KUALA LUMPUR 2012 WORLD GAS CONFERENCE

25th world gas conference

"Gas: Sustaining Future Global Growth"

Upgrading biogas to bio-methane :Green natural gas

Technology and cost

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Contents

- Introduction
- Background
- Green natural gas
  - ①Biomethane from biogas (fermentation method)
  - ②Biomethane from pyrolysis gas from woody biomass (Gasification method)
  - ③ New green gas from synthesis gas (H2 from wind power and CO2)
- Upgrading Technologies
  - ① Water Scrubbing
  - ②PSA Pressure Swing Adsorption
  - ③Chemical absorption
  - ④ Membrane separation
  - ⑤ Cryogenic separation
- Conclusion

Introduction

- Renewable energy will play an important role in preventing global warming.
- Natural gas is the cleanest energy among fossil fuel, but in the long future, CCS technology and renewable energy source needs to be introduced in order to reduce sufficient CO_2.
- At present the most promising method is to produce biogas from energy crops and organic waste by fermentation.
- From the view point of biogas production volume, gasification of organic waste such as woody biomass, garbage and sewage sludge will also be a promising method in the near future.
- In the long run, biogas from synthesis of H_2 from wind power and CO_2 will be a promissing method.
- Whether these can be realized will depend on production cost, especially upgrading cost.
- Here we explain the technologies and cost of the respective method.

Background1

Natural gas is the cleanest energy among fossil fuel and energy saving by natural gas is promising way, but in order to achieve 80% CO2 reduction, introduction of renewable energies such as solar, wind, and biomass energies including biogas is essential.

Heavy oil + Conventional burners
100

CO_2 emissions

Shift to natural gas
75

Use of highly efficient system by natural gas
45

Renewable natural gas
20

Efficient system by natural gas

High efficient gas furnace
Regenerative burner

Smart House with fuel cell

Greater use of NGV

Shift to low-carbon fuel

Coal 100

Oil 80

Natural gas 60

Natural gas 60 + Biogas 0

Renewable energy

Green natural gas

Biogas introduction is necessary to reduce CO_2 emissions

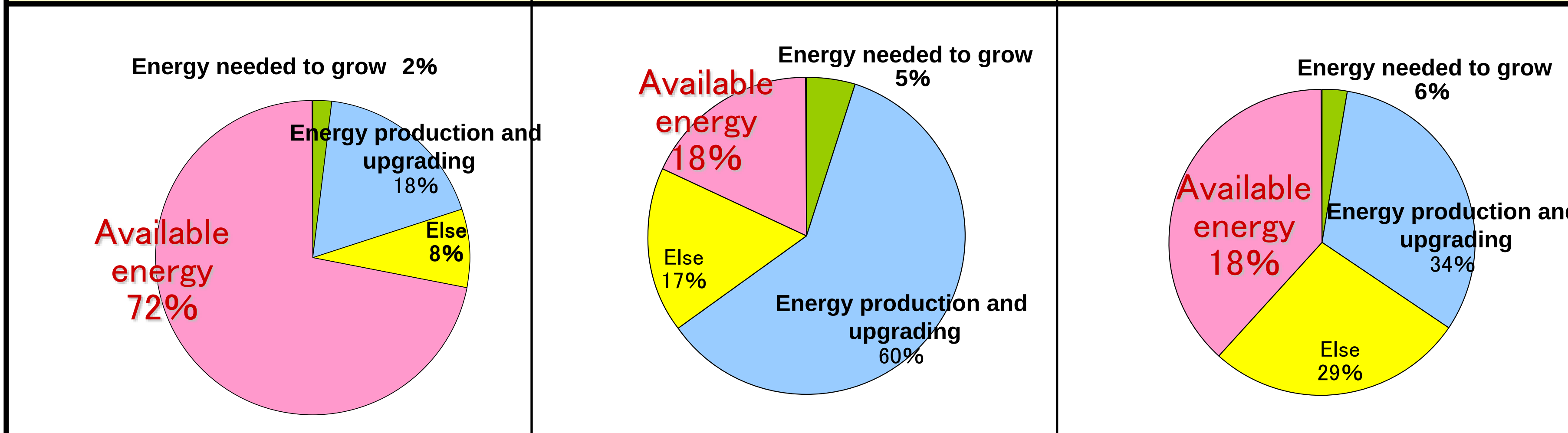
Background 2
Biogas is the most excellent among all biofuels

Biogas has the highest yield of available energy from energy crops among all bio fuels

① Only biogas can use not only fruit or berry, but also leaves, stalks and roots as energy source.
② Biogas requires smallest energy to produce available energy among all biofuels.

Comparison of energy yield （LCA evaluation）

Biogas	Bioethanol	Biodiesel oil



Type of biofuels	Produced energy	Actual available energy
Biogas	50,200	36,301
Bioethanol	19,801	3,614
Biodiesel oil	17,041	7,151

Unit： kWh/ha

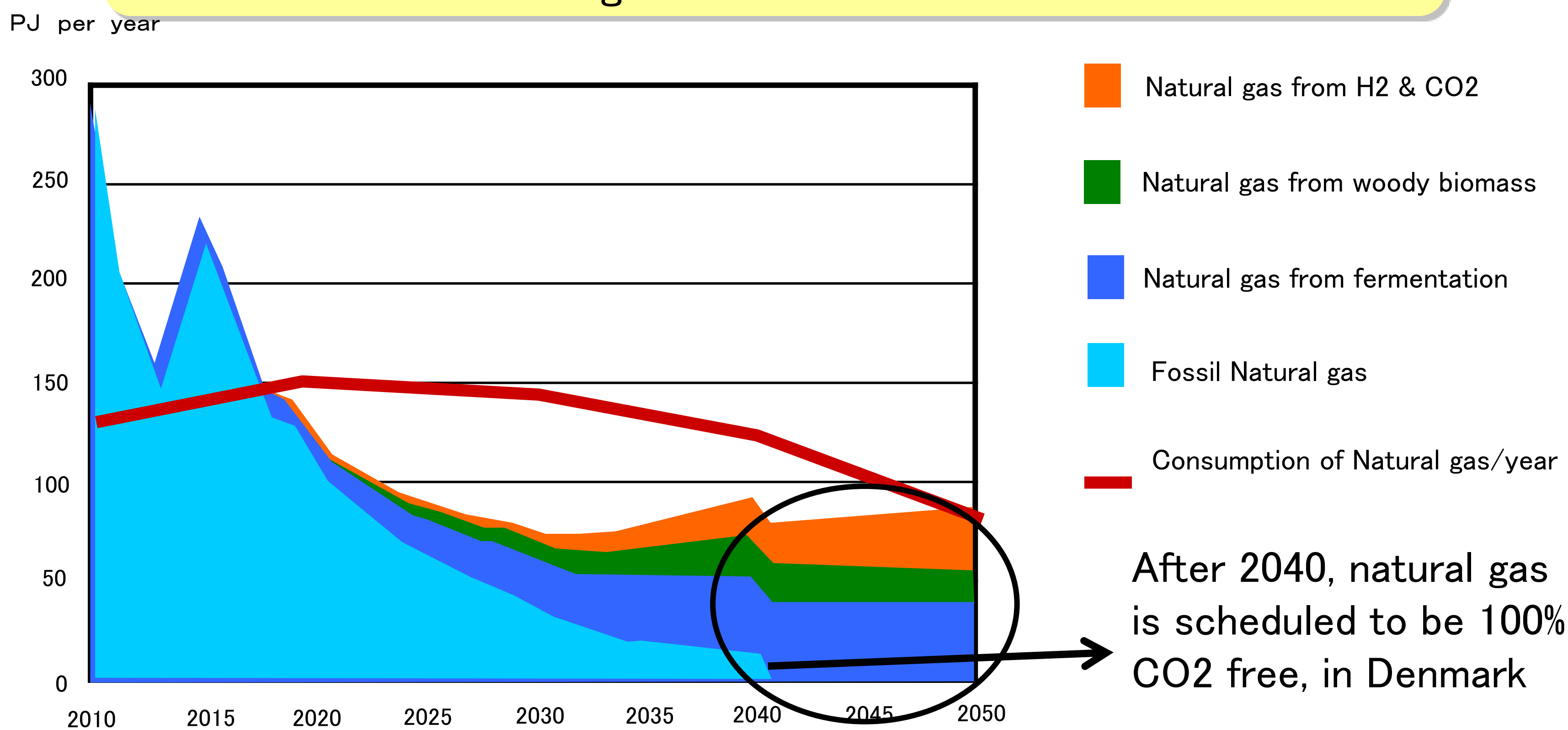
Biogas is thought as the best biofuel

Background 2

Green natural gas in the future

In order to reduce CO2 emission by 80%, in the advanced countries in EU, such as Denmark, Netherlands, Germany, renewable gas has been introduced as a Green natural gas.

After 2040 Natural gas will be 100% CO2 free : Denmark



- **Whether carbon free natural gas can be realized will depend on production costs, especially costs of upgrading biogas .**

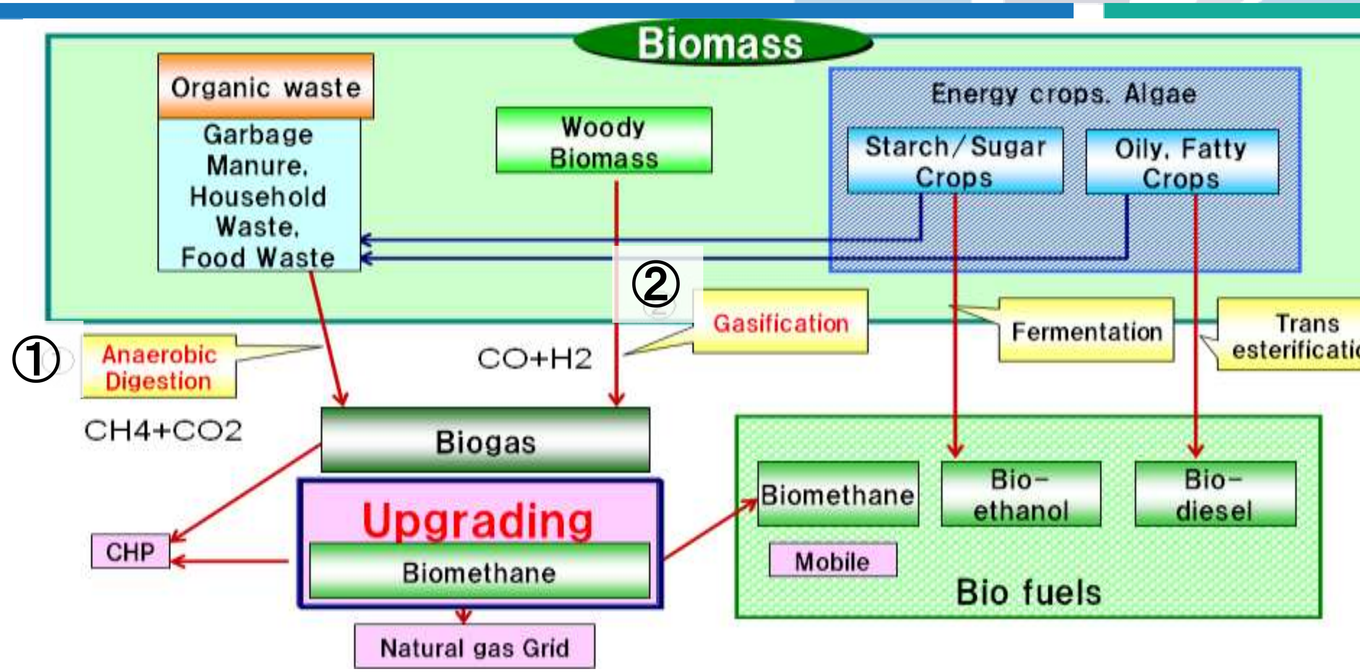
Green gas from renewables

①Bio-methane from fermentation method

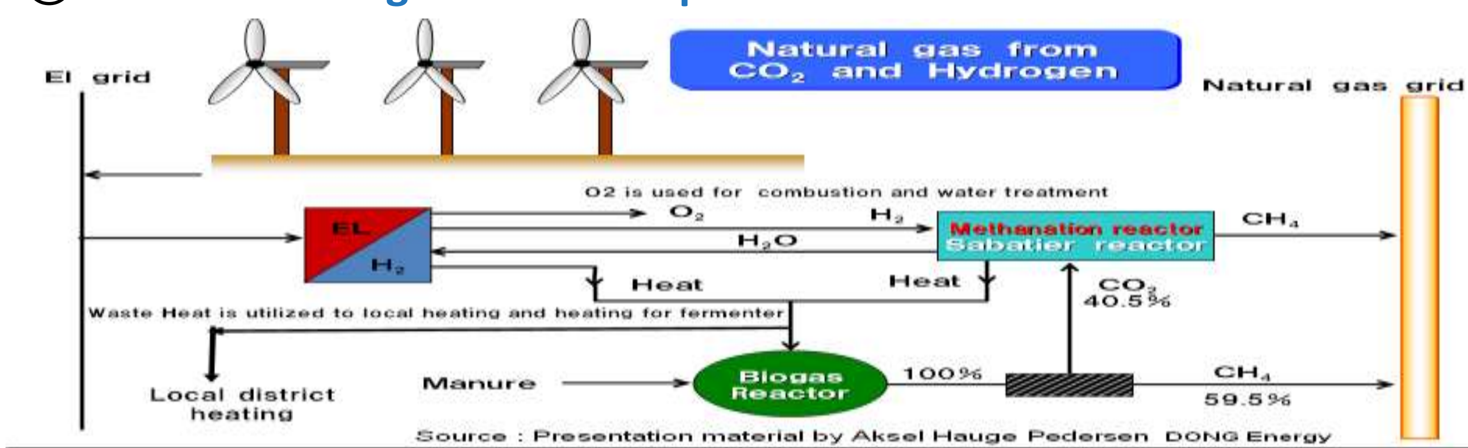
②Bio-methane from pyrolysis gasification method

③Green natural gas

from synthesis method with H2 from wind power and CO2



③ Green natural gas from wind power and CO2



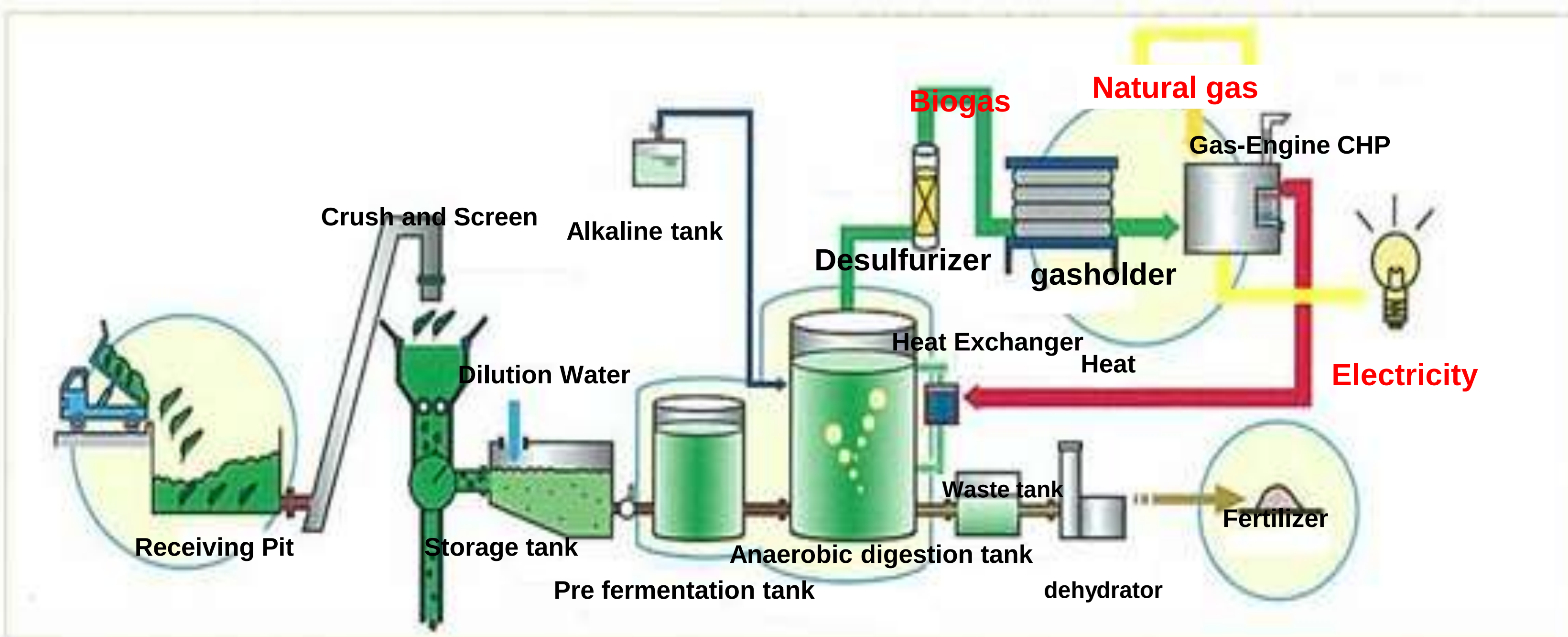
Biomethane from biogas Fermentation method

Anaerobic Digestion System

Microbial conversion of Biomass (i.e.. food waste) to Biogas under anaerobic condition.

System Feature

- **Energy recovery from organic waste with high water content**
- **Quiet drive with few moving parts**
- **Small energy requirement**

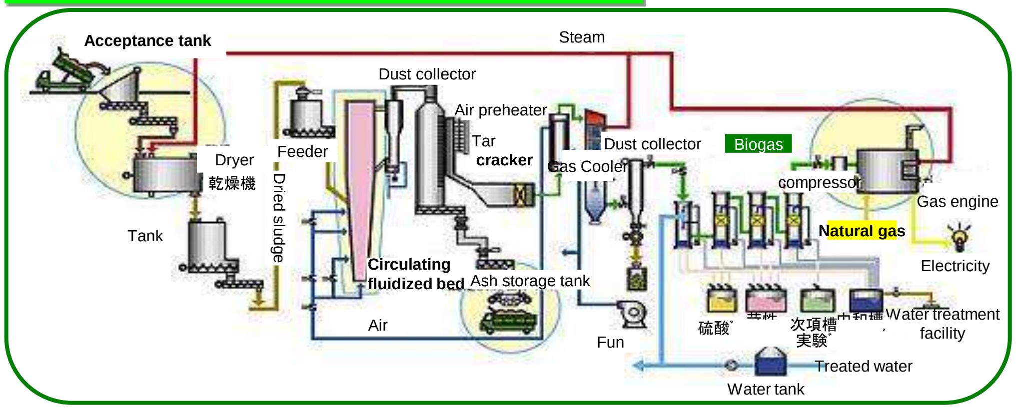


Biogas : Pyrolysis gasification 1
Example sewage sludge

Pyrolysis gasification

The pyrolysis gasification system is a technology that gasifies the biomass such as sewage sludge or wood biomass with partial combustion, and manufactures the gasification gas of which the principal ingredient is H2 and CO, etc.

The characteristic of the system



Tokyo gas test site
Capacity Treatment amount 15t/day
Dry-base
Power generation : 200～260kW

Almost all organic wastes can be available.

- **Great volume reduction can be achieved as same as the Incineration treatment.**
- **Yield of the gas is high .** *** Gasification efficiency 60-70%**
- **Sewage treatment plant needs a large amount of electric power, and can cover a large amount of power by biogas-fired cogeneration system.**
- **Sewage sludge can be dried by waste heat from cogeneration system.**

Biomethane from Biomass
pyrolysis process example 2

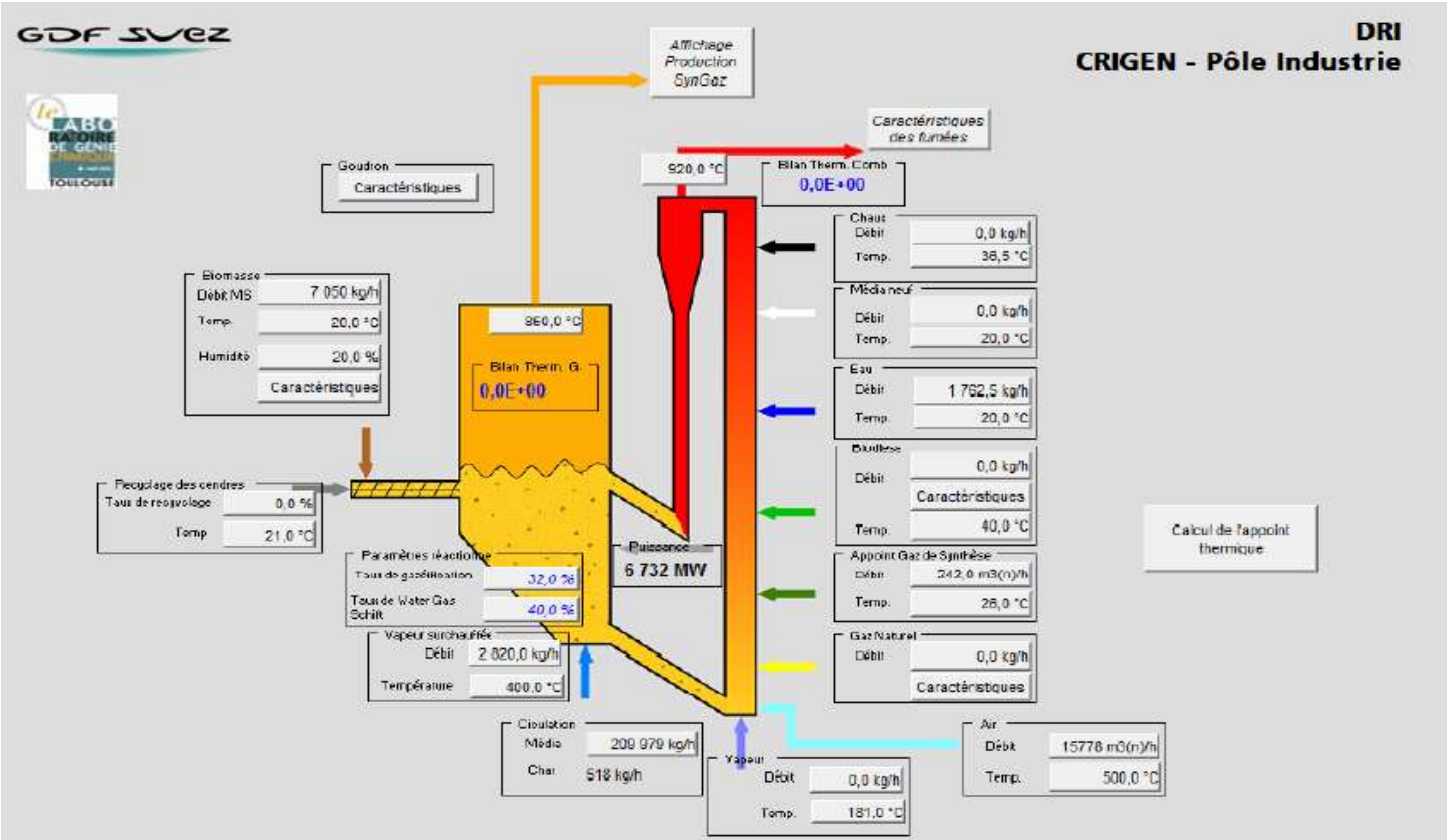
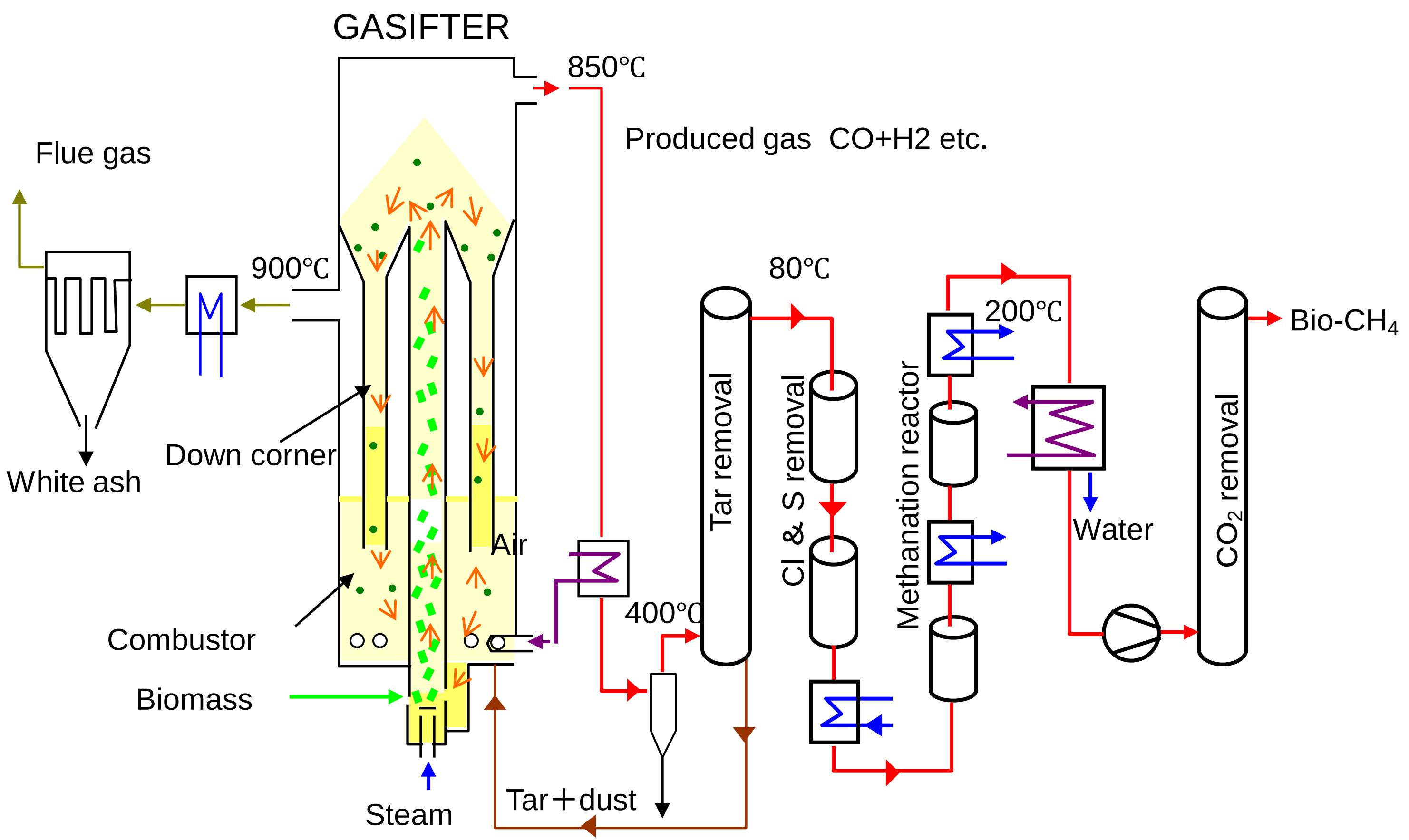


Figure 1: FICFB reactor - software interface of the 0D-model

Biomethane from Biomass
pyrolysis process example 3



Simplified process layout of MILENA－SNG system

Source: Comparing different biogas upgrading techniques   Eindhoven University of Technology, July 3, 2008

Comparison between biogas and natural gas

Biogas and natural gas in Japan

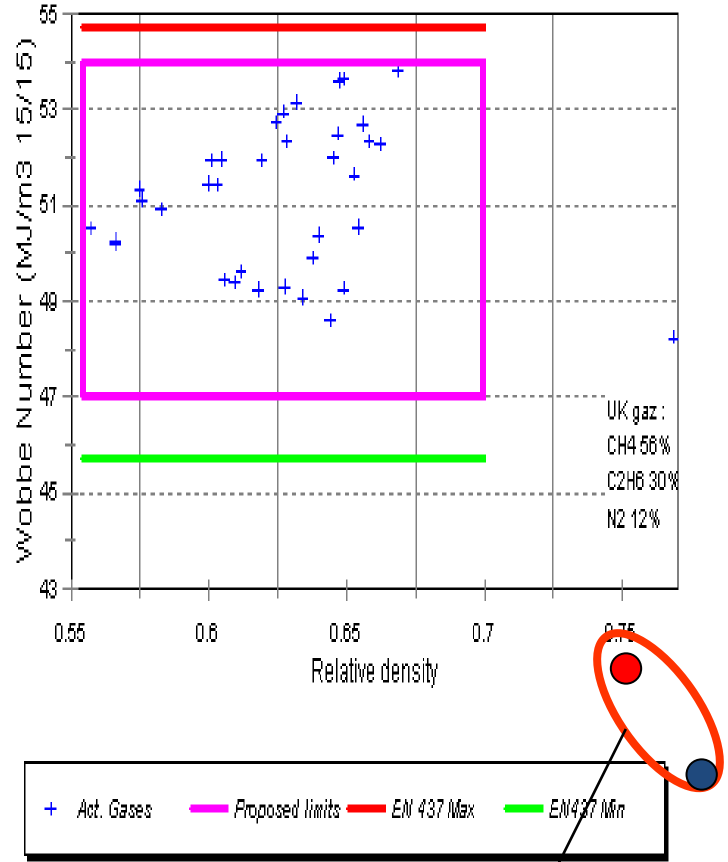
Item	Biogas		Natural Gas
Composition	A: CH_4=65% $CO2$=35%	B: CH_4=80% CO_2=20%	CH_4=88%, others C_2H_6, C_3H_8, C_4H_{10}
Calorific value (MJ/Nm³)	27.4	31.88	45
(kcal/Nm³)	6188	7616	10750
Combustion velocity (cm/sec)	21.4	27.13	36.8
CP (Combustion potential)	20.67	27.7	41.7
Wobbe Index (Calorific value/√specific gravity)	29.04	36.81	55.81
Specific gravity	0.89	0.75	0.65
Theoretical combustion air (m^3N/m^3N)	6.2	7.6	10.95
Others	Gas pressure, composition, quantity are fluctuating and contains toxic contents		Gas pressure ,composition are stable and contains no toxic content

A. Biogas from garbage.

B. Biogas from waste water

Natural gas : standard value of Osaka gas

Position of distributed gases in EU and biogas



Biogas position

Example of Upgrading level in Japan (CHP, NGV, Gas grid injection)

Item	unit	Crude Biogas	Ex. of Crude Biogas	Standard for CHP	Standard for NGV ※3	Ex. of Bio-Methane for NGV ※3	Standard for Grid injection ※4
CH_4	vo1%	58–80	59.7	58–80	≧97	98.2	No description
CO_2	vo1%	15–40	37	15–40	—	0.6	≦0.5
O_2	vo1%	0.5–2.0	0.4	0.5–2.0	≦4	0.2	≦0.01
N_2	vo1%	0.5–2.0	0.8	0.5–2.0	≦1.0	1	≦1.0
H_2S	PPM	200–3,000	330	10–100 ※2	≦0.1	＜0.1	≦1.0
Siloxane ※1	Mg/Nm^3	14.53	14.53	≦1	≦1.0	≦0.005	0
Heat value: HHV	MJ/Nm^3	21–32	23	22–32	39	39.3	45
Dew point	℃	0-30	0≦	0≦	≦-56	＜0.1-60	≦-60
Odorant Intensity	—	—	—	—	≧2,000	3,000	≧2,000
Conc. Odorant	Mg/Nm3	—	—	—	—	—	12-16

※1 Siloxane: Organic silicon compound contained in the shampoo and hair conditioner. Siloxane is included in the biogas of the sewage origin.

※2 The limit of the concentration of H2S depends on the CHP manufacturer.

※3 This standard is set by Kobe City

※4 This standard is set by Osaka gas

Upgrading system

1. **Biogas direct use onsite : CHP onsite etc**

   simple impurity removal system required : H_2S , Siloxane moisture

2. **Upgraded into biomethane : grid injection ,NGV**

   upgrading plant is required as below

Upgrading Technologies

① Water Scrubbing
②PSA Pressure Swing Adsorption
③Chemical absorption
④ Membrane separation
⑤ Cryogenic separation

Simple upgrading by removing impurity

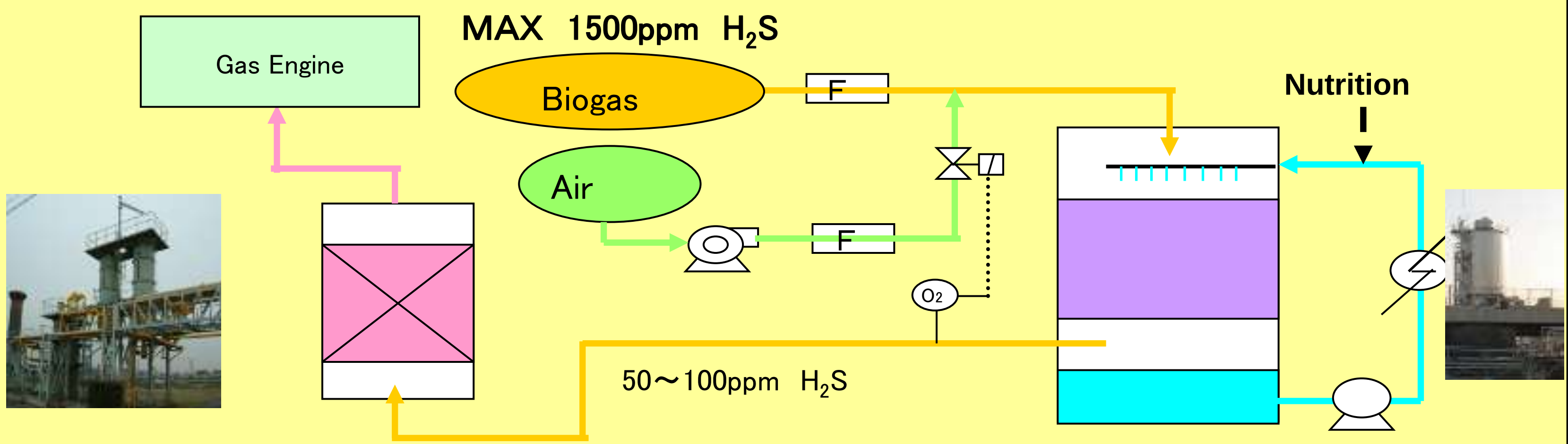
Onsite biogas direct utilization　Desulphurization System

Microbial desulphurization method combined with Dry catalytic desulphurization method

Operation cost of microbial desulphurization method is very low, but it can not completely remove sulfur.
Dry catalytic desulphurization method can remove sulfur completely, but operation cost is high .

Of course ,each technology will be applied alone, but large scale plant adopt the combined system.

Important affair : If the catalyst breaks through, pipeline or gas appliances such as CHP will be damaged, and if macrobiotics get damage and died, biogas content changes and in most dangerous case, the gas becomes the mixture state to easily blow up or burning itself. .
We often see that the customer maintenance of the system is not so good.



Dry Catalytic Method

$Fe_2O_3 + 3H_2S = Fe_2S_3 + 3H2O + 14.9$ kcal
$2Fe_2S_3 + 3O_2 = 2Fe2O_3 + 6S + 290$ kcal

Microbial Method

$H_2S + 1/2O_2$
→(sulfur oxidation bacteria)→
$S + H_2O$

Upgrading into biomethane : grid injection ,NGV

①High pressure Water scrubbing method

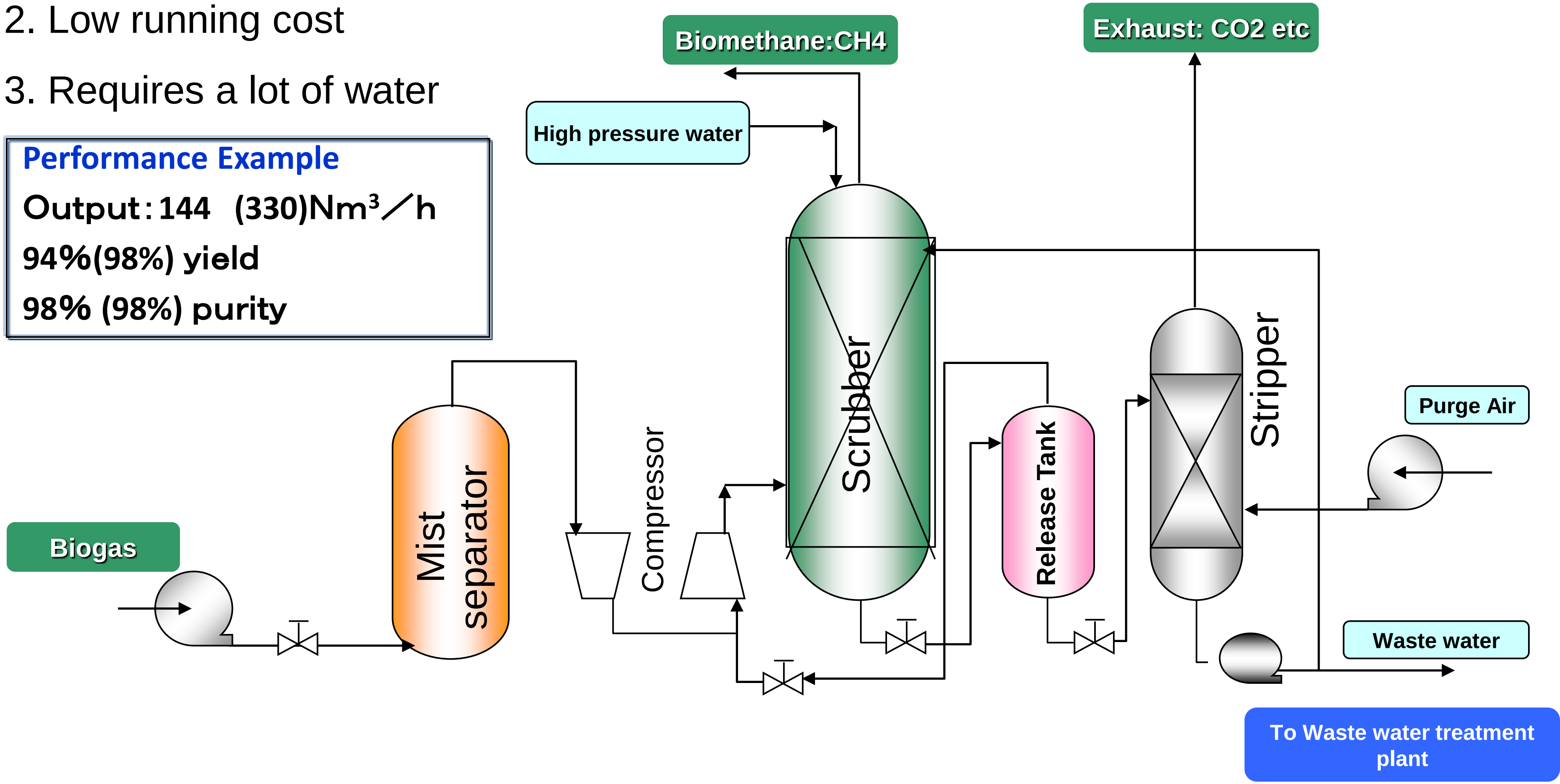
1. Very high impurity removing performance
2. Low running cost
3. Requires a lot of water

Performance Example

Output：144 (330)Nm^3／h

94%(98%) yield

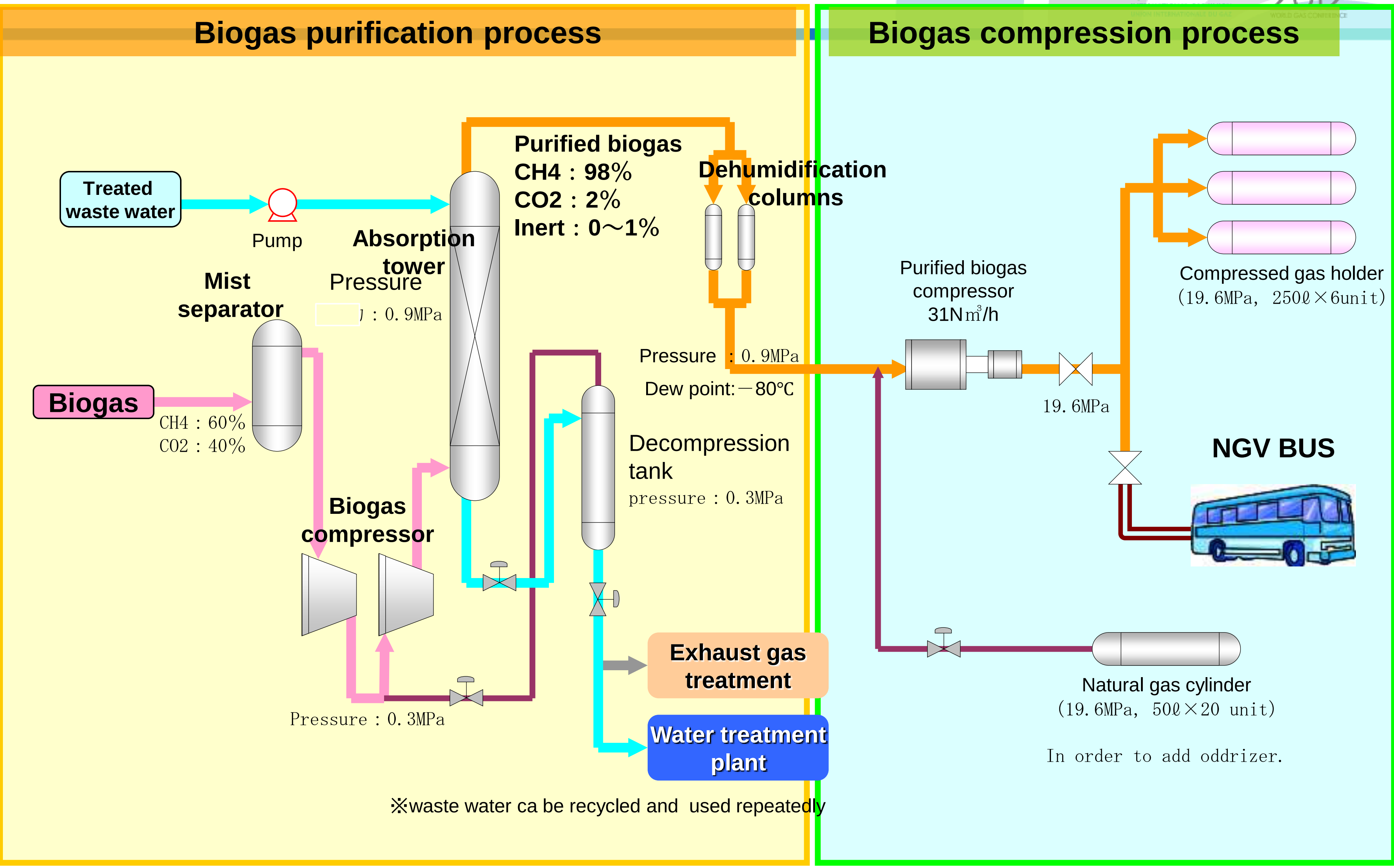
98% (98%) purity



Source: Comparing different biogas upgrading techniques Eindhoven University of Technology, July 3, 2008

Upgrading into biomethane : grid injection ,NGV

Example of High pressure water Purification of biogas at sewage treatment plant

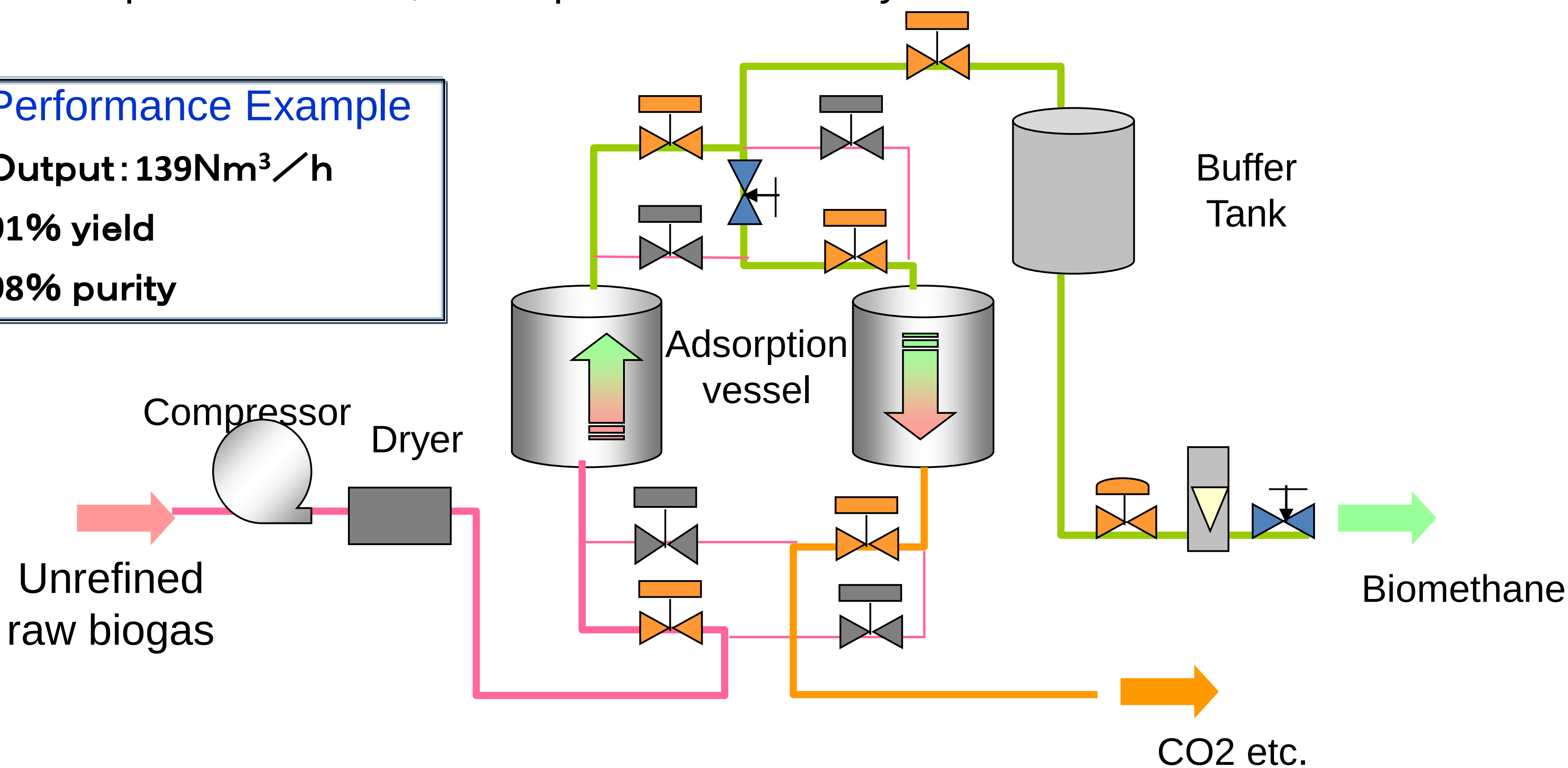


Upgrading into biomethane : grid injection ,NGV

② PSA Upgrading Method

1. CH4 yield is high.
2. CO2 and impurities are removed at high level.
2. Low power demand, but depend on electricity cost.

Performance Example
Output：139Nm³／h
91% yield
98% purity



Source: Comparing different biogas upgrading techniques Eindhoven University of Technology, July 3, 2008

Upgrading into biomethane : grid injection ,NGV

③Chemical absorption method

1. 2 chemical absorption systems are needed (For CO2 and H2S), or water scrubber is needed to remove CO2 .
   In order to remove CO2, chemical absorption column with amine solution (MEA &DMA) or water scrubber is needed.
2. Almost all H2S removed and H2S is converted Fe2S3
3. Running cost is relatively high and total system is complicated

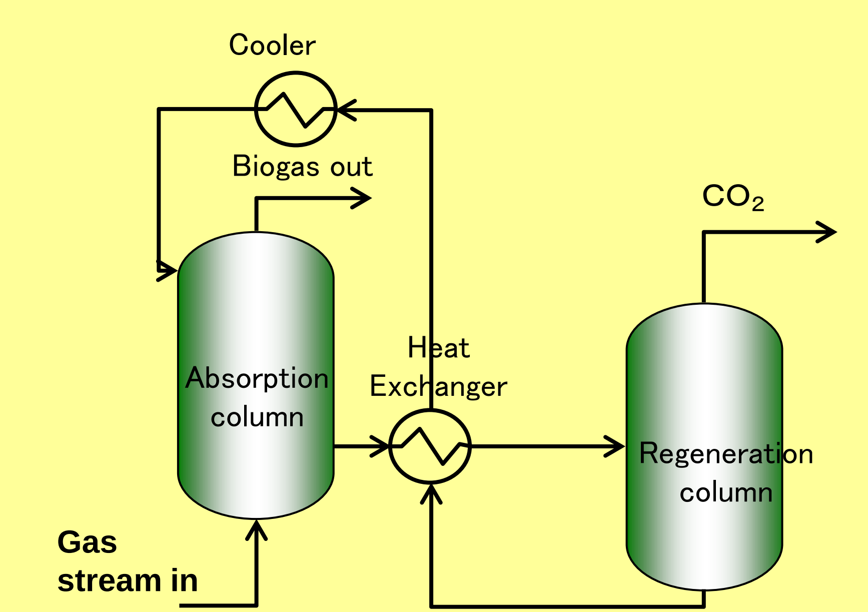
Performance Example

Output : 137Nm³／h

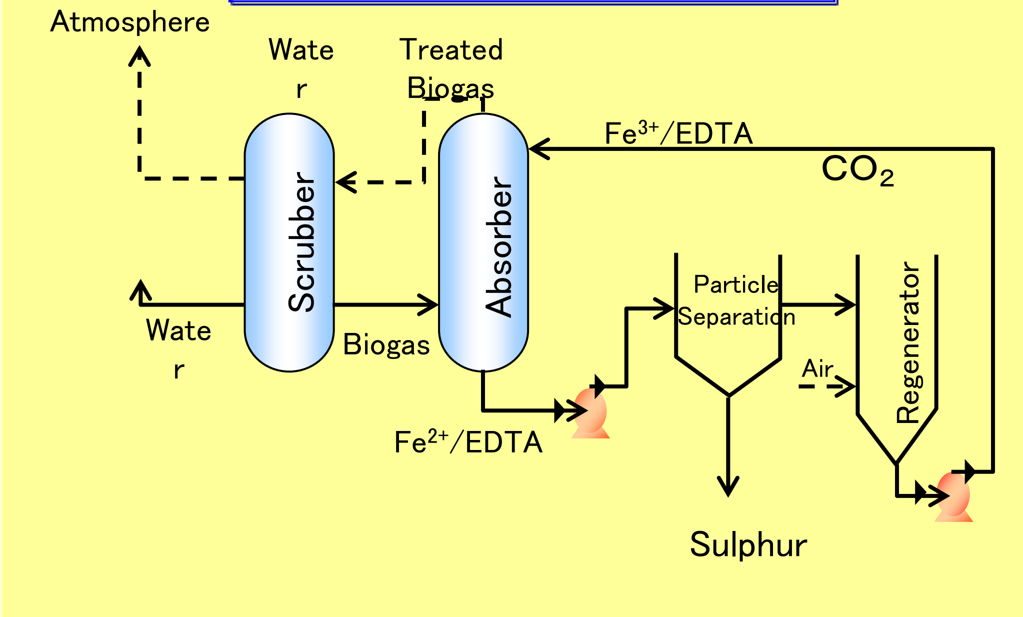
90% yield

98% purity

Chemical absorption for CO2



Chemical absorption for H2S



Source: Comparing different biogas upgrading techniques Eindhoven University of Technology, July 3, 2008

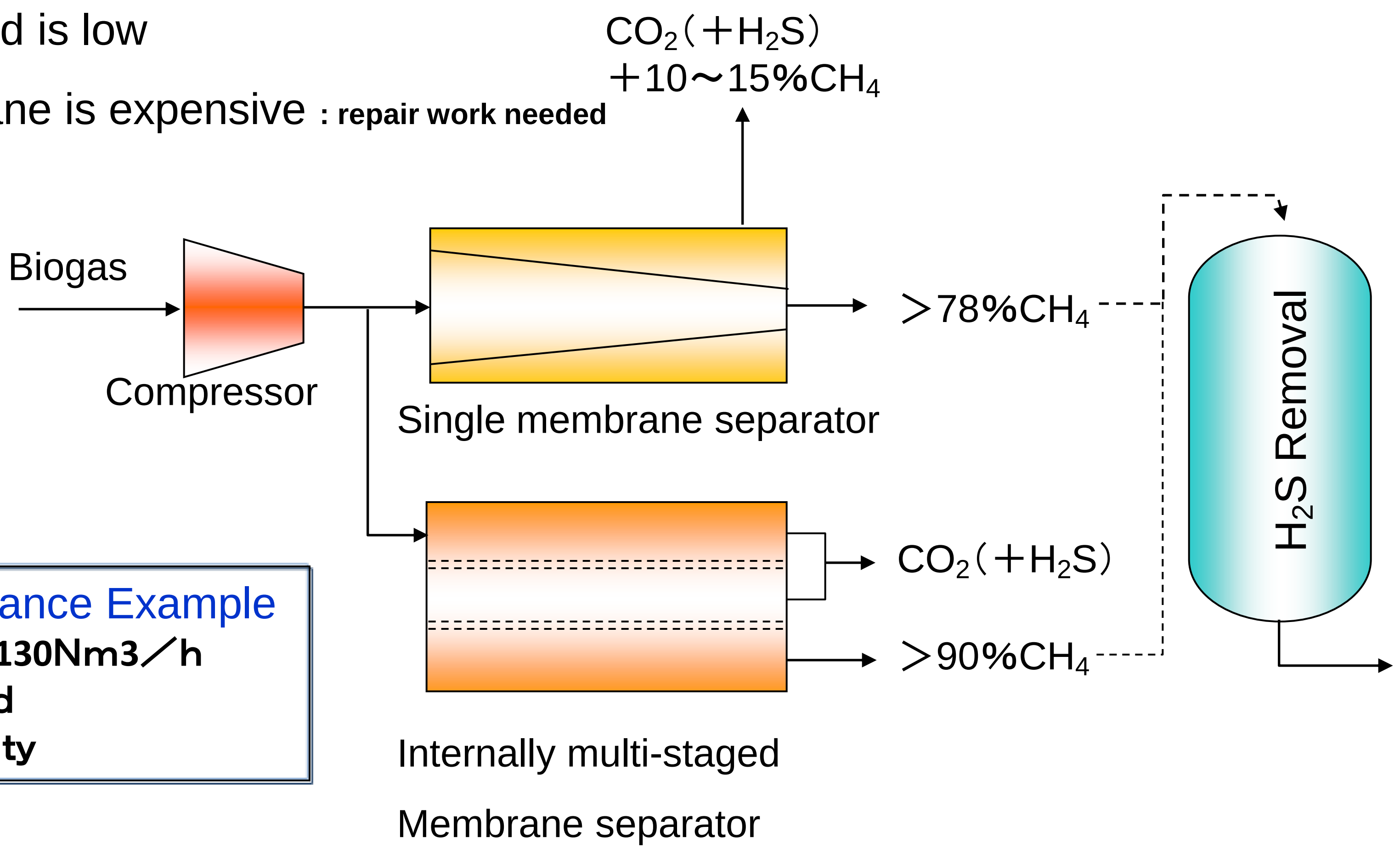
Upgrading into biomethane : grid injection ,NGV

④Membrane upgrading method

1.Suitable for small plant

2. Gas yield is low

3. Membrane is expensive **: repair work needed**



Performance Example
Output：130Nm3／h
78% yield
90% purity

Source: Comparing different biogas upgrading techniques Eindhoven University of Technology, July 3, 2008

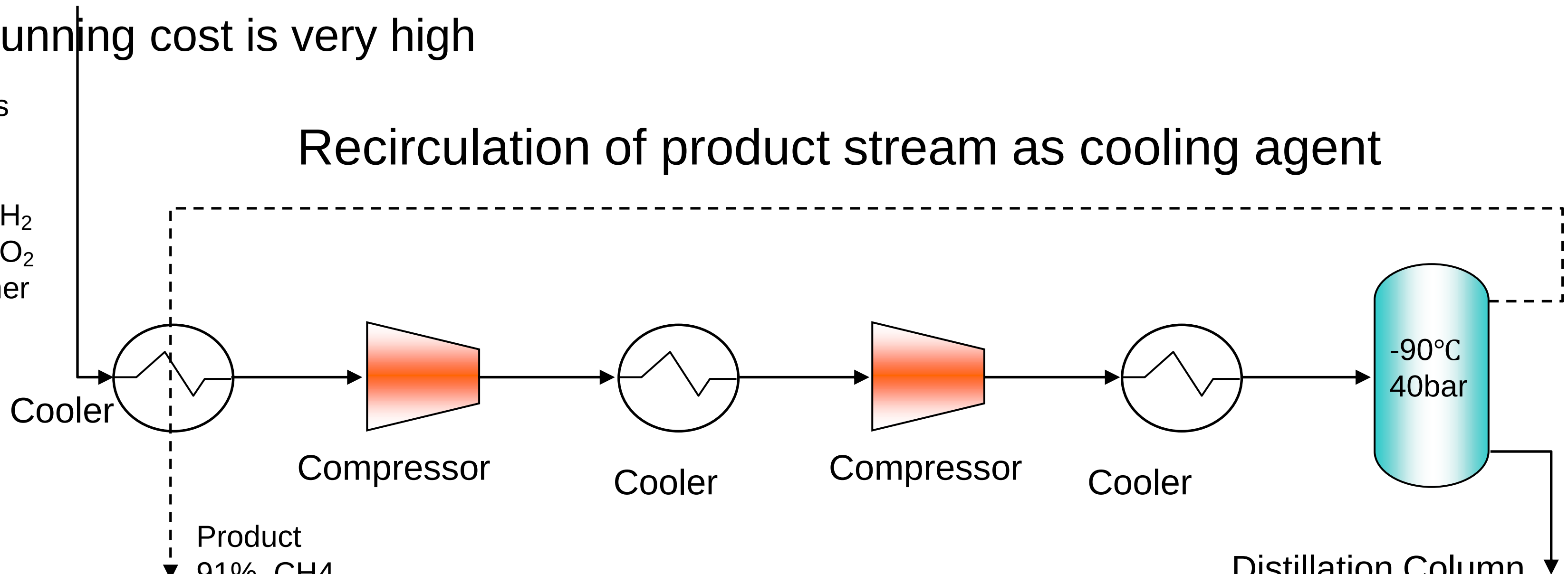
Upgrading into biomethane : grid injection ,NGV

⑤Cryogenic upgrading method

1.Suitable for Large plant

2. Gas yield is high

3. Running cost is very high



Performance Example

Output：1361m3／h

98% yield

91% purity

Source: Comparing different biogas upgrading techniques Eindhoven University of Technology, July 3, 2008

Upgrading into biomethane : grid injection ,NGV

Cost comparison between Upgrading technologies

Technique	Investment cost €	Running cost €	Upgrading Cost €/Nm3 biogas	Maximum achievable yield %	Maximum achievable purity %	Advantages	Disadvantages
Chemical absorption	869,000	179,500	0.28	90	98	・Almost complete H_2S removal	・Only removal of one component in column ・Expensive catalyst
High pressure water scrubbing	440,000	120,000	0.15	94	98	・Removes gases and particulate matter ・High Purity, good yield ・Simple technique, no special chemicals or equipment required ・Neutralization of corrosive gases	・Limitation of H_2S absorption due to changing pH ・H_2S damages equipment ・Requires a lot of water, even with the regenerative process
pressure swing adsorption	805,000	187,250	0.26	91	98	・More than 97% CH_4 enrichment ・Low power demand ・Low level of emissions ・Adsorption of N_2 and O_2	・Additional complex H_2S removal step needed
Cryogenic separation	908,500	397,500	0.4	98	91	・Can produce large quantities with high purity ・Easy scaling up ・No chemicals used in the process	・A lot of equipment is required
Membrane separation	749,000	126,750	0.22	78	89.5	・Compact and light in weight ・Low maintenance ・Low energy requirements ・Easy process	・Relatively low CH_4 yield ・H_2S removal step needed ・Membranes can be expensive

Source: Comparing different biogas upgrading techniques Eindhoven University of Technology, July 3, 2008

Conclusion

1. High pressure water scrubbing is the cheapest and best, if a lot of amount of water is available.

Upgrading cost 0.15 Euro/m3 biogas - 0.17 Euro/m3 Biomethane

2. Membrane type is easy to construct and operate .

Membrane separation is promising in the future.

3. PSA is available if a lot of amount of water is not available.

Running cot is cheap if plant scale is relatively small.

- **High Pressure water scrubbing method is the best overall performance :**
  - **high yield and purity**
  - **compact setup**
  - **no chemicals**
  - **only one waste stream**
- **Membrane type is most promising in the future.**

➡ **If a large amount of inexpensive raw matrials for biogas can be obtained , green natural gas can be fully realized.**

Thank you for your attentions!

Upgraded into biomethane : grid injection ,NGV

Standard of Biomethane of USA AGA Guideline

Anticipated Renewable Gas Composition

ANTICIPATED RENEWABLE GAS COMPOSITION	
Methane	95 to 97 percent
Carbon Dioxide	Less than 2 percent
Oxygen	Less than 0.2 percent
Hydrogen Sulfide	Less Than 4 parts per million
Moisture	Less than 7 lbs/million cubic feet
Nitrogen	Less than 2.75 percent
”Commercially Free” of objectionable matter（polychlorinated biphenyl, dust, gums, tars, other liquids, chemical constituents or particulate matter that may interfere with the merchantability of flowing gas）	

◆Recommendation based on AGA 4A guidelines, state and interchangeability requirements

◆National gas quality standards may not be appropriate― one size does not fit all

Upgraded into biomethane : grid injection ,NGV

Quality demands in different countries for utilisation of biogas as vehicle fuel

	Unit	France[1)]	Switzerland[1)]	Sweden
Wobbe index$_{lower}$	MJ/nm³			45,5
Wobbe index$_{upper}$	MJ/nm³			48,2
Water dewpoint	°C		5° lower than the lowest ambient temperature	
Energy content upper	kWh/nm³	10.7		
Water content, maximum	mg/nm³	100	5	32
Methane minimum	vol%		96	97
Carbon dioxide, maximum	vol%			3
Oxygen, maximum	vol%	3.5	0.5	1
Carbon dioxide, + oxygen + nitrogen, maximum	vol%	3	3	3
Hydrogen, maximum	vol%			0,5
Hydrogen sulphide, maximum	mg/nm³	7	5	23
Total sulphure	mg/nm³		14.3	
Particles or other solid contaminants, max. diameter	mm			5
Halogenated hydrocarbons	mg/m³	1	0	

Biogas from Biomass

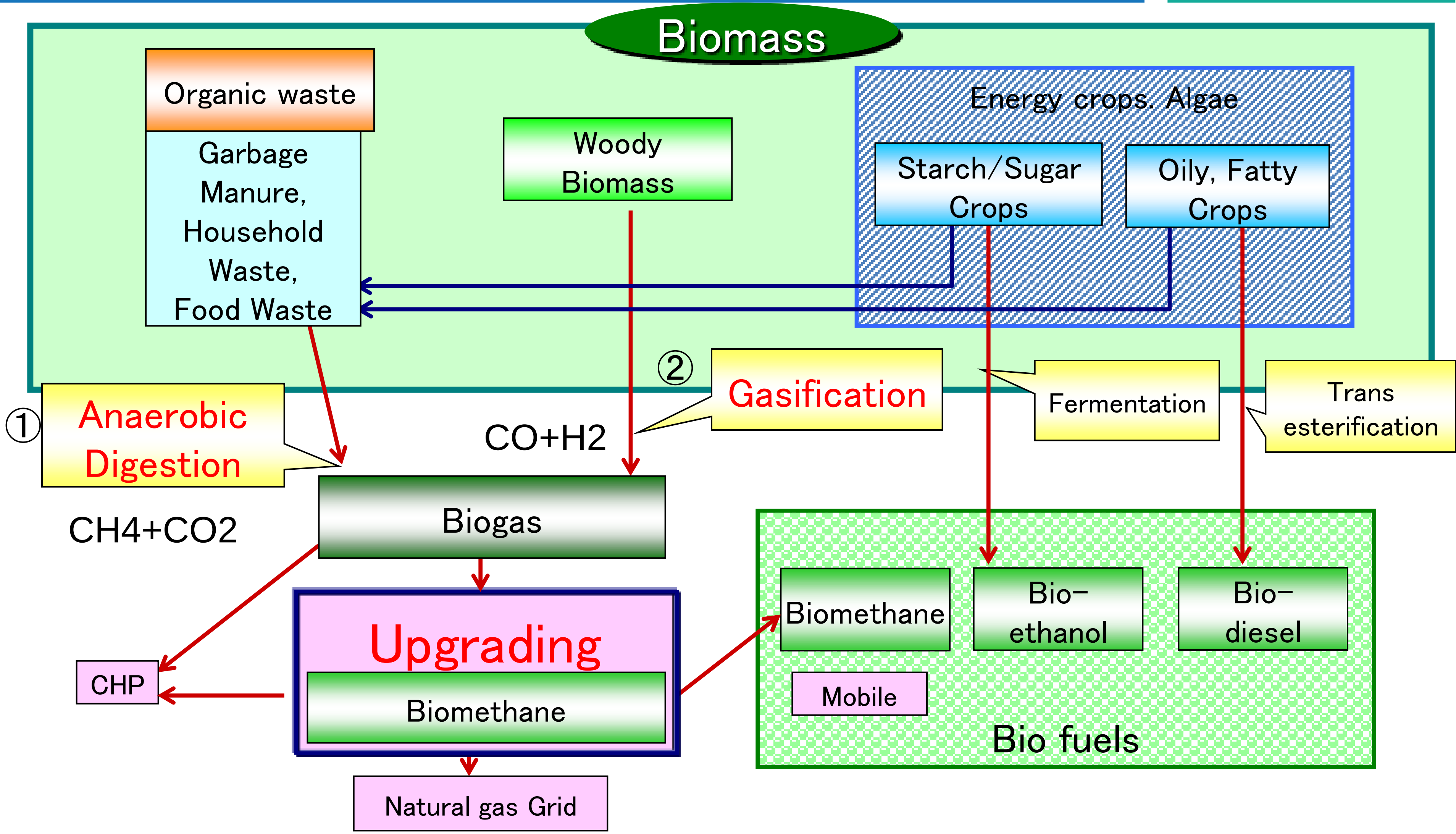
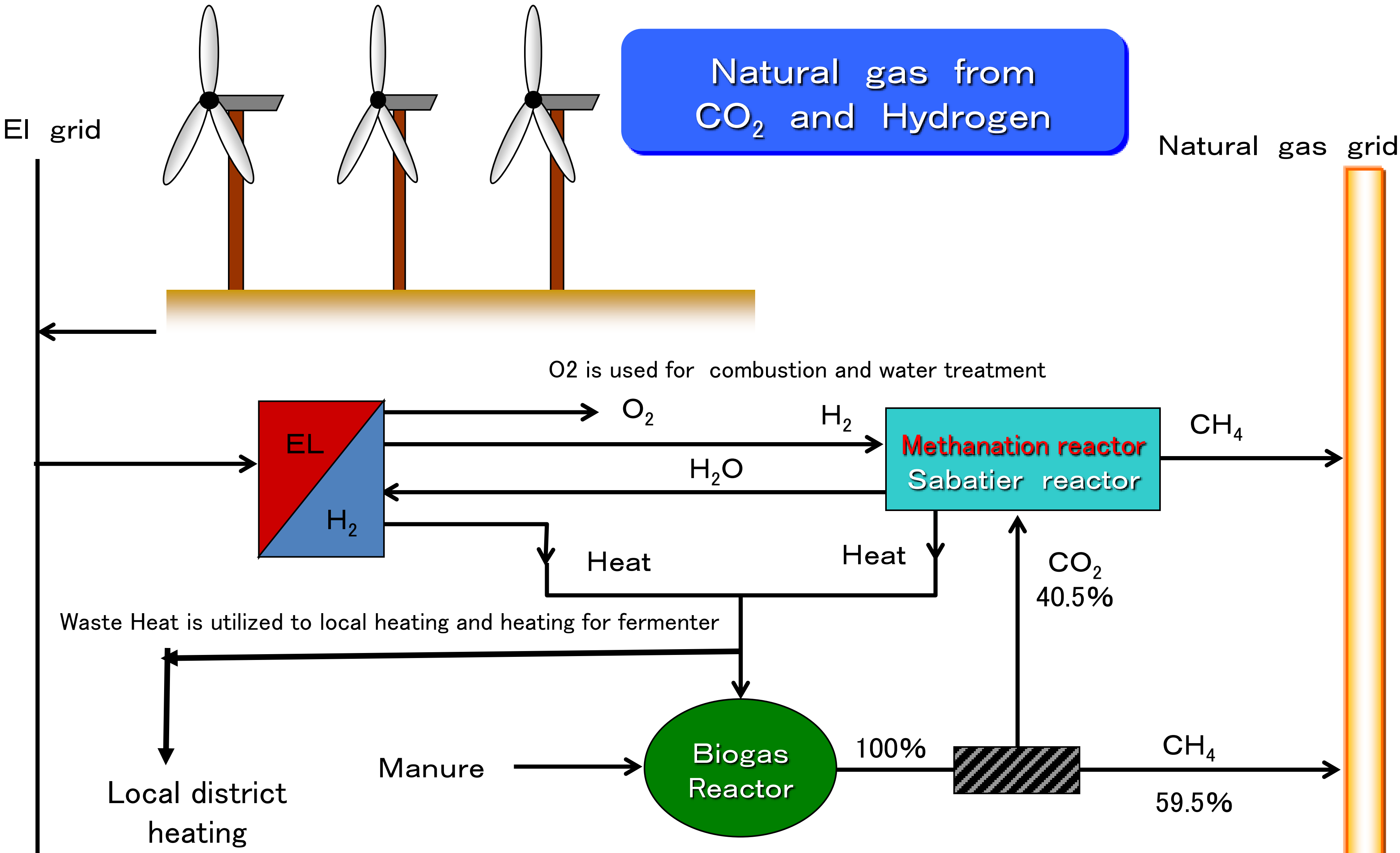


Figure 1. Overview of processing biomass into sustainable energy

Green natural gas from wind power and CO2



Source : Presentation material by Aksel Hauge Pedersen **DONG Energy**

Recommend standards for appliances in Japan

Appliance	Components									Source
	Methane	Heat value	H2S	Siloxane	CO2	O2	N2	others	Dew point	
Gas engine	60～70% allowance: Less than ±5%	21.56～25.12MJ/Nm³	Less than 10ppm	Less than 0.02ppm	—	—	—	Moisture: Under dew point at actual temp. Total: Less than 100ppm	—	※1
Fuel cell	60%	—	Less than 3ppm	Less than 1ppm	—	Less than 50ppm	N2: Less than 0.1% NH4: Less than 1ppm	Cl: Less than 1ppm HCl: Less than 1ppm SO2: Less than 1ppm Organic S: Less than 0.3ppm Moisture: Not saturated at room temp.	—	※2 ※3
Automobile	More than 97%	—	Less than 0.1ppm	Less than 1mg/Nm³	—	Less than 4%	—	Odorant intensity Less than 2000	Less than −51℃	※4
Source of city gas	—	More than 35.56MJ/Nm³	Less than 2ppm	—	Less than 4%	—	—	—	Under dew point	※5
Grid Injection	—	45MJ/Nm³	Less than 1.0mg/m³	Negotiation	Less than 0.5Vol%	Less than 0.01Vol%	Less than 1.0Vol%	Odorant conc. 12～16mg/Nm³	Negotiation	※6
Gas Cylinder supply	More than 85%	—	Less than 10ppm	-	Less than 15%	Less than 1%	1%以下	CO: Less than 1ppm	Less than −60℃	※7
Ref. Raw Biogas	60～65%	21～23MJ/Nm³	0.02～0.08%	20～50ppm	33～35%	—	0～3%	H2:0～2%	—	※8 ※9
Ref. Natural gas 13A	89.60%		—	—	—	—	—	Ethane Propane Butane	—	※10

Source: ※1: Engine maker catalogue
※2: Guide line for fuel Cell introduction 2008、NEF Japan
※3: Fuel Cell maker Catalogue
※4: Kobe city publication Higashi nada sewage treatment center
※5: Nagaoka city and Hokuriku gas
※6: Guideline for purchasing Biogas by Osaka gas
※7: Standard of C company
※8: Guideline for facility 2009: Japanese Sewage treatment association
※9: Guideline for biogas Japanese Ministry of Environment 2008
※10: Tokyo gas Home page

Contents

- **Current status of gas quality in Japan**
- Under these circumstances, the Japanese gas companies have established their own provisions for gas supply and has set the terms and conditions for quality of gas to be received from outside to maintain the quality of supply gas on the standard level for the gas appliances at their customers. This report explains the current status of gas quality issues in Japan and measures taken by gas utilities to secure the quality standard.

	Standard 13A	13A-1	13A-2	13A-3
CH4	88.9	85.0	55.0	98.0
C2H6	6.8	0	0	0
C3H8	3.1	15.0	15.0	0
C4H10	1.2	0	0	0
Others	0	0	H2 : 30.0	N2 : 2.0
Heat Value (MJ)	45.00	49.15	37.05	39.1
Heat Value (kcal/m3)	**10,750**	**11,741**	**8,851**	**9,840**
Specific Gravity	**0.638**	**0.705**	**0.494**	**0.563**
Combustion Velocity (cm/s)	37.00	37.70	47.30	36.00
Wobbe Index	**56.40**	**58.50**	**52.70**	**53.10**

Standard for Biomethane injection to the grid of Netherlands

Appendix 1： biomethane compostion requirements（Dutch）

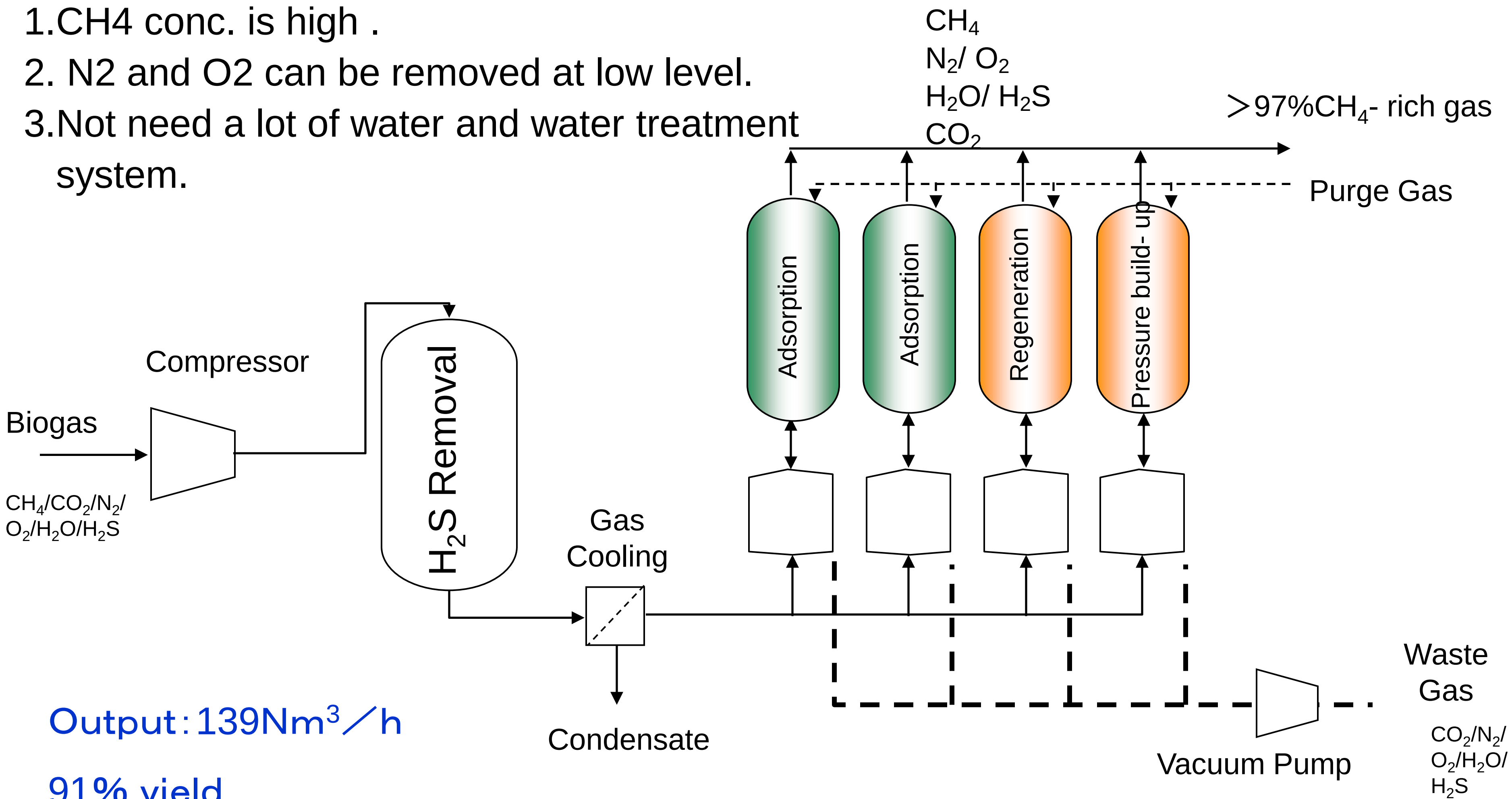
Items	Standard　Gastec	Unit
Calorific value	31.6–35.7	MJ/M^3
Wobbe-index	43.46–44.41 （G_TS）	MJ/M^3
Water dew point	＜0.10 (3 bar)	℃
Temperature	0–40	℃
H2S	5 （G_TS）	ppm
Mercaptan	10 （G_TS）	
Odorant（THT）	＞10, nom 15 ＜40 (GTS)	mg/m^3
Ammonia	Ammoniak:3	mg/m^3
Cl	50	mg/m^3
hydro Chloride (HCl)	1	ppm
Hydro cyanide (HCN)	10	ppm
Carbon Mono-oxide (CO)	1	Mol%
Carbon di-oxide （CO_2）	6	Mol%
BTX (Benzene. Toluene. Xylene)	500	ppm
Aromatische koolwaterstoffen	1（G_TS）	moj96

PSA Upgrading Method

1.CH4 conc. is high .

2. N2 and O2 can be removed at low level.

3.Not need a lot of water and water treatment system.



Output：139Nm^3／h

91% yield

98% purity

Source of Biogas & yield

	Sewage Sludge	Cattle Manure	Swine Manure	Poultry Manure	Municipal Waste	Food Factory Waste Water
Solid Content	2.5%	10%	10%	30%	25%	0.1%
Gas Yield	ave.10m^3/t	ave.25m^3/t	ave.45m^3/t	*ave.140 m^3/t	ave.150m^3 /t	ave.0.3m^3/t
Notes	300 plants in Japan	Dozens of plants in Japan		Unsuitable for anaerobic digestion due to high nitrogen content	Sometimes, ammonia removal required	Dozens of UASB Plants in Japan

＊Solid content of municipal waste：0～20% Dry type digester
10% Wet type digester

Standard for Biomethane injection to the grid of Netherlands

Appendix 1： biomethane compostion requirements（Dutch）

Items	Standard Gastec	Unit
Calorific value	31.6–35.7	MJ/M^3
Wobbe-index	43.46–44.41 （G_TS）	MJ/M^3
Water dew point	＜0.10 (3 bar)	℃
Temperature	0–40	℃
H2S	5 （G_TS）	ppm
Mercaptan	10 （G_TS）	
Odorant（THT）	＞10, nom 15 ＜40 (GTS)	mg/m^3
Ammonia	Ammoniak:3	mg/m^3
Cl	50	mg/m^3
hydro Chloride (HCl)	1	ppm
Hydro cyanide (HCN)	10	ppm
Carbon Mono-oxide (CO)	1	Mol%
Carbon di-oxide （CO_2）	6	Mol%
BTX (Benzene. Toluene. Xylene)	500	ppm
Aromatische koolwaterstoffen	1（G_TS）	moj96