DEVELOPMENT OF DIMETHYLETHER (DME) SYNTHESIS FROM NATURAL GAS AS AN ALTERNATIVE FUEL IN JAPAN

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1. INTRODUCTION

DME (Dimethylether, CH3-O-CH3) is a clean clear liquid produced from natural gas and oxygen, having a similar boiling point as that of LPG, allowing much easier transport, storage and distribution than super cryogenic LNG. Such a characteristic may justify utilization of relatively small natural gas resources as well as distribution to relatively small and diversified end users because of much less investment for logistic chain.

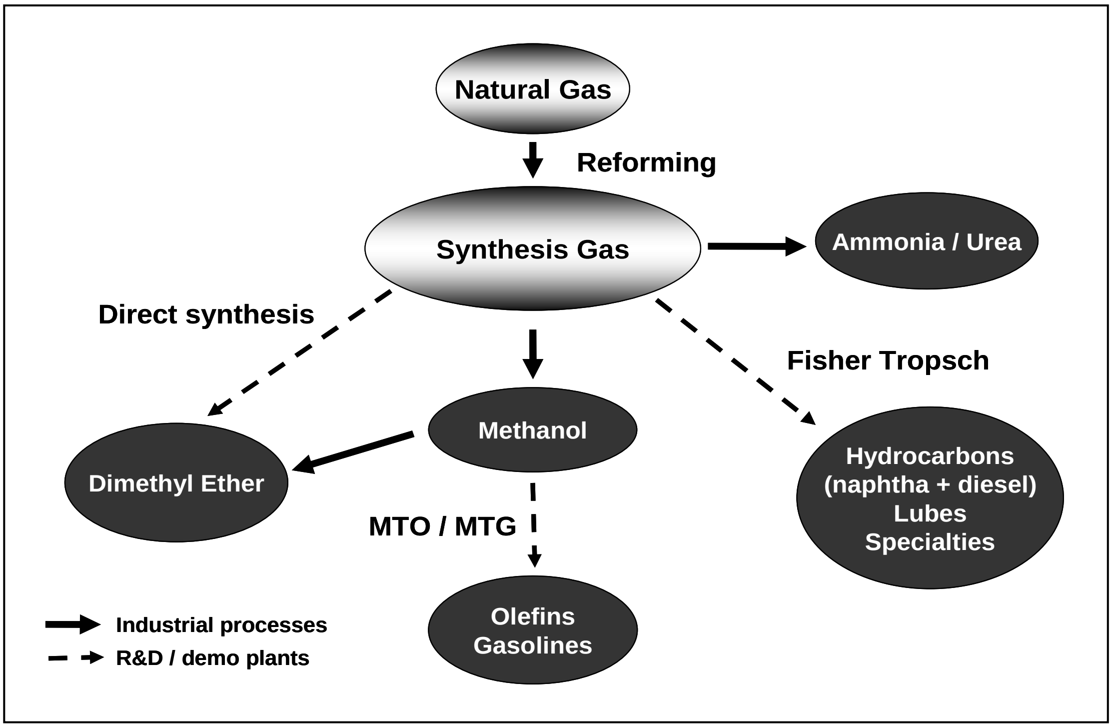
Current world commercial production of DME is very limited, around 150,000 tons per year, only for use as an aerosol propellant mostly for cosmetic use. However, DME has a big potential to grow as a clean alternative fuel, if a large scale production becomes available with a competitive price.

TotalFinaElf is one of the major suppliers of LNG in the world, particularly to Japan, exporting more than 5 million tons annually. However, seeking for development of a diversified application form of natural gas as a clean fuel in the near future, TotalFinaElf has decided to participate in a new development project of DME synthesis technology suitable for a large scale production. This development project has been initiated in Japan last year under a financial support by the Japanese government METI and led by JFE. This paper presents current status of DME development projects in Japan.

2. CHEMICAL CONVERSION ROUTES OF NATURAL GAS TO LIQUID

Since methane, a major component of natural gas, is a chemically stable compound, it is necessary first to go through a high temperature reforming to carbon monoxide and hydrogen before converting it to any type of liquid product. Once natural gas is reformed to CO and H2 (called as *Synthesis Gas*) by reforming with steam or oxygen in a conventional high temperature reforming process, there are three major chemical conversion routes from there as shown in **Figure 1**.

Figure 1 : Gas Chemical Conversion: Gas To Liquid (GTL)



Conversion to methanol is an already industrially established chemical conversion route with a long history, with a number of large scale industrial plants all over the world. Recently, two other conversion routes to liquid products have been developed; namely, to liquid hydrocarbons and DME.

Conversion to liquid hydrocarbons, such as kerosene and diesel, through Fisher-Tropsch synthesis process followed by subsequent refining process such as hydro cracking (GTL in a narrow definition) is now emerging as a commercial process. The products are used mostly for substitution of the conventional transportation fuels such as diesel fuel with a very low sulfur content, and high quality lubricant oils.

Conversion to DME through dehydration of methanol has been an industrial process since many years but only in a small scale industry for the use other than fuel. However, a large scale conversion of natural gas to DME as a clean fuel is now technically made available in one step reaction, and waiting for demonstration test with much higher efficiency than the conventional 2 step process.

3. PROPERTIES OF DME

DME is boiling at -25°C under atmospheric pressure, or at 6 bars at ambient temperature. Comparing with propane boiling at -42°C, this allows utilization of the existing LPG infrastructures with only a minor modification such as replacement of elastic sealants with more DME resistant material.

Figure 2 compares some physical properties of DME with other fuels. It is noted that although calorific value of DME in terms of weight is lower than methane, the same in terms of liquid volume or in terms of gas volume is equivalent or higher.

Figure 2 : Physical Properties of DME & Other Fuels

Properties	DME	Propane	n-Butane	Methane	Methanol	Diesel Oil	Coal
Net calorific value (kcal/kg)	6,900	11,000	10,930	12,000	4,800	10,000	6,400
Net calorific value (kcal/l)	4,620	5,440	6,230	5,040	3,790	8,400	n.a.
Net calorific value (kcal/Nm^3)	14,200	21,800	28,300	8,600	n.a.	n.a.	n.a.
Cetane number	55 ~ 60	5	10	0	5	40 ~ 55	n.a.
Viscosity (kg/ms at 25°C)	0.12~0.15	0.2	0.2		0.7	2 ~ 4	n.a.
Liquid density (g/cm at 20°C under pressure)	0.67	0.49	0.57	0.42	0.79	0.84	n.a.
Boiling point (°C)	-25	-42	-0.5	-162	65	180~370	n.a.

4. POTENTIAL MARKETS OF DME IN JAPAN

There are three major potential markets for DME after a large scale production has become available at a competitive CIF price with LNG. The major potential markets are fuel for power generation, LPG market for household and industrial use, and diesel fuel market for transportation. Advantages of DME over the conventional fuel in each market are illustrated in **Figure 3** and **Figure 4.**

Figure 3 : Major Potential DME Markets in Japan

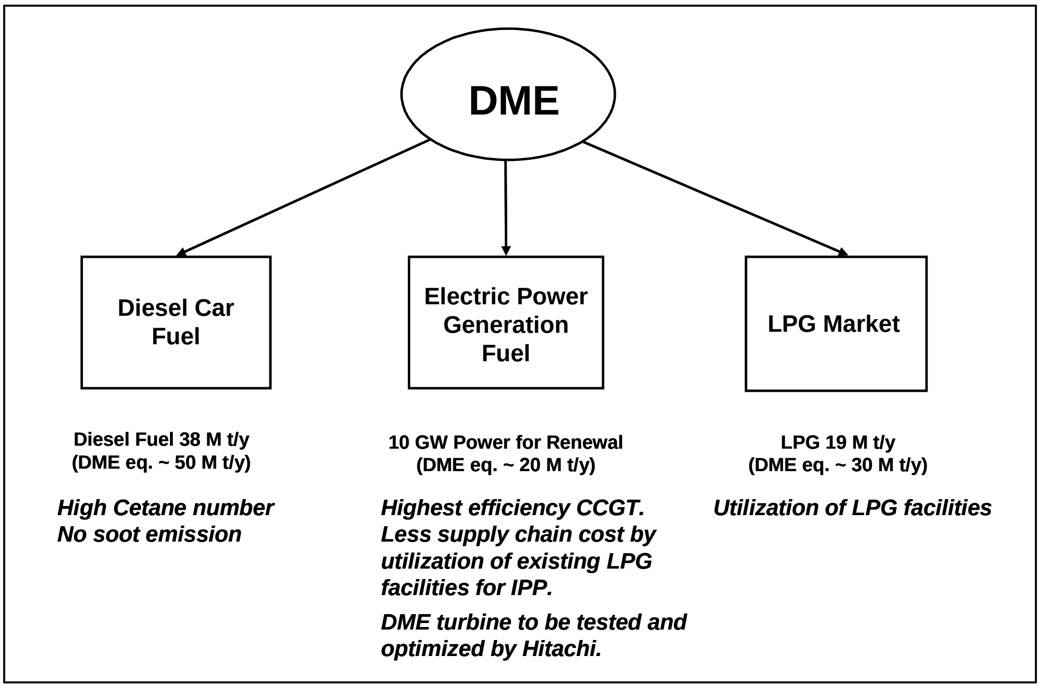


Figure 4 : Comparison with other fuels

- **DME-fired CCGT is most efficient for Power Generation (GE data).**

	DME	Natural Gas	Naphtha
LHV efficiency (%)	51.5	50.7	48.3

- **DME is suited for clean Diesel Car. (Hino / Isuzu / Nissan Diesel)**

	DME	Diesel Fuel
Cetane number	55 ~ 60	40 ~ 55
Soot emission	0	Smoke

- **DME can substitute LPG. (Idemitsu)**

	DME	Propane	Town Gas (13A-1)
Wobbe Index (MJ/Nm^3)	52	81	59
Maximum combustion speed (cm/s)	49	41	38
Stoechiometric air ratio	3	5	2.5

(Normal town gas burner can be used, just with minor adjustment of air intake.)

4.1 Clean fuel for electric power generation.

Use of DME as a clean fuel for power generation is promising by use of a high efficiency gas turbine combined cycle. According to some test conducted by GE(1), DME fired gas turbine showed highest LHV efficiency among other fuels such as natural gas and naphtha. World’s major gas turbine manufacturers like GE, Mitsubishi Heavy Industry and Hitachi are now developing DME-fired gas turbines with a minimal modification of the conventional ones.

For future power generation plants, new construction of nuclear power plants will be more difficult due to the opposition from the population. Coal and oil fired power stations will have to be limited to cope with Kyoto Protocol for reduction of CO2 emission, and will be replaced by the power plants firing more clean fuels such as natural gas or DME which reduces CO2 emission by about 30% from that of coal.

However, Japan is a unique country in that almost 100% of natural gas is imported as LNG from remote countries such as Indonesia, Australia and Middle East, which is economically justified only under a long term, large quantity import contract requiring a large investment. In relatively small and isolated plants remote from a large natural gas receiving terminal, use of DME is considered to be more attractive because of the far less investments required for transportation and storage than those for LNG. Moreover, recent move for deregulation of electric power business in Japan may also favor use of DME because of the same reason of lower investment cost for relatively small IPP and PPS entrants to the deregulated market. Considering a growth of electric power market as well as some renewal of old coal and oil fired power plants in the future in Japan, total potential market of DME in the field of power generation in Japan is estimated to be 10 to 30 million tons in a forthcoming decade (**Figure 5**).

Figure 5 : Market – Fuel for Power Generation

Power Generation Capacity in Japan (10 EPCOs)

Fuel	2001 (GW)	2011 projected (GW)	Δ (GW)
Nuclear	45	62	17 ?
Coal	29	43	14 ?
Oil	46	45	-1
LNG	62	69	7
Hydro	45	47	2
Others	3	4	1
Total	230	270	40

- **DME price to be more competitive than LNG at power plant gate.**
- **Projected demand increase 2001 ~ 2011: 40 GW**

  Nuclear and Coal may have to be replaced by safer and cleaner fuels.
  - Maximum 17 + 14 = 31 GW = DME eq. 60 M t/y
- **Replacement of existing Coal and Oil-fired power stations aged over 30 years:**

  Total ~ 10 GW = DME eq. 20 M t/y
- **By deregulation of power industry, monopoly of EPCOs will disappear, and new IPP and PPS players like Hitachi, JFE, Nippon Oil, city gas companies look at new energies more competitive.**

  IPP capacity of 200 MW (DME eq. 400 kt/y) ~ .
  DME distribution in Japan is as economical as LPG distribution system.

4.2 LPG Market

Fuel for household and industrial use can be a large potential market for DME considering a relatively high price of LPG in Japan, and a possibility of utilizing the existing LPG infrastructures with minor modifications. Japan consumes nearly 19 million tones per year of LPG of which 76 % is imported mostly from Saudi Arabia. Recent CIF price of LPG at Japanese port is about 380 US$/t or 6.4 US$/10^6BTU, which is much higher than estimated DME CIF cost of around 3.5 to 4 US$/$10^6$BTU.

There are already 36 existing primary LPG terminals and 120 secondary terminals throughout Japan for receiving LPG, as well as 4,600 tank lorries and 1,900 service stations constituting a wide distribution network which may be used for DME distribution as well(2).

In **Figure 4**, a comparison of combustion properties of methane, propane, DME and typical Japanese town gas are shown in terms of Wobbe Index (WI), Maximum Combustion Speed (MCP) and Stoichiometric oxygen and air for combustion. Although combustion speed is relatively high, DME has more or less similar combustion characteristics compared to LPG or 13A-1 grade town gas(3).

4.3 Alternative fuel for diesel cars.

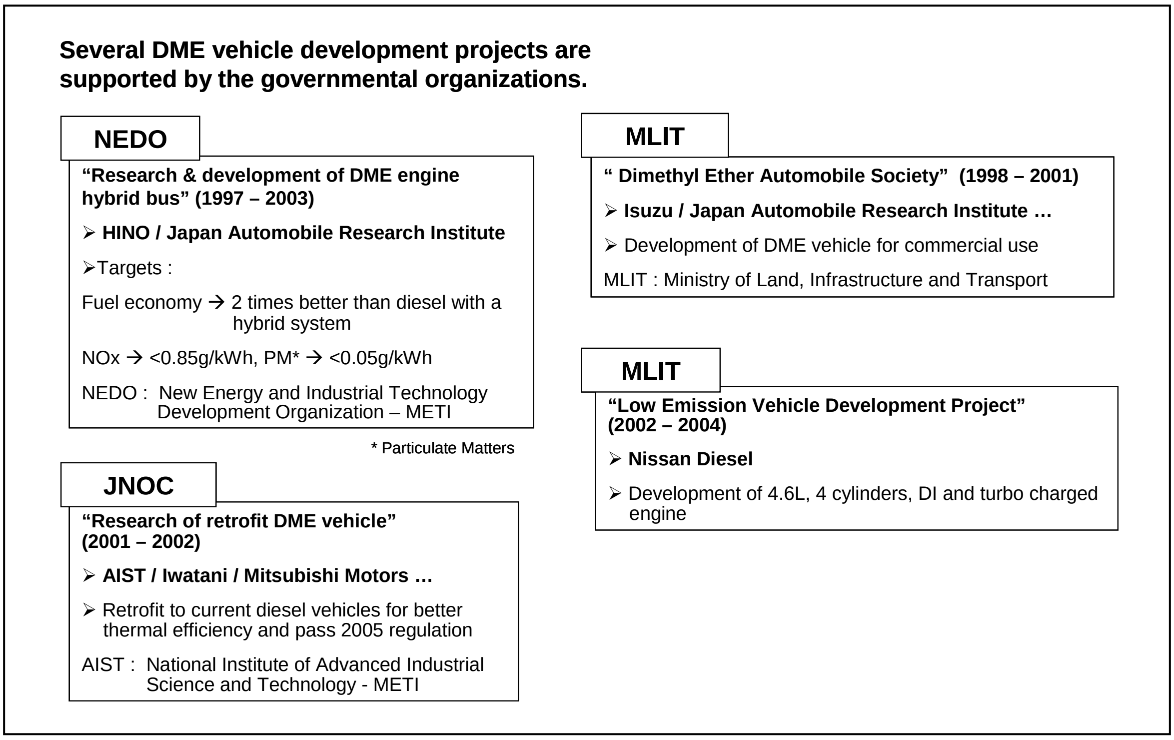
Substitute for diesel car fuel is also promising in view of DME properties such as no sulfur content, no soot emission, and a high Cetane number (55 ~ 60).

Current consumption of diesel fuel for automobile in Japan is about 38 million tones per year, mostly for heavy duty cars such as bus and trucks, having air contamination problem mostly due to soot and NOx emission.

Major diesel car manufacturers in the world are now trying to develop engines suitable for DME with a minimal modification of the conventional diesel engine. In Japan, major diesel car manufacturers such as Hino Motors, Mitsubishi Motors, Isuzu and Nissan Diesel are developing DME driven heavy duty cars under the support by the government organizations such as NEDO(4) , JNOC(5) and MLIT(6) with a target of producing a commercial model by 2006 (**Figure 6**). Required modifications of the conventional engine arise from DME properties such as lower boiling point, increased injection volume, low viscosity and low lubricity compared to diesel oil.

Development of automobile fuel market for DME may take more time than those for power plant fuel and LPG alternative, but once established, the size of the market should be very large.

Figure 6 : DME for Diesel Cars



5. NEW DME SYNTHESIS PROCESS DEVELOPMENT

The current small scale production of DME is using a conventional two step indirect process comprising methanol synthesis and dehydration of the methanol to DME. Those processes are licensed by the licensors such as Lurgi, Haldor-Topsoe, Mitsubishi Gas Chemical (MGC) and Toyo Engineering (TEC).

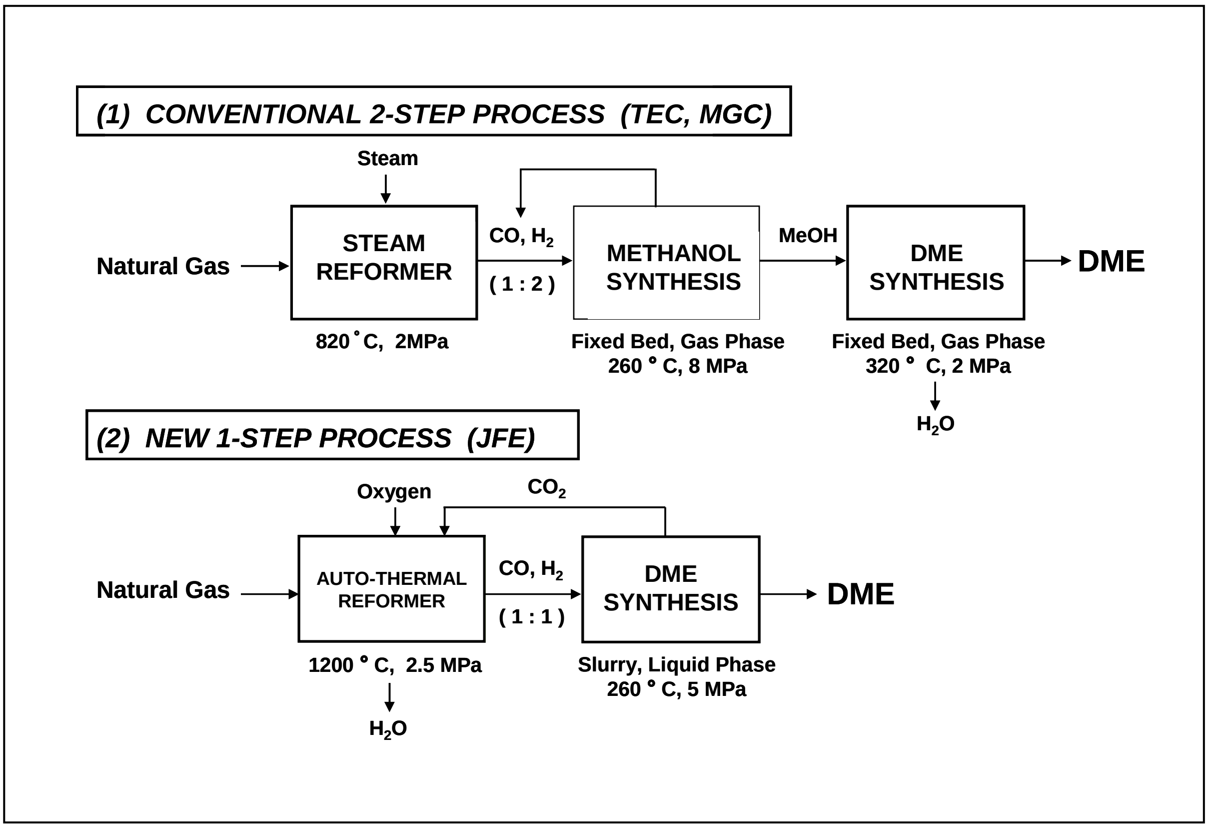
As the price of DME largely depends on the production cost, many efforts have been paid to simplify the process and improve efficiency. A number of one step DME processes have been proposed by such companies as Haldor-Topsoe and Air Products, but none of them have been commercialized yet.

A new one step direct synthesis process suitable for a large scale production of DME has been successfully developed by a Japanese major steel company JFE in a pilot plant of 5 t/d scale in 1998(7). Based on a successful result of operation of the 5 t/d pilot plant, a demonstration plant of 100 t/d scale is going to be built for confirmation of reliability of the process and for obtaining engineering data for scale-up in the next step to a commercial plant of 3,000 t/d order to be built by 2008 as a target.

The features of the process are in a proprietary catalyst having active sites deposited on one carrier for methanol synthesis, dehydration of methanol and shift reaction for converting produced water to CO and hydrogen, and a process using a slurry liquid phase bubbling tower type reactor with the catalyst particles finely suspended in a solvent, into which a mixture of CO and H2 gas is injected and bubbles up to the top of the tower, during which above three reactions takes place simultaneously.

A block flow diagram in **Figure 7** illustrates difference of the new process from the conventional one. The reaction is highly exothermic, and the heat is recovered as a medium pressure steam through multiple boiler tube bundles inserted in the liquid phase of the reactor. The bubbling tower reactor with catalyst slurry has advantages of relatively easy scale-up, easy removal of reaction heat, and continuous catalyst replacement. As the result of the reaction, CO2 is produced which is recycled back to the Auto Thermal Reformer in which CO2 is converted to CO.

Figure 7 : New 1-step process is proposed for DME production.



6. JFE-DME PROJECT BY DME DEVELOPMENT INC.

A consortium led by JFE with participation of 8 major Japanese companies – Toyota Tsusho, Hitachi, Idemitsu, INPEX, Japan LNG, Marubeni and TotalFinaElf, as an international oil and gas major, established a joint venture company named DME Development Inc. in late 2001 for execution of a 5 years development program of construction and test operation of a 100 t/d demonstration plant of JFE-DME process. The construction of the demo-plant is scheduled to be completed in the end of 2003, followed by several test runs in 3 years including final analysis and evaluation of the process viability for an industrial application. Total budget of the project is about 20 billion Yens (169 million US$), of which about 13 billion Yens (113 million US$) are subsidized by METI.

7. FEASIBILITY STUDY BY DME INTERNATIONAL CORPORATION

In parallel with the above development project, another company was established by the same member companies as above, under the name of DME International Corporation, for the purpose of a feasibility study of a commercial DME production including natural gas supply, plant site selection and construction plan, transportation of DME, receiving terminal locations and facilities, DME market as well as economic analysis and financing of the commercial project. The feasibility study is scheduled to be completed in 2004.

8. OTHER DME PROJECTS IN JAPAN

In addition to the above JFE projects in which TotalFinaElf is participating, there are two other projects by different groups of Japanese companies.

Nippon DME group is a consortium of Mitsubishi Gas Chemicals, Mitsubishi Heavy Industries, JGC and Itochu, now conducting a feasibility study of DME production in Australia using a conventional 2-step DME process.

Mitsui & Co. is now conducting a feasibility study of DME production in Iran using a 2-step DME process developed by Toyo Engineering Corporation.

All the projects have a target of starting DME production of 3,000 to 7,000 t/d around 2008.

9. PREPARATION FOR WORLDWIDE DME BUSINESS AS ALTERNATIVE ENERGY

Along with those development projects driven by several Japanese private companies, Japanese government is now encouraging related industries such as automobile manufacturers, electric power companies as well as the existing LPG logistic networks in Japan, to establish standards for application and handling of DME in each sector, and particularly to prepare laws and regulations including safety measures by 2006, so that the Japanese market will be ready to accept DME as a clean fuel by the time when a large scale production is supposed to start by several companies.

About 50 Japanese companies related to production, logistics and potential users of DME organized the "DME Forum Japan" for exchange of information and taking part in several workshops to develop infrastructure platforms for DME (**Figure 8**).

Several US and European companies related to DME business organized an international link as "International DME Association" (IDA), to which DME Forum Japan is participating as a member. Currently 17 member companies are participating in IDA including Shell International, BP, Lurgi, AIR Products, AB Volvo, Renault, Snamprogetti etc.

Figure 8 : Preparation for DME Markets in Japan

METI is driving:

- **Legislation and modification of laws and regulations**
- **Standardization**
- **Specifications for automobile fuel and household/industrial fuel**
- **Safety measures**

for transportation, handling and storage of DME by 2006.

Active Organizations in Japan:

- **Japan DME Forum (JDF)**

  Members from Government organizations such as JNOC, Academic Institutions, Japan LP-Gas Association and 60 major Japanese private companies in the field of E&P (JAPEX, INPEX), gas & power utilities, petroleum refining/marketing, engineering, manufacturing, transportation, etc. TotalFinaElf is a foreign member company.

  - Working in collaboration with IDA for international standardization.

- **Japan LP-Gas Association**

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