.399 4.58	0.279 6.9 10.4 339 2.506 4.79 0.267 7.2 9.9 341 2.478 4.76 0.262 8.1 9.3 350 2.432 4.71	0.269 6.5 10.5 325 2.522 4.81 0.268 6.8 9.9 334 2.481 4.78 0.265 7.3 9.5 344 2.465 4.71	0.418 5.7 10.6 310 2.545 4.86 0.438 6.2 10.2 331 2.517 4.81 - 7 9.7 340 2.503 4.74	0.274 5.6 10.3 240 2.5 4.77 0.27 6.4 10.1 293 2.46 4.7 0.266 7.2 10 300 2.42 4.62	0.428 5.1 11.2 301 2.491 4.64 0.445 6.3 10.6 314 2.494 4.62 0.456 6.8 10.3 320 2.458 4.56	0.446 5.5 10.6 268 2.53 - 0.467 6.2 10.7 290 2.49 4.69 0.46 6.7 10.3 310 2.49 4.68	0.408 6.7 10.3 325 2.42 4.63 0.412 7.3 10.1 330 2.39 4.57 0.421 8.1 10 340 2.35 4.58	0.405 6 10.6 315 2.44 4.69 0.425 6.5 10.3 325 2.4 4.67 0.417 7 9.8 335 2.4 4.61	0.404 5.6 10.6 285 2.43 4.73 0.415 6.2 10.5 320 2.43 4.71 0.418 6.8 10 330 2.45 4.76		3000 2900 2800
VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC BP Tq VE CO 2 VE CO 2 VE CO 2 VE VE CO 2 VE VE CO 2 VE VE CO 2 VE VE CO 2 VE VE CO 2 VE VE VE CO 2 VE VE VE VE VE VE VE VE VE VE VE VE VE	0.272 6.6 10.2 341 2.453 4.68 0.27 7.5 9.8 343 2.422 4.62 0.265 8.2 9.3 357 2.399 4.58 0.262	0.279 6.9 10.4 339 2.506 4.79 0.267 7.2 9.9 341 2.478 4.76 0.262 8.1 9.3 350 2.432 4.71 0.257	0.269 6.5 10.5 325 2.522 4.81 0.268 6.8 9.9 334 2.481 4.78 0.265 7.3 9.5 344 2.465 4.71 0.26	0.418 5.7 10.6 310 2.545 4.86 0.438 6.2 10.2 331 2.517 4.81 - 7 9.7 340 2.503 4.74 0.458	0.274 5.6 10.3 240 2.5 4.77 0.27 6.4 10.1 293 2.46 4.7 0.266 7.2 10 300 2.42 4.62 0.263	0.428 5.1 11.2 301 2.491 4.64 0.445 6.3 10.6 314 2.494 4.62 0.456 6.8 10.3 320 2.458 4.56 0.464	0.446 5.5 10.6 268 2.53 - 0.467 6.2 10.7 290 2.49 4.69 0.46 6.7 10.3 310 2.49 4.68 0.471	0.408 6.7 10.3 325 2.42 4.63 0.412 7.3 10.1 330 2.39 4.57 0.421 8.1 10 340 2.35 4.58 0.427	0.405 6 10.6 315 2.44 4.69 0.425 6.5 10.3 325 2.4 4.67 0.417 7 9.8 335 2.4 4.61 0.422	0.404 5.6 10.6 285 2.43 4.73 0.415 6.2 10.5 320 2.43 4.71 0.418 6.8 10 330 2.45 4.76 0.424		3000 2900 2800
VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> CO <sub>2</sub> CO <sub>2</sub> CO <sub>2</sub> CO <sub>2</sub> CO <sub>2</sub> CO <sub>2</sub> CO <sub>2</sub> CO CO <sub>2</sub> CO CO CO CO CO CO CO CO CO CO CO CO CO	0.272 6.6 10.2 341 2.453 4.68 0.27 7.5 9.8 343 2.422 4.62 0.265 8.2 9.3 357 2.399 4.58 0.262 8.7	0.279 6.9 10.4 339 2.506 4.79 0.267 7.2 9.9 341 2.478 4.76 0.262 8.1 9.3 350 2.432 4.71 0.257 8.6	0.269 6.5 10.5 325 2.522 4.81 0.268 6.8 9.9 334 2.481 4.78 0.265 7.3 9.5 344 2.465 4.71 0.26 8.2	0.418 5.7 10.6 310 2.545 4.86 0.438 6.2 10.2 331 2.517 4.81 - 7 9.7 340 2.503 4.74 0.458 7.3	0.274 5.6 10.3 240 2.5 4.77 0.27 6.4 10.1 293 2.46 4.7 0.266 7.2 10 300 2.42 4.62 0.263 8.3	0.428 5.1 11.2 301 2.491 4.64 0.445 6.3 10.6 314 2.494 4.62 0.456 6.8 10.3 320 2.458 4.56 0.464 7.4	0.446 5.5 10.6 268 2.53 - 0.467 6.2 10.7 290 2.49 4.69 0.46 6.7 10.3 310 2.49 4.68 0.471 7	0.408 6.7 10.3 325 2.42 4.63 0.412 7.3 10.1 330 2.39 4.57 0.421 8.1 10 340 2.35 4.58 0.427 8.6	0.405 6 10.6 315 2.44 4.69 0.425 6.5 10.3 325 2.4 4.67 0.417 7 9.8 335 2.4 4.61 0.422 7.7	0.404 5.6 10.6 285 2.43 4.73 0.415 6.2 10.5 320 2.43 4.71 0.418 6.8 10 330 2.45 4.76 0.424 7.2		3000 2900 2800
VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> CO <sub>2</sub> CO <sub>2</sub> CO <sub>2</sub> CO <sub>2</sub> CO <sub>2</sub> CO <sub>2</sub> CO <sub>2</sub>	0.272 6.6 10.2 341 2.453 4.68 0.27 7.5 9.8 343 2.422 4.62 0.265 8.2 9.3 357 2.399 4.58 0.262 8.7 8.9	0.279 6.9 10.4 339 2.506 4.79 0.267 7.2 9.9 341 2.478 4.76 0.262 8.1 9.3 350 2.432 4.71 0.257 8.6 8.9	0.269 6.5 10.5 325 2.522 4.81 0.268 6.8 9.9 334 2.481 4.78 0.265 7.3 9.5 344 2.465 4.71 0.26 8.2 9.2	0.418 5.7 10.6 310 2.545 4.86 0.438 6.2 10.2 331 2.517 4.81 - 7 9.7 340 2.503 4.74 0.458 7.3 9.5	0.274 5.6 10.3 240 2.5 4.77 0.27 6.4 10.1 293 2.46 4.7 0.266 7.2 10 300 2.42 4.62 0.263 8.3 9.4	0.428 5.1 11.2 301 2.491 4.64 0.445 6.3 10.6 314 2.494 4.62 0.456 6.8 10.3 320 2.458 4.56 0.464 7.4 9.9	0.446 5.5 10.6 268 2.53 - 0.467 6.2 10.7 290 2.49 4.69 0.46 6.7 10.3 310 2.49 4.68 0.471 7 10	0.408 6.7 10.3 325 2.42 4.63 0.412 7.3 10.1 330 2.39 4.57 0.421 8.1 10 340 2.35 4.58 0.427 8.6 9.4	0.405 6 10.6 315 2.44 4.69 0.425 6.5 10.3 325 2.4 4.67 0.417 7 9.8 335 2.4 4.61 0.422 7.7 9.5	0.404 5.6 10.6 285 2.43 4.73 0.415 6.2 10.5 320 2.43 4.71 0.418 6.8 10 330 2.45 4.76 0.424 7.2 9.6		3000 2900 2800
VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC UHC UHC UHC UHC CO <sub>2</sub> UHC UHC UHC UHC UHC CO <sub>2</sub> UHC UHC UHC CO <sub>2</sub> UHC UHC CO <sub>2</sub> UHC CO <sub>2</sub> UHC CO CO <sub>2</sub> UHC CO CO <sub>2</sub> UHC CO CO <sub>2</sub> UHC CO CO <sub>2</sub> UHC CO CO <sub>2</sub> UHC CO CO CO <sub>2</sub> UHC CO CO CO <sub>2</sub> UHC CO CO CO CO <sub>2</sub> UHC CO CO CO CO <sub>2</sub> UHC CO CO CO CO CO CO CO CO CO CO CO CO UHC UHC CO CO CO CO UHC UHC UHC UHC UHC UHC UHC UHC UHC UHC	0.272 6.6 10.2 341 2.453 4.68 0.27 7.5 9.8 343 2.422 4.62 0.265 8.2 9.3 357 2.399 4.58 0.262 8.7 8.9 365	0.279 6.9 10.4 339 2.506 4.79 0.267 7.2 9.9 341 2.478 4.76 0.262 8.1 9.3 350 2.432 4.71 0.257 8.6 8.9 361	0.269 6.5 10.5 325 2.522 4.81 0.268 6.8 9.9 334 2.481 4.78 0.265 7.3 9.5 344 2.465 4.71 0.26 8.2 9.2 355	0.418 5.7 10.6 310 2.545 4.86 0.438 6.2 10.2 331 2.517 4.81 - 7 9.7 340 2.503 4.74 0.458 7.3 9.5 350	0.274 5.6 10.3 240 2.5 4.77 0.27 6.4 10.1 293 2.46 4.7 0.266 7.2 10 300 2.42 4.62 0.263 8.3 9.4 313	0.428 5.1 11.2 301 2.491 4.64 0.445 6.3 10.6 314 2.494 4.62 0.456 6.8 10.3 320 2.458 4.56 0.464 7.4 9.9 327	0.446 5.5 10.6 268 2.53 - 0.467 6.2 10.7 290 2.49 4.69 0.46 6.7 10.3 310 2.49 4.68 0.471 7 10 350	0.408 6.7 10.3 325 2.42 4.63 0.412 7.3 10.1 330 2.39 4.57 0.421 8.1 10 340 2.35 4.58 0.427 8.6 9.4 357	0.405 6 10.6 315 2.44 4.69 0.425 6.5 10.3 325 2.4 4.67 0.417 7 9.8 335 2.4 4.61 0.422 7.7 9.5 353	0.404 5.6 10.6 285 2.43 4.73 0.415 6.2 10.5 320 2.43 4.71 0.418 6.8 10 330 2.45 4.76 0.424 7.2 9.6 351		3000 2900 2800
VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC BP Tq VE CO CO CO CO CO CO CO CO CO CO CO CO CO	0.272 6.6 10.2 341 2.453 4.68 0.27 7.5 9.8 343 2.422 4.62 0.265 8.2 9.3 357 2.399 4.58 0.262 8.7 8.9 365 2.389	0.279 6.9 10.4 339 2.506 4.79 0.267 7.2 9.9 341 2.478 4.76 0.262 8.1 9.3 350 2.432 4.71 0.257 8.6 8.9 361 2.417	0.269 6.5 10.5 325 2.522 4.81 0.268 6.8 9.9 334 2.481 4.78 0.265 7.3 9.5 344 2.465 4.71 0.26 8.2 9.2 355 2.447	0.418 5.7 10.6 310 2.545 4.86 0.438 6.2 10.2 331 2.517 4.81 - 7 9.7 340 2.503 4.74 0.458 7.3 9.5 350 2.495	0.274 5.6 10.3 240 2.5 4.77 0.27 6.4 10.1 293 2.46 4.7 0.266 7.2 10 300 2.42 4.62 0.263 8.3 9.4 313 2.44	0.428 5.1 11.2 301 2.491 4.64 0.445 6.3 10.6 314 2.494 4.62 0.456 6.8 10.3 320 2.458 4.56 0.464 7.4 9.9 327 2.45	0.446 5.5 10.6 268 2.53 - 0.467 6.2 10.7 290 2.49 4.69 0.46 6.7 10.3 310 2.49 4.68 0.471 7 10 350 2.45	0.408 6.7 10.3 325 2.42 4.63 0.412 7.3 10.1 330 2.39 4.57 0.421 8.1 10 340 2.35 4.58 0.427 8.6 9.4 357 2.43	0.405 6 10.6 315 2.44 4.69 0.425 6.5 10.3 325 2.4 4.67 0.417 7 9.8 335 2.4 4.61 0.422 7.7 9.5 353 2.453	0.404 5.6 10.6 285 2.43 4.73 0.415 6.2 10.5 320 2.43 4.71 0.418 6.8 10 330 2.45 4.76 0.424 7.2 9.6 351 2.49		3000 2900 2800 2700
VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC BP Tq Tq Tq Tq Tq	0.272 6.6 10.2 341 2.453 4.68 0.27 7.5 9.8 343 2.422 4.62 0.265 8.2 9.3 357 2.399 4.58 0.262 8.7 8.9 365 2.389 4.56	0.279 6.9 10.4 339 2.506 4.79 0.267 7.2 9.9 341 2.478 4.76 0.262 8.1 9.3 350 2.432 4.71 0.257 8.6 8.9 361 2.417 4.66	0.269 6.5 10.5 325 2.522 4.81 0.268 6.8 9.9 334 2.481 4.78 0.265 7.3 9.5 344 2.465 4.71 0.26 8.2 9.2 355 2.447 4.63	0.418 5.7 10.6 310 2.545 4.86 0.438 6.2 10.2 331 2.517 4.81 - 7 9.7 340 2.503 4.74 0.458 7.3 9.5 350 2.495 4.67	0.274 5.6 10.3 240 2.5 4.77 0.27 6.4 10.1 293 2.46 4.7 0.266 7.2 10 300 2.42 4.62 0.263 8.3 9.4 313 2.44 4.67	0.428 5.1 11.2 301 2.491 4.64 0.445 6.3 10.6 314 2.494 4.62 0.456 6.8 10.3 320 2.458 4.56 0.464 7.4 9.9 327 2.45 4.62	0.446 5.5 10.6 268 2.53 - 0.467 6.2 10.7 290 2.49 4.69 0.46 6.7 10.3 310 2.49 4.68 0.471 7 10 350 2.45 4.62	0.408 6.7 10.3 325 2.42 4.63 0.412 7.3 10.1 330 2.39 4.57 0.421 8.1 10 340 2.35 4.58 0.427 8.6 9.4 357 2.43 4.59	$\begin{array}{c} 0.405\\ 6\\ 10.6\\ 315\\ 2.44\\ 4.69\\ 0.425\\ 6.5\\ 10.3\\ 325\\ 2.4\\ 4.67\\ 0.417\\ 7\\ 9.8\\ 335\\ 2.4\\ 4.61\\ 0.422\\ 7.7\\ 9.5\\ 353\\ 2.453\\ 4.6\end{array}$	$\begin{array}{c} 0.404\\ 5.6\\ 10.6\\ 285\\ 2.43\\ 4.73\\ 0.415\\ 6.2\\ 10.5\\ 320\\ 2.43\\ 4.71\\ 0.418\\ 6.8\\ 10\\ 330\\ 2.45\\ 4.76\\ 0.424\\ 7.2\\ 9.6\\ 351\\ 2.49\\ 4.56\end{array}$		3000 2900 2800 2700
VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> VE CO 2 UHC BP Tq VE CO 2 VE CO 2 UHC BP Tq VE CO 2 VE CO 2 UHC BP Tq VE CO 2 VE CO 2 UHC BP Tq VE CO 2 VE CO 2 UHC BP Tq VE CO 2 VE VE CO 2 VE CO 2 VE CO 2 VE VE CO 2 VE CO 2 VE CO 2 VE VE CO 2 VE CO 2 VE VE CO 2 VE VE CO 2 VE VE VE VE VE VE VE VE VE VE VE VE VE	0.272 6.6 10.2 341 2.453 4.68 0.27 7.5 9.8 343 2.422 4.62 0.265 8.2 9.3 357 2.399 4.58 0.262 8.7 8.9 365 2.389 4.56 0.255	0.279 6.9 10.4 339 2.506 4.79 0.267 7.2 9.9 341 2.478 4.76 0.262 8.1 9.3 350 2.432 4.71 0.257 8.6 8.9 361 2.417 4.66 0.252	0.269 6.5 10.5 325 2.522 4.81 0.268 6.8 9.9 334 2.481 4.78 0.265 7.3 9.5 344 2.465 4.71 0.26 8.2 9.2 355 2.447 4.63 0.277	0.418 5.7 10.6 310 2.545 4.86 0.438 6.2 10.2 331 2.517 4.81 - 7 9.7 340 2.503 4.74 0.458 7.3 9.5 350 2.495 4.67 0.467	0.274 5.6 10.3 240 2.5 4.77 0.27 6.4 10.1 293 2.46 4.7 0.266 7.2 10 300 2.42 4.62 0.263 8.3 9.4 313 2.44 4.67 0.252	0.428 5.1 11.2 301 2.491 4.64 0.445 6.3 10.6 314 2.494 4.62 0.456 6.8 10.3 320 2.458 4.56 0.464 7.4 9.9 327 2.45 4.62 0.473	0.446 5.5 10.6 268 2.53 - 0.467 6.2 10.7 290 2.49 4.69 0.46 6.7 10.3 310 2.49 4.68 0.471 7 10 350 2.45 4.62 0.47	0.408 6.7 10.3 325 2.42 4.63 0.412 7.3 10.1 330 2.39 4.57 0.421 8.1 10 340 2.35 4.58 0.427 8.6 9.4 357 2.43 4.59 0.43	$\begin{array}{c} 0.405\\ 6\\ 10.6\\ 315\\ 2.44\\ 4.69\\ 0.425\\ 6.5\\ 10.3\\ 325\\ 2.4\\ 4.67\\ 0.417\\ 7\\ 9.8\\ 335\\ 2.4\\ 4.61\\ 0.422\\ 7.7\\ 9.5\\ 353\\ 2.453\\ 4.6\\ 0.43\\ \end{array}$	0.404 5.6 10.6 285 2.43 4.73 0.415 6.2 10.5 320 2.43 4.71 0.418 6.8 10 330 2.45 4.76 0.424 7.2 9.6 351 2.49 4.56 0.43		3000 2900 2800 2700
VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC BP Tq VE CO CO CO <sub>2</sub> UHC BP Tq VE CO CO CO <sub>2</sub> UHC BP Tq VE CO CO CO CO UHC BP Tq VE CO CO CO CO UHC BP Tq VE CO CO CO CO CO CO CO CO CO CO CO CO CO	0.272 6.6 10.2 341 2.453 4.68 0.27 7.5 9.8 343 2.422 4.62 0.265 8.2 9.3 357 2.399 4.58 0.262 8.7 8.9 365 2.389 4.56 0.255 9.2	0.279 6.9 10.4 339 2.506 4.79 0.267 7.2 9.9 341 2.478 4.76 0.262 8.1 9.3 350 2.432 4.71 0.257 8.6 8.9 361 2.417 4.66 0.252 9	0.269 6.5 10.5 325 2.522 4.81 0.268 6.8 9.9 334 2.481 4.78 0.265 7.3 9.5 344 2.465 4.71 0.26 8.2 9.2 355 2.447 4.63 0.277 8.5	0.418 5.7 10.6 310 2.545 4.86 0.438 6.2 10.2 331 2.517 4.81 - 7 9.7 340 2.503 4.74 0.458 7.3 9.5 350 2.495 4.67 0.467 7 5	0.274 5.6 10.3 240 2.5 4.77 0.27 6.4 10.1 293 2.46 4.7 0.266 7.2 10 300 2.42 4.62 0.263 8.3 9.4 313 2.44 4.67 0.252 8.8	0.428 5.1 11.2 301 2.491 4.64 0.445 6.3 10.6 314 2.494 4.62 0.456 6.8 10.3 320 2.458 4.56 0.464 7.4 9.9 327 2.45 4.62 0.473 7.6	0.446 5.5 10.6 268 2.53 - 0.467 6.2 10.7 290 2.49 4.69 0.46 6.7 10.3 310 2.49 4.68 0.471 7 10 350 2.45 4.62 0.47 7 5	0.408 6.7 10.3 325 2.42 4.63 0.412 7.3 10.1 330 2.39 4.57 0.421 8.1 10 340 2.35 4.58 0.427 8.6 9.4 357 2.43 4.59 0.43 9.1	$\begin{array}{c} 0.405\\ 6\\ 10.6\\ 315\\ 2.44\\ 4.69\\ 0.425\\ 6.5\\ 10.3\\ 325\\ 2.4\\ 4.67\\ 0.417\\ 7\\ 9.8\\ 335\\ 2.4\\ 4.61\\ 0.422\\ 7.7\\ 9.5\\ 353\\ 2.453\\ 4.6\\ 0.43\\ 8\end{array}$	0.404 5.6 10.6 285 2.43 4.73 0.415 6.2 10.5 320 2.43 4.71 0.418 6.8 10 330 2.45 4.76 0.424 7.2 9.6 351 2.49 4.56 0.43 7.8		3000 2900 2800 2700
VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> CO <sub>2</sub> CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC BP Tq VE CO CO CO <sub>2</sub> UHC BP Tq VE CO CO CO <sub>2</sub> UHC BP Tq VE CO CO CO <sub>2</sub> UHC BP Tq VE CO CO CO <sub>2</sub> UHC BP Tq VE CO CO CO CO CO CO CO CO CO CO CO CO CO	0.272 6.6 10.2 341 2.453 4.68 0.27 7.5 9.8 343 2.422 4.62 0.265 8.2 9.3 357 2.399 4.58 0.262 8.7 8.9 365 2.389 4.56 0.255 9.2 8.6	0.279 6.9 10.4 339 2.506 4.79 0.267 7.2 9.9 341 2.478 4.76 0.262 8.1 9.3 350 2.432 4.71 0.257 8.6 8.9 361 2.417 4.66 0.252 9 8.7	0.269 6.5 10.5 325 2.522 4.81 0.268 6.8 9.9 334 2.481 4.78 0.265 7.3 9.5 344 2.465 4.71 0.26 8.2 9.2 355 2.447 4.63 0.277 8.5	0.418 5.7 10.6 310 2.545 4.86 0.438 6.2 10.2 331 2.517 4.81 - 7 9.7 340 2.503 4.74 0.458 7.3 9.5 350 2.495 4.67 0.467 7.5 9.2	0.274 5.6 10.3 240 2.5 4.77 0.27 6.4 10.1 293 2.46 4.7 0.266 7.2 10 300 2.42 4.62 0.263 8.3 9.4 313 2.44 4.67 0.252 8.8 9.4	0.428 5.1 11.2 301 2.491 4.64 0.445 6.3 10.6 314 2.494 4.62 0.456 6.8 10.3 320 2.458 4.56 0.464 7.4 9.9 327 2.45 4.62 0.473 7.6 0.2	0.446 5.5 10.6 268 2.53 - 0.467 6.2 10.7 290 2.49 4.69 0.46 6.7 10.3 310 2.49 4.68 0.471 7 10 350 2.45 4.62 0.47 7.5 5 2.5	0.408 6.7 10.3 325 2.42 4.63 0.412 7.3 10.1 330 2.39 4.57 0.421 8.1 10 340 2.35 4.58 0.427 8.6 9.4 357 2.43 4.59 0.43 9.1 2	0.405 6 10.6 315 2.44 4.69 0.425 6.5 10.3 325 2.4 4.67 0.417 7 9.8 335 2.4 4.61 0.422 7.7 9.5 353 2.453 4.6 0.43 8 0.43 8	$\begin{array}{c} 0.404 \\ 5.6 \\ 10.6 \\ 285 \\ 2.43 \\ 4.73 \\ 0.415 \\ 6.2 \\ 10.5 \\ 320 \\ 2.43 \\ 4.71 \\ 0.418 \\ 6.8 \\ 10 \\ 330 \\ 2.45 \\ 4.76 \\ 0.424 \\ 7.2 \\ 9.6 \\ 351 \\ 2.49 \\ 4.56 \\ 0.43 \\ 7.8 \\ 0.6 \\ \end{array}$		3000 2900 2800 2700
VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC CO CO <sub>2</sub> UHC CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC CO CO <sub>2</sub> UHC BP Tq VE CO CO CO CO CO CO CO CO CO CO CO CO CO	0.272 6.6 10.2 341 2.453 4.68 0.27 7.5 9.8 343 2.422 4.62 0.265 8.2 9.3 357 2.399 4.58 0.262 8.7 8.9 365 2.389 4.56 0.255 9.2 8.6	$\begin{array}{c} 0.279\\ 6.9\\ 10.4\\ 339\\ 2.506\\ 4.79\\ 0.267\\ 7.2\\ 9.9\\ 341\\ 2.478\\ 4.76\\ 0.262\\ 8.1\\ 9.3\\ 350\\ 2.432\\ 4.71\\ 0.257\\ 8.6\\ 8.9\\ 361\\ 2.417\\ 4.66\\ 0.252\\ 9\\ 8.7\\ 2.57\\ 8.7\\ 1.52\\ 9\\ 8.7\\ 1.52\\ 9\\ 1.52\\ 1$	0.269 6.5 10.5 325 2.522 4.81 0.268 6.8 9.9 334 2.481 4.78 0.265 7.3 9.5 344 2.465 4.71 0.26 8.2 9.2 355 2.447 4.63 0.277 8.5 8.8	0.418 5.7 10.6 310 2.545 4.86 0.438 6.2 10.2 331 2.517 4.81 - 7 9.7 340 2.503 4.74 0.458 7.3 9.5 350 2.495 4.67 0.467 7.5 9.3	0.274 5.6 10.3 240 2.5 4.77 0.27 6.4 10.1 293 2.46 4.7 0.266 7.2 10 300 2.42 4.62 0.263 8.3 9.4 313 2.44 4.67 0.252 8.8 9	0.428 5.1 11.2 301 2.491 4.64 0.445 6.3 10.6 314 2.494 4.62 0.456 6.8 10.3 320 2.458 4.56 0.464 7.4 9.9 327 2.45 4.62 0.473 7.6 9.3	0.446 5.5 10.6 268 2.53 - 0.467 6.2 10.7 290 2.49 4.69 0.46 6.7 10.3 310 2.49 4.68 0.471 7 10 350 2.45 4.62 0.47 7.5 9.8	0.408 6.7 10.3 325 2.42 4.63 0.412 7.3 10.1 330 2.39 4.57 0.421 8.1 10 340 2.35 4.58 0.427 8.6 9.4 357 2.43 4.59 0.43 9.1 9 2.5 2.43 4.59 0.43 9.1 9 2.5 2.43 4.59 0.43 9.1 9 2.5 2.43 4.59 0.43 9.1 9 2.5 2.43 4.59 0.43 9.1 9 2.55 2.42 4.59 0.43 9.4 3.57 2.43 4.59 0.43 9.4 3.57 3.5	0.405 6 10.6 315 2.44 4.69 0.425 6.5 10.3 325 2.4 4.67 0.417 7 9.8 335 2.4 4.61 0.422 7.7 9.5 353 2.453 4.6 0.43 8 9 9.5 355 2.453 4.6 0.43 8 9 9.5 355 2.453 4.6 0.43 8 9 9.5 10.5	0.404 5.6 10.6 285 2.43 4.73 0.415 6.2 10.5 320 2.43 4.71 0.418 6.8 10 330 2.45 4.76 0.424 7.2 9.6 351 2.49 4.56 0.43 7.8 9.5		3000 2900 2800 2700
VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC BP Tq VE CO CO CO CO CO CO CO CO CO CO CO CO CO	0.272 6.6 10.2 341 2.453 4.68 0.27 7.5 9.8 343 2.422 4.62 0.265 8.2 9.3 357 2.399 4.58 0.262 8.7 8.9 365 2.389 4.56 0.255 9.2 8.6 379	$\begin{array}{c} 0.279\\ 6.9\\ 10.4\\ 339\\ 2.506\\ 4.79\\ 0.267\\ 7.2\\ 9.9\\ 341\\ 2.478\\ 4.76\\ 0.262\\ 8.1\\ 9.3\\ 350\\ 2.432\\ 4.71\\ 0.257\\ 8.6\\ 8.9\\ 361\\ 2.417\\ 4.66\\ 0.252\\ 9\\ 8.7\\ 375 \end{array}$	0.269 6.5 10.5 325 2.522 4.81 0.268 6.8 9.9 334 2.481 4.78 0.265 7.3 9.5 344 2.465 4.71 0.26 8.2 9.2 355 2.447 4.63 0.277 8.5 8.8 372	0.418 5.7 10.6 310 2.545 4.86 0.438 6.2 10.2 331 2.517 4.81 - 7 9.7 340 2.503 4.74 0.458 7.3 9.5 350 2.495 4.67 0.467 7.5 9.3 369	0.274 5.6 10.3 240 2.5 4.77 0.27 6.4 10.1 293 2.46 4.7 0.266 7.2 10 300 2.42 4.62 0.263 8.3 9.4 313 2.44 4.67 0.252 8.8 9 328	0.428 5.1 11.2 301 2.491 4.64 0.445 6.3 10.6 314 2.494 4.62 0.456 6.8 10.3 320 2.458 4.56 0.464 7.4 9.9 327 2.45 4.62 0.473 7.6 9.3 338	0.446 5.5 10.6 268 2.53 - 0.467 6.2 10.7 290 2.49 4.69 0.46 6.7 10.3 310 2.49 4.68 0.471 7 10 350 2.45 4.62 0.47 7.5 9.8 356	0.408 6.7 10.3 325 2.42 4.63 0.412 7.3 10.1 330 2.39 4.57 0.421 8.1 10 340 2.35 4.58 0.427 8.6 9.4 357 2.43 4.59 0.43 9.1 9 370	$\begin{array}{c} 0.405\\ 6\\ 10.6\\ 315\\ 2.44\\ 4.69\\ 0.425\\ 6.5\\ 10.3\\ 325\\ 2.4\\ 4.67\\ 0.417\\ 7\\ 9.8\\ 335\\ 2.4\\ 4.61\\ 0.422\\ 7.7\\ 9.5\\ 353\\ 2.453\\ 4.6\\ 0.43\\ 8\\ 9\\ 365 \end{array}$	$\begin{array}{c} 0.404\\ 5.6\\ 10.6\\ 285\\ 2.43\\ 4.73\\ 0.415\\ 6.2\\ 10.5\\ 320\\ 2.43\\ 4.71\\ 0.418\\ 6.8\\ 10\\ 330\\ 2.45\\ 4.76\\ 0.424\\ 7.2\\ 9.6\\ 351\\ 2.49\\ 4.56\\ 0.43\\ 7.8\\ 9.5\\ 358\\ \end{array}$		3000 2900 2800 2700 2600
VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC BP Tq VE CO CO CO CO CO CO CO CO CO CO CO CO CO	0.272 6.6 10.2 341 2.453 4.68 0.27 7.5 9.8 343 2.422 4.62 0.265 8.2 9.3 357 2.399 4.58 0.262 8.7 8.9 365 2.389 4.56 0.255 9.2 8.6 379 2.42	$\begin{array}{c} 0.279\\ 6.9\\ 10.4\\ 339\\ 2.506\\ 4.79\\ 0.267\\ 7.2\\ 9.9\\ 341\\ 2.478\\ 4.76\\ 0.262\\ 8.1\\ 9.3\\ 350\\ 2.432\\ 4.71\\ 0.257\\ 8.6\\ 8.9\\ 361\\ 2.417\\ 4.66\\ 0.252\\ 9\\ 8.7\\ 375\\ 2.45\\ \end{array}$	0.269 6.5 10.5 325 2.522 4.81 0.268 6.8 9.9 334 2.481 4.78 0.265 7.3 9.5 344 2.465 4.71 0.26 8.2 9.2 355 2.447 4.63 0.277 8.5 8.8 372 2.471	0.418 5.7 10.6 310 2.545 4.86 0.438 6.2 10.2 331 2.517 4.81 - 7 9.7 340 2.503 4.74 0.458 7.3 9.5 350 2.495 4.67 0.467 7.5 9.3 369 2.519	0.274 5.6 10.3 240 2.5 4.77 0.27 6.4 10.1 293 2.46 4.7 0.266 7.2 10 300 2.42 4.62 0.263 8.3 9.4 313 2.44 4.67 0.252 8.8 9 328 2.46	0.428 5.1 11.2 301 2.491 4.64 0.445 6.3 10.6 314 2.494 4.62 0.456 6.8 10.3 320 2.458 4.56 0.464 7.4 9.9 327 2.45 4.62 0.473 7.6 9.3 338 -	0.446 5.5 10.6 268 2.53 - 0.467 6.2 10.7 290 2.49 4.69 0.46 6.7 10.3 310 2.49 4.68 0.471 7 10 350 2.45 4.62 0.47 7.5 9.8 356 2.47	0.408 6.7 10.3 325 2.42 4.63 0.412 7.3 10.1 330 2.39 4.57 0.421 8.1 10 340 2.35 4.58 0.427 8.6 9.4 357 2.43 4.59 0.43 9.1 9 370 2.24	$\begin{array}{c} 0.405\\ 6\\ 10.6\\ 315\\ 2.44\\ 4.69\\ 0.425\\ 6.5\\ 10.3\\ 325\\ 2.4\\ 4.67\\ 0.417\\ 7\\ 9.8\\ 335\\ 2.4\\ 4.61\\ 0.422\\ 7.7\\ 9.5\\ 353\\ 2.453\\ 4.6\\ 0.422\\ 7.7\\ 9.5\\ 353\\ 2.453\\ 4.6\\ 0.43\\ 8\\ 9\\ 365\\ 2.26\\ \end{array}$	$\begin{array}{c} 0.404\\ 5.6\\ 10.6\\ 285\\ 2.43\\ 4.73\\ 0.415\\ 6.2\\ 10.5\\ 320\\ 2.43\\ 4.71\\ 0.418\\ 6.8\\ 10\\ 330\\ 2.45\\ 4.76\\ 0.424\\ 7.2\\ 9.6\\ 351\\ 2.49\\ 4.56\\ 0.43\\ 7.8\\ 9.5\\ 358\\ 2.45\\ \end{array}$		3000 2900 2800 2700 2600
VE CO CO <sub>2</sub> UHC BP Tq VE CO CO <sub>2</sub> UHC BP Tq VE CO CO CO <sub>2</sub> UHC BP Tq VE CO CO CO CO Tq UHC BP Tq VE CO CO CO Tq Tq VE CO CO CO Tq UHC BP Tq VE CO CO CO Tq Tq Tq VE CO CO CO Tq Tq Tq Tq Tq Tq CO CO CO Tq Tq Tq Tq Tq Tq Tq	0.272 6.6 10.2 341 2.453 4.68 0.27 7.5 9.8 343 2.422 4.62 0.265 8.2 9.3 357 2.399 4.58 0.262 8.7 8.9 365 2.389 4.56 0.255 9.2 8.6 379 2.42 4.52	$\begin{array}{c} 0.279\\ 6.9\\ 10.4\\ 339\\ 2.506\\ 4.79\\ 0.267\\ 7.2\\ 9.9\\ 341\\ 2.478\\ 4.76\\ 0.262\\ 8.1\\ 9.3\\ 350\\ 2.432\\ 4.71\\ 0.257\\ 8.6\\ 8.9\\ 361\\ 2.417\\ 4.66\\ 0.252\\ 9\\ 8.7\\ 375\\ 2.45\\ 4.61\\ \end{array}$	0.269 6.5 10.5 325 2.522 4.81 0.268 6.8 9.9 334 2.481 4.78 0.265 7.3 9.5 344 2.465 4.71 0.26 8.2 9.2 355 2.447 4.63 0.277 8.5 8.8 372 2.471 4.61	0.418 5.7 10.6 310 2.545 4.86 0.438 6.2 10.2 331 2.517 4.81 - 7 9.7 340 2.503 4.74 0.458 7.3 9.5 350 2.495 4.67 0.467 7.5 9.3 369 2.519 4.6	0.274 5.6 10.3 240 2.5 4.77 0.27 6.4 10.1 293 2.46 4.7 0.266 7.2 10 300 2.42 4.62 0.263 8.3 9.4 313 2.44 4.67 0.252 8.8 9 328 2.46 4.7	0.428 5.1 11.2 301 2.491 4.64 0.445 6.3 10.6 314 2.494 4.62 0.456 6.8 10.3 320 2.458 4.56 0.464 7.4 9.9 327 2.45 4.62 0.454 5.1 10.3 320 2.458 4.56 0.464 7.4 9.9 327 2.45 4.62 0.473 7.6 9.3 338 - 4.72	$\begin{array}{c} 0.446\\ 5.5\\ 10.6\\ 268\\ 2.53\\ \hline\\ 0.467\\ 6.2\\ 10.7\\ 290\\ 2.49\\ 4.69\\ 0.46\\ 6.7\\ 10.3\\ 310\\ 2.49\\ 4.68\\ 0.471\\ \hline\\ 7\\ 10\\ 350\\ 2.45\\ 4.62\\ 0.47\\ \hline\\ 7.5\\ 9.8\\ 356\\ 2.47\\ 4.61\\ \end{array}$	$\begin{array}{c} 0.408\\ 6.7\\ 10.3\\ 325\\ 2.42\\ 4.63\\ 0.412\\ 7.3\\ 10.1\\ 330\\ 2.39\\ 4.57\\ 0.421\\ 8.1\\ 10\\ 340\\ 2.35\\ 4.58\\ 0.427\\ 8.6\\ 9.4\\ 357\\ 2.43\\ 4.59\\ 0.43\\ 9.1\\ 9\\ 370\\ 2.24\\ 4.54\\ \end{array}$	$\begin{array}{c} 0.405\\ 6\\ 10.6\\ 315\\ 2.44\\ 4.69\\ 0.425\\ 6.5\\ 10.3\\ 325\\ 2.4\\ 4.67\\ 0.417\\ 7\\ 9.8\\ 335\\ 2.4\\ 4.61\\ 0.422\\ 7.7\\ 9.5\\ 353\\ 2.453\\ 4.6\\ 0.43\\ 8\\ 9\\ 365\\ 2.26\\ 4.62\\ \end{array}$	$\begin{array}{c} 0.404\\ 5.6\\ 10.6\\ 285\\ 2.43\\ 4.73\\ 0.415\\ 6.2\\ 10.5\\ 320\\ 2.43\\ 4.71\\ 0.418\\ 6.8\\ 10\\ 330\\ 2.45\\ 4.76\\ 0.424\\ 7.2\\ 9.6\\ 351\\ 2.49\\ 4.56\\ 0.43\\ 7.8\\ 9.5\\ 358\\ 2.45\\ 4.67\\ \end{array}$		<ul> <li>3000</li> <li>2900</li> <li>2800</li> <li>2700</li> <li>2600</li> </ul>

## Table 3.18: Vehicle Emissions [21]

G: gasoline; E3, E7 and E10: 3,7 and 10 vol.% ethanol in gasoline; M3, M7 and M10: 3,7 and 10 vol.% methanol in gasoline; EM3, EM7 and EM10: 3,7 and 10 vol.% ethanol and methanol in gasoline; CO and  $CO_2$  in vol.%; UHC in ppm. BP is brake power in KW, Tq is torque in Nm and VE is volumetric efficiency.

## Ternary Blends [24, 25]

Few Methanol Ternary Blends studied in different research are:

- 1. 6% Ethanol, 6% Methanol, 88% Gasoline
- 2. 3% & 10% ethanol & methanol in gasoline
- 3. 53% Methanol, 17% Butanol & 30% Gasoline
- 4. 5% Methanol, 5% Butanol, 90% Gasoline

#### Advantages of Ternary Blends:

- 1. Butanol & Methanol can complement each other for e.g. reduction of evaporative emissions.
- 2. In few experiments, engine performance improved than pure gasoline
- 3. Unburnt Hydrocarbons reduced

#### **Disadvantages of Ternary Blends:**

- 1. Few experiments revealed a decreased engine performance as compared to pure gasoline
- 2. Higher  $CO, NO_X$  and  $CO_2$  emissions than those of dual blends
- 3. Fuel consumption increases as compared to gasoline or dual blend systems.
- 4. Ternary blends provide lower BTE than M70 a higher brake fuel consumption than gasoline.

Air to fuel ratios are provided below

- Pure gasoline : 14.8
- Methanol : 6.4
- Ethanol : 9
- Butanol : 11.2

Methanol has the lowest A/F ratio signifying than dual fuel blends run on leaner air systems.

For lower level blends ( $\leq 15\%$ ) following modifications are essential:

- 1. Corrosion inhibitors
- 2. Fuel system (non-metal parts)

For High Level blends (≤ 85%), following modifications are imperative

- 1. Wetted system & surfaces
- 2. Fueling equipment

Central Pollution Control Board [26] commissioned a study to evaluate the emission performance of Methanol-Gasoline Blend through Indian Institute Of Petroleum, Dehradun in 1995-96 and their observations are as under:

Emissions, mg/km	Gasoline	M85	M100
FTP cycle			
THC	161.59	111.87	124.3
СО	733.37	683.65	870.11
Nox	490.99	379.12	285.89
Evaporative emission (mg/test)	1720	680	880
FTP test			
Benzene	7.79	4.38	0.32
Toluene	33.66	8.66	2.11
Buta-1-3-diene	0.19-0.50	0.44	2.05
Formaldehyde	4.78	13.87	21.76
Acetaldehyde	0.94	10.02	0.27

Table-3.19: Emissions form gasoline, M85 and M100 in a FTP Cycle

Source: AFDC

Volvo in their evaluation of DME and Methanol as fuel gives both fuels a high positive rating for climate impact, energy efficiency, fuel potential, vehicle adjustment and fuel costs as compared to other fuels. The key area which has to be addressed is the fuel infrastructure.

## 3.5.5 Phase Stability and Material Compatilibility [27, 28]

## 3.5.5.1 Phase stability

As is common for most alcohols blended in gasoline, methanol is fully soluble in water and also miscible with gasoline-type hydrocarbons (HC). The additions of some co-solvent alcohols (ethanol, propanols, or butanols) are generally required in methanol gasoline blends to provide adequate water tolerance (solubility) or phase stability under colder temperature conditions. As with most gasoline and alcohol fuel blends, inhibitors or additives are generally recommended with methanol blends to provide added protection against metal corrosion. Properly blended gasoline with methanol is typically compatible with materials commonly used in gasoline distribution systems as well as vehicle fuel systems.

Extensive product research, as well as years of commercial experience, indicate that properly blended methanol in gasoline has no adverse effect on vehicle performance. In fact, methanol-gasoline blends have cleaner burning properties that generally reduce CO, HC, PM and air toxics from most gasoline engine vehicles.

## 3.5.5.2 Material Compatibility

Many suppliers of fuel system components have examined the effect of gasoline blends at higher concentrations of methanol on various materials used in automotive fuel systems and in gasoline distribution systems. Also, considerable commercial experience for 5% methanol blends was acquired during the early 1980's. Except for a few materials, no significant detrimental effects were noted for most of the tested materials or those used in commercial practice. Based on experience developed by the oil refining industry, Table 3.7 lists the recommendations for commonly used materials in the storage, handling and distribution of gasoline that may contain 5% methanol.

Table 3.20a: Material Compatibility of Commonly Used Materials with Gasoline/ Mechanical/

Recommended	Not Recommended
Metals	
Aluminum	Galvanised metals
Carbon Steel	
Stainless Steel	
Bronze	
Elastomers	
Buna-N TM*	Buna-N TM*
Flurel TM	
Fluorosilicone	
Neoprene*	Neoprene*
Polysulfide Rubber	
Viton TM	
Polymers	
Acetal	Polyurethane
Nylon	Alcohol-based pipe dome
Teflon TM	
Fiberglass-reinforced	

Co-solvent Blends

\* = works fine for hoses and gaskets but not seals

Source: Methanol Institute

Material compatibility issues are a major concern for high level (>85%) Methanol in combustion engine for e.g. PU must be replaced by elastomers in vehicles systems. The material compatibility of low and high level methanol in gasoline is provided in Table 3.19b.

S. No.	Issue concern	Low Level (<5%)	High (>85%)
1.	Material compatibility <sup>a</sup>	No	Yes
2.	Fuel volatility <sup>b</sup>	Yes	Yes
3.	Lower Energy Density	No	Yes
4.	Blending with Ethanol	Yes	No
5.	Standards based on (4)	Yes	No
6.	Emission Reduction (Significant)	No	No
7.	Vehicle Retrofication cost	No	Yes
8.	Feasibility of utilizing in present fleet	No	Yes
9.	Storage & Distribution	No	Yes
10.	Fueling Station	No	Yes
11.	Public Safety	No	Yes

Table 3.20b: Material Compatibility of Methanol in low level and high level blends with Gasoline

\*Source: Methanol Fuel Blending & Methanol Compatibility Report, Methanol Institute, 2011

a = vehicle side & fueling infrastructure

b = increase in vapour pressure

## 3.6 GLOBAL METHANOL FUEL BLENDING REGULATIONS

In many regions of the globe, the blending of oxygenates such as alcohols and ethers is controlled by government regulations that specify the limits for the various oxygenates allowed in commercial gasoline. The maximum levels of oxygen from oxygenates in gasoline have generally been established to maintain and ensure the fuel blend's drivability performance in the vehicle fleet operating on the road at the time when the regulations had been implemented.

Table 3.21 summarizes the current fuel regulations for blending methanol in major gasoline market regions. Oxygenate blending regulations established in the 1980's in Europe and the U.S. set a maximum oxygen limit of 3.7 wt%, which reflects the drivability performance limits of the carburetted fuel metering systems that existed at the time. More recently, some provinces in China have established methanol blends with oxygen levels that are about twice as high as those established in the 1980's in Europe and the U.S. markets. The higher allowable oxygen levels in Chinese gasoline markets reflects the greater flexibility of current vehicle fuel system technology, which employs high pressure, multi-port fuel injection systems with computerized feedback control loops using oxygen sensors.

As a result of these advancements in fuel metering technology and improved materials, the vehicles on the road today can manage a wider range of oxygen levels and alcohol content in fuel without suffering a loss in drivability performance.

Table 3.21: Approved Methanol Gasoline Blends with Requirements for Co-solvent Alcohols
and Additives [28]

Market Region		Introduction Year	Maximum Volume % Methanol	Minimum Volume % Co-solvent	Maximum Wt % Oxygen	Corrosion Additives
U.S.A.	Sub Slim *	1979	2.75	> Methanol	2.00%	
U.S.A.	Fuel Waiver	1981	4.75	> Methanol	3.50%	Required
U.S.A.	Fuel Waiver	1986	5	2.5	3.70%	Required
Europe	EC Directives	1985	3.0	> Methanol	3.70%	
China	M 15	2007	15	For Water	-7.90%	Required
Shanxi	Standard			Tolerance		
* US EPA's S	Substantially Simila	ar for Regulatior	ו Commercial g	asoline		

Source: Methanol Institute Guidelines

#### Methanol as a fuel blend in other countries

- Australia : A15 (12% methanol, 3% ethanol, 85% gasoline)
- Israel : M15 & proposed M70
- Uzbekistan : M3 & M5 fuel blends

## 3.6.1 Global Methanol Transportation Initiatives [29, 30, 31]

Methanol blend fuel and pure methanol fuel are actually one of the very first types of alternative fuels available. The discovery of large global natural gas deposits, and cheap coal prices, methanol fuel blending research, pilot programs on methanol fueled vehicles, and other initiatives are becoming increasingly popular, particularly within the APMECA (Asia Pacific, Middle East, and Central Asian) region, where the need for reducing reliance on imported-oil is very critical. A drawback in mixing alcohols with diesel like methanol is the separation of two liquids very easily for which an emulsifier is needed to stabilise the blend.

#### 3.6.1.1 Australia

Australia has been testing GEM (Gasoline-Ethanol-Methanol) fuel blends in recent years; the test of A15 fuel (12% methanol, 3% ethanol, 85% gasoline) in non-modified cars has been running since 2012.

The Coogee (Coogee Energy Pty Ltd), methanol fuel blending research program involves an extensive laboratory test program in conjunction with a fleet of trial vehicles operating on various petrol methanol blend fuels. It is currently one of the largest, if not the longest, research programs into fuels and emissions in Australia.

The program reports annually and is informed by stakeholder engagement roadshows involving all levels of the Australian petrochemical industry, the automotive manufacturing and engineering industry, government regulators and consumer groups. Like ethanol, methanol is an alcohol which can be used as a liquid transportation fuel, either by itself or when blended with other fuels such as petrol.

Petrol-methanol blend fuels have a long history internationally, and are permitted for use in both Europe1 and the United States2 (among other countries). Such fuels are not prohibited in Australia, but do not easily fit within current State and Commonwealth fuel regulations which are based on petrol and petrol-ethanol blends.

Coogee is exploring the commercialisation of four methanol containing fuel blends:

- GEM6 (94% ULP, 3% methanol, 3% ethanol)
- GEM8 (92% ULP, 5% methanol, 3% ethanol)
- GEM15 (85% ULP, 12% methanol, 3% ethanol)
- GEM56 (56% methanol, 44% ULP)

## 3.6.1.2 Israel

In Israel, the need for energy security and environmental protection has pushed the country to complete successful M15 vehicle pilot program tests. More recently, Israeli government has also launched research on the potentiality of M70 fuel. Given the fact that Israel has just discovered two major gas fields, Leviathan and Tamar, with a combined reserve of roughly 700 billion cubic meters of natural gas, the development in methanol-blend fuel seems more promising than ever.

## 3.6.1.3 Central Asia

In Central Asia, which is extremely rich in natural gas deposits, countries are trying to mitigate high fuel price and utilize these assets through the development of methanol fuel and other related derivatives. Uzbekistan has tested M3 and M5 fuel blends, and Azerbaijan has constructed Central Asia's first methanol production in 2013.

#### 3.6.1.4 Europe

In Europe, 3% methanol in European gasoline standards is in place. The European Commission initiated the Renewable Energy Directive in 2009 to promote the application of renewable energy within Europe; the Directive has established an overall policy that requires EU to fulfill at least 20% of its total energy needs with renewable energy by 2020. In 2013, the Junior World Rally Championship (Junior WRC) used methanol-ethanol-gasoline mixture (37 %, 21% & 42% respectively)

#### 3.6.1.5 China

Lastly, China, the world's largest consumer and producer of methanol, has taken initiatives throughout the nation to promote methanol fuels standards ranging from M5 (5% methanol, 95% gasoline) to M100. China's Ministry of Industry and Information Technology (MIIT) announced the creation of a two-year pilot program in Shanxi and Shaanxi Provinces and in Shanghai in 2012, aiming at the development and promotion of M85-fuelled vehicles. In 2014, the MIIT further expand this initiative to include Gansu and Guizhou Provinces. The project has since expanded to several more locations and now comprises over 1000 vehicles in total. The Geely model SC7 used in the Pilot has met all initial drivability targets; ignition, driving, fuel shift, acceleration and durability. Emissions have met the China National 4 standard (equivalent to Euro 4), and formaldehyde emissions meet the MIIT requirement of 10mg/km. One fuel filling has allowed as much as a 320 km range, and average fuel usage is 15.3L M100/100km. Outside of the MIIT Pilot, there are now 470,000 taxis, trucks and buses running on high proportion methanol fuels across China. The number of used cars modified from gasoline to methanol has been accumulated is about 120000 units, with more than 30000 units in Shanxi province. Many provinces involves methanol utility for cars, such as Shanghai, Shaanxi, Guizhou, Henan, etc

The various methanol blends operating in different provinces of China is provided in Table 3.22:

Province	Local Methanol	Implemented
	Gasoline Standards	Since
Gansu	M15 & M30	2009
Guizhou	M15	2010
Hebei	M15 & M30	2010
Heilongjiang	M15	2005
Jiangsu	M45	2009

Table 3.22: Methanol blend	s in Chir	na for Road	Transportation	[32]
----------------------------	-----------	-------------	----------------	------

Liaoning	M15	2006
Shaanxi	M15 & M25	2004
Shandong	M15	2012
Shanghai	M100	2013
Shanxi	M5, M15, M85 & M100	2008
Sichuan	M10	2004
Xinjiang	M15 & M30	2007
Zhejiang	M15, M30 & M50	2009
Ningxia	M15 & M30	2014

Source: Methanol Institute, Stratas Advisors, January 2015

## 3.6.2 Indian Initiative on Methanol [33]

Indian Institute of Petroleum (IIP) in 1983-1986 conducted a fleet trail with M12 under the UNDP/UNIDO assisted programme on alternate fuel. M12 gasoline blend was used as the fuel in this study on 14 two wheelers of various makes. IIP also carried out some experimental studies on the two wheelers with methanol gasoline blends upto 20 %.

## Findings of the studies are summarized below:

- Operation beyond or over 15% methanol- gasoline blends was erratic and the engine started misfiring and hunting.
- With M15 it showed marginally better output and 3-4% improvement in fuel consumption.
- It established that upto 15% blends can be used without any engine modifications.
- Substantial reduction in carbon monoxide was recorded.
- No hot or cold driveability problems with M12 blends.
- Engine performance of M12 vehicles was found comparable to that of gasoline vehicles.
- Increase of wear with cast iron rings was observed.

In the year 1992, BIS standard was amended to facilitate the use of methanol in gasoline. Indian oil companies initiated a pilot scale project in November 1993 to market a methanolpetrol blend of 3% methanol called Petrol-M. This product was supplied from 10 selected retail outlets in the city of Baroda in Gujarat. Initially this project was taken up for a period of one year.

## The key findings of this project are:

- Blending, transportation and quality wise Petrol-M trail marketing was successful.
- A total quantity of 376 kl of the product was sold.
- It was comfortably used by cars, two-wheelers and three-wheelers.
- To tackle the apprehended problem of corrosive effect of methanol on engine parts, the oil industry used corrosion inhibitors.

CPCB also commissioned a study to evaluate the emission performance of methanolgasoline blends through IIP sometimes in 1995-96. CPCB estimated that if all the petrol driven vehicles in Delhi use a methanol-gasoline blend of 3% methanol and 97% gasoline, it may be possible to have 11% reduction in hydrocarbons emissions, 7% CO reduction and 30% NOx reduction compared to pure gasoline driven vehicles.

## 3.6.3 Adaptation for existing vehicles [24, 33]

Lower level methanol-blends (M5, M10, M15) can be directly used in most existing vehicles with little to no modification, as industry experience confirms. The small range of modifications that may need to be pursued are upgrades to the non-metal parts of the fuel system for anti-corrosiveness, the installation of corrosion inhibitors and the use of corrosion inhibitors and some co-solvent alcohols for increasing water tolerance. Although older vehicles with carbureted fuel systems (non-pressurized) would be negatively impacted in drivability with the addition of methanol, vehicles with fuel injector systems (pressurized) are relatively insensitive to the addition of methanol.

Since most of the global automakers are producing vehicles with fuel injection systems, the use of lower level methanol blend would produce little impact on the vehicles on the road. Additionally, by altering the computer program for fuel injection system, a car can be easily converted into a flexible fuel vehicle with adaptive mechanisms that allow it to use both methanol and gasoline at maximum energy output.

## 3.6.4 Advantages and Disadvantages

The advantages & disadvantages of Methanol as a fuel have been summarized as under:

## Advantages of Methanol

- Methanol has very lower ozone forming potential.
- Emissions of sulphur and sulphur compounds are virtually negligible.
- Very low evaporative emissions due to its low vapour pressure.
- Easy refueling.

- Methanol is the most practical carrier of hydrogen to run fuel cells.
- Methanol has high-octane quality.
- Easy availability of feedstock viz. coal, bio-mass & Black liquor etc.
- Methanol is quite cheaper compare to gasoline.

#### **Disadvantages of Methanol**

- High formaldehyde emissions.
- Acute toxicity.
- Low energy content compared to gasoline.
- Demands special lubricants and spare parts.

## 3.7 METHANOL FOR BIODIESEL

Another application for methanol in transportation is its crucial role in the production of environmentally-friendly bio diesel fuel.

In the process of making biodiesel fuel, methanol is used as a key component in a process called transesterification - methanol is used to convert the triglycerides in different types of oils into usable biodiesel fuel. In trans-esterification process [35] methanol react with the triglyceride contained in vegeTable oils, animal fats, or recycled greases, forming fatty acid alkyl esters (biodiesel) and the byproduct glycerin. The reaction is:

 $Oil + alcohol \rightarrow biodiesel + glycerin$ 

In other words, the refined bleached and deodorized oil is reacted with methanol to yield biodiesel as the main product with Glycerin as byproduct. The distillation plant enables recovery of solvent.

Several experiments have concluded that the best results of biodiesel are obtained when methanol is used. One such research undertaken by the scientists at the Kocaeli University, Department of Automotive engineering [36] on the effects of different alcohols and feedstocks revealed that the best results were obtained when an alkaline catalyst (sodium hydroxide) is utilized with methanol as the alcohol.

In terms of costs, a paper by Kulchanat Kapilakarn [37] on Comparison of Costs of Biodiesel Production from Transesterification states that methanol costs contribute about 15% of the total manufacturing expenses, while a good purity and costs balance is achieved at methanol to oil molar ratio of 6:1, at 70°C for 20 minutes with recovery of methanol. The study was based on palm oil.

## 3.7.1 Specifications

There are several **ASTM and EN specifications** available for bio-diesel depending on percentage blending. The first ASTM standard (ASTM D6751) was adopted in 2002. The ASTM specification for biodiesel is ASTM D 6751; in the EU, it is EN 14214. ASTM D6751-15a specifies quality for B100, 100% biodiesel. ASTM D7467-13 provides specification for B6 to B20. Blends up to 7% of fatty acid methyl ester (FAME) are allowed in diesel fuel defined by EN 590 (2009). EN 16709, introduced in 2015, covers B20 and B30 blends for use by captive fleets. The FAME component in EN 16709 is required to comply with EN 14214 and the diesel component with EN 590. The Methanol institute in this biodiesel primer
reports that few manufacturers in Europe have sanctioned the use of certain vehicles with B100 or B30 fuels, but the majority of vehicles are only approved for use with EN590 diesel, which contains a maximum of 7 vol% biodiesel.

**The Indian standard, IS 15607: 2005,** provides the specification of using B100 with diesel fuel meeting the requirements of IS 1460 'Automotive diesel fuel — Specification'

The Ministry of Road Transport and Highways (MoRTH), Govt. of India [38] came out with Central Motor Vehicles (Fourth Amendment) Rules, 2016 issued on 11<sup>th</sup> April, 2016 which provides the specification of B100.

# Mass emission standards for bio-diesel (B100)

- (1) The newly manufactured vehicles fitted with compression ignition engine compatible to run on diesel or mixture of bio-diesel up to hundred per cent Bio-diesel (B100) (hereinafter referred to as flex-fuel bio-diesel vehicle), shall be type approved as per prevailing diesel emission norms.
- (2) The compatibility of vehicle to level of bio-diesel blend or B100 shall be specified by the vehicle manufacturer and the same shall be displayed on vehicle by putting a clearly visible sticker.

S.No	Characteristic	Requirement	Method of Test, reference to	
1	Density@ 15 <sup>0</sup> C, kg/m3	860-900	ISO 3675 ISO 12185 D 4052	[P:16/P:32]
2	Kinematic Viscosity @ 40 0C, cSt	2.5-6.0	ISO 3104	[P:25]
3	Flash Point, Pensky-Martens Closed – Cup test(PMCC)0C , minimum	120	ISO 3679	[P:21]
4	Sulphur, mg/kg, maximum	10	D 5453	[P:83]
5	Carbon residue (Ramsbottom)(1) per cent by mass, maximum	0.05	D 4530 ISO 10370	
6	Sulphated ash, per cent by mass, maximum	0.02	ISO 6245	[P:4]
7	Water content, mg/kg, maximum	500	D 2709 ISO 3733 ISO 6296	[P:40]
8	Total contamination, mg/kg, maximum	24	EN 12662	
9	Copper corrosion 3 hours @ 500C, maximum	1	ISO 2160	[P:15]
10	Cetane No., minimum	51	ISO 5165	[P:9]
11	Acid value, mg KOH/g, maximum	0.5	EN 14101	[P:1/sec 1]

Table 3.23: B100 (Biodiesel) fuel specification, MoRTH, Govt. of India [38]

# TIFAC, DST, Govt. of India | Utilisation issues of Methanol and DME

12	Methanol(2), per cent by mass, maximum	0.2	EN 14110	
13	Ethanol(3), per cent by mass, maximum	0.2		
14	Ester content, per cent by mass, minimum	99.5	EN 14103	
15	Free Glycerol, per cent by mass, maximum	0.02	D 6584	
16	Total Glycerol, per cent by mass, maximum	0.25	D 6584	
17	Phosphorus, mg/kg, maximum	10	D 4951	
18	Sodium and Potassium , mg/kg, maximum	To report	EN 14108 and EN 14109	
19	Calcium and Magnesium, mg/kg,	To report	-4	
	maximum			
20	lodine value	To report	EN 14111	
21	Oxidation stability at 110	0C, h,	6	EN 14112
	minimum			
22	Mono-glyceride content, per	0.05	EN 14105	
	cent by mass, maximum			
23	Di-glyceride content, per cent by mass, maximum	0.01	EN 14105	
24	Tri-glyceride content, per cent	0.01	EN 14105	
	by mass, maximum			

Source: MoRTH, Govt. of India

# 3.7.2 Indian Scenario

The Government of India (GOI) approved the National Policy on Biofuels on December 24, 2009. The policy encourages use of renewable energy resources as alternate fuel to supplement transport fuels and had proposed an indicative target to replace 20 percent of petroleum fuel consumption with biofuels (bioethanol and biodiesel) by end of 12th Five-Year Plan (2017).

A recent government draft notification on use of bio-diesel allows the newly manufactured vehicles fitted with compression ignition engine compatible to run on diesel or mixture of bidiesel up to 100% bio-diesel will be type approved as per the prevailing diesel emission standards

The Government of India launched its biodiesel programme in 2015 as part of its efforts to cut energy imports and carbon emissions. It involved, as a part of initial run, selling of the biodiesel B5 blend to customers in some retail outlets of state-owned oil marketing companies (OMCs) in New Delhi, Vishakhapatnam, Haldia and Vijayawada. The Ministry of Petroleum and Natural gas has permitted direct sale of Biodiesel (B100) to bulk consumers like Railways, shipping and State Road Transport Corporations etc

In October 2015, the biodiesel inputs that are specifically listed as now exempt from the 12.5 percent central excise tax are refined, bleached and deodorized (RBD) palm stearin, methanol, and sodium methoxide.

Fuel scenario for India is provided in Table 3.24. It can be observed that the diesel requirement as a transportation fuel is projected to be 69 billion liters in 2020. India's bio-fuel production currently accounts for nearly 1 percent of global production.

Diesel demand increased by 7.5% to 74.6 million tonnes during 2015-16, and is projected to further go up by 7.7% to 78.11 million tonnes in 2016-17.

Calendar Year	2015	2016	2017	2018	2019	2020	2021	2022	2023
		1		B	illion liter	'S	1	1	1
Gasoline Total	28	30	32	35	37	40	43	47	50
Diesel Total	94	97	101	106	110	115	119	124	129
On-road	56	58	61	63	66	69	72	74	78
Agriculture	11	12	12	13	13	14	14	15	16
Construction	4	4	4	4	4	5	5	5	5
/mining									
Shipping/rail	5	5	5	5	5	6	6	6	6
Industry	10	11	11	12	12	13	13	14	14
*Heating	7	8	8	8	9	9	10	10	10
Jet Fuel Total	8	9	10	10	11	12	13	14	15
Total Fuel	130	136	143	151	159	167	176	185	195
Markets									

Table 3.24: Fuel Scenario in India [44]

Source: USDA, Ministry of Petroleum and Natural Gas

As per USDA [44] estimates based on industry and stakeholders feedback, currently, India has 5-6 large capacity plants (10,000 to 250,000 MT per year) currently utilizing 28 percent of the installed capacity to produce <u>125-140 million liters of biodiesel</u> from multiple feed-stocks such as inedible vegeTable oils, unusable edible oil waste (used-once), and animal fats. As per Emami Agrotech, which has a 300 TPD biodiesel plant in India, the total production capacity of all units was 1,500 TPD, while the combined production was only 500 TPD. Capacity utilisation of Emami plant at Haldia remained at 100 TPD (33%)

The biodiesel thus produced is purchased by small and medium enterprises, sold to experimental projects carried out by automobiles and transport companies (state sponsored or private trial runs), apart from minor sales to unorganized consumers such as cellular communication towers, brick kilns, progressive farmers, and to institutions that run diesel generators as source of power back-up.

The National Policy on Biofuels had proposed a 20% blending ratio for both biodiesel and ethanol by 2017. However, the current Government has decided to allow 100% bio-diesel for vehicles citing its low pollution level and less reliance on imported crude fuel.

As per Economic Times report (June 2016), [45] Mercedes in a communication to the Ministry of Transport has stated that their SUVs can run on 100% Biodiesel. The biodiesel scenario in India is provided in Table 3.25.

Calendar Year	2009	2010	2011	2012	2013	2014	2015	2016
Poginning Stooko		45	20	42	45	45	50	45
	0	40	30	42	40	40	50	40
Production	75	90	102	115	120	130	135	140
Imports	0	0	0	0	0	0	0	0
Exports	0	0	0	0	0	0	0	0
Consumption	30	52	60	70	75	80	90	100
Ending Stocks	45	38	42	45	45	50	45	85
		L	Product	ion	L	L		ı
Number of	F	F	F	F	C	C	G	6
Biorefineries	Э	5	5	5	0	0	0	0
Nameplate Capacity	450	450	450	460	465	480	480	500
Capacity Use (%)	17	20	23	25	26	27	28	28
		Feedstoo	ck Use (1,00	0 MT)*				
Used Cooking Oil	23	38	42	48	49	50	50	52
Animal Fats and	0	0	0	7	7	0		0
Tallows	3	0	0	(	1	0	5	Ö
Other Oils	19	50	58	65	70	75	85	85
Market Penetration								
Biodiesel, on-road use	30	26	30	35	38	40	45	50
Diesel, on-road use	40,400	42,625	49,343	49,354	49,605	49,605	53,284	57,244
Blend Rate (%)	0.06	0.07	0.07	0.08	0.08	0.08	0.08	0.09
Diesel, total use	70,000	71,041	75,866	82,238	82,256	82,674	88,807	95,407

Table 3.25: Biodiesel Scenario in India (Million Liters) [44]

Source: USDA

In India, a technical paper, titled "Application of Response Surface Methodology for Optimization of Biodiesel Production by Transesterification of Animal Fat with Methanol" [46] discusses the yield of biodiesel from animal fat with methanol as a transesterification agent with sodium hydroxide as catalyst.

The results of the experiment modeled on statistical basis predicted that the maximum animal fat methyl ester yield of 85.93% volume of oil is achieved at optimized parameters of (35% volume of oil) methanol, (0.46% weight of oil) catalyst concentration and reaction time of 90 minutes. A yield of 91% was obtained experimentally at the above parameters.

The detailed biodiesel specification in US, EU as compared to India is provided in Table 3.26.

Characteristic with unit		India ISI5607:2005	U.S.	EU
Ester content	mass %	96.5(min.) by GC	-	>96.5
Density	Kg/m <sup>3</sup>	0.86-0.9 ASTM D-4052	-	0.86-0.9
Viscosity	mm²/s	2.5-6.0 ASTM D-445	1.9-6.0	3.5-5.0
Flash Point	O	120(min) IP-170	>130	>120
Sulfur content	Mg/kg	50(max) ASTM D5453	<0.015	<0.001
T95	O	-	<360 (90%)	-
Carbon residue	mass%	0.05(max) ASTM D-	<0.05	-
(100%)		4550		
Carbon residue	mass%	0.05 (MAX) ASTM D-	-	<0.3
(Rams bottom)		524		
(on 10% distillation residue)				
Cetane number		48 (min) ASTM D-613	>47	>51
Sulfated ash	mass%	0.02(max) ASTM D-482	<0.02	<0.02
Water content	Mg/kg	500 (max) IP-386	<0.05 (vol %)	<500
Total contamination	Mg/kg		-	<24
Copper corrosion		One (max) IP-154	No.3	Class-I
Total acid number	Mg KOH/g	0.5 (max) ASTM D-974	<0.5	<0.5
Oxidation stability	hr.	1.5 (MAX) ASTM D- 5304	<3	<6 (EN14112)
lodine number		115 (max) proposed	-	<120
Methyl linolenate	mass%		-	<12
Poly unsaturated FAME	mass%		-	<1

Table 3.29: Detail Biodiesel Specifications in India, US and EU

Methanol content	mass%	0.20 (max) by GC	<0.2	<0.2
Monoglyceride	mass%	0.80 (proposed)	-	<0.80
Diglyceride	mass%		-	<0.2
Triglyceride	mass%		-	<0.2
Free glycerol	mass%	0.02(max) ASTM D- 6584	<0.02	<0.02
Total glycerol	mass%	0.25(max) ASTM D- 6584	<0.24	<0.25
Na+K	Mg/kg	To report by ICP-AES	<5	<5
Ca + Mg	Mg/kg	To report by ICP-AES	<5	<5
Phosphorous	Mg/kg	10.0(max) by ICP-AES	<10	<10
CFPP	O	-IP-309	-	<5/<-5/<-15
Pour point	°C	<b>=</b> IP-15	-	<0

Source: Indian Institute of Petroleum

# 3.7.3 Global Scenario [39, 40]

Globally, biodiesel are utilized in the transportation sector, the scenario is provided in Table 3.27. Biofuels account for roughly 1% of the total renewable energy bucket. In 2014, biodiesel grew at 14% over previous year. Liquid Biofuels are used mainly for passenger vehicles and heavy-duty road vehicle applications.

The global production of Biofuels for the past three years is provided in Table 3.27. Capacities for biodiesel production were added in United States, Brazil, Germany, Argentina and France in 2015. Biodiesel production fell at a slightly negative growth rate of -0.9% in 2015 over 2014.

Year	Production	Ethanol	Biodiesel	DVO
	(billion liters)			
2013	118.1	87.8	26.3	4.0
2014	127.7	94	29.7	4.0
2015	132.9	98	30.0	4.9

Table 3.27: Global Production of Biofuels

Source: REN, 2016

The global bio-diesel production and consumption is provided in Figure 3.5



Figure3.5: Biodiesel Global Production [42] Source: OECD/FAO (2015)

The biodiesel production by country in 2014 & 2024 are provided in Figure 3.5:



Figure 3.6: Biodiesel production share by country in 2014 and 2024 [42]

The future projections for biodiesel globally as provided by FAO are provided in Table 3.28 and Table 3.29

	PRODUCTION		Growth (%)	DOMESTIC	USE	Growth (%)
	(million l	_itres)	(1)	(million Li	tres)	(1)
	Average	2024	2015-24	Average	2024	2015-24
	2012-14est	2024	2013-24	2012-14est	2024	2013-24
NORTH AMERICA						
Canada	392	486	0.33	538	794	1.56
United States	5 149	4 723	0.41	5 719	6 633	2.19
EUROPE						
European Union	11 599	13 120	0.27	13 014	13 452	-0.34
of which second generation	52	185				
OCEANIA DEVELOPED						
Australia	63	280	11.96	72	276	11.04
OTHER DEVELOPED						
South Africa	77	268	17.55	77	268	17.55
SUB-SAHARAN AFRICA						
Mozambique	74	78	-0.07	29	42	3.70
Tanzania	63	101	4.70	6	38	14.97
LATIN AMERICA						
AND CARIBBEAN						
Argentina	2 565	2 923	1.17	1 043	1 429	0.62
Brazil	3 1 18	5 094	1.23	3 1 1 9	5 070	1.19
Colombia	666	968	3.34	665	968	3.37
Peru	98	108	0.03	275	272	1.57
ASIA AND PACIFIC						
India	300	792	12.89	433	900	8.65
Indonesia	2 044	6 789	7.62	1 007	5 638	9.92
Malaysia	240	619	5.42	105	294	11.28
Philippines	187	281	2.04	187	281	2.04
Thailand	944	1 001	1.01	944	1 001	1.01
Turkey	13	14	0.88	13	14	0.92
Viet Nam	28	145	10.02	28	145	10.14
TOTAL	27 913	38 569	2.13	27 568	38 297	2.14

Table 3.28: Global Biodiesel Projections [42]

Source: USDA, FAO, IEA

	SHARE IN DIESEL TYPE FUEL USE (%)				
	Energy s	hare	Volume s	share	
	Average	2024	Average	2024	
	2012-14est	2024	2012-14est	2024	
NORTH AMERICA					
Canada	1.9	2.1	2.1	2.3	
United States	2.3	2.4	2.5	2.6	
EUROPE					
European Union	5.3	5.9	5.7	6.4	
of which second generation					
OCEANIA DEVELOPED					
Australia	0.3	1.1	0.3	1.2	
OTHER DEVELOPED					
South Africa					
SUB-SAHARAN AFRICA					
Mozambique					
Tanzania					
LATIN AMERICA AND CARIBBEAN					
Argentina	6.7	9.5	7.3	10.3	
Brazil	4.9	6.5	5.3	7.0	
Colombia					
Peru					
ASIA AND PACIFIC					
India					
Indonesia					
Malaysia					
Philippines					
Thailand					
Turkey					
Viet Nam					
TOTAL	3.2	3.6	3.5	4.0	

Table 3.29: Global Biodiesel Projections in Diesel [42, 43]

Not available

Note: Average 2012-14est: Data for 2014 are estimated.

1. Least-squares growth rate (see glossary).

2. For total net trade, sum of all positive net trade positions.

In the EU, diesel cars are currently certified for blends with up to 7 % biodiesel by volume (fatty acid methyl ester (FAME) or dimethyl ether (DME); around 6.5 % in energy terms) and for petrol cars the limit is 10 % ethanol by volume (around 6.7 % in energy terms).

# 3.7.4 Global Bio-methanol Companies

# BioMCN, a part of OCI NV [41], established in 1974 is the first company in the world to produce and sell industrial quantities of high quality bio-methanol (installed capacity: 870,000 tonnes per annum)

BioMCN produces two types of methanol: bio-methanol and regular (also known as grey) methanol. Bio-methanol is produced from bio-gas sourced from waste digestion plants through the national gas grid by purchasing bio-gas certificates to label methanol as biomethanol. Europe and USA are leading countries to produce biodiesel. They account for 45% of the global production. Europe produces and consumes more than 30% of biodiesel world-wide.

Enerchem Incorporation operates a bio-methanol plant (Enerchem Alberta Biofuels) in Edmonton, Canada. The plant runs on a feedstock of post sorted municipal solid waste (after recycling and composting) with an annual capacity of 38 million litres (10 million gallons). The plant is a result of 10 years in R & D from pilot to full scale and commenced production in 2015. This plant has been certified by the International Sustainability and Carbon Certification (ISCC) system for the biomethanol production. It became the first ISCC certified plant in the world to convert municipal solid waste into biomethanol. The R & D facility of Enerchem is established as Enerchem Westbury, which is a demonstration unit testing unconventional feedstocks for converting them into methanol.

Under the European Renewable Energy Directive (RED) all EU countries must ensure that at least 10% of their transport fuels come from renewable sources by 2020.

# 3.8 METHANOL AS MARINE FUEL

According to Methanol Institute [47, 48], currently globally there are an estimated 90,000 marine vessels with a consumption of 370 million tonnes of bunker fuel. Marine fuels are classified into marine distillate fuels and marine residual fuels. Marine fuel properties are listed in ISO 8217:2010. The Table 3.30 summarizes their differences.

Name	Alias	Alias	Туре	Chain length
No. 1 fuel oil	No. 1 distillate	No. 1 diesel fuel	Distillate	9-16
No. 2 fuel oil	No. 2 distillate	No. 2 diesel fuel	Distillate	10-20
No. 3 fuel oil	No. 3 distillate	No. 3 diesel fuel	Distillate	
No. 4 fuel oil	No. 4 distillate	No. 4 residual fuel oil	Distillate/Residual	12-70
No. 5 fuel oil	No. 5 residual fuel oil	Heavy fuel oil	Residual	12-70
No. 6 fuel oil	No. 6 residual fuel oil	Heavy fuel oil	Residual	20-70

Source: Cheveron Fuels, IMO

These are also often referred to Bunker oil.

- Bunker A corresponds to the distillate fuel oil No. 2
- Bunker B is a No. 4 or No. 5 fuel oil
- Bunker C corresponds to the residual fuel oil No. 6

There are four major recognized marine fuels globally as under:

- 1. Marine Gas Oil (MGO), (distillate fuel)
- 2. Marine Diesel Oil (MDO) (residual fuel)
- 3. LNG
- 4. Intermediate and Residual Fuel Oil

Further, fuel grades and common industry names are provided in Table 3.30

Fuel Type	Fuel Grades	Common Industry Name
Distillate	DMX, DMA, DMB, DMC	Gas Oil or Marine Gas Oil
Intermediate	IFO 180 380	Marine Diesel Fuel or
		Intermediate Fuel Oil (IFO)
Residual	RMA-RML	Fuel oil or Residual Fuel Oil

#### Table 3.31: Diesel fuel types for marine applications [51]

Source: IMO

The sulphur content for MRO and MDO vary from approximately 0.10% to 1.50% and 0.3% & to 2.0% respectively. Most of the commercial vessels are operating on Heavy Fuel Oil (HFO). It is estimated that ships emit around 8% of global sulphur oxide (SOx) emissions and 15% of global nitrogen oxide (NOx) emissions annually.

Units		Methanol	LNG	Bunker Fuel
Molecular formula		СНЗОН	>90% CH4	CnH1.8nC8-C20
Carbon Content	(wt%)	37.49	~75	~87
Density	kg/l	0.79	0.44 (LNG)	0.85
Water Solubility		Complete	No	No
Boiling point	٦°	65	-162	150-370
Flash point	°C	11	-188	min.60
Auto ignition	°C	464	540	240
Viscosity	cSt@20°C	~0.6	n.a.	~13.5
Octane	RON/MON	109/89	120/120	-
Cetane No.	-	5	-	45-55
LHV	MJ/kg	20	45	42
Flammability limits	Vol%	7-36	5-15	1-6
Flame speed	cm/s	52	37	37
Heat of evaporation	kJ/kg	1178	n.a.	233
Stoichiometric AF ratio	-	6.45	17.2	14.7
Adiabatic flame temp.	C°	1910	1950	2100
Bulk modulus	MPa	777	848	1350
Sulphur content	%	0	0	3.5 max

Table 3.32: Methanol, LNG and Bunker Fuel Comparison [51, 52]

Source: Methanol Institute, IMO, Wartsila

**MARPOL Annex VI**, first adopted in 1997, limits the main air pollutants contained in ships exhaust gas, including sulphur oxides  $(SO_x)$  and nitrous oxides  $(NO_x)$ , and prohibits deliberate emissions of ozone depleting substances (ODS). MARPOL Annex VI also regulates shipboard incineration, and the emissions of volatile organic compounds (VOC) from tankers.

The revised emission standards set up by the IMO (MARPOL Annex VI) prohibit ships in Sulphur Emission Control Areas (SECAs) for emitting more than 0.1% of sulfur after 1<sup>st</sup> January 2015. The global sulfur cap will be reduced progressively from 4.5% to 0.5% by 2020. This target will be reviewed by the IMO in 2018. Moreover, in accordance with the IMO regulation, the European Commission has decided to also enforce the 0.5% sulfur cap in non-ECA areas by 2020.

# 3.8.1 Methanol-Past & Current Marine Applications

Methanol is widely regarded by the industry as one of the most promising alternatives for marine fuel in the medium to long term. Over the past few decades, the global shipping industry has experienced tremendous growth, with more than 50,000 commercial vessels sailing internationally every day. Methanol as a marine fuel finds its development since 2010. History of Methanol as a marine fuel from Methanol Institute is provided in Table 3.33:

Time Line	Development	Results
2010-2014	EffShip ("Efficient Shipping with Low Emissions")	Technology development contributed to
	and SPIRETH ("Alcohol (Spirits) and Ethers as	IMO's draft IGF code (International Code
	Marine Fuel)	of Safety for Ships using Gases or Low-
		Flashpoint Fuels) which governs the safe
		handling of LNG and methanol fuels on-
		board ships.
2013	Methanex signed an agreement with Mitsui OSK	Delivery was completed in April 2016 in
	lines (MOL) for building seven 50,000 DWT ships	Japan. Ships are chartered by Waterfront
	with MAN diesel & Turbo's ME-LGI flex fuel engine.	Shipping Company, Canada.
2015-2018	Lloyd's Register announced plans to design a	Funded by the German Government,
	whole new generation of cruise ships and ro-	designs for the new methanol ships will
	paxferries powered by methanol (Methaships).	be developed over the next three years.
	Partnering in the project are German Shipyard	
	Meyer Werft, German shipbuilder Flensburger-	
	Schiffbau-Gesellschaft and German methanol	
	distributor HELM AG.	
2015	Swedish ferry operator Stena Line, relaunched the	Running on methanol, Sox emissions are
	Stena Germanica featuring the world's first dual-	expected to be cut by 99%, Nox by 60%,
	fuel methanol propulsion system	particulates by 95%, and CO2 by 25%.
		€ 11.2 million funding for the work was
		provided under the European Union's
		Trans-European Transport Networks
		(TEN-T) program.
2016	Green Pilot project, Goteborg, ScandiNAOS AB the	Ongoing
	project, which began in March 2016, intends to	
	convert a pilot boat to methanol operation to show	
	how a methanol conversion of a smaller vessel can	
	be carried out in practice and to demonstrate the	
	emissions reductions that can be achieved.	

# Table 3.33: History of Methanol as Marine Fuel [51, 52, 53]

Source: IMO, EMSA

A study by the European Maritime Safety agency [52] (**Study on the use of ethyl and methyl alcohol as alternative fuels in shipping, 2015)** provides the following list of projects using Methanol as marine fuel:

Project Name	Dates	Project Type,	Fuels Tested	Ship Types
		Coordinator		
METHAPU Validation of	2006-	Prototype EU FP6	Methanol in	Car Carrier
Renewable Methanol Based	2009	Project,	Solid Oxide	(PCTC)
Auxiliary Power System for		coordinated by	Fuel Cell	
Commercial Vessels		Wärtsilä Finland		
Effship Efficient Shipping	2009-	Primarily paper	Methanol in	General to most
with Low Emissions	2013	study with some	laboratory	ship types, with
		laboratory testing,	trials, other	case examples
		coordinated by	fuels	of a short-sea
		SSPA Sweden AB	discussed in	ro-ro vessel and
		and ScandiNAOS	desk studies	a Panamax
				tanker
SPIRETH	2011-	Laboratory testing,	Methanol in a	Passenger
Alcohol (spirits) and ethers	2014	on-board testing	converted	Ferry
as marine fuel		(DME converted	main engine	(RoPax)
		from methanol) with	(in a lab). DME	
		an auxiliary diesel	(converted	
		engine, coordinated	from methanol	
		by SSPA Sweden	on-board) in	
		AB and	an auxiliary	
		ScandiNAOS	engine	
Methanol: The marine fuel	2013-	Conversion of main	Methanol	RoPax ferry
of the future (Also referred	2015	engines and testing		Stena
to as "Pilot Methanol" by		on-board, project		Germanica
Zero Vison Tool)		coordinated by		
		Stena AB		
MethaShip	2014-	Design study	Methanol and	Cruise Vessel,
	2018	coordinated by	DME	RoPax
		Meyer Werft		
Waterfront Shipping	2013-	Commercial Ship	Methanol	Chemical
Tanker newbuilding projects	2016	Construction	(Dual-Fuel	tankers
			Engines)	

Tahle	3 34.	Projects	usina	Methanol as	marine	Fuel	[52	531	
Iable	5.54.	FIUJECIS	using	Methanol as	manne	гuег	[JZ,	55	

LeanShips Low Energy and	2015-	Horizon 2020	Methanol,	2 cases: Small
Near to Zero Emissions	2019	project with 8	LNG, and	waterplane area
Ships		demonstrators (1	conventional	twin hull and
		methanol)	fuels with	trailing suction
		coordinated by	emissions	hopper dredger.
		DAMEN	abatement	
proFLASH	2015	Study of the effects	Methanol and	All
	(Phase 1:	of methanol and	LNG	
	preFLAS	LNG properties on		
	H)	fire detection and		
		extinguishing		
		systems,		
		coordinated by SP		
		Technical Research		
		Institute of Sweden		
SUMMETH Sustainable	2015	MARTEC II project	Methanol	Road ferry
Marine Methanol		coordinated by	(laboratory	
		SSPA, focused on	engine tests)	
		smaller marine		
		engines		

Source: European Maritime Safety agency



Figure 3.7: Timeline for Methanol based Marine Projects Source: Green Pilot, Kick off seminar, Göteborg June 15-16 2016 **SPIRETH** ("Alcohol (spirits) and ethers as marine fuel") project focused on two concepts for using methanol fuel on board as follows:

- DME: Development of a methanol to DME conversion process plant for shipboard operation, and testing the plant and the DME fuel mix on board an existing ship, using an adapted diesel auxiliary engine. Methanol was loaded and stored on the ship, and converted using the Haldor Topsoe OBATE TM (On board alcohol to ether) process.
- **Methanol:** Conversion of a full scale marine engine to run efficiently on methanol with pilot fuel ignition, and performance testing in a laboratory.

<u>The project began in 2012 and testing was completed in 2014</u>. For the DME fuel concept, work carried out included the design, installation, and operation of an OBATETM (On Board Alcohol to Ether) process unit for dehydrating methanol to a fuel mix of DME (60% by weight), water, and methanol. The unit was tested on-board the Stena Scanrail, a ro-pax ferry that sailed between Gothenburg and Frederikshavn.

The SPIRETH project group consisted of SSPA Sweden (project coordinator), ScandinNAOS (technical coordinator), Stena Rederi, Haldor-Topsøe, Wärtsilä, Lloyd's Register EMEA, and Methanex.

SPIRETH was co-financed by the Swedish Energy Agency, the Baltic Sea Action Plan Facility Fund (Nordic Investment Bank), the Nordic Council of Ministers' Energy & Transport Programme, and the Danish Maritime Fund, and the project partners.

For Methanol, the marine fuel of the future" is a pilot action to test the performance of methanol on the passenger ferry *Stena Germanica*, which traffics the route between Gothenburg, Sweden, and Kiel, Germany. Bunkering systems including a bunkering vessel are also being investigated as part of the project. The project was granted 50% support under the 2012 Trans-European transport network (TEN-T) multi-annual program. Project partners are Stena AB (coordinator), Wärtsilä Finland OY, Stena Oil AB, Seehafen KIEL GmbH & Co. KG, and Göteborgs Hamn AB.

The *Stena Germanica's* fuel system and one main engine were converted to methanol/MGO dual fuel operation and the vessel re-entered service on March 26, 2015 [6]. Conversion of the remaining three main engines is planned to take place during late 2015 to 2016 while the vessel is in service.

Waterfront Shipping, a subsidiary of the world's largest methanol producer, Methanex, has commissioned seven new 50000 DWT tanker vessels using MAN MELGI flex engines running on methanol, fuel oil, marine diesel oil, or gas oil. Mitsui OSK Lines Ltd. will own three of the vessels, and Marinvest/Skagerrak Invest and Westfal-Larsen will each own two. The ships are being built by Hyundai Mipo Dockyard and Minaminippon Shipbuilding Co., Ltd. Laboratory demonstration of the two stroke engine with methanol was reported in 2015. The engine uses a pilot injection of MGO or HFO to initiate combustion, and a fuel booster injection valve is used to raise fuel injection pressure to 600 bar. Methanol is delivered to the engine in liquid condition at a supply pressure of 8 bar.

In April 2016, Waterfront Shipping launched seven 50,000-ton marine vessels built with dual fuel engines that can run on methanol, fuel oil, marine diesel oil or gas oil. The innovative two stroke engines used in the Waterfront vessels were manufactured by MAN Diesel & Turbo SE.

#### SUMMETH (Sustainable Marine Methanol)

The SUMMETH project was launched in 2015 with the objectives of advancing technology, introducing methanol for coastal and inland waterways vessels to reduce carbon footprint and investigate methanol combustion concepts and fuel options that will lead to cost effectiveness.



Figure 3.8: SUMMETH Schematic Source: Green Pilot, Kick off seminar, Göteborg June 15-16 2016

# 3.8.2 Methanol and LNG-Cost Effectiveness

The technology and costs of retrofitting a ship based on methanol are far less than LNG. Typical retrofits are provided below for Methanol and LNG

# Methanol

- Cylinder heads, fuel injectors, fuel pumps, HP fuel oil pipes
- Ventilation systems
- Inerting system
- Fuel tanks

# LNG

• All except entablature & crankshaft to be replaced

Currently there are several ways that shipping companies can meet the new fuel Standards

- 1) Switching to low sulfur fuel,
- 2) Installation of scrubbers,
- 3) The use of LNG and
- 4) The use of methanol/methanol-diesel dual-fuel systems.

The price of marine gas oil with 0.1% Sulphur content is roughly 50% more expensive than the price of regular bunker fuel. Scrubbing is a method by which ships install on-board devices (called scrubbers) to remove SOx from exhaust gases. In this way, ships can continue burning high sulfur fuel while meeting the new emission standards. The most advanced scrubbers are capable of removing up to 97% of the sulfur dioxide emissions. However, the cost of installing scrubber equipment can vary between  $\in 1$  million and  $\in 5$ million per ship, depending on the ship size.

The switch to LNG-fueled engines is expected to contribute to a 95% reduction in SOx emissions, and to a nearly 90% reduction in PM and NOx emissions. However, viable refueling infrastructure investments are still needed. The US opened its first LNG bunkering facility in Port Fourchon (Louisiana) in early 2015 and trial refueling tests have already been carried out. LNG does not offer a profitable business model yet, as high capital costs outweigh fuel savings for many companies.

wethanol	Natural Gas	Diesel
0.79	0,44(as LNG)	0,85
65	-162	150-370
11	-188	min. 60
464	540	240
~ 0,6	na	~ 13,5
109/89	120/120	-
3	-	45-55
20	50*	42
7-36	5-15	1-6
52	37	37
1178	na	233
6,45	17,2	14,7
1910	1950	2100
	0.79 65 11 464 ~ 0,6 109/89 3 20 7-36 52 1178 6,45 1910	Initiality         Initial Gus           0.79         0,44(as LNG)           65         -162           11         -188           464         540           ~ 0,6         na           109/89         120/120           3         -           20         50*           7-36         5-15           52         37           1178         na           6,45         17,2           1910         1950

Table 3.35: Comparison of Methanol with Natural Gas and Diesel [50]

Source: Wartsila

# Methanol offers several advantages over LNG as a marine fuel

- 1. Does not require high pressure or cryogenic storage onboard or ashore
- 2. Adaptability for use in dual fuel engines
- 3. Conversion costs are lesser than LNG
- 4. The GHG emissions and energy content issues are taken care of with 4% methane slip and carrying larger capacity storage
- 5. Methanol can be converted to DME, which has also been proven to be a diesel substitute
- 6. Marine methanol fuel produces no sulfur emissions and very low levels of nitrogen oxide emissions.

In comparison to a conventional marine-diesel engine the most considerable things that differ are:

- The cylinder head, where an extra injector is added.
- A Fuel Block, that accommodates fuel for injection
- The fuel delivery system, a part of the piping is double walled to detect any leakage.
- A special ventilation system for possible leakage

**Diesel cycle engine operation involving methanol and ethanol fuels as obtained from EMSA is provided in Table 3.36.** Blue shaded rows describe marine engine projects, while green rows show land-based applications of heavy duty diesel engines.

Engine Fuels Engine speed Engine model	Comment
Manufacturer and type	
Wärtsilä         Dual fuel methanol         Medium speed         Retrofit kit for         Installe	d on the ropax
and MGO four-stroke Wärtsilä-Sulzer ferry St	ena Germanica
marine main 8 cylinder Z40S in 2015	
engine, pilot	
ignition	
MAN Diesel & Dual fuel – Slow speed two- ME-LGI series Methan	ol dual
TurboConventional fuelstroke marineintroduced 2013fuel englishing	gines installed
together with low main engine, <b>New</b> on cher	mical tankers to
flashpoint liquids pilot ignition production be delived	vered in 2016
methanol, ethanol, engine	
LPG, gasoline, or DME	
possible	
Scania Ethanol 95% with High speed 9- Scania ED9 Scania	ethanol engines
additives litre diesel <b>Production</b> have be	een used on
engine for use in engine public t	ransit buses for
trucks and many y	ears (first
buses operati	on in 1985)
Caterpillar Methanol 100% High speed 4- Adapted More th	an 5000 hours
stroke engine, Caterpillar 3406 operati	on in a test
261 kW, DITA Engine project	in long-haul
adapted with (retrofit for test trucks i	n 1987-1988
"glow plug" study)	
ianition, used in	
0, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1,	

Table 3.36: Different Engine Developed for Methanol (land and marine) [53]

Source: EMSA

Several sources indicate that a conversion kit, which is a stand-alone high pressure methanol pump with belonging oil unit for supply of sealing oil and control oil to the fuel injectors, will be required as well.

Installation costs of a small methanol bunkering unit have been estimated at around  $\in$ 400,000. A bunker vessel can be converted for approximately  $\in$  1.5 million. In contrast, an LNG terminal costs approximately  $\in$  50 million and an LNG bunker barge  $\in$  30 million.

Retrofit cost of a ship from diesel fuel to dual-fuel methanol/diesel fuel has been estimated to be € 250-350/kW for large engines (10-25 MW). This can be compared with retrofit to LNG fuel, which is in the order of  $\in$  1,000/kW.

# Stena indicates that the conversion costs to methanol are € 300 per KW, which is comparable to scrubber costs, whereas conversion costs to LNG is € 1000 per KW.

For the methanol option, investment cost for the retrofit used a value of EUR 350/kW reported for the conversion of the 24 MW Ro-Pax ferry Stena Germanica retrofit project carried out in 2015.

For the methanol new build, a cost of EUR 700/kW for the engine and auxiliary systems was used as reported in [68] in 2012, and this was updated to 2015 USD values using an inflation rate of 4% and currency exchange of 1 EUR to 1.12 USD. Given the limited experience with marine methanol installations, costs for this option should be considered approximate. Methanol retrofit costs are provided in Table 3.37

Fuel and compliance strategy	Retrofit	New builds (includes
		engine, generator, etc.)
MGO (engine upgrade, SCR/EGR)	150 000 + 63 \$/kW	120 000 + 542 \$/kW
HFO (scrubber & SCR)	489 \$/kW	926 \$/kW
LNG dual fuel 4 stroke plus tanks	664 \$/kW	1275 \$/kW
Methanol dual fuel 4 stroke	392 \$/kW	815 \$/kW
Ethanol dual fuel 4 stroke	392 \$/kW	815 \$/kW
Sour	on EMSA IMO Martaila	

# Table 3.37: Methanol Retrofit Costs for Marine Applications [52,53]

Source: EMSA, IMO, Wartsila

Wartsila provides following retrofits for methanol as a bunker fuel

- OBATE (Bunker Methanol and run on DME)
- Surface Ignition
- Fumigation
- Mixing Concept (Emulsion) •
- Ignition Improvers
- Pilot fuel assisted Diesel Combustion
- Premixed Combustion with Spark Plug or Pilot Fuel Ignition



Figure 3.9a: Schematic Diagram of Wartsila Methanol Marine Engine [54]



Figure 3.9a: Engine Piping of Wartsila Methanol Marine Engine [54]

Further, comparison between different methanol based engines as provided by Wartsila is summarized in Table 3.38. The Table provides positives (+) and negatives (-) of each prototype. As can be observed, the OBATE-DME system have possible ignition issues, while the Dual Fuel, there are concerns for degradation of engine oil. In Methanol-Diesel prototype, NOx was observed to be higher than for Otto concept.

OBATE-DME (Diesel)	Dual Fuel (Otto)	Methanol-Diesel (Diesel)
Positives		
+ clean, smokeless combustion	+ NOx Tier III without SCR/EGR	+ no knocking
+ sTable combustion	+ possible small modifications	+ no power reduction
+ no knocking	cost	+ cost effective adaption
		+ low NOx & low PM
		+ good back-up fuel performance
		+ experience of the concept from gas
<ul> <li>Negatives</li> </ul>		
<ul> <li>modifications of fuel</li> </ul>	<ul> <li>formaldehyde in exhaust</li> </ul>	<ul> <li>NOx higher than for DF concept</li> </ul>
preparation system	emissions	
<ul> <li>modifications of fuel injection</li> </ul>	<ul> <li>degradation of engine oil</li> </ul>	
system	<ul> <li>knocking behaviour</li> </ul>	
<ul> <li>modification of piston bowl</li> </ul>	<ul> <li>quit expensive conversion</li> </ul>	
<ul> <li>Cetane number of OBATE-</li> </ul>	cost from diesel	
DME is low		
<ul> <li>possible ignition problems</li> </ul>		

Table 3.38: Wartsila Marine Methanol Engine Concepts Comparison

Source: Wartsila

According to data from Jim Jordan and Associates, the total demand for methanol in 2013 was at 66 million tons, that's in comparison to the 372 million tons marine diesel demand.

# 3.8.1 Technology [52]

The IMO provides extensive information on the technology readiness on the following subsections for use of methanol as a marine fuel. These are provided from Table 3.39 to Table 3.43. These are provided under system component, technology readiness and remarks.

- 1. Bunkering
- 2. Storage
- 3. Pre-engine handling and processing
- 4. Combustion
- 5. Post Processing

System component	Technology	Remarks
	readiness	
Mechanical ventilation	Mature	Dependent on location of bunkering station
Coamings fitted	Mature	
Control from safe location	Mature	
Pipes self-drained, arranged for	Mature	
inerting and gas freeing		
System for cargo and fuel	Mature	Dependent on the ship type, relevant for
segregation		chemical tankers
Transfer coupling shall	Mature	
automatically close at disconnect		
Monitoring and control systems	Mature	
Drip trays	Mature	Below all possible leakage points

# Table 3.39: Bunkering of methanol

System component Technology Remarks					
oystem component	recimology	Kemarka			
	readiness				
Inlet and outlet piping	Mature				
Level indicators	Mature				
Arrangement for interting and gas	Mature				
freeing, by nitrogen installation					
Remotely operated shut-off valves	Mature				
and control system					
Filtering of Methanol	Mature	Especially for chemical tankers with			
		Methanol fuel service tank			
Drip trays	Mature	Below all possible leakage points			
Fire detection – IR CCTV	Relatively new,	This is due to methanol fire being invisible			
	but used in other				
	industries.				
Fixed foam fire extinguishing	Mature	For fuel tanks on weather deck			
system					

#### \_ . . . . ~ . ~ ... .

# Table 3.41: Methanol handling and processing before the main engine

System component	Technology readiness	Remarks
Double walled piping and corresponding ventilation of annular space.	Mature	Used for LNG as fuel systems
Liquid and vapour detection	Mature	
Remotely operated valves	Mature	
Filtering system	Mature	

Supply pump	Mature	
Circulation circuit	Mature	Keep supply higher than the
		fuel consumption
Double block and bleed valve configuration	Mature	
Arrangement for interting ang gas freeing, by	Mature	For drainage and purging of the
nitrogen installation		Methanol lines
Temperature and pressure control system	Mature	
Temperature regulation system	Mature	
Ventilation system of rooms containing equipment	Mature	
Drip trays	Mature	Below all possible leakage
		points.

Table 3.42: Combustion of methanol in the main engine

System component	Technology readiness	Remarks
Double-walled fuel pressure lines	Mature	All Methanol fuel lines to the main
		engine
Additional LFL engine monitoring	Relatively new application,	Detect LFL ignition controlling
systems		automatic shutdown
Additional sealings	Mature	Avoid leakage to the engine room.
Additional methanol fuel injection	Relatively new application,	Relevant for dual fuel system
system	built on a mature concept	
Combined sealing and cooling oil	Relatively new application	Due to the non-lubricant effects of
system to the injection valve		methanol
Liquid and vapour detection	Mature	
Purge return system	Relatively new application,	Purging and inerting of Methanol in
		the main engine
Fire detection to engine room –	Relatively new, but used in	This is due to methanol fire being
IR CCTV	other industries.	invisible

Table 3.43: Methanol handling and processing after the main engine

System component	Technology readiness	Remarks
Double block and bleed valve	Mature	Configuration needed to avoid
configuration for the Nitrogen injection		methanol vapour back to the
		nitrogen system
Remotely operated shut-off valves and	Mature	
control system		
Manual valves	Mature	
Liquid and vapour detection		
Double walled-piping	Mature	

So far, methanol ships have been powered by diesel concept engines which have been modified to run on both methanol and marine diesel.

Sweden's Stena Line [55] launched the world's first methanol-fuelled ferry in March 2015. Dual fuel technology is used, with methanol as the main fuel, but with the option to use Marine Gas Oil (MGO) as backup.

According to World Maritime News [56], methanol has been used in a full scale ferry installation in 2015 on the Stena Germanica and is being installed in new build chemical tankers for delivery in 2016.

According to Swedish fleet owners, Stena RoRo AB, [57] Methanol can be stored onboard and ashore in similar tanks as oil products. Bunker barges will be small chemical carriers for methanol compared to small gas carriers for LNG.

A diploma thesis [58] completed by researchers at the Department of Shipping and Marine Technology Chalmers University of Technology, Sweden in 2015 on methanol as a marine fuel brings out the following:

- 1. Methanol use was accepted by the responders mainly due to environmental factors
- 2. Methanol use was accepted as challenging due to investment costs and operational costs



Figure 3.9c: Small Ship powered by Methanol Source: Westfal Larsen

# 3.8.3 Emissions from Methanol as Marine Fuel

The International Maritime Organisation outlines the emissions from methane when considered as a marine fuel. It also acknowledges that combustion of methanol will also give rise to formaldehyde. However, the study by the IMO does not cover this aspect.

The emissions from methanol as a marine fuel are provided in Table 3.44

Compound	Emissions	MGO emissions (g/MJ	HFO emissions			
	(g/MJ methanol)	MGO)	(g/MJ HFO)			
CO <sub>2</sub>	69	75	77			
CH <sub>4</sub>	0	0	0			
N <sub>2</sub> O	0	0	0			
NOx	0.4	1	1			
SOx	0	0.04	0.5			
Source: IMO						

Table 3.44: Comparison of Emissions from combustion in marine engines [52]

The environmental impact from marine fuels sourced from Stena is provided in Figure 3.10. It clearly shows that that the emissions from methanol sourced from NG has lesser NOx and SOx as compared to HFO and MGO





# 3.9 METHANOL FUEL CELL

Different types of fuel cells include phosphoric acid, alkaline, molten carbonate, solid oxide, metal-air, and the proton exchange membrane and its important subset the direct methanol fuel cell (DMFC). The first fuel cell was invented back in 1839 by Sir William Robert Grove, physicist and inventor [59]. The direct methanol fed fuel cell is a subset of the PEM fuel cell.

DMFC is a subcategory of the proton exchange membrane fuel cell (PEMFC) that uses methanol as the fuel. It was invented and developed in 1990 [60]. A DMFC anode can draw hydrogen directly from liquid methanol. This action eliminates the need to have a fuel reformer, allowing the direct use of pure methanol as a fuel. Methanol provides several advantages as it is convenient to handle and easily available.

Methanol fuel is less expensive (per unit energy) and provides significantly higher volumetric and gravimetric energy density when compared to compressed hydrogen (at 1000 bar) and even liquid hydrogen [61]. Methanol fuel embodies ten times higher specific energy density than the state-of-the-art Li-ion batteries.

As per IEA report [62], an additional 15.7 GJ/tMeOH are required conversion of methanol (MeOH) from hydrogen and coal compared to the gas steam reforming route and additional 5.6 GJ/tMeOH compared to the coal partial oxidation route. The methanol route from hydrogen and  $CO_2$  requires the most energy due to its high stoichiometric hydrogen demand. This route is, however, interesting from a GHG-saving perspective

Direct alcohol fuel cell (DAFC) is a variant of PEM fuel cell. In case, methanol is used as fuel, it is called direct methanol fuel cell (DMFC); and similarly in the case of ethanol, it is called direct ethanol fuel cell (DEFC). In general, when a fuel cell uses PEM as electrolyte, it is termed as DAFC; and in the case of anion exchange membrane electrolyte, it is called direct alcohol alkaline fuel cell or direct alcohol AEM fuel cell (DAFC).

There are several types of fuel cells, and each operates differently based on different redox reactions, fuels, electrode materials, electrolytes and operating temperatures as provided in Table 3.45:

	PEMFC	DMFC	AFC	PAFC	MCFC	SOFC
Primary Applications	Automotive & stationary power	PorTable Power	Space Vehicle & Drinking Water	Stationary Power	Stationary Power	Vehicle auxiliary power
Electrolyte	Polymer(plastic) membrane	Polymer (plastic) membrane	Concentrated (30-50%) KOH in H2O	Concentrated 100% Phosphoric acid	Molten Carbonate Ceramic matrix of LiAIO2	Yttrium- stabilized Zirconia
Operating Temp. Range	50-100°C	0-60°C	50-200°C	150-220°C	600-700°C	700-1000°C
Charge Carrier	H+	H+	OH-	H+	CO3 =	O=
Prime Cell Components	Carbon-based	Carbon- based	Carbon-based	Graphite- based	Stainless Steel	Ceramic
Catalyst	Platinum	Pt-Pt/Ru	Platinum	Platinum	Nickel	Perovskites
Primary Fuel	H2	Methanol	H2	H2	H2, CO, CH4	H2, CO
Start-up Time	Seconds- minutes	Seconds- minutes		Hours	Hours	Hours
Power Density kW/m3	3.8 6.5	~0.6	~ 1	0.8 1.9	1.5 2.6	0.1 1.5
Combined cycle fuel cell Efficiency	50-60%	30-40%	50-60%	55%	55-65%	55-65%

Table 3.45: Types of Fuel Cell [63]

Source: RK Shah, IIT Delhi

It is well-known that fuel oxidation and oxygen reduction kinetics is faster in the presence of alkaline medium than acidic medium (Basu 2007). In the recent past, AEM-based DAFCs have become popular as fuel crossover is absent, which is predominantly present in PEM-based DAFCs.

The methanol dissociates into electrons, protons and carbon dioxide at the anode. The protons diffuse from anode to cathode through the polymer electrolyte membrane and electrons migrate toward the cathode through an external circuit. At the cathode, the electrons, hydrogen ions and oxygen from the air react to form water.

The reactions involved in direct methanol fuel cell are shown here (Basu 2007) [64]:

Anode (Pt/C) : CH3OH + H2O→CO2 + 6H+ + 6e- (1)

Cathode (Pt/C):  $3/2O2 + 6H + 6e \rightarrow 3H2O$  (2)

Overall : CH3OH + 3/2O2→ CO2 + 2H2O (3)

Equation (1) shows the methanol oxidation reaction in which 6 electrons are generated by electro-oxidation of a methanol molecule. The reversible cell potential at standard condition of a DMFC is calculated as 1.199 V. The methanol electro-oxidation reaction is a complex multi-step process.

	PEMFC	SOFC	MCFC	DMFC
Operating Temp. (°C)	80-150	800-	>650	80
		1,000		100
Fuel	H2	H2, hc	ng, hc	methanol
Electrical Efficiency (%)	35-40	<45	44-50	15-30
Applications	FCV	Station.	Station.	PorTable
	Power	Power	Power	Power
Lifetime (h) FCV	2,000	6,000	8,000	na
Power	30,000	20,000	20,000	
Target lifetime (h) FCV	4,000	40,000	40,000	
Power	20,000	60,000	60,000	na
	Source: Il	ΞA		

ahla	3 16.	Com	narieon	of	Difforent	اصر	Calle	
able	5.40.	COIII	parison	0I	Different	гuег	Cells,	IEA

The IEA in their fuel cell dossier (2007) [65], states that due to low efficiency (15%-30%) and low power density, Methanol based fuel cells are not suiTable for mobile or stationary use. However, they provide a very good option for replacing batteries for consumer use.

The main problem associated with DMFC [64] is that the methanol electro-oxidation reaction at the fuel electrode (anode) is very slow as compared to hydrogen. This leads to a far lower power for a given size of fuel cell. The second major problem is the methanol crossover from anode compartment to cathode compartment through the polymer electrolyte membrane.

Both these problems markedly reduce the performance of the DMFC compared to PEMFC.

There have been significant efforts towards the development of polymer electrolyte membranes for DMFCs in order to reduce the methanol crossover and increase their operating temperature (Kerres 2001).

There are a few standard approaches for reducing the methanol crossover:

- (a) use of active anode catalyst results in complete methanol oxidation and not being available to diffuse through the electrolyte
- (b) controlled use of methanol to the anode so that at the time of low current there is no excess methanol available, which can diffuse through the membrane

- (c) use of thick electrolyte, that may reduce the fuel crossover but it should not be at the expense of the electrolyte resistance
- (d) use of composite polymer electrolyte membrane that may reduce the methanol crossover

The development of polymer electrolyte membrane with reduced methanol crossover is an active area of research for DMFC [64]. Efforts to develop the desired membrane for DMFC include modification of the conventional polymer electrolyte membrane (Nafion®) properties by incorporating organic or inorganic materials (composite Nafion® membrane) or by developing alternative PEM (Savadogo 1998). In an effort to modify the existing Nafion® membrane properties, inorganic solid acids have been incorporated with the objective of serving the dual functions of improving water retention as well as providing additional acidic sites (Malhotra and Datta, 1997).

# 3.9.1 Policy in India [66]

India's policy on fuel cells and financial support is driven largely by four agencies, viz. Ministry of New and Renewable Energy (MNRE), Department of Science and Technology (DST), Department of Atomic Energy (DAE) and Council of Scientific and Industrial Research (CSIR). Under its NMITLI program, CSIR has provided a total budgetary support of about Rs 20 Crores during 2004-2013 for the development different fuel cell technologies.

Under MNRE, Chemical Sources of Energy Programme deals with the development and applications of fuel cell technology which produces electricity, water and heat through reaction between hydrogen and oxygen/air. The fuel cell technology offers high conversion efficiency, modularity, compactness and noise-free operations.

# 3.9.2 Research and Development

#### Direct Methanol Fuel Cells, Los Alamos National Laboratory [67]

Direct methanol fuel cells provide an alternative power source for mobile devices.



Figure 3.11: DMFC Source: LANL

# Technology Marketing Summary

LANL has developed an intellectual property portfolio in Direct Methanol Fuel Cells that may permit companies to participate in the emerging DMFC market while minimizing R&D risks and expenditures.

### Description

Direct Methanol Fuel Cells (DMFCs) represent an innovative, cutting-edge technology that can provide mobile power to devices such as cell phones, laptop computers, and digital video cameras. After decades of fuel cell research, scientists and engineers at Los Alamos National Laboratory (LANL) are working to remove the final obstacles preventing widespread adoption of DMFCs. LANL is now inviting participation from companies ready to cooperate with leading fuel cell researchers, in-license select technologies, and commercialize direct methanol fuel cell technology.

The Federal Aviation Administration (FAA) is considering the approval of DMFC power packs for use on airplanes. As with other potentially disruptive technologies, the participants in this entry market niche for extended in-flight mobile device power will enjoy a significant and sustained competitive advantage in the broader power pack market. The potential costs of ignoring this emerging technology are large. On the other hand, the cost and risk of "going it alone" and relying exclusively on internal development are also very high. Partnering with LANL represents an attractive alternative to these costly strategies.

#### **Benefits**

- Improved DMFC performance
- Reduced cost of R&D
- Reduced risk of R&D
- Reduced development cycle

#### Design freedom (IP) Applications and Industries

- High power density stacks
- Air breathing DMFCs
- Membranes

Catalysts

- Flow-field designs
- Bipolar plate designs

### Institute for Basic Science (IBS), South Korea [68]

Researchers from South Korea's Institute for Basic Science (IBS) have proposed a way to increase the efficiency of direct methanol fuel cells (DMFC) while reducing their production of toxic heavy metals.

DMFCs, which were invented in the early 1990s, use a liquid fuel that is easier to store and transport than other energy carriers such as hydrogen but have traditionally been seen as inefficient.

Scientists at the IBS Center for Nanoparticle Research have now found a way to prevent the fuel cell's catalyst becoming "poisoned" by carbon monoxide as part of the process, by reacting the gas with another dangerous byproduct, a carcinogenic form of chromium. The production of carbon monoxide hinders the chemical reaction that drives the fuel cell by blocking its platinum catalyst.

Reacting the carbon monoxide with the hexavalent chromium [Cr (VI)] effectively cleans the catalyst's surface by turning the reactants into carbon dioxide and the much less toxic trivalent chromium [Cr (III)].

The researchers showed that with this method the fuel cell could maintain a constant voltage for 10 hours and enhance its power density by 20 per cent at 70°C without producing Cr (VI). Methanol is seen as potential alternative fuel because of the lower carbon dioxide emissions it produces than conventional petrol or diesel and its relative ease of use compared to hydrogen.

## Dr. G. Sasi kumar [66, 69]

# Centre for Energy Research, SPIC Science Foundation, Tamil Nadu

Direct Methanol Fuel Cell (DMFC)

- -Developed 250 DMFC stack
- R&D being carried out on alternate fuels

Electrolysis of aqueous methanol-

Developed 60 lit/hour hydrogen generator, with very low power consumption, (1/3rd) compared to water electrolyser (MNES funded project).

Methanol electrolyser for hydrogen production with 60 lit/hour hydrogen production

# IIT Madras [66]

Titania nanotubes as an alternative catalyst support for Direct Methanol Fuel Cell

### Ingsman Energy & Fuel Cell Research Organization Private Limited [66]

Kottivakkam Nehru Nagar, Chennai, Tamil Nadu

Pt, PtRu and PtRuM (M = Mo, Ox etc) based catalysts are used as electrode catalysts for DMFC. The catalysts are prepared by impregnation, colloidal and microemulsion methods. Flexible Carbon materials are used as catalyst support. Efforts are being taken for increasing hydrophilicity of the carbon substrate to get better performance of the DMFC. A solution of methanol in water is used as fuel and it is supplied to the anode. Air, oxygen and hydrogen peroxide are used as oxidants. The performance of DMFC is tested with respect to different catalyst, fuel concentrations, electrolytes and catalysts supports.

#### 3.9.3 Global Market

The Global Direct Methanol Fuel Cell (DMFC) Market 2016-2020 report [70] predicts that the global DMFC market will grow with a CAGR of 40.47% during the period 2016-2020. Direct Methanol Fuel Cells (DMFC) Market could be worth 188.82 Million USD by 2020

As per marketsandmarkets.com [70], Direct Methanol Fuel Cells (DMFC) market is expected to grow from an estimated USD 92.65 Million in 2015 to USD 188.82 Million by 2020, at a CAGR of 15.3% from 2015 to 2020. Further it states that the DMFC market was dominated by SFC Energy AG (Germany), Ballard Power Systems Inc. (Canada), and Oorja Protonics (U.S.), in 2015. These market players have also been active in the competitive developments of the DMFC market.

In another online research, Technavio's market research analyst [71] predicts the global DFMC market to grow at a CAGR of more than 40% during the forecast period.

At present, governments worldwide are taking several initiatives, in terms of investments, R&D, and commercialization, to increase energy efficiency and reduce energy consumption. As a result, there has been an increased focus on energy-efficient products for energy generation and storage, including fuel cells. This has led to growing awareness among consumers about the use of DMFCs. Also, many end-users prefer using energy-efficient products such as DMFCs to expand their energy storage and reduce their operating expenses.

At present, lithium-based batteries are primarily employed in porTable applications. However, rapid technological advancements will enable DMFCs to replace lithium-based batteries.

Segmentation by application and analysis of the DFMC market

- PorTable
- Stationary
- Transportation

Further, various online reports [71] suggest that the porTable segment accounted for more than 81% of the market share during 2015 and is expected to retain its market leadership until the end of 2020. The military sector is the emerging area for DMFC applications in terms of porTable power. The defense industry's need for lightweight, porTable power solutions to reduce the weight borne by a soldier is driving the adoption of DMFCs. DMFCs are also used to power on-board communication systems, sensors, and provide continuous power for weapon systems during independent missions. Also, these devices help charge the batteries that supply power to equipment.

The report by E4tech, "The Fuel Cell Industry Review 2014" [72], provides insight into the global scenario of fuel cells by type and geographical locations. The report reveals that world over there has been development and deployment of fuel cell units of 1 KW to 20 KW in both developed and developing economies.

**<u>Ballard</u>** has been one of the more successful players in these markets with its <u>ElectraGen</u> <u>methanol reformer-based fuel cell products</u> [72]. It has continued to deliver units for the telecoms market through 2014, announcing new orders such as 13 units for Digicel in the Caribbean. It also announced in mid-2014 an agreement with Azure of China for licencing its telecom products for the Chinese market, also a target for FutureE, now part of Heliocentris.

The report includes India as one of the major end users of the fuel cells in terms of having focus on intelligent energy, which is basically the source of power in electricity distribution and space research.

In Asia, First Element Energy [73] signed a multi-year agreement with a major telecom operator in Indonesia to provide 300 base load methanol reformer fuel cell units for off-grid rural areas. These units are likely to use Nedstack fuel cells, with First Element Energy entering an agreement with Nedstack for at least 300 of its FCS XXL stacks

# 3.9.4 Applications

Methanol fuel cells have been reported for use in forklifts in combination of normal batteries [74]. These DMFC have reported to improve the working time, reduce operating costs and reduce GHG emissions by upto 66% (specific model: Ooja Model 3).

DMFCs are the ideal choice for small vehicles such as tuggers and forklifts. DMFCs are also best suited for porTable power usage in consumer electronic goods such as mobile phones, PCs, cameras, and laptops [75].

# 3.9.5 Global Market share

Geographical segmentation and analysis of the DFMC market have been provided for following regions:

- Americas
- APAC (Asia Pacific American Coalition)
- EMEA (Europe, Middle East & Africa)

During 2015, the EMEA region dominated the market, accounting for more than 40% of the market share. The demand for clean and reliable power sources, coupled with the growing investments in DMFCs, is contributing to the growth of the DMFC market in EMEA. Significant resources are being allocated for the R&D of clean technologies such as DMFC for use in stationary power and in vehicles. The Fuel Cells and Hydrogen Joint Undertaking (FCH-JU) that falls under the Horizon 2020, Europe's flagship research program, has funded several projects for the development of larger capacity DMFC to be used in the telecom sector and in new materials that would increase the durability of DMFC [75].

As per reports by Transparency Market Research [76], the global market for direct **methanol fuel cell (DMFC) is expected to reach 92,000 units by 2016** at an estimated growth rate of 45.3%. This tremendous growth in the DMFC market is expected as a result of the new generation of porTable electronics, with the need for longer power on times. Asia is expected to lead this market with a total share of 38%, followed by North America holding a share of 35% and Europe with 27%. The report further states that the direct methanol fuel cell revenue is expected to grow to USD 109 million from USD 17.5 million over 2016.

# 3.9.6 Major Players

The global DMFC market has few vendors. They work on various segments in developing DMFC products for stationary and porTable power. There are also some firms that are highly specialized and provide expertise in proprietary technology.
One of the main advantages of DMFCs is that they use the high energy density methanol as fuel. It burns slower than gasoline, producing energy for a longer period of time.

Major manufacturers around the world dealing in methanol based fuel cell applications are:

- Ballard Power
- DMFCC
- Enocell
- FuelCellsEtc
- Hitachi
- Neah Power Systems
- Oorja Protonics

# **Company Summary**

Summary of the companies along with the developments in the field of methanol fuel cell is provided below:

# Ballard Power Systems Inc.

#### Burnaby, British Columbia

The principal business is the design, development, manufacture, sale and service of fuel cell products for a variety of applications, focusing on our power product markets of Heavy-Duty Motive (consisting of bus and tram applications), PorTable Power, Material Handling and Telecom Backup Power, as well as the delivery of Technology Solutions including engineering services and the license and sale of our extensive intellectual property portfolio and fundamental knowledge for a variety of fuel cell applications.

The ElectraGen<sup>™</sup> family of fuel cell power generation systems includes systems fuelled by compressed hydrogen or liquid methanol, both of which provide reliable backup power for 'extended duration runtime' requirements.

Fuel cell manufacturer, Ballard Power Systems, has installed more than 100 of its methanol fueled fuel cell systems on rooftops in major cities around the world to provide backup power to critical telecom sites.

In May 2016, Ballard Power Systems announced that it has entered into a definitive agreement to sell certain of the Company's methanol Telecom Backup Power business assets to Chung-Hsin Electric & Machinery Manufacturing Corporation, a major Taiwanese power equipment company, for a purchase price of up to \$6.1 million.

# <u>Case Study of Ballard's Methanol Fuelled Backup Power System Installation of an</u> <u>ElectraGen™ ME backup power system for rooftop applications.</u>

Rooftop installations of fuel cell systems are straightforward, depending upon the logistics of the building and access to the rooftop.

The fuel cell system fits through standard size doors and service elevators, or alternatively, cranes or hoists could be used to lift the system onto the roof.

Ballard's methanol-fueled ElectraGen<sup>™</sup>- ME system is the ideal solution to provide telecom operators with reliable backup power at rooftop sites.

This fuel cell system addresses many of the challenges commonly found with rooftop locations;

1. Easier to Site The ElectraGen<sup>™</sup>- ME is a quiet, lightweight solution with low emissions and less vibrations compared to diesel gensets.

2. Code Compliance Ballard's fuel cell system is designed to be compliant with North American fuel safety codes such as NFPA 853, NFPA 30 and meets the requirements of municipal fire department codes.

3. Safer Fuel The ElectraGen<sup>™</sup>- ME uses HydroPlus<sup>™</sup> fuel, a methanol-water mixture, that is safer than alternative liquid fuels such as diesel or gasoline. HydroPlus<sup>™</sup> also eliminates challenges associated with the delivery and storage of fuel; the fuel can easily be hand carried to the rooftop for refueling.

Rooftop installations are inherently challenging, but fuel cell systems provide a cost effective alternative to batteries and diesel generators. Telecom operators are increasingly choosing backup power fuel cells at rooftop telecom sites.

# **Oorja Protonics, Inc**

45473 Warm Springs Boulevard, Fremont, California 94539

Oorja Protonics, Inc., develops and manufactures direct methanol fuel cell (DMFC)-based power systems that use methanol, combining a fuel cell and a traditional battery to provide a high-power solution that significantly reduces operating costs and greenhouse gas emissions. Oorja designs, develops, and commercializes reliable, economical modular DMFCs ranging in power from 1 to 5 kW, which have a wide range of applications for the telecommunications (wireless) and materials-handling industries, supplying backup power. The company was founded in 2005 in Silicon Valley and is funded by leading global investors.

#### **DMFC Overview**

Oorja is the first company to offer Direct Methanol Fuel Cells (DMFCs) powerful enough for applications like materials-handling and wireless cell towers, offering operational advantages that make them an excellent alternative to charging batteries from the grid.

# Model 3 — for Materials Handling and PorTable Applications

The Oorja Model 3 is a liquid fuel cell that operates as an on-board battery charger for a wide variety of Class III vehicles in the materials-handling industry.

Model T-1 — for Telecommunications and Stationary Applications

The Oorja Model T-1 is a liquid fuel cell that operates as a battery charger for a wide variety of stationary applications, including wireless base stations.

# **Enocell Limited**

BioCity Scotland Bo'Ness Road, Newhouse, Lanarkshire Scotland, ML1 5UH Enocell designs and manufactures direct methanol fuel cell (DMFC) modules. These can be integrated into a range of power products used to provide cost effective and energy efficient off-grid power.

Enocell's clean energy, "off grid" hydrogen fuel cell modules enable the creation of fully integrated, highly efficient power sources that generate cost effective electrical energy directly at the point-of-use. Each hydrogen fuel cell module is designed to fully integrate into a wide range of application specific products with power outputs ranging from 2.5 W to 1,000W. The 3 primary power markets for fuel cell technology include: Stationary, Transportation and PorTable power. The focus is in the Stationary and PorTable sectors in the 2.5W to 250W range, where annual worldwide growth is expected to be +16 to 20% over the next 3 years.

# Chung-Hsin Electric & Machinery Manufacturing Corporation

HEM has established a clear renewable energy vision based on PEMFC technologies. Since establishing the renewable energy center in 2008, CHEM has invested over one billion NTD in lab equipments and facilities focused on technology area such as PEMFC stacks, reformers, power conditioning and hydrogen storage methods. In addition to collaborating with academic and research institutions to develop advanced clean energy solutions, CHEM is also an active participant in Taiwan's National Demonstration Projects (NDP). CHEM is

the first company to publicly demonstrate successful operations of a hybrid stationary fuel cell system in Taiwan.

The company launched the product include 2kW/5W fuel cell backup power system (BPS), fuel cell Methanol water reformer, fuel cell module and fuel cell power converters, which could be operated without noise and pollution. Besides, they develop energy-saving air condition product and new refrigerant in response to the trend of energy-saving trend

# Direct Methanol Fuel Cell Corporation DMFCC

Direct Methanol Fuel Cell Corporation develops and manufactures disposable methanol fuel cartridges that provide the energy source for fuel cell powered notebook computers, mobile phones, military equipment and other applications being developed by electronics OEMs, such as Samsung and Toshiba, and other companies.

It has been projected that up to 22% of notebook computers and 2.5% of mobile phones will be powered by fuel cells in the future, which would result in demand for more than three billion cartridges per year.

#### Patented Clean Energy Technology

DMFCC has licensed an extensive portfolio of direct methanol fuel cell patents from Pasadena-based California Institute of Technology (Caltech) and the University of Southern California (USC). Caltech manages NASA's Jet Propulsion Laboratory (JPL) where the direct methanol fuel cell was invented in collaboration with professors at USC.

# SFC Energy AG

Eugen-Sänger-Ring 7, 85649 Brunnthal, Deutschland (Germany)

SFC fuel cells use liquid fuel. Every SFC fuel cell employs DMFC (Direct Methanol Fuel Cell) technology which transforms methanol directly into electrical current. That's a real advantage, especially for mobile applications, because liquid methanol is easy to transport anywhere in practical SFC fuel cartridges.

The annual sales are of the tune of 35,000 per year

All SFC's fuel cells are based on DMFC (Direct-Methanol-Fuel-Cell) technology. They use an eco-friendly catalytic process to convert methanol into electricity using a direct and efficient process without intermediate steps. This makes this technology one of the cleanest ways of generating electricity. In the reporting period January through March 2016, the SFC Energy Group generated sales of EUR 10.30 million, compared to EUR 12.61 million during the prior year period.

#### Serenergy, Denmark

The company was founded in 2006 and today employs more than 50 highly skilled people. Serenergy has it's headquarter in Aalborg (Denmark) but also significant activities at our partner company Fischer Group in Achern (Germany). Serenergy provide everything from fuel stacks and systems for OEM integration all the way to providing complete turnkey solutions for diesel generator replacement. Serenergy develop and manufacture fuel cell stacks and power systems based on the High Temperature PEM fuel cell technology.

HT PEM fuel cells are similar to LT PEM fuel cells but operate at higher temperatures (150-180 degrees Celsius).

Serenergy's HT PEM fuel cells are integrated with fuel reformers, thereby making it possible to use a wider quality of methanol. HT PEM fuel cells are ideal for commercial use. E.g. it is ideal to power vehicles as range extenders for batteries and small scale commercial buildings.

Furthermore, Serenergy's Methanol Fuel Cell Power Solutions are fuelled by a methanol mix, 60 % methanol and 40 % water, which means that it is less flammable than pure methanol.

#### UltraCell

A Bren tronics company

399 Lindbergh Avenue, Livermore, CA, 94551

UltraCell is a wholly owned subsidiary of Bren-Tronics Inc, the worldwide leader in military porTable power, and leverages over 40-years experience in delivering MIL-STD power to the world's toughest war fighters.

The company was founded in 2002 to commercialize an advanced Reformed Methanol Micro Fuel Cell (RMFC) technology invented at the U. S. Department of Energy's Lawrence Livermore National Laboratory (LLNL). This technology enables a breakthrough in micro fuel cell performance. UltraCell is the first to commercialize RMFC technology to provide clean renewable energy to power porTable electronics. UltraCell's XX25<sup>™</sup> micro fuel cell system is leading the industry with its ultra-compact size and light weight. The XX25 is the only system

in its class to have undergone extensive Military Specification qualification testing and field trials.

UltraCell's XX25 is 4 times lighter and 16 times smaller than any other competitive fuel cell in the market for comparable power output.

While both UltraCell's Reformed Methanol Fuel Cell technology and DMFCs convert methanol to electricity, UltraCell has many advantages over a DMFC or solid oxide solution, including

- Higher efficiency with faster startup times
- Smaller size and lighter weight
- Cleaner operations with less CO2 emissions, and no need for water management
- Better operation and storage capabilities at low temperatures and in harsh environments.

UltraCell fuel cells use a mixture of methanol and water, which is easier to handle than pure methanol or propane gas. UltraCell first converts, or reforms, the methanol into small amounts of hydrogen and carbon dioxide, and then feeds these products to the fuel cell reaction zone for electricity generation. UltraCell's technology allows for higher power generation in a compact, rugged package that is easily carried, just like a hardbound book.



Fig 3.12: Overview of the Reformed Methanol Fuel Cell (RMFC System)

Methanol Reforming: Automakers took interest in such reformers, because of the advantages to store methanol on-board as liquid, compactness of reformer, faster start-up and potentially lower cost. These reformers were demonstrated in PEM fuel cell vehicles, but no fuel cell vehicle manufacturer is currently using this technology.

# 3.9.7 Efficiency

According to a paper published by Dr. Jens T. Müller, Germany, DMFC [77] system efficiencies are typically between 20 and 30 % (methanol in Æ DC power out) which, for power conversion systems in the power range of 10 - 250 Watts, is an exceptionally high number.

In the DMFC there exists the problem of cross-over of methanol from the anode to the cathode side, leading to secondary reactions, mixed potentials, decreasing energy and power densities and hence a reduced performance. This cross-over is caused by permeation of methanol due to a concentration gradient, indirectly dependent on the operation current and by molecular transport due to electro-osmotic drag, directly related to proton migration through the membrane which increases with increasing current density

The following Table provides the purchase of fuel cells by various companies globally by DOE, US Government [78].

Company	Country	Fuel Cell Provider	# of Units	Notes
Jiangsu Communications Services Company, Ltd.	China	First Element Energy	2	Feasibility study and pilot project, consisting of the installation of fuel cell units at two sites – one fueled by compressed hydrogen gas and the other using a mixture of liquid methanol and water.
Ascend Telecom	India	Intelligent Energy	1	Over a six-month period, fuel cell improved site power availability significantly while reducing fuel usage by 18%.
Microqual Techno Limited	India	Intelligent Energy	N/a	Exclusive 15-year agreement to provide fuel cell power solutions to Microqual- installed mobile telecom base station equipment on existing electricity transmission towers
Reliance Jio Infocomm	India	Ballard Power Systems	100	The order is the first of a series of planned deployments in Jio's India network.
Telkomsel	Indonesia	Ballard Power Systems	N/a	Fuel cells will supply critical back-up power to sites on the island of Sumatra.
Digicel Group Limited	Jamaica	Ballard Power Systems	13	This purchase brings Digicel's total number of fuel cells to 25.
Vodafone	Netherlands	Ericsson (Ballard Power Systems)	1	This pilot project in Rotterdam is expected to reduce emissions by 33 tons a year.

Table 3.47: International Telecommunications Companies Purchasing Fuel Cells, 2014-2015

Warid Telecom	Pakistan	Ballard Power Systems	N/a	Field trial – fuel theft was reduced and reliability improved with the fuel cell system, both of which positively impacted operating cost of the network site.
Globe Telecom	Philippines	Ballard Power Systems	20	Methanol-powered units are installed on rooftop locations in Manila.
Vodacom (Vodafone)	South Africa	N/a	N/a	Vodacom began using hydrogen fuel cell systems eight years ago and now has more than 200 fuel cells deployed. The company is now testing methanol-fueled fuel cells.

**Several research points out to the fact that the** DMFCs can add value to special-purpose vehicles including ambulances and forklifts, for example, low noise/vibration performance or less toxic emission feature.

The EASME (European Commission) in a press release state [79], that the German company Siqens has developed a High Temperature Methanol Fuel Cell (HT-MFC) with outstanding technical and economical characteristics. The first product will be an eco-friendly and affordable system named EcoPort for the camping and boat market. EcoPort generates electrical power using renewable methanol liquid fuel. The Danish company Danish Power Systems manufactures the key fuel cell component, the MEA (Membrane Electrode Assembly), for the Siquens products.

The emission comparison for a methanol based fuel cell and diesel generator is provided below (2KW/5 KW):

	ElectraGen ME System	Diesel Generator
	Fuel Cell System with Methanol-	
	Water Reformer	
Exhaust Emissions <sup>1,2</sup>		
Nitrogen Oxides (Nox)	0.007 g/kWh	7.5 g/kWh
Carbon Monoxide (CO)	0.17 g/kWh	8.0 g/kWh
Sulfur Oxides (Sox)	0 g/kWh	12.0 g/kWh
Particulate Matter	0 g/KWh	0.8 g/kWh
Carbon Dioxide (CO <sub>2</sub> )	783 g/kWh	1,500 g/kWh
Noise Emissions <sup>3</sup>		
Decibel rating	Quiet: 52 dB at 1 m	Loud 68 dB at 7 m
	47 dB at 7 m	

Table 4.48: Methanol Fuel Cell Systems vs. Diesel Generator [80]

	ElectraGen ME System Fuel Cell System with Methanol- Water Reformer	Diesel Generator
System Efficiency		
System Efficiency (%)	33%	10-25%
Operational Costs		
Maintenance (visits per year)	1	2-4
Theft Costs (fuel, parts)	None	Fuel & Parts
Reliability	Few moving parts	Many moving parts

**Note 1**: ElectraGen<sup>™</sup> ME System emissions data from ida Tech

**Note 2**: Diesel generator emissions data from EPA standards for 2007 and newer generators, EPA Standards of Performance for Stationary Compression Ignition Internal Combustion Engines; Final Rule July 11,2006

**Note 3:** ElectraGen system operated at 75% power output during noise test Source: Ballard Power Systems, ElectraGen

Hiroaki Takaguchi and Masakazu Ohashi of Fujikura Company, Japan brings out in their paper based on 1 KW methanol based fuel cell that "increasing the power storage of the DMFC system can be realized by increasing of the fuel tank capacity without increasing of the entire system volume so much. Therefore, it can be said that the more power storage is required, the more demand for DMFCs will be increased as compared with diesel generators."

DESCRIPTION	TECHNICAL DATA
Max nominal power	800 w at 48v DC
Average nominal power (24 hour average)	650w at 48V DC BOL (at sea level25°c,
Average nominal power output 24 hours	15.6kwh
Nominal voltage	48V DC
Nominal charging	13.5 A
Lifetime for the generator	3000 hours
Start-up time	3-10 minutes
Automatic frost production mode	System temperature <5°c will initiate frost protection
	mode.
BACK UP TIME	
Methanol storage-internal	Min.24 Hours
Methanol Storage	Option –Backup time depends on external storage
	volume system prepared for supplying internal storage
	tank easy safe refilling

Table 4.49: Methanol Fuel Cell Specification

PHYSICAL DIMENSION	
Dimensions D*W*H	900*605*2,230mm/19" rack
Weight (DMFC generated0	-250 kg
Noise (at 1 m ) Db(A)	55 typical 63 peak
Heat power output	2,100 w
Required area/space around the unit	100 mm, in particular in front of the ventilation inlet to
	ensure optimal coolant distribution.
INTERFACE ELECTRICAL	
Start/stop signal	The DMFC generator will measure the voltage on the
	battery bank, and when minimum voltage is reached
	the DMFC generator will start and stop again, once the
	max voltage has been reached.
Charging voltage to battery bank9min/max)	48 V DC (min34V and max.54 V)
Supply voltage from battery bank (min/max)	48 V DC (min.34 V and max.54V)
METHANOL CONSUMPTION AND	
LOGISTICS	
Nominal consumption of methanol	=0.7 litre per hour (depends on operation conditions)
Quality	High purity methanol 100%
INSTALLATION REQUIREMENTS	
Ventilation	Min.air intake 700 Nm/hour
Temperature limits	Temperature for storage, transport and operational
	surroundings +5*c 40c unto 4000m with 20% reduced
	power output
Maximum angle of inclination	0°-3°
OPERATION	
HMI(HUMAN MACHINE INTERFACE)	ON/off button on DMFC generator with button blink
	patterns for normal and error states, webpage with
	additional information and settings
COMMUNICATION	
Remote monitoring	SNMP/HTTP

# 3.9.8 Potential in India

As per news reports [81], over 70% of India's 425,000 telecom towers experience power outages of approximately eight hours per day. Some 150,000 or so of these towers are off-grid. A good potential to introduce methanol based fuel cell or power options could provide an alternate sustainable source.

Electricity costs make up 40 percent of cell tower operating costs in India, compared to 12 percent for Europe, largely driven by the cost of diesel [82].

In October 2015, the U.K.-based company Intelligent Energy [82], announced a £1.2 billion (\$1.8 billion) deal with India's GTL Limited to back up about 27,000 cell phone towers, Intelligent Energy has deployed about 100 megawatts of fuel cells for telco tower backup power in India with customers including Microqual and ATL, and has about 400 megawatts under contract. But its new deal is with its own subsidiary, Essential Energy, which owns the energy management contracts for GTL's tower fleet

Intelligent Energy makes proton exchange membrane (PEM) fuel cells that run on pure hydrogen. PEM fuel cells are cleaner and more efficient

Ballard Power Systems [83] had also received purchase order in September 2015 from Aditya Birla Group (Aditya; www.adityabirla.com) for fifty (50) ElectraGenTM-H2 direct hydrogen modules that will be deployed in the Idea Cellular network in India (www.ideacellular.com)

Idea Cellular, is one of India's largest wireless service providers and is a member company of the Aditya Birla Group of companies. Idea Cellular has 165 million subscribers, including 37 million data users, and revenue of US\$5 billion which represents 18% market share. Idea Cellular has untaken extensive testing and trialing of Ballard's ElectraGenTM product since late-2013.

The Aditya Birla Group has been a leading innovator in the many industrial sectors in which it operates. Its chemical division, ABCIL, owns chemical processing facilities throughout India. A number of these plants generate hydrogen as a by-product of chemical production processes. As yet another business innovation, the Company plans to capture its low cost by-product hydrogen from select chemical plants and utilize it as a fuelling source for the newly ordered ElectraGenTM-H2 modules, which it plans to deploy in the Idea Cellular wireless network.

In April 2015, Ballard Power Systems [84] received a purchase order from Reliance Jio Infocomm Limited (RJIL) for 100 ElectraGen<sup>™</sup>-ME fuel cell backup power systems to be deployed in its wireless telecom network in India. Shipment of these initial 100 systems is expected to be completed in 2015.

The purchase order follows successful completion of an extensive 12-month trial by RJIL of fuel cell systems from various vendors, with Ballard's ElectraGen<sup>™</sup>-ME methanol-fueled system ultimately having been selected for use in backup power applications. This purchase order is the first of a series of planned deployments in RJIL's India network.

RJIL is a subsidiary of Reliance Industries Limited. As the only company with a pan-Indian broadband wireless access license, RJIL is in the process of building out a new 4G telecom network, which requires the acquisition of hundreds of new base station towers.

Railways are reported to be using as much as 5% of the total Diesel oil consumption within the country. Railways are also using near about 1.5% of the electrical energy consumed in India. So there exists a need for alternate energy sources and devices [85]

# 3.10 DIMETHYL ETHER (DME)

#### 3.10.1 Background

DME is the simplest ether with a chemical formula of  $C_2H_6O$ . The properties of DME are provided in Table 3.50

Chemical formula	H3C-O-CH3
Molecular weight	46.07
Oxygen content by mass	34.8 %
CAS Registry number	115-10-6
Boiling point @ 1 atmosphere	-24.825 °C
Critical temperature	126.85 °C
Critical pressure	5370 kPa
Liquid density @ 25 °C	656.62 kg/m3
Vapor pressure @ 20 °C	516.76 kPa
Flammability limits in air by volume %	3.4 – 18

Table 3.50: DME Properties [86]

Source: [86], Oberon Fuels

DME can be produced from a variety of feedstock

- Renewable: Biomass, Municipal Waste, Waste from Pulp and Paper Production
- Traditional: Coal and Natural Gas

# 3.10.2 DME Applications

DME finds end use in several sectors as produced in Table 3.51

End Use Sector	Remarks
Aerosol Propellant	Replaced chlorofluorocarbon
	Low volatility, no toxicity, no carcinogenicity and good
	water/alcohol solubility
	DME-based aerosol propellants are extensively used in room
	fresheners, deodorants, hair sprays, antiperspirants, and pain
	relieving sprays.
Refrigerant	Requires additives.
	Low pollution and good refrigerating effectiveness
Foaming Agent	polystyrene, polyurethane and thermoplastic polyester
	Good pore size, great flexibility and improved pressure
	resistance

Table 3.51: Applications of DME

End Use Sector	Remarks
Chemical Intermediate	Dimethyl sulfate, Dimethyl sulfide, Dimethyl carbonate and
	polycarbonates
Laboratory Reagent	<ul> <li>low-temperature solvent and extraction agent</li> </ul>
	<ul> <li>precursor to the useful alkylating agent, trimethyloxonium</li> </ul>
	tetrafluoroborate
Diesel Fuel	high cetane number, moderate modifications required
LPG substitute	Similar properties, less reliance on oil-based LPG in future
Synthetic Biofuels	can be manufactured from lingo cellulosic biomass
Power Production	performance comparable to natural gas
	especially in isolated or remote locations where it can be difficult
	to transport natural gas
Cleaning Material	Cleaning material for laboratory systems and some high
	precision, high value added cleaning applications, such as in
	electronics

Source: International DME Association

# 3.10.3 DME Historical Development

The following time line from the International DME Association summarizes the history of DME



Figure 3.13: DME development timeline Source: International DME Association

# 3.10.4 Global Commercial Applications

Globally, DME's utilisation has been in two major sectors

- 1. As an aerosol
- 2. As a fuel

Fuel uses can be further classified into two categories

- 1. Cooking fuel
- 2. Transport fuel

DME is being currently utilised as a cooking fuel in China. The possibility of using it as a transport fuel is being currently pursued in many countries. Due to DME's physical and chemical properties, (it can be liquefied at low pressure, 5 bars), it has been established as a potential diesel substitute. However, modest engine modifications are required for fuel systems and engine management systems. DME engines are modified compression ignition type. For seal systems, metal-to-metal seals using non-sparking metals have been shown to be the most effective type of seal [87].

In China, approximately 90% of DME is utilised as cooking fuel. The remaining 10% has been reported to be used for welding, cutting and brazing applications

# 3.10.5 Comparison on Calorific Value

On net calorific value basis, following can be deduced:

- 1.6 kg of DME is equivalent to 1 kg of LPG
- 1.25 m<sup>3</sup> of DME is equivalent to 1 m<sup>3</sup> of LPG
- 1.8 m<sup>3</sup> of DME is equivalent to 1 m<sup>3</sup> of diesel

# 3.11 DME as a LPG substitute

Among the various current applications of DME, LPG blending represents the largest market for DME. LPG scarcity is a great concern in the countries that have less gas reserves, as they have a reduced capability to replace LPG with natural gas. DME has emerged as a reliable source for such countries to minimize their LPG imports by blending DME in LPG (up to 20%) without any change in current infrastructure. DME is also implemented as an aerosol propellant under liquefied gases propellant category. The various other applications of DME include its use in the form of chemical feedstock, solvent, refrigerant and for welding & brazing operations. Oberon Fuels [88] cites the following advantages when using DME as a blended domestic fuel.

- Burns with no particulate matter and minimal NOx
- Sulfur-free
- Price competitive with that of diesel; not tied to the price of crude oil
- Meets or exceeds strict emissions standards
- Simpler engine results in lower maintenance costs
- No spark plugs required
- Compression ignited, resulting in higher efficiency
- Safe, rapid dispensing, similar to that of propane
- Spillage will not contaminate soil

# DME-LPG research in India

A research was carried out by LERC on the effects of various percentages (5%, 10%, 15% and 20%) of DME in LPG. The studies are broadly classified in to three categories:

- Effect of LPG-DME mixture on rubber components.
- Effect of LPG-DME mixture on metallic parts of cylinders, pressure regulators and
- Effect of LPG-DME mixture on the thermal efficiency of existing LPG burners being used at homes in India.

# Conclusions from the research

The rubber hose used for connecting the cylinder with the burner showed that there was an increase in the absorption of medium with the increase in percent DME in LPG blend.

There was no significant change in the chemical composition of the parent materials used for the manufacture of cylinder, valve and regulator when exposed up to 20% of DME in LPG mixture for ageing test for one month

# Standard for DME blend in LPG

A draft standard for a DME-LPG blend has been prepared by a Joint Working Group of the International DME Association and the World LPG Association in 2011 [102], which is provided in Table 3.52 along with suggested testing protocols.

The standard has been derived from Chinese, ISO, EN and ASTM standards applicable for LPG and DME.

Further as a technical requirement, it specifies that at a worldwide level, the quality of DME should be consistent with the DME standard prepared by the Working Group 13 (WG13) of the ISO TC28 / SC4 and the quality of LPG must meet the national requirements and/or standards.

Further, guidelines on packaging specify that propane cylinders used for DME-LPG blends should have appropriate seals made of HNBR (depending on additives and characteristics) or Teflon. Viton, the material usually used with LPG, is not compatible for use with DME-LPG blends containing DME at 20% weight.

Characteristics	Units	Limit	Requirements	Testing Protocol
Mass fraction of DME in DME-LPG blends	%(w/w)	Less than	20	Gas chromatography method
Vapor pressure at 40°C	Кра	Less than	1380	Visual inspection by pressure gauge or ISO 8973 and 3993
Components of C5+ (see Note 1)	%(w/w)	Less than	1	Gas chromatography with EN 27941 or ISO 7941
Ethyl Mercaptan (odorant)	ppm	More than	10	ASTM D5305
Evaporation Residues	%(v/v)	Less than	0.05	ASTM D 2158 / EN 15470 & 15471
Total Sulfur	ppm	Less than	40	EN 24260
Corrosion (copper strip)		Less than	1	EN 6251
Free water	ppm	Less than	60	Visual inspection by sedimentation and measurement of the volume of water extracted from the bottom of the tank

Table 3.52: DME-LPG Blend Draft Standard [102]

Note 1: Limits for these components are recommendations only; actual limits should be as specified in the governing LPG quality standard.

# Scope of Recommendations

The recommendations in this document cover the quality, manufacturing, packaging, labelling, marking, accessories, filling, transport, storage, safe handling, and quality control for DME-LPG blends.

The recommendations are applicable to LPG-DME blends used for cooking and heating applications in households, commerce, and industry.

# 3.12 DME and Diesel

The liquid density of DME is about 80% of diesel fuel, and specific energy content (lower heating value) is about 70% [91, 92]. The comparison of DME and Diesel properties are provided in Table 3.53

Property	DME	Diesel Fuel
Carbon content (mass %)	52.2	86
Hydrogen content (mass %)	13	14
Oxygen content (mass %)	34.8	0
Critical temperature (K)	400	708
Critical pressure (MPa)	5.37	3.00
Critical density (kg/m3)	259	-
Liquid density (kg/m3)	667	831
Cetane number >	55	40-50
Auto-ignition temperature (K)	508	523
Stoichiometry air/fuel ratio	9.0	14.6
Boiling point at 1 atm (K)	248.1	450-643
Enthalpy of vaporization (kJ/kg)	467.13	300
Lower heating value (MJ/kg)	27.6	42.5
Gaseous specific heat capacity (kJ/kg-K)	2.99	1.7
Ignition limits (vol% in air)	3.4/18.6	0.6/6.5
Modulus of elasticity (N/m2)	6.37E+08	14.86E+08
Kinematic viscosity of liquid (cSt)	<0.1	3
Surface tension (N/m)	0.012	0.027
Vapor pressure at 298K (kPa)	530	<<10

Table 3.53: Comparison of DME and Diesel Properties as fuel

Source: Oak Ridge National Laboratory study: Emissions and Performance Benchmarking of a Prototype Dimethyl Ether-Fueled Heavy-Duty Truck

# 3.12.1 Advantages and Disadvantages

Favourable and challenging factors as compared to diesel fuel for compression ignition (CI) engines are as follows:

# 3.12.1.1 Favourable

- High cetane number fuel (superior ignitibility in compression ignition engines)
- Similar energy efficiency and power ratings

In addition to above, the world's largest truck manufacturer, Volvo [89], which has done extensive trials on DME fuels in its trucks with 10 trucks, 1.2 million km, lists the following advantages of DME as a truck fuel

- Easy to store and transport (liquefies at low pressure)
- Not cryogenic, negligible fugitive emissions, no tank venting
- Clean, no soot combustion (no Particulate Filter required)
- Non-toxic
- 10% carbon reduction in combustion balance compared to diesel
- Low global warming potential (GWP = 0.3 @100 yr)
- Synthesis from variety of bio-based feedstock
- High well-to-wheel efficiency for GHG emission
- Potential RINS opportunities (where renewable feedstocks are used)
- Synthesis from natural gas provides opportunity for single fuel from NG/methanol pathway with diesel like efficiency

# 3.12.1.2 Challenges

- Does not contain long chain molecule
- Low critical point,
- Low viscosity,
- Negligible lubricity
- High vapor pressure (the fuel system needs to be pressurized to maintain DME in a liquid state)
- Seal and gasket material compatibility
- Combustion development

# 3.12.2 Driving and Implementation Concerns

The driving forces and implementation concerns for DME in India are provided below:

# Driving forces for DME as a fuel into the Indian market

- 1. Well researched and tested fuel over last 10-15 years in several countries
- 2. Existing use as cooking fuel in China without major safety concerns
- 3. Easy blending in LPG without any systems modifications
- 4. Established engine technology available in the market
- 5. Environmentally superior fuel with lesser soot & GHG emissions than conventional diesel

# Major implementation concerns in India are

- 1. Awareness among consumers
- 2. Awareness of DME as a substance and its behaviour among regulatory authorities like fire department, health department, etc.
- 3. DME material compatibility especially injection systems and leakages
- 4. DME's performance for Indian road conditions
- 5. DME fuelling stations (to combine with existing petrol/diesel or CNG, or both stations)
- 6. DME safety guidelines at consumer end

According to a paper published by The Energy Institute, Pennsylvania University in 2003, 25% addition of DME by weight into diesel fuel reduced fuel viscosity below the ASTM specification. This suggested that viscosity rather than miscibility is the limiting factor in blending DME with diesel fuel.

DME cannot be used as-is on the domestic trucking fleet, but with relatively modest engine modifications – mainly to the fuel system - diesel trucks can easily run with 100% DME.

# 3.12.3 DME Vehicle Emissions

There are several references for comparing DME emissions with conventional diesel ones based on different emission norms. Nox emissions for the DME truck fluctuate between about 30 and 100 mg/s. For the standard injection quantity DME produces less Nox as compared to diesel combustion, while for a comparable heating value, the Nox emission of DME is observed to be higher due to the presence of oxygen from increased amount of fuel supplied.

The emission results from two test cycles (steady state and HHDDT) for DME trucks are provided from the results of **Emissions and Performance Benchmarking of a Prototype Dimethyl Ether-Fueled Heavy-Duty Truck study [90]**. The specifications of the prototype DME truck with conventional diesel truck is provided in Table 3.54

	Prototype DME truck	Conventional Diesel Truck
Displacement [L]	13.0	11.0
Compression Ratio [-]	17:1	16.5:1
Max Torque [Nm]	2200	2050

Table 3.54: Prototype	DME truck	properties	[93]
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# TIFAC, DST, Govt. of India | Utilisation issues of Methanol and DME

Max Power [HP]	450	405
Fuel	DME	Diesel
Fueling	Common Rail	Direct Injection Unit injector
Max Rail Pressure [bar]	300	2400
Emissions Compliance	Euro V	U.S. 2010
After treatment	DOC	DOC, DPF, Urea SCR

Source: AFDC, US

The conclusions from the above tests were as follows:

- NOx emissions were within the expected range for the prototype DME truck based on the emission standard for which the engine was calibrated (Euro V). This NOx emission level was met without the use of NOx aftertreatment
- HC emissions were within the expected range for a truck compliant with the Euro V emission standard
- Under the steady-cruise conditions the CO emissions were below the detection limit

Overall emissions from DME fuelled vehicles are provided in Figure 3.14:



# **1. DME as Cleanest Diesel Alternative**

Source : R & D Group for Practical Use of DME Fuel Vehicle

Figure 3.14: Emissions from DME [88]

The emission results from two test cycles for DME trucks are provided in table 3.55 reproduced from the results of work carried out by both Volvo Truck and Isuzu:

	Cycles	NOx (g/KWh)	PM (g/KWh)	HC (g/KWh)	CO (g/KWh)
lsuzu	JE05	0.78	0	0.138	0.67
	In use e	mission test resul	ts- Japanese tru	ck after 76,000	miles
	Euro EEV	2.00	0.02	0.25	3
	limits (ETC)				
	PEMS 20 tons	1.66	0	0.25	2.34
Volvo	PEMS 60 tons	1.72	0	0.31	1.82
	In use emission test results – European trucks after 115,000 miles				

Table 3.55: Emissions from a DME fueled truck

Source: Aum Energy

The emissions-related benefits of DME as shown by Volvo Trucks certainly point to zero particulates, lower NOX, zero SOX and 10% lower CO<sub>2</sub> emissions but with equivalent fuel efficiency against a diesel engine.

Isuzu has been working on DME since 2001 and has focused on city buses and short-haul trucks in tandem with a programme to develop better diesel engines. It states that DME for Euro VI can be achieved with a simpler configuration than with a diesel engine:

- Simpler Exhaust After-treatment system (EAS) and also simple Exhaust Gas Recirculation (EGR) system, both of which have a cost benefit
- Fuel system modified to suit DME

Isuzu feels that DME is especially attractive in countries with Euro III standards where the equivalent diesel engine leads to higher emissions, with EAS not being feasible for such high sulphur fuels. A DME engine with an EGR fitted has similar characteristics to a CNG vehicle from a  $CO_2$  perspective, with higher thermal efficiency. It has a 4x better distance and time-to-fill ratio that CNG and even better than diesel.

Isuzu has been working with the Japan Government in relation to the legislation of technical standards for DME vehicles. In 2015, notification was received for the modified application, importantly noting that the measurement of particulate matter (PM) is no longer necessary. Isuzu is now expecting to enhance its DME test fleet in service of garnering further support.

Aside of new trucks, it is also felt by experts that DME can be used in a dual-fuel truck that is equipped with a retrofitted fuel storage and injection system for DME. Paralleling the manner in which LPG has been used in trucks, by adding a DME layer into the fuel system, the potential uptake of DME – and therefore impact on transport-related emissions – can be markedly accelerated through a retrofit programme. By focusing such a programme on the existing Indian truck fleet (primarily older Ashok Leyland and Tata Motors trucks), the delta between current and future emissions is expected to be markedly wide.

# 3.13 Research & Development

# 3.13.1 Germany

The German government and Ford are co-funding a three-year €3.5 million research project that began in September 2015 [100], which will test the first production cars to run on DME, and Oxy Methylene Ether (OME1), a liquid usually used as a solvent in the chemical industry. The objective is to provide power and performance of modern internal combustion engines with environmental benefits comparable to an electric vehicle.

For the project Ford European Research & Innovation Center, Aachen, Germany, will work together with RWTH Aachen University, the Technical University of Munich, FVV, TUEV, DENSO, IAV Automotive Engineering, and Oberon Fuels. Oberon Fuels will supply DME for the project. DENSO will supply the fuel injection equipment to the research partners.

It is estimated that DME from renewable energy sources could offer well-to-wheel emissions of about 3 g/km CO<sub>2</sub>. Bio DME research is being undertaken in the market and could provide a viable source of fuel in markets such as Scandinavia and Canada where ample feedstock is available.

#### 3.13.2 US

The Alternate Fuel Energy Center of the US Department of Energy reports that different experiments have been conducted over years with DME as a co-blend.

Modifications required to suit the fuel system in order to use DME include pressurised tanks in a leak-proof system. The pressure keeps the fuel in liquid form all the way to injection. Common rail technology is used to create the optimum injection pressure. Larger tanks may be used to compensate the lower energy content of DME which is approximately 55% relative to diesel on a volumetric basis.

Components which were modified to suit the requirements of DME trucks were [93]:

- 1. Tanks: DME is filled as a liquid via a special nozzle and stored in liquid form in the tanks.
- 2. Pump: a special fuel pump regulates the pressure in the common rail injection system.
- 3. Injectors: special DME injectors have been jointly developed by Volvo and Delphi.
- 4. Engine: the moving parts are identical to those in the diesel variant.
- 5. Engine management: the software has been modified to suit the new injection system.

The modified engine components consist of:

- High pressure fuel pump, common rail, and fuel injectors.
- Moderate proprietary changes due to DME properties:
- Higher fuel flow needed due to 67% energy content of diesel.
- DME fuel also includes:
  - o Lubricity improver for low fuel viscosity
  - Chemical properties  $\rightarrow$  seal & gasket materials
- DPF can be removed; however an oxi-cat is used for CO and HC reduction.
- EGR versus SCR is under investigation for NOx control.

# 3.13.3 Japan [94]

Field tests on two 3.5-ton, DME, trucks built by the Isuzu Advanced Engineering Center and registered for commercial use (green license plates) are continuing. The test vehicle in the Kanto region completed the field test at the end of July 2011 after driving a total of 100,000 km. As of the end of February 2012, the test vehicle in the Niigata region had been driven a total of 95,000 km, and the project was finished in 2013.

In Japan, two DME trucks are running (with business license plates), with the goal being to develop technical regulations for DME vehicles. The attitudes towards new fuels are changing in Japan has changed, and steps commercialize DME fuel are being accelerated.

# 3.13.4 India [95]

In July 1998, BP had signed a technical and commercial agreement with IOCL, GAIL and IIP to develop DME as a multi-purpose fuel in India. <u>The major end use of DME envisaged</u> <u>through this plan was to replace naphtha and diesel for power generation</u>. The research focused on four southern Indian states of Andhra Pradesh, Karnataka, Kerala and Tamil Nadu. The research concluded that DME can be stored, shipped, pumped and transferred with existing infrastructure used for LPG with modifications in seals and gaskets.

The project ultimately did not proceed due to a change in BP's position, but not because of a technical limitation.

# 3.14 DME Specifications

DME is comparable to LPG so it can be used as heating fuel, either mixed with LPG or in its pure form. DME also has very good auto-ignition qualities which makes it a replacement fuel for diesel.

The energy efficiency chain is a key issue for choosing DME, which has a better life cycle  $CO_2$  balance than most of the other alternative fuels. DME is a commodity which can be made from various raw materials, including natural gas, coal, black liquor, biomass, and wastes.

Various engines [96] as developed by vendors are provided below:

- Large vehicles: Volvo, SAIC, Isuzu (Bus), Mack trucks (part of Volvo Group)
- Small cars: Ford (in process)
- OBATE process catalyst: Holder Topse



Figure 3.15: VOLVO DME Engine, Source: IDA [96]



Figure 3.16: SAIC DME Engine, Source: IDA [96]



Figure 3.17: MAC Truck DME Engine, the MACK<sup>®</sup> MP8 engine [97]

ISO 16861:2015 [98] is applicable for DME used as heating fuel, industrial fuel, and to replace diesel fuel or gas oil. It does not deal with the possible additives necessary for specific end-use applications, for example, odorant typically added to heating fuel and lubricity improvers for DME used as replacement of diesel. Such additives are typically specified for the different end-use applications, at an appropriate level — national, regional, or international.

ASTM D7901 - 14b is the Standard Specification for Dimethyl Ether for Fuel Purposes [99]. This specification covers DME for use as a fuel in engines specifically designed or modified for DME and for blending with LPG. This specification is for use by manufacturers of dimethyl ether, by engine developers of purpose-built engines, in contracts for the purchase of DME for fuel purposes, and for the guidance of consumers of this type of fuel.

Comparison of DME with other potential fuels such as Methane, Propane, Butane and Diesel Oil are provided in Table 3.56:

Property	Methane	Propane	DME	Butane	Diesel oil
Chemical formula	CH4	C3H8	СНЗОСНЗ	C4H10	-
Boiling point (°C)	-161.5	-42.0	-25.1	-0.5	180 - 360
Liquid Density (g/cm3,	- 0.49	0.67	0.57	0.84	
20°C)					
Specific gravity of gas	0.55	1.52	1.59	2.00	-
(vs. air)					
Saturated vapor	-	9.3	6.1	2.4	-
pressure (atm, 25°C)					
Ignition point (°C)	650	470	235	430	250
Explosion limit (%)	5 – 15	2.1 - 9.4	3.4 – 17	1.9 - 8.4	0.6 - 7.5
Cetane number	0	5	55 – 60	10	40 - 55
Net calorific value	12,000	11,100	6,903	10,930	10,200
(kcal/kg)					
Net calorific value	-	5,4	4,6	6,2	8,6
(kcal/l) liquid					
Net calorific value	8,6	21,8	14,2	28,3	-
(kcal/Nm3)					

Table 3.56: Comparison of DME with other fuels

Source: AEGPL Conference Nice 6-8 June 2007 – F. Bollon, Total

While handling of DME is similar to propane, pumps, valves, and seals on DME tanks and DME infrastructure must be made of specific materials since there is a risk of seal and gasket failures with some materials. ASTM specification D7901 provides limited guidance on safety and handling of DME, including elastomer selection for gaskets and seals.

# 3.14.1 Material Compatibility

The following materials have been found to be compatible with DME [101]: Nitrile (NBR, BUNA-N), Hydrogenated NBR (HNBR), Silicone (VMQ), Fluorosilicone (FVMQ), Perfluoroelastomer (FFKM), Polytetrafluoroethylene (PTFE), and stainless steel. This material compatibility information has been generated by commercial DME handlers, as a general reference, and listed in ASTM D7901.



Figure 3.18: Volvo DME Truck

# 3.15 METHANOL STORAGE AND HANDLING GUIDELINES

Methanol must be stored in a dedicated location, where it is protected from heat and ignition sources. All electrical systems must be fully enclosed and explosion proof. In order to prevent the methanol from absorbing moisture, it must be stored in a sealed container. If the container is sealed, there should be an allowance for thermal expansion; otherwise, large changes in temperature may cause the methanol to expand and rupture the container.

Methanol is routinely stored in tanks farms consisting of above-ground, floating roof tanks and smaller, internally baffled floating baffle tanks. Tanks must be grounded to avoid hazards associated with static discharge.

Tanks and storage vessels should be fitted with dip-tube-filling to protect against ignition from static electricity generated as a result of liquid falling through air.

Methanol is not a static accumulator. Grounding is required for lighting systems, pipe racks, pumps, vessel, filters, and all other equipment near and potentially within range of methanol vapor. Tall towers and other equipment subject to lightning strike must be equipped with lightning arresters. Hoses must be grounded.

Best practice for tank storage (in particular, of large volumes) of methanol uses internal or external floating roofs to minimize methanol vapor space within the tank and to reduce the amount of air that can mix with that vapor and control the volume of vapor emission from tanks. Alternatively, inert gas blanketing can be used to prevent formation of explosive atmospheres within tank vapor spaces. Dry nitrogen is the preferred inert gas for blanketing. Blanket gas should be free of carbon dioxide to avoid corrosion in the presence of moist air, and to avoid product contamination that could increase methanol acidity. Commercially, methanol storage tanks include an internal floating roof to mitigate VOC emissions and are blanketed with nitrogen.

It is recommended that the outside of methanol tanks be painted with heat reflecting paint. This measure will reduce vapor losses from the tanks.

Methanol is non-corrosive to most metals at ambient temperatures; exceptions include lead, magnesium and platinum. Mild steel is usually selected as the construction material.

Many resins, nylons and rubbers, particularly nitrile rubber (Buna-N), ethylene propylene rubber (EPDM), Teflon and neoprene are used satisfactorily as components of equipment in methanol service

Methanex Corporation advises the following for methanol storage systems:

- 1. Dedicated systems including equipment labeling
- 2. Others- must be cleaned, flushed & sampled
- 3. Equipments must be protected against contamination
- 4. Compatible material of construction preferably Mild Steel (MS). Others like plastics, aluminum, copper alloys & zinc (including galvanized steel) not recommended.
- 5. Storage tanks (internal or external floating roofs) must be designed as per local laws applicable & engineering standards incorporating safety measures such as bunds, dykes, level indicators, conservation vents & pressure vacuum relief valves & earthling. Overflow pipes are not recommended.
- 6. Dry Nitrogen (free of CO2) blanketing is recommended for vapour spaces above storage limit inside tanks.
- 7. For earthling, carbide tipped clamps & dip tube fittings are suggested.
- 8. For piping, mild steel is recommended without any screwed connections. Non ferrous materials are not recommended in pipe materials.

# <u>The Indian standard IS7444.1974 provide storage guidelines for methanol, both for</u> <u>small and large storage facilities including packaging and labelling</u>

It states that Carbon dioxide or dry chemicals are considered most effective hand extinguishers for fires involving methanol.

Further, the standard specify that the tanks and equipment, pumps, piping and valves shall always be drained and thoroughly flushed with water before being repaired. No repair job shall be taken up while the equipment is in operation and the lines are full of methanol.

# For small storages, Methanol institute suggests the following standards:

- IFC Chapter 34.
- NFPA 30.
- OSHA CFR 49 1910.119 and other regulations pertaining to hazardous materials.
- Policies and procedures must also address safety considerations raised in a Hazard and Operability Study (HAZOP), performed prior to delivery of the first tanker truckload, tote, or drum of methanol.

- Methanex Corporation's Corporate Manual: Container Filling Best Practice, Document #CR3RC250.
- ISO 9001: 2000 Quality Management Systems.

# Methanol Truck Loading

Generally, loading pumps pump from tanks to the truck loading area. The trucks are loaded from the top via loading arm with a dip pipe to prevent static electric charges. Vapour recovery from the truck loading vent is provided to reduce methanol emissions. Piping and automatic valves are provided to allow ship loading from one methanol product tank and truck loading from the other tank.

# Shipping Terminal

A shipping terminal could use an inert gas to pad storage tanks for both gasoline and methanol, but for somewhat different reasons. The purpose in padding gasoline storage may be fire protection because of the relatively low concentration of the lower flammability limit. The purpose of padding methanol may serve multiple purposes: fire protection due to the wide flammability range, and to maintain purity in an area that has characteristically high humidity.

At normal liquid storage temperatures, vapor space for gasoline storage quickly exceeds the upper flammability limit; that of methanol at 36% does not. Methanol storage tanks may remain in the flammable range even at relatively high liquid temperatures.

#### Methanol Ship Loading

Methanol loading pumps pump product from the methanol product tanks to the jetty to load ships. Vapour recovery systems are provided to reduce methanol emissions from ship loading. The recovered methanol is pumped back to the crude/off-specification methanol tank. Methanol slops receiver and methanol slops load-out pump are provided to gather methanol-containing drains from the ship loading areas and vapour recovery system. These are pumped back to the crude/off-specification methanol tank. Firewater is pumped to fire monitors at the jetty from the main firewater pumps.

# 3.16 DME STORAGE & HANDLING

The storage, handling, distribution and safety aspects of DME are very similar to those of LPG, in order to the similarity in physical properties of these substances. One of DME's most important characteristics is its low ignition temperature, which is similar to that of diesel fuel.

Properties	Unit	DME	LPG
Vapor Pressure	kPA	530	520
Liquid Density	kg/m3	667	540
Heating Value	MJ/kg	28.8	46
Bottle Fill	%	85	80
Mass per Bottle Unit Vol.	kg/m3	567	432
Energy per Bottle Unit Vol.	GJ/m3	16.3	19.9

Table 3.57: DME and LPG properties

For maximum flexibility, it is desirable that storage tanks for DME be rated at 250 psig, but a rating of 185 psig is adequate. The tank should be rated for deep vacuum (20–25 inches of Hg). In general, tanks intended for propane service are adequate, but butane and isobutane tanks may not be.

The manways and other flanged openings of tanks used for flammable propellants storage should be equipped with an inert gasket having a melting point above 816°C (1500°F), e.g., a metal or an appropriate spiral wound or composite (graphite-based) gasket.

Pressure relief valves must be in accordance with ASME and CGA requirements for the specific propellant in storage. For DME service, Kalrez® perfluoroelastomer seats are recommended.

Workers must always wear a self-contained breathing apparatus when entering tanks or other confined areas where high concentrations of HP DME vapors might exist. They should use the buddy system and a lifeline.

			L	PG
	DME	Diesel	Propane	Butane
Formula	CH3OCH3 or	C8 to C25	C3H8	C4H10
	C2H6O			
Mole weight	46.07	≈200	44.11	58.13
Boiling temperature, oC	-25	≈150-380	-42	-0.5

Table 3.58: Comparison of DME with other fuels

# TIFAC, DST, Govt. of India | Utilisation issues of Methanol and DME

Vapor pressure @20°C, bar	5.1	-	8.4	2.1
Liquid viscosity @25°C, kg/ms	0.12-0.15	2-4	0.2	0.18
Liquid density @20°C, kg/m3	660	800-840	490	610
Gas specific gravity (vs air)	1.59	-	1.52	2.01
Lower heating value, kJ/kg	28430	42500	46360	45740
Explosion limit in air, vol %	3.4-17	0.6-6.5	2.1-9.4	1.9-8.4
Cetane number	55-60	40-55	5	-
Auto ignition temperature@ 1 atm, °C	235	206	470	365
Stoichiometric A/F, kg/kg	9.0	14.6	15.7	14.8
Latent heat of evaporation, kJ/kg	410	250	426	390

Due to its similar properties with LPG, Dimethyl ether can be stored and transported using conventional LPG tankers. According to Japan LPG Center and for cooking appliances, the upper limit for DME in the DME/LPG mixture is assumed to be about 20% to 25% wt DME (without appliances modifications). According to the Chinese producers replacing 1 kg of LPG by 1 kg of DME does not change significantly the duration for boiling 1 liter of water

The Technical Committee on Chemical Products of the Japan Industrial Standards Committee has already established a tentative standard for DME as fuel under the number TS K 0011 in 2005. But this Committee agreed that DME as alternative to diesel and DME as alternative to LPG may have separate technical specification and that the TS K 0011 is mainly a proposal for DME as diesel.

Troy A. Semelsberger, et.al in their paper titled "Dimethyl ether (DME) as an alternative fuel" provides the state that the most challenging aspects of a DME engine are related to its physical properties and not to its combustion characteristics. As the viscosity of DME is lower than that of diesel by a factor of about 20; there is an increased amount of leakage in pumps and fuel injectors. There are also lubrication issues with DME; resulting in premature wear and eventual failure of pumps and fuel injectors. Additives have been used to increase the lubricity of DME, and the commonly used additives have been those developed for reformulated diesel.

# 3.17 DME FILLING IN TRUCKS

High-speed filling equipment at 80 L/min has been developed by TOKICO TECHNOLOGY for DME medium-heavy duty trucks to be competitive against existing diesel oil filling speed 80L/min. Filling method is pressure balanced filling system having a vapor line that connects the vapor phase part of the fuel tank and the storage tank in parallel with the liquid filling line.

The storage tank and the fuel tank have an equal pressure thanks to connecting these two tanks by vapor line. Constant flow rate can be kept even though the temperature in the fuel tank is higher than that in the storage tank. Integrated nozzle has been developed by Miyairi Valve Mfg. to achieve a simple operation of connection and disconnection for liquid filling and vapor return lines simultaneously.

# Pressure balanced filling system



Figure 3.19: DME Fuelling in Truck

# 3.18 QUALITY STANDARDS OF DME

JIS standard K2180 of fuel DME was issued in March, 2013. JIS of DME fuel for the vehicle is at present under examination.

Table 3.59: JIS standard for	DME as a fuel
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ltem	Unit	Standard value
DME purity	mass %	99.5 or more
Methanol	mass %	0.050 or less
Water	mass %	0.030 or less
Hydrocarbon (C4 or less)	mass %	0.050 or less
Carbon dioxide	mass %	0.10 or less
Carbon monoxide	mass %	0.010 or less
Methyl formate	mass %	0.050 or less
Ethyl methyl ether	mass %	0.20 or less
Residue after evaporation	mass %	0.0070 or less
Total sulfur	mg/kg	3.0 or less

# ISO standard for DME

ISO 16861:2015 specifies the characteristics of DME used as fuel of which the main component is the dimethyl ether synthesized from any organic raw materials.

ISO 16861:2015 is applicable for DME used as heating fuel, industrial fuel, and to replace diesel fuel or gas oil. It does not deal with the possible additives necessary for specific end-use applications, for example, odorant typically added to heating fuel and lubricity improvers for DME used as replacement of diesel. Such additives are typically specified for the different end-use applications, at an appropriate level national, regional, or international.

ISO29945: Refrigerated non-petroleum-based liquefied gaseous fuels --Di-methyl ether (DME) --Method of manual sampling on shore terminals

#### ASTM

ASTM D7901 - 14b: Standard Specification for Dimethyl Ether for Fuel Purposes

# CHAPTER-4 SAFETY, HEALTH AND ENVIRONMENT

This chapter provides an overview of the different environmental, occupational health and safety aspects for Methanol and DME. The chapter describes issues of toxicity, flammability and greenhouse gas emissions in particular based on characteristics and other physical, chemical and thermal properties. GHG emissions have been described for methanol as a compound, as a fuel, both for in-land and marine applications along with emissions associated with methanol during production from different feedstocks and at plant level.

# 4.1 METHANOL

Methanol (UN 1230) is an aliphatic alcohol, a colourless volatile liquid with boiling point of 64.7°C at 760 mm Hg (= 1 atm) and viscosity of 0.614 mPa sec. There are small amounts of methanol are produced naturally in the human body, in animals and in plants and bacteria. Methanol also occurs in small amounts in fresh fruit and vegeTables [1]. Methanol is widely produced in nature by anaerobic microorganisms responsible for complex aromatic hydrocarbon biodegradation. Several references classify methanol or its solutions as non carcinogens. Methanol is not a persistent chemical and is broken down in the environment.

1	
	1-43 mg/l
Fresh fruits and canned juices	11-80 mg/l
(orange and grapefruit juices)	12-640 mg/l
	(average of 140 mg/l)
Beer	6-27 mg/l
50% grain alcohol	1 mg/l
Wines	96-329 mg/l
Beans	1.5-7.9 mg/kg
Lentils	4.4 mg/kg
Carbonated beverages	~56 mg/l

Table 4.1: Sample Methanol Level [1]

Source: Division on Earth and Life Studies, National Research Council

A material safety data sheet of Methanol is provided as annexure-1.
#### 4.1.1 Methanol Fuel Characteristics

There has been several public research as well as findings on the effects of Methanol as a fuel on emissions, environment and health. These reports also cover safety aspect of handling methanol. Chemical composition of methanol and other fuels are presented in Table 4.2. Methanol is a lighter fuel with good oxygen content than Ethanol.

Property	<b>CNG</b> CH4 83-99%; C2H6 1-13% (gas)	Propane C3H8 (gas)	<b>Methanol</b> CH3OH (liquid)	<b>Ethanol</b> C2H5OH (liquid)	Gasoline C4-C12 (liquid)	No. 2 Diesel C8-C25 (liquid)	Biodiesel C12-C22 (liquid)
Molecular Weight (gm/mole)	16.04	44.1	32.04	46.07	100-105	~200	~292
Chemical Composition (wt %)							
Carbon	75	82	37.5	52.2	85-88	87	77
Hydrogen	25	18	12.6	13.1	12-15	13	12
Oxygen	-	-	49.9	34.7	0	0	11

Table 4.2: Chemical C	Composition of	Selected	Fuels	[2]
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Source: Roberts and Roberts

The fuel characteristics chart as obtained from AFDC is given as annexure-2. Other characteristics including few engine related properties are provided in Table 4.3. The reference does not provides RON as it states that it is not applicable for oxygenates. Hence, Blending Octane numbers (BON) are shown in Table 4.3. However, Sayler's article on alcohol [4] and others have provided RON and MON values for methanol and ethanol. These are provided in Table 4.4. Anti-knock index (AKI) values are also provided as these are used in fuel stations in the US and EU. Methanol like its counterparts such as Ethanol, Butanol and Propanol has high octane value.

Table 4.3: Fuel properties [3]

	Gasoline	Diesel	FAME <sup>a</sup>	Methanol	Ethanol	E85 <sup>e</sup>	E-diesel <sup>e</sup>
Density, kg/m3	~750	~840	880	796	794	780	810-840
Viscosity at 40 °C, cSt (Viscosity at 20 °C, cP)	<1 (0.37- 0.44)	~2-4.5 (2.6-4.1)	3.5-5	- (0.59)	- (1.19)	-	~1.9-4.1
HFRR, μm		<460	<460				>350
Boiling point, °C	30-190	170-340	300- 340	64	78	30-190	109-340
Octane number, RON <sup>b</sup>	95-98			122-133 (BON)	121-130 (BON)	~100	

# TIFAC, DST, Govt. of India | Utilisation issues of Methanol and DME

Cetane number	Na	>45	>50		8		42-52
Vapour pressure RVP,	45-90c	<1	-	32	16	40-80	16
actual kPa (blend kPa <sup>°</sup> )				(210+)	(124)		
CFPP. °C		e.a. <-25					e.g. <-
							25°C
Flash point, °C	<0	>56	>100	7	13		<20; 32
Auto ignition	>340	~240		464	425		
temperature, °C		210		101	120		
Flammability limits, vol%	1.4-7.6	1-6		7.3-36	3.3-19	1.2-9.1	3.3-19
Flammability limits, °C	-45-(-20)	64-150		7.2-43	13-42		13-42
Heat value, MJ/kg	43	43	36	20	26	29.2	~41-42
Stoich. AFR	14.7	14.7	12.4	6.5	9.0	10.0	14.0
					Not		
Flame visibility	Visible	Visible	Visible	Unvisible	clearly	Visible	Visible
					visible		

na = not applicable a) Properties based on rape seed methyl ester. b) RON or MON octane numbers are not relevant for oxygenates. Thus blending octane numbers (BON) are shown here for ethanol and for ETBE. c) Raid Vapour Pressure varies in different countries and seasons d) Vapour pressure changes non-linearly when ethanol is added to gasoline, second value is blending vapour pressure e) varies depending on base diesel fuel *Source: AMF, IEA* 

Table 4.4: RON and MON values of Methanol and Etha	nol [5]
--	---------

Fuel	RON	MON	AKI = RON+MON/2	Energy in 1 liter, MJ
Methanol	109	89	99.0	15.8
Ethanol	109	90	99.5	21.1
European gasoline	95	85	90	32.6

Source: Saylor

A research by Liao et. al [8], show that addition of methanol if added moderately gasoline can improve the combustion performance at low temperature compared to pure gasoline due to improvement of blend evaporation.

The solubility, flammability, biodegradation and GHG emissions pertaining to Methanol are discussed in the subsequent sections

#### 4.1.2 Solubility

Methanol is miscible with ethanol, ether, benzene, most organic solvents and ketone. It indicates that methanol can easily blend with ethanol. However, it is not soluble in cyclohexane, heptane, hexane, pentane, 2,2,4-trimethylpentane.

It forms solutions in acetone, chloroform and is completely miscible in water @ 20 deg C.

# 4.1.3 Flammability

The flash point of methanol is 15.6 deg C (open cup) and 12 (closed cup). US National Library of medicines states that the air odor threshold for methanol has been reported as 100 ppm [8]. Vapors of both gasoline and methanol are explosive in confined spaces, and form vapor plumes when unconfined. A 75%/25% mixture of water and methanol (by volume) is considered to be a flammable liquid. Air, Methanol-air mixtures at 1.81 bar (26.25 psia) and 120°C (248°F) may explode with or without the addition oxygen and water.

			•			
Property/ Information	<b>CNG</b> CH4 83-99%; C2H6 1-13% (gas)	Methanol CH3OH (liquid)	Ethanol C2H5OH (liquid)	Gasoline C4-C12 (liquid)	No. 2 Diesel C8-C25 (liquid)	B100 Biodiesel C12-C22 (liquid)
DOT Number	UN 1971	UN 1230	UN 1170	UN 1203	UN 1202 NA 1993	-
DOT Hazard	2.1 flammable	3.6.1	3	3	3 flammable	3 flammable
Class or Division	gas	flammable liquid	flammable liquid	flammable liquid	liquid	liquid
DOT Guide Number	17	28	26	27	128	
STCC Number	4905755	4909230		4908178		
OSHA/NFPA Flammability Class		IB	IB	IB	2 combustible liquid	2 combustible liquid
Mfg Name	E.I. Du Pont	Allied Corp	Fisher Scientific	Shell Oil Company	Hess Corporation	NREL/TP- 54043672
DOT Packing Group	-	PG II	PG II	PG II	PG III	PG III
DOT Packaging (non-bulk/bulk)	302/302	202/242	202/242	202/242	203/242	203/242
Type of Shipping Container	cylinders only	bulk in tank cars; 1-119 gal DOT PG- II, performance- oriented	bulk in tank cars; 1-119 gal DOT PG-II performan ce-	tanker trailers, rail cars, pipelines	tank trailers, rail cars, pipelines	tank trailers, rail cars, pipelines

Table 4.5: Flammability Properties of Selected Fuels [2]

# TIFAC, DST, Govt. of India | Utilisation issues of Methanol and DME

		containers	oriented containers			
Container Hazards	rupture, BLEVE & rocket in fire	rupture, BLEVE & rocket in fire	rupture, BLEVE & rocket in fire	rupture, BLEVE & rocket in fire	Rupture, BLEVE & fire	Rupture, BLEVE & fire
Special Fire Hazards	yellow luminous flame visible in daylight; vapor trail flashes back; vapor may explode if ignited in confined area	blue flame invisible in daylight; vapor trail flashes back; vapor may explode if ignited in confined area	blue flame invisible in daylight; vapor trail flashes back; vapor may explode if ignited in confined area	yellow luminous flame visible in daylight; vapor trail flashes back; vapor may explode if ignited in confined area	yellow luminous flame visible in daylight; dense black smoke	yellow luminous flame visible in daylight; dense black smoke
Other Information	LNG liquid floats & boils on water; LNG produces visible heavier- than-air vapor cloud; vapor cloud from CNG gas release is beyond and invisible	liquid floats & mixes with water; near neutral vapor buoyancy	liquid floats & mixes with water; near neutral vapor buoyancy	liquid floats on water; negative buoyancy vapor cloud	liquid floats on water; low vapor pressure, formation of vapor cloud not expected	liquid floats on water; low vapor pressure, formation of vapor cloud not expected

Source: Roberts and Roberts

# USEPA in its consumer information [9] for Methanol Fuels and Fire Safety states the following advantages of methanol as a fuel as compared to gasoline

Property	Comparison with Gasoline
Volatility	Lower and emits 2-4 times less vapour
Flammability	Must have 4 times more vapour concentration to ignite
Vapour Density	Lighter than gasoline, slightly heavier than air, quick dispersion
	below combustion concentration
Heat Release	Lower, burns 25% faster, heat 1/8 <sup>th</sup> of gasoline fires

# Table 4.6: Fire Safety as compared to Gasoline

Source: US EPA

The variation of flash points with different concentration of methanol in water has been provided in Figure 4.1 from G.R. Astbury et. al [10]. The graph provides results from both measured as well as calculated estimations.



Figure 4.1: Flash point variation with methanol concentration [10]

It may be observed that low concentration of methanol of 10%, the flash point is slightly above  $50^{\circ}$ C and falls below  $50^{\circ}$ C to  $40^{\circ}$ C at concentrations between 11% and 19%. The flash point is around  $25^{\circ}$ C at concentration of 50% w/w methanol.

# 4.1.4 Fire Class

# **DOT Hazard Classifications:**

Class 3 - Flammable liquids (and Combustible liquids [U.S.])

Class 6 - Toxic substances and Infectious substances

Division 6.1 - Toxic substances

Following a leak inside the containment area, the resulting methanol pool should be completely covered with alcohol-resistant foam. If the containment area is adequately sized, the methanol spill can be diluted with at least four parts water to one part methanol to reduce the risk of fire. Methanol NFPA safety label is given in Figure 4.2



Figure 4.2: Methanol NFPA classification [11]

NFPA Rating Explanation Guide							
RATING NUMBER	HEALTH HAZARD	FLAMMABILITY HAZARD	INSTABILITY HAZARD	RATING SYMBOL	SPECIAL HAZARD		
4	Can be lethal	Will vaporize and readily burn at normal temperatures	May explode at normal temperatures and pressures	ALK	Alkaline		
3	Can cause serious or permanent injury	Can be ignited under almost all ambient	May explode at high temperature or shock	ACID	Acidic		
2	Can cause temporary incapacitation or residual injury	Must be heated or high ambient temperature to burn	Violent chemical change at high temperatures or pressures	OX	Oxidizing		
1	Can cause significant	Must be preheated before ignition can	Normally stable. High temperatures	**	Radioactive		
	irritation	occur	make unstable	₩	Reacts violently or explosively with water		
0	No hazard	Will not burn	Stable	₩ох	Reacts violently or explosively with water and oxidizing		

Figure 4.3: NFPA rating guide [12]

# 4.1.5 Static Charge

**Electrical conductivity** is the measure of a material's ability to allow the transport of an **electric** charge. Static electricity is the electric charge generated when there is friction between two things made of different materials or substances. Static charge occurs during several operations such as storage transfers, pouring and siphoning. The electrical conductivity of Gasoline, low sulfur diesel and methanol is provided in Table 4.7. Values of methanol have been reported from two sources which have difference of more than 20 times. Nevertheless, these are several magnitudes higher than diesel and low sulfur diesel.

Substance	Electrical Conductivity
Substance	(pS/m)
Diesel	25
Low Sulfur Diesel	5
Mathanal	3 x 10 <sup>5 (1)</sup>
Methanol	7 x 10 <sup>6 (2)</sup>
Water	5 x 10 <sup>8</sup>
(	1) Roberts

Table 4.7: Electrical Conductivity of Methanol and other fuels

(2) Methanol Handbook

Methanol-water solutions at 40:60 concentration and methanol: water, 30:70 mixtures can be ignited by a static discharge. The high values of electrical conductivity of methanol indicate that probability of static charge accumulation for methanol is very low. These also show that ignition by static charge can only occur in extreme conditions.

However, as a matter of good practice, bonding, grounding and turbulence quelling, and liquid stilling during handling procedures should be followed in the event the methanol is a blended fuel, or is contaminated with hydrocarbon and therefore has an unexpectedly low electrical conductivity

# 4.1.6 Odour

Methanol has a faintly sweet alcohol odor but does not makes its presence known until a concentration of 2000 ppm or above is reached, which is ten times higher than the safe limit of human exposure of 200 ppm [13]. Because the odor of Methanol is a poor indicator of concentration, it is essential that some quantitative measure of exposure be determined. This is necessary to ensure that the health of workers is not impaired and to determine compliance with any applicable regulations. Methanol has a characteristic alcoholic odor; (pungent odor when crude). Odour thresholds are provided in Table 4.8:

Threshold level	Value	Unit
Low	13.1150	mg/cu.m
High	26.84	g/cu.m
Irritating concentration	22.875	mg/cu.m

Table 4.8: Odour Thresholds for Methanol

Source: Methanol Institute, Safe Handling of Methanol

Odor threshold is highly variable in air and ranges over several orders of magnitude and provided by various agencies;

- i. California Environmental Protection Agency: 10 ppm to 20000 ppm
- ii. American Conference of Governmental Industrial Hygienists: 100 ppm to 1500 ppm
- iii. Stegink, L.D., et. al. 1981: 141 ppm
- New Jersey Dept. of Health and Senior Services: 160 ppm The range of accepted odor threshold values is quite broad. Caution should be used in relying on odor alone as a warning of potentially hazardous exposures

#### 4.1.7 Occupational Exposure Limits

The Occupational threshold as reported by various agencies are provided below [14]:

#### NIOSH REL:

- STEL (skin): 250 ppm (325 mg/m<sup>3</sup>)
- $\circ$  TWA (skin): 200 ppm (260 mg/m<sup>3</sup>)

# OSHA PEL:

• TWA (8-hour): 200 ppm (260 mg/m<sup>3</sup>)

#### • ACGIH TLV:

- o STEL (skin): 250 ppm
- o TLV (skin): 200 ppm
- NIOSH IDLH: 6,000 ppm

#### DOE TEEL:

- TEEL-0: 250 mg/m<sup>3</sup>
- o TEEL-1: 694 mg/m<sup>3</sup>
- o TEEL-2: 2,750 mg/m<sup>3</sup>
- TEEL-3: 9,300 mg/m<sup>3</sup>
- AIHA ERPG:
  - ERPG-1: 200 ppm
  - o ERPG-2: 1,000 ppm
  - ERPG-3: 5,000 ppm

The Acute exposure guidelines are provided in Table 4.8:

	10 min	30 min	60 min	4 hr	8 hr
AEGL 1					
(discomfort, non-disabling) –	670 ppm	670 ppm	530 ppm	340 ppm	270 ppm
ррт					
AEGL 2					
(irreversible or other serious,	11,000	1 000 ppm	2 100 ppm	720 ppm	520 nnm
long-lasting effects or impaired	ppm*	4,000 ppm	2,100 ppm	730 ppm	520 ppm
ability to escape) - ppm					
AEGL 3		14 000	7 200		
(life-threatening effects or	**	nnm*	7,200 nnm*	2,400 ppm	1,600 ppm
death) – ppm		ρμπ	ррш		
- Source: NIOSH, CDC, US					

|--|

Notes:

Lower Explosion Limit (LEL) = 55,000 ppm

\* = > 10% LEL; \*\* = > 50% LEL

AEGL 3 - 10 min = \*\* 40,000 ppm

For values denoted as \* safety consideration against the hazard(s) of explosion(s) must be taken into account

For values denoted as \*\* extreme safety considerations against the hazard(s) of explosion(s) must be taken into account

Level of Distinct Order Awareness (LOA) = 8.9 ppm

The minimal acute methanol dose to humans that can result in death is considered to be 300 to 1000 mg/kg by ingestion, and fatalities have occurred in untreated patients with initial methanol blood levels in the range of 1500-2000 mg/L [29].

Human toxicity values in terms of Half-lives of methanol in the body are roughly 2.5 to 3 hours at doses less than 100 mg/kg bw. At high doses (greater than about 1000 mg/kg bw), half-lives can be 24 hours or more [29]

In a study [45, 46] with cynomolgus monkeys with exposure to methanol vapour at 650, 2600 and 6000 mg/m<sup>3</sup> for 6 hours a day, 5 days a week and 4 weeks did not result in any toxicity during exposure period and post-exposure necropsy. A similar study with rats and same exposure levels did not reported any exposure related effects except for increased discharge around nose and eyes.

#### 4.1.8 Methanol Spills in Surface Water and Soils

Due to high solubility with water, any spill will be diluted quickly depending on marine conditions. The effect of type of water, tides as well as nature will play an important role. However, it has been observed that an M100 release in open water, as discussed in Scenario 2, will disperse to non-toxic levels (< 1%) at a much faster rate than a parallel Gasoline release. Methanol will vapourize faster than gasoline due to high vapour pressure. Results from hypothetical methanol release scenarios for surface water is provided in Table 4.10.

Scenario	Туре	Quantity of Release	Concentration (%)	Time (hr)
1	Instantaneous	10000 tonnes	0.36%	01
2	Continuous	10000 litres per	<1%	02
3		hour	0.13%	03

Table 4.10: Concentration of Methanol Release in water with Time [15, 16]

Source: Methanol Institute Study, Malcolm Pirnie, Inc,

The Henry's Law constant for methanol is 4.55 X 10<sup>-6</sup> atm-cum/mole. This Henry's Law constant indicates that methanol is expected to volatilize from water surfaces. Based on this Henry's Law constant, the volatilization half-life from a model river (1 m deep, flowing 1 m/sec, wind velocity of 3 m/sec) is estimated as 3 days. The volatilization half-life from a model lake (1 m deep, flowing 0.05 m/sec, wind velocity of 0.5 m/sec) is estimated as 35 days [28].

High concentrations of Methanol resulting from a large spill in an enclosed area will deplete the surface water of oxygen required to sustain aquatic life. Regardless, small quantities of Methanol introduced into mammals as a result of bioaccumulation from Methanol fuel releases can be rapidly metabolized, negating any long term effect.

Methanol's Henry's Law constant indicates that volatilization from moist soil surfaces may occur. The potential for volatilization of methanol from dry soil surfaces may exist based upon a vapor pressure of 127 mm Hg.

The reported half-life for Methanol biodegradation under anaerobic conditions ranges from 1 to 5 days (Howard et al., 1991). The half-lives are compared to reports of half-lives for Benzene to illustrate the relatively rapid degradation of Methanol.

	Half-Life (Days)		
Environmental Medium	Methanol	Benzene	
Soil	1-7	5-16	
Air	3-30	2-20	
Surface water	1-7	5-16	
Groundwater	1-7	10-730	

Table 4.44. Laff Lives of Mathemal and Danzana	[4 E	4 71	
	110,	, 171	

Source: Methanol Institute Study, Malcolm Pirnie, Inc,

Methanol is significantly less toxic to marine life than crude oil or gasoline, and many of the effects of short term exposure are temporary and reversible.

# 4.1.9 Methanol in Air

The treatment of methanol degradation in the atmosphere is provided from US National Library of Medicine (WISER) and OECD. Both reports similar fate of methanol and half-lives.

# WISER

Methanol, which has a vapor pressure of 127 mm Hg at 25 deg C, is expected to exist solely as a vapor in the ambient atmosphere. Vapor-phase methanol is degraded in the atmosphere by reaction with photochemically-produced hydroxyl radicals (SRC); the half-life for this reaction in air is estimated to be 17 days (SRC), calculated from its rate constant of 9.4X10<sup>-13</sup> cu cm/molecule-sec at 25 deg C.

# SIDS

As per OECD assessment on Methanol [29], it is degraded in the atmosphere by photochemical, hydroxyl-radical dependent reactions. The estimated elimination half-life is calculated to be about 17-18 days with a rate constant of  $0.93 \times 10^{-2} \text{ cm}^3$ /molecule-sec. Worldwide, air concentrations of methanol have been measured at ranges from 1.05 to 13.1 x 10-5 mg/L.

# 4.1.10 Groundwater Effects

Potential impacts from release of methanol in groundwater has been studied [6]. The paper suggests a limiting value (inhibition threshold) of methanol in groundwater as 10,000 g/liter citing several other references and 8000 g/liter as a safe estimate, above which methanol can become persistent in groundwater. It further concludes that a methanol plume could persist in groundwater at concentrations above 1 mg/l for a period of one to two years.

The effects of methanol on BTEX had been studied [7, 17]. BTEX is an acronym that stands for Benzene, Toluene, Ethylbenzene, and Xylene. Cosolvency is a chemical phenomenon whereby one chemical dissolved in water increases the aqueous solubility of a second chemical. BTEX show greater solubility in methanol than water. Effects of methanol on the co-solubility of BTEX compounds for M85 blend in gasoline from an American Petroleum Institute (API) study [6, 17] are shown in Table 4.4. The study was done to evaluate the possible impacts of MTBE and Methanol in groundwater. The study reveals that high concentrations of methanol have the potential to increase the levels of BTEX in groundwater by cosolvency effects.

Concentration	Solubility Change
Aqueous with concentration <8.5% v/v	No change in solubility
> 8% and < 25%	Linear increase with methanol conc.
> 25%	Exponential increase
44% (993 ppm)	Equilibrium

Source: API

Note:

The API report presents the findings of a natural gradient tracer test and related laboratory experiments that investigate the subsurface behavior and impacts of methanol and MTBE. The primary goals of the research were to:

1) Describe the transport and fate of methanol and MTBE in groundwater; and

2) Determine the influence of methanol and MTBE on the transport and fate of BTEX in groundwater.

The research was designed to compare and contrast the effects of groundwater contamination by three fuel blends:

- 1) 100% gasoline (control)
- 2) 90% gasoline plus 10% MTBE
- 3) 15% gasoline plus 85% methanol (M85)

Summarizing, Methanol is bio-degradable under aerobic and anaerobic conditions with a much faster rate in the former case. A study by Kevin D. White et.al [16] indicates that methanol can be biodegraded in any of the sub-soil conditions such as aerobic, anaerobic, acidic and neutral conditions. In another study by Frago [19], it was found that methanol was readily biodegradable over concentrations ranging from about 80 mg/L to about 200 mg/L at various soil depth levels. At concentration less than 3000 mg/l methanol is readily degraded in a wide range of subsurface condition. However, methanol concentration above 10,000 mg/l can inhibit the microbial population and degradation rate will be slow [5]. In surface water a typical degradation rate is 10 mg/l per day [13].

# 4.1.11 Methanol spillage Scenarios

The following describes what processes occur following a release of Methanol on land, in water and underground.

- Tanker truck or railway tank spill: Methanol released to soil and/or groundwater.
- Released from storage: spills, pool fire, evaporative explosions, on land or sea
- Barge spill: Methanol released to surface water.
- Underground storage tank leak: Methanol released to soil and groundwater.

A single rail car could release as much as 30,000 gallons (100 tonnes) of methanol if fully emptied during such an event. A typical truckload of methanol is 8000 gallons (24 tonnes).

Typical river barges can carry just less than 418,000 gallons, or ~1255 tonnes.

Methanol is stored at docks and marine terminals in floating roof tanks; these typically have elaborate leak detection and safety systems. Methanol is also stored in aboveground tank farms with aboveground piping and leak detection and fire suppression systems. While spills may occur in these mass storage facilities, the larger concern is the possibility of releases at smaller distribution facilities and from totes and drums

New, upgraded UST systems are double-walled and typically have an interstitial leak detection device or other leak detection mechanism. Leak detection depends upon a number of factors, such as the location, volume, and velocity of the leak. Most commonly, leaks occur at the joints or at the dispenser; if a leak occurs at the dispenser it may not be detected. Leak detection systems can be subject to human error because alarms can typically be just turned off without action being taken. Studies have found that while newer USTs are less likely than older, single-walled tanks to leak, even upgraded USTs experienced leaks. Release and consequence from process plants include but not limited to

• Release of high pressure (80 barg) flammable methane gas from synthesis equipment

This may form a flammable gas cloud and could cause an explosion, spray fire if the gas source continues to be fed or pool fire.

- Release of flammable methanol, which if ignited will result in a pool fire, either in tank bunds or on the sea in the event of breach of loaded ships at jetty.
  Fire may injure personnel, damage other infrastructure and potentially escalate beyond the boundary wall
- Release of flammable methanol, which if ignited will result in a pool fire. Fire may injure personnel and damage other infrastructure.

#### 4.1.12 Methanol Safety for Marine applications

The flashpoint of methanol is below the minimum flashpoint for marine fuels specified in the International Maritime Organizations (IMO) Safety of Life at Sea Convention (SOLAS). All laws and regulations concerning emission in the maritime industry are contained in the "International Convention on the Prevention of Pollution from Ships", which is commonly known as MARPOL 73/78.

# IBC Code - International Code for the Construction and Equipment of Ships Carrying Dangerous Chemicals in Bulk, Amended by Resolution MEPC.225

Methyl alcohol is listed in Chapter 17 "Summary of minimum requirements", indicating that specific requirements from the IBC code apply in addition to MARPOL Annex II. IBC Chapter 17 lists the ship type for methanol as Ship Type 3. Ship Type defines, amongst other requirements, where the tank carrying the product can be located. Ship type 3 has no distance requirements for the tank location from the outer hull.

# Lloyd's Register Provisional Rules - Provisional Rules for the Classification of Methanol Fuelled Ships

Lloyd's Register published its provisional rules for methanol fuelled ships in January 2015.

# 4.1.13 Personal Protective Equipment

Exposure to methanol can occur via inhalation, skin absorption, contact with the eyes, or ingestion, whenever methanol is used or handled. The level of risk of exposure to methanol will dictate the appropriate level of personal protective equipment required. At a minimum, safety glasses with side shields or safety goggles and task-appropriate gloves are recommended. Depending on the situation, additional personal protective equipment may be required.

Air Concentration of Methanol	Respiratory Protection
< 200 ppm	No protection required. Skin and eye protection may still
	be needed
200 ppm or greater	Protection required if the daily time-weighted-average
	(TWA) exposure is exceeded or if there are additional
	routes of exposure (skin, eyes, ingestion). A supplied air
	system must be used if protection is needed.
> 200 ppm sustained	A supplied air breathing apparatus (SCBA) system must
	be used (i.e., positive-pressure SCBA)
	Source: OSHA

#### Table 4.13: Respiratory Protection Guide [31]

#### 4.1.14 Green House Gas (GHG) Emissions

#### A. Methanol as compound

The greenhouse gas emission potential of several compounds are shown in Table 4.12 as provided by the IPCC [24]. The second and third columns respectively represent the methane and ozone contribution to the net GWP and the fourth column represents the net GWP. Methanol has one of the lowest GWP.

Organic Compound/Study	GWP <sup>CH4</sup>	GWP <sup>03</sup>	GWP
Ethane (C <sub>2</sub> H <sub>6</sub> )	2.9	2.6	5.5
Propane (C <sub>3</sub> H <sub>8</sub> )	2.7	0.6	3.3
Butane (C <sub>4</sub> H <sub>10</sub> )	2.3	1.7	4.0
Ethylene (C <sub>2</sub> H <sub>4</sub> )	1.5	2.2	3.7
Propylene (C <sub>3</sub> H <sub>6</sub> )	-2.0	3.8	1.8
Toluene (C <sub>7</sub> H <sub>8</sub> )	0.2	2.5	2.7
Isoprene (C <sub>5</sub> H <sub>8</sub> )	1.1	1.6	2.7
Methanol (CH <sub>3</sub> OH)	1.6	1.2	2.8
Acetaldehyde (CH <sub>3</sub> CHO)	-0.4	1.7	1.3
Acetone (CH <sub>3</sub> COCH <sub>3</sub> )	0.3	0.2	0.5

Table 4.14: Global Warming Potential (GWP)

Source: IPCC, 2006

#### B. Methanol with different feedstocks

Methanol has been reported to be a much cleaner fuel than gasoline in terms of GHG emissions. A report by [20] provides relative GHG emissions of methanol from various feedstocks as compared to gasoline. It has been depicted in Figure 4.4





A report by European Commission, JRC [35] states that methanol from natural gas, corresponds to production emissions of about 24 kg CO2/GJ fuel and 68.8 kg CO2/GJ fuels for the use of fossil methanol, resulting in a total of 92.8 kg CO2/GJ fuel, which is similar to diesel fuel emissions. Methanol produced from gasification of coal relies on cheap, widely available resource, but the GHG emissions are about twice as high as from natural gas at 182-190 kg CO2/GJ fuel. It further states that biomass-to-methanol/DME to be probably the most energy-efficient pathway to procuring transport energy by 2050.

Figure 4.5 provide GHG emissions for various scenarios of methanol production showing the impact of local conditions and production methods.



Source: European Commission [35]

The GHG emissions of methanol as compared to other fuels from different feedstocks are provided in Figure 4.6. The graph portray that methanol from farmed wood and waste wood have the least GHG emissions.

Methanol from natural gas has comparable well to tank emissions with ethanol produced from sugar cane [35].

Methanol from waste wood has been estimated to have a GHG intensity of 5.0  $gCO_2e/MJ$  in 2020 by EU commission in its Biofuel Pathways information which is the least among the gasoline pool pathways including those based out of ethanol. [25].



Figure 4.6: GHG Emissions of Methanol, LNG and Ethanol from feedstocks [32]

A typical methanol plant based on natural gas in the US has been reported to emit around 0.282 tonnes of CO<sub>2</sub> per ton of methanol [21].

The Well to tank (WTT) emissions for methanol production pathways are shown in Figure 4.7 [36]. One of the interesting point provided in the reference report is the exclusion of CCS option for methanol, as it was not considered a relatively important automotive fuel in the future for EU.





The scenario depicts emissions for the following:

- GPME1b: Piped NG (4000 km) to methanol, synthesis plant in EU
- GRME1: Remote NG to methanol, synthesis plant near gas field
- KOME1: Coal (hard, EU-mix) to methanol, synthesis plant in EU
- WFME1: Wood (farmed) to methanol
- WWME2: Wood (waste) to methanol via black liquor

As per China Coal Research Institute,  $CO_2$  emissions are 2.37-3.52 tons of carbon dioxide per ton of methanol based out of coal (0.119-0.176t/GJ), among which 0.079 - 0.117 tons are discharged in the processing and 0.040-0.059 tons in the public process [26].

Use of efficient technologies have led to significant reduction (about 40%) from methanol production as compared to decade ago. Emissions are to the tune of 3.8 lb of  $CO_2$ / gallon (0.455 kg of  $CO_2$  /liter) of methanol [27].

GHG emissions data from **California Energy Commission study [34], has been reproduced in Figure 4.8.** The emissions were analyzed on a well-to-wheels (WTW) basis. WTW emissions are divided into two components: the fuel cycle, or well-to-tank (WTT), emissions and the vehicle cycle, or tank-to-wheels (TTW). These are estimated for urban buses. GHG emissions include methane and nitrous oxides.



Figure 4.8: Weighted GHG emissions for methanol and DME from various feedstocks [34]

# C. Methanol and other fuels

GHG emissions data from an Australian study [33], is provided in Figure 4.9 for different kind of fuels. It can be observed that methanol's emissions (60.8 g/MJ) are comparable to LPG (60.2 g/MJ) and less than ethanol, RME diesel, petrol and automotive diesel. Methanol's GHG emissions are 7.6% less than diesel and 5.3% less than ethanol.



Figure 4.9: GHG emissions from various fuels [33]

# D. Methanol based vehicles

GHG emissions data from Pump to Wheels and Well to Pumps are provided in Figure 4.10 from California Air Resources Board [30]. It depicts, GHG emissions of various types of vehicles. It can be observed that methanol fuel cell cars have lower GHG emissions than gasoline or corn based ethanol vehicles and higher emissions than electric and hydrogen (from Natural gas) vehicles.

In terms of production of hydrogen fuel cells for vehicle, the US Department of Energy states [22] that overall emissions as compared to gasoline internal combustion engines could be reduced upto 35% from methanol route and 50% from natural gas in case of hydrogen to fuel cells production from methanol and natural gas. Another reference sustainable transport pathways, [23], states that FCVs using methanol or hydrogen made from wood reduce fuel-cycle GHG emissions by about 85 percent.

Methanol powered heavy buses have the ability to reduce upto 18% GHG emissions as compared to conventional diesel buses [34]



Figure 4.10: GHG emissions from different type of vehicles, Source: CARB

# 4.1.15 Effects on Ozone

Adding oxygenates generally reduces many ozone precursor emissions from vehicles such as CO, HC, and nitrogen oxides (NOx) by the addition of oxygen and octane, and by also improving fuel distillation temperatures.



Figure 4.11: Ozone yields for Fuels [37]

# 4.2 DIMETHYL ETHER

Dimethyl ether (DME) is also known as methoxymethane. Synonyms are dimethyl oxide, oxybismethane, methoxymethane, wood ether and others. The CAS registry number is 115-10-6, the EINECS number is 204-065-8. Dimethyl ether is a colorless gas with a faint ethereal odor. Dimethyl ether is used as solvent in chemical and petrochemical industry. It is shipped as a liquefied gas under its vapor pressure. Dimethyl ether burns with a visible blue flame and is non-peroxide forming in the pure state or in aerosol formulations.

DME (dimethyl ether) is a medium to high pressure propellant and an excellent solvent that is very soluble in water. DME is a chemically sTable compound that reacts or decomposes only under rather severe conditions. In aqueous solutions, the propellant is hydrolytically sTable over a wide pH range.

DME is a commodity which can be made from various raw materials, including natural gas, coal, black liquor, biomass, and wastes.

Dimethyl ether is reported as having a relative vapour density of 1.59 (air = 1), a density of 2.11 kg/m<sup>3</sup> as a gas at 0°C, of 669 kg/m<sup>3</sup> ( $\pm$  0.01) liquefied at 20 °C. DME has high water solubility, high vapor pressure, boiling point of -24.8°C and melting point of -141.5°C. Dimethyl ether is sTable but is extremely flammable and may form potentially explosive mixtures with air, but will not form potentially explosive peroxides.

Molecular Weight	
Molecular weight	: 46.068 g/mol
Solid phase	
Melting point	: -141.49 °C
Latent heat of fusion (1,013 bar, at melting	: 107.168 kJ/kg
point)	
Liquid phase	
Relative liquid density (Water = 1)	: 0.73
Liquid density (1.013 bar at boiling point)	: 735.2 kg/m <sup>3</sup>
Liquid/gas equivalent (1.013 bar and 15 $^\circ  ext{C}$	: 368.9 vol/vol
(59 °F))	
Boiling point	: -24.81 °C
Latent heat of vaporization (1.013 bar at	: 461.55 kJ/kg

Table 4.15: DME Gas	Properties	[37]
---------------------	------------	------

boiling point)	
Vapor pressure (at 20 °C or 68 °F) :	5.0924 bar
Critical point	
Critical temperature	: 127.15 °C
Critical pressure	: 53.4 bar
Critical density	: 271.4 kg/m³
Critical density	: 277.01 kg/m <sup>3</sup>
Triple point	
Triple point temperature	: -141.5 °C
Triple point pressure	: 0.0000305 bar
Gaseous phase	
Gas density (1.013 bar at boiling point) :	2.3622 kg/m <sup>3</sup>
Gas density (1.013 bar and 15 °C (59 °F)) :	1.993 kg/m <sup>3</sup>
Compressibility Factor (Z) (1.013 bar and 15	0.97735
°C (59 °F)) :	
Specific gravity :	1.59
Specific volume (1.013 bar and 25 °C (77	0.5207 m³/kg
°F)) :	
Heat capacity at constant pressure (Cp)	0.0681 kJ/(mol.K)
(1.013 bar and 25 °C (77 °F)) :	
Heat capacity at constant volume (Cv) (1.013	0.0588 kJ/(mol.K)
bar and 25 °C (77 °F)) :	
Ratio of specific heats (Gamma:Cp/Cv)	1.158
(1.013 bar and 25 °C (77 °F)) :	
Viscosity (1.013 bar and 0 °C (32 °F)):	8.2865E-05 Poise
Thermal conductivity (1.013 bar and 15 °C	15.616 mW/(m.K)
(59 °F)):	
Miscellaneous	
Solubility in water (1.013 bar and 20 °C (68	35 vol/vol
°F)) :	
Flammability Limits, In the air at 20° C below	
1,013 bar	
Lower	3.4
Upper	27
Auto-ignition temperature :	350 °C

Source: Air Liquide

# Regulatory information is provided below:

- EC No (from EINECS): 204-065-8
- CAS No: 115-10-6
- Index-Nr. 603-019-00-8
- Chemical formula C2H6O
- REACH Registration number: 01-2119472128-37

# 4.2.1 Flammability

DME is flammable. Its lower explosive limit (LEL) in air is approximately 60 percent larger than that of propane, i.e., comparing DME and propane, about 60 percent more DME than propane can be vaporized in air before the lower explosive limit is reached [38]. Similarly, the LEL of DME is approximately 85 percent larger than that of iso-butane. Nonetheless, pure DME is extremely flammable and only trained personnel using proper equipment should handle it. Flammable gas detectors are recommended. Infrared or sensing flame detectors can be used with all HP DME propellants.

# Table 4.16: NFPA 704, DME

Diamond	Hazard	Value	Description
	Health	2	Can cause temporary incapacitation or residual injury.
2 1	Flammability	4	Burns readily. Rapidly or completely vaporizes at atmospheric pressure and normal ambient temperature.
$\sim$	VInstability	1	Normally sTable but can become unsTable at elevated temperatures and pressures.

As an immediate precautionary measure, isolate spill or leak area for at least 100 meters (330 feet) in all directions.

LARGE SPILL: Consider initial downwind evacuation for at least 800 meters (1/2 mile).

FIRE: If tank, rail car or tank truck is involved in a fire, ISOLATE for 1600 meters (1 mile) in all directions; also, consider initial evacuation for 1600 meters (1 mile) in all directions.

# 4.2.2 Heat of Combustion

The heat of combustion of several flammable aerosol propellants is given in Table 4.17. Of the flammable propellants, the hydrocarbons release the largest amount of energy upon combustion while DME release nearly half of propane.

HP 152a	6.3
HP DME	26.5
Propane	44.0
Isobutane	42.8
n-Butane	43.3

Table 4.17: Propellant Heat of Combustion, kJ/g [38]

Furthermore, the heat of combustion of DME is about 35 percent less than the heat of combustion of hydrocarbon propellants. Water is effective in reducing the flame extension of High Purity (HP) DME propellant. To illustrate, a blend of 80 percent HP DME, 14 percent water, and 6 percent ethanol exhibits zero flame extension

# 4.2.3 Solubility

It is described as being soluble in methanol, ethanol, isopropyl alcohol, chlorinated hydrocarbons and toluene. Its water solubility is reported in the application to be 328 g/l (20 °C at 410 kPa).

# 4.2.4 Reactivity Profile

DIMETHYL ETHER is a colorless, highly flammable gas (b. p. -24° C), slightly toxic. Very dangerous fire and explosion hazard when exposed to flame, sparks, heat or strong oxidizers. Violent reaction with aluminum hydride, lithium aluminum hydride. Upon standing and exposure to air (oxygen) tendency to form explosive peroxides. When ethers containing peroxides are heated (distilled) they can detonate

# 4.2.5 GHG Emissions

DME combustion and emissions commenced in 1995 and it gained wider publicity in 1999 due to the efforts of International DME Association and Japan DME Forum (Japan DME Association), DME environmental impacts are known to be low. DME has been used for more than 50 years as a consumer product. This has been established as it is widely used as a spray propellant. It has been reported to be ozone saving substance. There was no known fuel application of DME before 1990.

Research indicates that the first ever pure DME operated engine was developed and tested by a joint venture of Haldor topsoe A/S and Technical University of Denmark. Japan's Ministry of Land, Infrastructure and Transport later conducted a single cylinder engine test run on pure DME in 1997 and observed very similar outcomes. The IARC (International Agency for Research on Cancer) in June 2012, listed exhausts from diesel engine as carcinogenic to humans. This was due to the fact that PM concentration was in the range of 10<sup>7</sup> and 10<sup>9</sup> particles/cm<sup>3</sup> with particle diameter less than 100 nm which are able to enter the respirator systems of human beings.

The operation of a DME engine requires a new storage system and a new fuel delivery system, while the engine itself does not need modification. For FTD and DME, similar engines to diesel fuel are required. Methanol can be used in engines similar to petrol engines

DME does not produce soot as there is no carbon bond as well as SOx emissions are zero. NOx emissions (upto 40% reduction has been observed) can be controlled with proper utilization of technology. After-treatment of exhaust gas can be simplified, DPF and SCR are unnecessary. The properties of DME and Methanol (from Japan DME association) along with methane and Gas oil are provided in Table 4.18 [39]. It can be observed that **DME cetane number is very comparable to Gas oil, has higher LEL, though it has a wider explosion limit.** 

Property	DME	Methane	Methanol	Gas oil
Chemical Formula	CH <sub>3</sub> OCH <sub>3</sub>	CH <sub>4</sub>	CH₃OH	-
Boiling point (°C)	-25.1	-161.5	64.6	180~360
Liquid density (g/cm³,20°C)	0.67	-	0.79	0.84
Gas density (vs. AIR)	1.59	0.55	-	-
Saturated vapor pressure (MPa,25°C)	0.6	-	-	-
Auto-ignition point (°C)	235	650	450	250
Explosion limit (%)	3.4~17	5~15	5.5~36	0.6~7.5
Cetane number	55~60	0	5	40~55
Lower Heating value (MJ/kg)	28.8	50.2	20.1	42.7
Lower Heating value (MJ/m <sup>3</sup> )	59.2	35.8	-	-

Table 4.18: DME and Other Fuels [39]

Source: Japan DME Association

Global Warming Potential (GWP) of DME and other substances are provided in Table 4.19. It can be observed that DME has one of the lowest GWP over different time zones as compared to baseline  $CO_2$  as well as methane and nitrous oxide.

As per China coal research Institute [26],  $CO_2$  emissions are 3.8-5.48 tons of carbon dioxide per ton of dimethyl ether or, 0.133-0.190 t/GJ, among which 0.090-0.129 tons are discharged in the processing and 0.043-0.061 tons in the public process.

Time horizon								
	20 years 100 years 500 years							
DME	1.2	0.3	0.1					
CO <sub>2</sub>	1	1	1					
CH <sub>4</sub>	56	21	6.5					
N <sub>2</sub> O	280	310	170					

Table 4.19: GWP of DME with other gases [40]

The global warming potential of different fuels (CBD-Compressed biogas, LBG-Liquefied Biogas, FTD- Fischer–Tropsch Diesel, Methanol and DME) from a study of biogas systems for utilizing it as a possible transportation fuel (city buses) by Elham Ahmadi Moghaddam, et.al [41] from Department of Energy and Technology, Swedish University of Agricultural Sciences (SLU), and Department of Chemical Engineering, Lund University is provided in Table 4.20.

The results indicate that methanol followed by DME has the least total GWP than compressed biogas and Liquefied biogas.

Table 4.20: Global warming potential (g CO<sub>2</sub>-eq./Nm<sup>3</sup> raw biogas) for the fuel scenarios studied <sup>a</sup> [41]

	CBG	LBG	FTD	Methanol	DME				
(g CO <sub>2</sub> -eq./Nm <sup>3</sup> raw biogas)									
Upgrading	289	298 <sup>°</sup>	35 (84)	70 (84)	73 (84)				
Compression	45	0	0	0	0				
Liquefaction	0	157	0	0	0				
Syngas/fuel	0	0	185 (449)	106 (127)	136 (156)				
synthesis									
Transport	8	1	1	2	2				
Fuelling station	18	6	5	8	10				
(g CO <sub>2</sub> -eq./Nm <sup>3</sup> raw biogas)									
Total GWP	360	462	226 (540)	187 (222)	221 (253)				

a Values not allocated to fuel for the GTL scenarios are given in brackets,

b Includes upgrading and a purification step

It should be borne in mind that for the purposes of this study, fuel consumption and GHG emissions were calculated using 1 Nm<sup>3</sup> raw biogas as the Functional Unit (FU). Therefore the low emissions in the FTD scenario were also due to poor yield of fuel.

A publication by European Parliamentary Research Service [42] provides an evaluation of various fuels including DME and biodiesel in terms of energy security, environmental impacts and vehicle performance among others.

The evaluation is based on the following assumption

- i. It is assumed that electricity is obtained from CO2-free and renewable sources
- ii. In the medium-long term hydrogen is produced by a mix of natural gas, coal (with CO<sub>2</sub> sequestration) and electricity from renewables.
- iii. DME is produced by black liquor (a cellulosic feedstock) and its well-to-wheel CO2 emissions are comparable with biodiesel produced by biomass.

The matrix is reproduced in Table 4.21 for six relevant parameters for this study. DME and Methanol based reformer engines (FCVs) have been given a clear positive impact in terms of long term security of supply over conventional fuels.

Fuel and	Long-term	Cost of	Energy	General safety	Environment	Vehicles
powertrain	security of	handling,	(conversion)	issues (toxicity,	al impacts	performances
technology	supply	storage and	efficiency	inflammability)	and CO2	(acceleration,
		transport	well-to-wheel		abatement	mileage)
Gasoline with			•		•	
ICE						
Conventional			•	•	•	
diesel ICE						
Biodiesel	•		•	•	•	
(from						
biomass) ICE						
DME ICEii	•	•	•	•	•	•
Direct	•					•
hydrogen						
FCVsii						
CO2 capture			•		•	•
and on board						
methanol						
reformer-						
FCVs						
Hybrid	•		•	•	•	
vehicles						

# Table 4.21: Evaluation of Fuels and Powertrain Technologies

#### TIFAC, DST, Govt. of India | Utilisation issues of Methanol and DME

Fuel and	Long-term	Cost of	Energy	General safety	Environment	Vehicles
powertrain	security of	handling,	(conversion)	issues (toxicity,	al impacts	performances
technology	supply	storage and	efficiency	inflammability)	and CO2	(acceleration,
		transport	well-to-wheel		abatement	mileage)
Electric						
vehicles						

Source: European Parliamentary Research Service, European Parliament,

#### Legend

- Clearly positive impact
- Impact unclear or ambiguous
- Clearly negative

The well to tank GHG emissions of different fuels from Semelsberger et.al [43] is provided in Figure 4.12 showing the feedstock as well. The authors state that the production of dimethyl ether is the most efficient process as compared to other fuels such as methanol, diesel, naptha, hydrogen, etc. from natural gas, biomass or electrolysis. As per the US Department of Energy, a complete vehicle fuel-cycle analysis, commonly called a well-to-wheels (WTW) analysis examines the use and emissions associated with fuel production (or well-to-tank [WTT]) activities and energy use and emissions associated with vehicle operation (or tank-to-wheels [TTW]) activities. Research state that excluding fuels produced from biomass, the well-to-tank GHG emissions trend inversely to the well-to-tank efficiencies



Another study [44] by Toyota Motor Corporation provides a summary of  $CO_2$  emissions for production of DME from natural gas pathways by different reference. It can be observed that the  $CO_2$  emissions are around 0.44 t- $CO_2$ /t-DME produced. The same study provides  $CO_2$  emissions for methanol production by natural gas as 315 kg  $CO_2$  per ton of methanol.

Reference	Feedstock	Product	Energy efficiency or energy consumption	CO2 emission or carbon efficiency (t-CO2/t-DME)	Cogeneration, etc.
Hansen, J. B. et al.[1995] (Haldor Topsøe)	Natural gas	DME		0.44	
	Natural gas	DME	69 %	0.446	No electricity cogeneration. Incremental
Wang, M.Q. et	Natural gas	DME	70 %	0.446	No electricity cogeneration. Leap- forward
al.[1999] (Argonne National Lab.)	Flared gas	DME	68 %	0.446	Flared gas as feedstock. No electricity cogeneration. Incremental
	Flared gas	DME	69 %	0.446	Flared gas as feedstock. No electricity cogeneration. Leap- forward
NEDO [2001-3]	Natural gas	DME	71 %	0.112 g-C/10kcal	Natural gas input : 1.114 Nm3 / t-DME
Haldor Topsøe[2001]	Natural gas	DME	71.2 %	355 kg-CO2/t-DME 12.3 g-CO2/MJ-DME	
Ahlvik, P. et al.[2001] (Ecotraffic)	Natural gas	DME	74 %		

Table 4.22: GHG emissions for DME production from Natural Gas

Source: Toyota Motor Corporation

# CHAPTER-5 OBSERVATIONS AND RECOMMENDATIONS

#### 5.1 OBSERVATIONS

Considering, Methanol and DME utilization in various parts of the World, three distinct scenarios as under can be observed

#### WORLD EXCEPT CHINA

#### Methanol

- 1. Chemical Feedstock for manufacture of traditional chemicals like Formaldehyde, Acetic Acid, MTBE, MMA, etc.
- Blending with Gasoline for use in transport sector & use as a marine fuel under serious consideration. However, only 3%-5% blending has been allowed in land vehicles.
- 3. Methanol Based Fuel Cells have matured technology for commercialization.
- 4. Methanol plants are running successfully in Europe and US. However, they face stiff capacity utilisation issues as well as pricing competition from China.
- Israel has brought out policy directives to reduce the dependence of oil in transportation by 60% by 2025 through the Fuel Choice Initiative under the Prime Minister's office.

#### DME

- 1. As aerosol in deodorants
- 2. Prototype vehicles using blend of DME and Diesel in trucks and cars
- 3. DME as a forming and blowing media in foams
- 4. Numerous researches have demonstrated and proven that DME to be a carbon friendly fuel with the potential to reduce 90% emissions with a total well to wheel efficiency of more than 20%
- Commercially DME has been found suitable for most applications with no expensive or extensive vehicle adaptation required. Most of the infrastructure used for LPG can be utilized for DME.

# CHINA

# Methanol

- 1. As chemical feedstock for manufacture of Formaldehyde, Acetic Acid etc.
- 2. Blending with Gasoline and direct use as transport fuel with various blends.
- 3. National standards on methanol blends as a transport fuel
- 4. MTO-Methanol to Olefins, plants in operation and planned

# DME

- 1. Predominantly, DME is used as a blend with LPG (upto 20%)
- 2. Research ongoing for use in ceramics industry

# INDIA

# Methanol

- 1. As feedstock for chemical Industry for manufacturing of Formaldehyde and Acetic Acid etc.
- 2. As Solvent in Chemical and Pharmaceutical Industry.
- 3. As transesterification agent for biodiesel

#### DME

- 1. As aerosol in deodorants
- 2. Possible blend with LPG for domestic fuel.

Methanol's utilization in India is mainly in the chemical sector. The installed capacity in the country is around 0.7 million metric tonnes with consumption of 1.8-2.0 million metric tonnes. The production in the year 2014-15 was 0.24 metric tonnes. The poor capacity utilization was primarily due to non-availability of Natural Gas (needed to run these units) at reasonable price, which hindered the methanol production and it had to be imported.

Methanol and DME has immense potential for use as a feedstock for several downstream chemicals as well as used as fuel in several applications. However, the utilization heavily depends on the availability of natural gas and utilisation of vast coal resources in our country

# 5.2 RECOMMENDATIONS

#### 5.2.1 Methanol

The ethanol blending introduced in 2003, could achieve a blending percentage of 2.3% in 2014-15. However, to achieve 10% blending levels by 2016-17, Government has permitted Oil Marketing Companies (OMCs) to sell Ethanol blended petrol with percentage of ethanol as per BIS Specification. They plan to achieve 5% ethanol blending across the country as a whole. This will result in substitution of 1350 million litres of petrol which will save the country over Rs. 6000 crore of foreign exchange in one year.

Presently many European countries have allowed blending methanol with gasoline upto 3% to gasoline with no regulatory, environmental and technological issues. Similarly, DME has also been researched for use in trucks and cars with change in fuel systems and additives. If Govt. changes fuel policy & allows 3%-5% methanol mixing in place of ethanol then it will ease pressure on alcohol based industry. Moreove Govt. has fixed a price of ethanol for blending at Rs.49.50 per litre while methanol is available at half the above price with assured supply.

#### 5.2.2 DME

For DME, as per Government's desire to supply LPG cylinder to poor people, the new demand for LPG can be met by mixing 5-9% DME to LPG. The present domestic demand is 16 million tonnes. The requirement of DME at 7-9% blending will be 1-2 million tonnes. The corresponding methanol demand will be 3 million tonnes.

#### 5.2.3 General

There is an imperative need to recognize methanol and DME as an alternate fuel in energy policies in India as they do not currently figure in any energy or environment related policies.

There has to be a strong collective effort in brining all stakeholders for sensitizing about the importance of methanol and DME in saving imports of crude oil.

Increased efforts in the direction of methanol and DME awareness along with setting up of pilot projects such as importing M100 cars and Diesel trucks could provide a platform for evaluation of the fuels in Indian conditions.

There has to be a strong policy driven growth for the utilisation of methanol and DME is sectors which are currently being in practice in China and elsewhere.

DME has to be manufactured in India for providing several costs advantages which could lead to an optimum utilisation of DME

#### **Utilisation of Coal**

It is observed that India's coal reserves are mainly spread over seven states. The noncoking varieties are spread over Chhattisgarh, Jharkhand, Orissa and West Bengal. It may be an appropriate opportunity for these states to make an effort to establish coal based chemical industry starting with methanol to olefins along with DME and other basic chemicals. This will give a much needed impetus for utilisation of methanol and DME in India.

#### Synthetic Natural Gas (SNG) from coal

We need to consider also reviving the existing natural gas based methanol units by way of making available natural gas to them. The present natural gas produced in the country are linked with Fertilizer & Thermal Power Units, leaving aside the Organic Chemical Industry high & dry. It may be a good idea if we utilize part of the Syngas produced for Methanol (in the new plant) is diverted to make Synthetic Natural Gas by putting a Methanation Unit, where CO & CO2 can be reacted with Hydrogen as per the following equation:

 $\begin{array}{l} \text{CO}+3\text{H}_2 \rightarrow \text{CH}_4+\text{H}_2\text{O} \\ \text{CO}_2+4\text{H}_2 \rightarrow \text{CH}_4+2\text{H}_2\text{O} \end{array}$ 

The Synthetic Natural Gas thus produced can be dried and piped to these existing Methanol Units lying idle due to non-availability of Natural Gas.

# CHAPTER-6 DEMAND FORECAST

# 6.1 INTRODUCTION

Several facts emerged during the study for methanol and DME application areas including forecast to 2025. From the Table 6.1, it is recognizable that the use of Methanol is indeed changing globally. Methanol is being recognised globally as Energy Feed rather than only feed stock for conventional chemicals and solvents (Formaldehyde; Pharmaceutical) production.

The Merchant Research Consulting Ltd. [1] describes the future world methanol market with two different scenarios.

#### **Optimistic Scenario**

This scenario depicts a bright future of methanol based on several experts and market players' perception on the utilisation of methanol as an important chemical feedstock as well as its application in Power Generation, Chemical Industries & Transportation. This is based on several advantages which methanol can offer such as environmental benefits, technologically attractiveness, and cost reductions over conventional fuels as well as lower energy costs.

#### Less Optimistic Scenario

This scenario is based on several past experiences on utilizing methanol as an energy source as well as price fluctuations associated with it. The article outlines that despite its robust growth, the Methanol Market suffers from a number of incongruities. Currently, global methanol production and consumption are in the state of equilibrium, and as such, equilibrium can be easily violated.

		2007		2016		2020
Demand	%		%		%	
Traditional Chemicals						
Formaldehyde	38.65	15,086	25.41	21,828	24	24,000
Acetic Acid	10.26	4,003	7.11	6,105	9	9,000
Methyl tert-Butyl Ether(MTBE)	18.17	7,094	11.78	10,124	8.5	8,500
Methyl Methacrylate	3.40	1,329	1.99	1,706	1	1000
Dimethyl terephthalate(DMT)	1.25	488	0.55	473	0.4	400
Methanethiol (Methyl Mercaptan)	1.07	416	0.60	513	0.4	400
Methylamines	2.92	1,140	1.81	1,559	1.5	1500
Methyl Chloride (Chloromethane)	4.32	1,686	2.52	2,166	2	200
Alternative Fuels						
Gasoline Blending	7.17	2,799	14.16	12,168	15	15,000
Biodiesel	2.09	817	1.42	1,220	5	5,000
DME	2.39	932	4.58	3,932	8	8,000
Fuel Cells	0.02	7	0.01	8	2	2,000
Methanol to Olefins	0.01	5	23.10	19,848	20	20,000
Others	8.12	3,169	4.96	4,259	5	5,000
Total		39034	100.00	85,909	100	1,00,000

|--|

Source: Derived Data from MMSA

The end use report analysed the past use pattern of Methanol, the present and the future use pattern resulting from economics of competitive Fuels, like decline in price of crude oil, natural gas etc., along with policy reforms globally, which could push the demand of methanol in the market. The Global chemicals demand [2] is provided in Figure 6.1.



Figure 6.1: IEA, Global Chemicals Demand [2]

The demand for chemicals including methanol by 2050 has been estimated by the IEA based on 2010 figures and further on two different scenarios related to climate change. The first scenario in 6DS, which is global temperature rise to 6°C and the second, is 2DS, which is the restriction of global temperature rise to 2°C. These are further bifurcated into low demand case and high demand case.

	2010	Low Demand 2050	High Demand 2050
Methanol	49	171	191
Ethylene	123	320	376
Propylene	77	208	243
BTX aromatics	105	283	331
Total HVC	304	810	950
Ammonia	159	259	300

Table 5.2: Demand of Chemicals in 2050, IEA, million tonnes [2]
#### 6.2 PROJECTED DOMESTIC DEMAND

The present demand of methanol in the country is limited to traditional chemicals like formaldehyde, acetic acid and some chemicals listed in Table 2.13. The present consumption is of the order of 1.8 million tonnes. It is observed that the demand in the sector is growing at the rate of 6% per annum. It is estimated that the demand in chemicals sector will grow to 3.0 million tonnes by 2025.

The automobile industry in the country is growing at the rate of 9% (excluding two and three wheelers, SIAM) and alongside gasoline demand. The Government has allowed blending of ethanol upto 10% in gasoline. The availability of ethanol in the country is limited and the price of ethanol allowed for ethanol blending is Rs49.50 per liter compared to methanol which is available at half the above price.

It is observed throughout the world that many countries are planning to blend methanol at 5% per liter. With blend of 5% methanol and 5% ethanol as co-solvent, India will be in comfortable position. The demand of gasoline presently is 23 million tonnes per annum with 11% growth rate. The methanol demand for fuel blending would be 2.0 million tonnes by 2025.

India with 1.33 billion people consumes 20 million tonnes of oil. On an average hotels and restaurants generate 0.1 million tonnes of waste oil per annum. The used cooking oil and other inedible oil and animal tallow can be utilised for biodiesel production. Methanol is utilized as a transesterification agent. As per press reports, India would require 6.75 billion litres of biodiesel (5% blending with diesel), and 4.5 billion litres of methanol for blending over the six years.

Government in the last 15 months (2014-2016) gave more than 40 million LPG connections to rural poor people. Presently, the demand of LPG is 21 million tonnes. With additional connections, the demand of DME could be more than 2.5 million tonnes requiring 3.0 million tonnes of methanol.

The domestic demand by 20205 has been estimated to be 10.5 million tonnes in India.

The domestic demand for methanol as estimated based on existing and prospective market scenario of end use sectors as well as assuming that methanol utilization shall gain in the recent future due to positive policy intervention in different sectors is provided below for the year 2025.

S.No.	Application Sector	Present Demand	Future Demand
		(million MT)	(million MT) 2025
1.	Chemicals & Pharmaceuticals	1.80	3.00
2.	Blending as transport fuel	0.00	2.00
3.	For manufacturing DME for use with LPG	0.00	3.00
4.	Bio – diesel	0.50	2.50
5.	Total Demand	2.30	10.50

Source: Derived In-house

# The demand for DME as a blend for LPG has been estimated at 3.00 million metric tonnes

The end use report is not only analysing the past use pattern of Methanol but also analyses the present and the future use pattern resulting from Economics of competitive Fuels, like decline in price of Crude oil, Natural Gas etc.

# 6.3 CONVERSION FROM FEED

IEA provide that the conversion from coal to methanol is 1.59 tons of standard coal equivalent per ton of methanol.

As per China Coal Research Institute, the comprehensive coal consumption in methanol production is 1.42-1.59 tons of standard coal equivalent per ton of methanol. Energy conversion efficiency can reach 43-48%, or even 50% in some large projects.

The comprehensive coal consumption here is  $2.18 \sim 2.40$  tons of standard coal equivalent per ton of dimethyl ether. Energy conversion efficiency can reach  $41 \sim 45\%$ .

The typical gas consumption for world-scale methanol plant ranges from 28 to 31 million Btu per metric ton of product based on LHV of the feed;

Southern chemical states that the production of methanol from natural gas consumes about 100,000 BTUs per U.S. gallon, or 33.33 million BTUs per metric ton.

International Gas union states that 1 billion cu. meter of gas should provided 1.1 million tonnes of methanol

Hence for meeting the demand of methanol in the next 10 years and if methanol is manufactured from coal, the estimated coal demand would be 16 million tonnes per annum, while the natural gas equivalent would be  $301 \times 10^{12}$  Btu per annum.



# **Product Safety Summary Sheet**

# **DuPont<sup>TM</sup> Dimethyl Ether**

**Chemical Identification, Product Identification or Common Name:** 

CAS number: 115-10-6 CAS name: Methane, 1,1'-oxybis-EC Number: 204-065-8 EINECS Name: Dimethyl ether

# **Product Uses and Applications:**

Dimethyl ether is used in industrial applications as an intermediate in the preparation and manufacturing of other basic organic chemicals, as a catalyst in industrial polymerization processes, as an alternative fuel, as a foam expansion agent, and as an aerosol propellant for a variety of products that include adhesives, sealants, foam in a can, coatings, paints, automotive care products, topical skin cooling sprays, over the counter treatments, hairspray, sun screen and a variety of other personal care and household products where its water solubility and strong solvency properties add value.

# **Physical Properties of the Chemical or Product:**

Dimethyl ether is a colorless gas with high water solubility, high vapor pressure, a boiling point of -24.8°C and a melting point of -141.5°C. Dimethyl ether is stable but is extremely flammable and may form potentially explosive mixtures with air, but will not form potentially explosive peroxides.

# **Exposure Potential:**

# Workplace exposure:

Dimethyl ether has a low boiling point and will typically vaporize to the atmosphere upon its release. However, because Dimethyl ether is handled as a liquified gas, it can leak as both a gas or a liquid. As a gas leak, there is potential inhalation exposure. As a liquid leak, there is potential frostbite exposure. Workers should follow the recommended safety measures contained within the (Material) Safety Data Sheet ((M)SDS) and on any product packaging. Employees should be trained in the appropriate work processes and safety equipment to limit exposure to chemical substances. Occupational use of this substance is considered to be safe provided the recommended safety measures given in the (M)SDS are followed.

#### **Consumer exposure**:

Dimethyl ether is mainly used as a propellant in aerosol products to dispense the contents of the can. The most likely consumer exposure route would be an inhalation exposure if the aerosol product is not used as directed.

# **Environmental exposure:**

Dimethyl ether environmental exposure can occur from accidental leaks during manufacture, distribution, handling, or use and when aerosol products are dispensed. Dimethyl ether is not expected to be persistent in the environment and is not bioaccumulative.

# **Health Information**

Note: The information contained in this section may be useful to someone handling the pure undiluted substance such as a manufacturer or transporter. For more information on health hazards and recommended protective equipment, please refer to the (M)SDS.

Effect Assessment	Result
Acute Toxicity	Inhalation: Misuse or intentional inhalation abuse may cause
	death without warning symptoms, due to cardiac effects.
	Other symptoms potentially related to misuse or inhalation abuse
	are anesthetic effects, light-headedness, dizziness, confusion,
	incoordination, drowsiness, or unconsciousness, irregular
	heartbeat with a strange sensation in the chest, heart thumping,
	apprehension, feeling of fainting, dizziness or weakness. Vapors
	are heavier than air and can cause suffocation by reducing
	available oxygen for breathing.
Irritation	Skin: Not an irritant. Contact with liquid or refrigerated gas can
	cause cold burns or frostbite.
	Eye: Not an irritant. Contact with liquid or refrigerated gas can
	cause cold burns or frostbite.
Sensitization	Not expected to cause skin sensitization.
Mutagenicity	Not a mutagen.
Carcinogenicity	Not carcinogenic.
Toxicity after repeated exposure	No toxicologically significant effects were found.
Toxicity for reproduction	No reproductive/developmental toxicity.

Exposures may affect human health as follows:

# **Environmental Information**

Note: The information in this chapter is intended to provide brief and general information of this substance's environmental impact. The results in the table below refer to testing performed with the non formulated, undiluted substance. The data does not replace the data given in the (M)SDS. For more information and recommended protective measures, please refer to the (M)SDS.

Effect Assessment	Result
Aquatic Toxicity	Slightly toxic to aquatic organisms.
Biodegradability	Not readily biodegradable.
Persistence	Persistent in the atmosphere. It is expected to rapidly volatilize from aquatic and soil compartments.
Bioaccumulation potential	Not expected to bioaccumulate.

## **Risk Management**

# Workplace Management:

Risk management measures for industrial site use include containment through engineering controls and the use of personal protective equipment (PPE) as appropriate. Engineering controls include the use of storage and shipping containers that are rated for the pressures and temperatures to which the material may be subjected, use of appropriate recycle and recovery equipment, and adequate ventilation at both storage and use locations. Always refer to the (Material) Safety Data Sheet ((M)SDS) for guidance on the appropriate personal protective equipment to be used and on the safe handling of this material.

Normal ventilation for standard manufacturing procedures is generally adequate. Local exhaust should be used when the potential for large amounts are released. Mechanical exhaust should be used in low or enclosed places. Under normal manufacturing conditions, no respiratory protection is required when using this product. Safe work practices include maintaining proper storage of material containers at safe temperatures and away from building air ventilation intake locations.

# **Consumer Risk Management:**

Dimethyl ether is mainly used as a propellant in aerosol products to dispense the contents of the can. The most likely consumer exposure route would be an inhalation exposure if the aerosol product is not used as directed. All aerosol products are formulated for safe consumer use when label directions are followed, and when done so, Dimethyl ether vapors will dissipate quickly, mitigating any exposure concerns. Use of aerosol products with adequate ventilation is always recommended.

# **Regulatory Information:**

Always refer to the (Material) Safety Data Sheet ((M)SDS) for guidance on regulatory restrictions that may govern the manufacture, sale, transportation, use and/or disposal of this chemical or product. Regulations may vary by region, country, state, county, city, or local government.

#### **First Aid Information:**

For all First Aid or Emergency information, consult the (Material) Safety Data Sheet ((M)SDS).

#### **Information Sources:**

Data is compiled from a variety of sources, including publicly available documents, internal data and other sources such as, but not limited to, Chemical Safety Reports and (Material) Safety Data Sheets ((M)SDS).

## **Contact Information:**

E.I. du Pont de Nemours and Company, Wilmington, DE 19880 USA Customer Service: Toll Free: 1-800-774-1000 Global: 1-843-335-5912 Hours: 8:00 a.m. - 7 p.m. EST

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	Gasoline/E10	Low Sulfur Diesel	Biodiesel	Propane (LPG)	Compressed Natural Gas (CNG)	Liquefied Natural Gas (LNG)	Ethanol/E100	Methanol	Hydrogen	Electricity
Chemical Structure [1]	C₄ to C <sub>12</sub> and Ethanol ≤ 10%	C <sub>8</sub> to C <sub>25</sub>	Methyl esters of C <sub>12</sub> to C <sub>22</sub> fatty acids	$C_3H_8$ (majority) and $C_4H_{10}$ (minority)	CH₄ (majority), C₂H <sub>6</sub> and inert gases	CH₄ same as CNG with inert gasses <0.5% (r)	CH <sub>3</sub> CH <sub>2</sub> OH	CH₃OH	H <sub>2</sub>	N/A
Fuel Material (feedstocks)	Crude Oil	Crude Oil	Fats and oils from sources such as soy beans, waste cooking oil, animal fats, and rapeseed	A by-product of petroleum refining or natural gas processing	Underground reserves and renewable biogas	Underground reserves and renewable biogas	Corn, grains, or agricultural waste (cellulose)	Natural gas, coal, or, woody biomass	Natural gas, methanol, and electrolysis of water	Coal, nuclear, natural gas, hydroelectric, and small percentages of wind and solar
Gasoline Gallon Equivalent [4]	97% - 100%	1 gallon of diesel has 113% of the energy of one gallon of gasoline.	B100 has 103% of the energy in one gallon of gasoline or 93% of the energy of one gallon of diesel. B20 has 109% of the energy of one gallon of gasoline or 99% of the energy of one gallon of diesel.	1 gallon of propane has 73% of the energy of one gallon of gasoline.	5.66 pounds or 123.57 cu ft. of CNG has 100% of the energy of one gallon of gasoline. [2][5](q) 6.38 pounds or 139.30 cu ft. of CNG has 100% of the energy content of one gallon of diesel [2][5](q)	5.38 pounds of LNG has 100% of one gallon of gasoline and 6.06 pounds of LNG has 100% of the energy of one gallon of diesel (r)	1 gallon of E85 has 73% to 83% of the energy of one gallon of gasoline (variation due to ethanol content in E85). 1 gallon of E10 has 96.7% if the energy of one gallon of gasoline. [3]	1 gallon of methanol has 49% of the energy of one gallon of gasoline.	1 kg or 2.198 lbs. of H <sub>2</sub> has 100% of the energy of one gallon of gasoline.	33.70 kWh has 100% of the energy of one gallon of gasoline.
Energy Content (Lower heating value)	112,114 - 116,090 Btu/gal (g)	128,488 Btu/gal (g)	119,550 Btu/gal for B100 (g)	84,250 Btu/gal (g)	20,160 Btu/lb [2](q)	21,240 Btu/lb (r)	76,330 Btu/gal for E100 (g)	57,250 Btu/gal (g)	51,585 Btu/lb (g)	3,414 Btu/kWh

	Gasoline/E10	Low Sulfur Diesel	Biodiesel	Propane (LPG)	Compressed Natural Gas (CNG)	Liquefied Natural Gas (LNG)	Ethanol/E100	Methanol	Hydrogen	Electricity
Energy Content (Higher heating value)	120,388 - 124,340 Btu/gal (g)	138,490 Btu/gal (g)	127,960 Btu/gal for B100 (g)	91,420 Btu/gal (g)	22,453Btu/lb [1](g)	23,726 Btu/lb (g)	84,530 Btu/gal for E100 (g)	65,200 Btu/gal (g)	61,013 Btu/lb (g)	3,414 Btu/kWh
Physical State	Liquid	Liquid	Liquid	Pressurized Liquid	Compressed Gas	Cryogenic Liquid	Liquid	Liquid	Compressed Gas or Liquid	Electricity
Cetane Number	N/A	40-55 (a)	48-65 (a)	N/A	N/A	N/A	0-54 (b)	N/A	N/A	N/A
Pump Octane Number	84-93 (c)	N/A	N/A	105 (f)	120+ (d)	120+ (d)	110 (e)	112 (e)	130+ (f)	N/A
Flash Point	-45 °F (o)	165 °F (o)	212 to 338 °F (a)	-100 to -150 °F (o)	-300 °F (o)	-306 °F (p)	55 °F (o)	52 °F (o)	N/A	N/A
Autoignition Temperature	495 °F (o)	~600 °F (o)	~300 °F (a)	850 to 950 °F (o)	1,004 °F (o)	1,004 °F (p)	793 °F (o)	897 °F (o)	1,050 to 1,080 °F (o)	N/A
Maintenance Issues			Hoses and seals may be affected by higher-percent blend. Lubricity is improved over that of conventional diesel fuel.		High-pressure tanks require periodic inspection and certification.	LNG is stored in cryogenic tanks with a specific hold time before the pressure build is relieved, the vehicle should be operated on a schedule to maintain a lower pressure in the tank.	Special lubricants may be required. Practices are very similar, if not identical, to those for conventionally fueled operations.	Special lubricants must be used as directed by the supplier and M-85- compatible replacement parts must be used.	When hydrogen is used in fuel cell applications, maintenance should be very minimal. High-pressure tanks require periodic inspection and certification.	It is likely that the battery will need replacement before the vehicle is retired.

	Gasoline/E10	Low Sulfur Diesel	Biodiesel	Propane (LPG)	Compressed Natural Gas (CNG)	Liquefied Natural Gas (LNG)	Ethanol/E100	Methanol	Hydrogen	Electricity
Energy	Manufactured	Manufactured	Biodiesel is	Approximately	CNG is	LNG is	Ethanol is	Methanol is	Hydrogen is	Electricity is
Security	using oil, of	using oil, of	domestically	half of the LPG	domestically	domestically	produced	domestically	produced	generated
Impacts	which nearly	which nearly	produced,	in the U.S. is	produced from	produced	domestically.	produced,	domestically	mainly
	1/2 is imported	1/2 is imported	renewable,	derived from	natural gas and	from natural	E85 reduces	sometimes	and can be	through coal
	(n).	(n).	and reduces	oil, but no oil is	renewable	gas and	lifecycle	from	produced	fired power
			petroleum use	imported	biogas. The	renewable	petroleum use	renewable	from	plants. Coal is
			95%	specifically for	United States	biogas.	by 70% and	resources.	renewable	the United
			throughout its	LPG	has vast		E10 reduces		sources.	States' most
			lifecycle (i).	production.	natural gas		petroleum use			plentiful and
					reserves.		by 6.3% (I).			price-stable
										fossil energy
										resource.

#### Notes

[1] Standard Chemical Formulas represent idealized fuels. Some table values are expressed in ranges to represent typical fuel variations that are encountered in the field

[2] The type of meter or dispensing equipment being used to fuel vehicles must be taken into consideration. For fast-fill stations that dispense CNG with Coriolis flow meters, which measure fuel mass and report fuel dispensed on a "gallon of gasoline-equivalent" (GGE) basis, the lbs./GGE factor should be used. For time-fill stations or other applications that use traditional residential and commercial gas meters that measure/register in units of cubic feet, the CF/GGE factor should be used.

[3] E85 is a high-level gasoline-ethanol blend containing 51% to 83% ethanol, depending on geography and season. Ethanol content is lower in winter months in cold climates to ensure a vehicle starts. Based on composition, E85's lower heating value varies from 83,950 to 95,450 Btu/gal. This equates to 73% to 83% the heat content of gasoline.

[4] GGE table values reflect BTU range for common gasoline baseline references (E0, E10, and indolene certification fuel)

[5] See Compressed Natural Gas Gasoline & Diesel Gallon Equivalency Methodology at http://afdc.energy.gov/fuels/equivalency\_methodology.html

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# Central Pollution Control Board Ministry of Environment & Forests, Govt of India, Parivesh Bhawan, East Arjun Nagar, Delhi - 110032 MATERIAL SAFETY DATA SHEETS 377 Methyl alcohol

# 1. CHEMICAL IDENTITY

Chemical Name : Methyl alcohol

Chemical Classification: Flammable, Toxic Trade Name :

Synonyms: Methanol, Wood alcohol, Wood spirit, Colonial spirit, Columbian spirits

Formula : CH4C	)		CAS No: 67	-56-1 <b>UI</b>	N No:	1230	
Regulated Identifica	tion						
Shipping Name : M	lethanol			Hazchem	Code :	: 2WE	
Codes / Label : C	lass 3, Fla	mmable, Toxic	c Haza	ardous Waste	ID No	: 17	
HAZARDOUS INGRE	DIENTS	C.A.S. No.	HAZARDO	OUS INGREDI	ENTS	C.A.S. No.	
1 Methyl alcohol		67-56-1	3				
2			4				
2. PHYSICAL / CHEN	IICAL DAT	A					
Boiling 64.7 Pt. °C:	Phys	sical State: L	quid	Appearance	e: Colo	ourless, watery	
Melting -97.8 Pt °C:	Vapo @ 35	our Pressure s°C mmHg:	127 mm Hg deg C	at 25 Odour	: Alcoh pungo crude	nolic odour; ent odour when e	
Vapour 1.1 Density(Air =1):	1 So wa g/*	olubility in ater at 30°C 100ml:	Miscible @ : deg C	20 Others:	Miscib ether k ketone organi	le with etahnol, penzene, es & other c solvents.	
Specific Gravity (Wa	<b>ter =1 ):</b> 0	.8100 at 0 deg	C	pH :	Neutra	al	
3. FIRE / EXPLOSION	N HAZARD	DATA					
Flammability :	Yes	<b>LEL:</b> 6	Fla	sh Point °C ir	<b>OC:</b> 1	16.1	
TDG Flammability:	3	<b>UEL:</b> 36.5	Fla	sh Point °C ir	<b>CC:</b> 1	12.2	
Autoignition Temper	ature °C :	385					
Explosion sensitivity	v to impac	t: Stable					
Explosion sensitivity	/ to static	Electricity: Va	apours may b	e explosive.			
Hazardous Combustion Products : Emits acrid smoke and irritating fumes.							
Hazardous Polymeria	zation: W	/ill not occur.					
Combustible Liquid:	Yes	Explosive Ma	terial: No	Corrosi	ve Mate	erial No	
Flammable Material:	Yes	Oxidiser :	No	Others:			
Pyrophoric Material:	No	Organic Perc	xide: No				
4. REACTIVITY DATA	4						
Chemical Stability	: Stable						
Incompatibility with other material	: Strong of tetrachlo	xidisers, beryli ride + metals (	um dihydride Al, Mg, Zn), (	, metals (K, M dichlorometha	g), carb ne, oxic	oon Jants.	

# Hazardous

# Reaction Products

# 5. HEALTH HAZARD DATA

Routes of entry: Inhalation, Ingestion, Skin and Eyes

5

# Effects of Exposure / Symptoms:

Exposure to vapours causes eye irritation, headache, fatigue, drowsiness. High concentration can produce central nervous system depression and optic nerve damage. 50,000 ppm will probably cause death in 1-2 hrs. Is absorbed through skin. Swallowing may cause death or eye damage.

# Emergency Treatment :

Inhalation: Remove the victim from exposed area & apply artificial respiration if breathing has stopped.

Skin: Flush with plenty of water for 15 mins. Seek medical aid.

**Eyes:** Flush with plenty of water for 15 mins. Seek medical aid.

**Ingestion:** If victim is conscious and alert, give 2-4 cupfuls of milk or water. Get medical aid immediately. Induce vomiting by giving one teaspoon of syrup of Ipecac.

LD50 (oral-rat) mg/kg:	5628	STEL	<u>.</u> : 250 ppm	n (310 mg/mm3), skin
LC50 (rat) mg/kg:		Odou	Ir Threshold:	2,000 ppm
Permissible Exposure Limit:	200 ppm (260 mg/m3), skin	TLV (ACGIH) :		200 ppm (260 mg/m3), skin
NFPA Hazard	Health	Flammability	Reactivity	Special
Signals	1	3	0	

# 6. PREVENTIVE MEASURES Personal Protective : Avoid contact with liquid or vapours. Provide air-supplied respirator. (Do not use organic cansiter mask). Wear boots, safety goggles, protective apron and rubber gloves. Provide eye wash and basin nearby. Handling : Use spark-proof tools and explosion proof equipment. Avoid breathing dust, vapor, mist, or gas. Avoid contact with skin and eyes. Use only in a chemical fume hood. Storage : Store away from heat, ignition source, sparks. Keep away from heat, and

Precautions

7. EMERGE	NCY / FIRST	AID MEASURES						
FIRE:								
Fire Exting	Fire Extinguishing Media: CO2, dry chemical powder, alcohol foam, water mist/fog.							
Special Pro	ocedure	: Keep the containers cool by spraying water if exposed to heat or flame.						
Unusual Ha	azards	: Container may explode in a fire.						
EXPOSURE Inhalation:	E: First Aid N Remove the v stopped.	<b>leasures:</b> <i>v</i> ictim from exposed area & apply artificial respiration if breathing has						
Skin:	Flush with ple	enty of water for 15 mins. Seek medical aid.						

Eyes: Flush with plenty of water for 15 mins. Seek medical aid.

flame.

2

**Ingestion:** If victim is conscious and alert, give 2-4 cupfuls of milk or water. Get medical aid immediately. Induce vomiting by giving one teaspoon of syrup of Ipecac.

Antidotes / Dosages: Baking soda in a glass of water.

# SPILLS :

**Steps To Be Taken** : Shut off leaks if without risk. Drench with water.

Waste Disposal Method: Seal all the waste in vapour tight plastic bags for eventual disposal.

# 8. ADDITIONAL INFORMATION / REFERENCES

Periodic medical check up is recommended if exposed. Dangerous fire hazard when exposed to heat, flame, and oxidisers.

9. MANUFACTURERS / SUPPLIERS DATA	
NAME OF FIRM :	Contact person
MAILING ADDRESS :	in Emergency :
TELEPHONE / TELEX NOS :	Local Bodies involved :
TELEGRAPHIC ADDRESS :	Standard Packing :
OTHERS :	Trem Card Details / Ref :

# **10. DISCLAIMER**

Information contained in this material data sheet is believed to be reliable but no representation, guarantee or warranties of any kind are made as to its accuracy, suitability for a particular application or results to be obtained from them. It is up to the manufacturer/ seller to ensure that the information contained in the material safety data sheet is relevant to the product manufactured / handled or sold by him as the case may be. The Government makes no warranties expressed or implied in the respect of the adequacy of this document for any particular purpose.

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