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DME as a carrier of Renewable Energy

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Increasing importance of Renewable energy

- Overseas dependence of energy supply in Japan was 82% in 2009 and has risen with shutdown of nuclear power plants.
- As measures for energy supply security and global warming, the domestic renewable energy has been developing, but its resource amount is limited.
- The electricity, which is generated from renewable resources such as solar and wind power rich in remote area abroad, could be converted into energy carrier to be easily transported and used in Japan. This idea is considered as one of future promising options.

History of Global Energy System Concept

- 1973 The First Oil Crisis
- 1974 PORSHE(Plan of Ocean Raft System for Hydrogen Economy)(proposed by Prof. Ohta of Yokohama National Univ.)
- 1979 The Second Oil Crisis
- 1986-1998 Euro-Quebec Hydro-Hydrogen Pilot project (Study of Liquid Hydrogen marine transportation)
- 1990-1995 Conceptual study of CO_2 Global recycle system (proposed by Dr.Sano of Osaka National Research Institute)
- 1992 Rio Earth Summit
- 1993-2002 World Energy Network Project by NEDO
- 2004 Argentine gas company CAPSA-CAPEX studied economics of "Patagonia wind hydrogen export plan" targeted to 2030.
- 2008 System economics study of Patagonia wind hydrogen export to Japan for Power generation(The Institute of Applied Energy)
- 2009 Proposal for Canadian wind and hydro hydrogen to be converted to DME for export (Blue Fuel business initiative)

Physical properties of Renewable energy carrier

- Temperature and pressure condition of DME transportation is mild and its energy density is large by weight and by volume. It can be treated safely and non hazardous.

	Liquid hydrogen	Liquid ammonia	Methanol	MCH	DME	CO_2	Toluene
Molecular formula	H_2	NH_3	CH_3OH	C_7H_{14}	CH_3OCH_3	CO_2	C_7H_8
Liquid density [kg/m^3]	70.8	700	795	774	670	1100	867
Boiling point [^{o}C @0.1MPa]	-253	-33.4	64.4	101.1	-25	(-50)*2	110.6
Vapor pressure [MPa @25^{o}C]	-	1.02	0.0129	0.0061	0.53	(0.7)*2	0.0039
Energy density by weight [MJ/kg]	120.8	19.2	21.1	(7.4)*1	28.8	-	-
Energy density by volume [MJ/L]	8.5	13.4	16.8	(5.7)*1	19.3	-	-
Explosion limit [%]	4 - 75	15 - 28	6.7 - 36	1.2 - 6.7	3.4 - 27	-	1.1 - 7.1
Toxicity allowance [ppm]	-	25	200	400	-	-	50

*1: Calorific value of transported $3H_2$ ($C_7H_{14} \Leftrightarrow C_7H_8+3H_2$)

*2: Transportation condition of liquid CO_2

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Conversion process and Utilization technologies

・Synthesis pressure of DME is lower than that for Ammonia and Methanol synthesis. DME production technology is established.

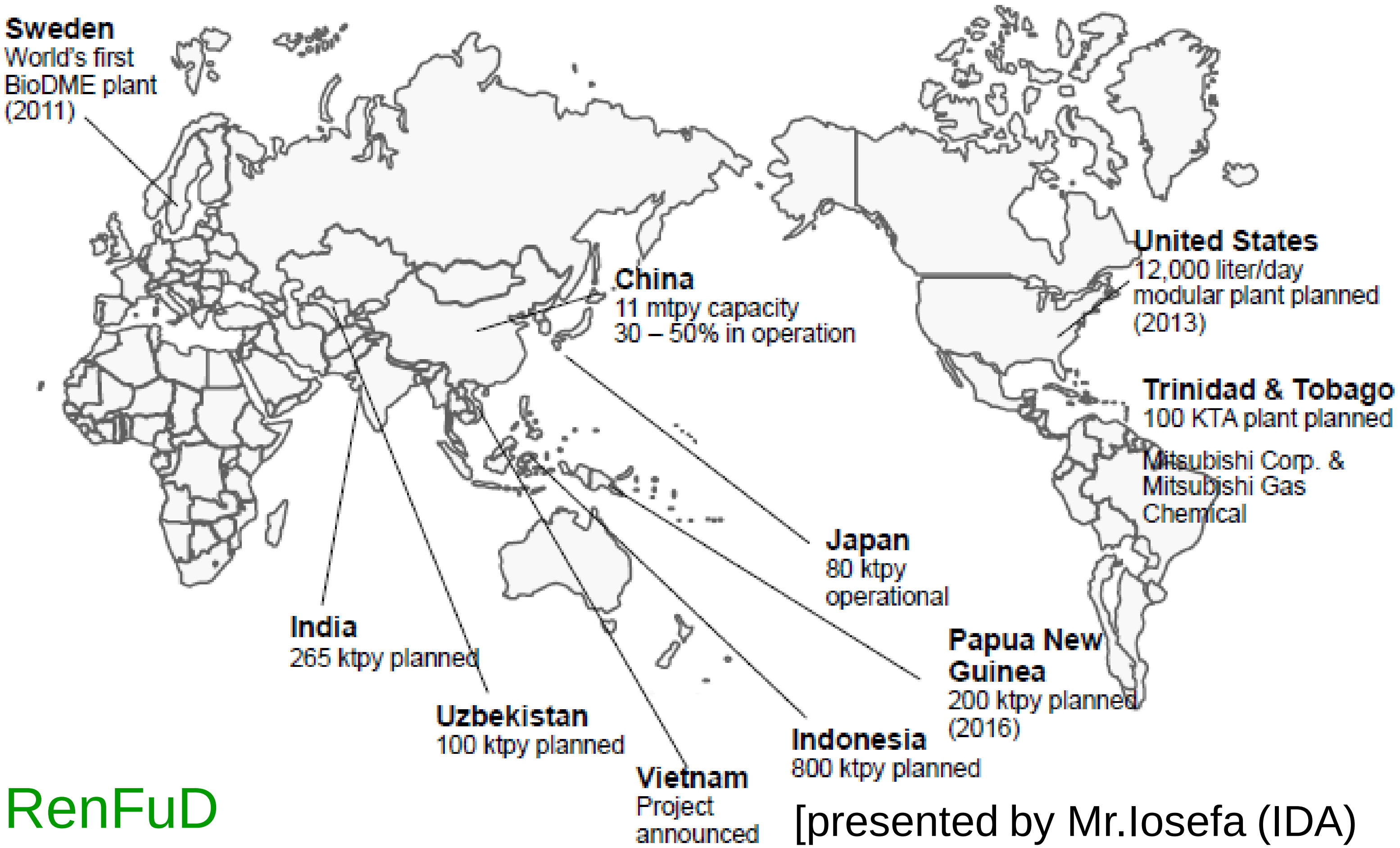
・DME combustion and DME engine technology are demonstrated including their durability. Temperature of DME steam reforming is relatively low and the reformer has bee developed

	Liquid hydrogen	Liquid ammonia	Methanol	MCH	DME
Conversion Auxiliary material	-	N_2 (Air separation)	Liquid CO_2	Toluene	Liquid CO_2
Process	Liquefaction	Synthesis	Synthesis	Hydrogenation	Synthesis
Temp. [ºC]	-253	400-500	210-260	150-200	240-280
Pres. [MPa]	ambient	20-30	8-10	3	5
Usage **Combustion** **Engine**	Safety problem SI engine	Safety problem SI engine NOx removal	Smokeless combustion SI engine	(not used as fuel)	Smokeless combustion CI engine
H_2 generation Process	Evaporation	Pyrolysis NH_3 removal	Steam reforming	Dehydro-genation	Steam reforming
Temp. [ºC]	ambient	700	220	350	330
H_2 amount [kg/kg]	1	0.18	0.19*1	0.06	0.26*1
Reaction heat [MJ/H_2-kmol]	0.9	30.5	16.5	68.3	20.6

*1: including H_2 from Steam

DME project trends in the world

- In China, 79 companies have 15million ton of annual production capacity in total, but the operation rate is 20-30% in 2012.
- In Trinidad and Tobago, a construction of 100,000 ton/year DME plant is determined.



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[presented by Mr.Iosefa (IDA) at DME5(2013)]

Production and Utilization of DME in Japan

• 80,000 ton annual production plant of Fuel DME production company, which is installed in Mitsubishi Gas Chemical Niigata, produces DME by dehydration of imported methanol, and supplies it to neighboring users.

- Boiler fuel of food factory: Ichimasa , Sato food
  Gas oil and LPG is replaced by DME. Thermal efficiency is equivalent.
- Truck fuel of transport company: Niigata Un'yu, Tri-Net Logistics
  Drivability of DME truck is equivalent to diesel trucks, no odor and no soot are appreciated.

DME plant in Niigata

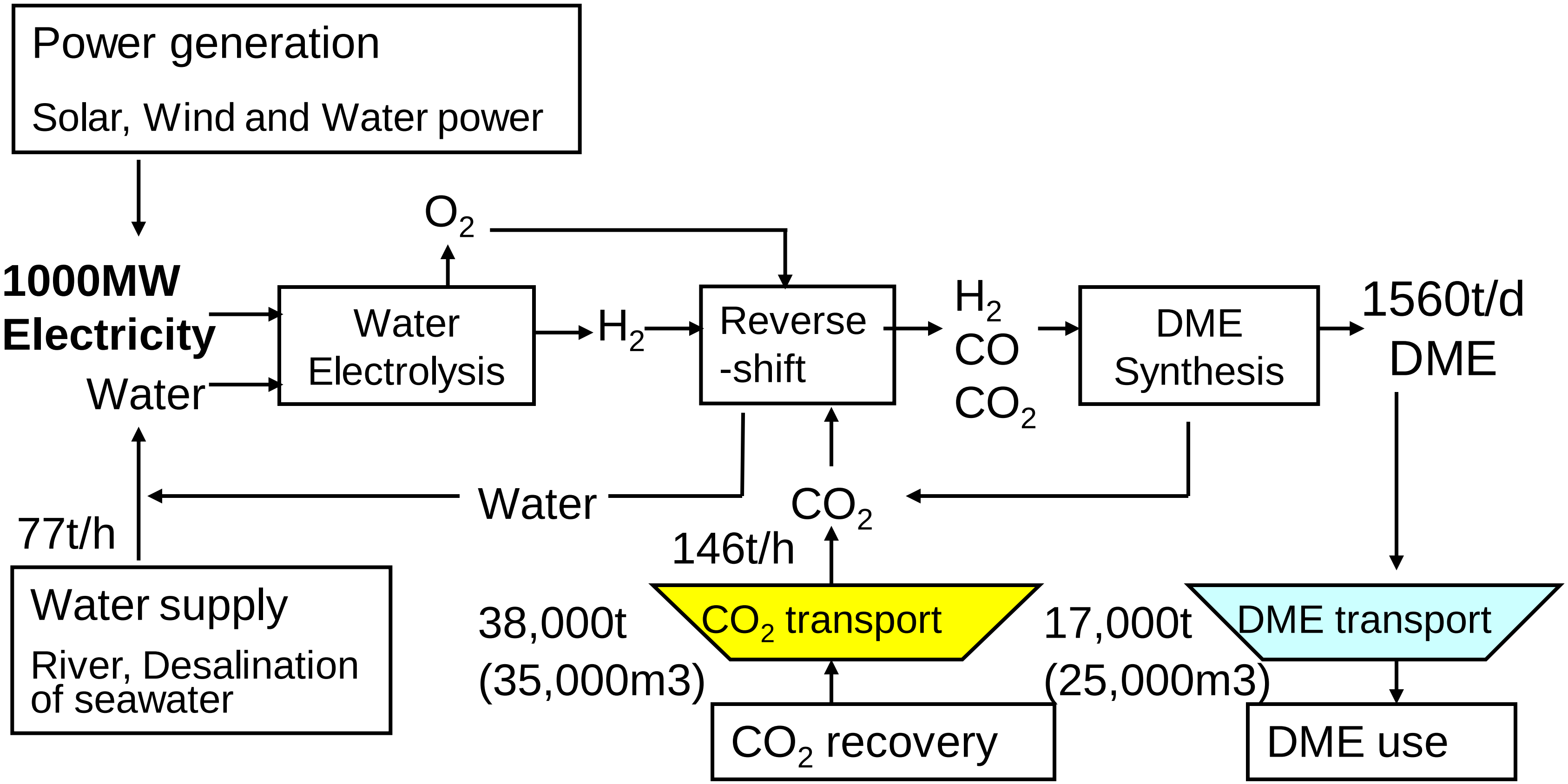
Boiler in Ichimasa

Truck of Niigata Un’yu

[Ohno：Proceeding of ASIADME7(2011)]

DME production process from Renewable energy

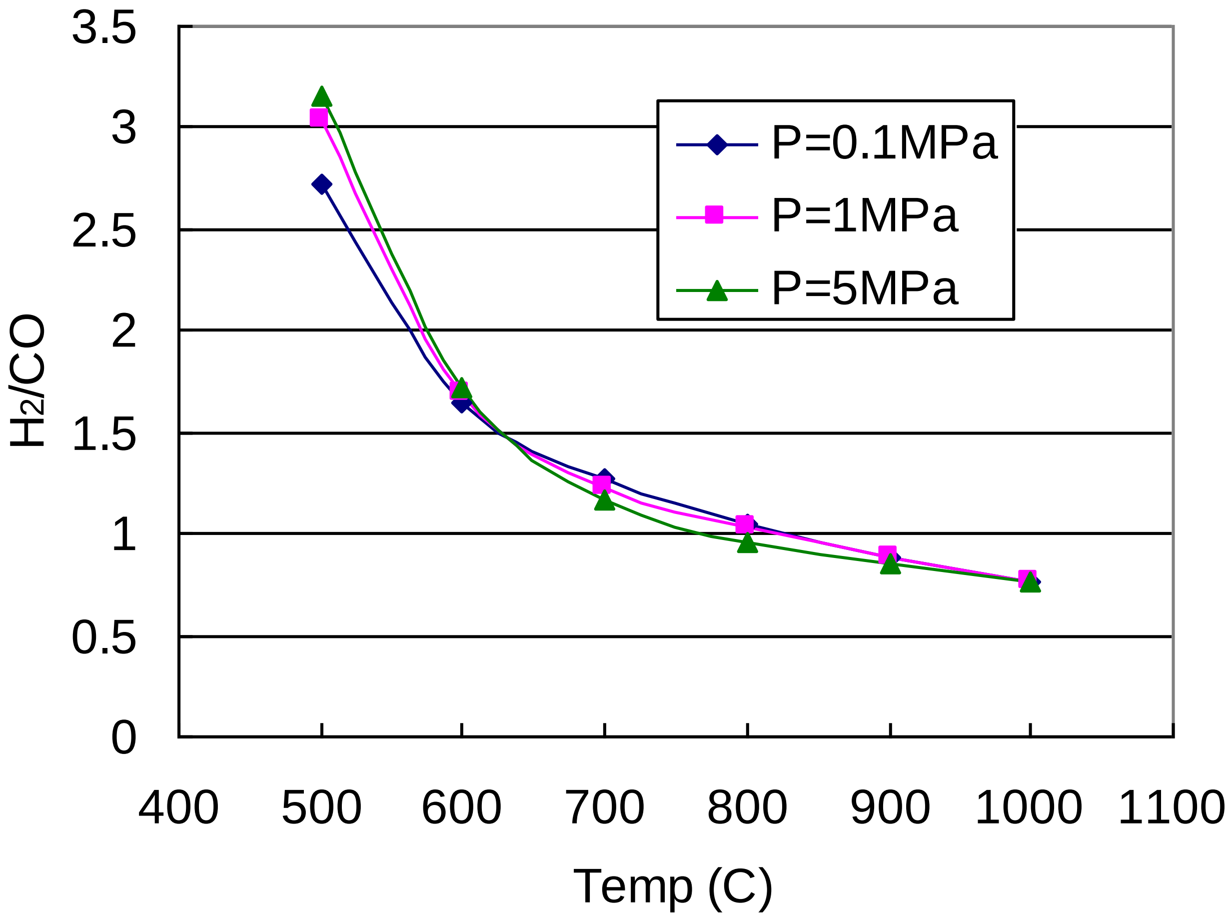
- H_2 generated by water electrolysis is converted into synthesis gas by reverse shift reaction with CO_2 to produce DME.
- CO_2 is recovered as liquid CO_2 at power plants in energy consumption areas and transported to DME production site by return DME transport low temperature ship.



Reverse shift reaction condition (H_2/CO)

- With higher temperature, H_2/CO goes down to $H_2/CO=1$ at 800ºC.

$$H_2+CO_2 \leftrightarrow H_2O+CO$$



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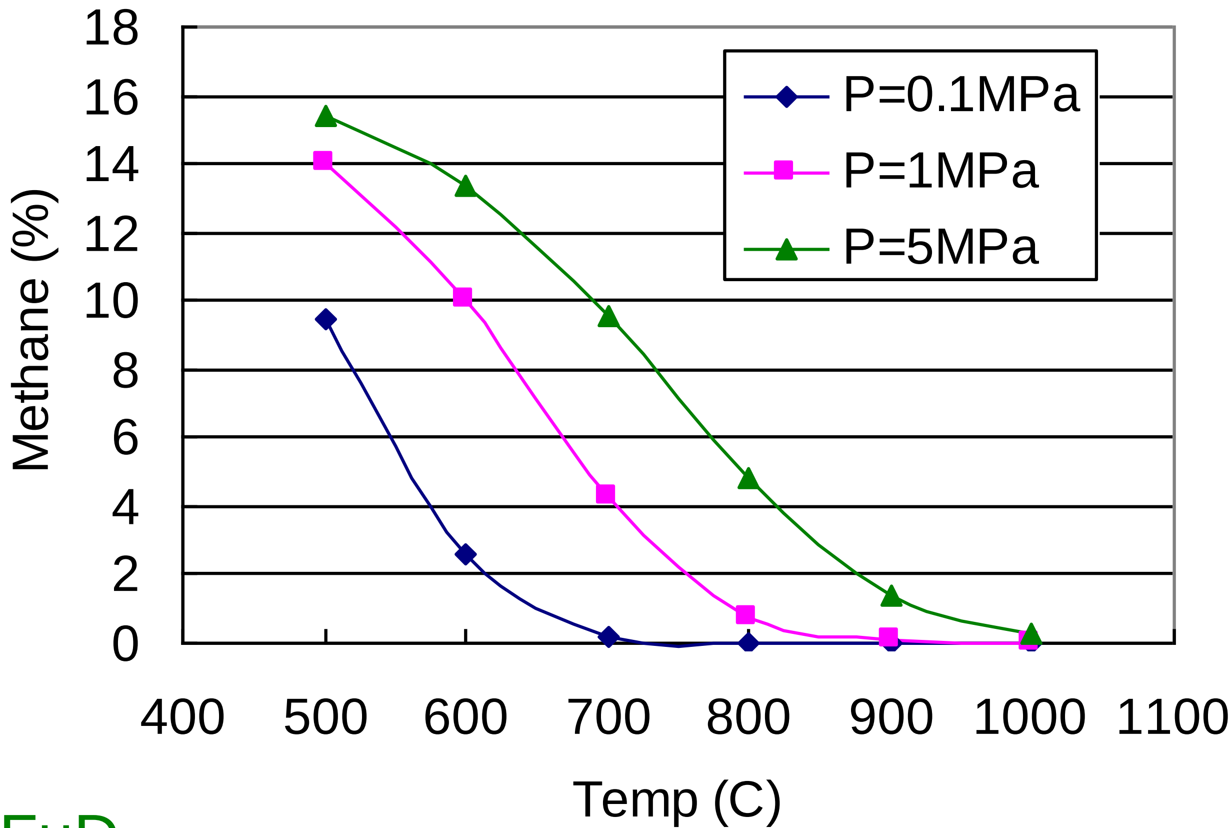
Reverse shift reaction condition (CH_4 formation)

•With higher pressure, equilibrium methane content is higher. In order to suppress methane formation, reaction temperature should be higher than 700ºC at ambient pressure.

$$CO+3H_2 \leftrightarrow CH_4+H_2O$$



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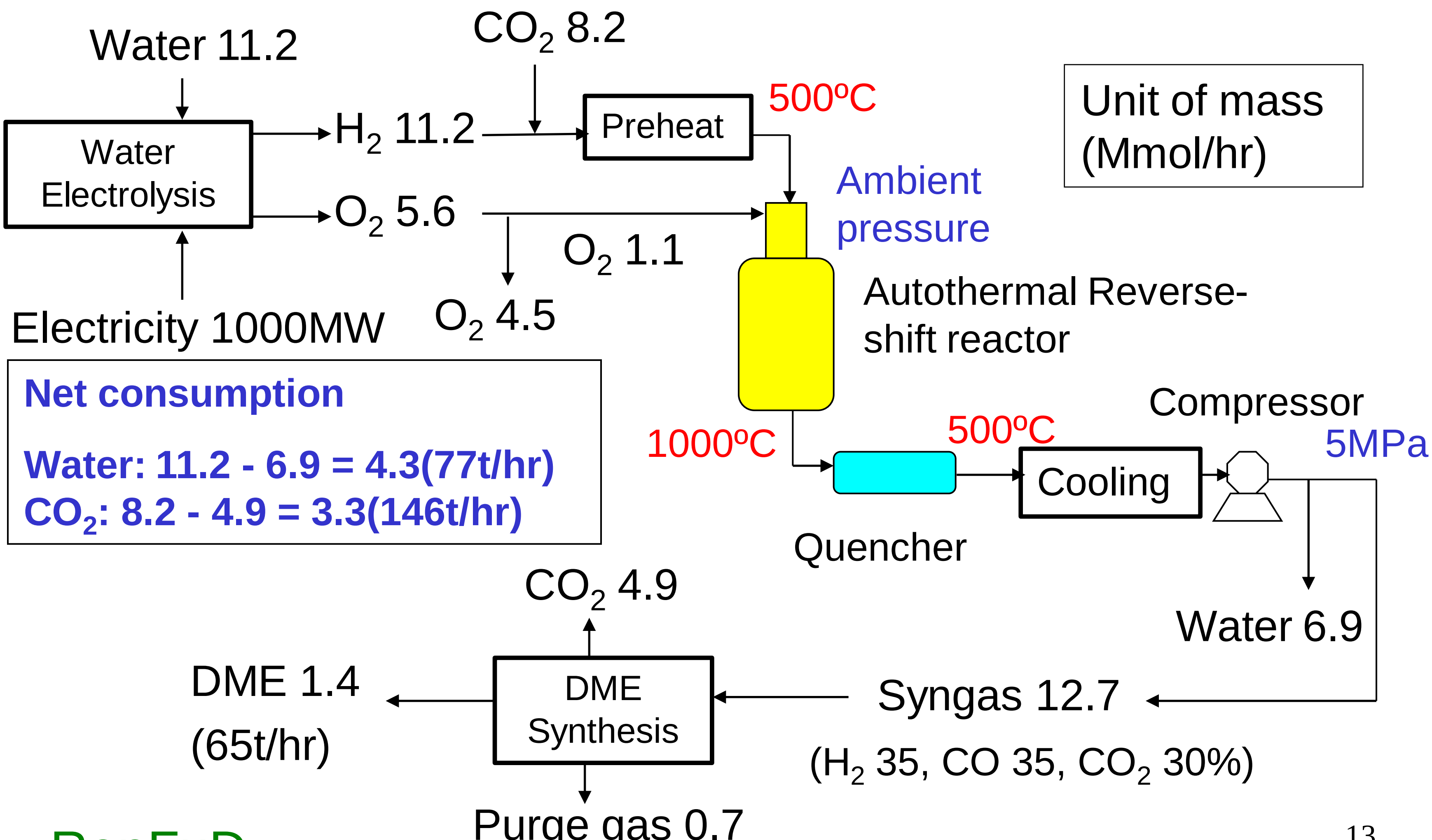
Auto-thermal reverse shift reaction process

- In H_2 obtained by water electrolysis, saturated water and a trace of O_2 remains. For liquefaction, it is necessary to dry and deoxygenate it. As for synthesis gas feed, removal of a trace of O_2 in H_2 , a trace of H_2 in O_2 and residual water is unnecessary.
- In order to suppress the methanation reaction, the feed gas reacts at the temperature higher than 800 ℃ and the product gas is rapidly cooled in a quencher in order that the reaction stops at H_2 / CO = 1.
- By using O_2 by-produced by water electrolysis, the feed gas react sat high temperature, the reaction rate is sufficiently large, the catalyst is considered unnecessary. (Requires experimental verification)
- Reactor system is a similar one to the secondary reformer of natural gas, a proven high-temperature reactor, engineering challenges are small.
- High-pressure steam recovered in a quencher is used for driving the compressor.

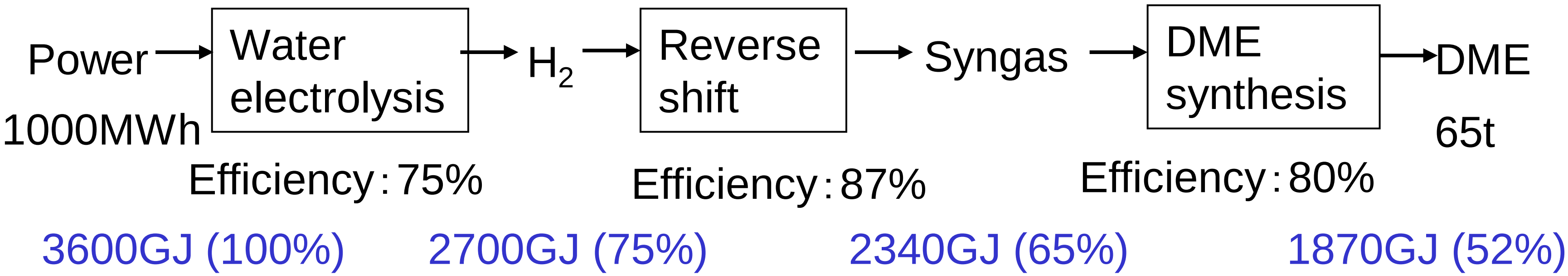
Total process flow from Power to DME

- From 1000MW of Electricity, 77t/hr (1850t/d) of Water and 146t/hr (3500t/d) of CO_2 , 65t/hr (1560t/d) of DME is produced.



Conversion efficiency estimates from Power to DME

- Given the electric power consumption of water electrolysis 4kW / Nm^3-H_2 (efficiency 75%) and cold gas efficiency 70% from H_2 to DME, conversion efficiency from power to DME is estimated to be 52%.



(1) Water electrolysis $7.5H_2O + \text{Power} \rightarrow 7.5H_2 + 3.75O_2$

(2) Auto-thermal reverse shift

$$7.5H_2 + 5.5CO_2 + 0.75O_2 \rightarrow 3H_2 + 3CO + 2.5CO_2 + 4.5H_2O\downarrow$$

(3) DME synthesis $3H_2 + 3CO + 2.5CO_2 \rightarrow CH_3OCH_3 + 3.5CO_2$

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(4) Total system $3H_2O + 2CO_2 + \text{Power} \rightarrow CH_3OCH_3 + 3O_2$

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(5) Utilization $CH_3OCH_3 + 3O_2 \rightarrow 3H_2O + 2CO_2 + \text{Energy}$

Conclusion

- DME is an energy carrier of high energy density. Storage and transport of DME is easy. DME is not toxic.
- In consumption areas, DME can be directly used as fuel (power generation, home, transport). Utilization technologies are proven.
- DME has high transport density as a carrier of H_2 energy. Energy requirement for H_2 generation from DME is small. Steam reforming technology of DME has also been established.
- Technical challenge for DME conversion is the only syngas production by reverse shift reaction, other technologies are proven.
- Energy efficiency from power to DME is estimated to be 52%.
- If DME production from natural gas or coal goes on ahead, DME production from renewable energy including biomass could be introduced easily.