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Closed cycle and continuous operations by a thermo-chemical water-splitting IS process

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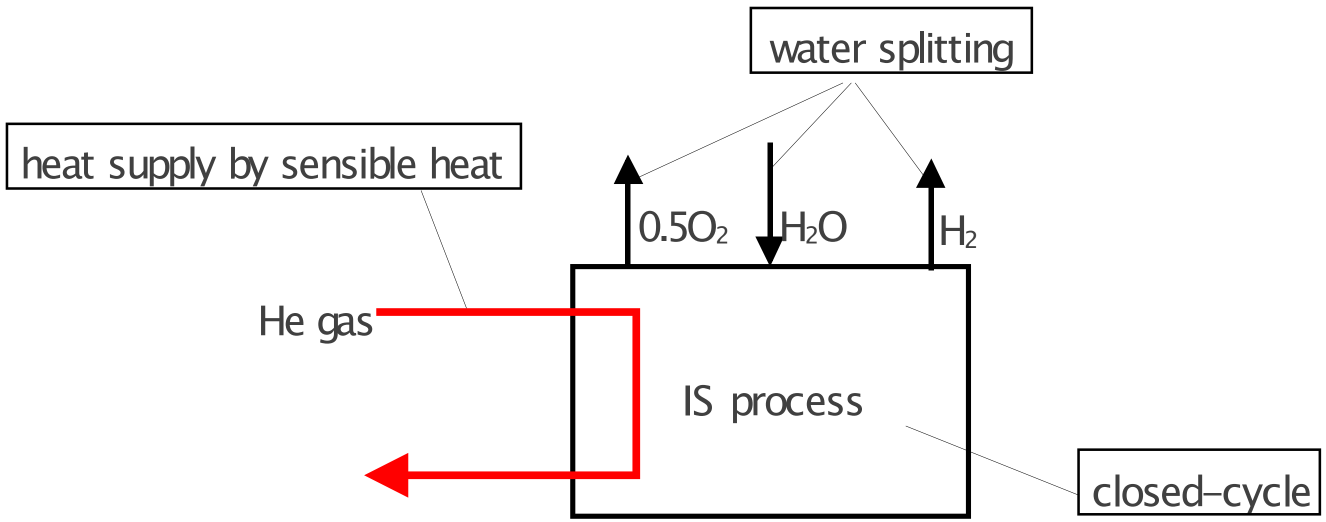
Purpose of the study

・Desirable and unique feature
→ IS process can be operated on continuous and closed-cycle condition

・All chemicals circulate through the process changing chemical forms by three reactions



Development <u>operational methods</u> to realize **closed-cycle water splitting** process driven by **helium gas heat**

Outline

- Problems with close-cycle water splitting process by heat absorption
- Operational methods to maintain mass balance
- Techniques to regulate Bunsen solution composition
- A method to allocate heat for O_2 and H_2 production sections in strict proportion

For simple discussion

Reactions for IS process

$$
\begin{aligned}
\cancel{2H_2O} + \cancel{SO_2} + I_2 &\longrightarrow \cancel{H_2SO_4} + 2HI \\
\cancel{H_2SO_4} &\longrightarrow \cancel{H_2O} + \cancel{SO_2} + \frac{1}{2}O_2 \\
2HI &\longrightarrow H_2 + I_2
\end{aligned}
$$

Supposing SO_2 to be limiting reactant

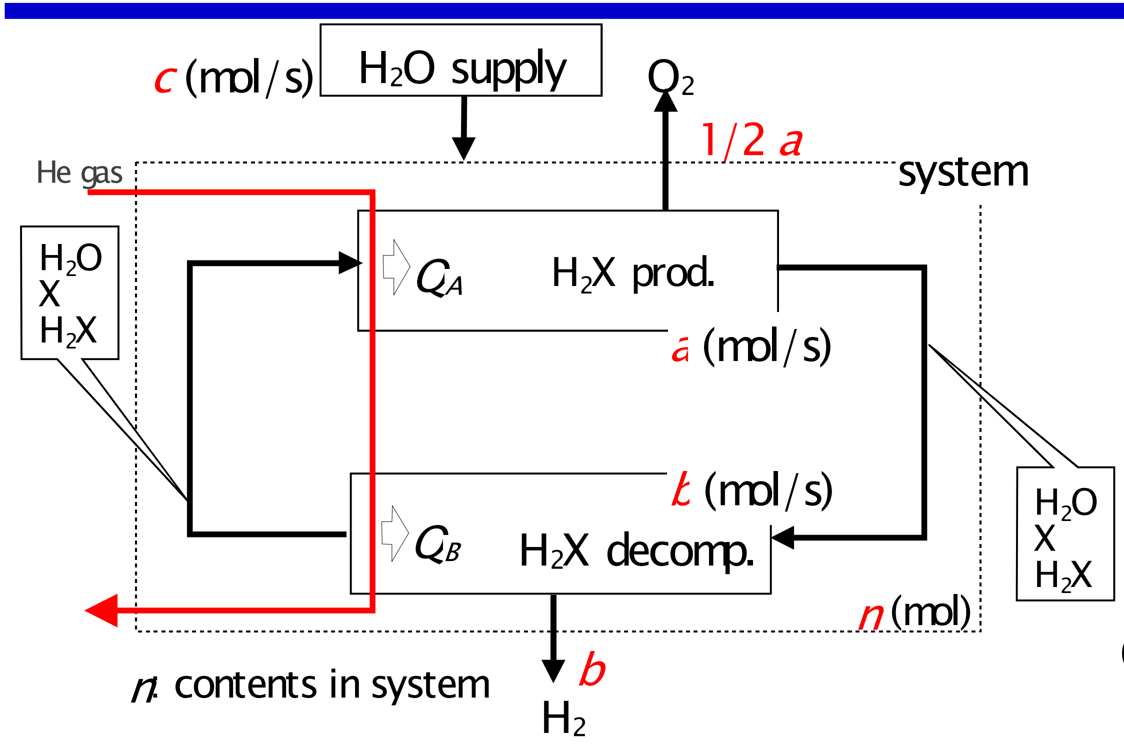
Simplest reaction scheme

$$
\begin{aligned}
H_2O + X &\longrightarrow H_2X + \frac{1}{2}O_2 \\
H_2X &\longrightarrow X + H_2
\end{aligned}
$$

I_2 = X, X: imaginary substance

Employ simplest themochemical cycle of two step reactions

Problems on closed-cycle operation



$$\frac{dn_{H_2O}}{dt} = c - a$$

$$\frac{dn_X}{dt} = b - a$$

$$\frac{dn_{H_2X}}{dt} = a - b$$

①Process becomes steady on *a*=*b*=*c*

②On a=b=c, Q_A:Q_B should be strict proportion

①Closed-cycle condition, ②Water splitting by heat absorption via He gas

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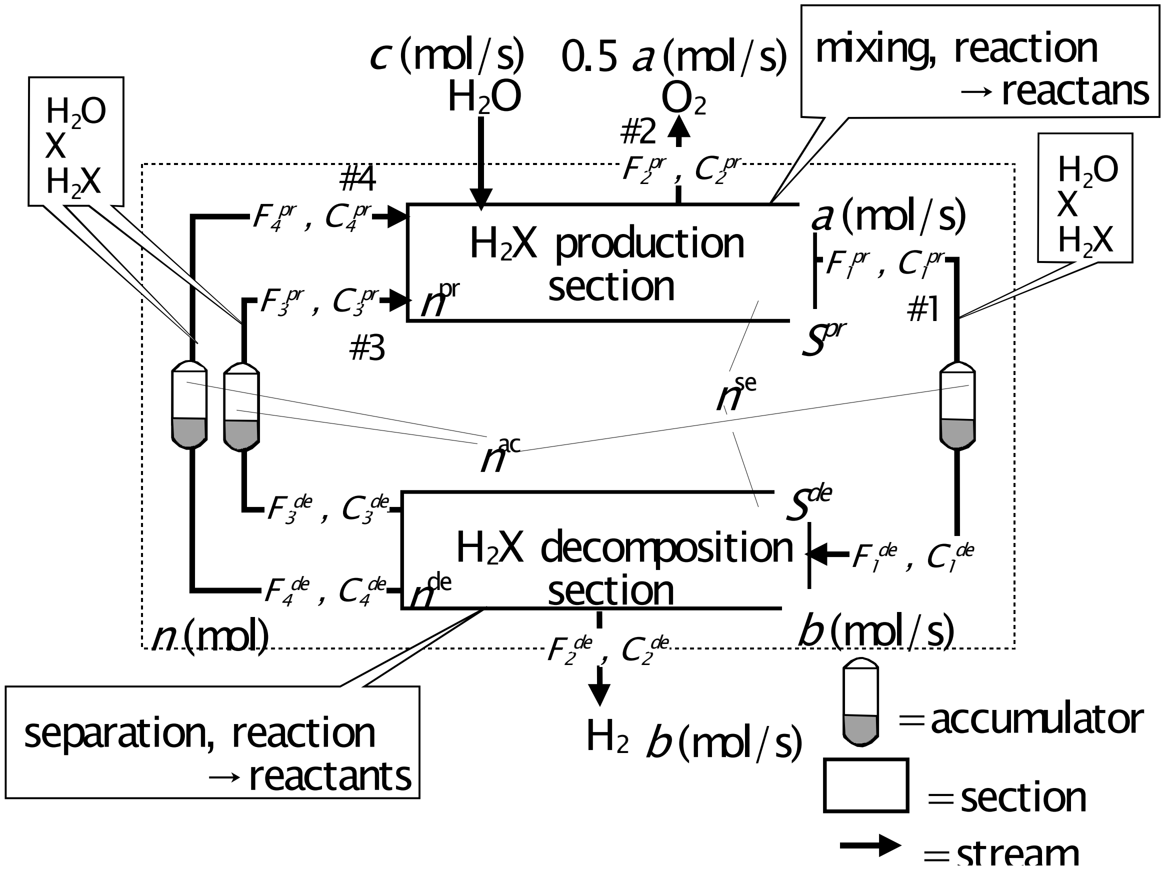
Stable hydrogen production becomes difficult

Challenges

Develop operational methods to maintain MB (*a*=*b*=*c*) and HB (Q_A/Q_B = const.)

For $a=b=c$, requires manipulated variables



C: matrixes to indicate compositions,
F: flow rates, S: amount of reaction per unit time

To install accumulators, divides contents variation

$$\frac{dn}{dt} = \frac{dn^{\mathrm{se}}}{dt} + \frac{dn^{\mathrm{ac}}}{dt}$$

Modularizing reaction sections

$C=const.$, $dn^{se}/dt = 0$

$$CF + S - \frac{dn^{\mathrm{se}}}{dt} = 0$$

⇩

$$F = C^{-1}(-S)$$

F are fixed uniquely to S

Manipulated variables to control S (e.g. a, b) → feed flow rate F

For *a*=*b*=*c*, requires controlled variables

Contents variations in accumulators

$$-\begin{pmatrix} F_1^{de}+F_1^{pr} \\ 0 \\ F_3^{de}+F_3^{pr} \\ F_4^{de}+F_4^{pr} \end{pmatrix} = (C^{pr})^{-1} \begin{pmatrix} -a+c \\ -a+b \\ a-b \\ 0 \end{pmatrix}$$

Deference between input and output of accumulators

Overs and shorts

Trial case

St#1: GA's composition ($HI/I_2/H_2O$=1/3.8/5.3)

St#3: pure H_2O

St#4: I_2 + a bit H_2O,HI

St#1 #2 #3 #4

$$C^{pr} = \begin{pmatrix} 0.552 & 0 & 1 & 0.01 \\ 0.396 & 0 & 0 & 0.98 \\ 0.052 & 0 & 0 & 0.01 \\ 0 & 1 & 0 & 0 \end{pmatrix}$$

H_2O

X = I_2

H_2X = 2 HI

H_2 or O_2

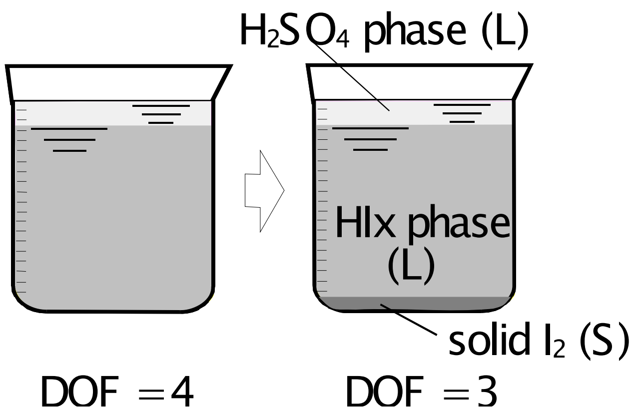
Trial case

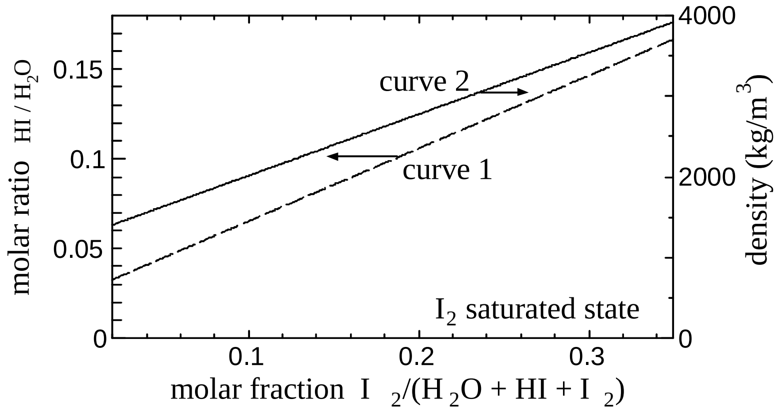
$$-\begin{pmatrix} F_1^{de}+F_1^{pr} \\ 0 \\ F_3^{de}+F_3^{pr} \\ F_4^{de}+F_4^{pr} \end{pmatrix} = \begin{pmatrix} 21.0(a-b) \\ 0 \\ (c-a)-11.5(a-b) \\ -9.53(a-b) \end{pmatrix}$$

Detects overs and shorts of reactions (*a*-*b*, *c*-*a*)

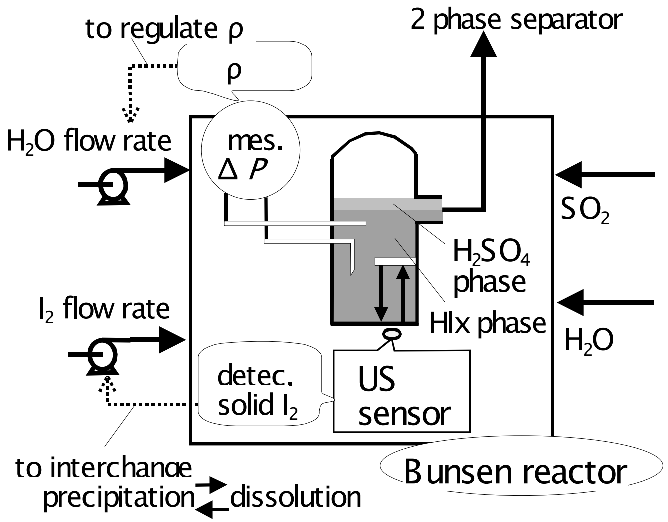
→ level variation of accumulators = Controlled variables

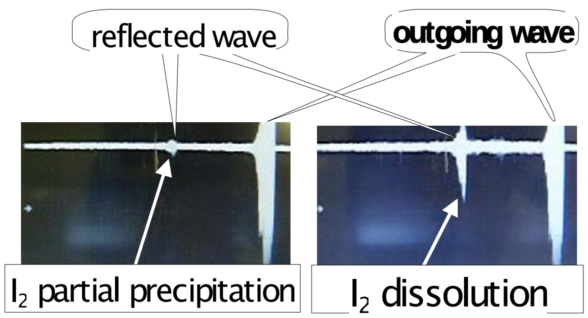
For *C*=const. , techniques of maintaining Bunsen solution composition





On I_2 saturated condition, to regulate density of HIx Soln. maintains Bunsen composition

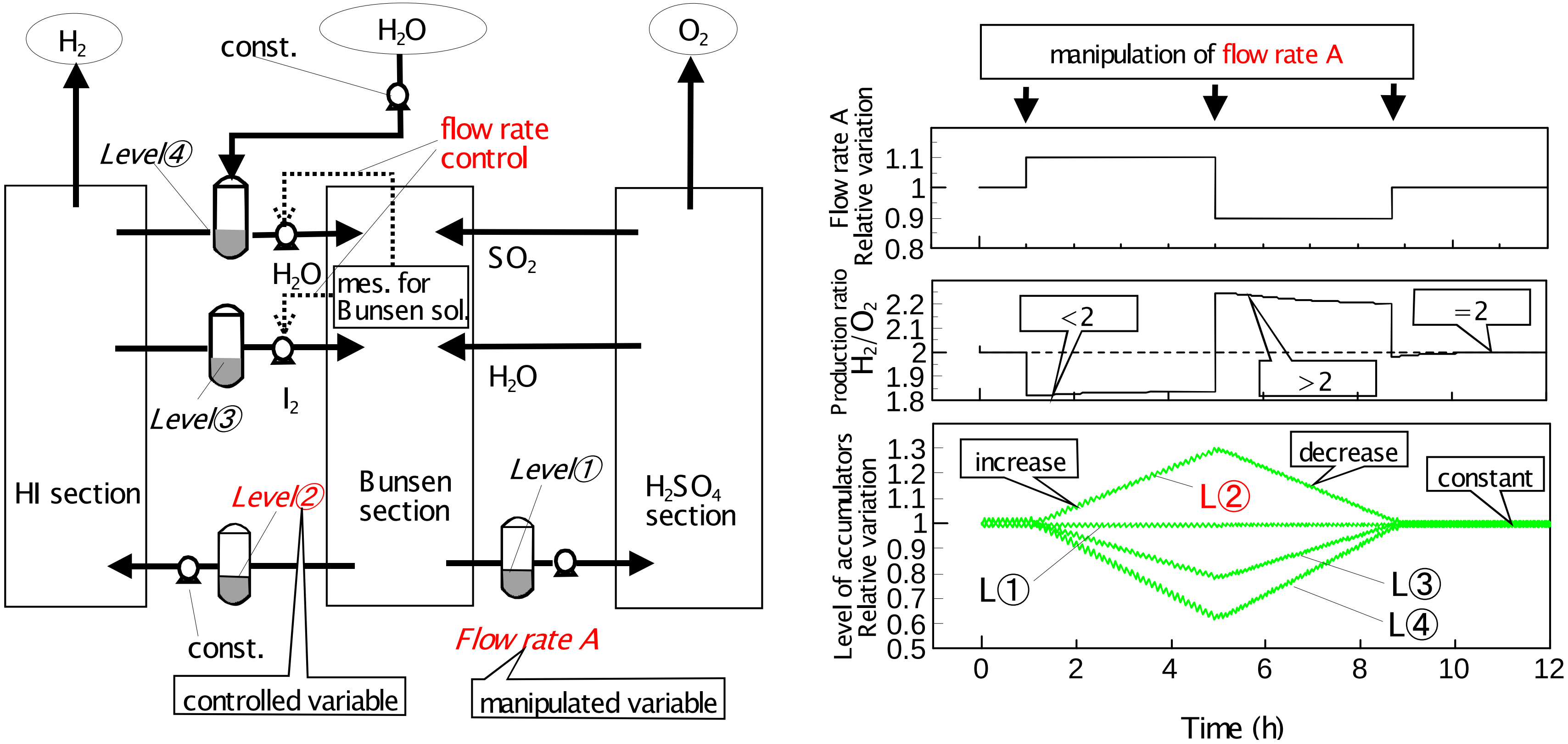




In plant operation, DP sensor and US sensor control flow rate of H_2O and I_2 recycling from other section → Bunsen solution is able to maintain regular composition

Computer simulation of control method for a=b=c

Level② varies according to production ratio which can be controlled by flow rate A

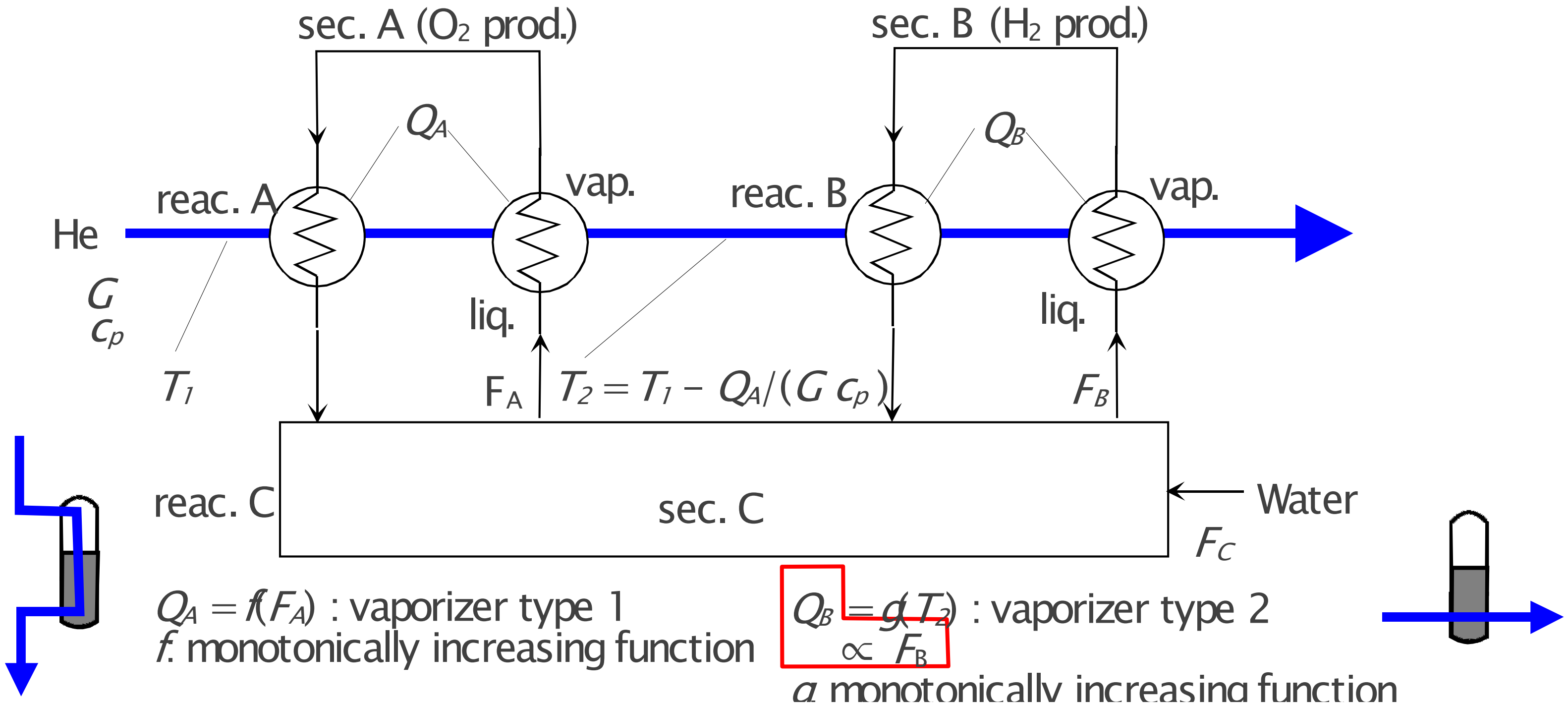


Computation → Operational methods was confirmed

Bench test → the methods was verified by accomplish of 1 week H_2 production

For long-term operation, stable H_2 production is able to conduct on manipulating flow rate A and B

For Q_A/Q_B = const., one of configurations for IS process with He gas supply



Cascade heat absorption system via two heat sinks (Q_A, Q_B)

Heat should be allocatd for Q_A, Q_B in strict proportion

F_A manipulation → controls ratio of Q_A to Q_B (Q_A ↑ → Q_B ↓)

F_B determines from Q_B

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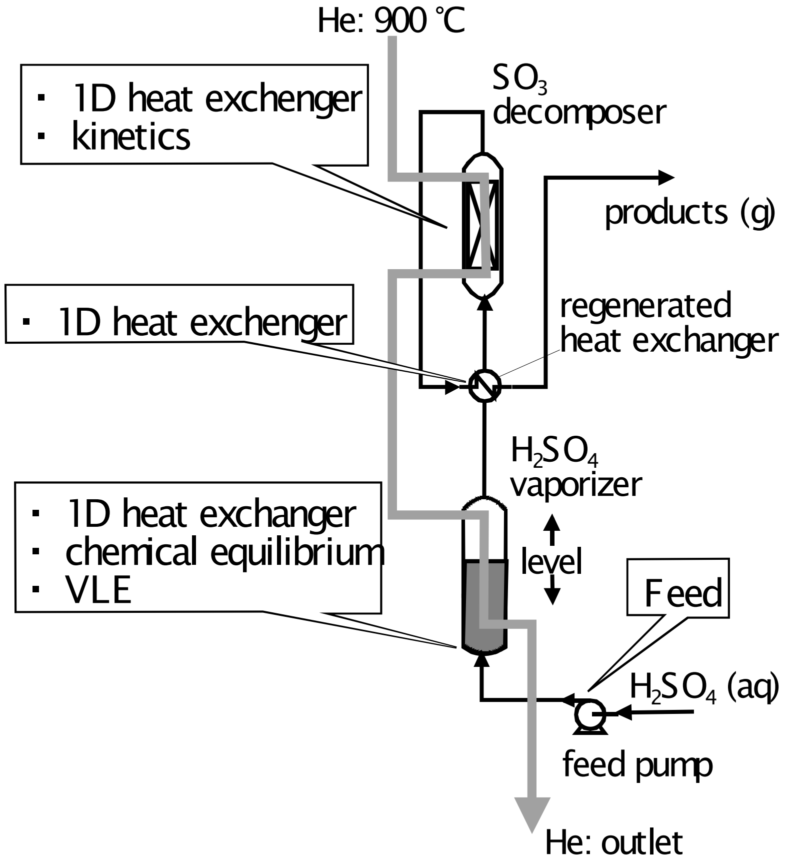
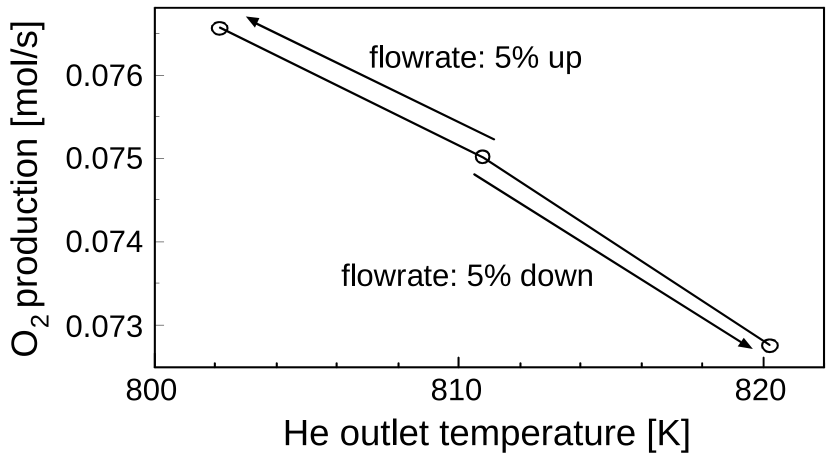
Manipulate flow rate A and B, according to He gas condition

Computer simulation for O_2 production system

Manipulate flow rate A to control inlet temp. for H_2 prod. section





- O_2 production decays with reducing feed rate of H_2SO_4(aq.)
- While He outlet (=inlet for H_2 prod. system) temperature increases

Key point to maintain heat balance is confirmed

Conclusions

・Essential problems with close-cycle water splitting process by heat absorption were declared.

・Operational methods to maintain mass balance were developed.

・ Techniques to regulate Bunsen solution composition were devised.

・ The methods and techniques were confirmed by computer simulation and the bench-scaled H2 production test.

・A method was discussed to allocate heat for O_2 and H_2 production sections in strict proportion.