Dimethyl Ether Production from Biomass

Guangzhou Institute of Energy Conversion (GIEC)
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R&D in GIEC

- Biomass Energy
- Gas Hydrate
- Solar Energy
- Ocean Energy
- Geothermal Energy
- Energy Strategy

Biomass Energy:
- Energy Crops
- Biomass Thermal Utilization
- Biomass Synthetic Fuel
- Solid waste

President of Chinese Academy of Sciences, Dr. Yongxiang Lu Visited our Lab. Oct, 2003

Biomass resources-energy Cycle

Global Biomass Resources

- **Wood residues:**

  Sawdust, wood chips, wood waste, pellets, crate discards, wood yard trimmings

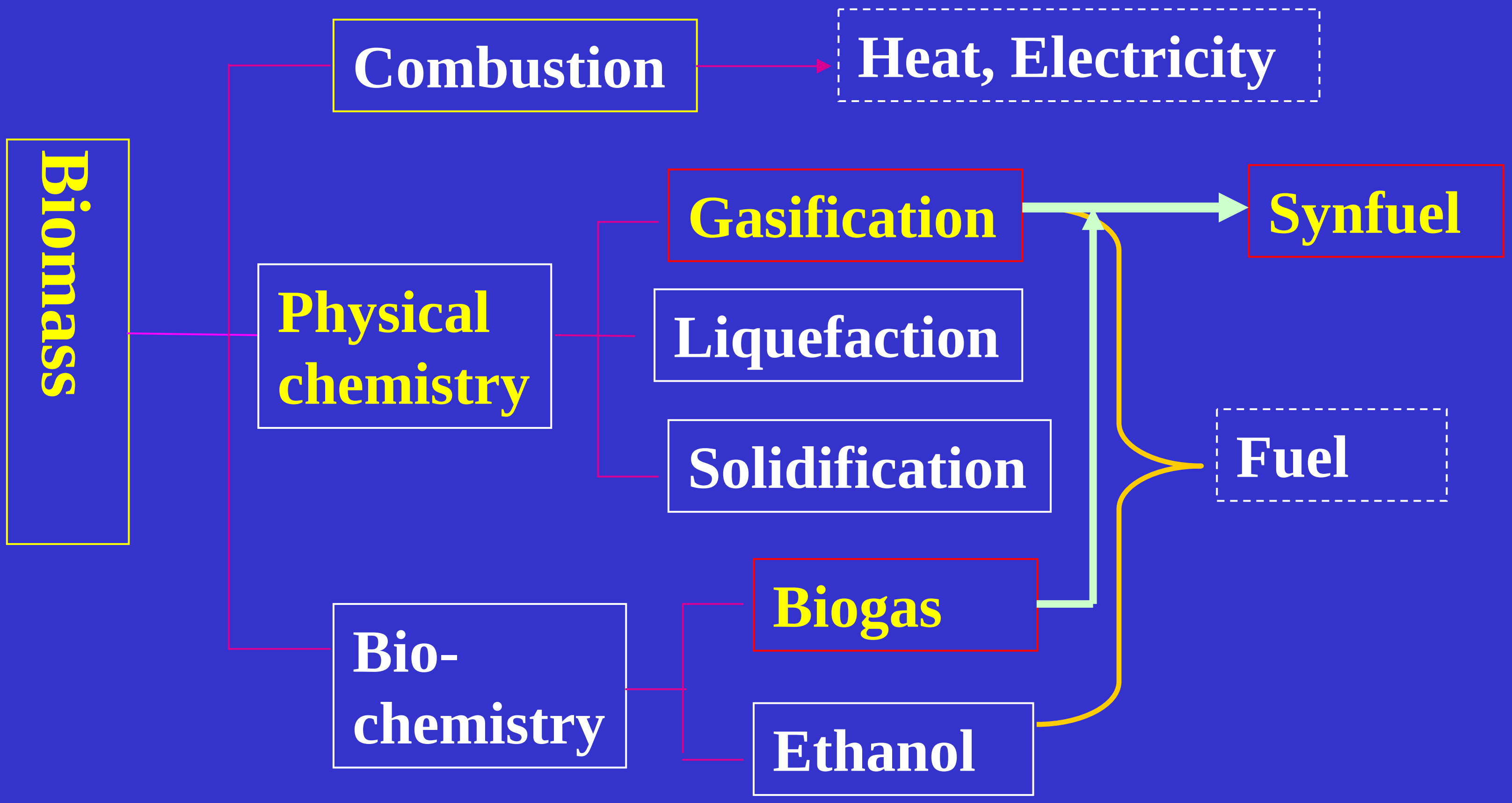
- **Agricultural residues:**

  Corn stover, rice hulls, coconut shell, bagasse, animal waste

- **Energy crops:**

  Miscanthus, hybrid poplar, switchgrass, salix, banagrass

Biomass Conversion Technologies

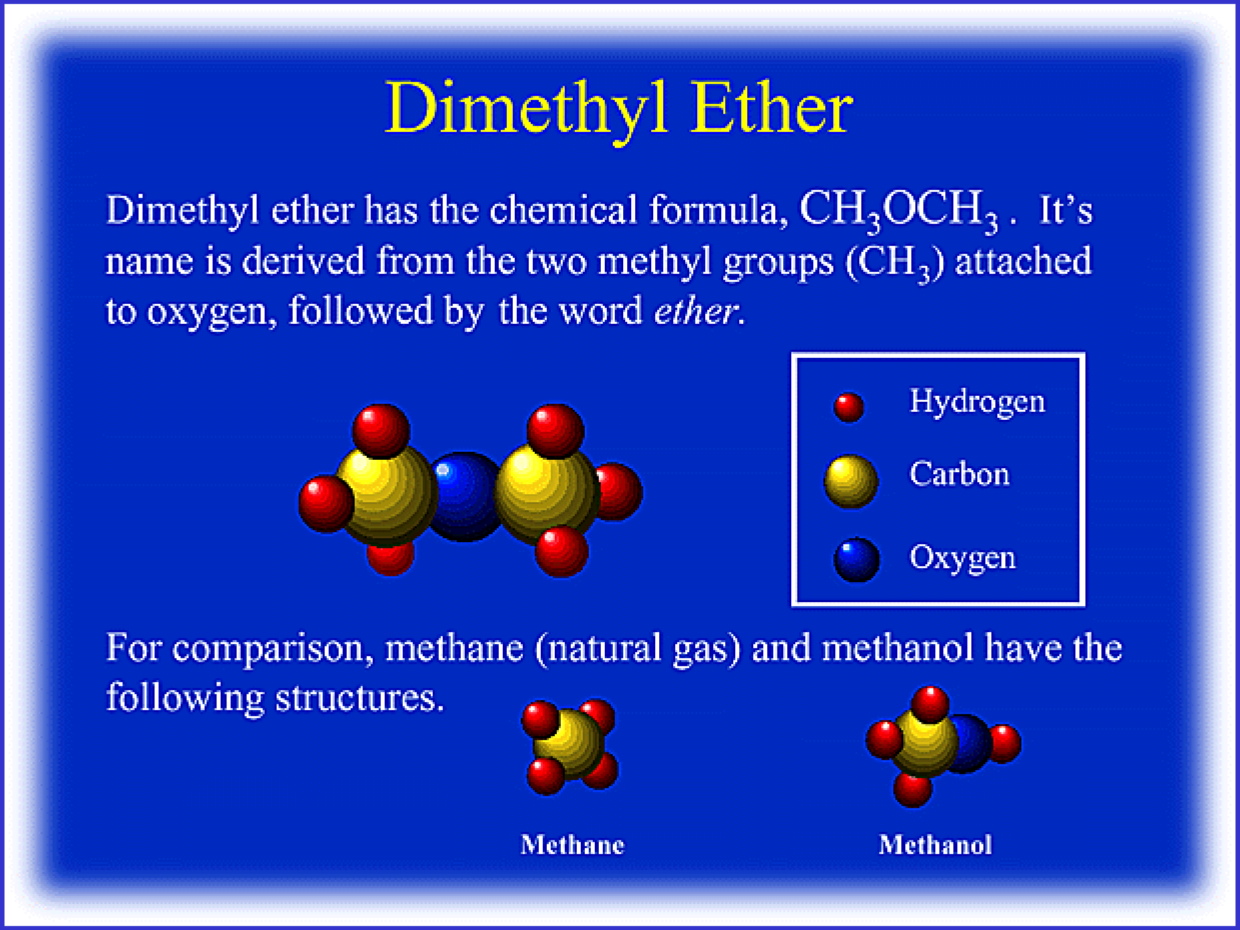


$CO + 2H_2 \rightarrow CH_3OH$ -90.4KJ/mol

$2CH_3OH \rightarrow CH_3OCH_3 + H_2O$ -23.4KJ/mol

$CO + H_2O \rightarrow H_2 + CO_2$ -41.0KJ/mol

$3CO + 3H_2 \rightarrow CH_3OCH_3 + CO_2$ -245.2KJ/mol



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Usage of DME

Aerosol propellant

LPG Substitute

Diesel Substitute

Large-scale Fuel gas/ steam combined cycles for electricity generation

Small-scale distributed electricity/heat/cold combined supply

Chemical intermediate material

Properties of DME and LPG

	DME	LPG
Vapor pressure（60℃，MPa)	1.35	1.92
Calorific value（kJ/kg)	28410	45760
Explosion limit（%）	3.5	1.7
Theoretical burned gas value （m^3/kg)	6.96	11.32
Theoretical air value For combustion（m^3/kg)	7.46	12.02
Premixed gas calorific value（kJ/m^3)	4219	3909
Theoretical temperature of combustion（℃）	2250	2055

Physical properties of DME and other fuel

	DME	Diesel	Propane	Butane	Methanol
MW	46.07	190~220	44.11	58.13	32.01
Boiling point / ° C	-24.9	180~360	-42	-0.5	65
Vapor pressure /kPa	5.1		8.4	2.1	0.32
Liquid density /g•cm^{-3}	0.668	0.84	0.501	0.61	0.79
Liquid viscosity /x10^{4} Pa•s^{-1}	0.15	5.35~6.28	0.10	0.18	0.768
LHV/MJ•kg^{-1}	28.43	42.5	46.36	45.74	19.5
Cetane number	55~60	40~55			5
Vaporization heat /kJ •kg^{-1}	410	250	370	358	1110

Advantage of DME

- Easy substitute of LPG for cooking and home heating
- Safely distributed and stored
- Clean substitute for diesel fuel without emitting soot and particle matters
- At low cost in large quantities
- Low toxicity, not corrode to metals
- High cetane number

Source of DME

- methanol tail gas
- Liquid phase methanol dehydrogenation process(two steps)

$$2CH_3OH(l) \xrightarrow{H_2SO_4} CH_3OCH_3 + H_2O - 23.4KJ/mol$$

- Gas phase methanol dehydrogenation process(two steps)

$$2CH_3OH(g) \xrightarrow{\text{solid acid}} CH_3OCH_3 + H_2O - 23.4KJ/mol$$

- Direct synthesis from syngas (based on coal, biomass, NG…..)
  - two phase (gas-solid)
  - three phase (gas-liquid-solid)

Basic steps in DME production from biomass

Main Reactions in Gasification

1 Pyrolysis	Biomass $\rightarrow$ Coke + Tar + Gas (CO_2, CO, H_2O, H_2, CH_4, C_nH_m) $C_nH_m \longrightarrow C_2H_4 + C_2H_6 + C_2H_2$ Tar $\longrightarrow$ (x_1CO_2, x_2CO, x_3H_2O, x_4H_2, x_5CH_4, $x_6C_nH_m$)
2 Combustion	$2CH_\alpha O_\beta + O_2 \longrightarrow CO_2 + CO + H_2O$ $2CO + O_2 \longrightarrow 2CO_2$
3 Gasification	$CH_\alpha O_\beta + H_2O \longrightarrow CO + H_2$ $CH_\alpha O_\beta + CO_2 \longrightarrow CO + H_2O + H_2$ $CO + H_2O \longrightarrow CO_2 + H_2$ $C + H_2 \longrightarrow CH_4$ $CH_4 + H_2O \longrightarrow CO + 3H_2$

Effect of gasifying agent and catalysts

Conditions			
Steam Catalyst	No No	Yes No	Yes Yes
H_2	20.67	28.18	41.97
O_2	0.62	0.85	0.11
CH_4	7.55	8.16	6.00
CO	40.47	39.32	23.14
CO_2	27.06	19.45	27.18
C_2H_2	0.28	0.26	0.14
C_2H_4	3.21	3.57	1.34
C_2H_6	0.14	0.20	0.08
Gas yield (m^3/kg)	1.14	1.51	1.59
H_2 yield (g/kg)	16.5	32.2	86.9

gas cleaning-up

Remove of particles

Remove tar

- **Spray water**
- **Bubble water bathing**
- **filtrate**
- **Catalyst**

Reforming

	H_2	CO	CO_2	CH_4	N_2	others
Syngas	31.5	14.8	18.6	5.4	21.3	4.4
reformed gas	41.6	27.8	3.4	2.7	19.1	5.4

Gasification condition: 1073K, ER of 0.28, S/B of 0.70
reforming condition:1023K ,addition of 0.54Nm3 biogas/Kg biomass (dry basis)

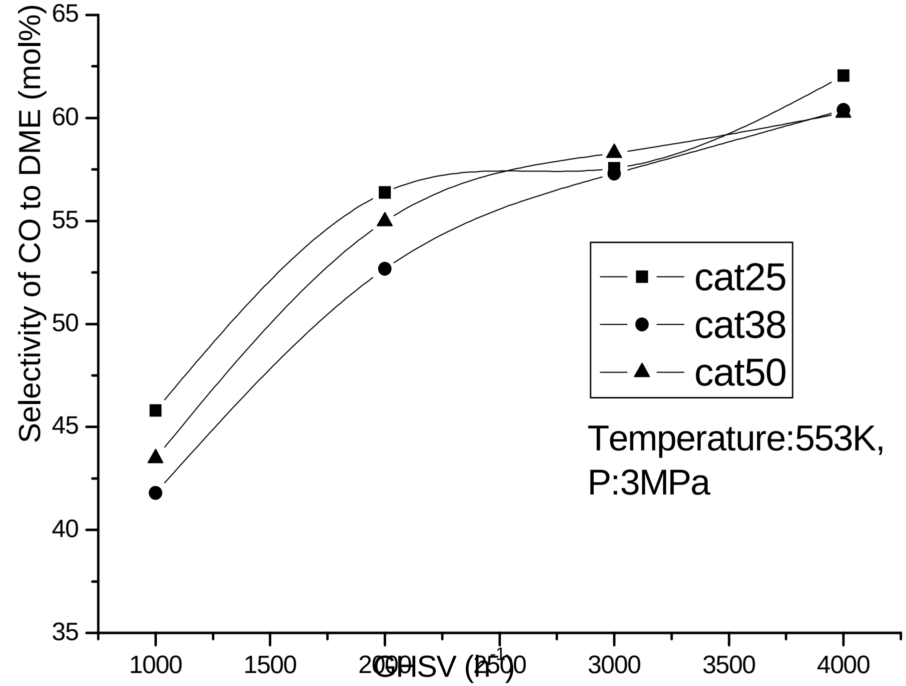
Effect of feed composition on the DME synthesis

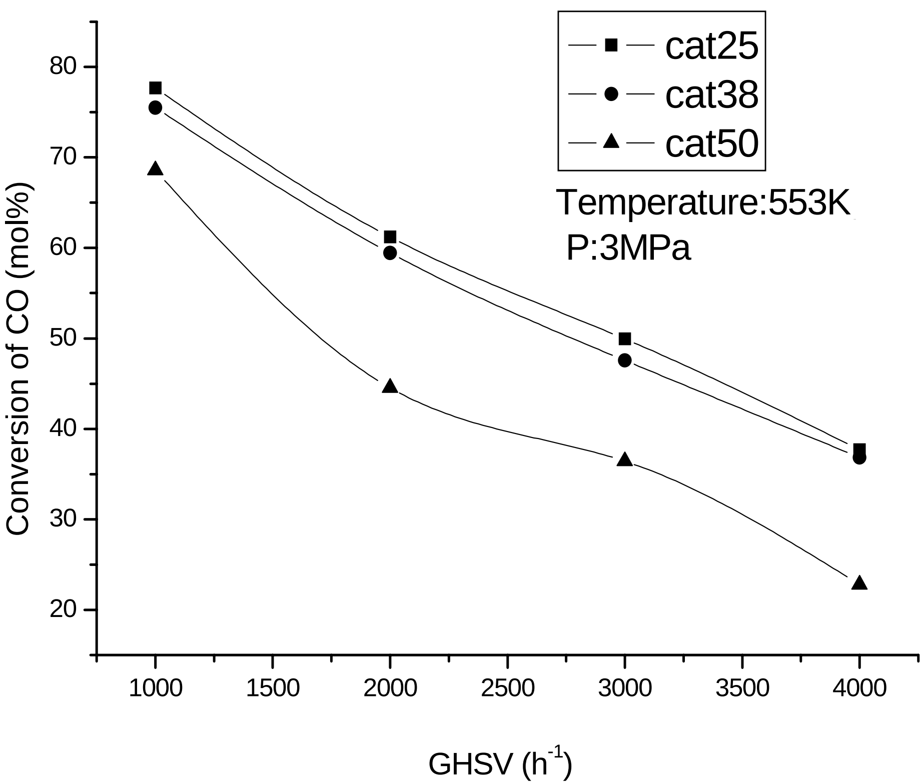
	H_2(V %)	*CO(V %)*	*CO_2(V %)*	*Conversion of CO (%)*	Selectivity of DME (%)
1	48	48	4	17.4	59.6
2	52	44	4	19.3	64.4
3	56	40	4	21.5	65.1
4	60	36	4	24.5	63.4
5	64	32	4	27.4	62.9
6	72	24	4	33.1	66.5

Effect of catalyst composition on the DME synthesis

Cat	Content of HZSM-5 (wt.%)	Conversion of CO (%)	Selectivity of DME (%)	Yield of DME($Kg.m^{-3}.h^{-1}$)	Selectivityof CO2 (%)
Cat1	83	75.1	63.6	459	35.0
Cat2	75	71.2	65.7	449	34.7
Cat3	60	62.2	66.2	395	34.7
Cat4	50	45.2	69.4	328	34.0
cat5	33	24.0	48.9	113	37.4

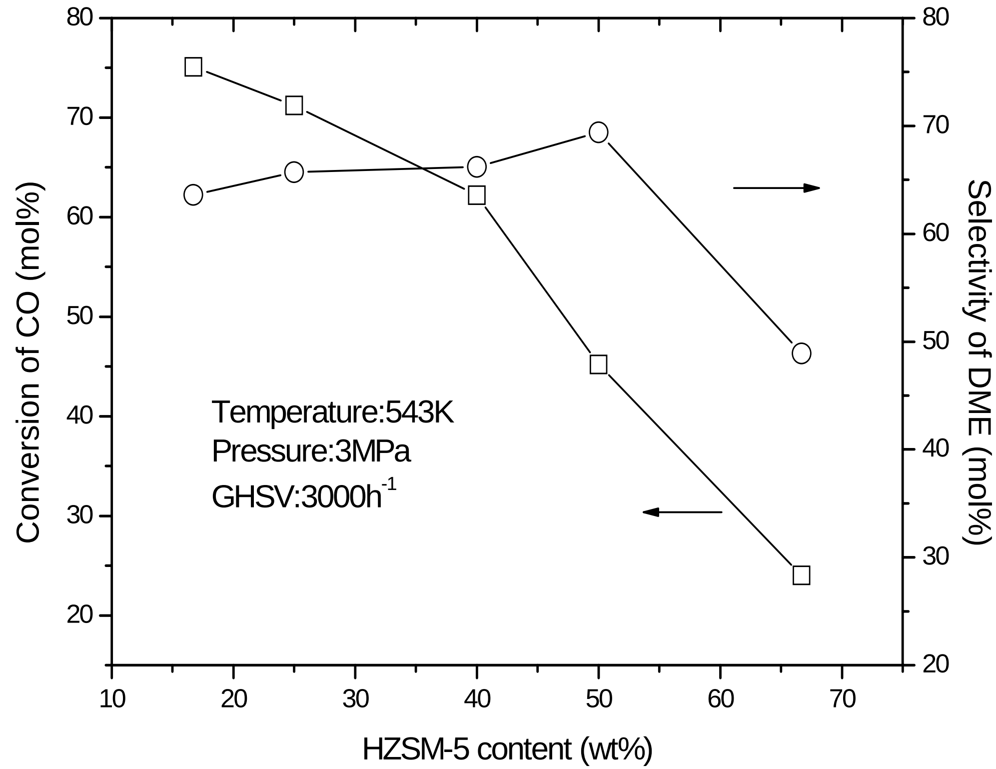
The effect of Si/Al ratio on the selectivity of DME with the GHSV

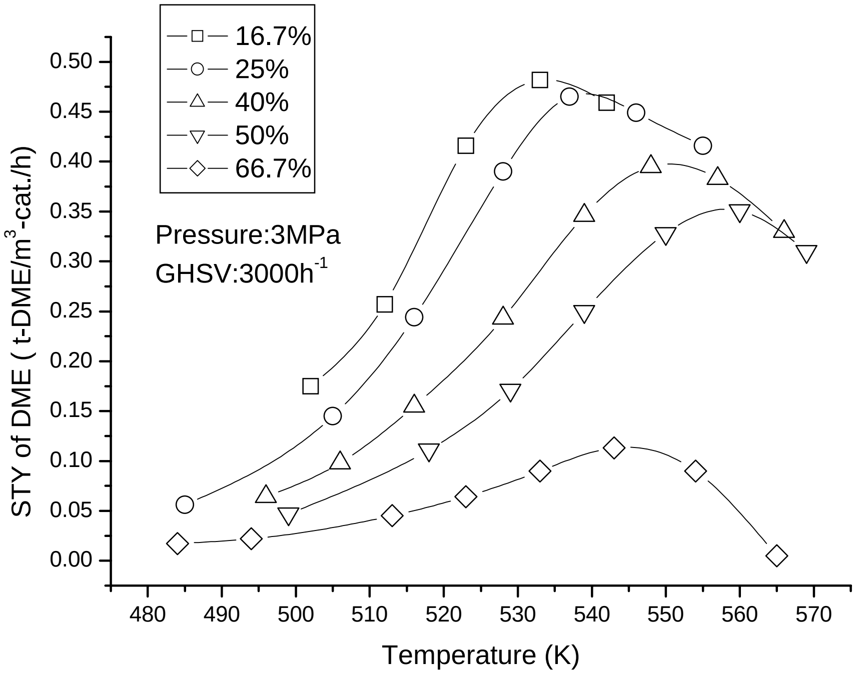




The effect of Si/Al ratio on the conversion of CO with the GHSV

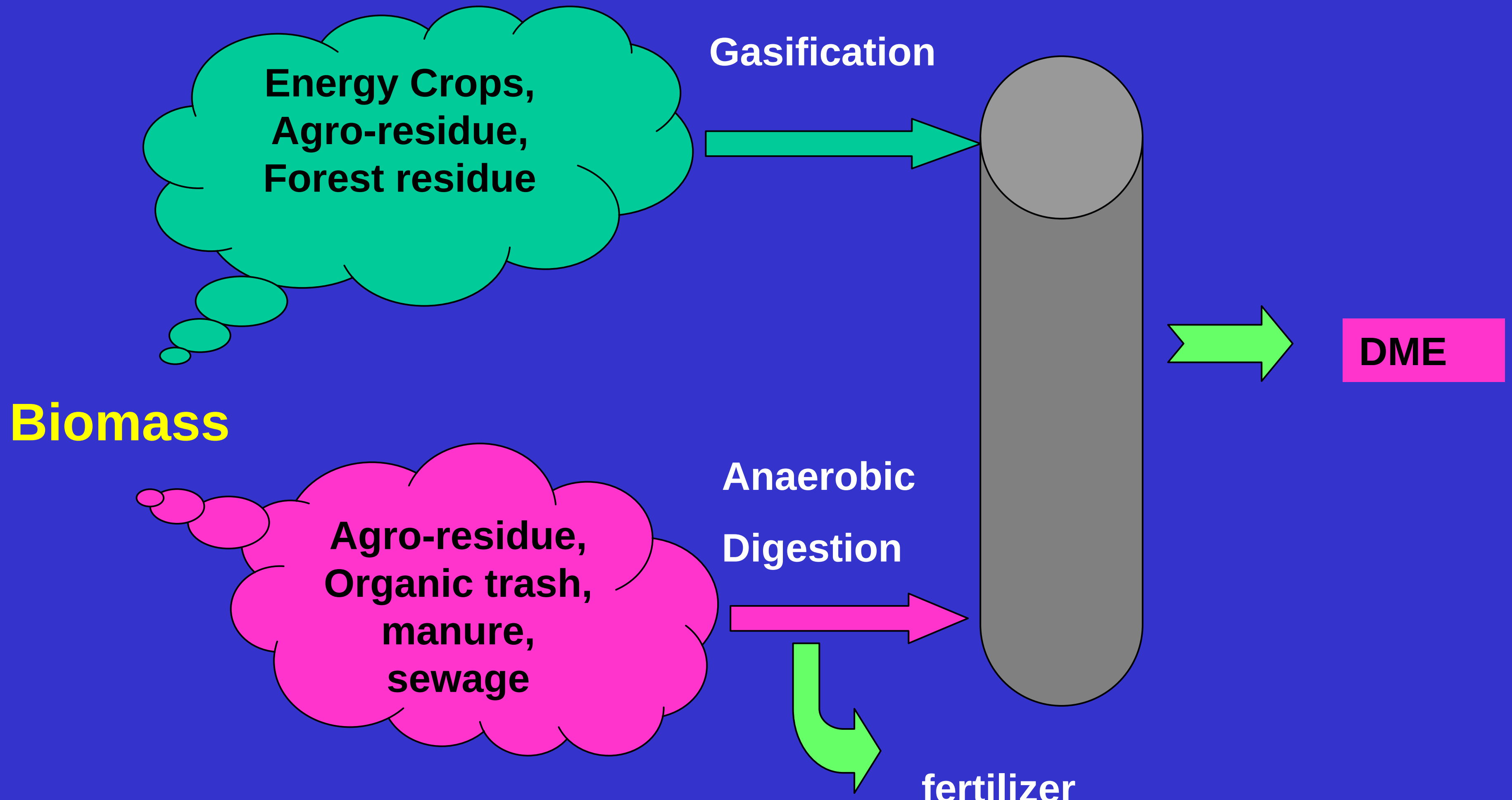
The effect of content of HZSM-5 on the conversion of CO and the selectivity of DME



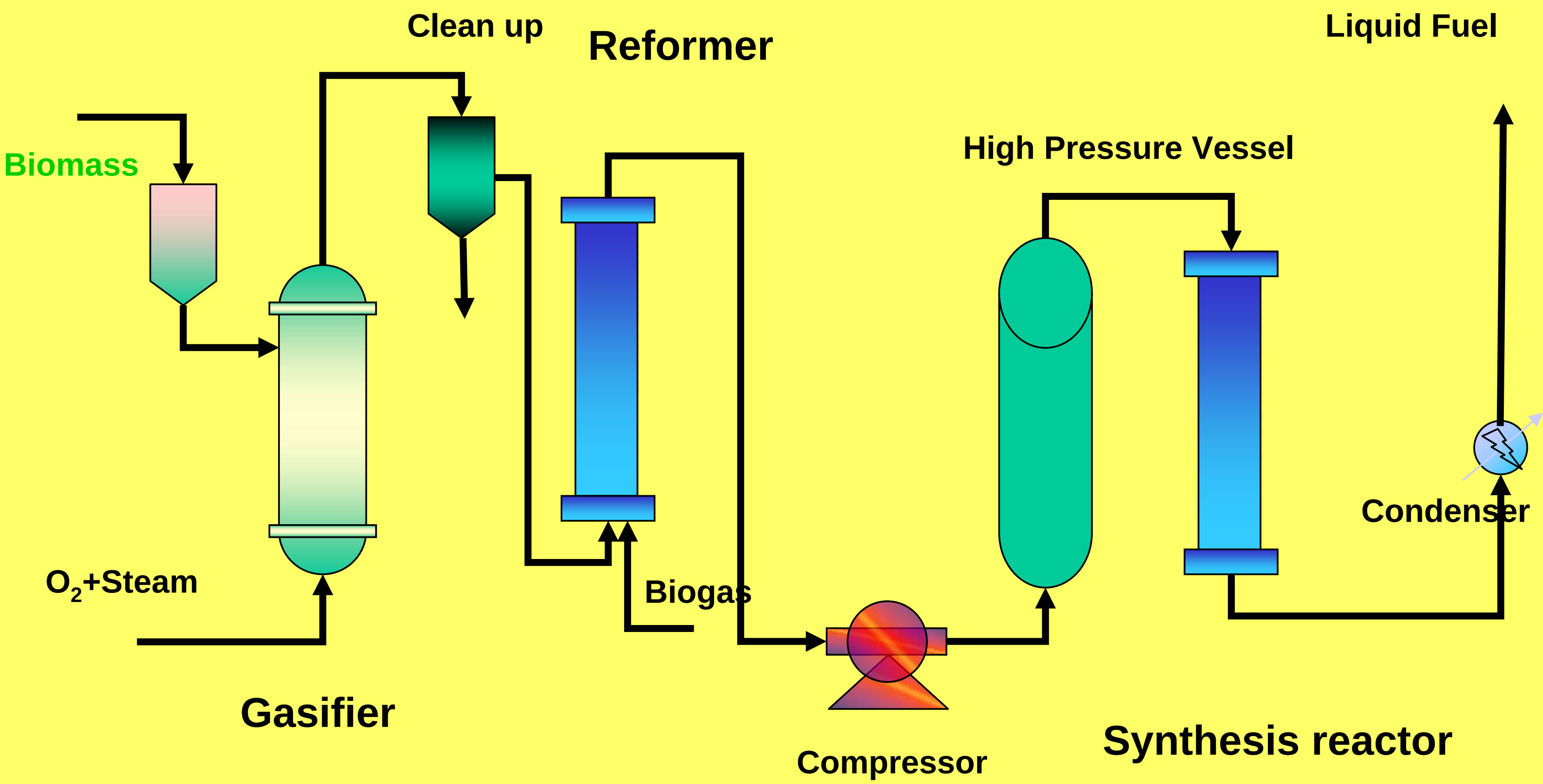


The effect of contents of HZSM-5 on the space time yield of DME with the temperature

Co-reforming of biogas and bio-syngas



Flow chart of Biomass To Liquid (bench scale)



Typical composition of biogas and bio-syngas(vol%)

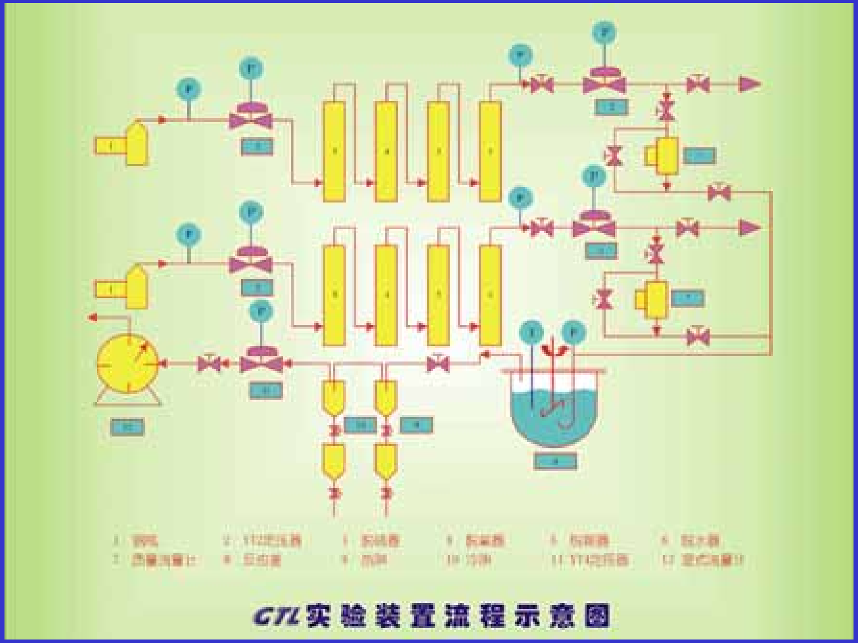
	H_2	CO	CO_2	CH_4	other
Bio-syngas	22	40	30	5	3
Biogas	-	-	20	80	-

$$CH_4 + CO_2 = 2\,CO + 2H_2 \qquad (1)$$

$$3\,H_2 + 3\,CO = CH_3OCH_3 + CO_2 \qquad (2)$$

$$3\,CH_4 + CO_2 = 2\,CH_3OCH_3 \qquad (3)$$

Slurry reactor for DME synthesis



DME Synthesis Equipment in our lab

Biomass Gasification for Generation

New Energy Building in GIEC

Thank you for your Attentions!

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