I4. Synthesis of Bio-LPG from Biomass-derived Syngas

Tomoko OGI, Masakazu NAKANISHI,
National Institute of Advanced Industrial Science and Technology
Kaoru FUJIMOTO
University of Kitakyushu

IEA Bioenergy Conference
Vienna Austria, November 13 , 2012

Introduction: About JAPAN –Energy Status, now-

Primary energy sources

	2008	2009	2010	2011
hydraulic	653PJ	648PJ	699PJ	640PJ
geothermal	23PJ	24PJ	22PJ	22PJ
nuclear	2 218PJ	2 420PJ	2 576PJ	1 436PJ
coal	5 455PJ	4 409PJ	5 024PJ	4 765PJ
petroleum	11 088PJ	9 647PJ	9 964PJ	9 814PJ
natural gas	3 944PJ	3 678PJ	3 970PJ	4 431PJ
TOTAL	23 282PJ	20 827PJ	22 255PJ	21 107PJ

(petroleum + natural gas) 14-15EJ

fossil-LPG is about 6% of imported petroleum and natural gas.

$$\frac{750\text{-}800\text{PJ}}{14\text{-}15\text{EJ}} \approx 6\%$$

Energy applications

	2008	2009	2010	2011	
LPG	16 245kt	15 081kt	14 644kt	15 008kt	750-800PJ
municipal gas	35 727Mm^3	32 954Mm^3	35 206Mm^3	35 109Mm^3	
petroleum oil	207 670ML	193 996 ML	197 209ML	193 056ML	
gasoline	57 247ML	57 447ML	58 368ML	56 864ML	
diesel oil	32 246ML	32 247ML	33 057ML	44 646ML	
electric power	913 138GWh	846 725GWh	901 522GWh	859 663GWh	

About JAPAN –Strategy- why LPG? Why bio-LPG?

- **New National Energy Strategy (2006)**
  - Petroleum oil dependency of transport energy will be brought down from 100% to 80% till 2030.
  - 500,000kl liquid bio-fuel will be introduced.
- **Next Generation of Vehicles and Fuel Initiative (2010)**
  - The second generation liquid bio-fuel was nominated.
- **Act of Sophisticated Methods of Energy Supply Structures (2010)**
  - Use of non-fossil energy sources and the effective use of fossil energy resources are promoted.
  - LPG suppliers are mandated to introduce bio-gas.
- **Basic Energy Plan for Japan (2010)**
  - LPG is classified to be distributed source of energy.

-------March 11, 2011---the East Japan Great Earthquake

Strategy-…Why LPG?
…then East Japan Great Earthquake

An earthquake of unprecedented force
A tsunami of unspeakable destructiveness
….then   A radioactive awakening

Japan convulses, grieves, moves on

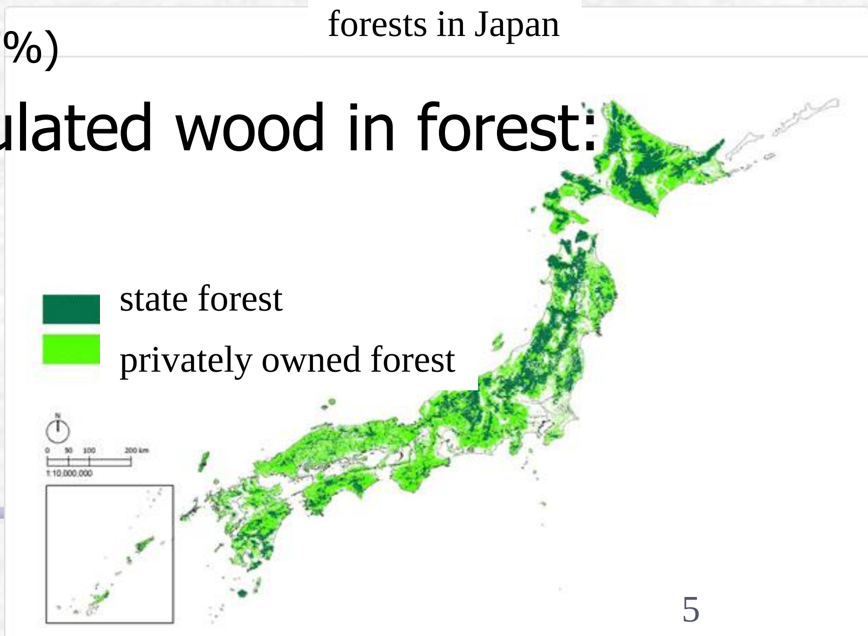
At that time, from that day, LPG has been supplied and used as local energy for heat, cooking….

- Basic Energy Plan for Japan (2010)
  - LPG is classified to be distributed source of energy.
    - LPG is supplied to more than 90% area of Japan.
  - ***LPG is very useful especially in disaster***.

About JAPAN –Forest- Why bio-LPG?

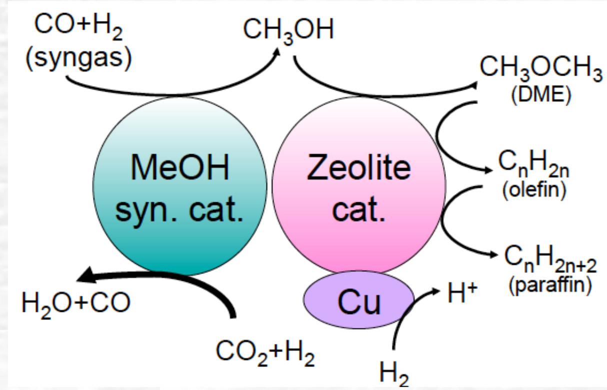
- New National Energy Strategy (2006)
  - Petroleum oil dependency of transport energy will be brought down from 100% to 80% till 2030…. → Development of substitutive Bio-fuel
- About 68.5% of land are of Japan is forest:
  - forest area: 24 979kha
    - Total land area: 36 450kha
    - 3rd highest in the world
      - 1st: Republic of Finland (72.9%)
      - 2nd: the Kingdom of Sweden (68.7%)
  - Estimated amounts of accumulated wood in forest: 4432Mm^3

In Japan, forest residues and agricultural wastes have great potential as resources of fuel materials*….(but cost for collection?)*



National (NEDO) Project:

Synthesis of LPG from Biomass-Derived Syngas (FY2010-2013)



direct LPG synthesis
hybrid catalyst

$$CO + CO_2 + H_2 \rightarrow C_nH_{2n+2}$$

bio-LPG

bio-Syngas
(CO, CO_2, H_2)

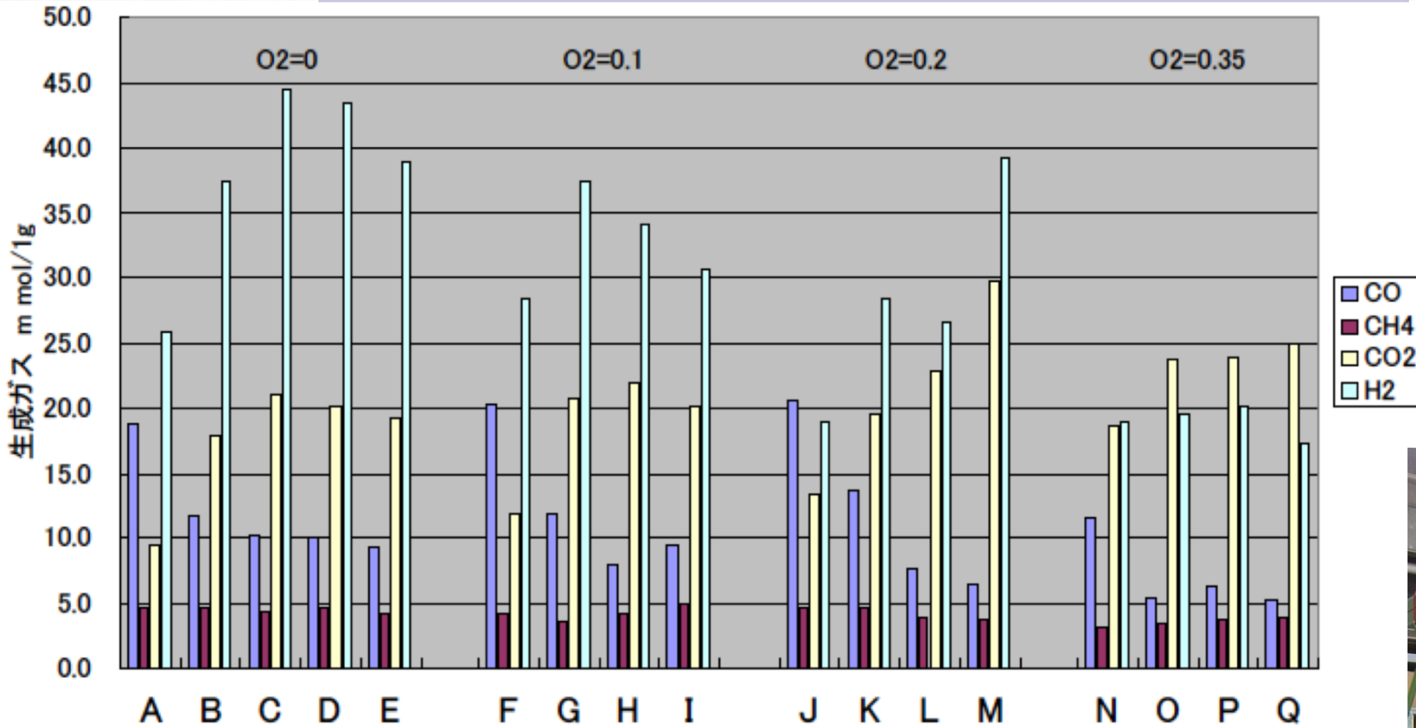
Lab-scale
gasifier(AIST)

Composition control
for catalytic
synthesis

Lab-scale LPG synthesis reactor
(Japan Synthesis Gas/University of Kitakyushu)

Gas properties obtained from lab-scale gasifier

C	H	O	N	S	Ash
48.6%	6.1%	45.1%	0.0%	0.0%	0.3%

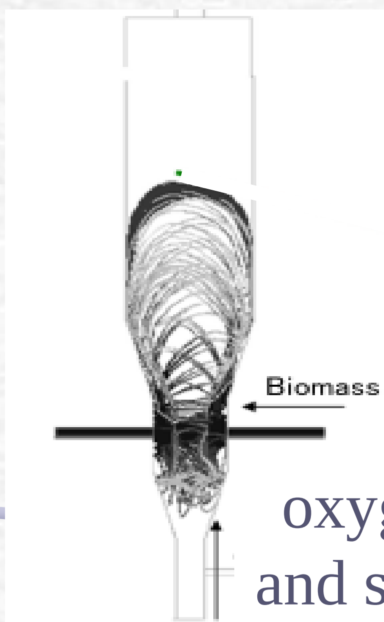


- Japanese cedar wood chips

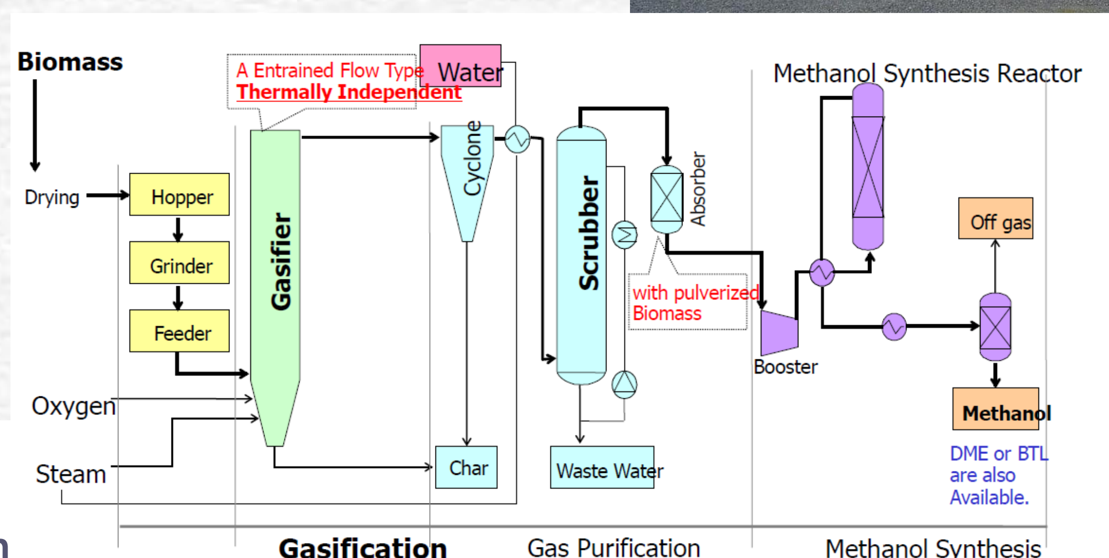
O2/C \ H2O/C	0.5	2.5	5	10
0	A	B	C	D
0.1	F	G	H	I
0.2	J	K	L	M
0.35	N	O	P	Q

Entrained-flow Biomass Gasification

- 100-200t/day-scale commercial plant (plan)
- Cold gas efficiency is 75% or higher.
- 0.1%-tar and 1%-char yields, when operating recycle systems
- H_2, CO, CO_2 contents are highly controllable by adjusting H_2O, O_2 and biomass feed rates.
  - H_2 increases when increasing H_2O.
  - H_2 and CO decrease when increasing O_2.
  - CH_4 content: 8-10%



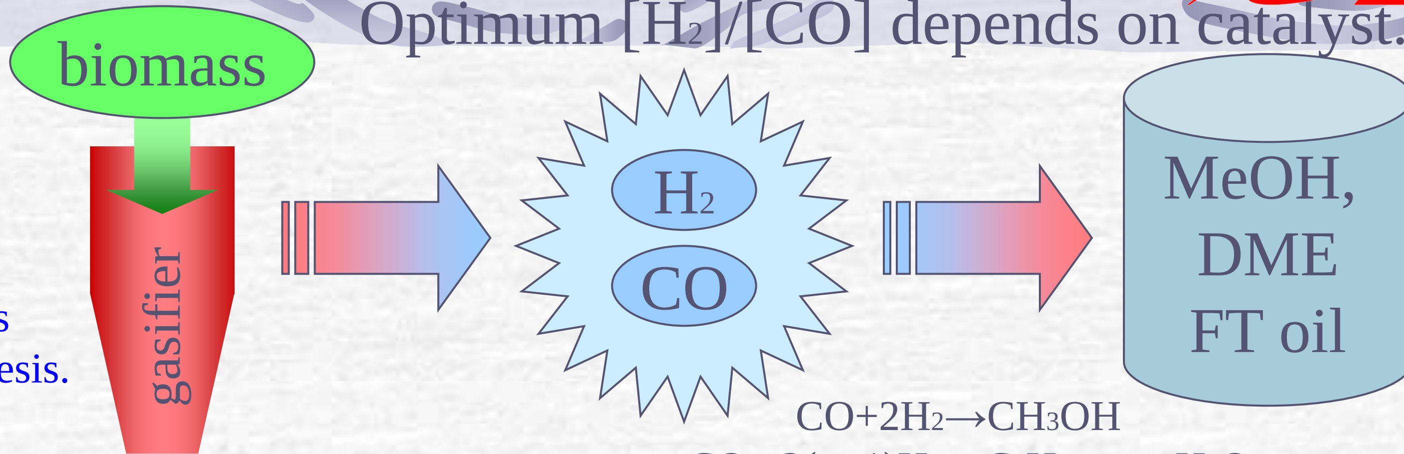
oxygen and steam



2t/d-scale test plant (MHI)

Ordinal BTL (MeOH, DME, FT oil) process

Optimum $[H_2]/[CO]$ depends on catalyst.



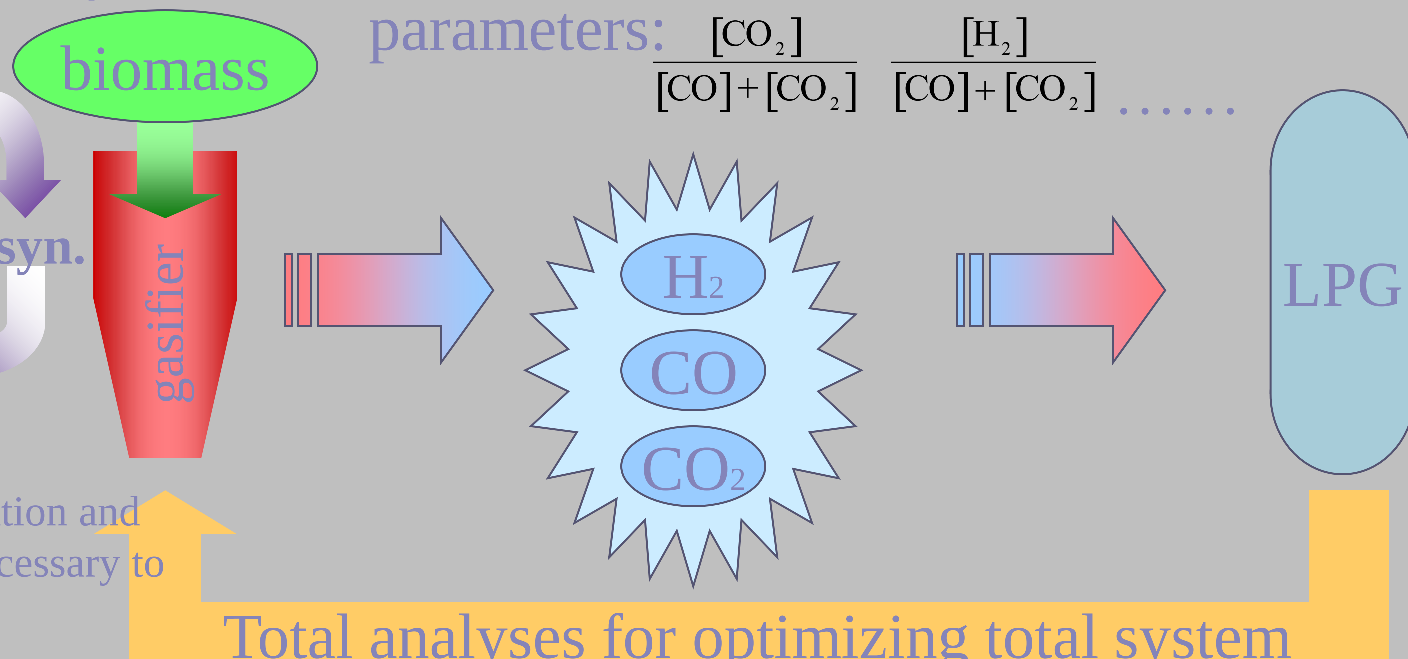
Purpose of gasification:
To obtain gas compositions suitable for catalytic synthesis.

$CO + 2H_2 \rightarrow CH_3OH$

$nCO + 2(n+1)H_2 \rightarrow C_nH_{(2n+2)} + nH_2O$

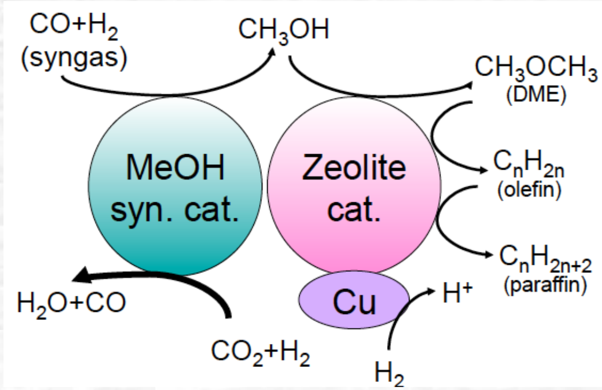
Bio LPG synthesis process

parameters: $\frac{[CO_2]}{[CO]+[CO_2]}$ $\frac{[H_2]}{[CO]+[CO_2]}$ ......



Total analyses of gasification and catalytic synthesis are necessary to optimize total system.

National (NEDO) Project:
Synthesis of LPG from Biomass-Derived Syngas (FY2010-2013)



direct LPG synthesis
hybrid catalyst

$$CO + CO_2 + H_2 \rightarrow C_nH_{2n+2}$$

bio-LPG

bio-Syngas
(CO, CO_2, H_2)

Composition control
for catalytic
synthesis

Lab-scale
gasifier(AIST)

Lab-scale LPG synthesis reactor
(Japan Synthesis Gas/University of Kitakyushu)

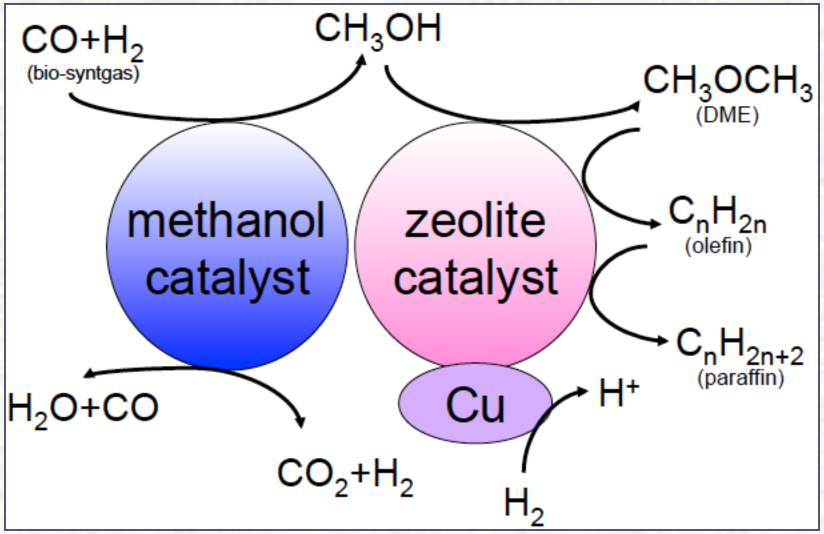
direct LPG synthesis catalyst

- a hybrid of methanol and zeolite catalysts
- One-path process
- 80%-CO conversion rate at moderate conditions
  - 260^{o}C and 2.0MPa

} Simple and low-cost reactor

- Bio-LPG is synthesized from H_2, CO and CO_2
  - Reversible and irreversible reactions proceed simultaneously.

$$2CO + 4H_2 \leftrightarrow 2CH_3OH$$
$$\leftrightarrow CH_3OCH_3 + H_2O$$
$$\rightarrow C_nH_{2n} + H_2O \rightarrow C_nH_{2n+2}$$
$$H_2 \rightarrow 2H^+$$
$$CO + H_2O \leftrightarrow CO_2 + H_2$$

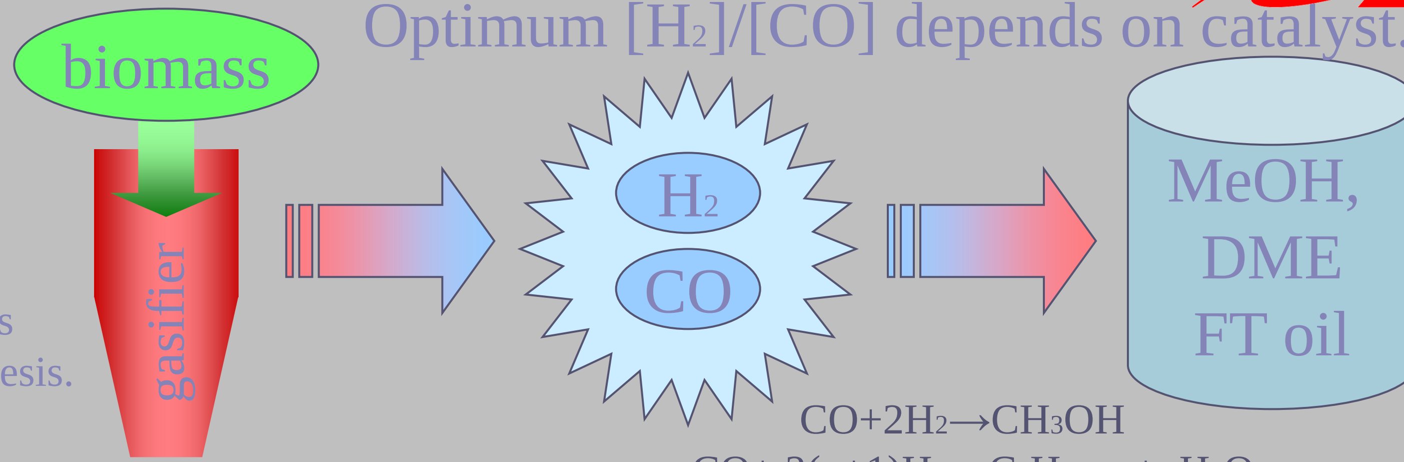


- Synthesis properties depend on H_2, CO, CO_2 contents.
  - optimum conditions: $\frac{[H_2]}{[CO]+[CO_2]} \geq 2.5$ $\quad 0.1 \leq \frac{[CO_2]}{[CO]+[CO_2]} \leq 0.4$

Ordinal BTL (MeOH, DME, FT oil) process

Optimum $[H_2]/[CO]$ depends on catalyst.

Purpose of gasification:
To obtain gas compositions
suitable for catalytic synthesis.

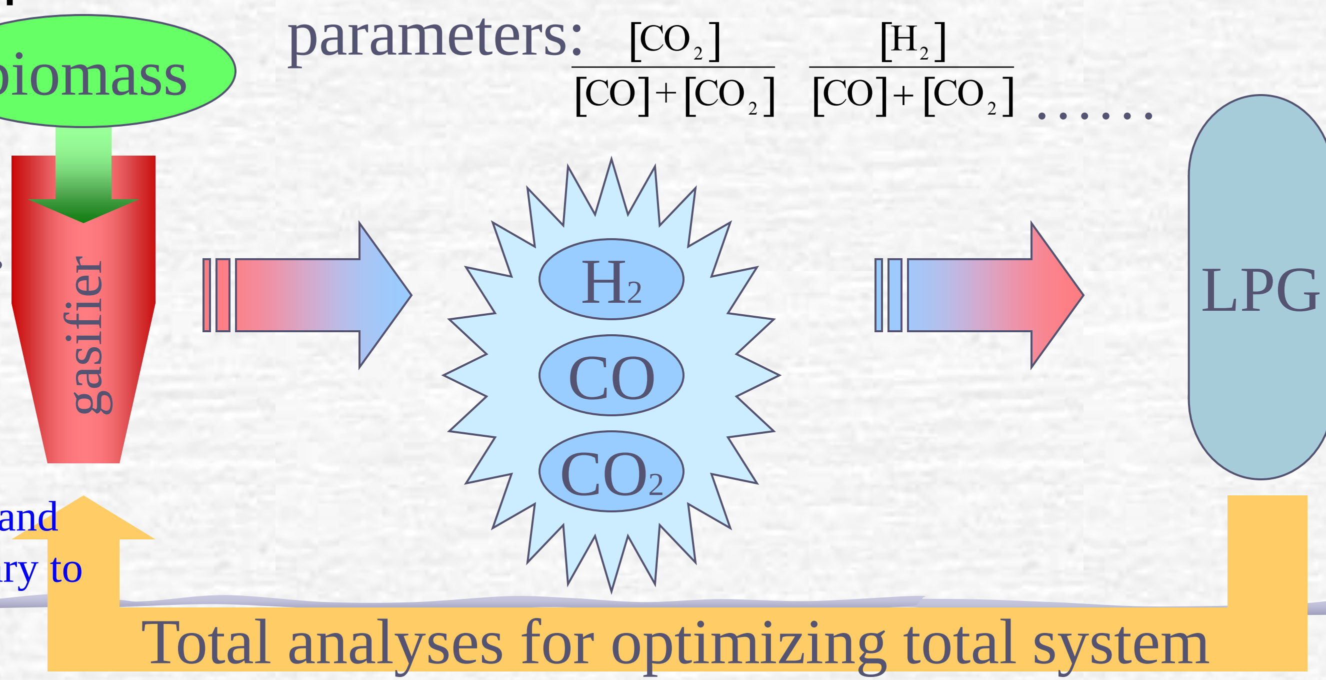


$CO + 2H_2 \rightarrow CH_3OH$

$nCO + 2(n+1)H_2 \rightarrow C_nH_{(2n+2)} + nH_2O$

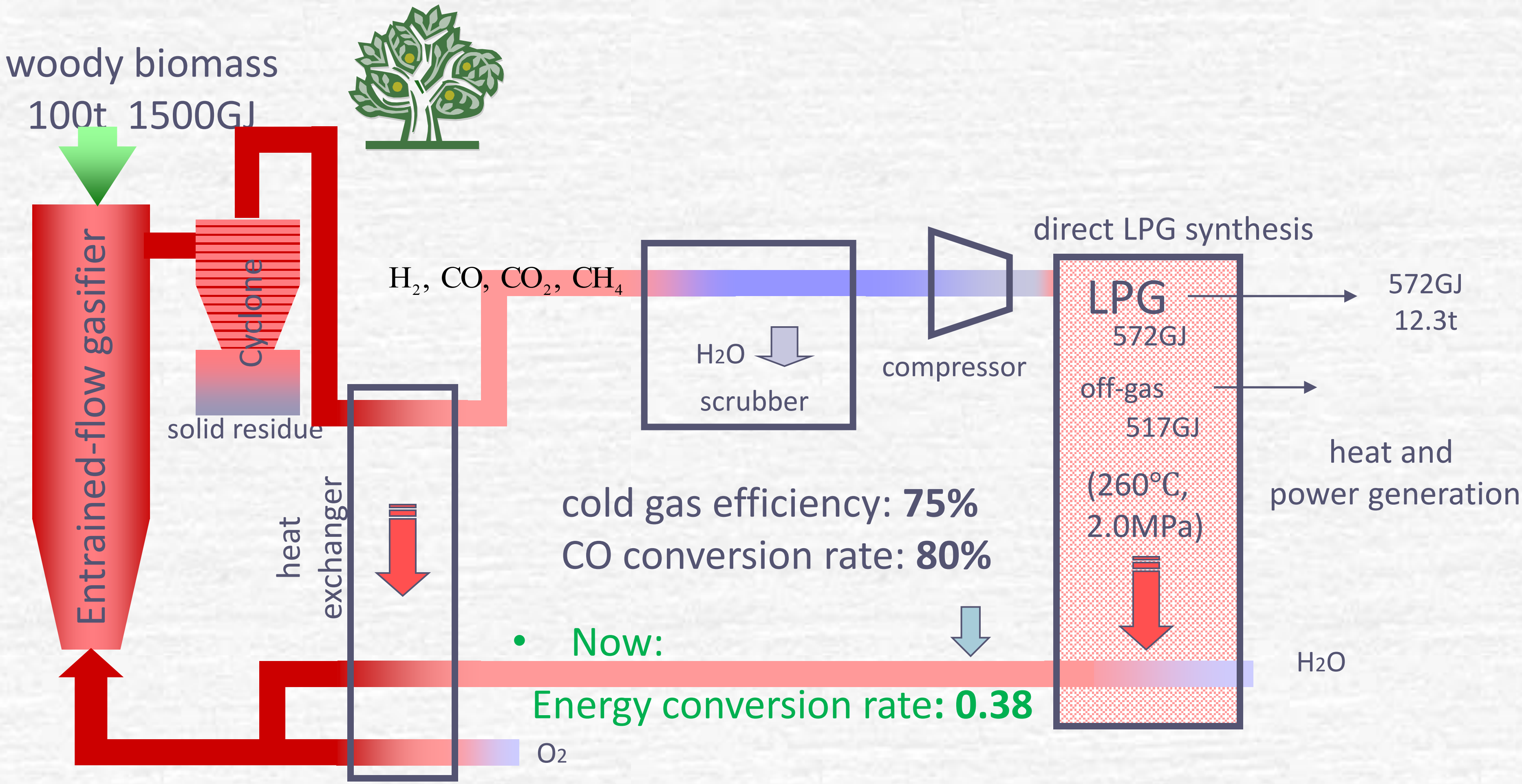
Bio LPG synthesis process

parameters: $\frac{[CO_2]}{[CO]+[CO_2]}$ $\frac{[H_2]}{[CO]+[CO_2]}$ ……



Total analyses of gasification and catalytic synthesis are necessary to optimize total system.

Integrated system of gasification and LPG synthesis

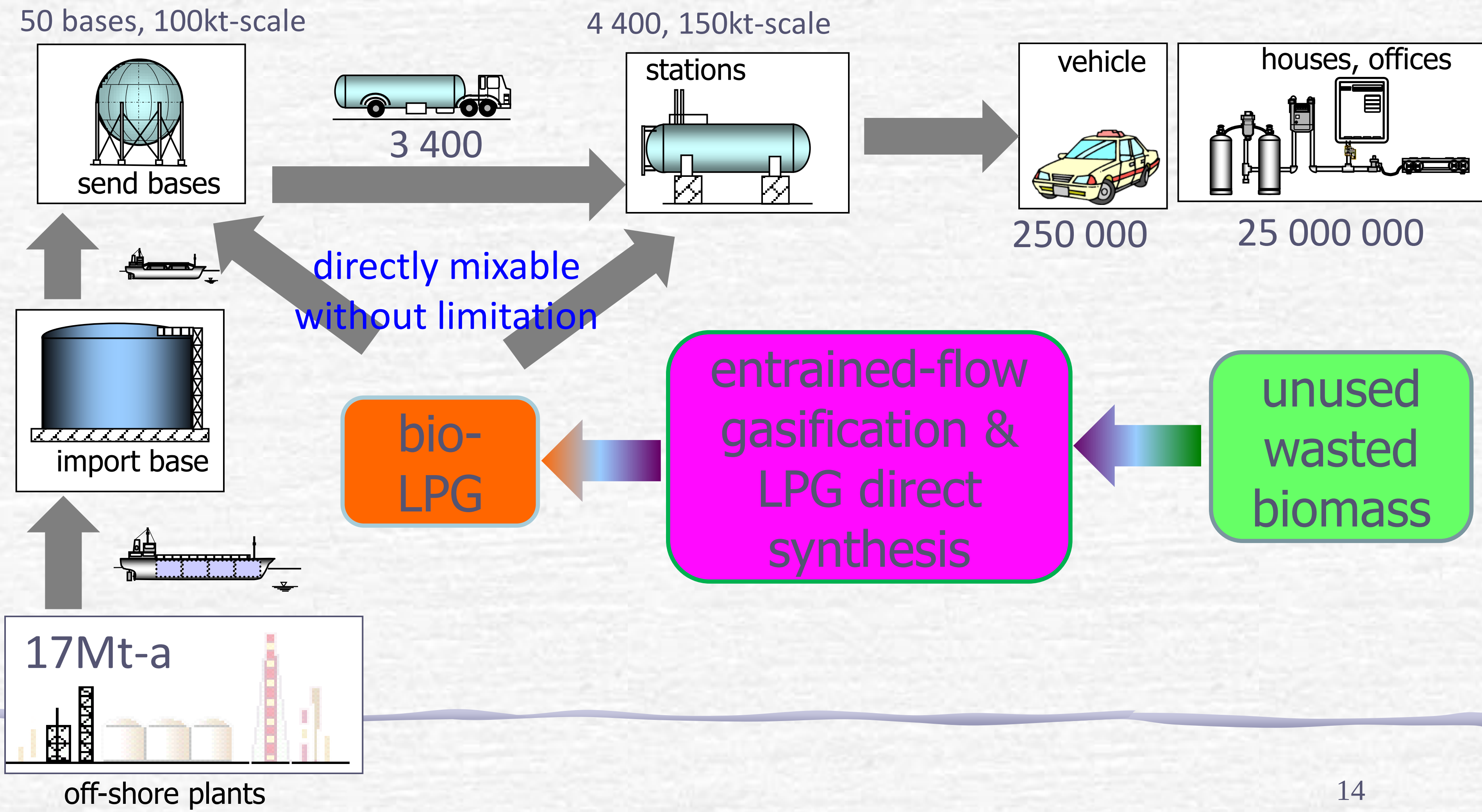


*Catalytic gas reforming (CH4 reforming & Shift reaction)

$$CH_4 + H_2O \rightarrow 3H_2 + CO \qquad CO + H_2O \rightarrow H_2 + CO_2$$

LPG supply chain and bio-LPG plant

- Bio-LPG is suitable for present LPG supply chain.
- Bio-LPG is directly mixable without limitation.



Conclusion

- System of woody biomass gasification(entrained-flow)-direct catalytic LPG synthesis is a promising process

  high cold efficiency gasification & high CO conversion to direct LPG synthesis

  (but subjects to be solved…..)

- Bio-LPG is suitable for Japanese LPG supply chain and for local product for local consumption.
  - Bio-LPG of about 5.8kt is producible at a 100t/d-scale plant in each year.
    - 750 million Japanese yen (>9 million US dollar).
    - 130 000 yen/t-LPG.
  - Bio-LPG of about 288kt is producible if 50 LPG bases have own plants.
    - about 2% of LPG consumption.

- Subjects of the further study
  - catalytic gas reforming to increase H_2 and CO
  - low cost ultra clean-up
  - to acquire engineering data of LPG synthesis reactor
  - effective recovery of heat

Acknowledgement

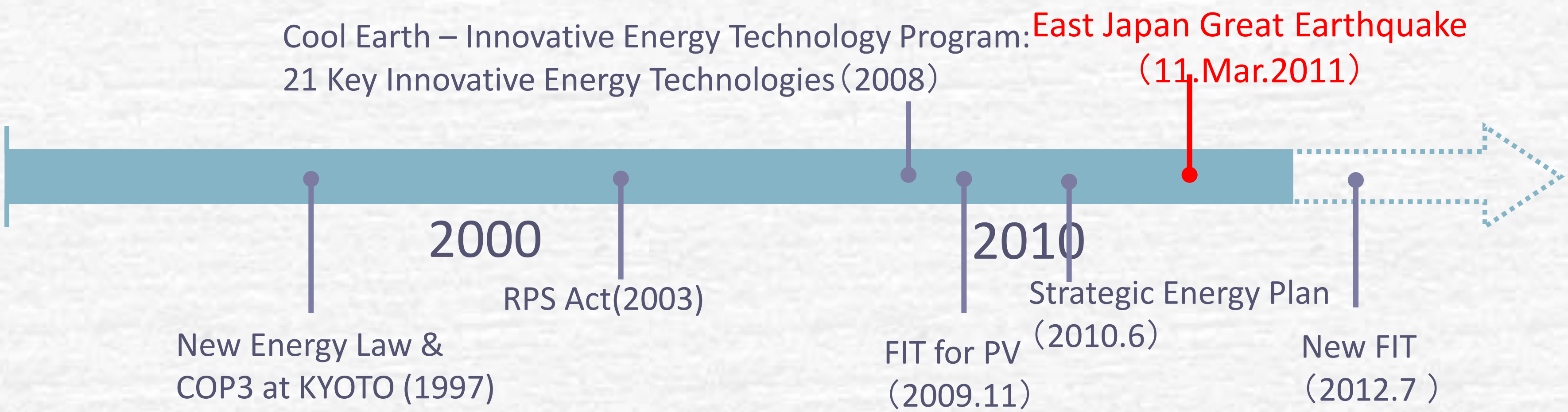
- This research has been performed and funded by NEDO biomass project.
- Authors thank to Dr. Takeno and Dr. Matsumoto (Mitsubishi Heavy Industries Ltd.,)for variable discussion about biomass gasification.

Thank you for your kind attention!!

Before 3.11/ After 3.11….discontinuity

Before 3.11

Review of Basic Energy Plan (June 2010) ---
--Enforcement of introduction of Nuclear and renewable energy
Nuclear (& hydraulic, “zero emission” energy) ⇒ ~50%



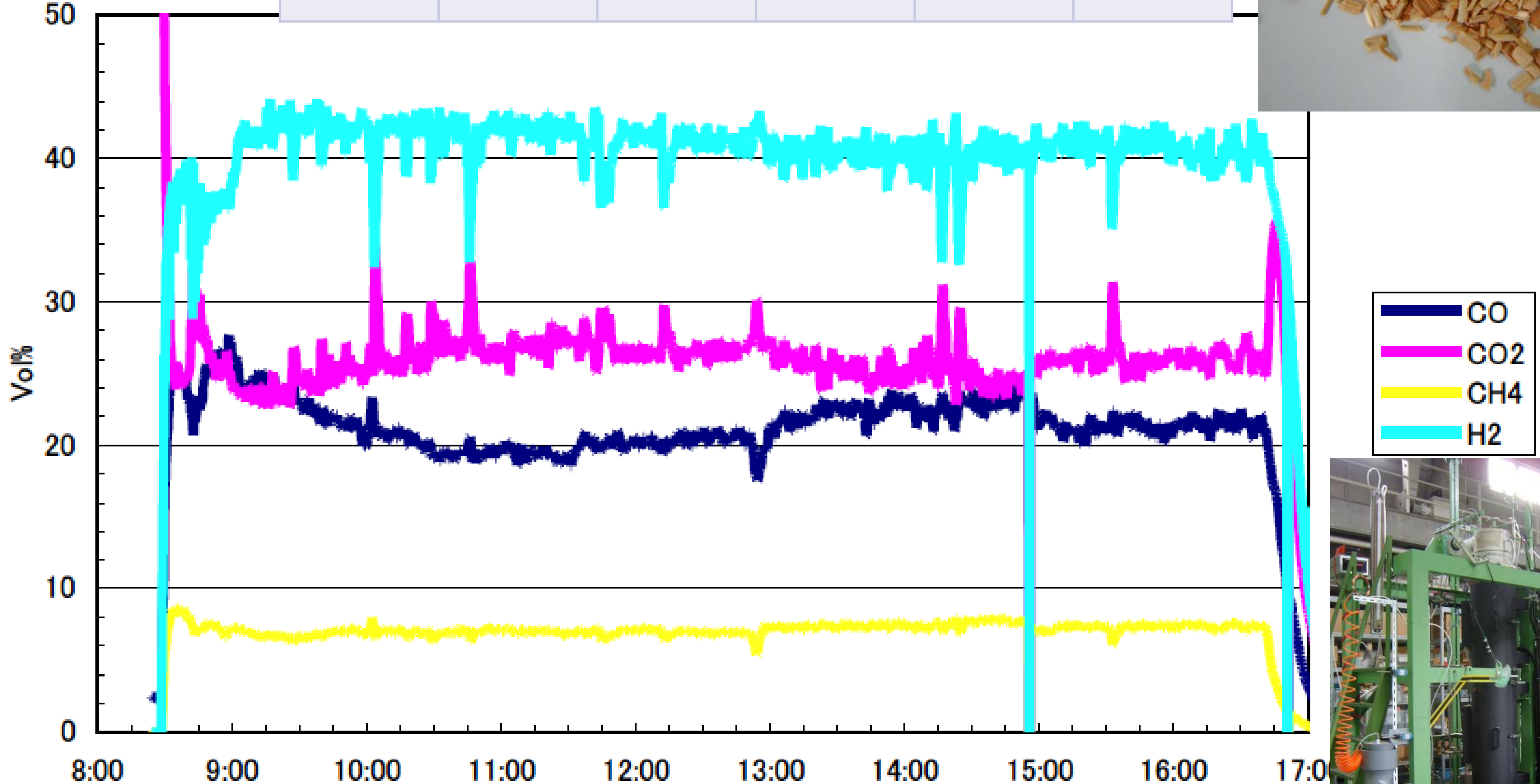
After 3.11

Again, Review of Basic Energy Plan ---
--Enforcement of introduction of renewable energy,
especially solar and wind ?
⇒ now under discussion…

Gas compositions of lab-scale gasifier

- Japanese cedar wood chips

C	H	O	N	S	Ash
48.6%	6.1%	45.1%	0.0%	0.0%	0.3%



Integrated system of gasification and LPG synthesis

Because amount of recoverable/usable heat is limited, H_2O and O_2 feed rates (gasification agent) are limited.

woody biomass
100t 1500GJ

Practical gas compositions

$$\frac{[H_2]}{[CO]+[CO_2]} \le 1.5 \qquad \frac{[CO_2]}{[CO]+[CO_2]} \ge 0.5$$

Optimum gas compositions for LPG synthesis

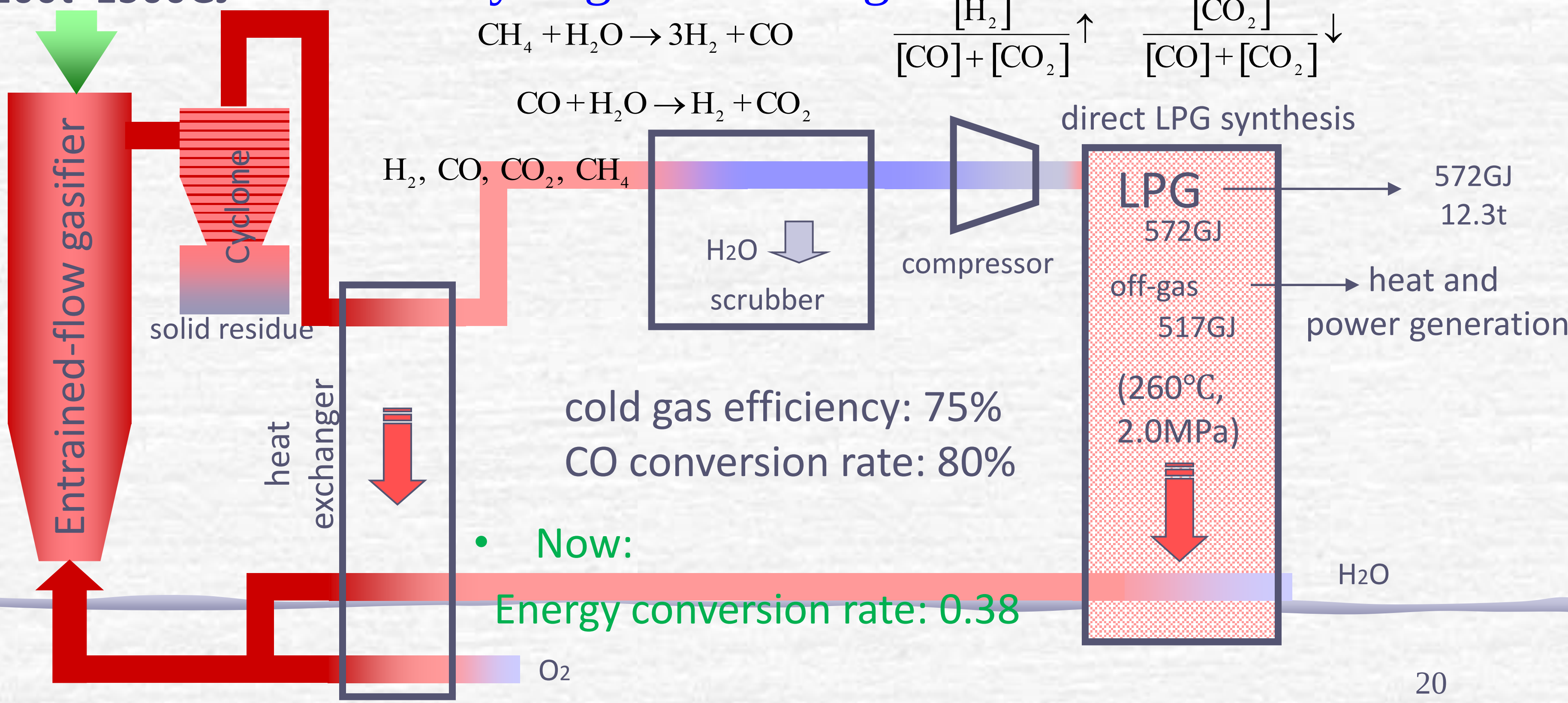
$$\frac{[H_2]}{[CO]+[CO_2]} \ge 2.5 \qquad 0.1 \le \frac{[CO_2]}{[CO]+[CO_2]} \le 0.4$$

Catalytic gas reforming

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

$$CO + H_2O \rightarrow H_2 + CO_2$$

$$\frac{[H_2]}{[CO]+[CO_2]} \uparrow \qquad \frac{[CO_2]}{[CO]+[CO_2]} \downarrow$$



cold gas efficiency: 75%
CO conversion rate: 80%

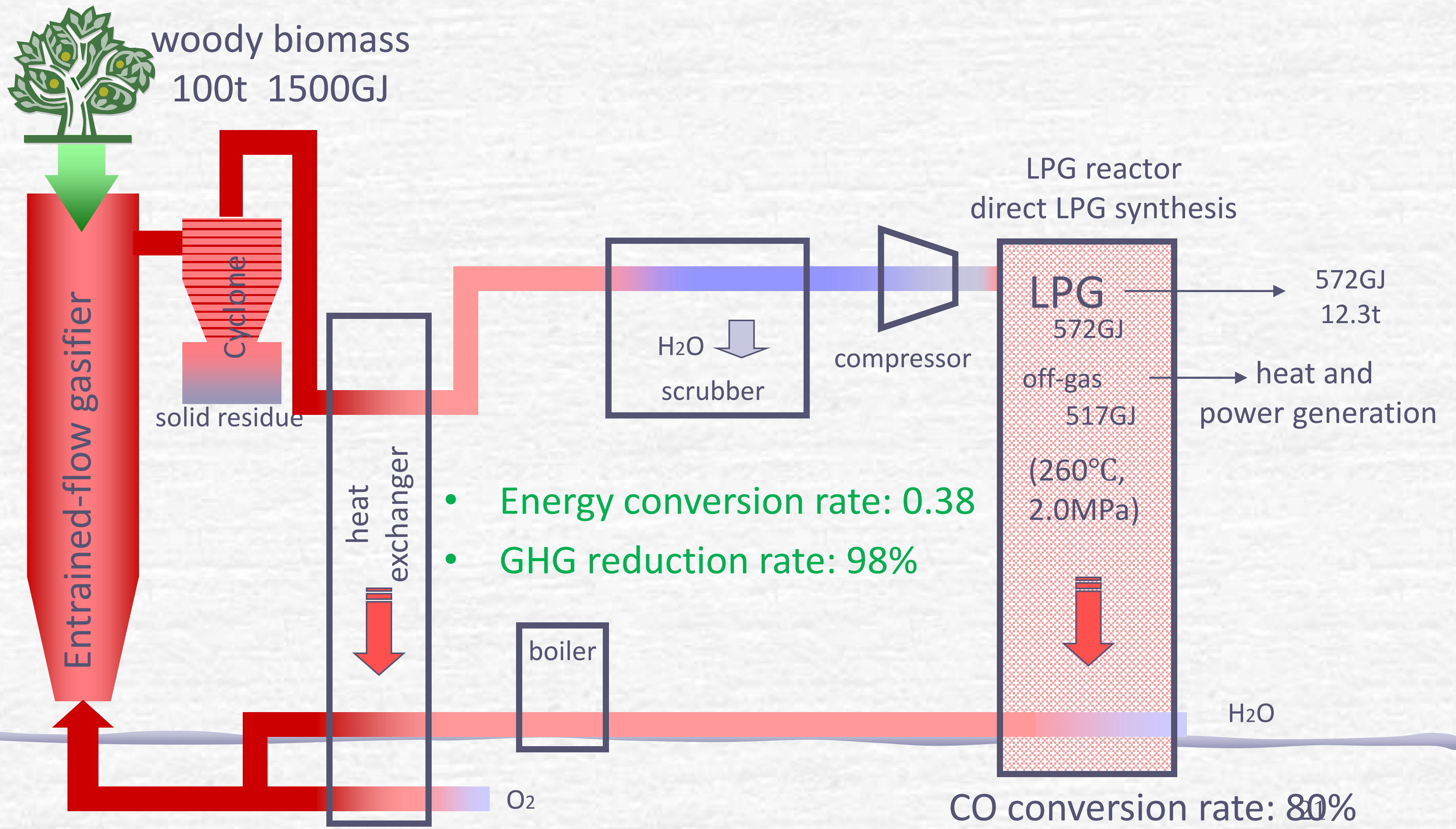
- Now:

Energy conversion rate: 0.38

Integrated system of gasification and LPG synthesis

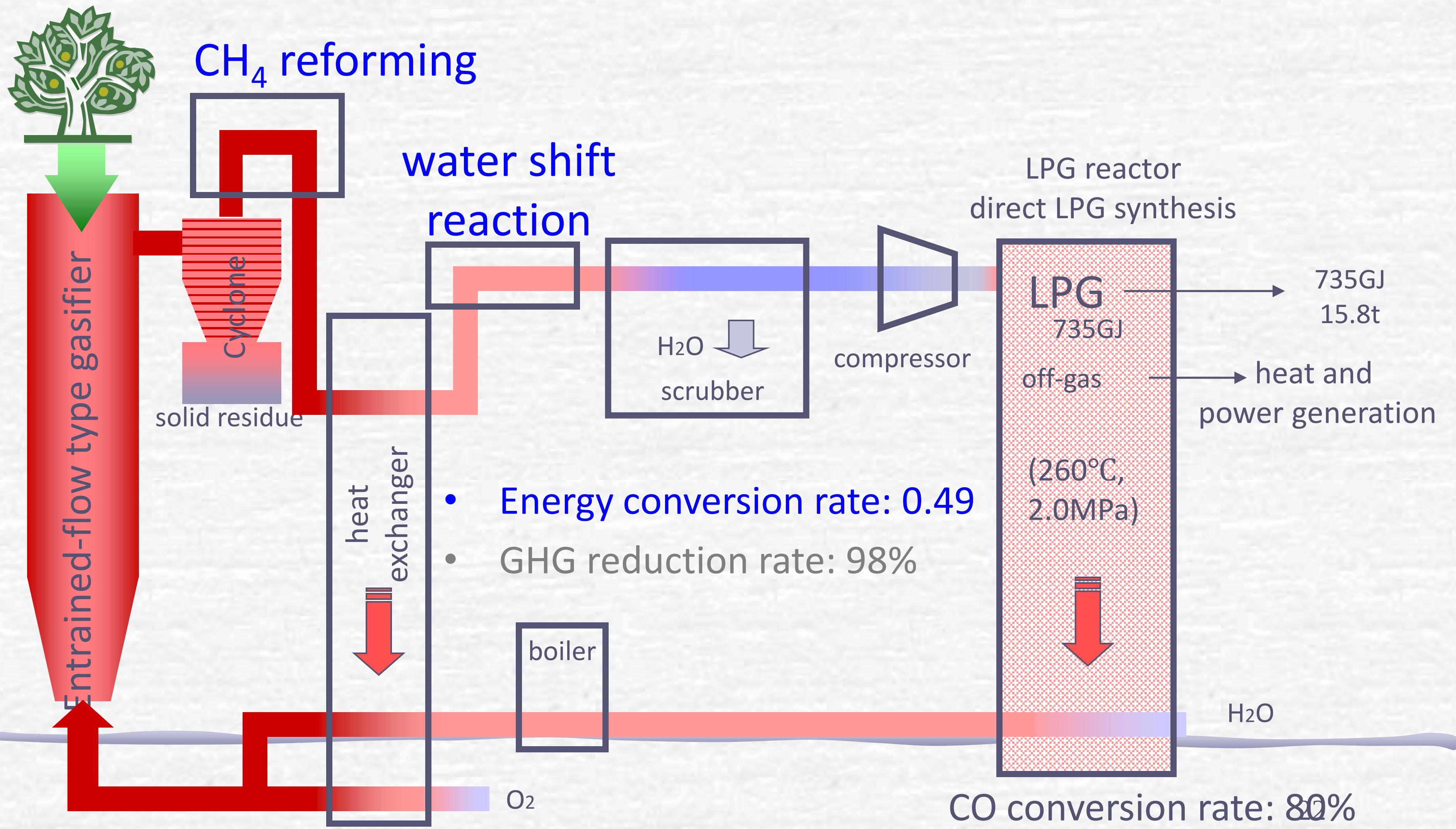
- Entrained-flow Biomass gasification
- Direct LPG Synthesis

} simple, low cost and high efficiency

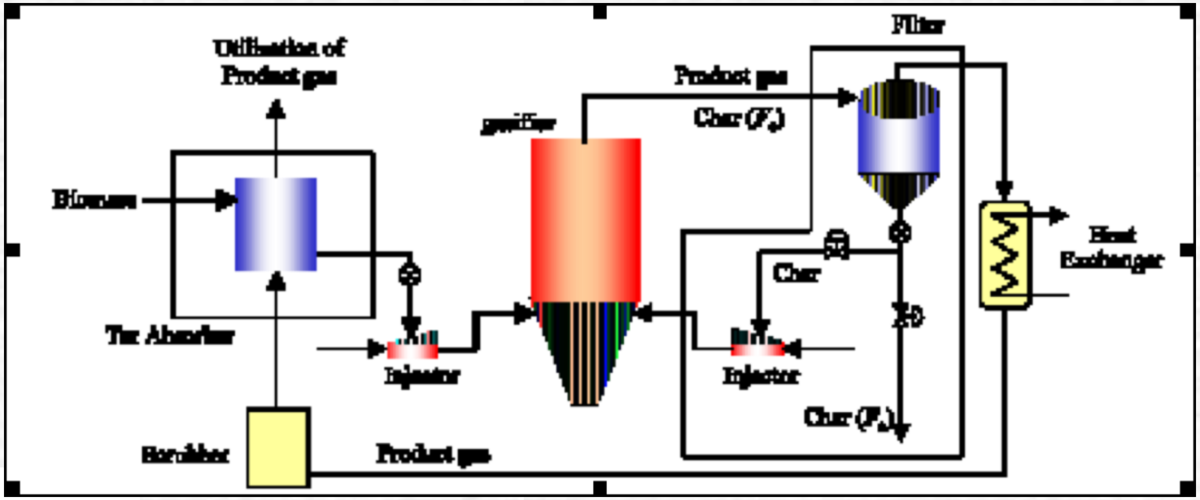


Targets of last 2-year study

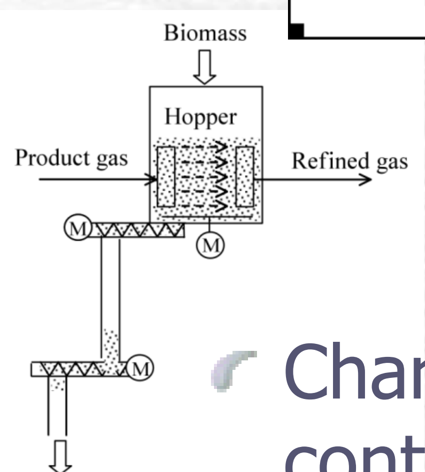
- to improve energy conversion rate to 0.49 &
- to acquire engineering data for a commercial plant



Development of High-Efficiency Biomass Gasification Process by Removal and Recycle of By-product

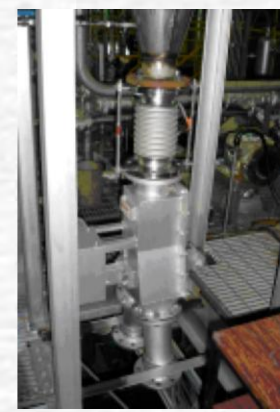


filter



Char yield: 5% -> 1%
Tar yield: 1% -> 0.1%

- Char recycle system and continuous tar absorber combined with biomass feeding devices



branched damper