Hydrogen Production from Supercritical Water
-Mechanism of Catalytic Reactions of Biomass by Ruthenium(IV) Oxide-

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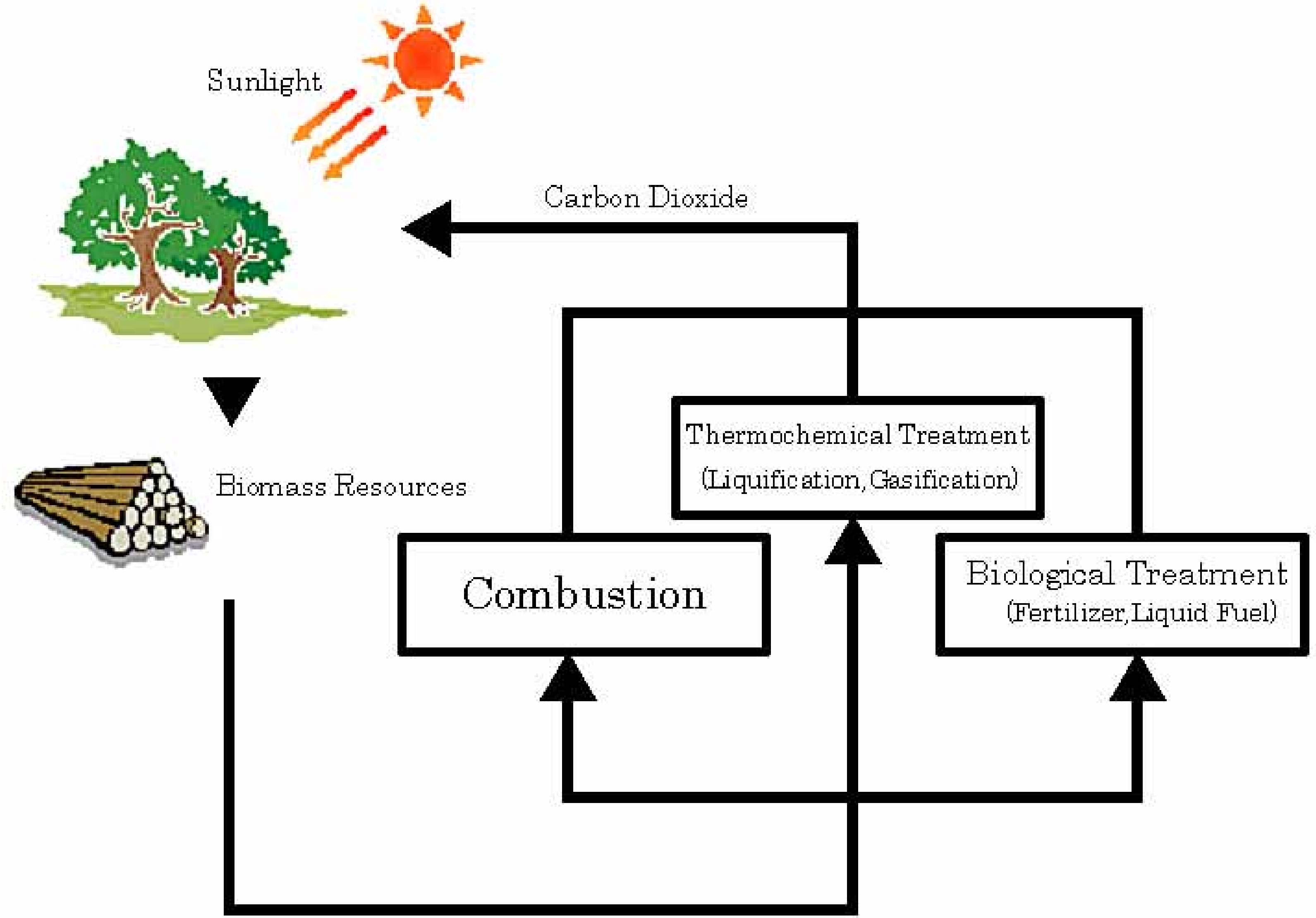
Biomass is recyclable fuel source



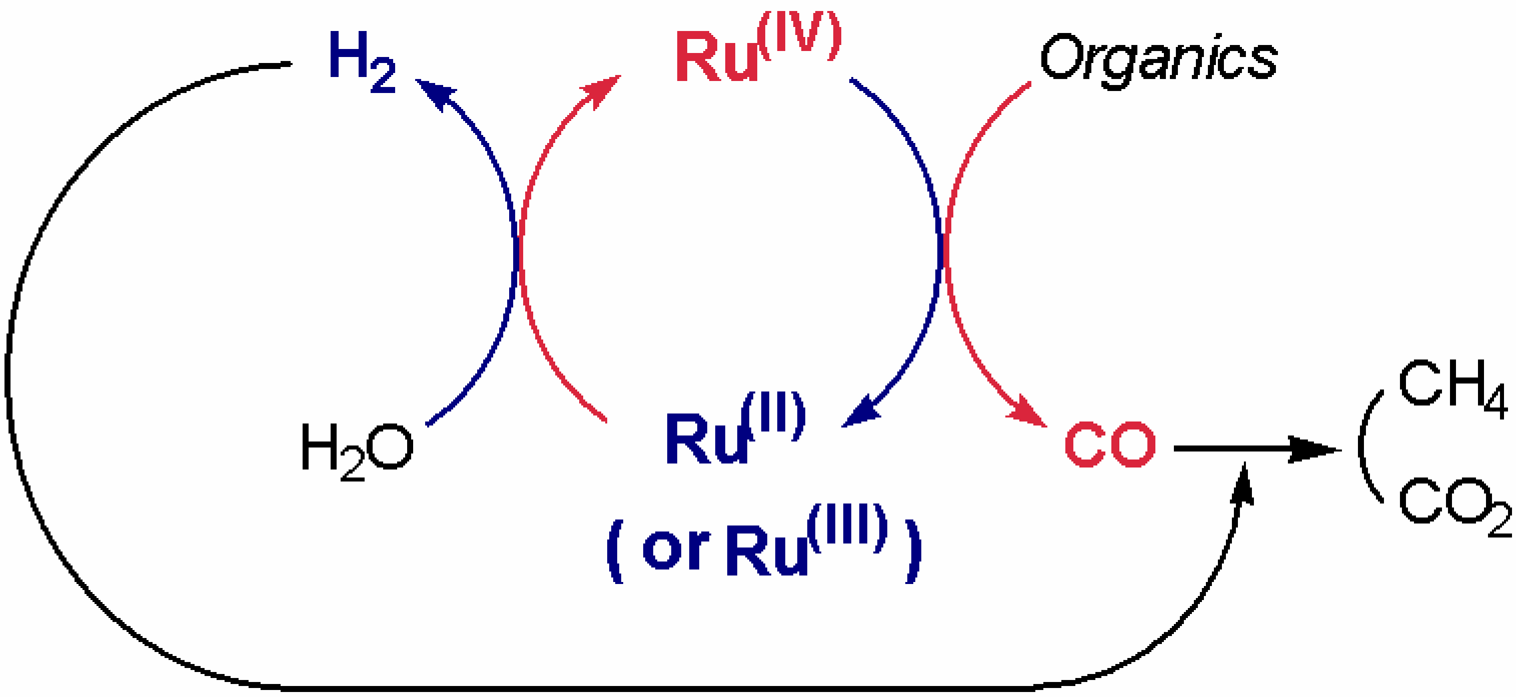
Problems in exploitation of biomass

Low combustion efficiency because of containing high oxygen atom ratios	Almost all biomass is solid,which makes difficult to deal as fuels
↓	↓
Enhance their efficiency(containing high H/C ratio) for use as high quality fuels	The necessity of reforming to liquid or gas to ease treatment

Decomposition ratios and gas distributions for organic compounds in the presence of RuO_2 catalyst in supercritical water

Organic compounds	Carbon conversion(%)	O/C ratio	Product distribution(%)		
			CH_4	CO_2	H_2
Naphthalene	96.7	-	48.8	42.7	8.4
Polyethylene	100.6	-	66.6	28.0	5.3
Polypropylene	99.9	-	66.5	26.9	6.5
Porystylene	100.7	-	53.7	39.4	6.9
PET	97.2	0.40	37.3	51.0	11.5
cellulose	97.0	0.83	34.2	50.9	14.6

Mechanism of the gasification catalysis by RuO_2



Hydrogen produced from water

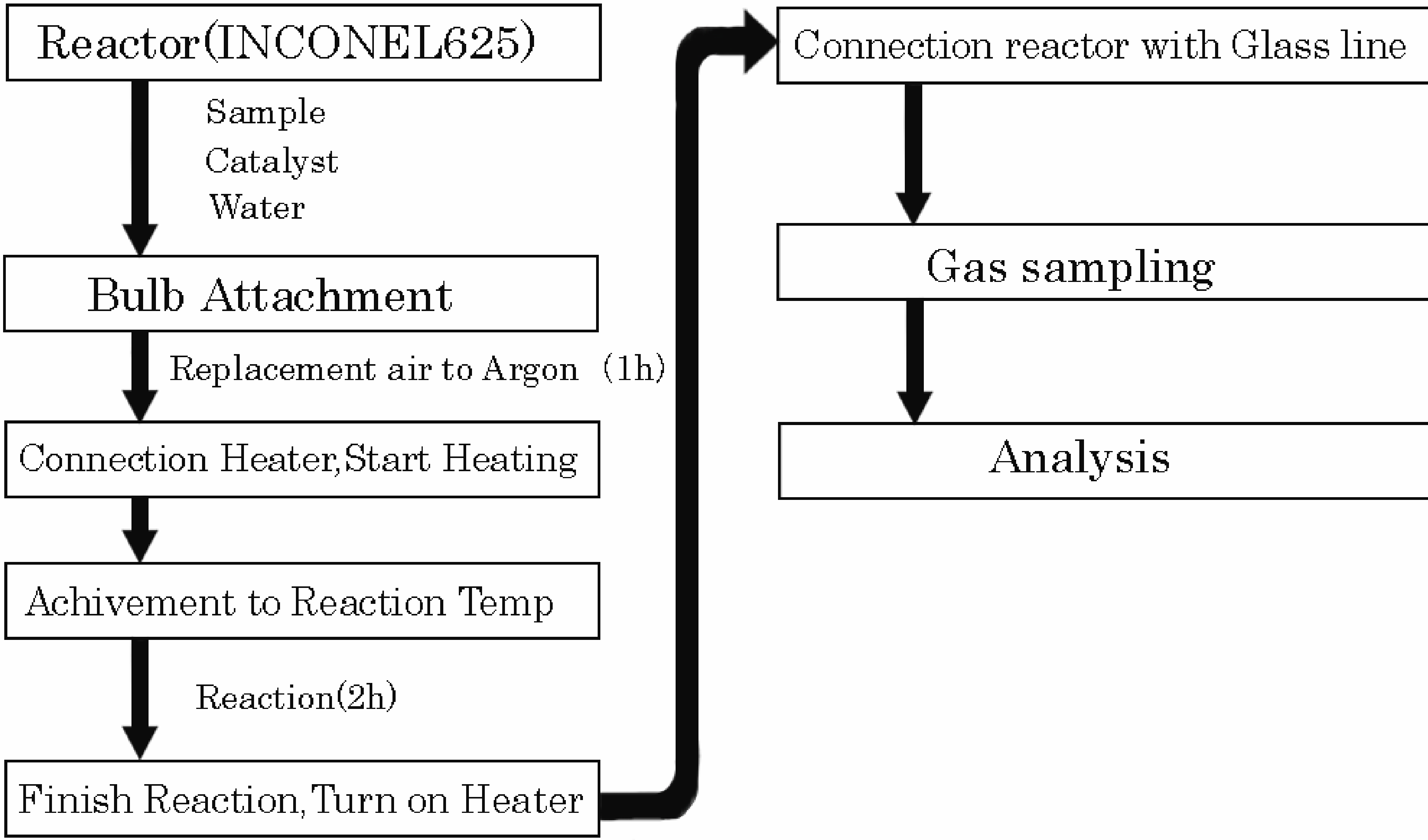
Experiment

Gasification of biomass in SCW using RuO_2 as a catalyst

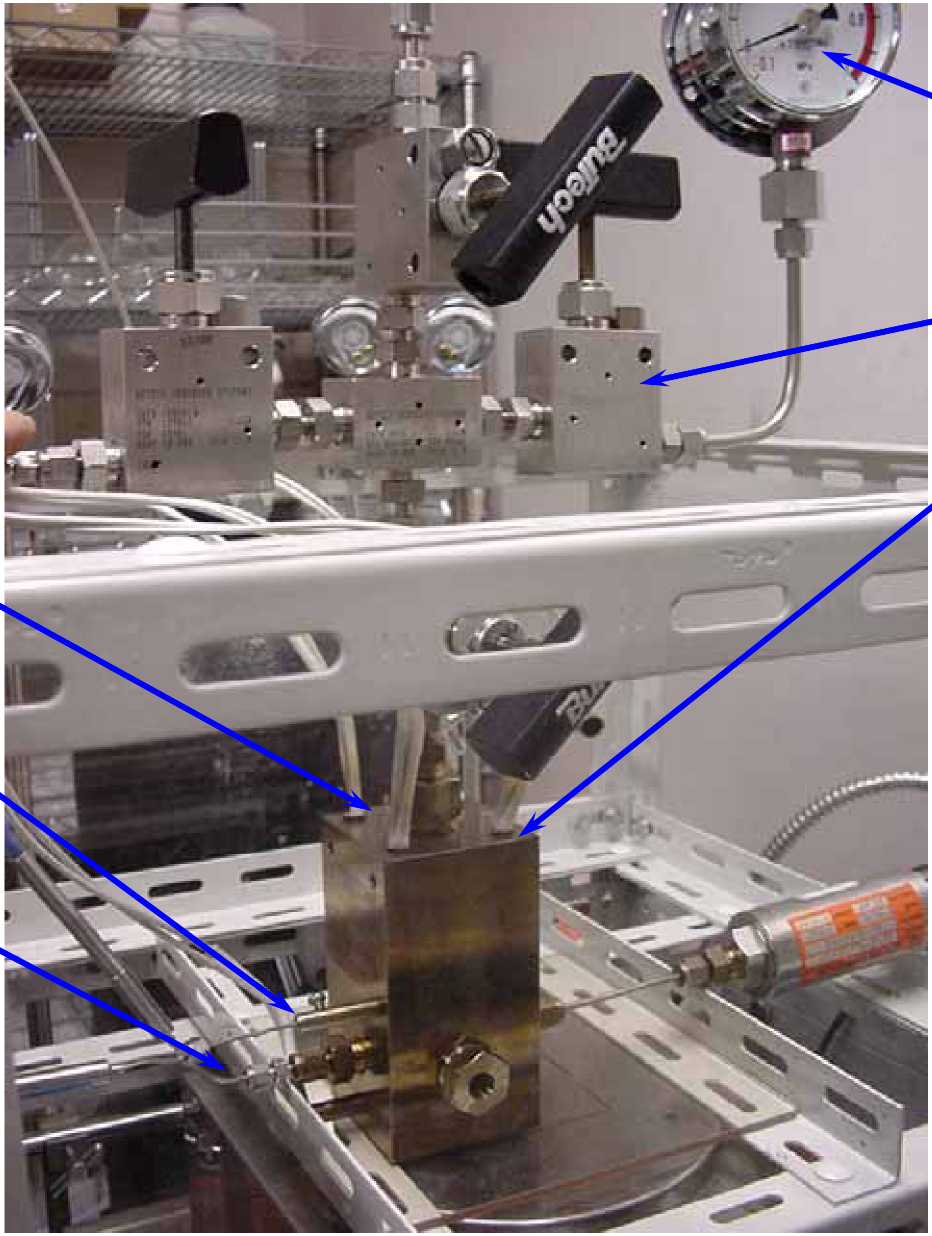
Experiments were carried out for the following samples

- Cellulose and lignin (main compounds of biomass)
- mixtures of cellulose(75%) and lignin(25%) (for the simulation of biomass)
- Pulp (main sample used in this experiment)
- Paper sludge and recycled paper from Tomoekawa Paper Company

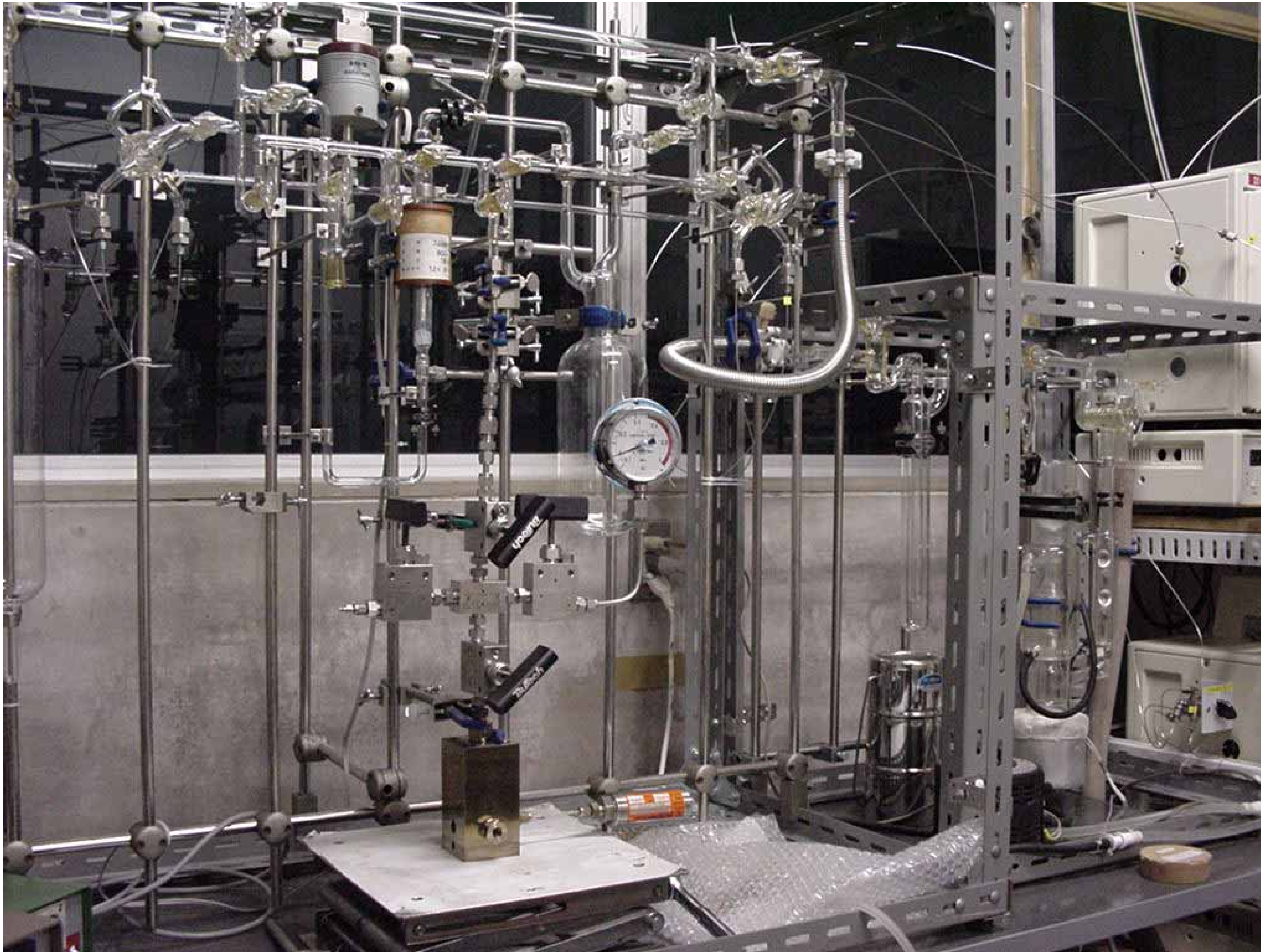
Experimental Procedure



Picture of experimental apparatus(1)



Picture of experimental apparatus(2)



The decomposition ratios for four different samples in the presence or absence of catalyst in SCW

Sample	SCW	SCW+RuO_2
Cellulose	32.0	97.0
Pulp	17.8	71.3
Mixtures (cellulose and lignin)	10.6	32.0
Lignin	8.5	7.9

(Sample:100mg Catalyst:20mg Temp:450℃ Time:2h) Unit：%

Gas. ratio=100×[C in gas products] / [C in samples loaded]

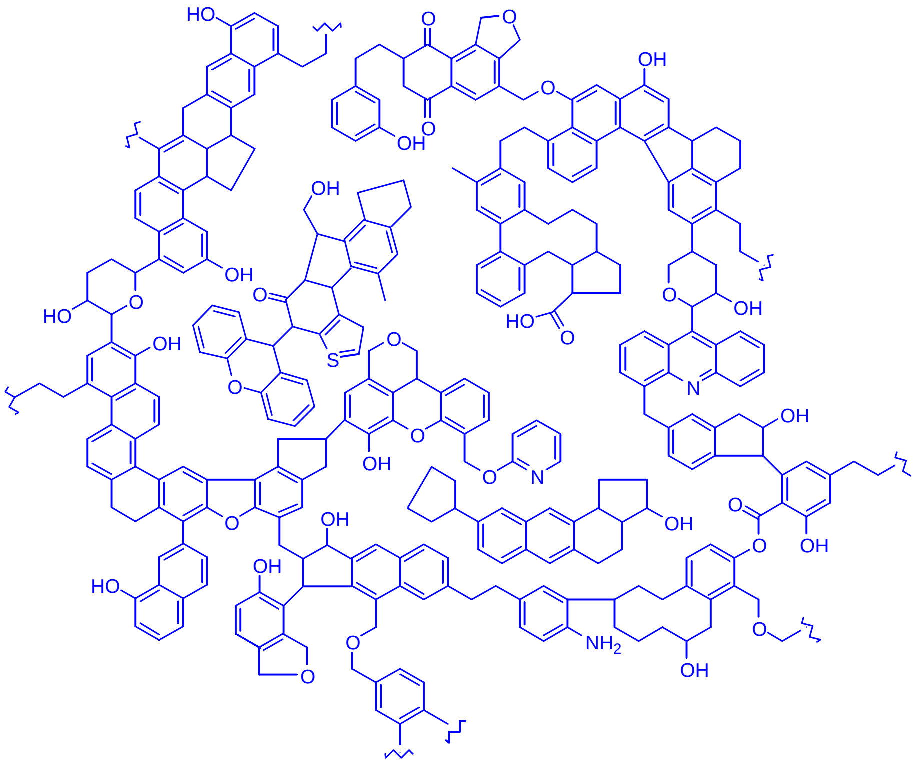
The decomposition of coal and lignin in supercritical water.

Sample	SCW	SCW+RuO_2
Lignin	8.5	7.9
Coal(Yallourn)	9.5	42.6

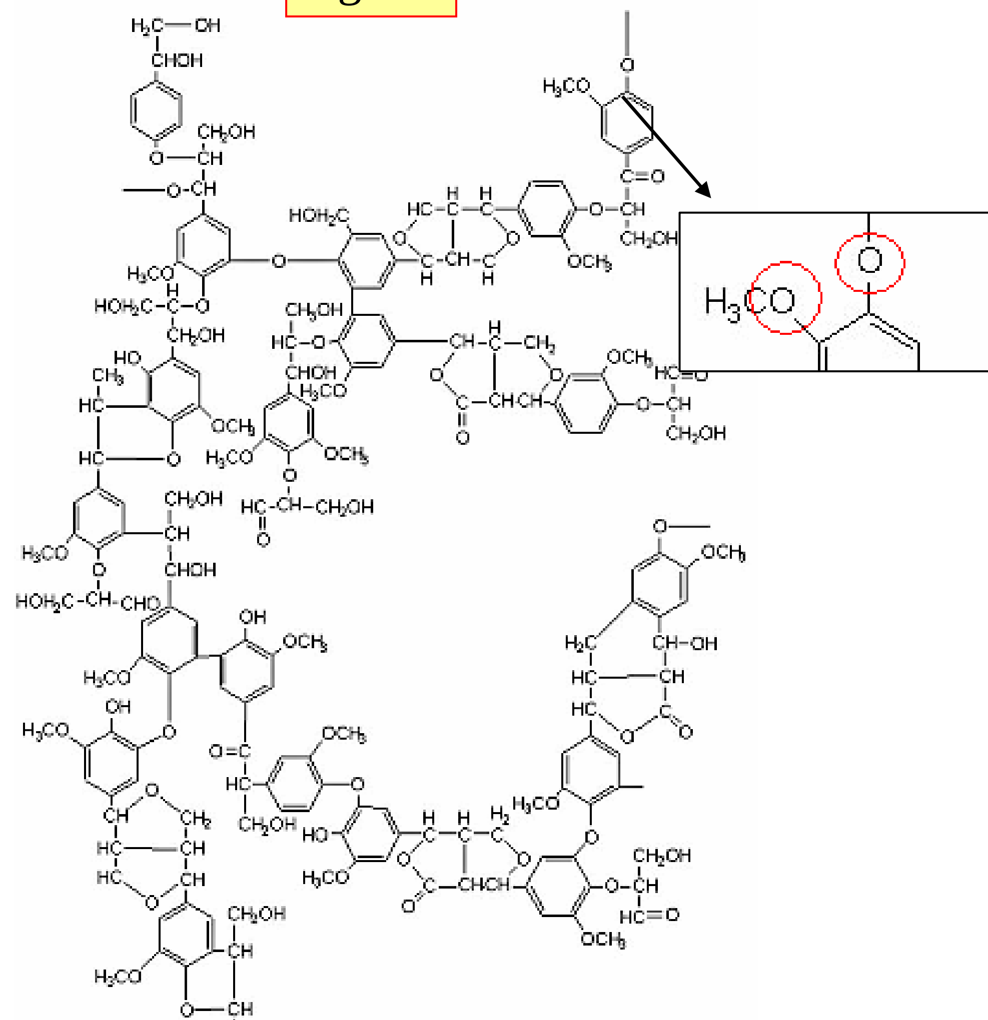
(Sample:100mg Catalyst:20mg Temp:450℃ Time:2h) Unit：%

Structures of coal and lignin

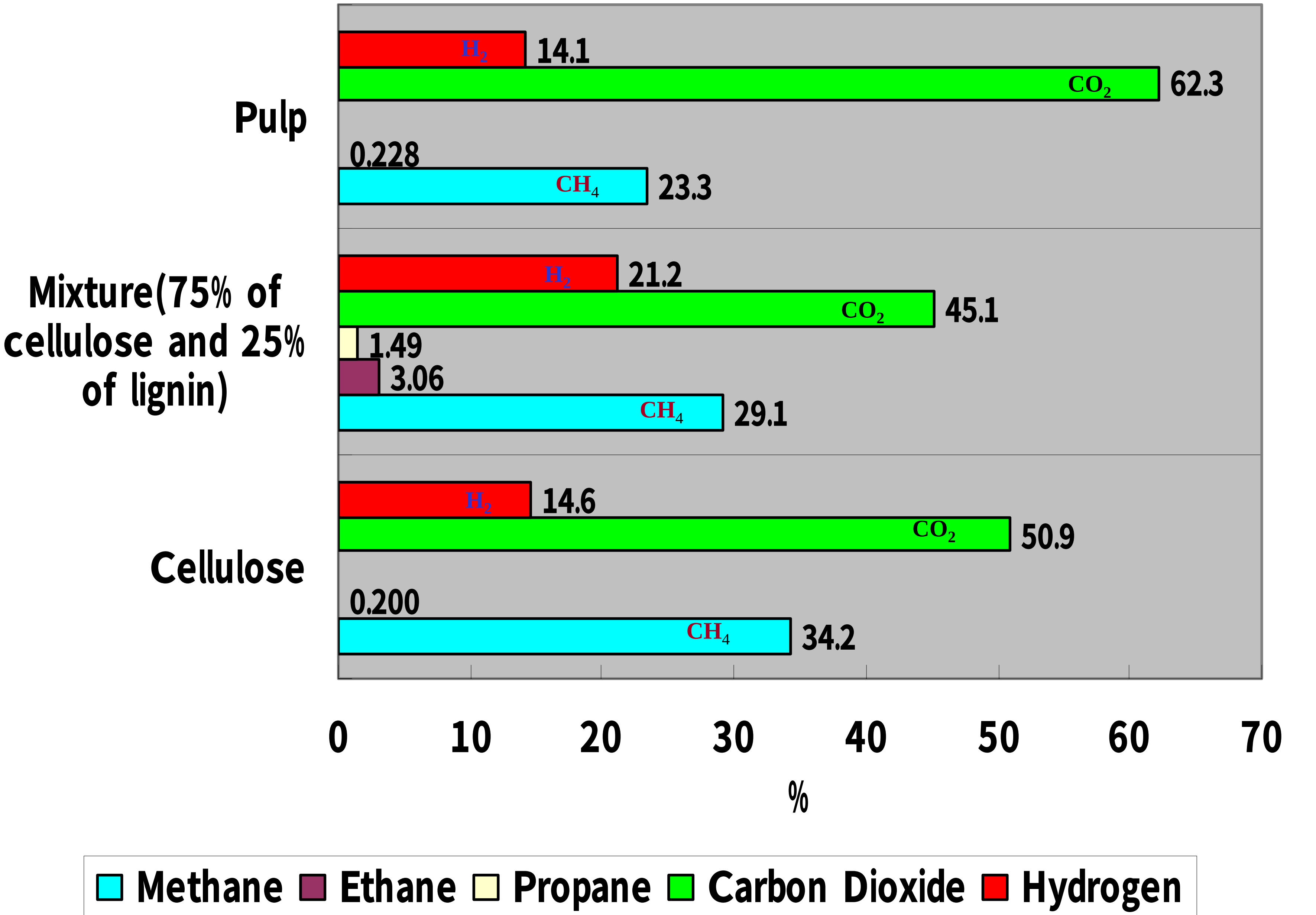
Bituminous coal



lignin



Gas species produced from each samples

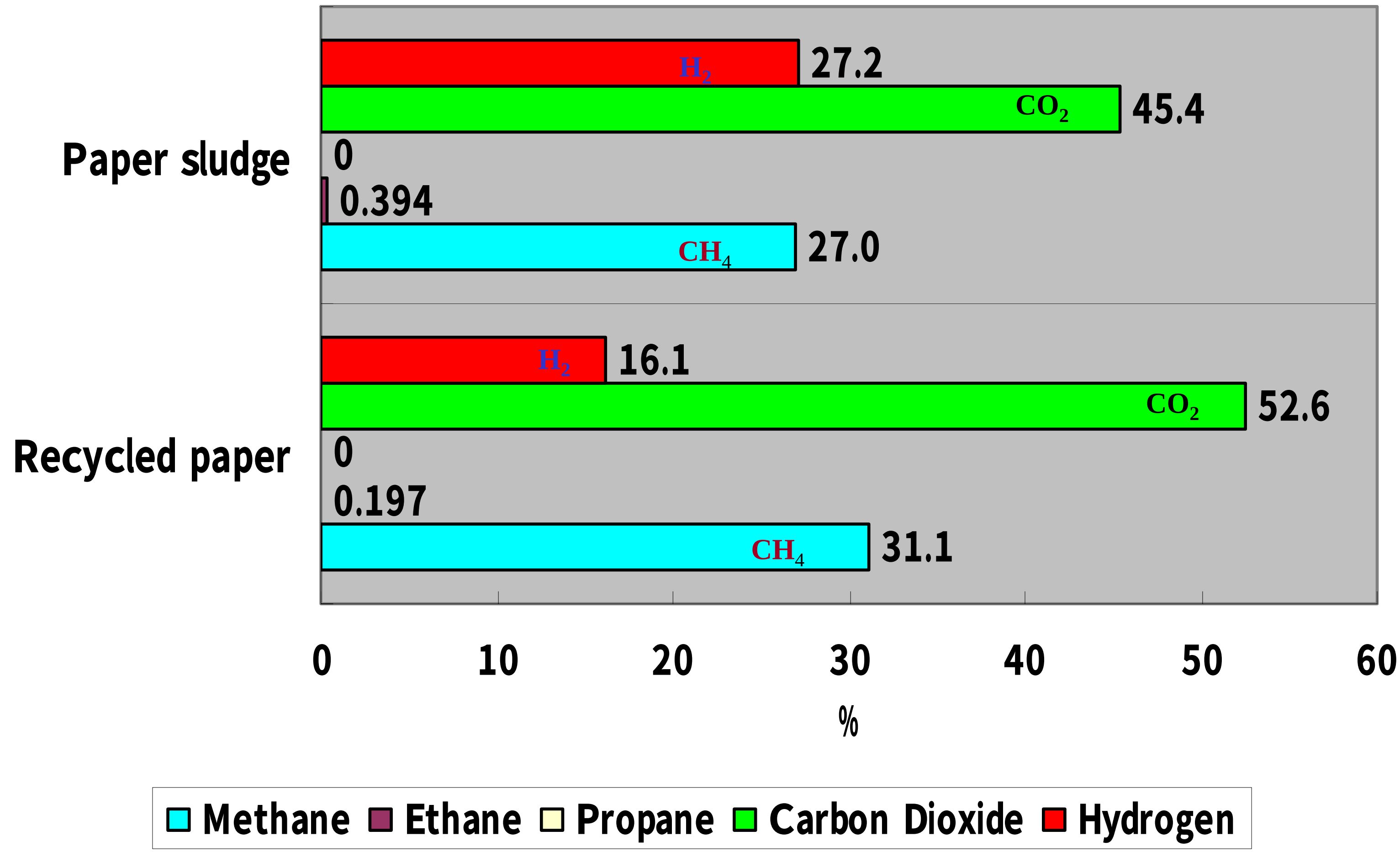


Amount of gas(L) produced from 100g of pure cellulose and pulp

samples / produced gases	Cellulose	Pulp
CH_4	32.1L	19.0L
H_2	13.7L	11.5L

Amount of gas was calibrated under the standard condition.

Gas species produced from paper sludge and recycled paper



(Sample:100mg Catalyst:20mg Temp:450℃ Time:2h)

Amount of gas(L) produced from 100g of paper sludge and recycled paper

produced gases \ samples	Paper Sludge	Recycled Paper
CH_4	8.64L	23.3L
H_2	8.70L	12.0L

Amount of gas was calibrated under the standard condition.

Confirmation of production of fuel gases such as methane and hydrogen

→This method is available about disposing of wastes

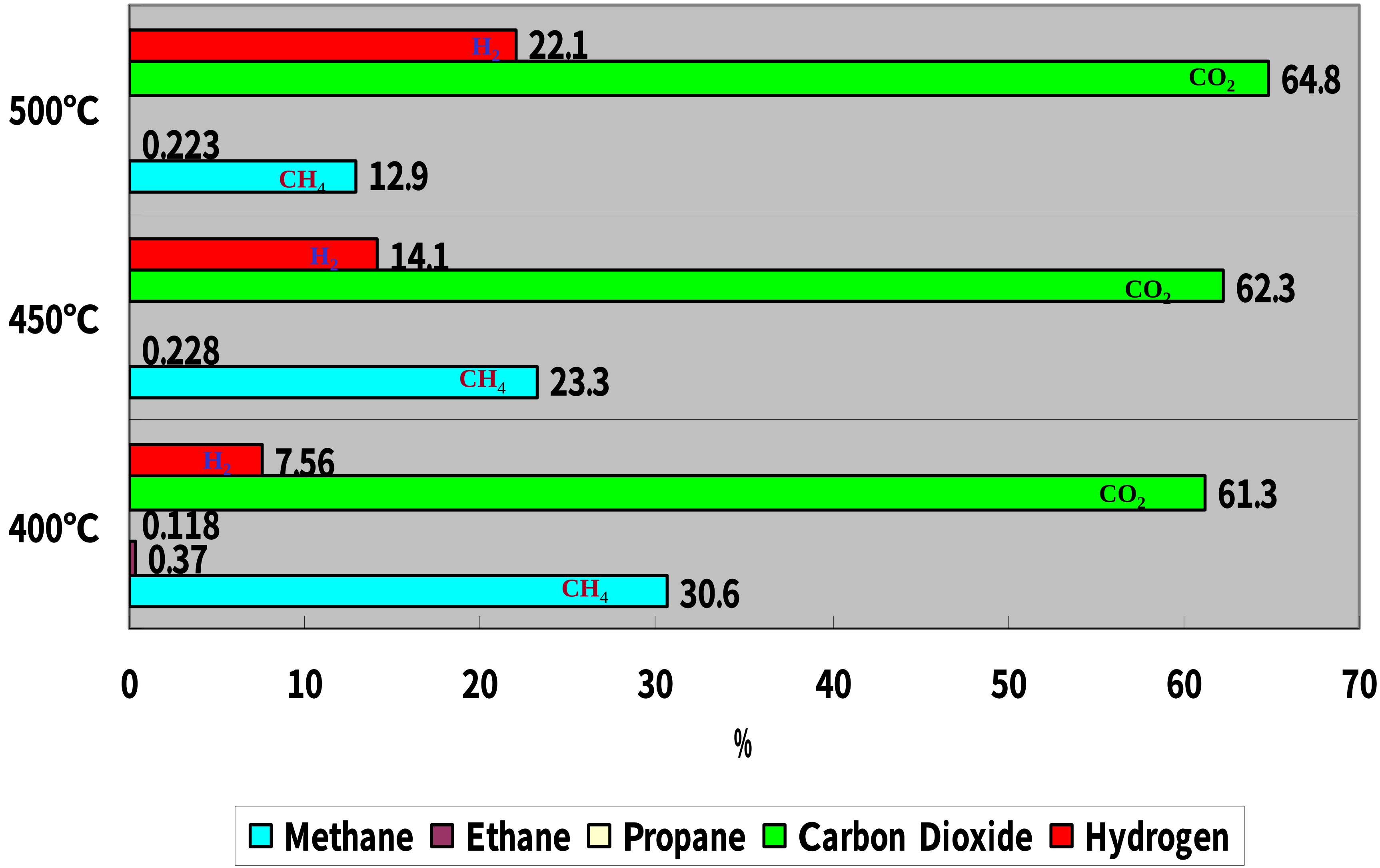
Treatment of industrial wastes from paper company

Paper sludge

Recycled paper

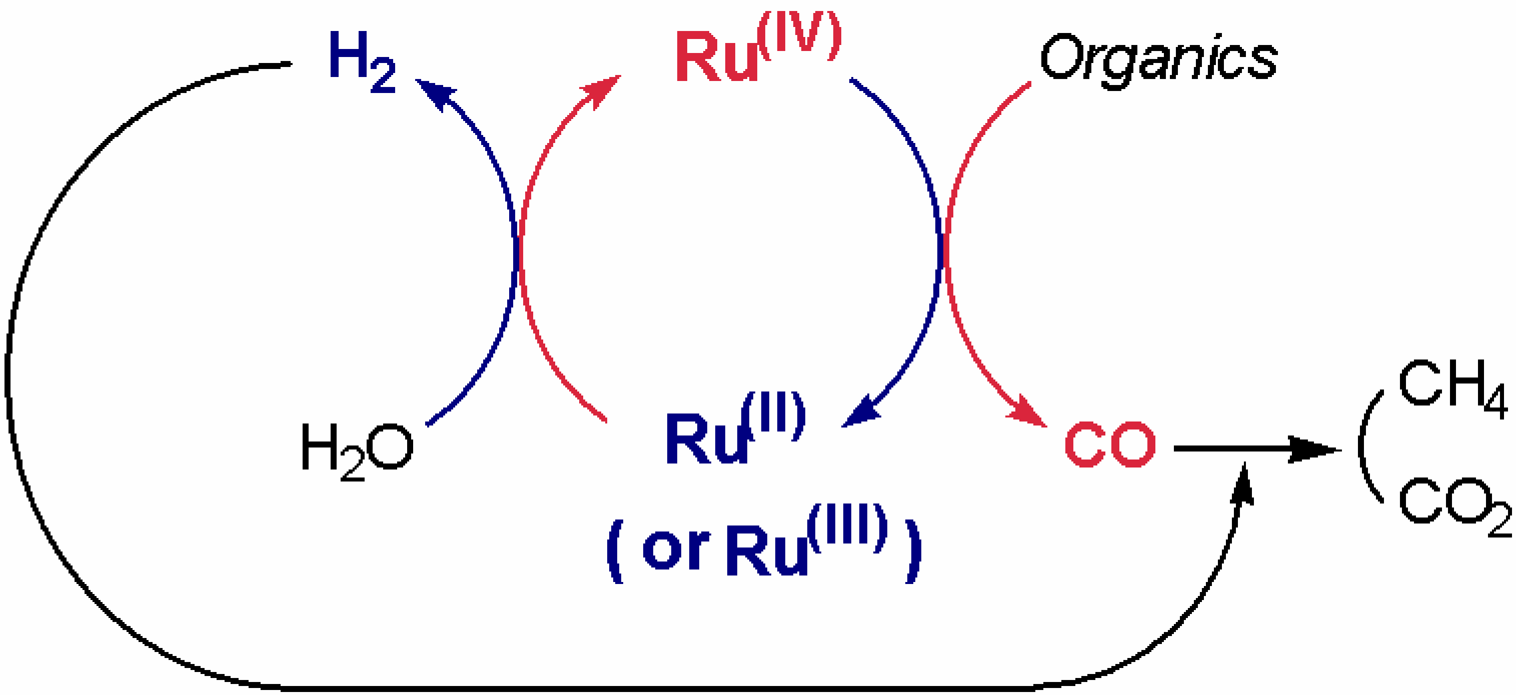
Organic residues are negligible →This method enables to decompose waste containing biomass.

Effect of temperature on the productions of gasses from pulp



(Sample:100mg Catalyst:20mg Time:2h)

Mechanism of the gasification catalysis by RuO_2



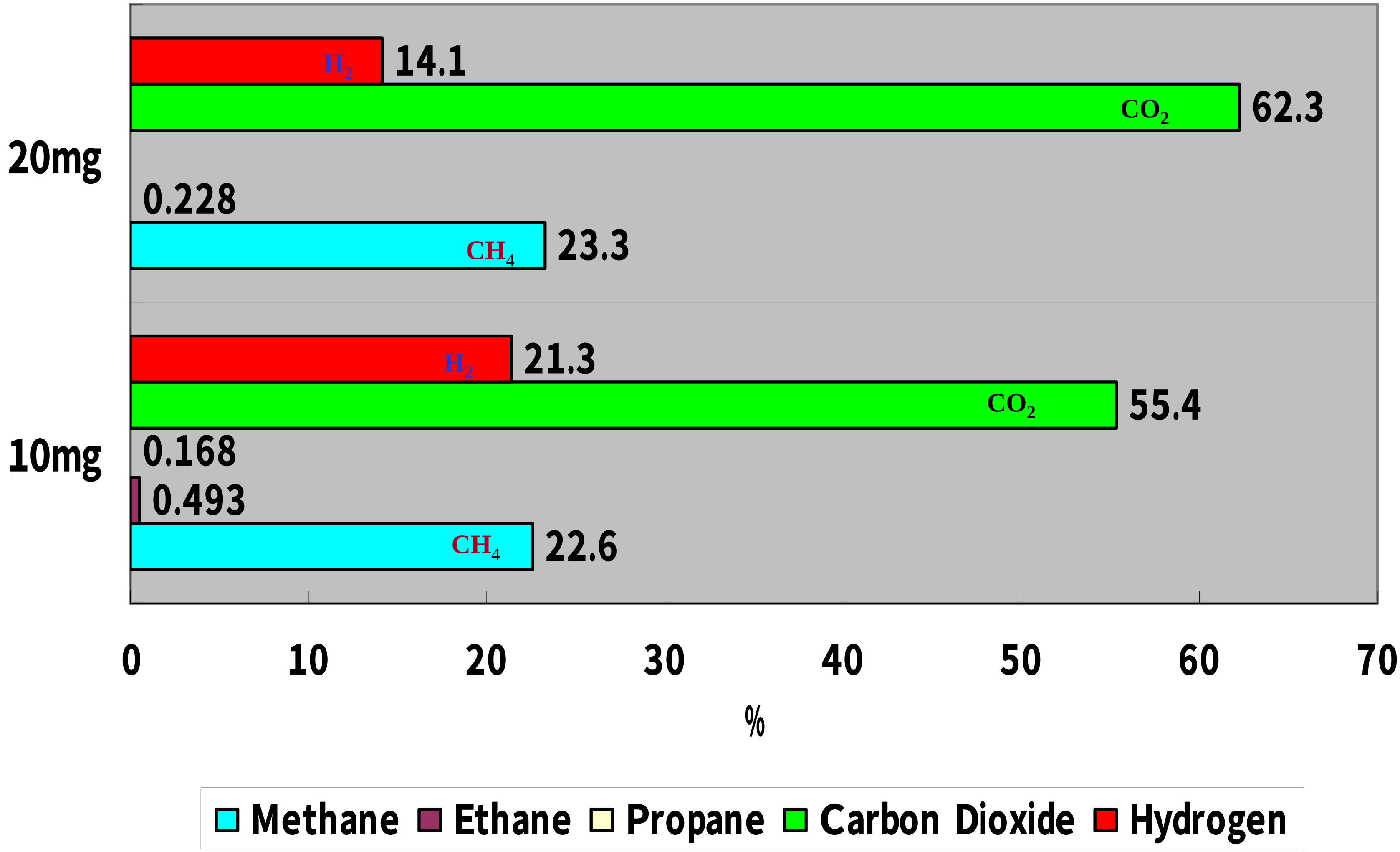
- $CO + 3H_2 \rightarrow CH_4 + H_2O$
- $2CO + 2H_2 \rightarrow CH_4 + CO_2$

Amount of gas(L) produced from 100g of pulp at different temperatures

temp / produced gases	400℃	450℃	500℃
CH_4	24.7L	19.0L	11.8L
H_2	6.09L	11.5L	20.2L

Amount of gas was calibrated under the standard condition.

Change in gas distributions versus the amounts of catalyst(10 mg and 20mg)



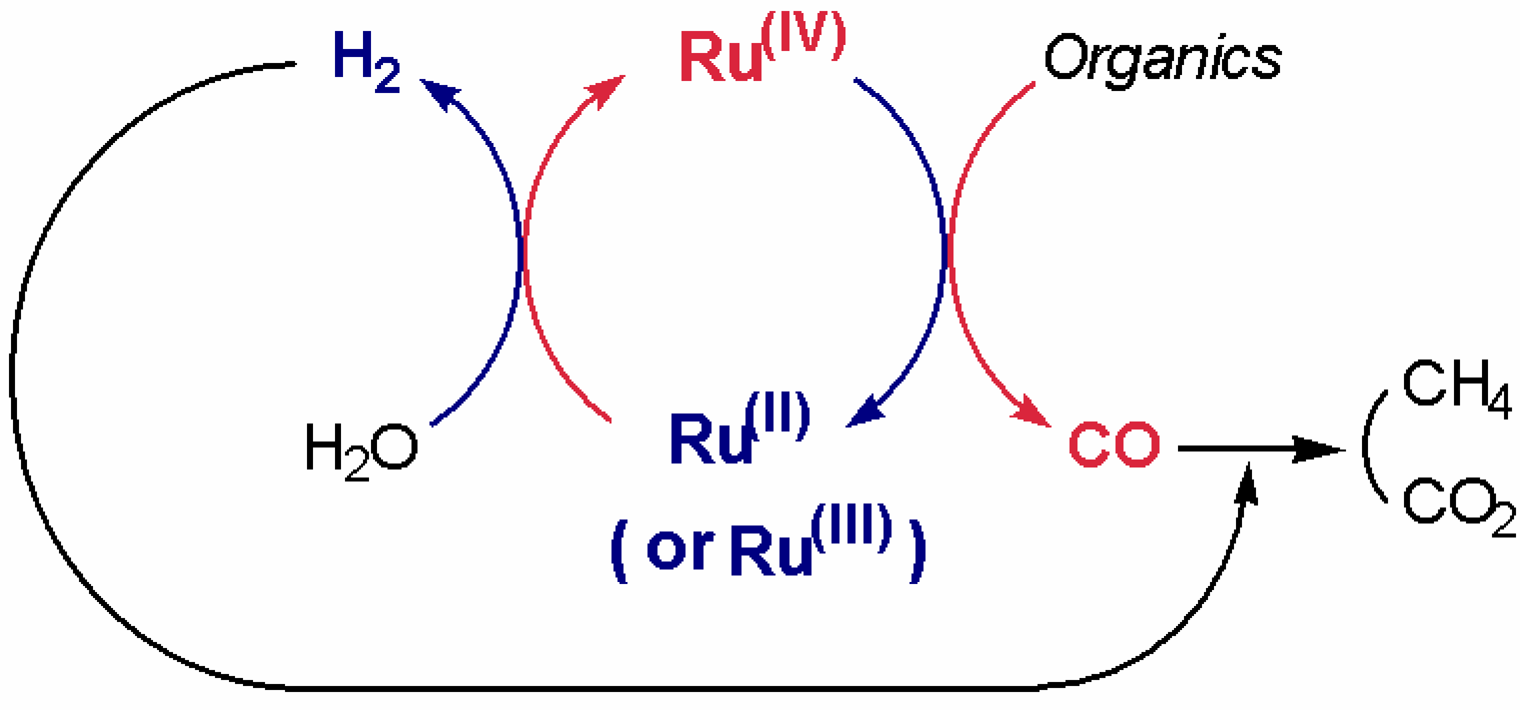
(Sample:100mg Temp:450℃ Time:2h)

Change in amount of RuO_2 catalyst for the gasification of biomass

cat / produced gases	10mg	20mg
CH_4	14.7L	19.0L
H_2	13.8L	11.5L

Amount of gas was calibrated under the standard condition.

Mechanism of the gasification catalysis by RuO_2



Existence of Ru2+ was confirmed by the UV absorption spectrum

Comparison of catalytic reactions between RuO_2 and Ni for the decomposition of biomass

	Methane	Hydrogen	Gasification ratio
RuO_2(450°C)	19.0L	11.5L	71.3%
RuO_2(500°C)	11.8L	20.2L	72.4%
Ni(450°C)	14.7L	13.9L	50.1%

(Sample:100mg of pulp Catalyst:20mg(RuO_2)/40mg(Ni) Temp:450℃ Time:2h)

Each Organic residues after reaction

Ni(450℃)

RuO_2(450℃)

Comparison of catalysts between RuO_2 and Ni for the gasification of naphthalene

	Gasification ratio
RuO_2(450°C)	96.7%
Ni(450°C)	26.3%

(Sample:100mg of Naphthalene Catalyst:20mg(RuO_2)/40mg(Ni) Temp:450℃ Time:2h)

RuO_2 is much stronger catalyst for the treatment of Organic compounds than Ni

Conclusions

- The present method using RuO_2 as a catalyst in SCW enables to decompose biomass and to produce fuel gases.
- The gases produced are H_2, CH_4, and CO_2
- Hydrogen production ratio increases with temperature up to 22.1% at 500℃
- RuO_2 catalyst is superior in catalytic efficiency to other catalyst such as Ni catalyst for decomposition of organic compounds.