PRODUCTION OF METHANOL AND DME

August, 2016

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ABBREVIATIONS

BFB	Bubbling Fluid Bed
BGL	British Gas/Lurgi
BHEL	Bharat Heavy Electricals Ltd.
BTL	Biomass to Liquid
CBG	Compressed Bio Gas
CFB	Circulating Fluid Bed
COG	Coke Oven Gas
CRI	Carbon Recycle International
CTL	Coal To Liquid
CSIR	Council of Scientific & Industrial Research
DME	Di-Methyl Ether
EF	Entrained Flow
FCIPT	Facilitation Centre for Industrial Plasma Technologies
FT	Fischer–Tropsch process
GE	General Electric
GHG	Green House Gas
GAIL	Gas Authority of India Ltd.
GNFC	Gujarat Narmada Valley Fertilizer and Chemicals Ltd.
GTL	Gas to Liquid
HHV	Higher Heating Value
HTS	High Temperature Shift
IGCC	Integrated Gasification Combined Cycle
IICT	Indian Institute of Chemical Technology
IIT	Indian Institute of Technology
IISc	Indian Institute of Science
IOC	Indian Oil Corporation
JnNURM	Jawaharlal Nehru National Urban Renewal Mission

JSW	Jindal Steel Works
KBR	Kellogg Brown & Root
KOGAS	Korean Gas
KWH	Kilo Watt Hour
LPG	Liquefied Petroleum Gas
L&T	Larsen & Toubro
LTS	Low Temperature Shift
LVOC	Large Volume Organic Chemicals
MHI	Mitsubishi Heavy Industries
MMTPA	Million Metric Ton Per Anum
Mtpa/MTPA	Million Ton Per Anum
MSW	Municipal Solid Waste
MTBE	Methyl Tertiary Butyl Ether
MTO	Methanol To Olefin
MTP	Methanol To Propylene
MW	Mega Watt
MWe	Mega Watt Electrical
NTPC	National Thermal Power Corp. of India
PBT	Persistent, Bioaccumulative and Toxic
PDIL	Projects & Development India Ltd.
PE	Polyethylene
PF	Phenol Formaldehyde
PFB	Pressurised Fluid Bed
POX	Partial Oxidation
PPX	Poly Para Xylene
PTA	Purified Terephthalic Acid
RCF	Rashtriya Chemicals & Fertilizers Ltd.
SNG	Synthetic Natural Gas
TEL	Tetra Ethyl Lead
TERI	The Energy Research Institute

TPD	Ton Per Day
UCG	Underground Coal Gasification
UF	Urea Formaldehyde
WtE	Waste to Energy
WTW	Well To Wheel

FOREWORD

Methanol & DME Economy – Production Issues

Methanol and Di Methyl Ether (DME) are emerging as alternative liquid fuels for transportation. While methanol could be used directly or, blended with gasoline, DME is suitable for Diesel engines.

The use of methanol and DME – a dehydrated form of methanol- as alternative transportation fuel was initially fuelled by their excellent burning characteristics and lower GHG emission. With price advantage of natural gas, methanol and DME penetrated into the liquid transportation fuel market. Subsequently, coal has also been used, particularly in China, to produce methanol and DME for fuel application.

Till 2012, global methanol production was much less than the installed capacity, but during the last few years, the demand has increased and many new facilities are coming up around the world. It is expected that by 2020, the production of methanol will exceed 100 Million tonnes. The present demand for DME is of the order of 5 Million Tonnes per annum, which is expected to grow by about 15% per year during the next few years. At this time, the major use of DME is for blending with LPG but the use as diesel substitute is expected to raise the requirements many folds.

Unlike gasoline or diesel, which are mostly produced from petroleum crude, methanol and DME could be produced, such as bio mass via syn gas, or via reforming of bio gas. With increasing concern about GHG emission, from energy usage, the fuels produced from renewable sources are increasingly favoured over the non renewable sources. From bio mass virtually carbon neutral fuel is possible to be produced. Further, the large methanol / DME plants based on fossil fuels could easily reduce the impact to the environment by capturing the carbon produced during the processing of the hydrocarbon source to methanol/DME.

However, the current production of methanol is largely based on fossil sources with only between 1-2 % of the total methanol being produced from biomass.

In India all the methanol plants are based on natural gas or naptha. Although there is great demand for methanol in India, the availability of natural gas and price of naptha along with the low import price of methanol, is preventing building of new plants.

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 CO_2 stream coming out of factories or plants e.g. large power plant, steel plant etc.

Keeping in view the current high growth trajectory of our Country, sharply increasing energy requirements being mostly met through imports, NITI Aayog has constituted a core team for working on all aspects of Methanol Economy and evaluating technologies, prioritizing R&D, nucleating and pursuing scaling up efforts. Three different groups have been constituted to focus of issues related to R&D, Production and Utilization of Methanol and DME and come up with a road map.

Towards getting a status paper for consideration and evolving a road map for our country, this survey report broadly consists of collation of information on the following aspects :

- Potential availability of high ash coal and biomass for methanol & DME production
- R & D efforts in the sector– National & International
- Status of available technologies:
- Evaluating Feasibility
- Issues and challenges & areas for improvement in the production technology
- Setting R&D priorities

This report is an outcome of culling out information available in literature, public domain besides inputs from experts and organizations like- Methanol Institute and International DME Association.

Keeping in view the feasibility and viability of operation, this survey report has covered aspects related to processing of different feedstock simultaneously, production flexibility to address market needs and possibility of integrating existing methanol plants with DME. The report has also covered problems associated with bio mass collection and their sustained supply.

The preparation was guided and orchestrated 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.

H. S. Karanagale

Chairman- Expert Group

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EXECUTIVE SUMMARY

THIS LITERATURE SURVEY REPORT WAS PREPARED AT THE INSTANCE OF TIFAC (INDIA) WITH THE OBJECTIVE OF CREATING A ROAD MAP FOR METHANOL ECONOMY FOR LONG TERM ENERGY SECURITY OF THE COUNTRY.

Methanol and Di Methyl Ether (DME) are emerging as alternative liquid fuels for transportation. While methanol could be used directly or blended with Gasoline, DME is suitable for Diesel engines. Methanol is a liquid at ambient temperature but the boiling point of DME is little lower. It could be handled like Liquefied Petroleum Gas (LPG). DME has excellent flammability and is a better replacement for LPG. During the last few years the use of methanol and DME as fuel has increased significantly. Methanol demand is growing at a robust 6 to 8 % annually (Ref. 124). The demand for DME is also increased and much of the methanol demand is because it is used to produce DME. In India, the use of both methanol and DME as fuel component is very low at present. Currently, there is surplus production of methanol in the world but the demand in India is much more than the indigenous production.

The use of methanol and DME as alternative transportation fuel was initially fuelled by their excellent burning characteristics and lower GHG emission. Subsequently, with the price advantage of natural gas, methanol and DME derived from natural gas penetrated into the liquid transportation fuel market. Recently, coal is also widely used, particularly in China, to produce methanol and DME for fuel application.

Unlike Gasoline or Diesel which are mostly produced from petroleum crude, methanol and DME could be produced from renewable sources, such as biomass via Syngas or via reforming of biogas. With the increasing concern about GHG emission from energy usage, the fuels produced from renewable sources are increasingly favoured over the non-renewable sources. From biomass virtually carbon-neutral fuel can be produced.

To sustain the increasing energy demand in the developing countries, dependence on fossil fuel will remain for many years to come, till viable renewable energy is available and delivered to the user. The large methanol/DME plants based on fossil fuels could easily reduce its impact to the environment by capturing the carbon produced during the processing of the hydrocarbon source to methanol/DME. Therefore, the current trend in the world is to have more focus on capture of carbon dioxide if fossil fuel is used for production of methanol/DME and smaller plants from biomass and MSW which again produce carbon neutral fuel. It may be noted that with the progressive developments in technology, these gasification plants are becoming cheaper to build and operate.

In India all the methanol plants are based on natural gas or naphtha. Although there is great demand for methanol in India, the availability of natural gas and price of naphtha along with the low import price of methanol, is preventing the building of new plants.

The utilization of biomass in India is not very well organized. Much of this is burnt as such in several biomass based power plants. Since Late 90's several plants were operating in India based on gasification technology, developed by Indian Research groups. These were small units producing as low as 20 KWH energy. These plants were operating without any technological issues and were economically viable (Ref. 125). Therefore, it is very much possible to build up DME plants based on small scale bio gasifiers with indigenous design from TERI, IISc. or from other local sources.

Although India is having many biogas plants through anaerobic digestion, most of them are small capacity and in most cases cater the local requirements at a very low investment cost. It may not be worth to consider this segment for methanol or DME production. Larger biogas plants could be planned with the available digestible biomass from big animal farms or similar sources and convert the available biogas to methanol or DME via steam reforming.

The MSW is another good source of low cost hydrocarbon feedstock for power generation. India generates about 50 Mil Tons of MSW per year which could easily produce more than 1500 MW of power. While disposal of the waste and generation of power is in focus, production of chemicals was never considered in India so far from MSW. It is worth considering methanol/DME plants in some of these cases.

There are several emerging technologies in the area of methanol/DME production. The most promising is the use of plasma arc for gasification and carbon dioxide hydrogenation. These technologies have great promise for waste disposal and carbon dioxide fixing. Plasma based technology can handle wide variety of feed materials with production of, harmless slag. It is suitable for gasification of assorted biomass or solid waste in small and medium scale. The economics of conversion of carbon dioxide to methanol with hydrogen depends on the availability of low cost renewable hydrogen and concentrated carbon dioxide near the production facility. Geothermal energy is one of the cheapest sources of electricity, which could be used to split water for hydrogen.

In this report all the avenues for production of methanol and DME in India have been explored. Since methanol production in India is less than the demand, several large scale methanol plants can easily be installed.

At present, there is no production capacity of DME in India and the use of methanol as fuel is also negligible. Since our present objective is to introduce methanol as transportation fuel component, the only option is to produce from methanol by dehydration.

From this foregoing discussion we can converge on the following road map:

1. Installation of at least one large scale coal based IGCC with co-production of methanol and/or fertilizer and power, with carbon capture.
2. If coal bed methane is available in reasonable quantity, appropriate capacity reformer based methanol/DME plant may be considered.
3. At least one each demonstration plant for biomass (agricultural waste) and MSW based gasification for methanol/DME production with conventional and proven gasifier technology could be considered.
4. Plasma gasifier could be considered for at least one demonstration or Pilot unit at present. This may work out to be more economical for small scale carbon neutral methanol or DME production with single step DME, in smaller scale from very low grade feedstocks.
5. R & D facilities for carbon dioxide hydrogenation in pilot plant scale and possible integration with renewable hydrogen production related R & D projects.
6. Catalyst development and Pilot plant for single step liquid phase DME production from syngas.
7. R & D programme in development of chemical looping for gasification without air separation unit.
8. To pool all the available domestic resources for gasifier technology, operating experience and research laboratories to participate in the movement for biomass conversion to synthetic fuels.

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CHAPTER 1. INTRODUCTION

Long term Energy Security of the country is of utmost importance for any nation. With the objective of development of a road map, Methanol Economy is very important since methanol can be produced from renewable resources, unlike fossil based transportation fuels.

This report proposes that both methanol and DME (Di-Methyl Ether) have potential to replace fossil fuels for energy storage and transportation. The interest in these from the energy arises from the fact that unlike fossil fuels, methanol/DME can be produced from both fossil fuels as well as from renewable resources, including municipal and agricultural waste. Both methanol and DME also provide the opportunity to fix carbon dioxide, provided hydrogen is produced without carbon footprint.

The replacement of fossil based transportation fuels is important to prevent carbon dioxide emission. Methanol/DME when produced from biomass has a lower carbon emission than conventional fossil fuels. If merely 5% of conventional diesel/gasoline is replaced with these alternative fuels, Green House Gas (GHG) emissions could be reduced significantly (Ref. 1).

This report will also survey all the established and emerging technologies for biomass gasification and syngas conversion to methanol and DME. Finally an attempt will be made to draw a road map for India to usher these new fuels with the prime objective to reduce the carbon foot print or Well to Wheel GHG emission.

1.1 CHARACTERISTIC FEATURES OF METHANOL & DME

Although both methanol and DME have several common features, they have some major differences in their physical characteristics as well as in their properties as alternative transportation fuels.

Both methanol and DME are simple forms of hydrocarbon containing oxygen. Methanol is completely miscible with water while DME has limited solubility, due to the difference in polarity. The main difference in physical properties is in the boiling points. DME boils at -24.9° C while methanol's boiling point is about 65° C. Therefore, at ambient temperature methanol is a liquid while DME is a gas.

The Physical properties of Methanol and DME are summarized in Table 1 & 1A:

Table 1. Physical Properties of Methanol (IS 7444)

Sr.No	Property	Value
1	Colour	Colourless, Water White
2	Boiling Point	64.5°C at 760 mmHg
3	Density (g/ml)	0.791 3 at 20°C
4	Hygroscopicity	None
5	Odour	Pure material has a slight alcoholic odour. Other grades may have pungent oily odour.
6	Flash Point	
	• Open Cup	16°C
	• Close Cup	12°C
7	Reactivity	Not dangerously active
8	Solubility	Miscible in all proportions in water
9	Corrosivity	Slightly corrosive to metals especially in presence of moisture. Exceptions – lead and aluminium
10	Freezing point	-97.6°C
11	Vapour density (air=1)	1.11
12	Flammable limits, percent by volume in air at STP	7.3 to 36
13	Vapour pressure	at 0°C – 52 mmHg
		at 20°C -96mmHg
		at 40°C -253 mmHg
14	Auto – ignition Temperature	470°C
15	Refractive Index at 20°C	1.3312
16	Latent heat vaporization	262.8 cal/g at 64.7°C
17	Latent heat of fusion	16.4 cal/g at -97°C

Table 1A. Physical Properties of DME

Chemical Formula	$H_3C\text{-}O\text{-}CH_3$
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
Vapour pressure @ 20°C	516.76 kPa
Flammability limits in air by volume %	3.4 – 18

As regards combustion characteristics, both of them burn with blue flame without any smoke. The net calorific value for DME is higher than methanol (31.7 vs. 22.9 MJ/Kg. HHV), therefore the energy produced per unit volume is about 30% higher for DME. Methanol has a very high Octane number (Anti Knock Index of 98.65) so it can be added into gasoline to augment its Octane number. Due to their different burning characteristics, methanol is suitable as additive for Gasoline engines. Although a fair percentage of methanol can be added to Gasoline, there are several problems such as higher vapour pressure, separation in presence of water etc. Therefore, generally less than 3 % methanol is added with Gasoline for use with unmodified Gasoline engines. In addition to blending with Gasoline, methanol is widely used as a clean liquefied hydrogen carrier for fuel cells. Fuel cells which directly use methanol also exist, where an on-line reformer is not required for hydrogen generation.

On the other hand, DME has a much higher Cetane No. (55 to 60), which makes it suitable for Diesel engines. It is infinitely soluble with Diesel, at least at ambient temperature, and even at below 0°C, 30% DME remains dissolved. Therefore, blending of up to 30% DME with Diesel is feasible without any major modification of engines. Pure DME is also possible to be used as fuel, using pressurized fuel storage and delivery system, but this requires major modifications in the Diesel engine.

Regarding emission from DME or DME Diesel blends as fuel, there is reduction in smoke and particulate matter, but no significant benefit on GHG emission unless DME is produced from renewable resources.

As compared to fossil based transportation fuels, where completely sulfur free fuel is difficult or expensive to produce, both methanol and DME could easily be produced as zero sulfur fuel. Since the current growth in use of both methanol and DME are for their use in transportation fuels, the specification is required to compatible with the engine. For production of DME the methanol used by Fuel DME Production Co. Ltd., Japan is shown Table 2. The DME produced is more than 99% pure:

TABLE 2

Federal Grade AA: Purity of Methanol ≥ 99.9%	
Characteristics	**Requirement**
Acetone, wt. percent max	0.002
Ethanol, wt. percent max	0.001
Acidity (as acetic acid) wt. percent max	0.003
Appearance	Free of opalescence, suspended matter and sediment
Carbonizable substance colour, Pt-Co scale max	No.30
Colour, Pt-Co scale max	No.5
Distillation range at 760 mmHg. Max	1.0°C (and shall include 64.6 ± 0.1°C)
Specific gravity at 20/20°C, max	0.7928
Non-volatile matter, wt. percent max	0.001
Odour	Characteristic, non-residual
Permanganate time	No discharge of colour in 30 minutes
Water, wt. percent max	0.1

Source: Ref. 128, DME Promotion Project in Japan, by Akira Ishiwada, Fuel Production Co. Ltd., Nov 2011, Presented in 7th. Asian DME Conference

The ASTM specification for Fuel grade methanol is shown is Table 2A (Ref. 140). This range of products contains 70 to 85% methanol and the rest is other hydrocarbons.

TABLE 2.A: Standard Specification for Fuel Methanol (M70-M85)

Fuel Methanol (M70-M85) for Automotive Spark-Ignition Engines (ASTM D 5797 – 07)			
Properties	**Class 1**	**Class 2**	**Class 3**
Methanol + higher alcohols, min, volume%	84	80	70
Hydrocarbon/aliphatic ether, volume%	14–16	14–20	14–30
Vapor pressure, kPa	48–62	62–83	81-103
Lead, max, mg/L	2.6	2.6	3.9
Phosphorus, max, mg/L	0.2	0.3	0.4
Sulfur, max, mg/kg	160	200	300
FOR ALL CLASSES			
Higher alcohols (C2–C8), max, volume %	2		
Acidity, as acetic acid, max, mg/kg	50		
Solvent washed gum content, max, mg/100 mL	5		
Unwashed gum content, max, mg/100 mL	20		
Total chlorine as chlorides, max, mg/kg	2		
Inorganic chloride, max, mg/kg 1 Water, max, mass%	0.5		
Appearance	This product shall be visibly free of suspended or precipitated contaminants (clear and bright). This shall be determined at indoor ambient temperatures unless otherwise agreed upon between the supplier and the purchaser		

Specification of DME as prepared by International DME Association is shown in Table 2B (Ref. 66).

TABLE 2.B: Specifications for DME as per International DME Association

Characteristic	Unit	Limit	DME Spec for End users
Purity	Mass %	Max.	98.50
Methanol	Mass %	Max.	0.05
Water	Mass %	Max.	0.03
Hydrocarbons	Mass %	Max.	1.00
CO2	Mass %	Max.	0.10
CO	Mass %	Max.	0.01
Methyl Formate	Mass %	Max.	0. 50
Ethyl Methyl ether	Mass %	Max.	0.20
Residue after evaporation	Mass %	Max.	0.007
Sulfur	mg/kg	Max.	3.0

It is evident from the foregoing discussion that both methanol and DME have great potential as transportation fuels with much lower environmental impact. While methanol can be used as a blend with Gasoline or directly in fuel cells, DME is ideally suited for Diesel engines either as blend or as regular fuel. However, due to its low boiling point, major modifications are required both in the engine as well as in any pure DME handling system.

1.1.1 HAZARDOUS AND TOXICOLOGICAL PROPERTIES OF METHANOL & DME

Methanol is highly inflammable and also toxic to human beings. The fire and explosion data for methanol is shown in Table 3A. These data was adopted from the data sheet compiled by ScienceLab.com, Inc. (Ref. 163).

Table 3A: Fire and Explosion Characteristics of Methanol

Sr.No	Property	Observations & Attributes
1	Flammability	Flammable
2	Auto Ignition Temp.^{0}C	464
3	Flash Point ^{0}C	Close Cup: 12, open Cup: 16
4	Flammable limits %	6: Lower and 36.5: Upper
5	Products of combustion	Carbon monoxide, carbon dioxide and water
6	Fire hazards in presence of various substances	Highly inflammable in presence of open flame and sparks but non-flammable due to shock
7	Explosion hazard in presence of various substances	-- As above-
8	Firefighting media & instructions	Small fire: Dry Chemical powder Large fire: Alcohol foam, water spray or fog
9	Special remarks of fire hazards	Explosive in the form of vapour when exposed to heat or flame. Vapour may travel considerable distance to source ignition and flash back, when heated to decomposition, it emits acrid smoke and irritating fumes, may burn with near invisible flame.
10	Special remarks on explosion hazard	Forms an explosive mixture with air, explosive when mixed with chloroform + sodium methoxide and diethyl zinc. It boils violently and explodes.

The Toxicological & Ecological Information on Methanol is summarized below. These data was adopted from Methanol safety Data Sheet prepared by Methanex Corporation (Ref.164).

Potential Health Effects:

Inhalation: Causes mild central nervous system (CNS) depression with nausea, headache, vomiting, dizziness, incoordination and an appearance of drunkenness. Metabolic acidosis and severe visual effects can occur following an 8-24 hour latent period. Coma and death, usually due to respiratory failure, may occur if medical treatment is not received. Visual effects may include reduced reactivity and/or increased sensitivity to light, blurred, double and/or snowy vision, and blindness.

Eye Contact: Moderate eye irritant.

Skin Contact: In general, primary alcohols such as methanol are not considered to be irritant to the skin. Repeated or prolonged exposure to methanol may cause dry, itchy, scaling skin (dermatitis).

Skin Absorption: Can be absorbed through the skin and cause harmful effects as described in "Inhalation" above.

Skin Sensitization: Not considered to be a sensitizer.

Respiratory Sensitization: Not considered to be a sensitizer

Ingestion: There have been reports of accidental or intentional ingestion of methanol although ingestion is not a typical route of occupational exposure. Ingestion of as little as 10 ml of methanol can cause blindness and 30 ml (1 ounce) can cause death if victim is not treated. Ingestion causes mild central nervous system (CNS) depression with nausea, headache, vomiting, dizziness, incoordination and an appearance of drunkenness. Metabolic acidosis and severe visual effects can occur following an 8-24 hour latent period. Coma and death, usually due to respiratory failure, may occur if medical treatment is not received. Visual effects may include reduced reactivity and/or increased sensitivity to light, blurred, double and/or snowy vision, and blindness.

Birth Defects/Developmental Effects: has caused teratogenic and fetotoxic effects, in the absence of maternal toxicity in animal studies.

Reproductive Effects: Not considered a reproductive toxin.

Acute toxicity

Ingestion

LD50 (oral, rat): 5600 mg/kg

LD50 (oral, rabbit): 14200 mg/kg

Dermal

LD50 (dermal, rabbit): 15800 mg/kg

Inhalation

LC50 (rabbit): 81000 mg/m3/14h

LC50 (rat): 64000 ppm/4h

Eye Damage/Irritation

Moderate eye irritant.

Skin Corrosion/Irritation

Not considered to be an irritant.

Sensitization

Not considered to be a sensitizer.

Repeated Dose Toxicity

No relevant data found

Chronic Toxicity and Carcinogenicity

Not listed by IARC, NTP, ACGIH OR OSHA as a carcinogen.

Teratogenicity, Embryotoxicity and/or Fetotoxicity

Methanol has produced fetotoxicity in rats and teratogenicity in mice exposed by inhalation to high concentrations that did not produce significant maternal toxicity.

Reproductive Toxicity

Not considered to be a reproductive toxin.

Mutagenicity

There is insufficient information available to conclude that methanol is mutagenic.

Ecological information

LC50 (96h, fish): 15400 -29400 mg/l

EC50 (48h, daphnia): > 10000 mg/l

EC50 (72h, algae): 22000 mg/l Selenastrum carpricornutum (Pseudokichnerela subcapitata)

Persistence and degradability

Readily biodegradable

Bioaccumulation

Does not bioaccumulate. Partition coefficient: n-octanol/water 0.77

Mobility in Soil

Mobile in soils

PBT/vPvB

This substance is not considered to be persistent, bioaccumulating nor toxic (PBT). This substance is not considered to be very persistent nor very bioaccumulating (vPvB).

The complete information on safety and handling of methanol is available in Material Safety Data Sheet for methyl alcohol compiled by Methanex Corporation (Ref. 164).

Information of flammability hazards of DME is summarized in Table 3B (Ref. 14).

Table 3B: Flammability hazards of DME

Tabulated hazards summary	
Flammability	Highly flammable
Vapor density w.r.t air	Heavier than air
Gas/Air Mixture	Explosive
Distance Ignition possibility	Possible
Extinguishing agent	Powder, Carbon dioxide, Foam
Decomposition Products	Carbon monoxide, Carbon dioxide, water
Reactivity	Reacts violently with Aluminium hydride, Lithium Aluminium hydride

Source: Ref. 14. DME Safety Data sheet Aerosol Supplies Australia Pty, Ltd

DME is fairly safe as regards to its toxicity and environment impact due to its short half-life. Some of the toxicological and ecological properties are summarized below (excerpted from Shell safety data sheet for DME, Ref. 73):

Likely Routes of exposure:	mainly Inhalation, also through eye and skin contact
Acute Oral Toxicity:	Not expected to be a hazard
Acute Dermal Toxicity:	Not expected to be a hazard
Acute inhalation Toxicity:	Low toxicity by inhalation
Skin corrosion/irritation:	Expected to be non-irritant to skin
Serious eye damage/irritation:	Expected to be non- irritant to eyes
Respiratory irritation:	Not expected to be a respiratory irritant
Respiratory or skin sensitisation:	Not expected to be a sensitizer

Aspiration Hazard:	Not considered an aspiration hazard
Germ cell mutagenicity:	No evidence of mutagenic activity
Carcinogenicity:	Not expected to be carcinogenic
Reproductive / Developmental Toxicity:	Not expected to impair fertility, not expected to be a developmental toxicant
Additional Information:	Rapid release of gases which are liquids under pressure may cause frost burns of exposed tissues (skin, eye) due to evaporative cooling. High gas concentrations will displace available oxygen from the air; unconsciousness and death may occur suddenly from lack of oxygen

It should be noted that the toxicological and environmental impact of DME is much lower compared to most of the conventional liquid hydrocarbon based transportation fuels. This is one of the main reasons for recent trends in the use of DME as a substitute of diesel.

1.2 USE OF METHANOL & DME

Methanol is primarily used for manufacture of other chemicals such as formaldehyde, acetic acid, MTBE etc., as denaturing agent or as common laboratory solvent. Traditionally, methanol was manufactured from destructive distillation of wood. It is also produced naturally through the metabolism of many varieties of bacteria. It is only during the 1970s that methanol gained importance as feedstock for olefins and synthetic gasoline production or as gasoline blending component and for manufacture of Methyl Tertiary Butyl Ether (MTBE), which is again an Octane boosting additive for gasoline. It is also one of the major feedstock for bio diesel production (Ref. 23).

The different uses of Methanol are tabulated in Table 4:

Table 4: Use of Methanol for Different Applications

Sr.No	Product	2007		2016		2025		Application Area
		%	MMTA	%	MMTA	%	MMTA	
1	Formaldehyde (HCHO)	38	15.2	28	21.6	14.7	22	Pharma, Automobile, Wood Industry (Adhesive), UF/PF Resin, Insulation Industry
2	Acetic Acid	11	4.5	9	7.0	8.6	8.8	PTA (Art Textile), Adhesive Paints
3	MTBE/TAME	11	4.5	8.5	6.5	7.5	7.9	As Oxygonte in Transport Fuel, replacement of TEL
4	MeOH as Gasoline Blend	7	2.8	19	14.63	21.5	22.7	Transport Fuel Blend
5	Bulk Olefins for Polyolefins & other LVOC (i.e. MTO/MTP)	NIL	NIL	8	6.2	11.5	11.4	Polyolefins (PE, PPX other LVOC)
6	Chloromethane/ Methyl A	5	2.0	4	3.1	3.9	4.1	Silicones
7	As solvents for Pharma, Construction Industry etc.	16	6.4	11	8.5	10.1	11	Pharma Process + Construction chemicals
8	As fuel cell feed							
	Total		**35.4**		**67.53**		**87.5**	

** These facts emerged during the study (some Methanex, icis etc) for methanol application areas including forecast to 2025*

The non-fuel use of DME is mostly for aerosol preparation. The fuel related usage of DME is as LPG and Diesel substitution or as blending component.

1.3 GLOBAL DEMAND & PRODUCTION OF METHANOL AND DME

Till 2012, global methanol production was much less than the installed capacity but during the last few years, the demand has increased and many new facilities are coming up around the world. It is expected that by 2020, the production of methanol will exceed 100 Million ton. The global production of methanol is going to be nearly doubled between 2011 and 2020. The rise in demand will only come from fuel usage, while the use as feedstock for formaldehyde etc. will decline significantly.

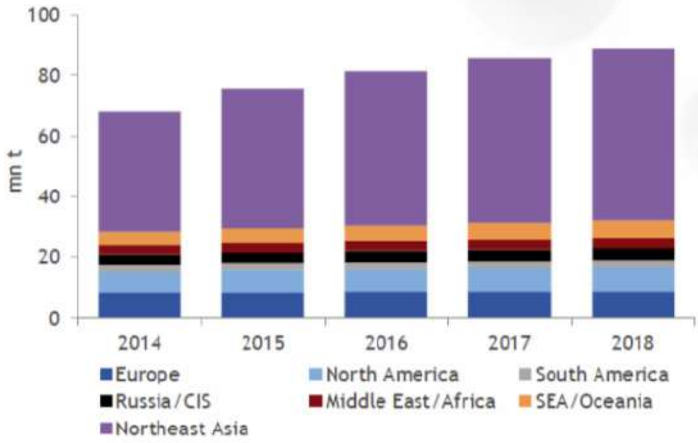
The present demand for DME is of the order of 5 MT per annum, which is expected to grow by about 15% per year during the next few years. At this time the major use of DME is for blending with LPG but the use as diesel substitute is expected to increase by many folds, in the near future.

In addition to the use of methanol and DME as transportation fuels, the recent trend is to use methanol as a feedstock for olefin production, particularly in China. Several new gas based methanol plants are coming up for exporting to China. In the last few years this application has grown as the sixth largest methanol derivative. Methanol demand is expected to grow and it is expected that during the next five years an average growth rate of almost 7% with usage of methanol as feedstock for olefin production is likely to become the second largest methanol derivative. (Ref. 129)

The methanol industry spans the entire globe, with production in Asia, North and South America, Europe, Africa and the Middle East. Worldwide, over 90 methanol plants have a combined production capacity of about 100 million metric tons (almost 33 billion gallons or 90 billion litres), and each day more than 100,000 tons of methanol is used as a chemical feedstock or as a transportation fuel (60 million gallons or 225 million litres). Methanol is also a truly global commodity, and each day there is more than 80,000 metric tons of methanol shipped from one continent to another (Ref. 24).

The global methanol demand, growth and future projection up to 2018 is shown in the Fig. 1 and Table 5.

Fig. 1: Global Methanol Industry Demand



Source: Ref. 130: Argus JJ&A, Methanol Demand Remains Robust, Global Methanol Industry Demand Global

Table 5. Growth in Global Methanol Demand (*1000 Ton)

Country	2014	2015 E	2016 E	2017 E	2018 E	TOTAL
Asia	7,467	10,034	8,214	6,794	7,446	39,955
North America	364	166	144	142	139	955
South Africa	19	8	28	45	53	153
Europe	63	116	149	163	163	654
Russia	17	3	44	64	65	193
Middle East	74	99	156	71	72	472
Africa	11	2	7	11	11	42
TOTAL	**8,015**	**10,428**	**8742**	**7290**	**7949**	**42,424**

Source: Ref. 131 ,Chapter V - Regional Methanol Market Analysis – World 97, MMSA, Global insight, Asian perspective, (page: 101)

It may be clearly seen that the global demand is practically fuelled by North East Asia. Accordingly, the demand growth is also very high in this region.

While demand in North America is fairly steady for the last few years, due to the methanol and synthetic Gasoline demand in China, several new production facilities are coming up as shown in table 6:

Table 6: North America Methanol expansion forecast

North America Methanol Expansion Forecast 2012-2016				
(000 Metric Tons)				
New Projects and Re-starts with High Probability				
Name	Location	Ownership	Capacity	Timing
Re-starts				
OCI-Beaumont	Beaumont, TX	OCI	750	Q3 2012
Lyondell	Channelview, TX	Lyondell Base II	740	Q4 2013
Relocations				
Former Coastal Plant	Pampa, TX	G2X Energy	65	Late 2014
Methanex	Geismar, LA	Methanex	1,000	Q4 2014
New Plants				
Celanese	Clear Lake, TX	Celanese	1,300	Q3 2015
Total			3,855	

(Source: Ref. 132, Methanol Fuel drivers: Public Policy, Economics and the Environment, Gerg Dolan,)

The world's largest plant is likely to come up in Texas City which will produce 7.2 Mil.Ton/year. Most of the other plants have capacities of between 1.5 to 3 Mil.Ton/year. All these plants are gas based.

The main driver of methanol market for use as fuel is China. To feed Chinese market several large plants have been announced in 2015 in USA. The first one is going to be the largest methanol plant in the world as shown in Table 7.

Table 7. New Facilities For China

Location	Capacity M tons/year
Texas City, Louisiana	7.2
St. Lames Parish, Louisiana	3
Tacoma, Washington	1.6
Oregon	1.6
Oregon	1.6

Source: Ref. 133, Market outlook: ‘Mega-mega’ methanol, plants planned in US to feed China, MTO, 26 September 2014 09:02 Source: ICIS Chemical Business

Already several coal based methanol plants are operating and many more are coming up in China. About 80% of the methanol produced in China is from coal. However, much of the current demand is for olefin production. Production is almost doubled from 60 Mil.Ton between 2015 to 2018 for both Methanol and methanol derived olefin production. The demand of DME was rather low in 2014, hence some of the plants were not operating in full capacity. (Ref. 134)

Although there is an increase in demand of methanol for fuel application and the production capacity in China is going to increase but there is some uncertainty due to current surplus capacity and lower growth of fuel market in North America. The current growth rate of methanol demand may slow down after 2020 due to alternate carbon neutral energy usage as transportation fuel.

CHAPTER 2. PROCESS & TECHNOLOGY FOR METHANOL AND DME

With the growth and demand for both methanol and DME as alternate fuel, the conventional wood distillation process was not able to cope up with the enhanced demand. BASF was the first to acquire a patent on production of synthetic methanol via Syngas (synthesis gas). The first plant was started in 1923. This established the main production route for both methanol and DME, which is still being followed today. The current production of methanol is largely based on fossil sources with only between 1% and 2% of the total methanol being produced from biomass. The carbon footprint for methanol/DME is no better than that of fossil based transportation fuels. This is because the syngas is usually produced from fossil fuels, either natural gas or coal. With the increasing concern about GHG emission from transportation fuels, alternative sources of hydrocarbon feedstocks became important. This includes wood, solid waste, biomass and other renewable resources.

The present emphasis is to produce bio methanol because all the benefits of using methanol/DME as fuel will only be realized when they are produced from non-fossil sources. The environmental benefits surpass the higher cost of production of methanol using biomass in place of natural gas.

Regarding technologies for production of methanol, the established process uses syngas produced from fossil fuel sources, while there are many technological challenges. Presently, intense research activities are directed towards the area of biomass gasification. Several demonstration plants are operating around the world. However, only a few plants are operating as full commercial ventures.

The simplest way to produce DME is dehydration of methanol. The possibility of using DME as direct substitute or as blending component for Diesel was realized during the last decade of the 20th Century. DME is intimately related to methanol since it is the dehydrated form. In addition to the simple dehydration of methanol, it could also be directly produced from syngas in a single step, thereby avoiding the formation of methanol as intermediate. The issues regarding fossil fuel or biomass as the feedstock for syngas production hold good for DME as well.

The current focus is towards the production of methanol/DME via syngas from advantageous feedstocks such as low grade coal and solid waste (Fossil or biomass), which are otherwise burnt or incinerated, and from by-products of different industries such as steel plants, cement plants or refineries.

The most common route for production of both methanol and DME is via syngas although there are numerous available sources of feedstock for syngas production. The traditional route for methanol and DME production could be summarized as:

Carbon Source + oxygen (or air) → Syngas (CO + hydrogen) → methanol → DME + water

In addition to the wide variety of fossil and non-fossil based feedstocks for syngas production, there are variations in the types of gasifiers for conversion of carbon source to syngas as well as for further transformation to methanol/DME.

2.1 MANUFACTURE OF SYNGAS

There are two distinctly different types of feedstock for syngas: from hydrogen deficient feedstocks such as coal, coke or residual hydrocarbons, biomass and hydrogen rich fuels such as methane (natural gas) or naphtha. The easiest way to produce syngas is from hydrogen rich fuels via steam reforming.

2.1.1 CHEMICAL REACTIONS INVOLVING SYNGAS FORMATION

2.1.1.1 STEAM REFORMING OF NATURAL GAS OR NAPHTHA

Natural gas is one of the most important sources of syngas production, due to its low cost and lower GHG emission compared to coal, and the ease of conversion either to hydrogen or to syngas. Natural gas and lower hydrocarbons such as ethane, naphtha or biogas are easily converted to syngas following the pathway as shown below:

$$CH_4 + H_2O \leftrightarrow CO + 3\,H_2 \quad \Delta H = +206 kJ/mol$$

This reaction is known as steam reforming. However, this reaction is highly endothermic; therefore external energy is required to be supplied to the process.

With steam reforming of natural gas or lower hydrocarbons, the hydrogen to carbon monoxide ratio is of the order of 3 to 4. This ratio is not favourable for production of methanol since for methanol production; stoichiometric ratio of hydrogen to carbon monoxide is about 2. However, steam reforming is suitable when hydrogen production is the objective. For hydrogen production, the carbon monoxide in the steam reformate is used to generate hydrogen by shift reaction:

$$CO + H_2O \leftrightarrow CO_2 + H_2 \ \Delta H = -41 kJ/mol$$

This carbon dioxide is separated by pressure swing absorption to recover pure hydrogen.

Steam reforming is carried out using Nickel catalyst at about 700°C to 1000°C. For higher hydrocarbons, a pre-reformer is installed in the upstream methane reformer to convert the higher liquid hydrocarbons to lighter hydrocarbons in presence of hydrogen before entering into the methane reformer. The main advantage here is the flexibility to process higher hydrocarbons for production of hydrogen. The reaction temperature of the pre-reformer is about 400 to 500°C. The catalyst used in pre-reforming is also based on Nickel, but to prevent coke formation, some noble metal such as Rhodium is deposited on the supported Nickel catalyst.

While steam reforming is a simple process to produce hydrogen, it is energy intensive. Moreover, the higher ratio of hydrogen to carbon monoxide makes this process unviable for direct use in methanol production. However, the presence of excess hydrogen may be very conveniently used to reform some carbon dioxide produced during the reaction to convert this into carbon monoxide. Thereby the desired ratio of 2:1 for hydrogen and carbon monoxide could be achieved for production of methanol.

2.1.1.2 PARTIAL OXIDATION OF NATURAL GAS, OTHER HYDROCARBONS (POX)

Another major route for production of syngas from lower hydrocarbons or natural gas/biogas is partial oxidation. This route is particularly suitable for production of methanol due to two reasons, namely,

a. Less external energy is required to be supplied, and
b. The ratio of hydrogen and carbon monoxide is of the order of 2, which is the stoichiometric ratio for methanol synthesis.

The main difference here is that oxygen is added in place of steam and normally no catalysts are used. The main reactions are shown below:

$2\ CH_4 + O_2 \rightarrow 2\ CO + 4\ H_2\ \Delta H = -38kJ/mol$

It may be noted that even if the carbon monoxide is converted to hydrogen by shift reaction, only two molecules of additional hydrogen will be available, making 6 molecules of hydrogen from 2 molecules of methane as compared to 8 by methane reforming as shown below:

$2\ CH_4 + O_2 + 2\ H_2O \rightarrow 2\ CO_2 + 6\ H_2$ (POX)

$2\ CH_4 + 4\ H_2O \rightarrow 2\ CO_2 + 8\ H_2$ (Steam Reforming)

Although the energy requirement is much higher for steam reforming compared to POX, this is often preferred, at least for small scale hydrogen production. On the other hand, POX is the preferred route for large scale syngas production for methanol.

There are two major strategies for POX as regards the use of an oxidizing agent. The oxygen could be added either as air or as pure oxygen. Both options have pros and cons. Although oxygen separation facility preceding the POX unit adds to the investment, it offers several benefits. Addition of oxygen in place of air is favoured for syngas production since this route saves cost in post purification of syngas before sending to methanol reactor. In addition to this, pre separation of air is particularly attractive when carbon dioxide sequestering and / or NOx control is desired, since the carbon dioxide from oxygen fired gasifiers is more concentrated than that of air fired gasifiers. It is easier and cost effective to capture carbon dioxide from concentrated flue gas (Ref. 2).

There are several types of gasifier systems with combinations of steam reforming, shift reaction and partial oxidation. Some of the available technologies are summarized in the subsequent sections.

2.1.1.3 AUTO THERMAL REFORMING

Auto thermal reforming is a combination of both non-catalytic partial oxidation and reforming in a single reactor system. The combination of these two exothermic and endothermic reactions in sequence permits the operation without any addition of energy from external sources. Recently this technology is gaining popularity due to availability of proven technologies from reputed licensors as well as inherent advantages of this technology.

By proper adjustment of hydrocarbon to oxygen ratio in the partial combustion zone and addition of steam in the catalytic reforming zone, it is possible to achieve equilibrium. The H_2/CO ratio is between 1.5 and 3, which is most suitable for methanol production.

Although at present there are relatively few such units in operation world-wide, several large scale units are operating. The potential for this technology is very high for conversion of natural gas to syngas for methanol or DME production.

In addition to the commercially established routes for production of syngas from natural gas or lower hydrocarbons (up to naphtha), there are several other technologies such as Catalytic Partial Oxidation, Dry Reforming with carbon dioxide, and Chemical Looping.

2.1.2 SYNGAS PRODUCTION FROM DIFFERENT HYDROCARBON SOURCES

While coal, coke, natural gas and biomasses are the major carbon sources, there are several other sources from which syngas can be manufactured. The solid waste from domestic origin, food waste, agricultural waste, effluent gases, liquids and solids from different industry are very often utilized for production of syngas. In addition to the advantage on the cost of hydrocarbon source, the other benefits are reduction of carbon footprint and waste disposal problem.

2.1.2.1 SYNGAS FROM HEAVY RESIDUE, COAL, BIOMASS OR SOLID WASTES

While normal combustion of solid fuel will essentially produce hot gases after complete combustion, the term gasification has a special meaning. Gasification implies that the fuel is not completely burnt. Technically it could be termed Partial Oxidation. The key is the combustion of the fuel with less than stoichiometric ratio of oxygen to convert it to syngas. Operating pressure used is around 30 Bar and temperature of the order of 1000 to 1500^0 C.

Regarding the basic technology for conversion of solid hydrocarbons or coal, both follow similar chemical pathways, as also the reactor configurations. However, there are several specific issues for coal, heavy hydrocarbon residues and biomass. Complete combustion of coal or other residual solid hydrocarbons produces energy. Similarly, gasification also produces energy but to a lower extent. The main difference is that complete combustion produces a large amount of carbon dioxide while gasification produces much less carbon dioxide. The energy is delivered in the form of a mixture of carbon monoxide and hydrogen. Power plants based on gasification may be coupled with production of syngas and methanol or DME, to recover a major part of the hydrocarbon in the fuel as high grade transportation fuel or chemicals. For large scale plants it could be coupled with combined cycle to recover energy from the product gases, before converting them into useful chemicals. The fuel efficiency of a coal gasification power plant with combined cycle can be more than 50%. In addition to the energy efficiency, with the use of oxygen in place of air, the produced carbon dioxide is in concentrated form therefore, syngas cleaning or carbon sequestering is easier and the size of the gasification equipment is lower.

The wide variation of heating value and moisture content of biomass as well as coal has to be taken into account before estimation of expected methanol/DME production. The quantity of feedstock is directly proportional to the heating value of the feed (Ref. 118).

2.1.2.1.1 GASIFICATION TECHNOLOGIES AND REACTORS FOR GASIFIERS

Besides air or oxygen, gasification can be carried out even with steam or carbon dioxide, but the energy requirement is too high to sustain a stand-alone facility.

Gasification is the heart of the process, and several modes of operation are possible for gasification. Technologies for most of these variations are established, while some of them are still in the development stage.

The major gasifier configurations are:

- Moving Bed and Fixed Bed
- Fluidized Bed
- Entrained Bed
- Transport Bed

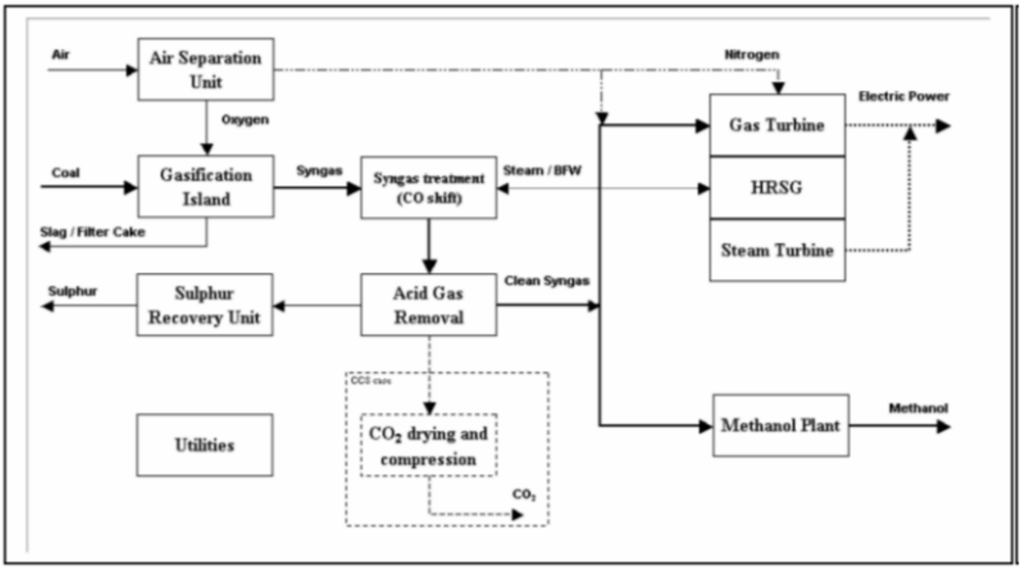
The names themselves imply the modes of operation. For the Moving Bed, there could be co-current or counter-current flow of gas and carbon source. The main characteristics for the different configurations are summarized in table:

Table 8: Characteristics of Different Gasifiers

Parameters	Moving Bed	Fluid Bed	Entrained bed
Energy Usage	low	high	low
Carbon Conversion	poor	medium	high
Heat and Mass Transfer	poor	good	excellent
Feed Particle Size	50mm (approx) (not suitable for highly coking coal)	small	Small below 100 mesh
Oxygen requirement	low	moderate	high
Operating Temperature	low	moderate	high
Operating Pressure	low	moderate	high

Since both Fluidized Bed and Entrained Bed reactors can operate at higher temperature and pressure, they are suitable for gas turbines. Entrained Bed gasifiers are more convenient because of the feed flexibility, including capability to handle high ash coal. The operating temperature is higher than the fusion point of the ash, so it flows easily out of the gasifier. Since the recent focus is towards power and chemical production from different types of solid fuels, entrained bed gasifiers are popular. A simplified Flow Sheet for gasification with power and chemical production is shown in Figure 2.

Fig. 2: Co- Production of Chemical & Power



Source: Ref. 3. Production of Electric power and Chemicals in a carbon constrained Environment, Guido Collodi.

The advantage here is that the plant could produce either methanol or power depending upon market demand. Due to the combined cycle the energy efficiency is also high, leading to lower carbon emission.

In case of Moving Bed Gasifier, the bed moves freely, therefore this is suitable only for non-coking coals. Also the operating temperature is lower, and large amount of tar is produced. The reactor size is larger than modern fluidized bed or Entrained Bed Gasifiers. Almost all the technology licensors have their own technology with some innovative component built in. However, at present, most of the new gasifiers are based on fluidization, which could be circulating or Entrained bed, or even high speed transportation.

The different types of gasifiers have certain common features, such as: handling of slurry or dry powders, though the temperature, pressure and contact times differ widely. As a result, they widely differ in their carbon conversion efficiency. Interestingly, the carbon conversion in fluidized and entrained bed gasifiers is higher, particularly for low grade coals. Due to their ability to operate at higher pressure and temperature, and ability to handle different types of feed including biomass, these reactors are particularly suitable for chemical production from syngas, which requires higher pressure. Most of the new installations coming up are based on fluidized bed gasification, preferably with oxygen firing.

At this point it is worth mentioning that several reports are available on coal/biomass or municipal solid waste gasification with plasma. The biggest advantage here is that the molten slag, which comes out of plasma gasifiers, typically operating at 3000^0C, are vitreous when solidified. Hence no toxic chemicals leach out from the vitrified mass. Also the overall power requirement is quite low, compared to incineration (Ref. 4, 5, 6, 7).

Considering the quality of Indian coal, fluid bed gasifiers with high pressure operation are most suitable for immediate consideration, while for long term plans, we may explore the development of plasma gasifiers.

2.1.2.2 SYNGAS FROM BIOGAS

Biogas is the product from digestion of biodegradable non cellular material such as food or animal waste, including sewage sludge. The average composition of the biogas from anaerobic digester is about 65 +/- 10% methane; the balance is carbon dioxide with a little hydrogen. The carbon dioxide may be separated and the methane is used as natural gas in the Reformer. In view of the fact that the biogas contains a fair amount of carbon dioxide, it is possible to convert it to syngas by Dry Reforming also.

Production of biogas can be economically done without much investment and the product gas is reformed to syngas. However this anaerobic digestion is suitable only for certain specific types of biomass such as agricultural waste, manure, municipal waste, plant material, sewage, green waste, food waste, cake after oil extraction etc. Landfill gas is also biogas and easily reformed to syngas. There are many installations for making methanol/DME in small scale from biogas. With the recent growth of biodiesel production, large amount of oil cake is available. This could be easily used in bio-methanation units along with other easily bio digestible materials to produce biogas.

2.1.2.3 GASIFICATION OF BLACK LIQUOR

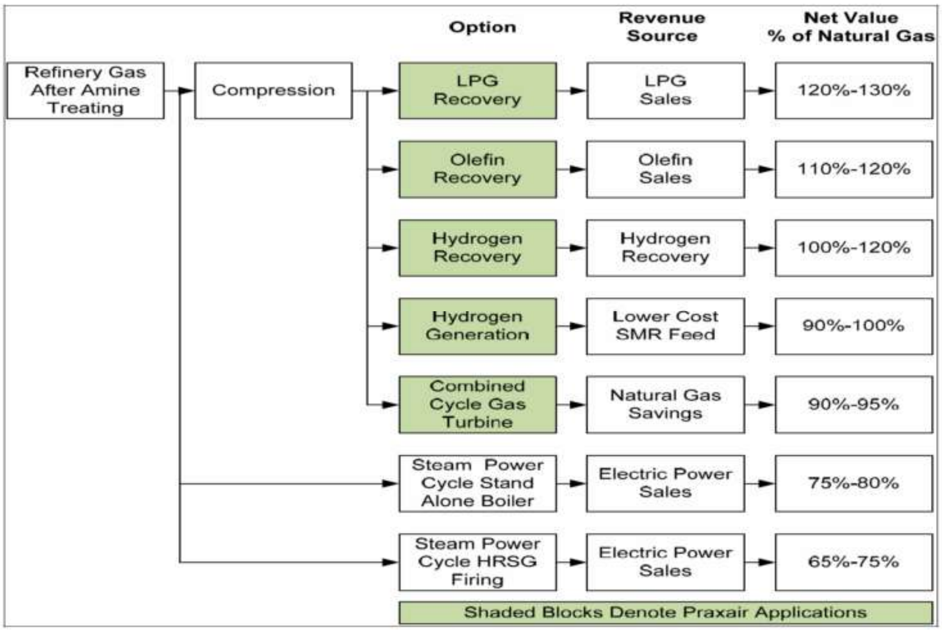
Black liquor is a problematic by-product from paper mills; about 1.7 to 1.8 ton of black liquor (dry basis) is produced for manufacture of one ton of pulp. Black liquor contains lignin, hemicelluloses and about 30% inorganic chemicals. Many paper mills use this black liquor as an energy source. Before use in a combustor water is removed in multiple effect evaporators and the concentrated liquor is burnt to recover the chemicals, which are recycled. In the United States, most of the black liquor is converted into electricity. Although production of energy from black liquor is an attractive option as an energy source with great reduction in GHG emission, it is more attractive to produce syngas from black liquor by gasification. The balance energy requirement of a paper mill could be met by burning low grade wood waste. The additional investment for a paper mill for production of methanol/DME from black liquor could be recovered in about 4 years as estimated in 2003 by ALTENER (Energy Framework Program) of the European Union (Ref. 9).The WTW energy for DME and synthetic diesel from black liquor shows the lowest GHG emission (Ref. 10).

2.1.2.4 SYNGAS FROM REFINERY OFF GASES

Petroleum refining is another process industry consuming a large amount of hydrocarbon source as feedstock, for production of transportation fuels and energy. These refineries produce fuel gas of different compositions. In fact, the diversity of composition, nature and the impurities of these off gases make their handling rather complex. Secondly, the hydrogen demand of the refineries is ever increasing. Most of the refineries produce hydrogen from naphtha or natural gas (if available) by steam reforming. The available fuel gases are normally burnt but there is interest in using these gases in the steam reformer, to save naphtha or natural gas.

Refinery off gases is a large source of low calorific value hydrocarbon gases. Therefore, after recovering the specific hydrocarbons from these dilute gas streams, they use these gases in their naphtha reformer to be converted to hydrogen. Refineries which manufacture MTBE (Methyl Tertiary Butyl Ether) for gasoline octane boosting, may produce methanol. The possibilities for utilization of off gases are shown in Fig 3.

Figure 3: Off GASES from Refineries



Source: Ref. 15. Technologies for refinery off gas utilization, NPRA 2010 MEETING PHOENIX AZ AM-10-178 Ramona Dragomir, et.al.

Refineries primarily focus on the recovery of valuable chemicals from these dilute streams, and production of hydrogen from the balance hydrocarbons.

2.1.2.5 SYNGAS FROM REFINERY RESIDUE AND PET COKE

To dispose of the heavier fractions of crude, many refineries also have a coking unit, which produces coke as a solid saleable product. There is always a possibility to put up a residue gasification plant using petroleum coke and other heavy residues for power and methanol production through IGCC. Therefore, for a refinery, it is feasible to put up gasification plant and produce methanol, but the economics may not be very favourable, particularly when the conversion to hydrogen is possible within the available existing infrastructure.

With regard to refinery residue, tars and heavy oil or coke, the conventional disposal route is to burn for generating power, if no other suitable outlet is available. However, with the recent developments of gasification technology coupled with IGCC, co-production of hydrogen is becoming popular. Since at present most of the refineries have a large hydrogen demand, IGCC of residue, coke and other solid waste is most economical compared to reforming naphtha for hydrogen generation. In case surplus feedstock is available after satisfying the hydrogen requirement for the refinery, the syngas could be used to convert to methanol/DME. This would be advantageous relative to investment, since large scale gasifiers are more economical.

Petroleum coke is especially attractive feedstock since it contains much lower ash and volatile content. However, it generally contains more sulfur and other metals as compared to coal. Pet coke could be used solely or by mixing with coal to reduce the overall ash content in the feed to the gasifier.

2.1.2.6 OFF-GASES FROM STEEL PLANT

Steel production facilities generate large volume of gases with low calorific value (about 3 -5 KWH/Nm^3). Coke oven gas contains methane and hydrogen, blast furnace gases contain carbon monoxide and hydrogen, and converter gas contains mostly carbon monoxide. A typical composition of different gases from steel plant is shown in Table 9.

Table 9: Off GASES from Steel plant

Steel Production Gas Type	Coke Gas	Blast Furnace Gas	Converted Gas
Source	Coke Oven battery	Blast Furnace	Converter
Input	Coal	Coke and Iron ore	Pig iron
Output	Coke	Pig iron	Steel
Hydrogen %	50-70%	5%	-
Methane %	25-30%	-	-
Carbon Monoxide %	-	20%	60%+
Lower heating value kWh/Nm³	~5.0	~0.9	~3

Source: Ref. 12. Blast furnace coke: News EIC Content 2013, Manchester Central, October 14, 2013, Energy Connect at Manchester Central, connected UK SME's and Energy Industry.

Since most steel plants use these low grade gases from different sections for power generation, there is not much reported information around utilization of these gases for syngas production. However, there may be some usage where such gases are mixed with natural gas, if available locally, for use in the gasifier.

There are some reports from Sweden during 2013, where techno-commercial feasibility was established when these gases are integrated with biomass gasification plant for production of methanol. It was found that among several options considered biogas addition works out to be most economical. (Ref. 13)

For the Steel plants using air for combustion rather than oxygen, for any conversion to syngas from these gases for methanol production, requires a nitrogen separation step. Therefore, it may be difficult to use the, off gases directly for methanol production. However, it may be possible to process at least the coke oven gas but for most of the steel plants the availability of this gas will be uneconomical for a reasonable capacity methanol plant. With syngas available from other sources, such as biomass or other fuels this is worth considering if surplus coke oven gas is available (Ref. 13). In a theoretical study it has been shown that there is a possibility of utilizing blast furnace off gases along with a combined cycle power generation unit (Ref. 70, 71). However, this strategy makes the operation more complicated and probably suited for grass root plants only.

There are several options with coke oven gas and the simplest option is generation of power or use as fuel in different sections of the plant or even exported. Methanol or hydrogen could be produced after partial oxidation of both cooled and hot coke oven gas. It could also be used for direct reduction. The choice depends upon the configuration of the complex and local economics. (Ref. 135)

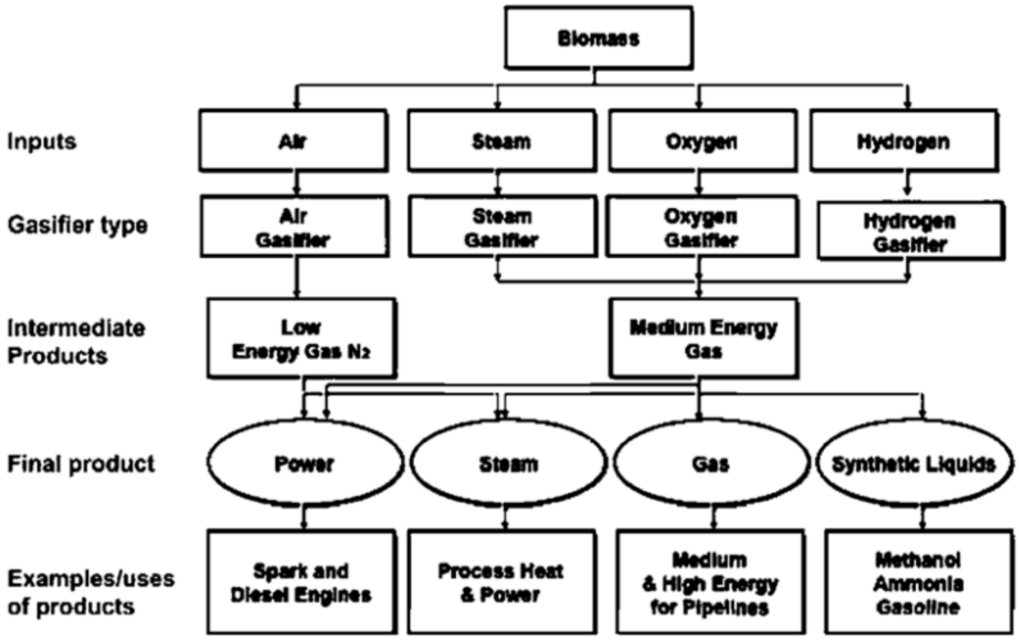
Coke oven gas (COG) is rich in hydrogen and therefore has a relatively high heating value of 17.6 MJ/m3, compared with 3.5 MJ/m3 for blast furnace gas. About 40% of the coal and coke energy input is converted into blast furnace gas. The carbon dioxide content of blast furnace gas is high. About 70% of COG is used in iron and steel production processes 15% to heat coke ovens and 15% for power generation. At most steel plants, COG is used to heat and to fuel equipment such as boilers and reheat furnaces. The boilers supply steam for electricity generation, turbine-driven equipment such as pumps and fans and for process heat. The overall efficiency can be improved if the coke oven is fired with blast furnace gas and the COG is put to a higher quality use, e.g. power generation. Combined cycle is preferred over steam cycles. Some plants convert COG to chemicals. (Ref. 136)

2.1.2.7 GASIFICATION OF BIOMASS TO SYNGAS

Biomass such as corn, sugar beet, wheat etc. is traditionally converted to ethyl alcohol by fermentation. More recently, lignocellulosic materials such as straw, wood, rice husk, cereal plants, wood scraps etc. are converted to ethanol by enzyme digestion and hydrolysis. In addition to this biochemical route, these lignocellulosic materials could be burnt for energy recovery. In India this is the most common usage of the surplus lignocellulosic materials after direct utilization as cattle feed whenever possible. The combustion and power generation of course comes with lower GHG penalty, while gasification and conversion to bio fuels such as methanol or DME is more rewarding even the investment is higher, particularly for too small a scale.

The wide variation in types of biomass, with high volume and moisture content, is a major issue for their use far away from the source. In Fig.4 shows different biomass gasification products and their uses.

Fig. 4: Biomass Gasification Products & their Uses



Source: Ref. 63: Gasification, Producer Gas and Syngas, by Samy Sadaka

The problem of collection, transportation prevents construction of large size biomass gasification plants for methanol/DME production. The problem is handled in several ways:

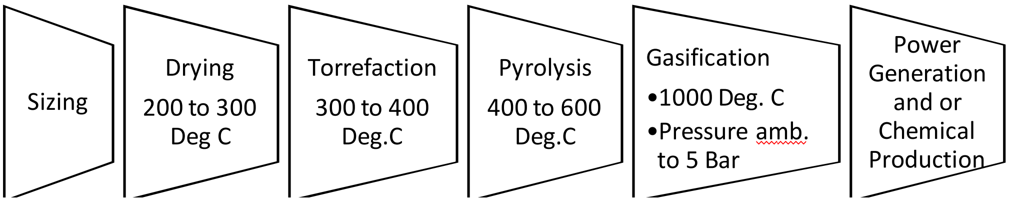
1. Breaking away from the concept that only Mega Scale Syngas and methanol plants are feasible. In fact today many skid mounted gasification and methanol/DME plants are operating in the world, successfully.
2. Preliminary treatment of the biomass at the point of origin to reduce its weight.
3. Design of the gasifier for processing multiple types of biomass feedstocks
4. Use of available biomass in the large gasifiers for coal or solid residues to the extent possible.
5. To locate the plant closer to the source where sustained supply of adequate quantity of at least one type of biomass is assured.
6. In addition to the lignocellulosic materials the plant is designed with the capability to process MSW from local source.

Although the combustion equipment of biomass is similar to that used for power generation or syngas production, gasification is more complex to control.

Due to these inherent constraints there are some limitations for building Mega methanol/DME plants based on biomass. The disadvantages of having smaller capacity are compensated with positive gains through utilization of waste, much lower penalty for GHG emission and availability of fuels at the user end without transportation over long distances. Putting these together, particularly if cost tag is attached with the WTW carbon emission, methanol/DME is a winner even if produced in moderate scale from waste biomass.

While pretreatment of coal or coke for gasifiers is simpler, due the wide variation in characteristics of available biomass, the preparation of biomass for the gasification reactor requires attention. Generally there are several pretreatment steps before the biomass is fed to the gasifier, such as Sizing, Drying, Torrefaction (especially suited for wood), Pyrolysis etc.

The typical operating conditions are shown below:



Sizing includes chipping, cutting, pulverizing, milling, screening etc. to produce suitable uniform sized product.

Drying is carried out either by heating with available gas or preferably with sunlight, if possible, to reduce the moisture content to an acceptable level for transportation.

Torrefaction is particularly suitable for wood where wood chips are heated for a short time in absence of oxygen to make them dry and brittle. This step removes the balance moisture and makes the wood easier to handle in subsequent stages.

Pyrolysis is also carried out in absence of oxygen with the objective to extract valuable volatile components from the biomass. This step helps in avoidance of tar formation in the gasifier.

There are several types of gasifier designs depending upon the type of biomass and size of the gasifier as shown in Table10.

Table 10: Status of Biomass Gasifier technology & Applications

Gasifier Type	Heat and power Application	BTL Application	Developers
EF	No past commercial heat and power applications using dedicated biomass	Construction of biomass demonstration plants ongoing. Most significant experience so far in integrating biomass gasification with fuel production, as a result of coal to liquid fuels experience	Several developers, with differing company sizes, and some large players having established designs based on fossil feedstocks. Participation by large industrial players in several projects
BFB	Well established heat and power applications, but only to modest scales using biomass	Currently scaling up to larger systems, and BTL applications with plants under construction	Technology developers are smaller companies, with only a few interested in BTL
CFB	Well established heat and power applications, good experience in scaling up CFB for biomass	Early days of BTL applications, currently undergoing testing at pilot plants	Limited number of developers, one dominant (strong research base, with large industrial players on-board), others small
Dual	Earlier stage of technology development, heat and power applications successfully demonstrated	Early days of BTL applications, carrying out slipstream testing at a CHP plant	Few and small technology developers, but some interested in BTL
Plasma	Established power applications, but focused on MSW and was waste feedstocks. Limited experience with other biomass	Very early days of scaling up to larger systems, some very small waste destruction plants also testing liquid fuels production	Several technology developers of different sizes, and many interested in BTL

Source: Ref. 11, Review of technologies for gasification of Biomass and wastes, NNFCC Project 09/008, June 2009

To summarize, biomass gasification is more complex compared to fossil fuel based gasifiers. Before selection of suitable gasifier design, and the process scheme, the objective and characteristics of the hydrocarbon source must be taken into consideration. The critical properties are ash content, moisture content, density, particle size etc. For example, Entrained Bed gasifiers can be designed for a wide variety of feedstock, but for a given design cannot accept a wide variation of feedstock. On the other hand, for Fluidized Bed gasifiers there is the problem of ash management with feedstock having low ash melting temperature.

The most versatile gasifier, which can handle almost any type of materials, is based on Plasma Arc Furnace. Such gasifiers can even handle municipal sludge, producing non leachable vitreous mass from the inorganic materials present in the biomass. Since the input power of the plasma torch can be controlled at will, this technology offers tremendous feed flexibility with regard to calorific value of the feed. More than 40 installations are currently operating world-wide, and many more are coming up (Ref. 6).

2.1.3 PURIFICATION AND CONDITIONING OF SYNGAS

The Syngas received from the gasifier requires to be conditioned before it goes into methanol/DME production. The impurities in product gases from gasification are particulate matters, CO_2, H_2O, CH_4, CxHy aliphatic hydrocarbons, benzene, toluene, tars and inorganic impurities (mainly H_2S, NH_3, HCl) etc. A simplified flow sheet for syngas cleaning is shown below:

2.1.3.1 TAR REMOVAL FROM SYNGAS

Apart from particulate removal the two critical issues are sulfur and tar removal. Maximum efforts are taken to reduce tar formation in the gasification step itself. The high temperature gasifiers such as Entrained bed gasifier; the syngas is almost tar free. This is one of the main advantages of operating the gasifier at higher temperature. While the low temperature gasifiers, this becomes important since most of the subsequent process units or turbines are having stringent limits of tar concentration. Tar formation is also a major issue particularly for MSW processing. In addition to control in the gasifier itself and through physical separation with cyclones etc, the chemical treatment is necessary. The chemical routes are: by increasing reaction rates of tar decomposition by thermal cracking, catalytic cracking or by plasma cracking. (Ref. 137).

Tar reforming is carried out in a tar reformer to remove tars, light hydrocarbons, and ammonia before any additional gas treating or cooling. Reforming must occur prior to cooling the syngas to prevent tar condensation and deposition on downstream equipment. In the tar reformer, tars (mono and polyaromatic compounds) and light hydrocarbons such as methane, ethylene, and ethane are converted to H_2 and CO. Ammonia is converted to N_2 and H_2.

2.1.3.2 SULFUR REMOVAL FROM SYNGAS

For sulfur removal, the amine is mostly used. An amine unit with a high circulation rate can reduce the syngas sulfur concentration to below 10 ppm. The liquid phase oxidation systems such as LO-CAT^{TM} for sulfur removal from GASES uses iron based catalyst for removing H_2S, but for very large scale syngas with high carbon dioxide concentration, this is not very much economical. In amine unit, both carbon dioxide and sulfur are simultaneously removed by amine absorption. Subsequently, ZnO guard/polishing beds removes the balance of the sulfur. It is also possible to place the LO-CAT^{TM} unit after the amine unit, followed by ZnO guard bed. This reduces the unnecessary flow of carbon dioxide in the LO-CAT^{TM} unit as well as increases the life of the guard bed. After polishing step the sulfur content in syngas is less than 1 ppm. (Ref. 138) carbon dioxide removal is also possible either by cryogenic route or by membrane separation.

2.1.3.3 SHIFT REACTION FOR HYDROGEN TO CARBON MONOXIDE RATIO CONTROL

Special consideration is required particularly for carbon dioxide and the hydrogen to carbon ratio. When hydrogen is the target product from syngas, the carbon monoxide is converted into hydrogen through shift reaction. On the other hand when methanol is the target product, the shift reaction is required only if the hydrogen to carbon monoxide ratio is less than 2. For gasification or partial conversion of hydrocarbon to syngas, the ratio is closer to 2 but in case of gas reforming the ratio is close to 3. For altering the ratio of H_2 to CO from the syngas after reforming, there are two options, namely, removal part of the H_2 from syngas and reconstituting the mixture. The other alternative is reforming the carbon dioxide present in syngas or by external addition of carbon dioxide, to generate additional CO. This is actually reverse shift reaction. Another important aspect is the concentration of carbon dioxide in syngas. Although the theoretical requirement of stoichiometric ratio of H_2 to CO is 2, actually it is not the absolute ratio of these two components only. This ratio is very much sensitive to the presence of carbon dioxide as shown below:

H_2 - CO_2 /CO + CO_2 = 2 or more

This indicates that for even small quantities of carbon dioxide present in the syngas, the actual hydrogen to carbon monoxide ratio needs to be much higher in the conventional processes for methanol conversion. Therefore, maximum care is taken to keep the carbon dioxide concentration as low as possible. Recently, several technologies have become available where much higher concentration of carbon dioxide is tolerated in methanol synthesis from syngas. It should also be noted that for production of FT Diesel the theoretical ratio of 2 is applicable and the presence of carbon dioxide does not affect the conversion. For products other than methanol, the hydrogen to carbon dioxide ratio requirement is different (Ref. 16). In methanol synthesis, H_2 will react preferentially with CO_2 over CO to form methanol. This results in a significantly lowered methanol yield, greatly impacting the process efficiency. In FT synthesis, CO_2 acts as diluents only.

The equilibrium of this reaction shows significant temperature dependence and the equilibrium constant decreases with an increase in temperature, that is, higher carbon monoxide conversion is observed at lower temperatures. On the other hand the kinetics is favoured at higher temperature. In order to take advantage of both the thermodynamics and kinetics of the reaction, the industrial scale water gas shift reaction is conducted in multiple adiabatic stages consisting of a high temperature shift (HTS) followed by a low temperature shift (LTS) with intersystem cooling. The initial HTS takes advantage of the high reaction rates, but is thermodynamically limited, which results in incomplete conversion of carbon monoxide. To shift the equilibrium toward hydrogen production, a subsequent low temperature shift reactor is employed to produce a carbon monoxide exit composition of less than 1%. For hydrogen production the low temperature shift reaction is necessary but for methanol production this step could be avoided. The transition from the HTS to the LTS reactors necessitates intersystem cooling.

The catalytic water-gas shift reaction is initially carried out in a high-temperature shift (HTS) reactor at 300-450°C and the gas leaving the HTS reactor is cooled and passed through a low-temperature shift (LTS) reactor. Due to the different reaction conditions, different catalysts must be employed at each stage to ensure optimal activity.

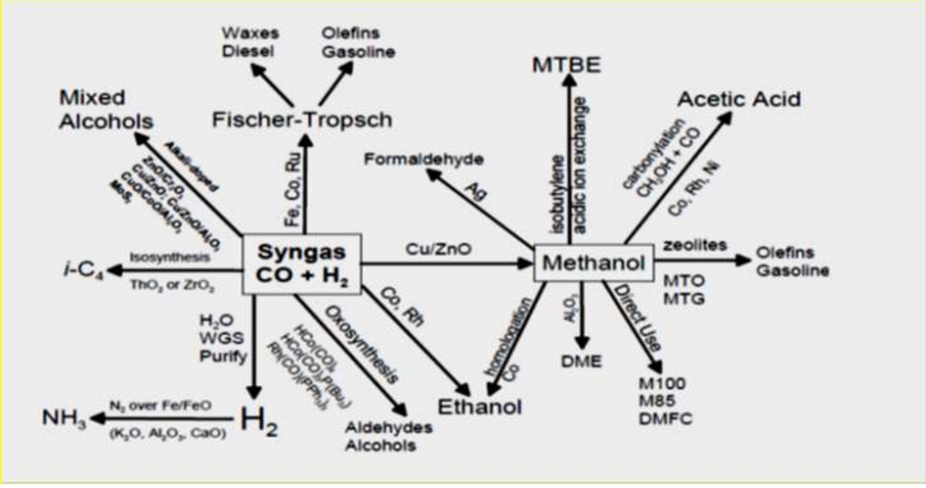
The typical composition of commercial HTS catalyst has been reported as 74.2% Fe_2O_3, 10.0% Cr_2O_3, and 0.2% MgO. The chromium acts to stabilize the iron oxide and prevents sintering. The operation of HTS catalysts occurs within the temperature range of 310 to 450^0 C. The temperature increases along the length of the reactor due to the exothermic nature of the reaction. As such, the inlet temperature is maintained at a level to prevent the exit temperature from exceeding 550^{0}C. Industrial reactors operate at a range from atmospheric pressure to 8 MPa. While both the HTS and LTS catalysts are commercially available, their specific composition varies based on vendor. (Ref. 139) Depending upon the composition of feed syngas and the target hydrogen to carbon monoxide ratio, the catalyst and operating conditions are chosen.

The typical composition of commercial LTS catalyst has been reported as 32 -33% CuO, 34-53% and ZnO, 15-33% Al_2O_3. The active catalytic species is CuO. The function of ZnO is to provide structural support as well as to prevent the poisoning of copper by sulfur. The Al_2O_3 prevents dispersion and pellet shrinkage. The LTS shift reactor operates at a range of 200 to 250^0 C. Low reaction temperatures must be maintained to prevent the copper from thermal sintering. The lower temperatures also reduce the occurrence of side reactions. Noble metals such as Pt supported on Ceria have been reported for LTS.

2.2 CONVERSION OF SYNGAS TO METHANOL/DME

The syngas is the building Block for FT Diesel, methanol and other hydrocarbons such as olefins, DME, and other alcohols and aldehydes. The different products from syngas with and without going via methanol are shown in Fig. 5.

Fig. 5: Different Products from Syngas



Source: Ref. 17, P.L. Spath and D.C.Dayton

While FT diesel production process from syngas can handle a wide range of hydrogen to carbon monoxide ratio, for methanol production this ratio has to be more than 2. The typical operating conditions for FT Diesel are 150 to 300^0 C, in presence of Cobalt or Iron based catalyst in fixed bed or slurry reactors. A wide range of products from jet fuel to waxes and lubricants may be produced with proper catalyst design and operating conditions (Ref. 18).

2.2.1 MANUFACTURE OF METHANOL

With regard to methanol there are several options. Syngas conversion to methanol as intermediate for other chemicals is well established technology. However, with the recent trends to use methanol as gasoline and DME, coupled with the recent interest in producing olefins as well as synthetic gasoline, it has become important to use the syngas to directly convert to the desired product without going via methanol.

Once the synthesis gas of the correct composition is manufactured, methanol is produced by high pressure reaction over catalyst in fixed bed. The pressure for the older generation catalyst and process was close to 100 bar. The conversion and selectivity are high. The natural gas reforming process results in a considerable hydrogen surplus in syngas. If an external source of CO_2 is available, the excess hydrogen can be consumed and converted to additional methanol.

The main reaction which governs the formation of methanol from syngas is

$$CO + 2H_2 \leftrightarrow CH_3OH \ \Delta H = - 90.84 \text{ kJ/Mol.}$$

Due to the equilibrium, the reaction is favoured at higher pressure and lower temperature. The other possible reactions are:

$$CO_2 + 3\ H_2 \leftrightarrow CH_3OH + H_2O\ \Delta H = -\ 49.43\ kJ/Mol$$

The overall reaction for a mixture of CO and CO_2 could be written as:

$$CO + CO_2 + 5\ H_2 \leftrightarrow 2\ CH_3OH + H_2O$$

It may be noticed that these reactions are also exothermic and equilibrium limited. This route provides opportunity to fix available carbon dioxide while using syngas where the hydrogen concentration is higher in syngas.

Yet another option is direct oxidation of methane to methanol, since it is just addition of one oxygen atom in a molecule of methane. However this is not yet commercially used.

Unlike the methane reforming process with steam, the synthesis of methanol is highly exothermic, taking place over a catalyst bed at moderate temperatures. Most plant designs make use of this extra energy to generate electricity needed in the process. Control/removal of the excess energy can be challenging.

The catalyst used in industrial low-pressure synthesis is based on copper oxide-zinc oxide-alumina (Cu/Zn/Al2O3) in the process developed by ICI of England. This catalyst is extremely active and highly selective. The catalytic reactor operates from 5-10 MPa and 200-280^{0}C, with modern applications on the lower end of these operating conditions. Generally these catalysts are prepared in tablet form. They are shipped in their fully oxidized form and must be activated/reduced in-situ by passing H_2/N_2 (1 mol% H_2) over the catalyst bed. This must be carefully controlled at low temperature to preserve crystalline structure and physical integrity to ensure optimal performance. The copper based catalyst system is much less robust system than the previous catalysts and is more susceptible to poisoning and deactivation. The catalyst is particularly sensitive to chlorine and sulfur. With sulfur levels below 0.025 ppmv and chlorine levels below 0.0125 ppmv, the catalyst life of two to four years can be expected. (Ref. 47)

The new process developed by Air product is in slurry phase. An inert mineral oil and powdered catalyst slurry is used as a reaction medium and heat sink. As the feed gas bubbles through the catalyst slurry forming MeOH, the mineral oil transfers the reaction heat to an internal tubular boiler where the heat is removed by generating steam. The ability to remove heat and the large oil slurry inventory allows the LPMEOH™ reactor to operate at isothermal conditions. This process can handle carbon monoxide rich syngas with wide compositional variations. Due to the ability to process CO-rich syngas, an upstream water-gas-shift (WGS) unit to increase the syngas H_2/CO ratio is not needed. Also carbon dioxide removal step could be avoided. It is possible to make full utilization of feed H_2, if Carbon dioxide is available (Ref. 34).

2.2.2 PRODUCTION OF DME

Technically, the process of producing DME form methanol consists of simple dehydration of methanol to DME as per the reaction shown below:

$$2\ CH_3OH \rightleftarrows CH_3\ CO\ CH_3 + H_2O\ \Delta\ H - 50.6\ kJ/Mol$$

This is an exothermic and equilibrium reaction: therefore, the reaction can be reversed depending upon the concentration of the different reactants and the equilibrium constant.

DME is produced via fixed-bed catalytic dehydration of methanol obtained from syngas. Until 1975, DME was produced as a by-product (3-5 wt%) during high-pressure methanol synthesis. The new low pressure methanol synthesis route does not give any DME as a by-product. Therefore, as an alternative for DME production, dehydration of methanol over solid acids is the preferred technology.

In conventional DME production by dehydration of methanol, the feed is pumped at about 10 to 12 Atm. pressure and mixed with recycled methanol before it is evaporated in the reactor. The dehydration reaction is conducted in an adiabatic reactor loaded with a dehydration catalyst. The operating temperature range is of the order of 290- 400^0 C with about 80% conversion of methanol. The reactor effluent is cooled and the DME is separated from methanol and water. The recovered methanol is sent back to the dehydration reactor. The catalyst used is acid catalysts based on γ alumina or silica alumina. However, it is the convenient route for small-scale manufacture of DME for chemicals and fuel applications, at least till the market is fully developed. (Ref. 90)

Compared to the two step synthesis of DME, the single step process is economically and technically more attractive. In this case both methanol synthesis and dehydration is carried out in single reactor. At present, the single step process of DME production is carried out with bi-functional catalyst. This route is preferred for dedicated plants for DME, but the technology is yet to get matured. Moreover, synthesis of a bi-functional catalyst is a challenging task, since the presence of two kinds of active sites on the surface may affect its overall catalytic properties

Liquid or slurry phase process for DME is also available from Air products. These slurry phase technologies can handle higher concentration of carbon dioxide in syngas. Technology for Dehydration of DME is also available from Fuel DME Production Co.Ltd, DME Institute through Licenser (Mitsubishi Gas Chemical/JGC), Japan. (Ref. 128)

The selection of the particular route is normally based on the overall economics, desired product flexibility and type of feedstock with its consistent availability. For large scale plants however it is preferred to go via methanol production since it offers product flexibility depending upon the market demand. Once methanol is available it is easily converted either to target chemicals or to DME, hydrogen or synthetic gasoline.

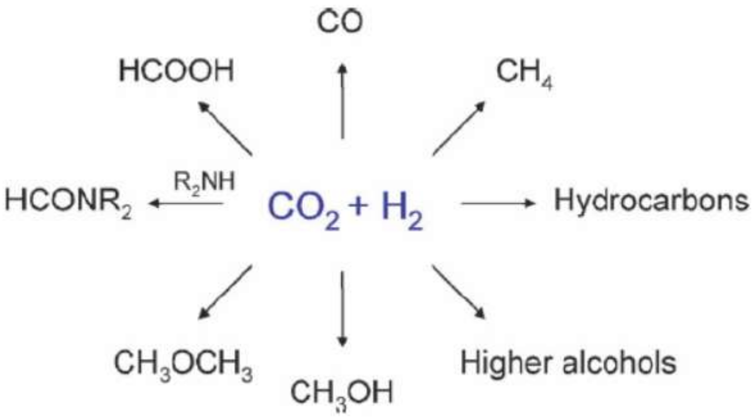
2.3 METHANOL FROM CARBON DIOXIDE

This is another very interesting development in methanol/DME production. Large numbers of publications have appeared in literature where new catalysts are reported to convert carbon dioxide and hydrogen into methanol/DME. There are several approaches such as use of concentrated or dilute carbon dioxide from atmosphere, use of Solid Oxide Fuel Cell with biogas or syngas avoiding direct use of hydrogen, direct conversion of carbon dioxide to carbon monoxide with solar energy or conversion of carbon dioxide and natural gas to form syngas, and even direct conversion of hydrogen and carbon dioxide to methane by Sabatier Reaction. (Ref. 28, 94, 95, 96, 97)

Methanol can also be produced from carbon dioxide via carbon monoxide formation with coal or directly converted to methanol with (Ref. 38, 98, 99, 100). Recently, a commercial plant started operating in Iceland. The name of the plant honors George Olah, Nobel Prize Laureate in chemistry and co-author of the book “Beyond Oil and Gas: The Methanol Economy”. In 2015 CRI expanded the plant from a capacity of 1.3 million litres per year to more than 5 million litres a year. The plant now recycles 5.5 thousand tons of carbon dioxide a year, which would otherwise be released into the atmosphere. All energy used in the plant comes from the Icelandic grid, which is generated from hydro and geothermal energy. Germany also operates a similar plant (Ref. 101).

Since this route offers duel advantage of fixing carbon by creating value added products, this technology requires special attention. Shown below are the possibilities of producing different chemicals using Carbon dioxide as feedstock. Different possible products from Carbon dioxide is shown in Fig. 6.

Fig. 6: Different Products from Carbon dioxide



Source: Ref. 141. Recent advances in Catalytic Hydrogenation of carbon dioxide, by Wei Eang et.al. Chem.Soc.Rev., 2011,40,3727

The three major reactions are: methane, carbon monoxide and methanol formation as shown below:

$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O$ Δ H 298 K = - 252.9 kJ mol $-^1$

$CO_2 + H_2 \leftrightarrow CO + H_2O$ Δ H 298 K = 41.2 kJ mol $-^1$

$CO_2 + 3H_2 \leftrightarrow CH_3\ OH + H_2O$ Δ H 298 K = - 49.5 kJ mol $-^1$

It could be noticed that methane formation is highly exothermic, while methanol formation is mildly exothermic but carbon monoxide formation is mildly endothermic. Also all these reactions are equilibrium controlled.

For methanation of carbon dioxide large numbers of catalysts are reported in the literature and Ni on silica is most widely studied. Several other catalysts are also reported such as VIIIB metals (e.g., Ru and Rh) supported on various oxides (e.g., SiO_2, TiO_2, Al_2O_3, ZrO_2, and CeO_2) (Ref. 141).

The conversion to carbon monoxide is actually reverse of Low Temperature Shift reaction. Therefore, the catalyst system is very similar to LTS based on Cu/Zn. Many new catalysts are reported in literature which includes nickel, Noble metals etc. RANEY nickel is also an active catalyst for hydrogenation and appears to have high reactivity for methanation reaction. This reaction can also be speeded up by electrochemical route. Recently, Brookhaven National Laboratory announced a process using ionic liquid to speed up this reaction using the commercial catalysts. (Ref. 142). Due to its endothermic nature, reaction is favoured at high temperature.

Methanol formation produces heat during the transformation. Decrease in reaction temperature and increase in reaction pressure favours this hydrogenation reaction. Typically, catalysts used in CO_2 hydrogenation are those for methanol synthesis from CO hydrogenation. Large numbers of catalysts are reported in the literature using Cu, Zn, Gallium, Palladium, Zirconium etc on Silica support. Noble metal catalysts are also reported. Due to its importance development of more efficient catalyst is actively pursued by many research groups around the world. It is also possible to carry out this reaction in liquid phase as in carbon monoxide hydrogenation at lower pressure. Direct conversion to DME is possible by using a duel function catalyst by incorporating acid function through addition of H ZSM 5 in conventional methanol catalyst. An extensive review is published is published in the Journal of Royal Society of Chemistry, Chem. Soc Review during 2011 by Wei Eang et.al on the recent developments on catalyst for carbon dioxide hydrogenation. (Ref. 141)

Carbon Recycle International CRI has been very active in this area and they have set up similar plant for methanol in Iceland with hydrogen from geothermal source. The process uses solid copper and zinc oxide catalysts operates at 250^0c and 100 atmosphere pressure. The technology may be available from them. (Ref. 101)

This route practically depends on the availability of cheap renewable hydrogen. The simplest way for getting hydrogen is from electro splitting of water. A recent estimate of investment and production cost for electricity from different routes clearly shows that geothermal energy is by far the cheapest carbon free electricity. The cost of geothermal energy is almost 50% lower than any other route (Ref.

143). Therefore, the success depends only on availability of geothermal energy near carbon dioxide source.

A recent computation study indicates that there is a possibility of utilizing the available hydrogen in ammonia plants to convert to methanol/DME by using carbon dioxide. This could reduce the carbon footprint without much penalty (Ref. 56). The hydrogen from Chlor Alkali industry could be captured for carbon dioxide reforming. These are possible small scale options to reduce carbon emission from fossil fuels (Ref. 57). The same is true with hydrogen from steel plant or refineries.

2.4 CATALYST AVAILABILITY FOR SYNGAS AND CHEMICAL PRODUCTION

Conversion of hydrocarbon to chemicals involves several steps from reforming or gasification, gas conditioning to methanol/DME production. Excluding the gasification process all the other steps are highly dependent on catalyst. Approximately 1.3 Ton of different catalysts required for a plant producing 1 Ton of methanol per hour. The generic nature of the different catalysts was discussed in the respective sections. The overall economics and the performance is very much dependent upon the catalyst. With the diversity of feed nature and composition and desired product slate as well as the available hardware, the catalyst and operating conditions have to be synchronized. The demand of catalyst in this area is growing fast not only for the mega plants coming up but also for replacement catalyst. (Ref. 47)

While many of these catalysts are available in the open market, most of the technology licensors tie up with a catalyst manufacturer for a complete package for the specific process segment. This is desirable in one respect that the accountability of the technology licensor to demonstrate the stipulated performance is ensured but on the other hand, the replacement of the catalyst could be expensive, when better catalysts are available in the market.

There are several suppliers of different catalysts for syngas production and processing. The major players are Johnson Matthey, Haldor Topsøe, Clariant. All these catalyst companies not only supply catalysts but also license technologies through their partners. Most of them also get associated with the user to choose better catalyst and optimising the process including trouble shooting such as change in feedstocks etc. They also offer custom catalyst for the customers. In the area of syngas processing and methanol / DME or hydrogen production area new catalysts are being developed.

Johnson Matthey offers full range of catalyst for the entire chain and offers a new technology for tar reforming, which is essential particularly for biomass and MSW conversion to methanol, since the tar and shoot is much more in the syngas generated from these renewable sources. (Ref. 144)

Haldor Topsøe is also having catalyst and service portfolio. They offer full range of catalyst and technology for integrated plant for both methanol and ammonia. Haldor Topsøe's first plant is operating since 1992. For large scale gas based methanol plants with auto thermal reformer, they offer complete technology with catalyst and gasifiers. Both in large scale hydrogen production and carbon dioxide reforming they have very dominant position in the market. (Ref. 145)

Clariant also offers broad range of catalysts which include catalysts designed for the production of ammonia, methanol, hydrogen, synthetic natural gas (methanation), and various processes in gas to liquid (GTL), coal to liquid (CTL) and biomass to liquid (BTL). Clariant is one of the leading global suppliers of catalysts used in synthesis gas processes. Additionally, the company develops and offers catalysts and adsorbents for CO_2 conversion and SNG (Synthetic Natural Gas) technologies. Various catalysts and adsorbents are also offered for the gas processing industry. (Ref. 146)

BASF, and UOP also offering and actively working on development of several catalysts related to of gas processing, CO_2 conversion and biofuels.

In India, Sudchemie, associated with Clarion supplies several grades of catalysts for ammonia synthesis, gas purification, reforming, Shift catalyst, and for methanation etc.

Since this area is going through a high growth phase and renewable transport fuel market is growing, many research laboratories, catalyst manufacturers and technology licensors are teaming up to bring more efficient catalysts in the market.

CHAPTER 3. CURRENT STATUS OF TECHNOLOGY AND TRENDS

In the previous sections we have discussed the basic routes of production of syngas, methanol and DME from different hydrocarbon sources. In this section we shall look into the present trend of commercial production of these products including problems and issues.

3.1 PRESENT COMMERCIAL PRODUCTION ROUTES

At Present there are large numbers of methanol production units all over the world. The total production capacity of methanol during the 2013 was about 100 Mil. Tons while the demand was about 65 Mil. Ton. 35% of the total production is being used in fuel. The consumption for DME was about 8% (Ref. 21). The global demand for methanol is as a building block for various chemicals, but the fuel application is growing fast. Therefore, the unused capacity is progressively reducing. China is the largest producer of methanol in the world and also the major user of methanol and methanol derivatives as fuel. The use of methanol and DME is growing at fast rate in several countries in the world including North America. The current methanol production capacity in India is about 1.5 Mil. Tons. Since the demand of methanol in India for chemical production is higher than its production, India is one of the largest importers of methanol (Ref. 25). Most of the large methanol plants in the world are based on natural gas, while in China both natural gas and coal are used. All the methanol plants in India are based on natural gas or naphtha; there is no coal based methanol plant in India. These units produce syngas through Steam Reforming.

While the popular technology for reforming of natural gas or naphtha is Auto-thermal reforming, gasification is gaining importance over reforming. When heavier feedstocks such as hydrocarbon residue, coal, coke or solid waste biomass or MSW are used, reforming is not feasible. In such cases gasification is the only option to produce syngas.

The most important development in methanol/DME production scenario is use of biomass for production of syngas for methanol. Due to the inherent issues with biomass, large scale mega plants are not feasible. Several demonstration units and a few commercial plants are operating based on biomass gasification.

3.2 RECENT TRENDS IN GASIFICATION PROCESS

For gas as well as solid carbon source, including coal, solid waste based methanol plants produce syngas via POX (Partial Oxidation). Many of the plants use pure oxygen as the oxidant source, with IGCC for simultaneous power generation. Although investment is high, IGCC with oxygen firing and carbon dioxide capture makes the plant practically carbon neutral. All these technologies are commercially available, and many plants are operating in several parts of the world. Generally, the investment per unit basis is lower and profitability is higher as the capacity of gasifier increased. 3000 TPD coal based methanol plant are being considered in China.

The production of methanol from bio mass is gaining momentum. This includes agricultural waste, lignocelluloic and domestic waste, MSW (Municipal Solid Waste) as well as heavy petroleum residue. For biomass based plants, to have a viable capacity with sustainable feed supply round the year is a challenge. Therefore, most of the efforts are around designing a gasifier which is able to handle multiple feedstocks. A comprehensive summary was published in 2009 by E4 technologies (Ref. 11). Due to the requirement of feed preparation and syngas cleaning, the cost of production of syngas from biomass is always higher than that of natural gas based plants. However, the economics of the biomass gasification route is very much dependent on the local conditions (Ref. 26). The cost of available biomass, sustained feed availability or use of multiple biomass feeds for uninterrupted operation, plant capacity etc. are the main factors. If, however, we consider carbon credit alone, then the biomass route is invariably economical.

Although technology is still at early stage, with the experience gained by many demonstration and pilot plants all over the world, it would be possible to estimate the technical and economic feasibility of a commercial plant.

3.3 PROCESSING OF DIFFERENT FEEDSTOCKS SIMULTANEOUSLY

The success of biomass gasification depends on sustainability, input cost and the ability of the plant to process locally available cheap biomass sources. As a general practice, many plants currently operate with a variety of feedstocks. A recent report from China indicates the possibility for co-processing syngas from biomass and biogas from a digester simultaneously to produce methanol/DME (Ref. 27).

From the available technologies it appears that no commercial technology is available for processing different types of feedstocks in the same plant. There are some demonstration plants which are designed to process a few selected feedstocks. In addition to the processing of varieties of biomass, even standard coal / Petroleum coke based gasifiers could co-process solid wastes of biological origin. Some currently operating Demonstration/Pilot plants are designed to process anything from glycerin to black liquor (Rec. 28).

In addition to the gasification of biomass and solid waste, the biogas produced from landfill and anaerobic digesters could also be co-processed profitably even at a moderate scale. Maverick Oasis offers a technology for economically viable production of methanol at smaller scale (Ref. 29). Oberon is offering a skid mounted DME plant based on natural gas and biogas for 3,000 to 10,000 Gal/day capacity (Ref. 30). Oberon has recently announced a 45 Thousand Gallon DME unit based on bio waste in California (Ref. 31).

With the recent drop of glycerin price there is interest in its conversion to useful products. Methanol/DME is the most attractive option. In 2008 Bio MCN commissioned a pilot plant for glycerol based DME production (Ref. 32). Black liquor is another convenient source for bio methanol, hence a number of studies have been reported during the last several years. A detailed feasibility study was conducted by the European Commission, which established the technical and economic feasibility of production of methanol /DME from black liquor (Ref. 9). Recently, Chemrec started operating a Pilot plant for production of DME from black liquor (Ref. 33). Although there is wide diversity in the types of biomass, with the experience gained in operating gasification, gas cleaning, and syngas conversion steps for many years, it seems possible to put together the available knowledge and technology to design and operate bio methanol/bio DME plants with confidence.

At present a large number of biomass based heat/power generation plants are operating all over the world, including in India. Many of these plants handle varied types of biomass and waste. With the recent development in medium size gas turbines for power generation, the economic viability is further improved to produce power from biomass with low carbon penalty. However, there are very few plants commercially operating for production of methanol/DME. With the increasing interest in bio based liquid fuels, these biomass based combustion units could be reengineered to produce methanol/DME. Since the feed pre-treatment and combustion furnaces are already in position, what is required is to modify the gasifier and post treatment of the syngas, using available technologies.

The conventional methanol synthesis process from syngas requires CO_2 free syngas, which means that carbon dioxide separation unit must be installed, before feeding to the conventional methanol reactor. This adds up to a high cost burden on a medium size bio methanol plant.

Recently, several reports have been published where the methanol reactor is operated in slurry phase rather than conventional low temperature high pressure gas phase. This slurry route can handle a wide variety of syngas compositions as well as the presence of carbon dioxide in the syngas. Therefore, there is also a possibility to do away with the conventional shift reactor to adjust the H_2 / CO ratio in the syngas produced from the gasifier. This new development will be very handy for small scale bio methanol plants. Air Products offers such liquid phase technology. Ohio University reports a laboratory study on one-step liquid phase DME synthesis using dual catalyst system at 1000 psi and 250^0C with copper, zinc and aluminium based catalyst (Ref. 35).

Carbon dioxide reforming is one of the viable routes to produce methanol/DME with negative carbon footprint. A large number of publications are available in the literature that underlines this point. Some amount of carbon dioxide could be recycled in the methane reformer, but large scale utilization of carbon dioxide is of interest.

An exhaustive review was published in “Renewable and Sustainable Energy Reviews” in 2014, in which the nature of different types of biomass and their processing strategy is discussed. Although the review was for power generation based on biomass, the information is applicable to bio methanol plants as well (Ref. 36).

3.4 PRODUCTION FLEXIBILITY TO ADDRESS MARKET NEEDS.

At present there is a global surplus in methanol production capacity. The demand for methanol for production of Formaldehyde etc. is not growing. For a new dedicated plant for DME production with assured demand, it is possible to convert syngas directly to DME in a single step. Due to very low capital cost and natural gas price this is the preferred feed for syngas production in USA and Middle East. On the other hand, China and many other developing countries are forced to use coal as the carbon source. The carbon penalty is obviously higher for coal based methanol/DME plants.

It is projected that use of methanol and DME will increase many fold as transportation fuel, mainly as liquid energy carrier. The focus on bio methanol will increase because this is a key route for reduction of carbon footprint. For methanol produced from natural gas or coal, its use as fuel offers marginal benefits in emission. However, carbon capture at the production unit provides the opportunity to control carbon dioxide emission at the source itself; thereby the GHG impact of the fuel is significantly reduced. With the recent stress on environmental impact, large scale methanol plants based on coal or natural gas are designed for Integrated Gasification Combined Cycle along with coproduction of methanol and chemicals. The new units use oxygen rather than air as oxidizing medium and very often incorporate a carbon separation and sequestering facility. This combination gives all the required flexibility, and most of the associated technologies are matured.

It must be understood that the economics still favour the use of transportation fuels derived from fossil hydrocarbon sources. Till now, all the possible alternative transportation fuels such as electricity, hydrogen, fuel cell, bio diesel, methanol/DME are either costlier, or the fuel distribution infrastructure is not ready or is prohibitively expensive. Therefore, fossil based transportation fuels still enjoy the major market share. The future of any of the alternative transportation fuels is still not very clear. However, as compared to hydrogen or electricity based vehicles, methanol/DME has stronger prospects for the near future, due to the fact that the use of blended fuel or even neat methanol/DME is possible. The cost of methanol/DME compared to gasoline or diesel remains a challenge, but in the countries where carbon footprint is the driving factor these alternative fuels offer benefit.

Another important point favouring methanol and DME is that they can be produced from a wide variety of waste materials which otherwise would have to be disposed of at a cost. Although there are some limitations on the capacity due to feedstock availability constraints, biomass or waste based plants are typically much smaller than fossil fuel based plants. Coupled with the cost of feed pretreatment etc. very often the cost of methanol produced from waste may be more than that of produced from natural gas or coal. On the flip side, the limitations of size and cost of production are overcome by social and environmental benefits.

It is envisaged that in the near future, medium capacity plants for methanol/DME with multiple types of feedstock derived from biomass or organic waste will come up. These plants will be using simplified and novel low investment technologies. On the other hand, large scale plants based on coal with co-production of methanol/DME and power through combined cycle will also be developed. Some of these will also have carbon separation and sequestering facility.

It is projected that the growth of methanol and DME will be high in Asian countries. An exhaustive survey on the forthcoming projects was released in 2007 by The Catalyst Group. (Ref. 37) The report projected that China is going to lead the DME market in the near future. It is to be noted that most of these capacity expansions were projected to be coal based.

3.5 RECENT DEVELOPMENTS AND OPERATING PROTOTYPES

Carbon dioxide reduction with hydrogen is a dream technology, provided hydrogen is available from non-fossil sources. Several demonstration plants are operating at present and research interest is growing in this area. However, the benefit of utilization will only come if hydrogen is available from non-carbon sources. Currently a 4000 MT /year plant is operating in Iceland for methanol production using geothermal electricity, wind mill derived hydrogen, and carbon dioxide from flue gas (Ref. 38). Although there are not many plants operating in commercial scale, several groups such as Haldor Topsøe and Johnson Matthey are seriously working towards development of technology utilizing carbon dioxide.

Recently, Enerkem Inc. of Canada has commissioned a commercial scale waste to Biofuel plant in Alberta, Canada. The municipal waste after compacting is gasified in a bubbling bed gasifier and the syngas in converted into methanol (Ref. 39). Canadian Biomass news reported (August 2010) the commercial operation of wood biomass to methanol via syngas in Soperton, Georgia. (Ref. 40). Maverick Synfuels has recently announced the technology for conversion of landfill and biogas to methanol. The proposed unit will be skid mounted (up to 25 TPD methanol) and can be assembled in a very short time (Ref. 29). During 2003, DME Development Corporation of Japan reported a demonstration plant for direct DME synthesis using natural gas in a slurry reactor. After operating a small pilot plant for several years, they had built a 5 TPD DME plant, which successfully produces DME by single step reaction with a small amount of methanol. They had subsequently built and tested a 100 TPD plant successfully, at Hokkaido, Japan in 2004. Since then, many more facilities were created. As of 2008 the production capacity of DME had been expanded to about 80,000 TPY by the joint venture company Fuel DME Production Co. Ltd (Ref. 41).

Oberon Fuels is operating a Demo/Pilot plant for converting biogas and other hydrocarbon rich waste streams to higher valued commodities such as DME. Using its proprietary small-scale process, Oberon makes DME and methanol from various methane and carbon dioxide sources. In 2013, Oberon Fuels' pilot plant, in Brawley, California, produced the first fuel-grade DME in North America. This ASTM D7901 compliant fuel is currently being used in North American demonstrations of DME-powered heavy-duty trucks (Ref. 42). The nameplate capacity of the plant is 4500 Gallons. Korean Gas has developed a 10 TPD Pilot plant for single step DME from reformed Syngas, and based on successful experimentation for several years, they have decided to build a larger plant of 300,000 TPA capacity of DME. The engineering was done by Unitel Technologies of Chicago, USA (Ref. 43).

Recently, Clariant announced that it has supplied a proprietary developed CO_2-SNG catalyst for the methanation unit of Audi's new power-to-gas facility in Werlte, Germany. The so-called "e-gas plant" was started up in June 2013 and it will produce an average of 1.4 million cubic meters of renewable synthetic methane per year, chemically binding some 2,800 metric tons of CO_2. The plant was developed, constructed and built by Stuttgart-based plant manufacturer ETOGAS GmbH (formerly SolarFuel). The technology can be also used to store surplus energy in the gas pipeline system and to balance energy supply against demand. Clariant is also working with Foster Wheeler and other groups for coal based Methanation plants. (Ref. 146)

A summary of the demonstration plants is shown in Table 11:

Table 11: List of Operating Demonstration Plants

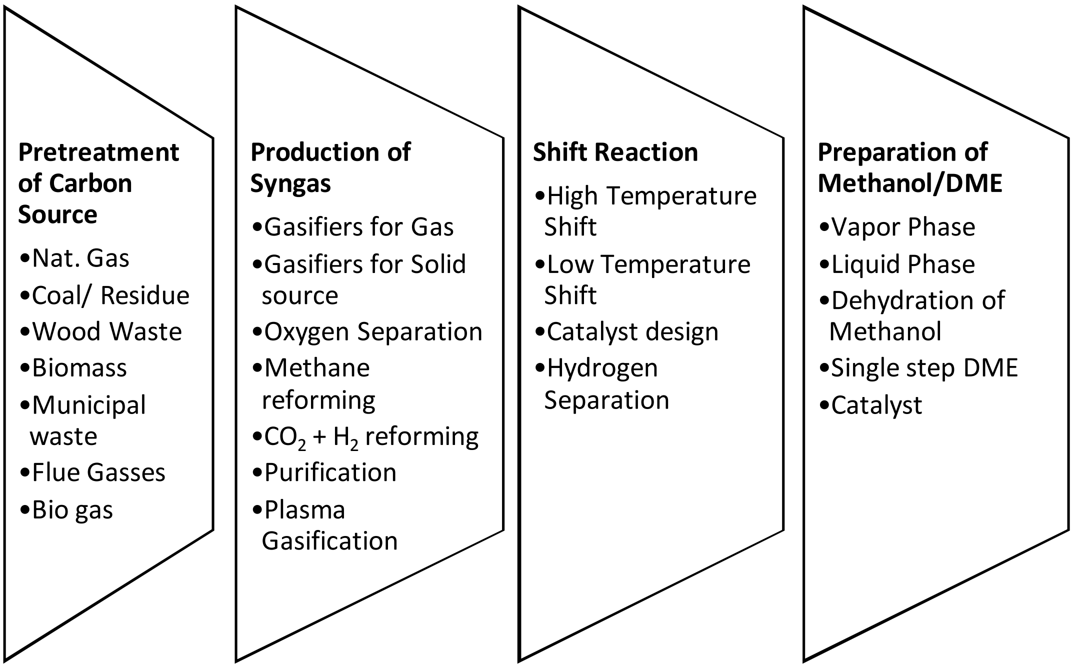
Sr. No.	Developer	Feed	Product	Capacity	Reference
1	CRI International	Geothermal electricity& CO_2	Methanol	4000 MTPA	38
2	Enerkem Inc	MSW	Biofuel	-	39
3	Soperton, Georgia	Wood, Biomass	Methanol	-	40
4	Maverick Synfuels	Landfill Biogas	Methanol	25TPD Skid mounted	29
5	DME Dev. Corp. Japan	Nat Gas	DME	%TPD, Pilot Plant,100 TPD and design of 80,000TPY	41
6	Oberon	-	DME	4500 Gal/Yr.	42
7	Korean Gas	Nat Gas	DME	10 TPD, 300,000 TPA on design	43
8	Clariant	CO_2 & Power	synthetic methane	1.4 million cubic meters/year	146

From the foregoing discussion it is clear that it is technically feasible to produce methanol/DME from different feedstocks with the available technology basket from different sources. With regard to biomass gasification for production of methanol/DME, there is a possibility of putting together available technologies, which are not fully matured yet. There is lot of development in this area and many groups are aggressively working towards development of viable technology. However, the main problem with biomass based plants is the cost and sustained availability of biomass.

3.6 AVAILABILITY OF PROVEN OR EMERGING TECHNOLOGIES

Conversion of carbon or hydrocarbons to foundation block chemicals such as methanol or DME appears to be simple, but the overall process has hidden complexities. Although there has been Intensive research during the last several decades, there are still many technology gaps, and scope of improvement is extensive. There are many new developments in the process and catalysts for different segments of the production chain, but there are not many proven technologies yet.

As a basis for discussing the proven and emerging technologies, here is a break-down of the individual components of the carbon source to methanol/DME production chain:



We can see that right from the source of hydrocarbon, to methanol/DME production, there are many possibilities, and several of them are not yet fully matured for commercial application. Further, the low cost of production of methanol/DME from natural gas prevents other possibilities for technology development. However, with the recent interest in reduction in GHG emission and using gasoline/Diesel compatible liquid fuels from renewable resources, as well as the increased problems of disposal of waste, the use of non-fossil sources for methanol production is gaining importance. In the following sections the current status of available technologies is elaborated for some of these areas, particularly from coal and from renewable sources.

3.6.1 PRETREATMENT OF CARBON SOURCE

Feed pre-treatment for natural gas is well established and most of the licensors can design suitable gas cleaning systems depending upon natural gas quality. However, for coal and biomass, the picture is entirely different due to the diversity of types of these solid hydrocarbon sources. In the case of coal, there is a wide variance in the characteristics of coal and ash content, and its softening point. This also includes the underground gasification of coal. There are many coal based methanol plants in China, and their modern high temperature gasifier designs, which operate above the ash melting point, can handle low melting high ash coals. The current technology to convert all types of coal to syngas is fairly matured, using high temperature and pressure gasification in entrained bed gasifiers with oxygen. Although slurry bed gasifiers are available, the gasification efficiency is relatively low, therefore dry coal is preferred. Large scale coal gasifiers operate with processing capacity of the order of 2000 Ton/day producing 1000 T/Day of DME (Ref. 45).

For varieties of biomass such as wood, agricultural waste, municipal waste, paper mill black liquor, refinery off gases, land fill and anaerobic digester biogas etc. the picture is quite different. Due to their inherent nature, each of these types of feedstocks has to be treated using a specific scheme suitable to the feed characteristics. There are however several reports of demonstration plants for some of these feedstocks individually or co-processed with different renewable feedstocks, and also sometimes with coal. Technologies for feed preparation for incineration or power generation from all these types of biomass are available. The key requirement is to make necessary adjustments to suit the gasification reactor for syngas production.

Biogas from Anaerobic digesters, refinery, steel or cement plant off gases, is often processed along with other feedstocks, depending upon their composition. Sometimes specific pretreatment or mixing ratio adjustments are required before feeding into the reactor (Ref. 15 & 44). As such there is not much challenge in the availability of these technologies, but for each case a specific scheme has to be derived.

Dry reforming of methane with carbon dioxide is another route to produce syngas, although this is especially suited for hydrogen production via shift reaction. The feed preparation requirement for natural gas is only the removal of sulfur by hydro-treating and passing through Zinc Oxide for complete sulfur removal. When higher hydrocarbons such as naphtha are used, a pre reforming section is necessary. Technology for this is available from many licensors (Ref. 46).

3.6.2 PRODUCTION OF SYNGAS

Steam reforming of natural gas is a well-established route to make syngas and hydrogen. Methane reforming reactors operate at above 800^0 C and at 1.5 – 3 MPa pressure. Typically the hot methane and steam is passed through tubes filled with Nickel Oxide catalyst on support. Several companies such as Haldor Topsøe, BASF, United Catalysts and ICI are suppliers of these catalysts.

Technologies for partial oxidation and gasification of natural gas, and solid or liquid hydrocarbon sources based on fossil fuels, are well established. Technology variations are in the gasifier design, operating temperature, pressure, energy management system, oxygen separation, carbon capture etc. Most of the commercial plants operate without any catalyst, and the technologies are matured and can be easily sourced from many available options.

Complete technology stacks covering gasification, syngas production and shift reaction for gas or coal based units for large scale IGCC plants are available from Lurgi, GE, Conoco Phillips, Shell and a few other companies. There are several players who are developing new types of gasifiers and other related processes. Many of them have been operating demonstration plants or even small and medium size plants for commercial production of syngas. The most active players in developing new gasifier designs are KBR, Future Energy, MHI, BGL etc. (Ref. 48).

Production of syngas from biomass is receiving good attention in recent times. There are many medium sized biomass based combustors and gasifiers operating today. There are several power generation units based on renewable feedstocks producing syngas for burning. India also has many small and medium size combustion units operating today. However, there are very few operating plants in the world processing biomass for DME/Methanol manufacture: Broomfield, CO – Range Fuels Inc. in Soperton Georgia, Haldor Topsøe' technology in Chemrec from paper mill waste in Sweden, Enerkem's woody mass to methanol at Edmorton, Alberta (Ref. 33,36,39 &40) etc..

The most important part of syngas purification is Tar removal. This is particularly necessary for low grade carbon sources both from fossil and renewable origin. For both gas turbines as well as for chemical synthesis this is very important. Envitech offers technologies for gas cleaning systems (Ref. 49). Since special attention is required for syngas cleaning when using a low grade source, which is the preferred feed stock, several organizations are working in this area including Johnson Matthey, Clariant, Haldor Topsøe etc. For Mercury and Sulfur removal, technologies are readily available.

Many small and medium capacity Plasma gasifiers are operating in the world but most of them are deployed for power generation rather than methanol/DME production (Ref. 6). This technology is particularly suitable for Biomass and low grade renewable carbon source as well as for low grade coal gasification, for effective ash control. However, commercial operation at a scale suitable for methanol/DME production as standalone unit for low grade source is still far off.

3.6.3 SYNTHESIS FOR METHANOL/ DME FROM SYNGAS

The next step for methanol / DME production is to bring both H_2 and CO together in a methanol reactor. Typically this reaction is carried out in vapour phase at about 30 to 50 bar pressure and 130 - 150^0 C. The technology for methanol synthesis from syngas is well established and several reputed licensors can supply the technology. However, DME is a relatively new product. Although it involves simple dehydration of methanol, technologies have not been perfected yet in large commercial scale, and not many large operating plants exist.

There are a few pilot plants/demonstration plants operating with liquid phase slurry reactors, where the syngas containing carbon dioxide can be easily handled. It is worth looking into this technology, since it will reduce the cost of methanol / DME production significantly. A small scale methanol plant could be economically feasible, where the separation of carbon dioxide is not required, and methanol or DME can be produced in a slurry reactor (Ref. 34).

Haldor Topsøe A/S (HT) has developed and demonstrated an integrated process for the direct production of DME from synthesis gas on a pilot plant scale. Based on their extensive experience in syngas production, methanol synthesis, and DME-related pilot plant work, HT and BP Amoco have identified proven technology for the construction of Greenfield DME plants with capacities in the range of 8-10 thousand tons per day.

NKK Corporation (Tokyo) and the Centre for coal utilization of Japan have jointly developed a new process for DME by utilizing sub bituminous coal. They have demonstrated this technology in a pilot plant of 5 tons per day capacity.

Biomass based syngas production units are typically smaller scale than coal or natural gas based units. Therefore, these plants are normally designed for a single product, either methanol or DME. There are several demonstration plants for direct conversion of syngas to DME in liquid or slurry phase reactors. In 2006, JEE group reported the operation of a 100 T/Day direct DME plant using Biomass derived syngas. The DME synthesis is carried out in Slurry Bed Reactor at a temperature of about 260^0 C and 5 MPa pressure. This is essentially a low cost technology, and the most important part is the dual function of the catalyst, where both the methanol synthesis and dehydration takes place in the single reactor. Both the catalysts and the technology are being developed by several groups such as Haldor Topsøe, Air Products and many others (Ref. 19). Another study was reported in 2009, where HZSM 5 based catalyst was used to convert biomass derived Syngas directly in a 100 T/year Pilot plant with fixed bed reactor (Ref. 20). Unitel Technologies reported operation of a demonstration plant of 10 TPD for direct synthesis of Syngas to DME for a Korean Group, Korea Gas (KOGAS) and after successful Demonstration a 900T/day plant is being considered (Ref. 43). They have also built and successfully commissioned a demo plant in early 2014 in southern California, USA, where high-purity DME stream was produced. They offer the technology for natural gas or biogas based plants with reformer and synthesis to methanol and to DME by catalytic distillation. According to their claim 300 TPD DME plant is feasible and economical (Ref. 22).

As it appears, there is not much commercial experience in direct synthesis of DME, but there is strong interest in having a viable technology for single step DME synthesis in medium scale from biomass sources.

CHAPTER 4. INDIAN SCENARIO

The current consumption of methanol in India is primarily for the manufacture of chemicals such as acetic acid. Use as fuel or fuel additives is not prevalent. Currently, India imports a large amount of methanol.

4.1 CURRENT METHANOL PRODUCTION CAPACITY AND ECONOMICS

Current methanol consumption in India is 1.5 Million Tons per annum. The demand is growing at about 10% and is expected to continue to be met through imports. The current production and imports are shown in Table 12.

Table 12. Methanol Production in India

Year	Installed Capacity	Actual production, In 1000 Ton	Consumption In 1000 Ton
2013-13	474.3	254.9	1469.22
2013-14	474.3	307.26	1534.78
2014-15	474.3	209.83	1801.99

Source: Ref. 147, Methanol production in India, Chemicals and Petrochemicals Statistics at a Glance 2015 (1)

It could be seen that India has almost double production capacity than what is produced. The increase in demand is met by import, which is steadily increasing. The reason for the low capacity utilization is non availability of gas and globally lower price of methanol. The import price prevailing during January 2015 was between Rs.16 to 17 per Kg. (Ref. 148) The two major end-use segments for methanol are chemical and energy. In the chemical segment, methanol is used for production of Formaldehyde, Acetic acid, Di-Methyl Terephthalate (DMT) and a range of solvents. The consumption of methanol in the energy segment is as blending component for petrol and Methyl Tertiary Butyl Ether (MTBE), Tertiary Amyl Methyl Ether (TAME) and Dimethyl Ether (DME). In India, the usage pattern for methanol has remained unchanged over a period of time, with formaldehyde sector accounting for the bulk of the consumption, while usage in the energy segment is not picking up.

Considering the diverse uses of methanol and its potential for use in the energy sector the industry estimates that current demand growth of 10% would be sustained with relatively higher growth in the energy segment. It is estimated that by end of XIIth Five Year Plan period, demand for methanol would reach 2.5

Million Tons, thus providing substantial opportunities for domestic industry in this sector. The current production capacity in the country is 0.385 Million Tons thereby creating gap of 2.115 Million Tons, which would primarily be met through imports from Middle East and China. Due to insufficient domestic production, in FY09 the net import of methanol was 1.06 Million Tons i.e. more than 4 times the domestic production of 0.24 Million Tons. Imports have grown from 0.5 Million Tons in FY07 to 0.8 million Tons in FY10. Investment opportunity exists for a world scale capacity of over 2 Million Tons, requiring an investment of approximately $0.9 billion (Rs. 4,000 Crore) (Ref. 25).

Feedstock availability continues to be a major concern for Indian chemical industry. Availability as well as pricing of natural gas and naphtha at competitive cost is major constraints. The poor quality of Indian coal makes production of methanol through this route uncompetitive at prevailing pricing for coal in India. As a result, the industry is primarily dependent on import of methanol, the basic building block, from Middle East and China.

Large production capacity of methanol established in Middle East and China will continue to put pressure on Indian industry. Viability of local production in the absence of any fiscal and regulatory support from the Government will continue to be of concern. Methanol production from pet coke and coal may be incentivized to make the production economically viable.

The industry is currently operating plants which are much below global scale, hence there is a need for consolidation and establishment of world scale plant. This can be achieved with creation of favourable investment climate in the country. The capacity of methanol plants is increasing to reduce investments, taking advantage of the economy of scale. The capacity of a world scale plant has increased from 2500 MTPD a decade ago to about 5000 MTPD today. Even larger plants up to 10,000 MTPD or above are considered to further improve the economics. (Ref. 149) There are five main producers of methanol in India. Gujarat Narmada Valley Fertilizers Company Ltd (GNFC) is one of the leading producers of methanol in India. GNFC, Deepak Fertilisers, and Assam Petrochemicals use technology from ICI to produce methanol, while Rashtriya Chemicals and Fertilizers Ltd (RCF) and National Fertilizers Ltd use technology from Haldor Topsøe Ltd. (Ref. 50). The production of the major manufacturers is shown in Table 13:

Table 13: Production of Methanol by Major manufacturers in India

Company	GNFC	Deepak Fertilizers & Petrochemicals Corp. ltd.	RCF	TOTAL
Installed Capacity (Ton/Year)	1,88,000 [1] 50,000	1,00,000 [2]	220 TPD [3] = 80,000	418000

Source: 1= Ref. 150, 2=Ref. 151, 3= Ref. 152

GNFC is the largest producer of methanol in India. Assam Petrochem Ltd., is building a 500 TPD methanol plant at Namrup based on gas. Most of the methanol plants in India produce Syngas from natural gas, however the recent focus is to switch to coal, as is prevalent in China (Ref. 51). There has been a proposal to set up a 1500 TPD methanol and 14 mil Cu ft./Day pipe gas per day from Ranigunj coal (Ref. 55).

Although there are no methanol plants in India based on coal, there are a few high ash coal gasification plants coming up in India. This, at least, will open up the door for large scale syngas production from coal. Shriram EPC Ltd., Chennai was planning coal gas plant of 150,000 Nm^3/h at Orissa from high ash coal and Zindal has announced their plant for 100,000 Nm^3 / h. Envirotherm is likely to provide the technology developed by British Gas and Lurgi (Ref. 52).

In India, BHEL had been operating a coal based IGCC power plant at Tiruchchirappalli for 6.2 MW power since 1998. This was the second coal based IGCC plant in the world. The technology was based on pressurized moving bed technology and successfully delivered 400,000 KWHr energy (Ref. 53). However, the coal used was not high ash coal. Since then there have been plans to set up more coal based IGCC units. India operates many coal based power plants, which use air in the combustor. A good summary is available in the document prepared by TERI. It appears that although India had started early in coal gasification with IGCC, neither chemical production nor carbon sequestering was actively pursued, although India has spent about 10 million US$ for a zero emission project as observer member/partner with USA (Ref. 54).

In summary, there is a huge potential for utilization of Indian coal for production of methanol/DME and power. Technology for IGCC is under active consideration, but for carbon capture and utilization of carbon dioxide we are at the starting point. We need to plug this gap before we embark upon coal based power and methanol/DME units. Without carbon capture, the environmental benefits of methanol as a fuel will not be realized. The cost is a major concern.

4.2 AVAILABILITY OF FEEDSTOCK FOR PRODUCTION OF METHANOL

Natural Gas is the most preferred feedstock for methanol production. Due to the availability of natural gas in the country most of methanol plants are not able to utilize the full production as indicated in the previous section. The other resources are coal, Pet coke, Biomass or MSW and off GASES from refineries, steel plants etc. Although India has good reserve of coal, the quality of coal is of concern.

Indian production of coal had been progressively increasing but the demand is also growing hence the balance is met by import. India had a total installed electricity capacity of around 250 gigawatts. Around 60 per cent of this is coal-fired. Indian coal reserve is about 301.56 Billion tonnes as on 1.4.2014

- Currently Indian coal is only used for power generation
- Only one plant for fertilizer production –via syngas air Gasification
- Coal washing requires large amount of water
- The average ash content is more than 40% and due to presence of large amount of silica and alumina, the ash fusion temperature is high.

4.2.1 INDIAN COAL AS FEEDSTOCK FOR METHANOL

There has been concern about cost of washing vs. transportation of unwashed coal. It is preferred to locate the gasification plant near the coal mines, so that the unwashed coal could be directly utilized. The main issue here is that the washing improves the efficiency of the electricity generation and the overall cost of production is lower. However, with the increasing problems of water usage and the difficulty in washing for several types of Indian coal, this may be revisited. As such, technologies are available today to clean the syngas as well as there are gasifiers which can handle even 50% of ash. Modern gasifiers operating at high temperature and pressure can handle high ash coals but the carbon emission is higher than washed coal. Therefore, the use of unwashed coal is not permitted to burn beyond 1000 Km of the mines or in densely populated areas, due to higher carbon dioxide emission (Ref. 88). For use of unwashed coal, the plant has to be located closer to the mines. It is to be noted that the gas produced by UGC or from coal bed methane is most suitable for converting to methanol/DME.

4.2.1.1 CHARACTERISTICS OF INDIAN COAL

The most important is the quality of Indian coal. The different grades of coal produced in India are shown shown in Table 14.

Table 14. Characteristic Features of Indian Coal

Grade	Useful heating value Kcal/kg	Ash %	Gross Cal Value Kcal/kg
A	>6200	<19.5	>6454
B	5600-6200	19.6-23.8	6049-6454
C	4940-5600	23.9-28.6	5597-6049
D	4200-4940	28.7-34.0	5089-5597
E	3360-4200	34.1-40.0	4324-508
F	2400-3360	40.1-47.0	3865-4324
G	1300-2400	47.1-55.0	3113-3865

Source: Ref. 102. Indian Thermal Coal Classification: Coal in India, 2015, Australian Gov. Department of Energy & Science, Office of the Chief Economist, WW.INDUSTRY.GOV.AU/OCE

Much of the Indian coals are difficult to wash and the nature of the coal is also non caking type. Although there are several coal based plants for methanol and/or DME in China but the quality of Chinese coal is much better than Indian coal. The Gross Calorific Values for most of the Indian coals vary in the range of 3500 to 4000 kCal/Kg while for the coal which is imported in India from Indonesia the range is between 54 to 6500 kCal.kg (Ref. *102)*. This clearly implies that for processing the same quantity of coal, the chemical output in weight basis will be almost half of what would have been expected from good quality coal. Since the plant cost is directly proportional to the amount of coal processed, the investment cost for Indian coal based methanol or DME plant will be proportionately higher. Moreover there is practically no commercial experience in the world to process non caking coal with 50% ash for methanol or DME production.

The Table 15 indicates the additional cost for using low grade coal for gasification.

Table 15: Additional Cost for Processing Low Grade Coal

Process Units	Increased Moisture	Increased Ash	Increased Sulfur
Fuel Preparation	+	+	
Gasifier	+	+	
ASU	+	+	
Slag Handling		+	
Heat Recovery	?	+	
Sulfur Removal			+
Steam Cycle		+	

Source: Ref. 104. An Overview of coal based Integrated gasification Combined Cycle (IGCC) Technology, by Ola Maurstad, September, 2005, MIT LFEE 2005 = 002 WP

4.2.1.2 PROCESSING HIGH ASH COAL FOR METHANOL PRODUCTION

In the earlier Section we have discussed about different types of gasifiers. The recent trend for power as well as liquid fuel production is to use the Entrained bed gasifies. Although high pressure Fluid bed reactors are used. There are several reasons for the preference towards Entrained bed gasifiers, particularly for chemical production. The most important is it produces tar free syngas. Due to its high temperature operation, the combustion takes place in few seconds resulting smaller reactor size. Since these reactors generally operate at the temperature higher than the gas melting temperature, the ash is easily removed from the reactor as liquid form. Many of the modern gasifiers are operating at above 2000^0C. and higher pressure than 40 bar. As for example, Udhe Prenflow Reactor can operate under this process condition with 99% carbon conversion. They reported to have licensed this gasifier technology to Mozambique for a 9,500 Barrels/day plant processing 37% ash. (Ref. 119) While most of the high ash coals will melt at this temperature, due to the non-coking nature of Indian coal there could be some concern. However, the ash melting point could be manipulated with addition of lime, etc. The main issue here is the loss of energy due to the large amount of molten ash going out of the reactor when high ash coal is processed.

In a recent presentation L & T has reported that they are working on a patent taken by Indian Oil where a two stage gasifier is to be used to process high ash Indian coal. Here the first stage will operate at lower temperature and the second gasifier at higher temperature. Most of the ash and tar will be removed in the first stage itself and the clean syngas will be produced in the second stage at higher temperature and pressure (Ref. 154). Since the gasifier is the one of the major cost centre, its overall economic benefits to be evaluated.

To reduce the overall concentration of ash, high ash coal could be co processed with either Pet coke or biomass. There are several reports of successful gasification with oxygen for processing pet coke with coal to reduce the impact of high ash content of coal and almost negligible ash in the pet coke. Although some of them are operating for power generation only but the quality of the tar free syngas is suitable for methanol production. The ease of carbon emission control in these oxygen fired units is also very important for future up gradation (Ref. 153).

With our current interest to use Indian coal for methanol production, the high pressure operation is desirable so that the cost of compression of syngas could be avoided. With the entrained bed gasifiers operating at above 40 bar, the low pressure liquid phase methanol production process is worth considering. A detailed study is reported by Air Products where the reactor is operated at 500 psig only. It has been shown that methanol production cost is about 70% lower than that of conventional gas phase reactor (Ref. 93).

The low calorific value, high ash content and non-coking nature bring restriction on the choice of suitable gasifiers for good quality syngas production. Also makes the economics unfavourable to some extent. The ash content adds up to the cost for almost every step in the process. Therefore, it is often debated if the washing of coal is desirable or low grade coal should be used as such. The cost of washing vs. the additional penalty for using non washed high ash coal must be evaluated carefully before taking the decision.

4.2.1.3 MANAGING RESIDUES AND SLAG FROM GASIFIERS

While handling of Indian coal with high ash content, its disposal becomes an important issue. Almost half of the coal processed returns as bottom ash, fly ash or as slag. Unless it is disposed efficiently, the operation cannot sustain for long.

The non-combustible material in coal is returned as ash from a coal based furnace. There are three different types of these by products, depending upon its characteristics. It contains arsenic, mercury, lead, and several other heavy metals. Due to these contaminations adequate care is necessary in safe handling and disposal of these materials. There are mainly three types of ash as indicated below:

- Fly ash, a very fine, powdery material composed mostly of silica made from the burning of finely ground coal in a boiler.
- Bottom ash, a coarse ash particle that is too large to be carried up into the smoke stacks so it forms in the bottom of the coal furnace.

- Boiler slag, molten bottom ash from slag tap and cyclone type furnaces that turns into pellets that have a smooth glassy appearance after it is cooled with water.

Indian coals from Odissa region indicates that the major components of the ash are Silica, Alumina and Iron oxides while the lime content is low. As a result the fusion temperature is generally high for Indian coal ash. The ash fusion temperature varies within 1150 to 1600^0C. The sulfur present in the coal is mostly organically bound, therefore not much is left in the ash. A typical ash analysis is shown in Table 16.

Table 16. Chemical Composition of Typical Indian Coal Ash from Odisha

Samaleshwari Block of 1b Valley Coal field Orissa			
Ash composition (Wt.%)	**A Depth: 20–24 m**	**B Depth: 100–140**	**C Depth: 217–260 m**
Al_2O_3	21.46	20.55	21.29
SiO_2	62.59	48.32	56.54
Fe_2O_3	5.51	21.47	13.44
CaO	1.73	1.98	2.33
MgO	0,60	0.50	1.05
Na_2O	0.11	0.14	0.16
K_2O	1.05	1.21	1.14
P_2O_5	1.57	1.67	1.02
TiO_2	1.72	1.44	1.65
SO_3	0.06	0.04	0.15

Source: Ref. 162. Composition, mineral matter characteristics and ash fusion behaviour of some Indian Coals, S. Chakaraborty et al. Fuel, 150, (2015) 96-100

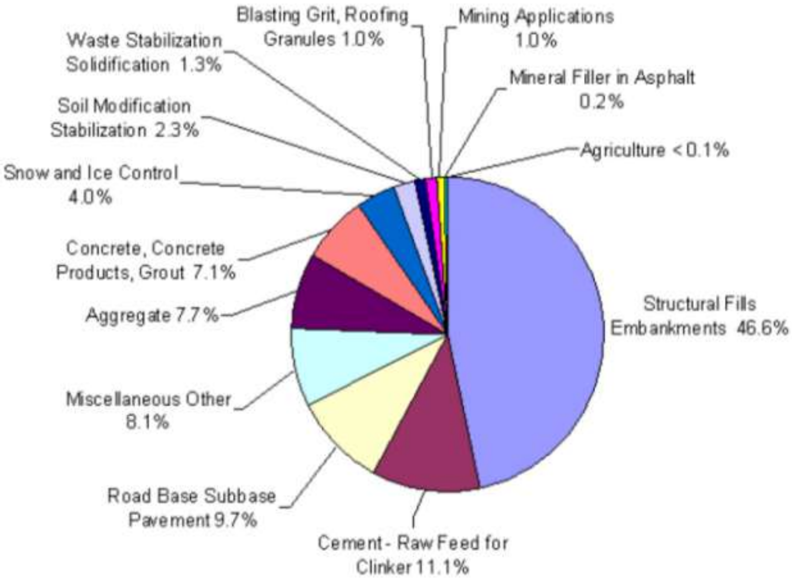
The fly ash makes up more than half of the coal leftovers. Fly ash particles are the lightest kind of coal ash is collected from the exhaust stacks of the power plant. About 99 percent of the ash is recovered through filters and electrostatic precipitators. Fly ash particles are an ideal ingredient in concrete. The recycling process also renders the toxic materials within fly ash safe for use.

The Bottom ash is the coarser component of coal ash, it settles to the bottom of the power plant's boiler. Bottom ash is not quite as useful as fly ash although it is used as structural fill and road-base material. However, it has certain risks for ground pollution due to leaching. The toxicity of the ash should be checked before using. Most of the countries have certain regulation regarding the disposal and usage.

The boiler slag is the molten form of coal ash that can be found both in the filters of exhaust stacks and the boiler at the bottom. Boiler slag can be included in roofing shingles (a reasonably safe application) and in structural fill. The molten ash, after solidification is crushed and is used as aggregate in lightweight concrete masonry units and raw feed material for production of Portland cement. Bottom ash has also been used as a road base and sub base aggregate and structural materials. To meet required specifications, the bottom ash or slag may need to be blended with other natural aggregates prior to its use. Discarded bottom ash and boiler slag are either landfilled or transferred to storage lagoons. When sluiced to storage lagoons, the bottom ash or boiler slag is usually combined with fly ash. This blended fly ash and bottom ash or boiler slag are referred to as ponded ash. Approximately 30 percent of all coal ash is handled wet and disposed of as ponded ash. The bottom ash is also used as snow and ice control on roads and pavements in some countries (Ref. 155, 156).

The different applications of ash are shown in Fig. 7.

Fig. 7: Different use of Coal Ash



Source: Ref. 155. Coal Bottom Ash/Boiler Slag Material Description

4.2.2 FEEDSTOCKS FROM INDIAN REFINERIES.

India has recently emerged as one of the global players in refining industry. The current production capacity is about 215 MMTPA (Ref. 157). There are about 23 refineries in India but only 8 are more than 10 MMTPA capacity.

4.2.2.1 PETROLEUM COKE FROM INDIAN REFINERIES.

Total Petcoke generation in India in 2013 was about 12 MMTPA and new refining capacity of about 10 MMTPA will be added soon. Reliance alone produces about 6.4 MMTPA at single point at Jamnagar (Ref. 8). Therefore a surplus availability is expected.

Most of the plants are of smaller capacity and coker is not available in all the refineries. However several large refineries having coker unit are considering the option for producing power and hydrogen through IGCC. As for example, Reliance is going ahead with installing a Pet coke gasification facility at Jamnagar, which will produce hydrogen as well as feedstock for chemicals. It is also likely to have carbon capture facility (Ref. 8). Many other refineries are also considering similar projects. For smaller refineries with coker, a group of refineries may decide to go for a gasification plant to produce methanol or DME. This will ensure economic capacity and uninterrupted supply of feedstock. Presently, most of the Indian refineries whether having coker or not disposing the residue in their captive power plant. There is a possibility of using these residual materials or coke and co process with coal or biomass. The price offered by the methanol plant has to be more than the revenue generated by refineries by selling the petcoke in the market or use the residue in their power plants.

4.2.2.2 OFF GASES FROM INDIAN REFINERIES

The possible usage of refinery off GASES has been discussed in the earlier section. The scenario is not much different in India. The earlier practice of burning as flare has almost non-existent today and all the hydrocarbon GASES are being used by the refineries in different sections and even for recovery of some valuable hydrocarbons. These quantities are not sufficient for standalone methanol plant. It may be possible to use some of the lower hydrocarbon streams via reforming in small scale. Since there are several streams of low calorific value gases at different locations of a refinery, there are often some logistic problems in mixing and processing them together. Refineries could explore the best economic solution for use of such low calorific value hydrocarbon GASES, including methanol, DME or syngas production.

4.2.3 BIOMASS AS FEEDSTOCK FROM INDIAN SOURCE

India has several bio gas based plants for power generation, however these account for only about 5% of the total power generation in the country. The largest three plants are of 1 to 1.5 MW each, in Tamil Nadu. All these plants only produce power (Ref. 114). There are many small and medium capacity gasification plants for power generation operating in India, based on Indian technology for the gasifier. These plants generate producer gas having hydrogen to carbon monoxide ratio of the order of 1. About 2 Kg of Biomass or wood chips is required for 1 KWH. Many of these plants deliver power at reasonable cost (Ref. 125).

Ministry of New and Alternative Energy of India has been quite active in the area of utilization of mixed Biomass and waste for production of bio fuels but most of these development projects funded are for bio ethanol or bio gas production including bio CNG (Ref. 64). TERI has been doing intensive research in the area of Biomass gasification for power generation in India since 1980. They can provide technology for gasifiers but are not focused towards methanol production via syngas (Ref. 65).

4.2.3.1 AVAILABILITY & UTILISATION OF BIOMASS IN INDIA

Under the 11th Plan period (2007 -12) the Government of India plans to add as much as 1700 MW of power production through biomass and bagasse cogeneration in various states. It has been indicated earlier that we have large potential for utilizing more biomass. Although at this time there is some utilization of biomass in India directly or indirectly, there is still about 25% surplus biomass which remains unutilized (Ref. 68).

Power generation projects from biomass in India during 2016 account for 4831.33 MW. About 32% of the total primary energy use in the country is still derived from biomass and more than 70% of the country's population depends upon it for its energy needs. The current availability of biomass in India is estimated at about 500 Million Metric Tons per year. Studies sponsored by the Ministry have estimated surplus biomass availability at about 120 – 150 Million Metric Tons per annum, covering agricultural and forestry residues corresponding to a potential of about 18,000 MW. This apart, about 7000 MW additional power can be generated through bagasse based cogeneration in the country's 550 Sugar mills, if these sugar mills were to adopt technically and economically optimal levels of cogeneration for extracting power from the bagasse produced by them. The most commonly used route is combustion. The advantage is that the technology used is similar to that of a thermal plant based on coal, except for the boiler. The Ministry has been implementing biomass power/co-generation programs since the Mid-Nineties. A total of approximately 500 biomass power and cogeneration projects aggregating to 4760 MW capacity have been installed in the country for feeding power to the grid. In addition, around 30 biomass power projects aggregating to about 350 MW are under various stages of implementation. Around 70 Cogeneration projects are under implementation with surplus capacity aggregating to 800 MW (Ref. 67). Bioenergy has remained critical to India's energy mix. The current potential of surplus agro and forest residues to energy is estimated at 16,881 MW along with an additional "waste to energy" potential of 2,700 MW (REF. 68).

4.2.3.2 MUNICIPAL SOLID WASTE (MSW) AS FEEDSTOCK IN INDIA

In India, MSW is a problem in almost all the cities. India generated about 188,500 Tons of MSW per day in 2012. The average composition of this MSW is 51% organics, 17.5% recyclables (paper, plastic, metal and glass), and the average calorific value is 7.3 MJ/kg (1745 kcal/kg). The compost yield from mixed MSW is only about 6 to 7%, and 60% is discarded as compost reject and used as landfill. The calorific value of these rejects is quite high (2,770 kcal/kg.) In Mumbai alone, from open landfill fires, pollutants of the order of about 22,000 TPY are emitted. From the rejects of the compost, about 58 million barrels of oil equivalent energy could be produced per year (Ref. 105). From the report of Govt. of India it is estimated that about 1400 Sq KM of land will be required between 2009 and 2047 for disposal of MSW from Hyderabad, Mumbai and Chennai only. During 2041 India will generate about 230 million TPY MSW per year ie.630,000 TPD (Ref. 106). Most of the towns/cities in India do not have proper action plans for implementation of MSW rules. Waste collection is observed only for 70% of total waste generation and the remaining 30% is lost in the urban environment. There is a large gap between waste collection and processing. Most of the Municipalities have no sanitary landfill facility and follow dumping for disposal of MSW (Ref. 107).

So far conversion of Waste to Energy was considered as the best way to reduce the detrimental impact of the large amount of waste generated. This is practiced in almost all the developed and many developing countries. Govt of India recognizes that the energy created from MSW is renewable energy. Several years back India had set up WtE plants in some cities but the experience was not up to expectations. With recent developments in technology it is now possible to operate WtE plants quite efficiently. The estimated potential for power generation from MSW in India during 2017 is expected to be about 5200 MW. Since 1000 TPD capacity MSW plants are quite standard and the technology is well established, only the large cities can have such facilities for power production. However, the cost for installation per ton of MSW processed is of the order of Rs. 23,00,000 while the cost of facility for composting is about Rs. 2,00,000. Since all the MSW cannot be used for feed in composting, WtE is the only available option. WtE is also less polluting compared to composting.

Through Jawaharlal Nehru National Urban Renewal Mission (JnNURM), several cities and towns have developed collection, transportation, sanitary landfill and composting facilities. The full potential for power production has not been realized yet (Ref. 105).

The Waste to Energy (WtE) projects based on Municipal Solid Waste (MSW), installed in the country as of 31st March 2015 account for just 154 MW. On the other hand there is a possibility to produce up to about 6000 MW from this source. For same reasons, so far, there has been limited focus on recovering energy from waste. All this capacity has been developed on mixed waste and incineration/ combustion /biodegradation of waste is carried out after its processing at the energy recovery site, which is certainly less optimal that segregating MSW at source. It is estimated that about Rs. 20 Crores will have to be invested per MW of power generated from MSW i.e. Rs.27 Crore per Ton of MSW processed. There could be some reduction if it is segregated at the collection point, a process which is not up to the mark at present (Ref. 108, 117).

Many state Governments are keen on tapping this source of energy (Ref. 74). Several plants are planned in the near future to leverage this opportunity (Ref. 75).

At present there are several small scale biogas producing plants in India. Since the cost of setting up a bio digester is lower and it is able to handle smaller quantities of bio digestible agricultural and food waste, during 2014 - 15 proposals for setting up of 94 bio digesters to produce 2213 KW of power at a cost of Rs. 33 Crores were mooted for Govt. support. Many of them had been approved (Ref. 109). Due to availability and logistics problems, large scale plants are not coming up. The largest biogas plant in India is in Satara district, Maharashtra, which produces 25,000 cubic meters of biogas per day from 600 tons of sugarcane waste obtained from sugar mills in the vicinity. Gas obtained is converted to Compressed Bio Gas (CBG) and used as fuel. This plant uses an advanced Continuous Stirred Tank Reactor for faster anaerobic process. Another large biogas plant has been developed under the National Biogas and Manure Programme by the Ministry of

New and Renewable Energy. This plant produces nearly 936,000 cubic meters of biogas per day (Ref. 110). 23 additional large biogas plants are also being planned.

It may be pointed out that so far in India the objective was to use MSW only for power generation, not for production of chemicals. This is a new trend, particularly with the growth of use of methanol/DME as transportation fuel. Although it is more complex to produce chemicals from MSW via gasification, there are several operating plants in the world now. Technically there is not much of an issue since the gasification of MSW is already an established technology. The technology for syngas cleaning and syngas conversion is essentially same. The only issue is that it will have more investment cost for air separation and subsequent methanol/DME production. It is worth considering installing at least one 1,000 TPD unit for methanol/DME production.

Since the MSW generation from small cities and towns is much lower, using conventional technology may not be viable. The other agricultural and biomass waste also could be treated simultaneously. It may be worth to consider the emerging Plasma gasifier technology with oxygen firing and methanol/DME production as a trial case.

Good MSW management is most crucial for India since it will reduce the increasing demand of land for landfill, produce renewable energy or fuel, as well as reduce pollution. The cost of treating MSW should be viewed holistically with the direct investment as well as the social and environmental benefits.

The Indian plasma gasification unit near Pune is producing 1.6 MW/Day by processing only 72 Tons of MSW. The capital costs of Plasma assisted waste to energy plants are higher than that of the conventional solid fuel gasifiers. This higher cost could be justified by the fact that it is freeing urban land and will manage the mounting waste in the cities. Again, the investment cost will further increase for oxygen firing and chemical production, in place of power (Ref. 127). A recent estimate for a 3000 TPD MSW Plasma based plant is about US $ 450 Million (INR 3,150 Crores approx.). This proposed plant only will produce power and not methanol. The cost of a conventional incinerator is also of the same order (Ref. 6). Since the cost of conversion of MSW is always high as compared to waste wood and other biomass, the plasma will still be more expensive. Again for oxygen firing and methanol conversion cost will have to be added. Unless support from the State is provided, the chemical production from waste may not catch up. Japan is very active in plasma based gasification. India is also already one of the players in plasma gasification.

4.2.3.3 BIOMASS AVAILABILITY FROM PAPER MILLS IN INDIA

Indian Paper industry is one of the world's fastest growing industries. It grew at a compounded annual growth rate of 6.7% over FY 06-11. Among the top producers of paper, India ranks at 20th position with an estimated production of 10.9 Mtpa. The Indian sector accounts for about 2.6% of the global production, estimated at 390 Mtpa. In 2012, India recorded paper consumption of 9.3 kg/capita vis-à-vis global average of 58 kg/capita. Currently there are 759 pulp and paper mills with an installed capacity of 12.7 Mtpa, producing paper, paper board and newsprint. The production is anticipated to grow to 14.0 Mtpa by the year 2016. However, this is one of the most polluting industries. Most of the black liquor produced is used for recovery of chemicals and the balance is burnt to generate energy. Since the average size of these paper mills is rather small, it is not economical to produce syngas or methanol. It has been suggested by an expert committee to install efficient multi-fuel high-pressure boilers, turbines and producer gas plants to utilize the biomass as a source of clean fuel, to reduce the carbon footprint of the mills (Ref. 69). The possibility of producing methanol or DME was not considered.

4.2.3.4 PROBLEMS ASSOCIATED WITH BIOMASS COLLECTION AND SUSTAINED SUPPLY

One of the most difficult aspects of biomass utilization in large scale is its collection and consistent production. Further, agricultural waste materials are not available round the year. Another concern is that much of the biomass could otherwise be used as compost for manure and biogas production. The biomass which could be easily converted to biogas or compost by anaerobic digestion should be utilized for this purpose and the biogas possibly could be diverted for syngas production along with other biomasses.

The diversity of physical characteristics and moisture content are key challenges, in addition to sustained availability around the year. Clubbing of some biomasses could be possible for similar pre-treatment of this carbon source. Transportation and collection are also a problem due to excessive moisture content and low bulk density. The optimization of the transportation network and medium of transportation, as a part of logistic support, can ensure the consistent supply of biomass to power plants, while it can reduce transportation cost as well (Ref. 36). Biomass also has costs prior to entering the gasification unit. This is not only for the collection, transportation, drying or pre-treatment but also opportunity cost against demand for other usage. In India, much of the residual biomass is already in use as cooking medium, at least in rural areas. Therefore, it very often becomes uneconomical to implement a biomass based plant with a single type of feedstock.

Regarding MSW, only few cities have segregated collection systems for different types of waste. This is one of the major issues in India around MSW management. However, rag packers help in direct recycling of much of the usable waste. Compared to many countries India is better placed in this area.

Most of the biomass based power plants which operate without gasification or even with gasification where syngas is prepared, the composition of the flue gas or syngas is not critical. Such units can tolerate much variation in the feedstock for sustained operation. On the other hand, the syngas composition as well as impurities is very critical for converting syngas to methanol or DME. Therefore, additional care needs to be taken in dealing with wide variations in feedstock. The plant has to operate mainly with one or two major feedstocks. A very large biomass based methanol/DME plants may not be feasible.

Larger plants with multiple feeds must account for the treatment and cost for different feed materials and the transportation from different sources. All these add to the upfront and operational cost. A feasible option is to treat the biomass at relatively smaller scale at the points of origin and then transport to a larger scale methanol/DME plant. The pre-treatment generally results in smaller quantities for transportation. Pelletisation is of course an established option. The other viable option is to produce oil /char by pyrolysis and then transporting the residue to the gasification plant, while the distillate could find use locally (Ref. 77).

For domestic waste, if it could be isolated at the collection point, the anaerobically digestible materials could be converted to biogas and the gas then transported by means of pipeline to the gasification plant as indicated earlier. However, this may not be feasible if the processing plant is not very close.

The Edmonton plant in Canada is one example of an operating plant for production of methanol which uses MSW after segregation. From MSW, the non-compostable and non-recyclable solid wastes are sorted. The organic materials are transferred to the Edmonton composting facility, the metals and cardboard materials are recycled directly, and the non-compostable and non-recyclable wastes are used as feedstock for the biofuel plant. This facility has been operating since 2014 for co- Processing of solid waste, coal and agricultural residue (Ref. 78).

4.2.4 AVAILABILITY OF SYNGAS OR FUEL GASES FROM STEEL PLANTS

Steel plants in India use large amounts of fuel for supply of energy, mostly coal or natural gas for the Blast furnace and coke oven plants. This sector contributes around 3% to the Gross Domestic Product (GDP). The average consumption of steel during 2011-12 was 70.92 Mt (59 kg per capita). The production of crude steel capacity has grown to 89.29 Mt annually. The projected estimates of crude steel production and capacity by 2020 is expected to reach 136 Mt with per capita consumption of 90 kg. There are three major process routes in steel making: 45% steel is produced by Blast Furnace –Basic oxygen Furnace (BF-BOF) route; 24% and 31% by electrical furnace such as Arc furnace and Induction furnace routes respectively. The product gases after the operation still contain significant combustible materials. The available gases with low calorific value are coke oven gas and blast furnace gas. Most of these gases are utilized in power or heat recovery (Ref. 70).

The list of major steel plants in India is shown in Table 17.

Table 17: Steel Plants in India

Name	Location	Owner
Tata Iron and Steel Corporation(TISCO)	Jamshedpur, Jharkhand	Tata Steel
Visvesvaraya Iron & Steel Plant	Bhadravati, Karnataka	SAIL
Bhilai Steel Plant	Chattisgarh	SAIL
Durgapur Steel Plant	Durgapur, West Bengal	SAIL
Bokaro Steel Plant	Jharkhand	SAIL
Chandrapur Ferro Alloy Plant	Chandrapur, Maharashtra	SAIL
IISCO Steel Plant	Asansol, West Bengal	SAIL
Salem Steel Plant	Tamil Nadu	SAIL
Rourkela Steel Plant	Odisha	SAIL
Vijaynagar Steel Plant	Hospet, Bellary, Karnataka	Jindal Steel and Power
Vishakhpatnam Steel Plant	Vishakhpatnam, Andhra Pradesh	Rashtriya Ispat Nigam

Source: Ref. 158. Iron and Steel Industry in India, Wikipedia

Recently some new technologies have been introduced in India which uses Syngas from different sources. The Thermal Reactor System developed by Praxair uses partial oxidation technology to convert various GASES like coke oven gas into a high quality Syngas. Jindal Steel has recently commissioned a Direct Reduction Plant at Angul, Odessa using Syngas produced from coal gasification. This plant use Indian coal, Pet coke and refinery residue as feedstock. JSW Steel Ltd. uses a melter/gasifier to simultaneously produce hot metal and gas at Toranagallu, Karnataka. This gas is exported to the Direct Reduction Plant. They are also replacing some of their natural gas consumption at Dolvi, Maharashtra. These are very recent developments. The simplified flow sheets indicare that these plants use oxygen in place of air. These technologies were provided by Midrex Technologies (Ref. 160).

Tata Steel has developed a technology to produce hydrogen from the quenching section by Thermo Splitting of water. This is a novel technology. This could provide a good source for hydrogen. (Ref. 76). Currently, they are probably using this internally and looking for a partner for commercial exploitation of their hydrogen production technology, in 2011. (Ref. 159)

With the recent trend of modernizing of large steel plants with Direct Reduction and Gasification with oxygen, there is some possibility of production of Methanol or DME with proper selection of available feedstocks as well as integrating with biomass gasifiers or digesters. This will require careful consideration for case to case basis to ensure availability of adequate quantity of gas at right quality.

It is known that the steel plants are struggling with reduction of carbon dioxide emission. If hydrogen could be produced within the plant, probably it will be one of the best options to put up a demo plant for CO_2 hydrogenation to methanol. This will not only reduce the emission burden but also avoid hydrogen handling and transportation. Even if the carbon dioxide utilization is not feasible, this hydrogen could be easily reacted with blast furnace gas or even with the available coke oven gas to fix the hydrogen. With the methane present in coke oven gas there is a good possibility of using some carbon dioxide for reforming of this methane. Such possibilities also could be explored.

4.2.5 OFF GASES FROM CEMENT INDUSTRY IN INDIA

India is the 2nd largest cement producer in the world. The current installed capacity of more than 380 MTPA with production of about 272MTPA. The average Kiln Capacity is about 4500 TPD. Approx. 7% of India's man-made CO_2 Emissions come from this industry. The current focus is waste heat recovery and reduction of GHG emission (Ref. 72). As such, not much gas having useful calorific value is available from the cement industry off GASES.

4.3 PROCESSING OF DIFFERENT FEEDSTOCKS SIMULTANEOUSLY

Presently the largest Syngas producer in India is the fertilizer industry. The breakup of the feedstock is approximately 56:26:12:6 for natural gas: naphtha: Fuel oil: coal or Residue (Ref. 58). Most of the technologies deployed by the majority of fertilizer manufacturers are steam reforming for production of hydrogen. Therefore, few options are available for using heavier feedstocks than naphtha. However, there is a possibility of replacing some of the feed gas with biogas or other flue gases. In such case the gases need to be economically available in proximity.

On the other hand there are large numbers of coal based power plants in India. Most of these plants operate in complete combustion mode. The coal is normally fired with air rather than oxygen. Practically none of them has carbon capturing capability. As it has been noted, the prerequisite for syngas production via partial oxidation should be free from nitrogen. If a power plant operates in IGCC mode then both power and syngas could be made. The syngas could be either burnt for direct power generation or used for methanol production. If air is used as firing agent nitrogen needs to be separated after combustion. Alternatively, the air could be separated before combustion. This co-processing capability adds to lots of flexibility to the operating plant to cope up with variable demand for power. The excess power during low demand period could be stored in the form of methanol. It is also possible to produce ammonia using the nitrogen from the air separation unit.

Unfortunately, today India has only negligible capacity operating in IGCC mode. Probably only one plant at Trichi is operating in this mode with coal. In the near future we may have some plants coming up with coal gasification. As per projection, IGCC will be introduced commercially in India during 2037 and during 2042 - 2047 there is likely to be only 30% of the total coal based power production from IGCC gasifiers (Ref. 59). Therefore, possibility for linking the existing power plants for syngas or methanol production is minimal at least in the near future. However, carbon dioxide capture and conversion to methanol from these power plants may be possible if carbon free hydrogen is available nearby.

Only about 12% of the power plants today are operating with natural gas. Many of them are operating with Combined Cycle (Ref. 60) but none of them produce syngas with IGCC mode via partial gasification. Therefore, no syngas is available from these plants as well. It seems that in power sector there is not much possibility to produce methanol, unless some major changes are carried out or additional capacity is created. Recently BHEL has started working on a 370 MW

Combined Cycle power plant at Karnataka, but again it is apparently not via gasification (IGCC) (Ref. 61).

It is technically complex to process coal and gas simultaneously in the same plant. While coal based ammonia plants go via syngas, the gas based plants use Steam Reforming route. Therefore, it is impossible to process coal and gas together in an ammonia plant. It could however be possible to process heavy residual fuels or even biomass in solid fuel based ammonia plants. At least this could reduce the GHG burden to that extent.

Mixing of all kinds of solid waste / residue feedstock is possible in fluid bed gasifies. There are many operating plants handling different types of feedstocks either simultaneously or in blocked out operation. In India, most of our biomass or agricultural residue is utilized in heat or power generation, with complete combustion or partial combustion, to produce low calorific value Producer gas. Since the Producer gas is the product of gasification using air rather than oxygen, this gas contains large amount of carbon dioxide and nitrogen, making it uneconomical to convert to methanol (Ref. 62). Although it is a good way to reduce carbon emission impact, such plants as are not suitable for producing syngas for methanol production. However, with addition of oxygen separation facility upfront the combustor these plants could be easily converted to methanol plant.

Adding small quantity of biomass with coal in large gasifier is one of the most viable options for producing methanol/DME from low value feedstock, while at the same time reducing carbon dioxide emission, at least to the extent the agricultural residue and bio wastes are used. There are several plants operating with mixed feedstock. The coal provides the bulk of the continuous source of feedstock for sustaining the economic sized plant. Many industrial wastes are also used for producing methanol; for example, glycerin is used in Biofuel production in Netherlands, black liquor is also used in several installations, carbon-dioxide reforming with renewable hydrogen in Iceland, etc. Depending on the local conditions it is possible for integrated production with Bio-Ethanol from sugarcane, co-feeding biomass feedstock and fossil fuels, and co-production of heat, electricity and other chemicals. Co-feeding of renewable feedstock in natural gas or coal based methanol production facilities can be used to reduce the environmental impact of conventional methanol production. In the process, the available biomass feedstock is optimally used (Ref. 79).

Co-firing of biomass has been demonstrated and used in all types of boilers ranging from 30 to 700 MWs. Biomass co-firing has been used extensively in the Scandinavian countries in relatively small sizes (up to 50 MWs). In the 1990s, many power plants demonstrated this option in Europe, Japan and United States, and then proceeded to use it commercially. Biomass may include switch grass, sawdust, wood wastes, Municipal Solid Wastes and other waste fuels. In most cases, the use of biomass is limited to a maximum of 15 percent of the total feed. Many countries in the world are co-processing biomass with coal. However, India's experience in gasification of Indian coal with IGCC is limited, although there are many Circulating Fluid Bed Combustors. Therefore, producing syngas from these existing plants may not be a very attractive option (Ref. 80).

4.4 POSSIBILITY OF INTEGRATING EXISTING METHANOL PLANTS WITH DME

In India there are several methanol manufacturing units but the total production for methanol is far below the present demand within the country. Only 0.37 million tons of methanol are produced in India as against a total requirement of 1.3 million tons (Ref. 55). Therefore, there is practically no commercial incentive for the methanol manufacturers to produce DME. However, if required for development purposes, DME could be easily produced from methanol. In near future surplus methanol availability from Indian source is not expected. Of course, the advantage of cheaper imported methanol could be considered for producing DME.

Conversion of methanol is straight forward if surplus methanol is available from the existing plants. The dehydration plant could be easily set up in the Methanol plant location itself.

4.5 CURRENT R&D SCENARIO IN INDIA

Indian R&D is always active in exploring novel scientific ideas and emerging technologies. In the area of utilization of coal as liquid fuel through Fischer–Tropsh Synthesis, research work was initiated at Central Fuel Research Institute, Dhanbad, at pilot plant scale during the early sixties. Subsequently, the pilot plant activities around coal liquefaction were shifted to IICT Hyderabad. In 1999, Oil India had set up a gasification pilot plant for 25 Kg/day at Dhuliajan. IOC had set up a pilot plant for gasification recently (Ref. 81). Many laboratories and research institutes are also working in smaller scale on different aspects of coal gasification, syngas purification and catalyst development etc.

PDIL Sindri was very active in developing catalysts for shift reaction and processing high ash coal in their Research facility at Sindri. Even during the early sixties many such catalysts were developed and many of them were commercialized. Today, there are several laboratories including National Chemical Laboratory, IITs and the recently started National Centre for Catalyst Research in IIT Chennai which are quite active in developing novel catalyst systems for different applications, including coal and syngas conversion.

India's first IGCC demonstration unit has been operating since 1988. Based on this experience, a plant for 100 MW was also considered by Govt. of India to be set up by BHEL. This proposed IGCC plant was based on the Pressurized Fluidized Bed (PFB) concept and was ideally suited for the high ash (35% to 45%) Indian coal. Since there was not much international experience available with PFB, BHEL R&D facilities were used, for arriving at the design of the ~100 MW plant (Ref. 82). The feasibility was established but the plant has not come up yet.

Prior to this, a joint study was carried out by CSIR India and USA in 1991. It was decided to set up demonstration units during 8th and 9th plan. It was proposed to replace natural gas by coal gas, through installation of coal gasifiers in the Combined Cycle plants for smaller units (20 to 100 MW) and installation of IGCC for new units of 300 MW during the 10th plan (2002 to 2007). However, nothing much has happened in this direction for the introduction of IGCC technology (Ref. 83).

During mid-90s, Indian Oil, GAIL and Indian Institute of Petroleum started working with AMOCO to introduce DME in India. The plan was to bring DME from Qatar for seeding Indian market by 2004. This was the time, when DME had just started getting attention around the world. China also had a similar tie up with AMOCO at that time.

Plasma is a comparatively new route for gasification and India has an operating plant based on this process, near Pune, with imported technology. The Facilitation Centre for Industrial Plasma Technologies (FCIPT), Institute for Plasma Research, Gandhinagar is also quite active in utilizing plasma to dispose medical and other waste. They have already established credibility in developing systems for hospital waste management. They are able to design small scale (15 to 20KG/Hr.) gasifier for MSW (Ref. 5). With the operating experience of the Pune unit and support from Institute for Plasma Research, it should be possible to put up a pilot plant to establish the technical and commercial feasibility for production of methanol from biomass, low grade coal or municipal waste using Plasma processes.

On production of methanol or DME directly from syngas, at this moment there is no decent capacity plant in any research establishment in India. However, most of IIT's and other research centres are exploring many novel options for the process and catalysts for syngas conversion to chemicals.

In the area of In situ gasification and underground gasification, Indian R&D had been very active and several agencies have been working in this area. However, this is yet to be fully exploited for commercial benefits (Ref. 84).

On utilization biomass and generation of renewable energy, Govt. of India has drawn up an exhaustive R&D programme for 11th Plan period (Ref. 85). This list covers almost all the areas of Technology development for utilization of biomass. However, this list does not cover methanol or DME production via gasification and syngas production.

There are many laboratories working on production, storage and utilization of hydrogen. A list of all the R&D activities in this area and the research organizations working on different projects is available in the report by Govt. of India (Ref. 86). The thrust area is to generate hydrogen from renewable resources. This activity could be easily linked with carbon dioxide reforming for production of methanol and DME. This strategy will not only help to reduce carbon dioxide emission but also produce valuable fuel. It is worth looking into this possibility of putting up a pilot unit by integrating hydrogen production from renewable resources and available carbon dioxide to produce methanol.

Indian Oil and Gas Sector has a good R&D track record for improving upon the imported technologies as well as developing technologies which could compete with the best available in the world. Also our Universities, Research Institutes and IITs are able to conceptualize and demonstrate novel technologies in laboratory scale. However, the main problem is the proper integration between different groups for the complex multidisciplinary projects. We need to establish mission oriented projects with full thrust and commitment from all stakeholders. An overview of Indian R&D in Oil and Gas Sector and the different ongoing projects is available in a recently published report (Ref. 87). It is seen that Indian R&D groups in the Oil and Gas Sector are working in almost all contemporary areas related to low carbon energy.

We have seen that there several technologies are available for gasification for pulverized coal. Among them Entrained bed or fluid bed gasifiers are gaining popularity because these gasifiers can deliver clean tar free syngas. With this experience of handling of high ash coal gasification, it may be possible at least to design a medium capacity Demonstration plant for syngas and methanol/DME production. The ash fusion point could be manipulated and the ash content could be moderated by adding Petcoke with high ash coal.

4.5.1 NEW DEMONSTRATION PLANT DESIGN.

In view of the recent developments in syngas, methanol and DME production, particularly on the feedstock selection, technology and syngas conversion we need to build and operate few Demonstration plants to develop indigenous capability. In all these three areas as well as catalyst development for different chemical conversion processes, there are significant developments in recent times. In this section an attempt has been made to identify few promising areas and where Indian R & D has the capability to design suitable demonstration plants.

4.5.1.1 BIOMASS TO METHANOL/DME

With India's experience in biomass combustion and the information available from the technology suppliers for gasification and gas cleaning, it is possible to design and operate a demonstration plant in India via gasification with oxygen and subsequent methanol/DME production. This plant could be designed with maximum possible flexibility as regards feedstocks, so that varied types of feedstocks could be tested and operating issues and economics could be estimated for different feedstocks.

4.5.1.2 PLASMA GASIFICATION OF BIOMASS

India already has some experience in operating a Plasma gasifier for power generation from MSW with air for gasification. At present the syngas from this Plasma gasifier is further burnt to generate power. It may not be difficult to design a suitable capacity demonstration plant for production of syngas for methanol/DME using oxygen as the oxidizing medium. During design stage, flexibility could be ensured so that any type of available feedstock can be tested. Indian capability for designing Plasma Arc furnace could be used to develop the design, else the gasifier can be imported.

4.5.1.3 CARBON DIOXIDE HYDROGENATION

Since this is another very promising route and India depends more on coal based power as well as chemical production, this route of carbon fixation and chemical production will be very attractive for India

It is reported that India has about 10,000 MWe of geothermal power potential, but excluding some direct use of the heat energy, no power plant is working with geothermal energy. Different orogenic regions are – Himalayan geothermal province, NagaLushai geothermal province, Andaman Nicobar Islands geothermal province and nonorogenic regions are – Cambay graben, Son NarmadaTapi graben and few other locations (Ref. 161). For Demonstration plant, one of these locations could be chosen or other industrial source of hydrogen and carbon dioxide could be selected. Technology could be outsourced or developed through pilot plant studies.

4.5.1.4 LIQUID PHASE DME PRODUCTION FROM SYNGAS

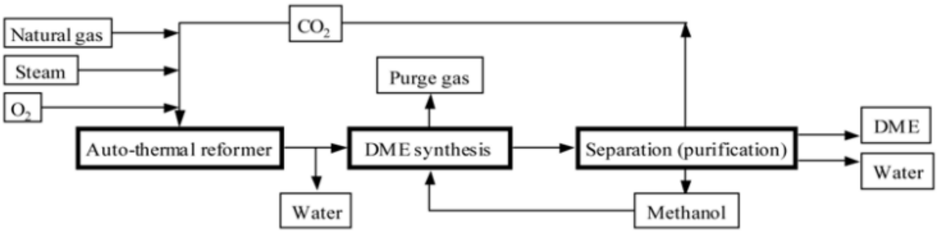
In this emerging process, the syngas is reacted in a slurry phase reactor in presence of powdered catalyst. This reaction takes place at moderate temperature and pressure. The most important feature is that unlike the conventional methanol reactor where the hydrogen to carbon monoxide ratio has to be closer to 2 and tolerance of the carbon dioxide concentration is low, this liquid phase process can handle H_2/CO ratio from 0.5 to 2 (Ref. 41). It is claimed that the liquid phase one step DME synthesis can tolerate any amount of carbon dioxide with syngas. Both these features and the simplicity of the synthesis process are most suitable for small scale DME plants using available syngas, where not much needs to be done to adjust the H_2/CO ratio or to remove the carbon dioxide, which is often an expensive step (Ref. 91).

This route offers low pressure methanol production with less stringent limitation on syngas composition as well as the hardware is simple. Only the novelty is in the catalyst formulation. It may not be very difficult to develop a catalyst and technology, in near future.

In recent times this route is getting lot of attention particularly for biomass gasification and syngas utilization. It is observed that biomass gasification and single step DME production is a more economical solution than using the syngas for power production (Ref. 92 & 93).

A simplified flow sheet of direct DME synthesis is shown in Fig. 8.

Fig: 8. Simplified Flow Sheet for Direct DME Synthesis



Source: Ref. 41. Direct Dimethyl Ether Synthesis, Takashi Ogawa_ et. Al, Journal of Natural Gas Chemistry, 12 (2003) 219 to 227.

CHAPTER 5. PROBLEMS & ISSUES TO BE ADDRESSED

From the foregoing sections, the following issues are emerged which need to be addressed to meet our objective to produce methanol/DME by eco-friendly and economic means.

1. At present, India has huge shortage of methanol in the country, therefore, the question of producing DME in those plants is rather difficult.
2. Majority of the units for methanol production are gas based and due to shortage of gas availability, industry is exploring coal based units for methanol production.
3. India has many coal based thermal power plants and several of them are using modern gasifiers but practically none of them are operating under IGCC mode, although some of them are operating with combined cycle. Hence there is no availability of syngas from these power plants.
4. India has a large number of small and medium size biomass gasifiers, which operate for generation of power or heat energy. Only few large biomass co-gasifiers have come up recently for producing power and few of the smaller ones are operating via gasification.
5. India has a large number of micro to medium size anaerobic digesters which produce methane rich gas. This biogas is generally used for lighting or directly for combustion. It is possible to divert the surplus gas for gasification and DME production, provided sufficient quantity of such gas is available.
6. Refineries in India have an ever increasing demand of hydrogen and this is met by natural gas or naphtha reforming. There is a possibility of producing methanol from these plants provided surplus syngas is available.
7. Most of the refineries produce some disposable residue and many of them make Petcoke, which is sold. There is a good case to use this coke and residue for production hydrogen and syngas for methanol production. However, very often the total availability of feedstock is lower than the desired economic size for IGCC plant. Some large refineries are now planning for coke based IGCC plants to dispose the coke and residue and to produce hydrogen and or methanol. Another good option is to co process Petcoke and high ash coal together for large methanol plant.
8. The coke oven and blast furnace gases from steel industry contain hydrogen and carbon monoxide respectively. Most of them are currently used for

heating within the plant itself. If economics permit these could be utilized for methanol production.

9. Technology to produce hydrogen from the quenching section in steel plant by Thermo Splitting of water is available indigenously. This is a novel technology. This could provide a good source for hydrogen (Ref. 76).
10. Traditional chlorine production by electrolysis is associated with hydrogen generation, which does not have much use by the chlorine industry. However, many of them produce hydrochloric acid.
11. Indian urea production is also short of the demand which is met by import. Moreover, typically the urea plants produce hydrogen rather than syngas, although syngas is available as intermediate. It may not be feasible to divert syngas for methanol production (Ref. 89).

The economic feasibility and technical viability is the prime issue. An attempt has been made in the subsequent sections to consolidate the available information which may help in decision making process.

5.1 ECONOMIC FEASIBILITY AND TECHNICAL VIABILITY FOR PRODUCTION OR DEMO PLANT

5.1.1 COMMERCIAL PLANT FOR POWER, METHANOL / DME FROM INDIAN COAL

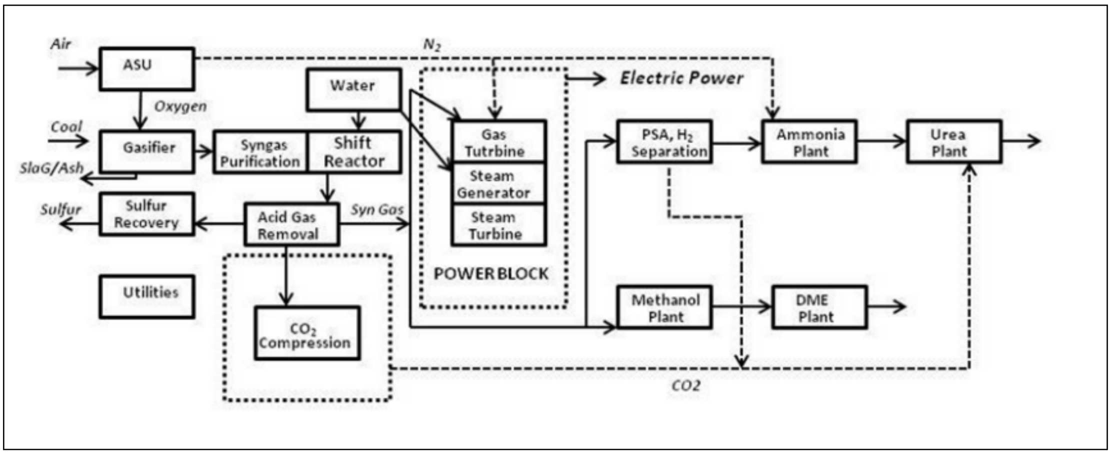
For large scale plants, technical viability, even utilizing Indian coal, is really not an issue although we do not have much experience. There are many proven technologies which can handle high ash coal, and India also has experience in IGCC at least at one plant. In terms of economic viability, this is feasible if the capacity is large enough. It may be noted that India had been considering IGCC for power generation for many years but no concrete development had taken place so far. It is expected that a few plants will soon come up based on coal or petroleum coke. Probably none of these plants are designed for production of methanol. However, hydrogen production is on the agenda in some cases, along with power production. The hydrogen is important because most of the large IGCC plants are under consideration by large refineries, which would desire to produce hydrogen to reduce the usage of naphtha.

With the intention of producing methanol in large scale from Indian coal, we may consider large IGCC oxygen based plant for power generation and methanol/DME and /or Fertilizer production. This strategy will have two benefits, namely, the capacity of the plant could be adequate to be economical, and the concentrated carbon dioxide from the unit could be easily captured if required, in future.

IGCC with electric power and methanol /Urea co-production is an attractive option, although it is sensitive to the selling price of methanol and Urea. The provision for carbon dioxide capture requires additional investment and the cost of power generated goes up but it is compensated if the carbon Tax is considered, making it economically viable (Ref. 3).

A simplified flow sheet for a large complex for production of methanol/DME, Ammonia/Urea and power is shown in Fig. 9. It may be noted that barring the slag from the coal ash practically no other major pollutant is generated from this complex.

Fig. 9. Block Flow Diagram for Coal Based Power, Fertilizer and Methanol Complex

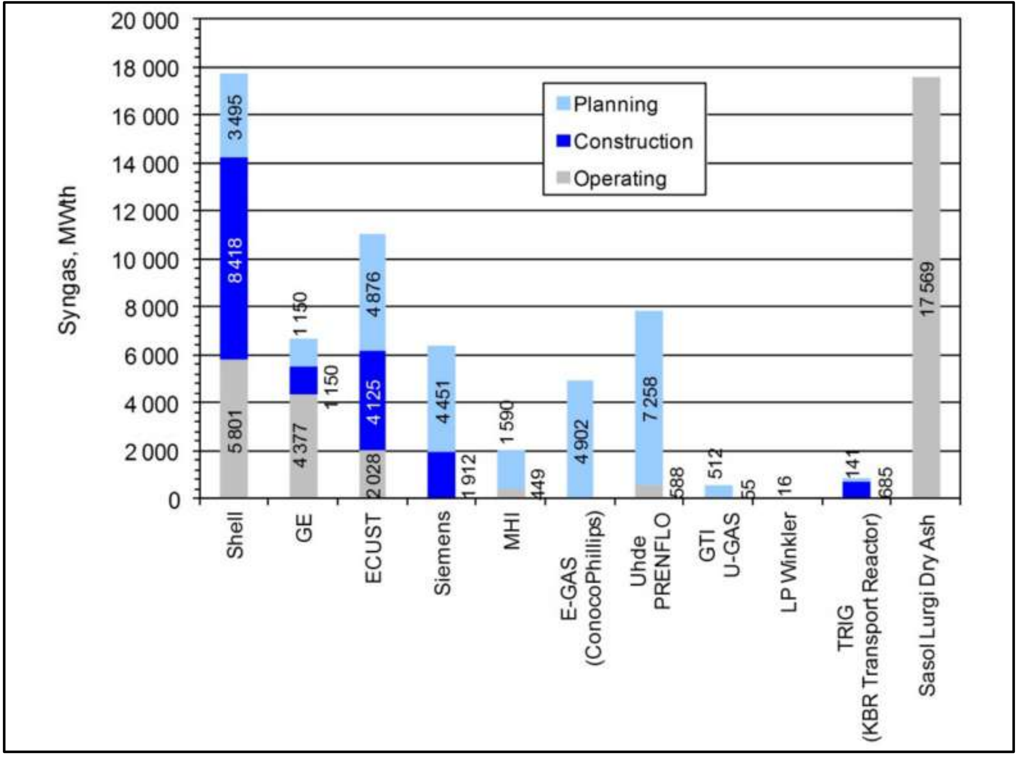


Source: Ref. 3. Production of Electric Power and Chemicals in a Carbon Constrained Environment Guido Collodi.

Regarding the availability of Technology there are many licensors actively participating in several new projects. The Technology suppliers for different operating and upcoming units, clearly indicating that there is no dearth of technology availability, as illustrated in Fig. 10.

Fig. 10: Technology Licensors for Gasification & Syngas Manufacture

Total capacity of reactors using coal as the main fuel, breakdown by technological groups (current and forecast by 2016).



Source Ref. 103. Cost estimation of coal gasification and motor fuels, by Marek Sciazko and Tomasz Chemielniak.

Regarding economically viable capacity, a comprehensive study was carried out by Marek and Tomasz, (Ref. 103) where they have considered several options as summarized below:

a. Only at about 5,600,000 TPY coal consumption to produce 1 mil. Tons of liquid fuels such as Propane and FT Diesel, the plant starts to be profitable. The investment is of the order of 230.7 Thousand US $/ Ton /Day of coal processed. This unit includes the carbon capture and sequestering with oxygen Firing and power generation through steam turbine (Combined Cycle).

b. The economically feasible capacity for single point delivery for hydrogen production is about 500,000 TPY coal processed. The investment cost with all other features the investment is of the order of 306.2 Thousand US $/ Ton /Day of coal processed.

c. For production of methanol also the economic capacity is 500,000 TPY but the investment cost for similar installation as above is little higher, about 314 US $ Thousand US $/ Ton /Day of coal processed.
d. Polygeneration of both power and methanol from either of the two identical gasifiers, with total capacity of about 500,000 TPY becomes economically feasible. These units operate in IGCC mode. This option adds flexibility since the plant can easily be switched to power or methanol production depending upon the selling price and demand levels.

This estimate is based on 2008 US $. However, this is a preliminary estimate and the accuracy is only about +/- 30%.

As compared to IGCC based power plants, the polygeneration plants having option for producing both power and methanol/DME are more economically attractive, particularly when carbon dioxide emission is to be controlled. Part of the carbon dioxide produced during gasification and shift reaction is used within the plant for reforming and delivered along with methanol, as in the case of other units producing FT diesel or methanol only.

While using Indian coal, there are several issues. Most of the technical issues have been discussed in Section 4.2.1.

There are many reports indicating that compared to power generation from coal even using IGCC, production of chemicals as well as power is more rewarding. Although the investment cost is high, the benefits of reduced environmental penalty and possibility of using low grade coal could justify putting up large coal based plants for power and chemical production in India, with IGCC and carbon capture facility. To avoid long distance transportation of coal, it is desirable to locate such plants near coal mines. However, Government support is required for such a massive investment.

It is observed that the quality of Indian coal is deteriorating with time hence this issue also should be kept in mind before investing in large scale coal based methanol plant. It may be noted that the heating value of the order of 13 MJ/Kg, ie, almost half of the good quality coals used eleswhere and methanol yield will also be proportionately reduced.

It is virtually impossible to have an accurate estimate of investment cost and economic viability since there are large number of variables. Some of these are: Type of feedstock (calorific value, single feed or multi feed), choice of gasifier, capacity of plant, geographical location, strategy of carbon capure, target product (single or multiple) etc. However, an attempt is made to summarise the notional cost of gasification plants for different feed and configuration in Table 18.

Although there is wide variation but it could give some general idea. The cost figuires are rounded up and should be considered only as indicative.

Table.18: Investment Cost for Different Feedstocks, Capacity and Products

Feed	Calorific value MJ/Kg	Configuration	Net Power Output Watt Hr/Kg	Alternative products In KG/Ton	Investment cost, US $ per KW or equiv for power production only	Source / Reference
NG	47.3	NGCC	7.2	1255 Kg Me. or 900 DME	718 without CC 1497 with CC, only power	Ref. 120
Coal	22 to 29	IGCC	3	580 Me or 416 DME	2500 without CC 3650 with CC, only power	Ref. 120
Wood biomass or Switch Grass	14 to 20	IGCC	1.3 to 1.7	250 – 325 Me eq.	1327 to 4225 (for equivalent power)	Ref. 121
MSW	5 to 10		0.5	180 M or 140 DME eq.	Only power 2426 without CC	Ref. 105
Lignite	15	Air fired	1 approx		500 MW 750 and 250 MW 1000 in 2011 in India	Ref. 122
NG	47.3	DME via Gasification	384 MW hr.eq , Plant output	67 T Me Eq DME/hr	997 (DME 1000 TPD and Methanol 217 TPD)	Ref. 123

NG: Natural Gas, NGCC: Natural Gas Combined Cycle, Integrated Gasification & Combined Cycle (Oxygen Fired), CC: Carbon Capture

The utility and feedstock consumption for production of methanol depends on the process scheme, feedstock type and export or import of power. Estimated raw material & utility consumptions for production of 1 MT of methanol from different hydrocarbon feedstocks and processes is shown in Table 19. It should be noted that autothermal reformer consumes more gas but exports power with lower consumption of steam and water as compared to that of steam reformer. Therefore, this option is more economical for gaseous hydrocarbon feedstocks. However, these figures are only indicative because the calorific value of coal is varying widely and the purity of methanol is also not fully defined.

Table 19: Feedstock & Utility Consumption per MT for Methanol

Inputs	Per MT of Methanol	Methanol from Coal	Methanol from NG (Auto Thermal Reformer)	Methanol from NG (Steam Gas reformer)
Coal	MT/MT	1.72	-	-
NG	SM3/MT	-	842	795
Oxygen	MT/MT	1.07	0.72	-
Steam	MT/MT	0.168	0.138	0.9 to 0.98
Power	KWH/MT	--	(-) 0.25	65 to 68
Water	M3/MT	15 to 18	4 to 5	6.5 to 6.7

The cost of a large scale IGCC plant based on coal gasification, oxygen firing and carbon sequestering with provision for producing both methanol and power is of the order of 2000 Euro (approx. 1,40,000 INR) per KW of power (Ref. 126) . The overall energy efficiency for coal conversion is about 50 to 55%. With time, the efficiency is increasing due to better design and the investment cost is also reducing. On an average about 1Tonne of coal is required to produce little over 2 MW of power. When I Ton of coal is converted to methanol or DME via IGCC, about 500 Kg of methanol or 350 Kg of DME is produced. Most of the IGCC based methanol plants also produce some power for its internal consumption and some surplus for the grid. The investment cost depends mostly on the location, feed characteristics and the plant sophistication level. There is wide variation in product mix, technology selected, operating and emission control strategy, feedstock type etc.

In Assam one gas based plant for 500 TPD of methanol at a cost of 1028 Crores is being considered. However, this plant is based on Natural Gas. West Bengal Government is also considering a plant for producing 1500 Ton of Methanol per day and fuel gas from Coal.

5.1.2 ECONOMIC FEASIBILITY FOR BIOMASS BASED PLANTS.

A feasibility report was prepared by Envitech recently for 6 MW Biogas power Plants (in 3 Blocks) for 135,000 MT/year of manure and agricultural residue/forage crops. About 45 million KWh Green power exported to the grid plus solid and liquid Fertilizer for fertilizing 72 Hectares. This plant would cost about 10 Million Euro (approximately Rs. 100 Crores) (Ref. 111).

It is expected that the share of biomass in the world will soon be of about 60% of the renewable power produced, which will be about 20% of total energy produced from all sources. It is thus worth looking into this option to produce renewable electricity. This electricity could be used to generate hydrogen for conversion to methanol with carbon dioxide. Both these technologies are available, and the cost is much lower with all the associated environmental benefits (Ref. 112).

The production of biogas by anaerobic digestion (Biomethanation) is the cheapest way to convert a major portion of organic wastes. Therefore, before using the biomass for gasification, possibility of conversion to biogas through Boimethanation must be explored. Use of this biogas for power generation or methanol production however depends on the overall economics.

Biomass gasification is more versatile than biogas production, since this route does not require specific types of biodegradable materials. A plant would produce syngas via gasification followed by methanol to Gasoline section. Assuming the cost of the methanol to gasoline section is about 20% of the total investment, the investment for processing 2000 TPD Biomass is of the order of 350 Million US $ (Approximately Rs. 2,500 Crore) . The rate of return for this plant producing synthetic Gasoline is difficult to estimate since IRR is sensitive to the Gasoline selling price. All the associated assumptions and estimates are available in this report (Ref. 113).

In another estimate it is seen that a processing plant of 4000 Kg/Hr for MSW and other Biomass producing about 2,300 KWH energy, will cost about Rs. 38.5 Crores for power generation via syngas. Although this plant will produce Producer gas, it will not use oxygen and will not have any facility for Shift reaction or methanol synthesis reactors (Ref. 116). However, for this scale it is possible to use liquid phase methanol reactor where there could be significant reduction in cost. In liquid phase synthesis the separation of carbon dioxide and Shift reactor may not be required. The only addition will be a liquid phase methanol reactor and air separation unit. Therefore the cost for a methanol plant will not be much more than that of the power plant. In general the additional cost for ASU and methanol reactor adds up to about one third of the base cost (Ref. 103).

It is clear that a small plant for methanol production may not be very economically viable. However, when we focus towards waste management, it is worth considering and could be compared with the normal practice of producing energy. In India our waste usage is much lower than the world standard. Assuming about 30% additional cost for a waste to methanol plant over the combined cycle power plant, we can at least set up few demonstration units within the country. With liquid phase methanol synthesis, it may be possible to develop a small capacity viable unit for methanol production from bio waste. There will not be much feed pre-treatment or gas post treatment. There is strong justification for an indigenous research project for development of such a Pilot unit with conventional gasification as well as plasma based.

5.2 SUSTAINED SUPPLY OF FEEDSTOCK

Availability of coal in large quantity for mega scale and IGCC plant with power and methanol production is not a problem, particularly if it is located near the mines. Transportation over a long distance not only adds to the cost but also risks interruption during transit. The issue is that the plant has to be matched with the demand in the surrounding area. If methanol is produced along with power this will provide better flexibility to balance the demand and production between power and methanol or DME.

Currently, there are not many large biogas plants in the country to supply adequate quantity of biogas for reforming and methanol/DME production. However, as discussed earlier, large dedicated biogas plants may be considered for conversion to syngas and methanol/DME.

Regarding MSW, the most important is the development of proper collection system. Both for biomass and MSW, seasonal variation has to be taken into account to ensure the sustained supply of feedstocks at reasonable cost.

For immediate DME requirement, sustained methanol supply will not be an issue since it is likely to be available in the market and it does not take very long time to set up dehydration plants.

5.3 SCALE OF FACILITY OR DISTRIBUTED SMALL SCALE UNITS

Due to the fact that India has a large gap between methanol production and consumption, large mega plants are necessary not only to reduce dependence on import but also for supply security. Currently our methanol demand is largely as intermediate feedstock, but with widespread use of methanol and DME, our energy security will also be an issue. We are already vulnerable, and this will further aggravate when the conventional transportation fuels produced from the refineries is replaced by methanol/DME. Although mega methanol plants would be based on Fossil fuels, the possibility of carbon capture and sequestering will play a big role towards its preference as transportation fuel.

Biomass and MSW based gasification plants must be geographically distributed to overcome the logistical challenges of transportation and handling. Large or medium size cities can provide adequate quantity of feedstock for economic sized methanol plants (after considering all the environmental benefits). Also the city itself will provide a ready market for the product if methanol/DME consumption develops, as expected.

For smaller areas, only in a few cases nearby areas can join for supply of MSW and waste biomass for gasification, but this again has to be evaluated against the power generation vs. methanol production benefits, due to the lower investment for power production.

5.4 SPECIFIC ISSUES FOR ECONOMIC & FUEL SECURITY

The profitability of operating a production unit and the necessity of the country very often does not go hand in hand. Presently we are having easy availability of imported methanol with the price of about 15 to 20 Rs./Kg (equivalent to about 2 lit of gasoline). Again with the coal price between Rs. 3500 to 4000 per Ton the commercial incentive for a coal based methanol plant with low grade Indian coal is rather low. However, if the fuel security is kept in mind, the financial incentive has to be compromised and state has to come forward to move such major investments.

The average cost of methanol plant is between US $ 500 to 700 /Ton per year of methanol from natural gas via reforming (Ref. 115). This is equivalent to about 0.6 KW power plant. The cost for production of methanol from biogas will also fall in the similar line since biogas is practically methane. It is worth exploring the possibility of producing methanol from biogas, generated for large scale digesters.

This will be a low cost option as well as the methanol will be from renewable source. The investment cost in this case is about half to one third of that of the solid fuel based gasification plants. In a recent report for new wood based methanol and power plant for 1000 T wood gasification per day, producing about 320, TPD methanol and power per day the investment cost mentioned was US $416 Mil (INR 2,900 Crores approximately) (Ref. 47).This cost is much higher as compared to a power plant for 1000 TPD biomass to power plant even by gasification which, on the higher side, may be up to INR 1700 Crores.

The cost of 200 to 400 KT/Yr methanol plant based on biomass and waste is of the order of Euro 300 to 500/Ton depending upon the scope of the project and feedstock type (Ref. 28).

An estimate for a 115 tons DME per day from dehydration of 165 Tons of methanol will cost about INR 40, Crores (Ref. 90).

On an average the cost of coal to methanol plant along with power is about 5000 US $ per KW equivalent for average quality of coal, with carbon capture. The expected cost for high ash Indian coal it could be even more. Therefore, it is not at this point economically feasible to jump to a mega methanol plant on high ash Indian coal. Since it is essential for National fuel security and carbon neutral fuel production, such venture should be undertaken. In addition, some demonstration units could be considered to test new gasifiers for successful application with high ash non caking coal.

5.5 AVAILABILITY OF TYPES OF BIOMASS IN INDIA

The biomass production and its current handling have already been covered in Section 4.3. This source is practically unused in India for production of value added chemicals. About 20% of our liquid fuel needs could be met through local production of small scale bio methanol plant. As such it may not look economically very attractive to convert this waste to methanol/DME. However, considering the dual benefits of totally carbon neutral or even carbon negative liquid fuel production and smart management of mounting bio waste being generated in the country, such projects could be commercially viable with some push from the State.

5.6 PRODUCTION & DISTRIBUTION COST OF METHANOL & DME

In the previous sections we have discussed the production cost of methanol for different feedstocks. The production cost of DME could be different depending upon the production scheme. The conventional route for dehydration of methanol either in standalone facility or located in the existing methanol plant, will be similar. This cost is easier to estimate depending upon the capacity and the technology. Not much information is available on the dehydration plant but it could be extrapolated from similar dehydration plants in chemical industry. The other route is the direct production of DME from syngas. From most of the limited available information it seems that the investment cost for direct DME production is similar to equivalent capacity methanol plant. Due to the uncertainty of future of DME and surplus methanol availability in the world there are not many direct DME plants excepting few in China, Japan or Korea. In several countries the preferred option is to have a mega complex for production of fertilizer, methanol and power to neutralize the market forces for the changing prices of these products.

In India the situation is quite different. There is shortage for power as well as methanol and the fluctuation of power tariff in India is controlled, dedicated methanol or DME plants could be considered. The choice is between dedicated methanol plant and dehydration plant for DME or only dedicated DME plant has to be made depending upon the national strategy of introduction of DME in the country.

Regarding distribution and transportation of methanol and DME there is no special issue since methanol can be transported as blend with gasoline to the fuel delivery point and DME could be handled in similar fashion as LPG. Only for substitution of diesel, the diesel engine fuel handling system has to be modified but the delivery of neat DME to the fuelling station will be similar to the LPG handling infrastructure. No significant additional cost in distribution is envisaged.

Unlike large scale liquid fuel production facilities (refineries or methanol plants) where the products will have to be transported to the user point which sometimes quite cost intensive, the bio methanol or DME offers a significant advantage since it could be produced in smaller scale, close to the user, thereby reducing the cost of transportation.

5.7 RETROFITTING OLD EQUIPMENT TO PROCESS NEW FUEL

The question of retrofitting old equipment to process new fuels is rather difficult in India. All the methanol units in India are natural gas or naphtha based and chemical is produced via steam reforming. The only possibility is to co-process available biogas or off GASES from refinery or steel plants to reduce the usage of natural gas. As indicated earlier there are also not many coal based fertilizer plants in India. The power plants typically are air fired. As such these plants are not very much suitable for methanol production. Also with the shortage of fertilizer production capacity in India, the scope of utilizing the spare gasifier for methanol/DME production is also limited. It may be worthwhile to consider some of the proposed coal based power plants to use oxygen fired gasifier and part of the syngas is diverted towards methanol /DME production system. This will not only generate low cost DME but also make these plants capture ready, which may justify the additional cost.

CHAPTER 6. SUMMARY & CONCLUSIONS

Methanol and Di Methyl Ether (DME) are emerging as alternative liquid fuels for transportation. During the last few years the use of methanol and DME as fuel has increased significantly. Methanol demand is growing at a robust 6 to 8 % annually. In India, the use of both methanol and DME as fuel component is very low at present. Currently, there is surplus production of methanol in the world but the demand in India is much more than the indigenous production, due to its use and feedstock for other chemicals.

Unlike Gasoline or Diesel which are mostly produced from petroleum crude, methanol and DME could be produced from renewable sources, such as biomass via syngas or via reforming of biogas. With the increasing concern about GHG emission from energy usage, the fuels produced from renewable sources are increasingly favoured over the non-renewable sources. From biomass virtually carbon neutral fuel is possible to be produced.

The availability of biomass resources is much lower than the total demand of fuels. It is estimated that about 20% of the fossil based fuel is possible to be replaced with biomass. To sustain the increasing energy demand in the developing countries, dependence on fossil fuel will remain for many years to come, till viable renewable energy is available and delivered to the user. The current trend in the world is to have more focus on capture of carbon dioxide if fossil fuel is used for production of methanol/DME.

In India all the methanol plants are based on natural gas or naphtha. Although there is great demand for methanol in India, the availability of natural gas and price of naphtha along with the low import price of methanol, is preventing the building of new plants. There are several proposals for putting up of large methanol plants from Indian coal and also from petroleum coke.

The utilization of biomass in India is not very well organized. Much of this is burnt as such in several biomass to power plants based on complete combustion mode. Since Late 90’s several gasification units were operating in India based on gasification technology developed by Indian Research groups. These were small units producing as low as 20 KWH energy. So far in India, only generation of power was considered from biomass. Production of chemicals was never in the agenda.

Although India is having many biogas plants through anaerobic digestion, most of them are small capacity and in most cases cater the local requirements at a very low investment cost. It may not be worth to consider this segment for methanol or DME production.

The technology for all the possibilities for production of methanol & DME based on coal or other hydrocarbon feedstocks are available locally or from overseas licensors. Even if some of these technologies are not fully matured, particularly for small scale gasification and chemical production, demonstration plants could be designed and operated.

There are several emerging technologies in the area of methanol/DME production. The most promising is the use of plasma arc for gasification. India is in an advantageous position in this technology because India has an active Research and Technology Group to promote plasma technology for waste disposal as well as there is an operating plant for gasification of MSW. A Pilot unit can be set up to test the suitability of different feedstocks for gasification with oxygen and subsequent conversion of the syngas to methanol/DME in liquid phase reactor.

To meet the objective of carbon neutral production of transportation fuels, several new options are being considered. Most of these possible options are in the laboratory or in the concept stage. For the larger time frame and future technology development, Indian R & D could be encouraged in working in the following emerging areas:

Development of catalyst and process for:

- ✓ CO_2 methane reforming - for biogas conversion
- ✓ CO_2 hydrogenation to syngas and single step DME from syngas
- ✓ Dual function catalyst for single Step DME Synthesis.
- ✓ Methanol synthesis catalyst for syngas with high CO_2 concentration
- ✓ Catalyst for gasification of biomass
- ✓ Chemical looping & oxygen carrier
- ✓ Ongoing Research activities in India for direct hydrogen production from Sunlight could be linked with the proposed R & D activities for methanol/DME synthesis from carbon dioxide and hydrogen
- ✓ Development of Larger Scale Plasma Gasifier, and many more

From this foregoing discussion we can converge on the following road Map:

1. Setting up a methanol dehydration plant in an operating methanol plant or as standalone unit for production of DME to cater the immediate requirement.
2. Installation of at least one large scale coal based IGCC with co-production of methanol, and power, with carbon capture.
3. If coal bed methane is available in reasonable quantity, appropriate capacity reformer based methanol/DME plant may be considered.
4. At least one each demonstration plant for biomass (agricultural waste) and MSW based gasification for methanol/DME production with conventional and proven gasifier technology could be considered. This will help us to establish the holistic benefits for waste to methanol production.
5. Plasma gasifier could be considered for at least one demonstration or Pilot unit at present. This may work out more economical for small scale power and methanol production or even single step DME production in smaller scale from very low grade feedstocks.
6. R & D facilities for carbon dioxide hydrogenation in pilot plant scale and possible integration with renewable hydrogen production related R & D projects.
7. Catalyst development and Pilot plant for single step liquid phase DME production from Syngas.
8. R & D programme in development of chemical looping for gasification without air separation unit.
9. To pool all the available domestic resources for gasifier technology, operating experience and research laboratories to participate in the movement for biomass conversion to synthetic fuels.

The investment cost of production of methanol or DME will be higher for both fossil fuels and, biomass than that of importing methanol at present. Therefore, Government support is required to move in this direction. This will not only help India in ensuring energy security but also managing the countries growing bio waste and associated environmental impact.

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