Steam based biomass gasification processes for syngas and hydrogen production

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Tokyo, Japan

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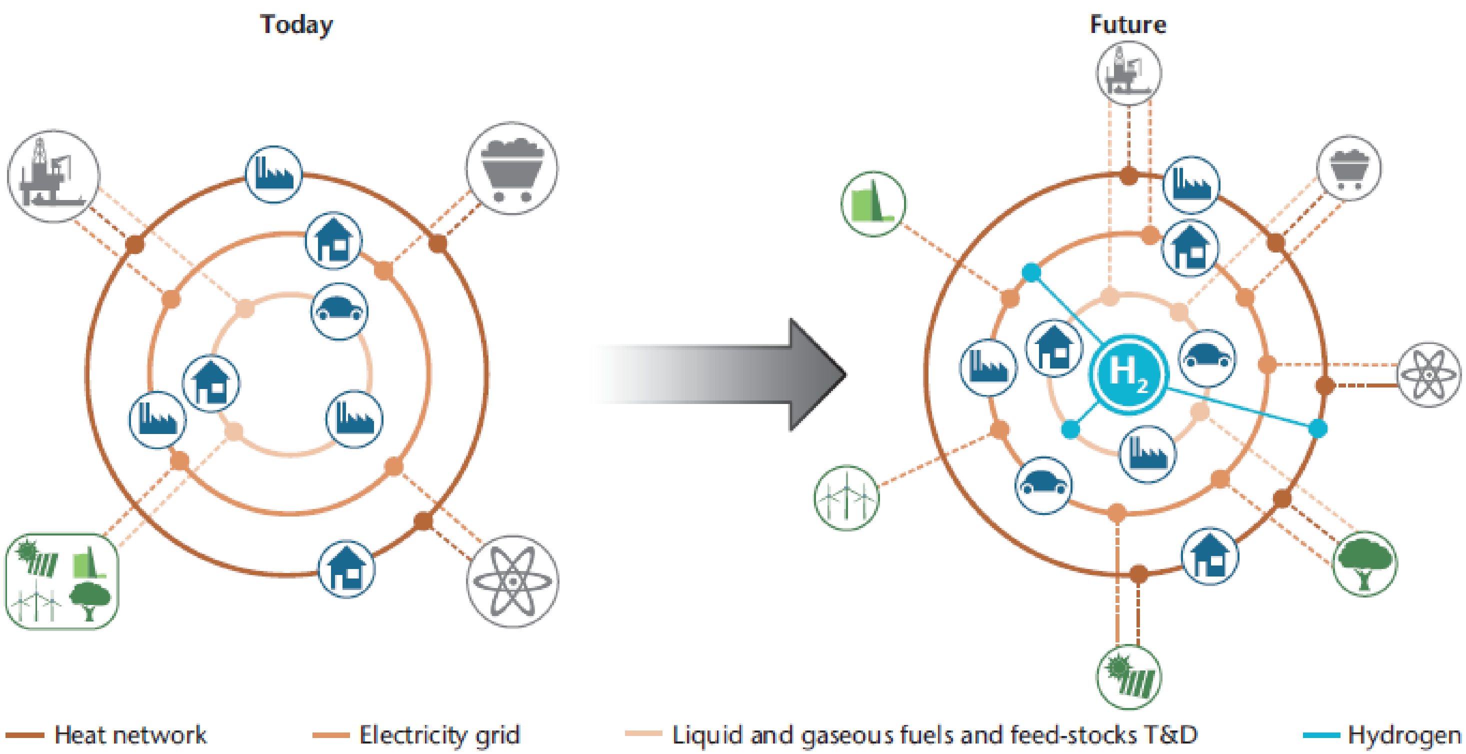
✓ Potential of Hydrogen



➢ FCEV fleet (Targets) announced by hydrogen initiatives (2020)

Europe:~350 000, Japan:100,000, Korea:50,000, United States: ~20,000

Source: Technology Roadmap Hydrogen and Fuel Cells

OECD/IEA, 2015 International Energy Agency

Heating Applications of Bio-Pellet Made from Ecological-Hazard Plant in Small and Medium Enterprises to Enhance Utilization of Renewable Energy in the APEC Region

✓ Background

INPUT (Biomass)

- Woody waste
- Thinning
- Sawmill waste
- Cow dung
- Livestock waste
- Sewage sludge
- etc.

OUTPUT (Product)

Hydrogen or Power & Heat

BLUE Tower II – Third pilot plant

(Shibukawa Technology Development Center of JBEC*)

*Japan Blue Energy Co. Ltd.

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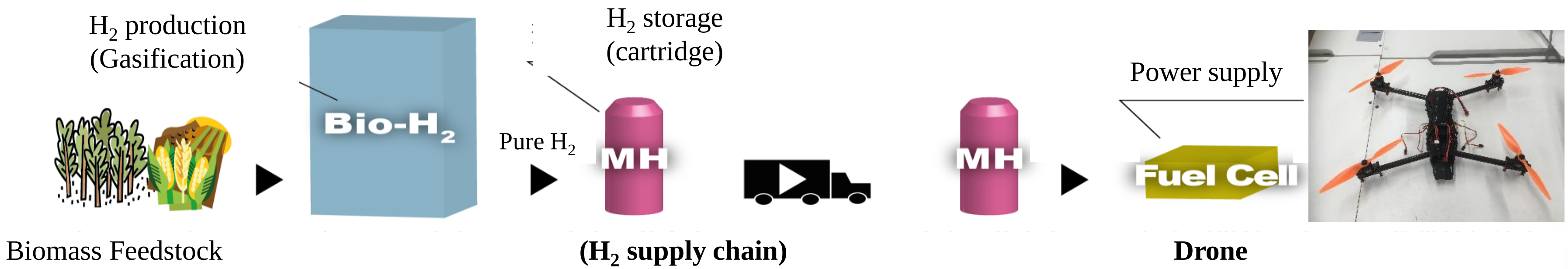
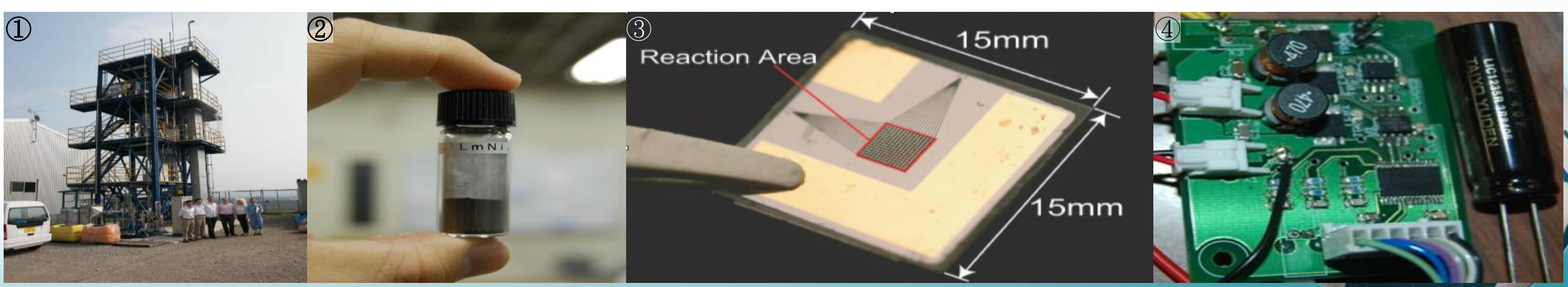
✓ Our Strategy -R&D of Fuel Cell Drone by Bio-H_2 fuel supply-

① Combination of Bio-H_2 production technology and a cell phone
② Expansion of Bio-H_2 application.

Prof. K. Dowaki (Project leader)	: Gasification technology, Gas Cleaning Technology・LCA
Prof. T. Gunji	: Removal technology of contaminants in Bio-syngas
Prof. M. Hayase	: Small scale PEFC in consideration of CO and H_2S tolerance
Dr. N. Katayama	**:** H_2 storage system (metal hydride)・power converter circuit





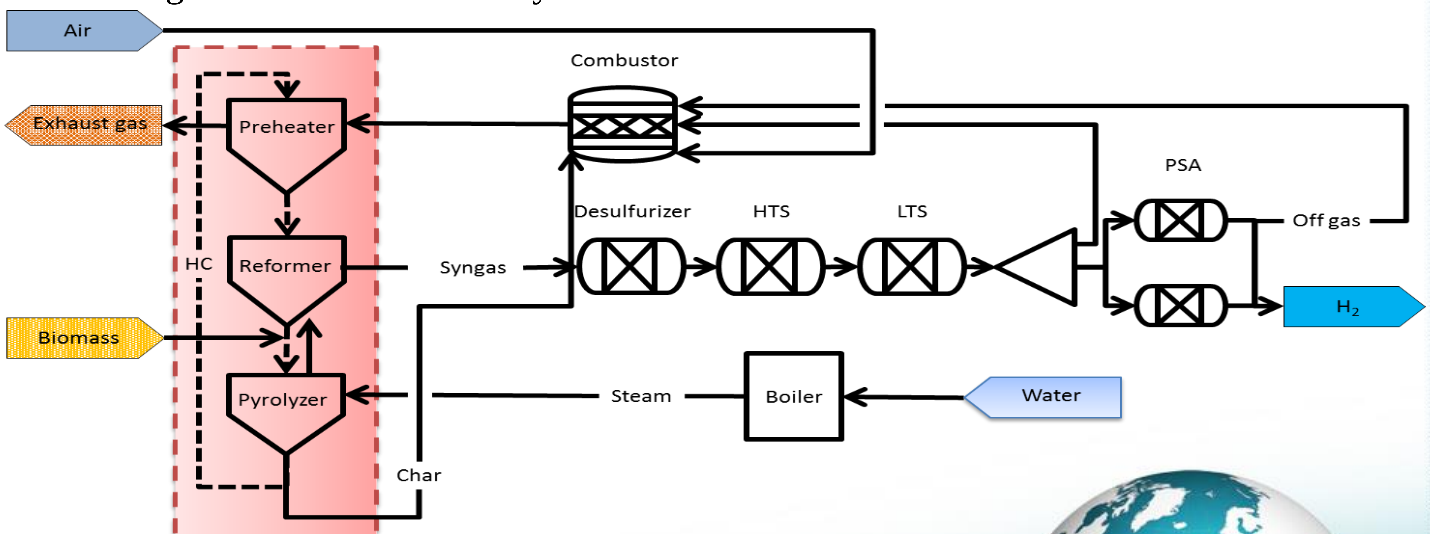
東京理科大学

Heating Applications of Bio-Pellet Made from Ecological-Hazard Plant in Small and Medium Enterprises to Enhance Utilization of Renewable Energy in the APEC Region

✓ Gasification Technology

Basic contents

- The gasifier type is the biomass pyrolysis system in a reductive atmosphere.
- The system has 2 furnaces of pyrolysis+reforming zone and pre-heater.
- H_2 concentration in syngas would be comparatively high (>40 vol.%).
- The plant capacity would be the range of 5 to around 70 t/day.



Biomass gasification process

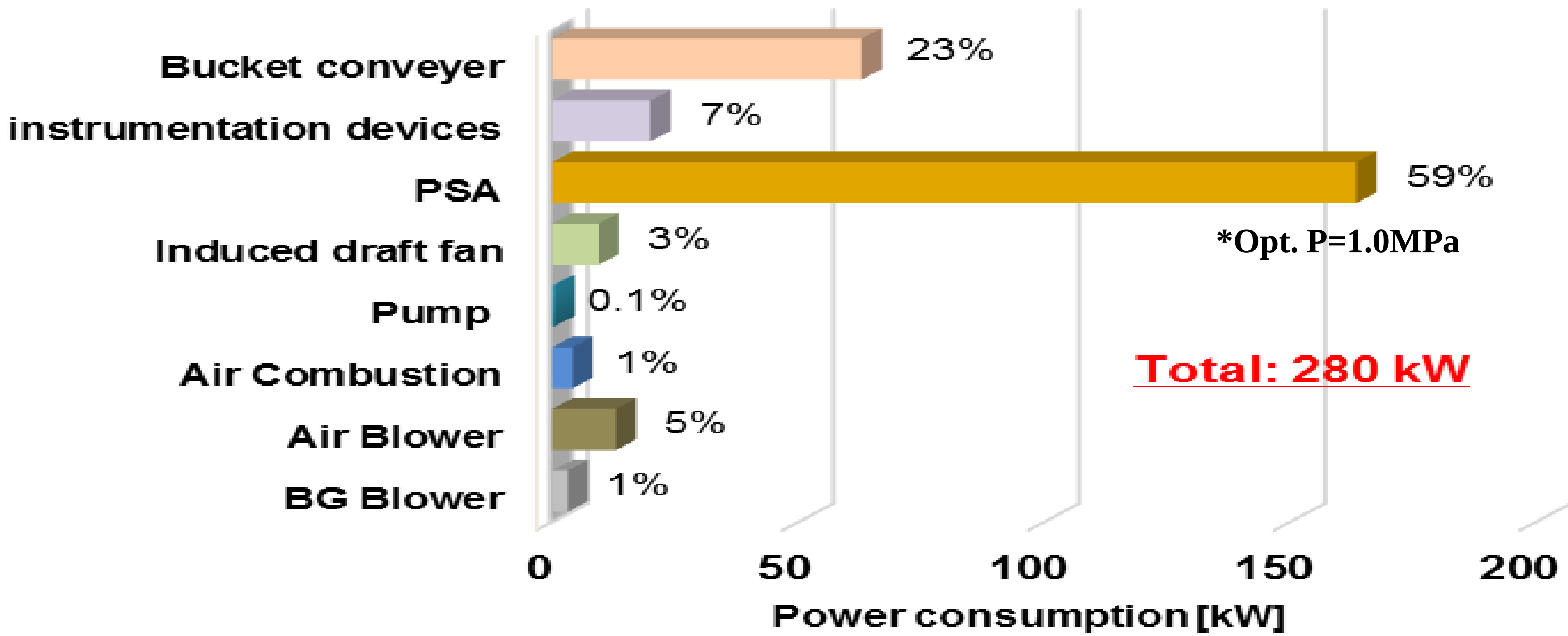
Our tasks in this study

- Confirmation of syngas yields and concentrations due to experiments.
- Confirmation of adsorption performance due to experiments.(CO_2 adsorption /H_2 purification)
- Process design of H_2 production system and estimations of production rate and auxiliary power
- Removal of impurities in syngas.
- Calculation of Eco-footprint of Bio- H_2 on basis of LCA concept.

✓ Reduction of auxiliary in Bio-H_2 plant

- In the previous LCA study on BT process design in use of the simulator of ASPEN-PLUS, we clarified that the highest impact energy consumption is due to the auxiliary power of PSA.

Reduction of energy consumption by our proposals will be achieved.

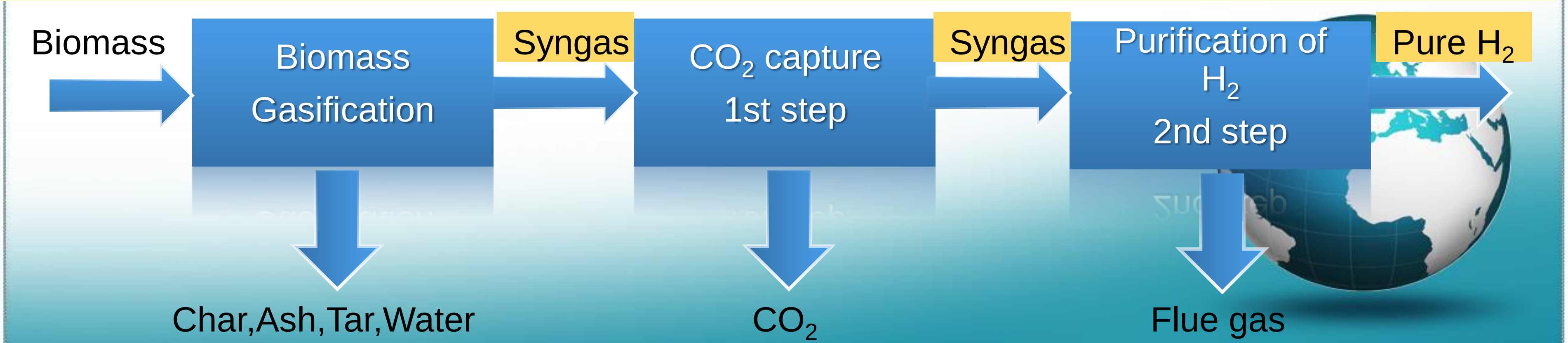


✓ Development of 2-step PSA

□ Performance test in use of "2-step PSA apparatus"

① Confirmation of gaseous yields and concentrations
② Preparation of bio-syngas
③ Execution of adsorption tests
- -Different species of absorbent (form and pore)
- -2-step PSA controls (pressure and temperature)
- -Combination of absorbents

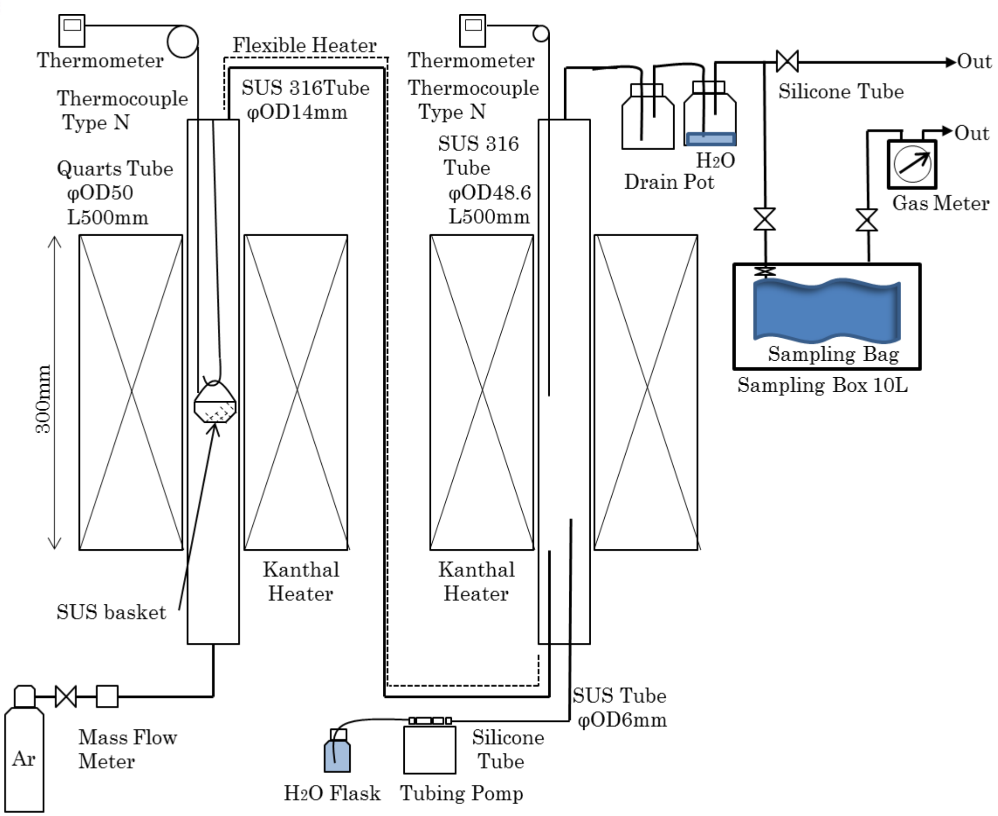
a. Power saving due to low pressure/low temperature controls and a reduction of amount of a working gas fluid (ex. 0.8MPaG->0.5MPaG, CO_2 removal)
b. Achievement of CO_2 adsorption and H_2 purification with higher efficiencies



Heating Applications of Bio-Pellet Made from Ecological-Hazard Plant in Small and Medium Enterprises to Enhance Utilization of Renewable Energy in the APEC Region

✓ Fabrication of apparatus (Gasification Process)

- Confirmation of the performance
- Data acquisition for the static modeling (**AspenPlus**)



Proximate Analysis	Waste W		J. cedar (Reference)
Moisture	6.02	wt.%	37.70
Ash	0.35	wt.%	2.20
Volatiles	82.92	wt.%	83.50
Fixed carbon	10.71	wt.%	14.30
Ultimate analysis			
Carbon	50.9	wt.%	50.41
Hydrogen	7.3	wt.%	5.52
Nitrogen	0.13	wt.%	0.31
Oxygen	41.27	wt.%	43.76
Chlorine	0.01	wt.%	0.01
Sulfur	0.01	wt.%	0.02

Measurement of gaseous yields

Note: This apparatus consists of pyrolysis zone and reforming zone.

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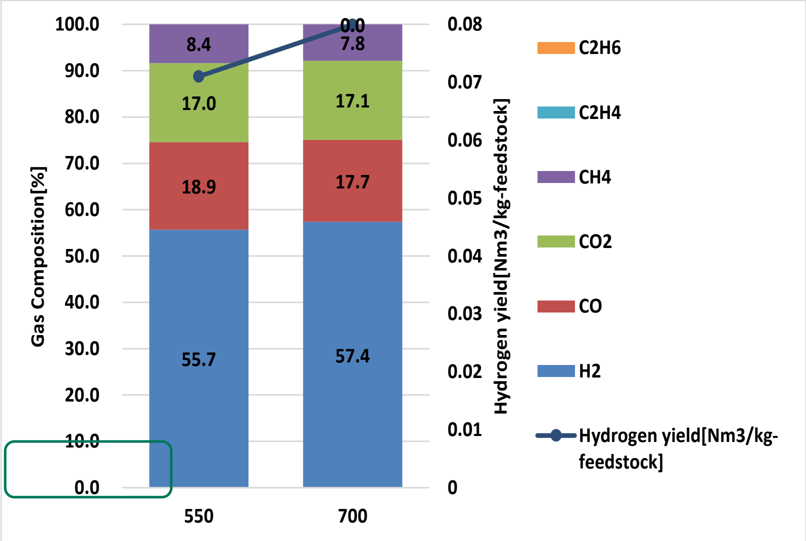
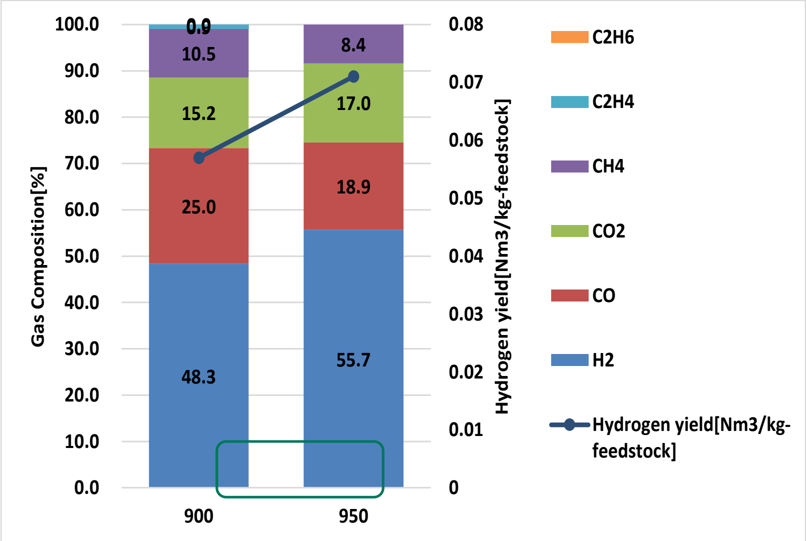
✓ Effects of pyrolysis and reforming temperatures



Pyrolysis Temp. [deg.C](Reforming T=950)



Reforming Temp [deg.C] (Pyrolysis T=550)

Performance (summary)

Pyrolysis Temp. [deg.C]	550	550	700
Reforming Temp. [deg.C]	900	950	950
Syngas [L/g-feedstock]	1.02	1.10	1.19
Char [g/g-feedstock]	0.2	0.2	0.2
Tar [g/g-feedstock]	0.02	0.04	0.008
Cold gas efficiency [%]	71	68	73

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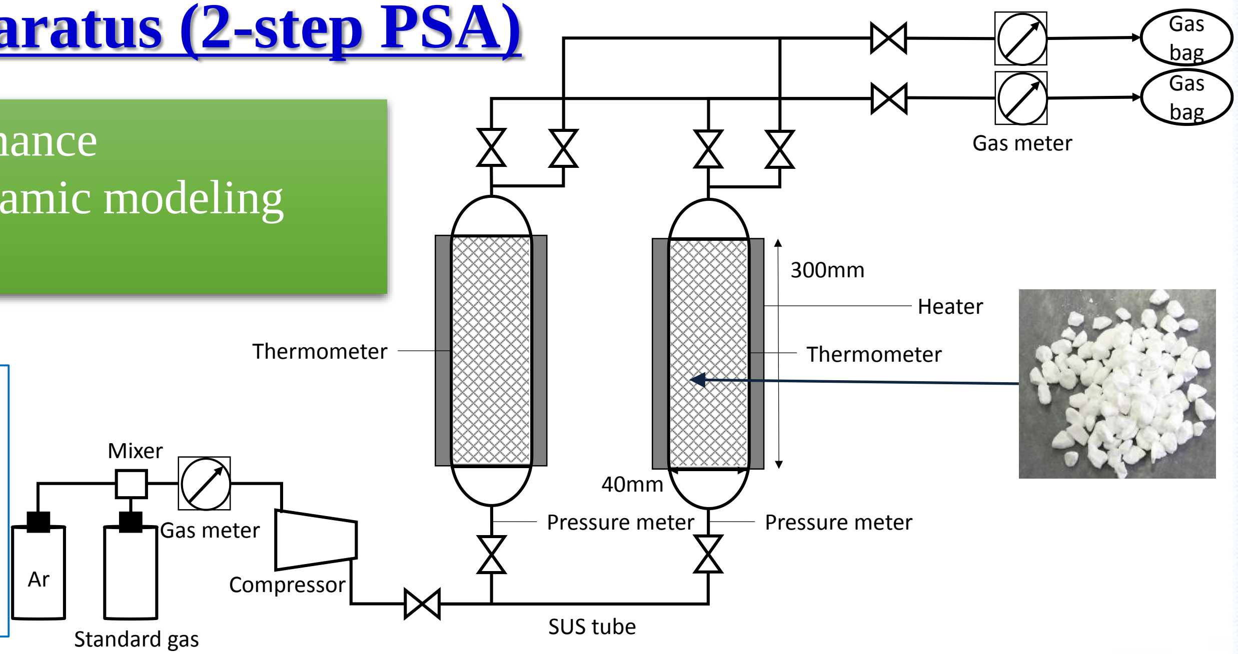
✓ Fabrication of apparatus (2-step PSA)

- Confirmation of the performance
- Data acquisition for the dynamic modeling (**gPROMS**)

- Adsorbent volume : 200 ml
- Opt. Temp. : RT
- Opt. P : 0.4 MPaG
- Feed gas : H_2 55%, CO 20%, CH_4 8%, CO_2 17%
- Opt. time : 5 min



Measurement of PSA performance

Adsorbents characteristic

Specification	HAS-Clay	Zeolite A-3	Zeolite A-4	Zeolite A-5	Zeolite F-9	Activated carbon (Kuraray Coal)	Activated carbon (CMS)
Chemical composition	$SiO_2 \cdot Al_2O_3 \cdot H_2O$	$MeO \cdot Al_2O_3 \cdot mSiO_2 \cdot nH_2O$ (Me: Cation)				Carbon	Carbon
Particle size [mm]	>2.0	2.36-4.75	2.36-4.75	2.36-4.75	2.39-4.75	4-5.5	2.36-4.75
Pore diameter [nm]	<0.02	0.3	0.4	0.5	0.9	0.5-10	0.5

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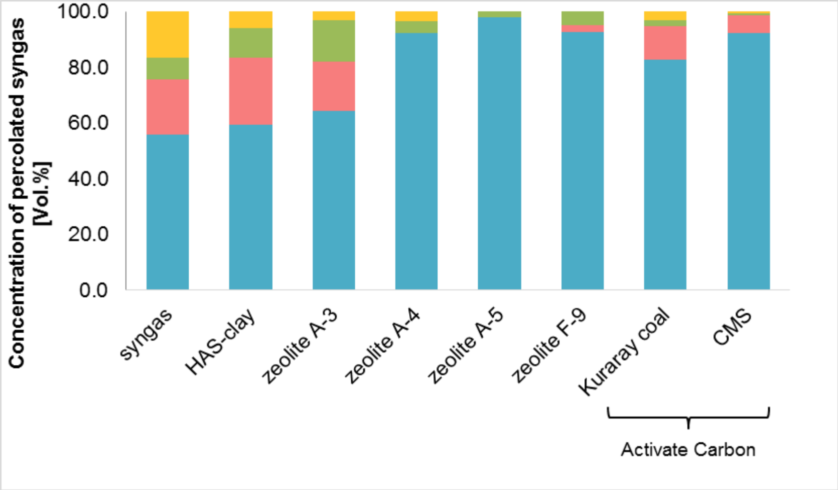
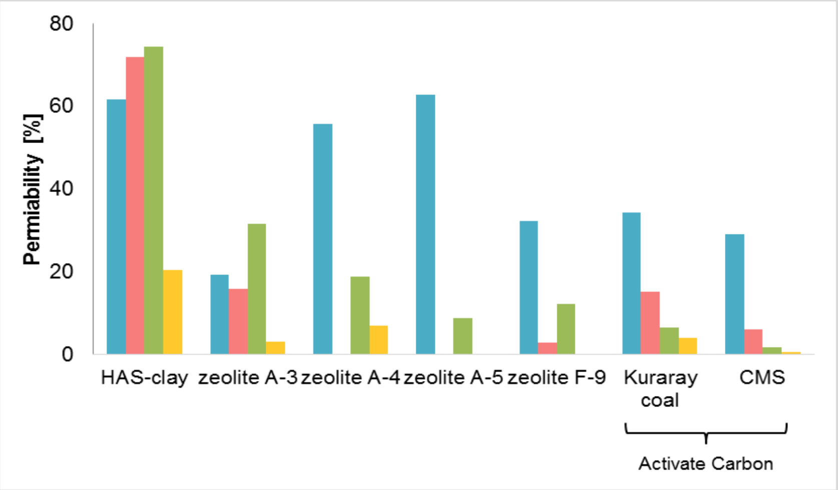
✓ Result of adsorption test (1)





<HAS-clay>

- ✓ Only CO_2 permeability was worse in comparison to the other gas components.
- ✓ That of H_2 was relatively higher.

<Zeolite A-5>

- ✓ The gaseous components percolated in the absorbent were H_2 and CH_4.
- ✓ H_2 permeability was highest among the candidates.
- ✓ The concentration of H_2 which passed through Zeolite A-5 was 90% or more.

Our proposals

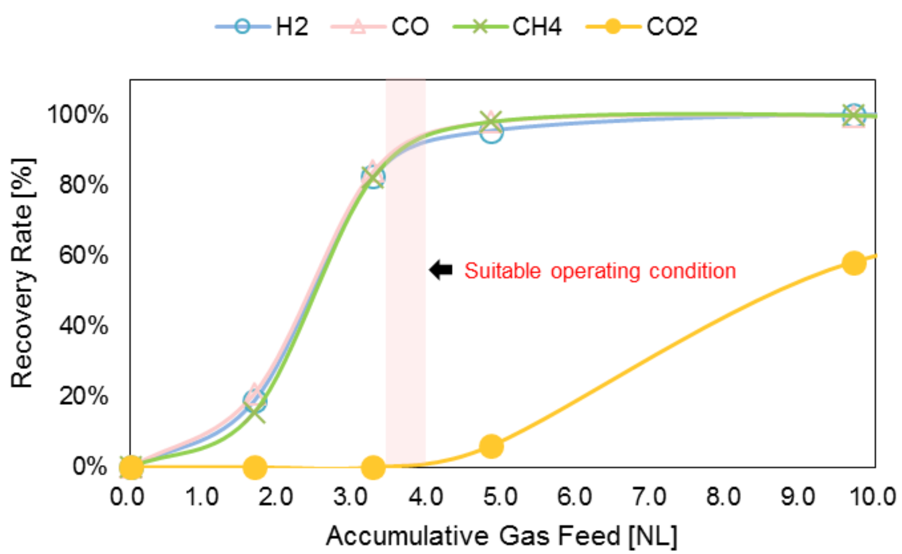
- At the 1st step, HAS-clay is employed in order to adsorb CO_2 selectivity.
- At the 2nd step, Zeolite A-5 is employed in order to purify H_2.

✓ Result of adsorption test (2)

In order to make only CO_2 component separated from HAS-clay at 1st step, the breakthrough curve was measured.

<Condition>

- ✓ Gas flow rate (Syngas(10%)+Ar(90%)) : 13.1 NL/min
- ✓ Operating pressure : 0.4 MPaG
- ✓ Operating temperature : Atmospheric (28 to 32 deg.C)
- ✓ Amount of HAS-clay : 200 cc



- H_2 and CO_2 are likely to be separated individually by the combination of HAS-clay at 1st step with Zeolite A-5 at 2nd step, and the gas flow control in consideration of CO_2 retention time.

✓ LCA study on Bio-H_2 production

- Based on our experimental results, we designed the process of target system.
- We argued the optimal condition in consideration of LCA concept.

<Definition of Eco footprint>

H_2 fuel production efficiency[%]

$$\eta_{energy} = \frac{Q_{H_2}}{W_1 + W_2 + H_1(T_1) + H_2(T_2) + Q_{syn} - Q_{og}}$$

CO_2 emission of H_2 fuel [g-CO_2/MJ-H_2]

$$FCO_2 = \frac{C_1 + C_2 + C_{aux} - \alpha C_{fs}}{Q_{H_2}}$$

The coefficient of α can be set up by the test of CO_2 assimilation in use of model plant (e.g. Arabidopsis thaliana).

Q_{H2} :LHV of H_2 [MJ/h]
Q_{syn} :LHV of syngas [MJ/h]
Q_{og} :LHV of off gas [MJ/h]
W_1 :first step of PSA [MJ/h]
W_2 :second step of PSA [MJ/h]
$H_1(T_1)$:sensible heat of first reactor[MJ/h]
$H_2(T_2)$:sensible heat of first reactor [MJ/h]
C_1 :CO_2 emission of first reactor [g-CO_2/h]
C_2 :CO_2 emission of second reactor [g-CO_2/h]
C_{aux} :CO_2 emission of auxiliary [g-CO_2/h]
C_{fs} : CO_2 emission due to carbon neutral [g-CO_2/h]
α :the percentage of adsorbed CO_2 gas [-]

- In the case of the combination of HAS-clay with Zeolite A-5,

✓ η_{energy} : 82.8%, FCO_2 : -56.6 g-CO_2/MJ-H_2 (164kW→112kW, Reduction by 31%)

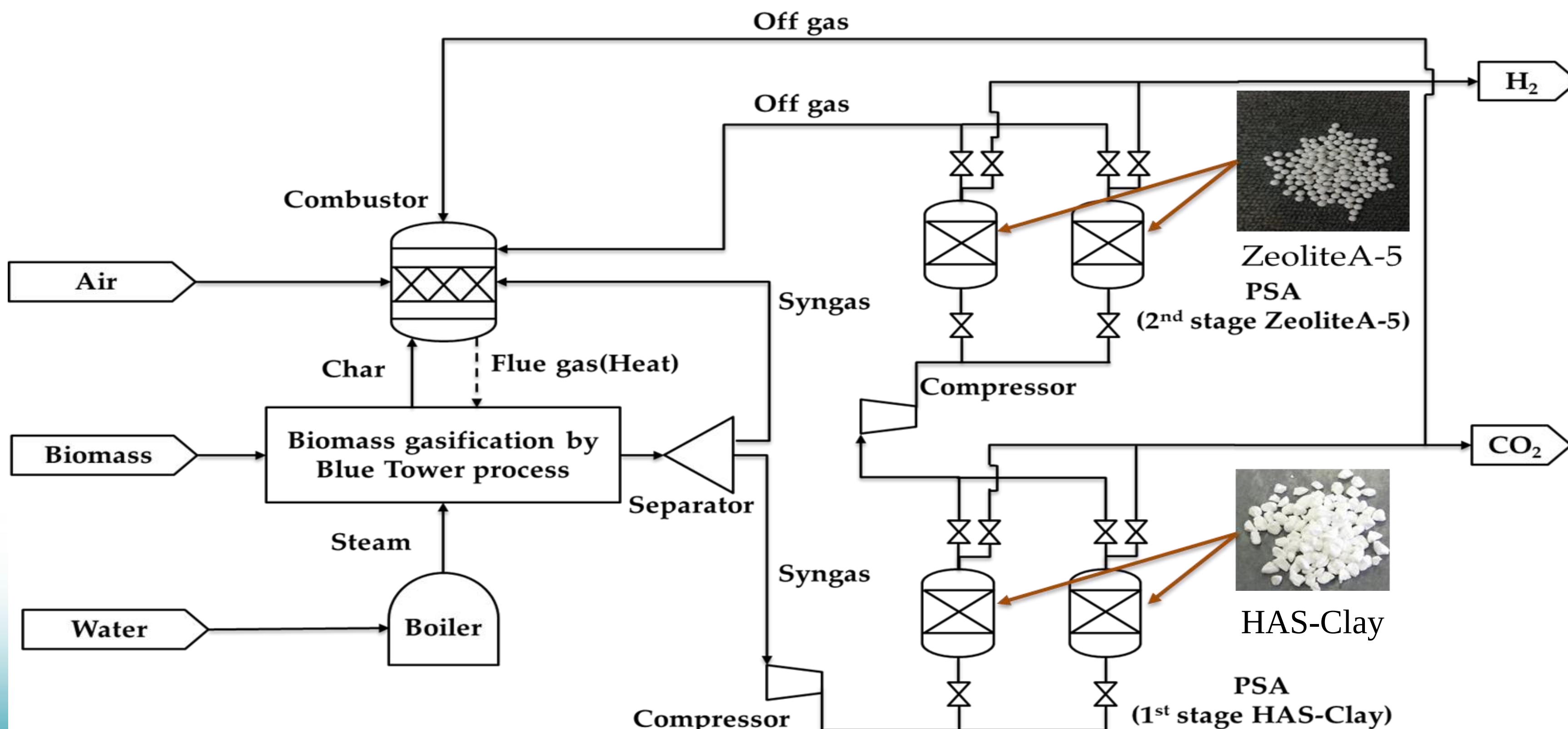
- In the conventional case[1],

✓ η_{energy} : 79.0%, FCO_2 : 57.4 g-CO_2/MJ-H_2

(1) Y. Watanabe et al. :*J. Life Cycle Assessment, Japan*, **9**(1), 20-36 (2013)

✓ Dynamic Simulation of 2-step PSA

- 1st stage, CO_2 adsorption
- 2nd stage, H_2 purification



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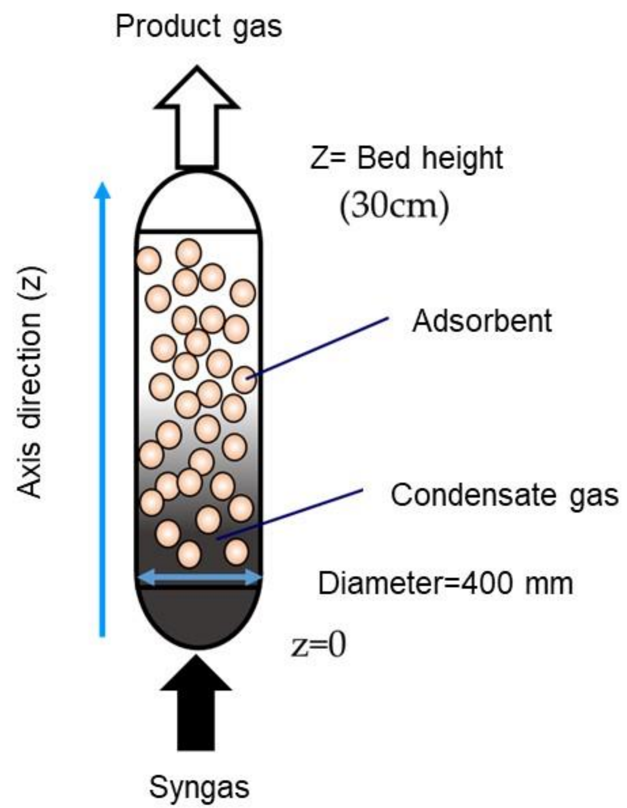
✓ Modeling



Fig, Schematics model

- **Mass balance**

$$\varepsilon_{bed}\frac{\partial C_{g,i}}{\partial t} = \frac{\partial}{\partial z}\left(\varepsilon_{bed} D_{ax,i}\frac{\partial C_{g,i}}{\partial z}\right) - u\frac{\partial C_{g,i}}{\partial z} - (1-\varepsilon_{bed})a_p k_f (C_{g,i}-C_{s,i})$$

Non constant; Diffusion; Convection; Adsorption

- **Heat balance**

Consideration of heat transfer between surface of inner vessel and gas flow.

$$(\varepsilon_{bed}C_g Cp_g + \rho_{bed}Cp_s)\frac{\partial T}{\partial t} = -\frac{\partial}{\partial z}\left(K_L\frac{\partial T}{\partial z}\right) + \varepsilon_{bed}C_g Cp_g \frac{\partial T}{\partial z}u + \rho_{bed}\sum_{j=1}^{Comp}\Delta H_j \frac{\partial q_j}{\partial t} + \frac{2h_w}{R_{in}}(T-T_{wall})$$

Non constant; Diffusion; Convection; Heat generation; Surface –gas flow

- **Pressure loss(Blake-Kozeny)**

$$-\frac{\partial P}{\partial z} = 180\frac{\mu(1-\varepsilon_{bed})^2}{\varepsilon_{bed}^3}\frac{\mu u}{Dp^2}$$

- **gPROMS (finite element method)**

✓ Simulation conditions

- PSA Cycle: Compression->Refinery->Decompression->Purge
- Number of cycles (in this simulation): 3

Note: Simulation parameters (physical properties) are used by the reference data [1][2]

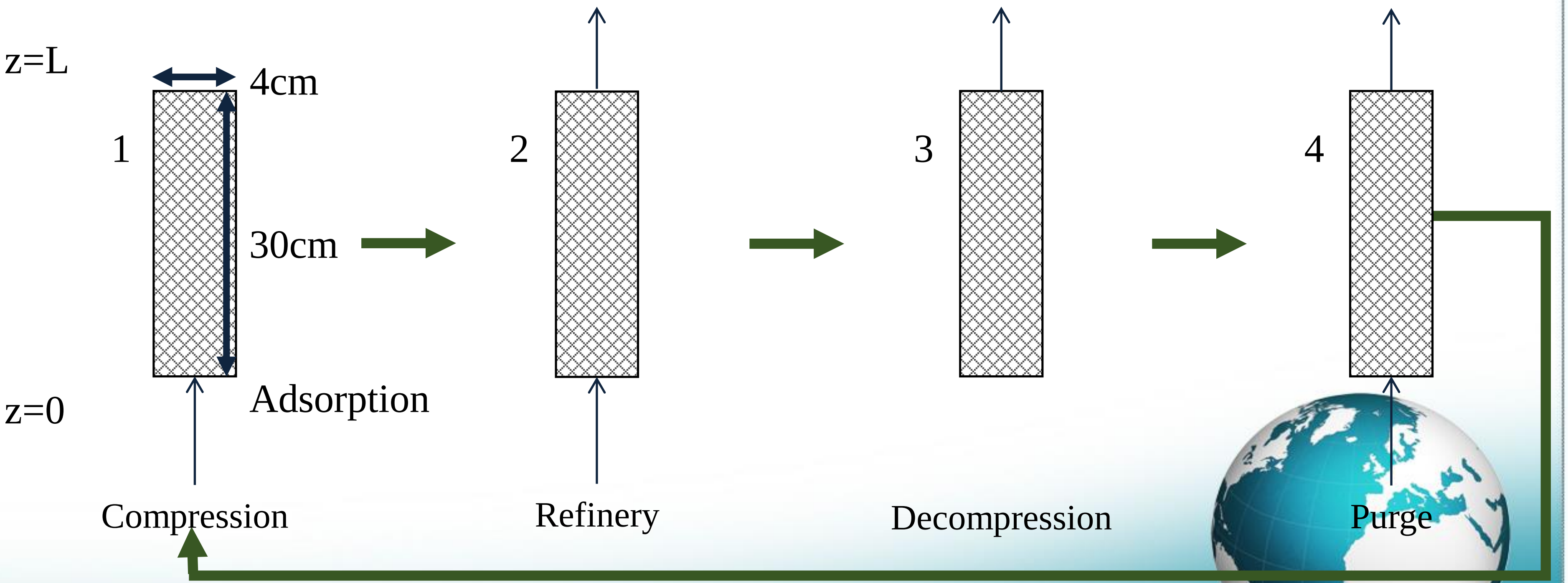


Fig. PSA cycle

[1] Jinsheng X, Yuzhi P, Pierre B, Richard C; International journal of hydrogen energy. 2016, 41,8236-8245
[2] Jaeyoung Yang and Chang-Ha Lee, ind. Eng . Chem. 1997, 36, 2789-2798

✓ Results at 1st stage (HAS-Clay)

- Confirmation of selective CO_2 adsorption
  - Recovery efficiencies of H_2,CO and CH_4 are higher.
- Conc. of CO_2 is high in purge process.
  - CO_2 : 97.47% (adsorption efficiency)
- Temperatures in compression and refinery processes increase.
  - Physical adsorption

	H_2	CO	CH_4
Flow rate 1st [%]	88.30%	88.42%	82.09%

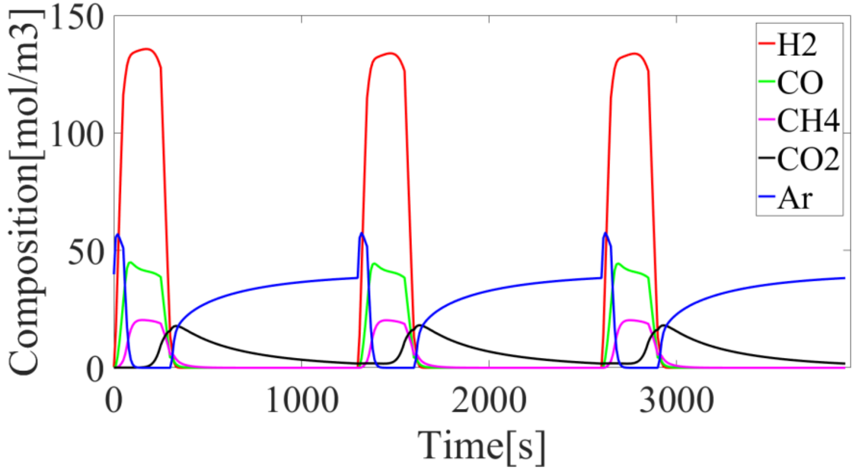


Fig. Molar fraction [mol/m^3]

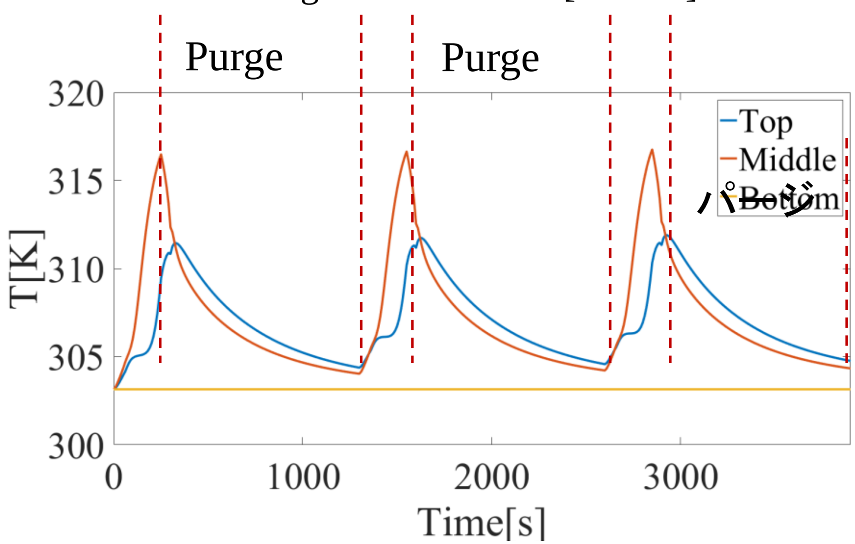


Fig. Inner temperature [K]

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✓ Results at 2nd stage (Zeolite A5)

- H_2 Conc. : 99.18%
- H_2 recovery eff. : 78.14%
  - Advantage point is to improve the product quality (concentration) in comparison to the conventional PSA without CO_2 adsorption
  - Reduction of auxiliary power: approx. 30% abatement [1]

	H_2	CO	CH_4	CO_2
Flow rate 2nd [%]	99.18%	0.77%	0.04%	0.003%

Only H_2 gas can pass through.
Sequestration of H_2 can be achieved.

[1] Dowaki, K. et al.: IEEJ Transactions on Electronics, Information and Systems , **128**(2), 168-175 (2008)

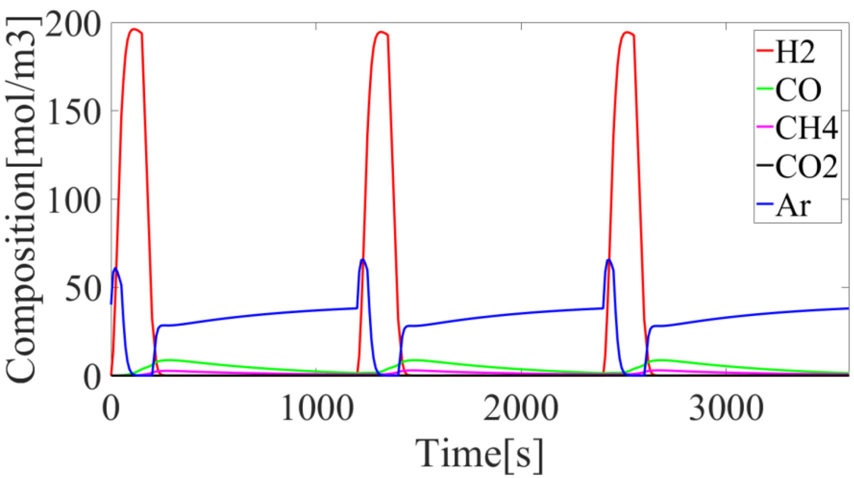

Fig. Molar fraction [mol/m^3]

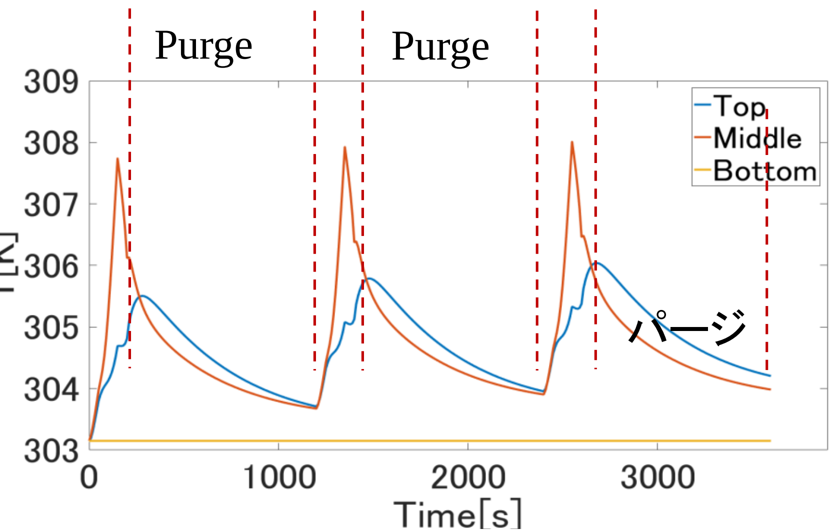

Fig. Inner temperature [K]

✓ Impurities problems on the operation by Bio-H_2?

- Contaminations of bio-syngas: HCl, H_2S, NH_3 etc.
- FC applications→Polymer Electrolyte Fuel Cell (PEFC) (present)

1. HCl (Hydrogen chloride)

- Pt dissolution (Use of catalyst on FC electrodes)

2. H_2S (Hydrogen sulfide)

- Performance drop

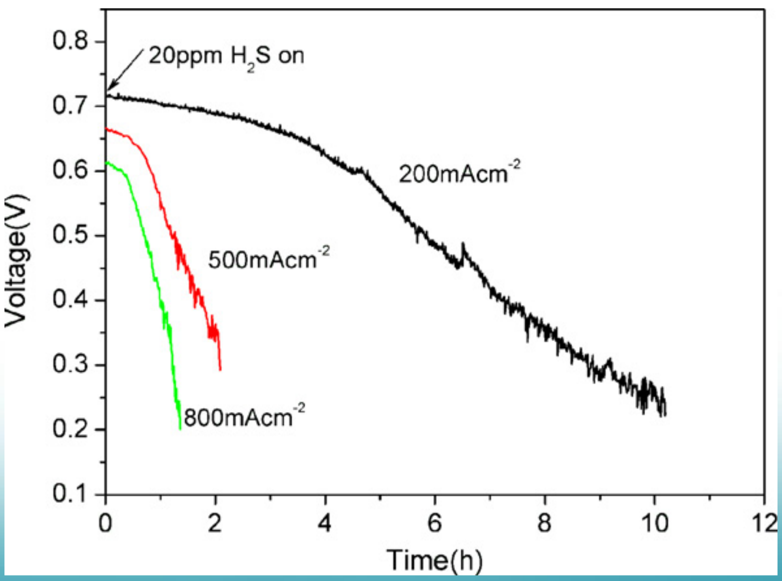

Fig. Effect of current density on the performance deterioration during exposure to 20 ppm H_2S/H_2. T_{cell} =70 °C, humidification temperatures of the anode and cathode: room temperature and 70 °C.

Source: W. Shi et al. / Journal of Power Sources 164 (2007) 272–277

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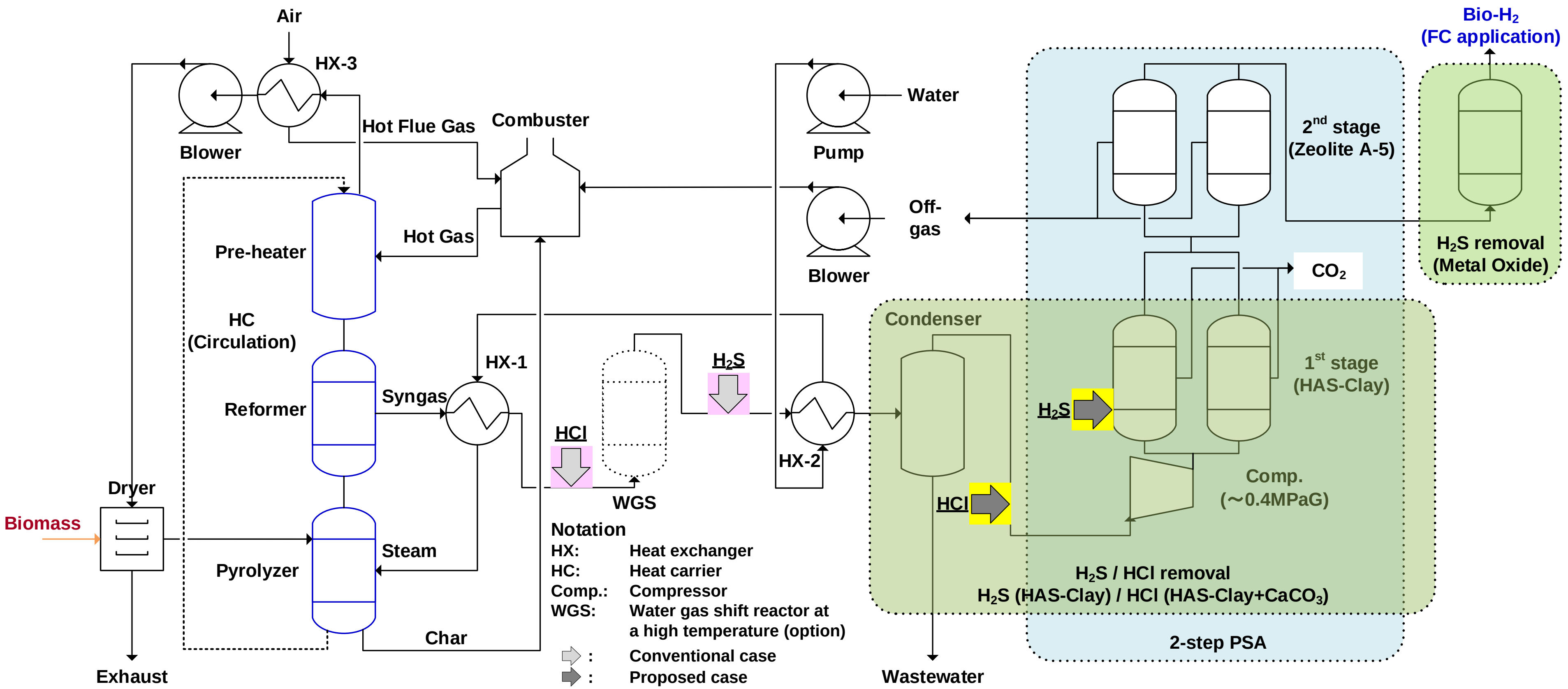
✓ Where shall the impurities be removed?

- Forethought of operation profile in the plant
- Minimum consumption of adsorbents (Economic and Environment)

◆ Process design



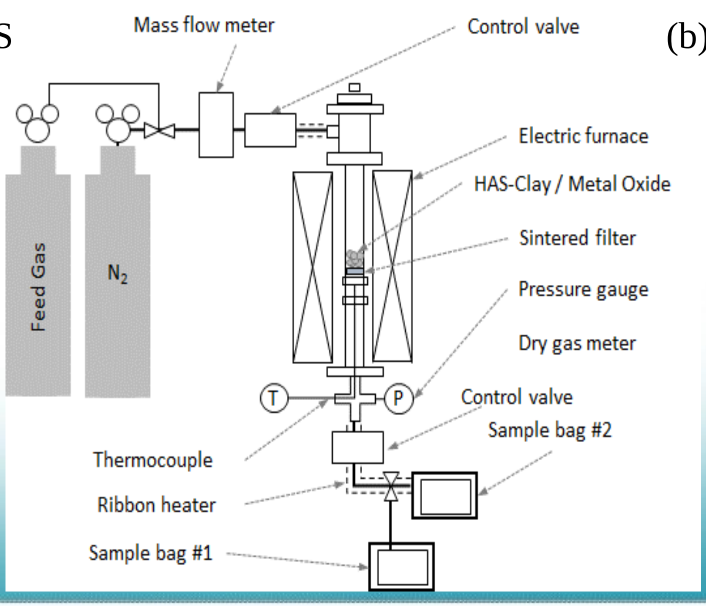
✓ Estimation of breakthrough curve (Removal Tests)

➢ Adsorbent candidates

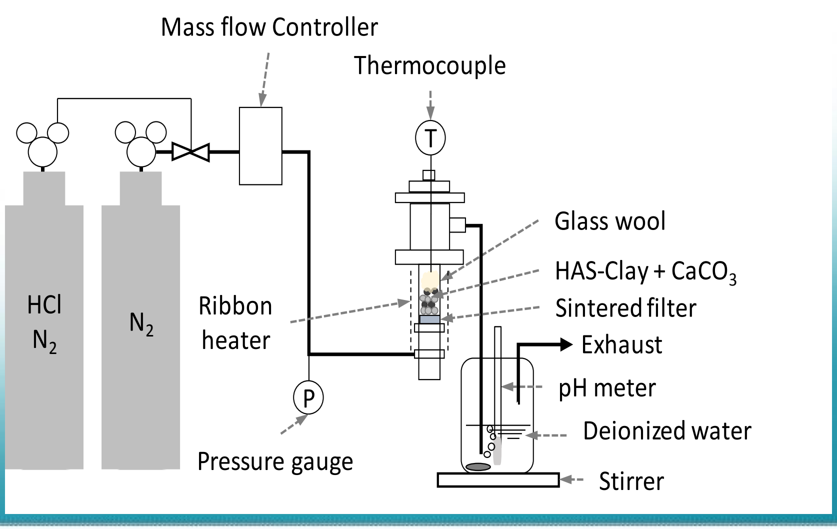
Specification	HAS-Clay	Zinc oxide	Iron oxide	Calcium carbonate
Target Impurities	H_2S/HCl	H_2S	H_2S	HCl
Chemical composition	$SiO_2 \cdot Al_2O_3 \cdot H_2O$	ZnO	Fe_2O_3	$CaCO_3$
Particle size [mm]	2.2-3.35 (H_2S) Powder (HCl)	2.2–3.35	2.2–3.35	12×10^{-3}-15×10^{-3}
Pore diameter [nm]	<0.02	-	-	-

Note: HAS-Clay means synthetic substances of hydroxyl aluminum silicate and clay.

(a) H_2S



(b) HCl

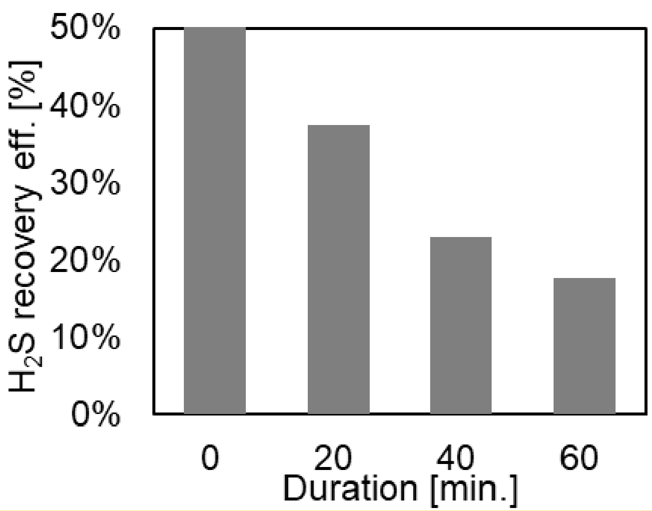


✓ Absorption performance of HAS-Clay(Results of H_2S (1))

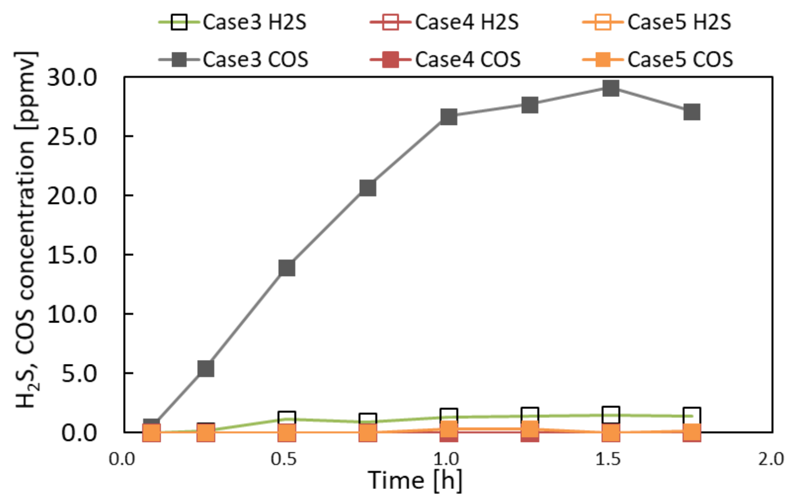
➢ Condition

1. H_2S: 30 ppmv, flow rate : 50 Nml/min. , 40 deg.C and 0.4 MPaG, Sample weight : HAS-Clay (2 g), Space velocities (SV) : 2,915 h^{-1}
2. H_2S: 100 ppmv, flow rate : 250 Nml/min. , 40, 80, 120 deg.C and atmospheric pressure, Sample weight : ZnO (1.3 g) or Fe_2O_3 (0.95 g), Space velocities (SV) : 8,784 h^{-1} (constant)

(a) Physical Adsorption (HAS-Clay)



(b) Physical Adsorption (Zeolite A-5)

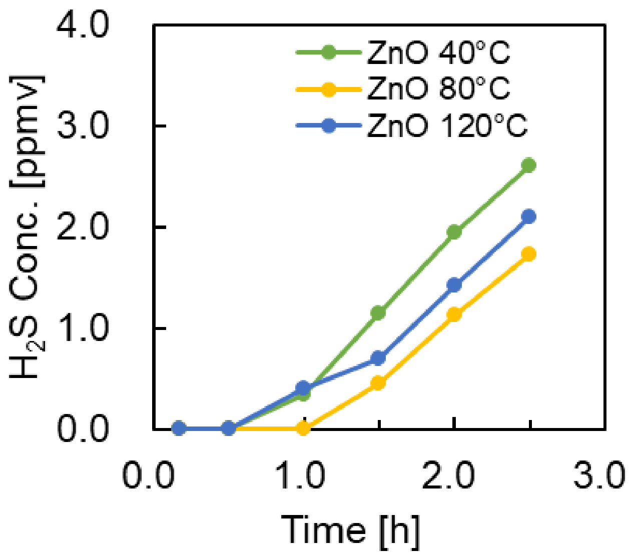


Note:

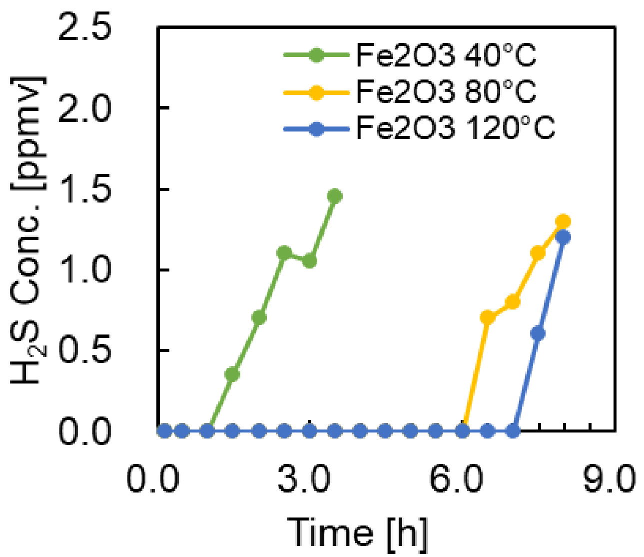
- ✓ In 2-step PSA (the combination of HAS-Clay and Zeolite A-5), almost H_2S can be eliminated.
- ✓ Prevention of $H_2S+CO_2=COS+H_2O$ because of an absorption of CO_2 by HAS-Clay.
- ✓ Chemical adsorption is a complementary use.

✓ Estimation of breakthrough curve (Results of H_2S(2))

(a) Chemical Adsorption (ZnO)



(b) Chemical Adsorption (Fe_2O_3)



➢ **Sulfur capture capacity (Definition)**

$$S_{cap} = \frac{t_{BT} \times \dot{V} \times C_{PG} \times At_{as}}{V_m \times W_{sorbent}} \times 100$$

t_{BT} : Breakthrough time [min]

C_{PG} : Conc. of pollutant [ppmv]

$\dot{V}$: Flow rate [L/min]

V_m :Molar volume [L/mol]

At_{as} : Atomic weight (=32.07)

$W_{sorbent}$: Adsorbent weight [g]

Table Sulfur capture capacity

Temp. [°C]	ZnO*	Fe_2O_3*
40	0.24	0.54
80	0.31	1.65
120	0.28	1.69

*Unit: g-S/100 g-sorbent

✓ Absorption performance of HAS-Clay(Results of HCl(1))

➢ Condition

1. HCl: 1,160 ppmv, Flow rate: 200 Nml/min, 100-200 deg.C and atmospheric pressure
   Sample weight : HAS-Clay (0.1 g) and/or $CaCO_3$(1.0g)
   Space velocities (SV) : 3,725-32,000 h^{-1} (see **Table**)
2. Estimation of the effect of blend effect vs. mono-adsorbent.

$CaCO_3+HCl \rightarrow H_2O\downarrow + CO_2\downarrow$ (adsorption effect of HAS-Clay)

Note: In general, Ca based adsorption is worked at the temp. of >600 deg.C.

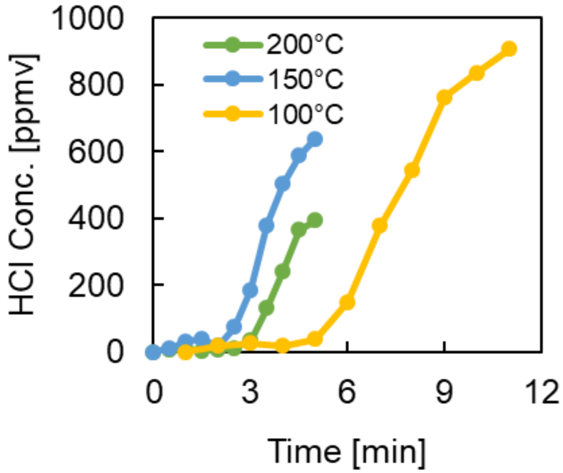
Table Combination of samples and SVs

	Specimen		
	#1	#2	#3
$CaCO_3$ [g]	1.00	0.00	1.00
HAS-Clay [g]	0.00	0.10	0.10
Space Velocity [h^{-1}]	4,216	32,000	3,725

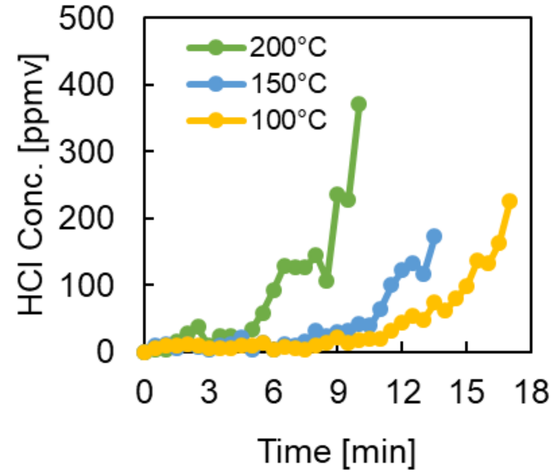
Based on the experimental results, the estimation of adsorption effect of blend case (Cl capture) was carried out.

✓ Estimation of breakthrough curve (Results of HCl (2))

(a) $CaCO_3$



(b) HAS-Clay



(c) Blend

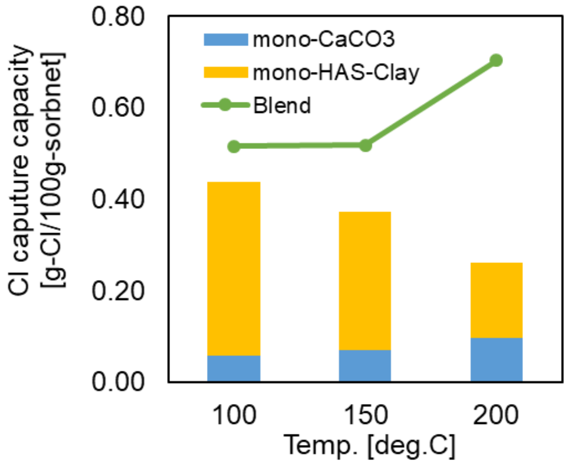


Table Chlorine capture capacity

Temp. [°C]	$CaCO_3$*	HAS-Clay*	Blend*
100	0.06	4.18	0.52
150	0.08	3.32	0.52
200	0.11	1.79	0.70

*Unit: g-Cl/100 g-sorbent

Heating Applications of Bio-Pellet Made from Ecological-Hazard Plant in Small and Medium Enterprises to Enhance Utilization of Renewable Energy in the APEC Region

✓ Impact analysis

➢ Purpose

1. Due to reduction of amount of chemicals (adsorbent), the eco-burden in consideration of LCA is to be visualized.

➢ Conditions

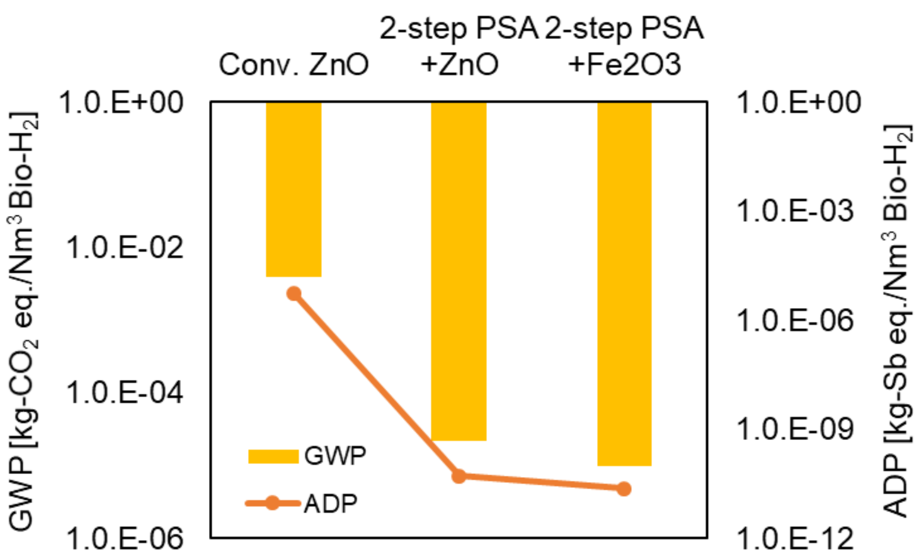
1. Functional unit: 1 Nm^3 Bio-H_2 (4N)
2. Estimated Index: Abiotic metal depletion potential (ADP), global warming potential (GWP)
3. Software: SimaPro 8.2 software (Impact analysis: the Centrum voor Millieukunde Leiden (CML) method
4. Conventional case (H_2S): ZnO (Conv. ZnO) (Capture capacity: 2.81 g-S/100 g-sorbent)
5. Initial concentration (H_2S): 200 ppmv
6. Proposed case: 2-step PSA+ZnO (0.24 g-S/100 g-sorbent), PSA+Fe_2O_3 (0.54 g-S/100 g-sorbent) *Note: Temp. 40 deg.C
7. Conventional case (HCl): Na_2CO_3 (Conv. Na_2CO_3) (Capture capacity: 5.35 g-Cl/100 g-sorbent)
8. Proposed case (Blend case): HAS-Clay+$CaCO_3$ (0.70 g-Cl/100 g-sorbent)
9. HAS-Clay is assumed to be regenerable.
10. Calculation

$$\text{Imapct Potential} = \text{Inventory Value} \times \text{Characterisation Factor}$$

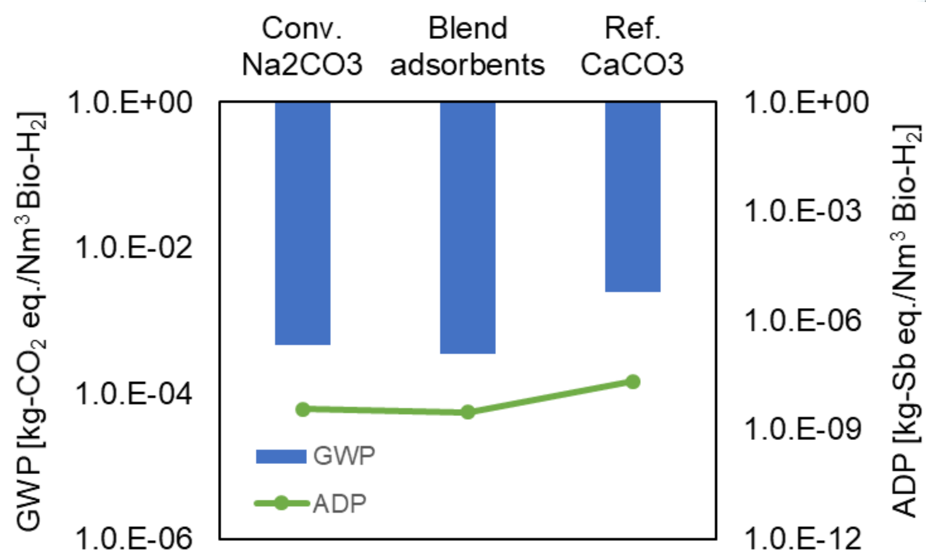
Heating Applications of Bio-Pellet Made from Ecological-Hazard Plant in Small and Medium Enterprises to Enhance Utilization of Renewable Energy in the APEC Region

✓ Estimation of GWP and ADP

(a) H_2S



(b) HCl



☐ Advantages due to HAS-Clay use

- The eco-indexes of GWP and/or APD was remarkably improved in comparison to the conventional cases (H_2S).
- In the case of blend of HAS-Clay and $CaCO_3$, GWP and ADP in comparison to the conventional case were improved by 25.4 % and 19.4 %, respectively (HCl).

✓ Conclusions

- In our group, Bio-H_2 production system using the gasification process of Blue Tower is developing.
- The design policy is based on LCA indexes to obtain the eco-benefit of biomass feedstock.
- Looking at the entire system, the key technology is the reduction of external energy consumption besides an assurance of steady operation.
- Also, the technology of impurities removal would be extremely important to match a fuel specification for FC application.
- In this case, the candidates have to be selected appropriately, since the adsorbents are associated with eco-burden.

✓ Conclusions (continued)

- HAS-Clay which we concerned in this study has good potentials to reduce the auxiliary power and eliminate the impurities in product gas.
- The characteristic of HAS-Clay, especially, CO_2 adsorption, can promote the elimination of H_2S and HCl, too.
- Simultaneously, the consumption of metal oxide would be reduced due to these characteristics.
- Using the eco-index on basis of LCA (GWP and ADP), the obvious advantages can be obtained.
- In our future tasks, the adsorption performance of other impurities (e.g. NH_3) will be analyzed.

Thank you for your attention!