# DME Production Process from Coal & Biomass

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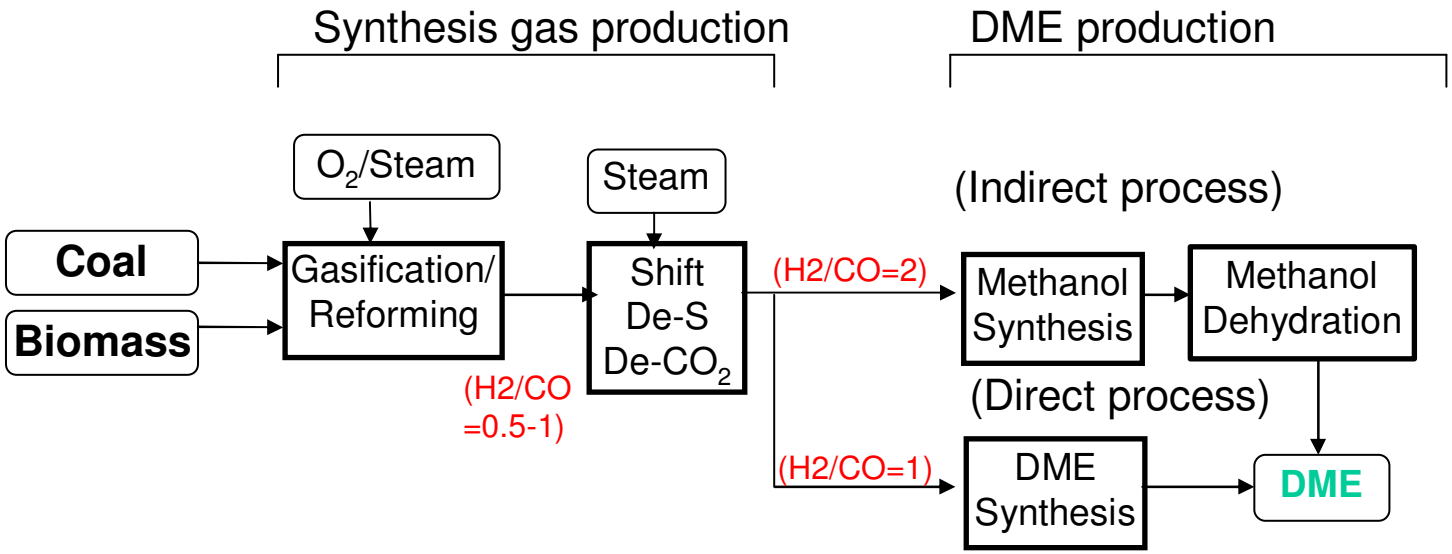
# DME production from Coal & Biomass

- Coal resource is relatively abundant, but limited for growing future use.
- Biomass resources is abundant and renewable, and carbon neutral, but, dispersed and bulky, inadequate for long distance transportation.
- Efficient conversion into DME is important to secure resource and control $CO_2$ emission.



# DME production from Coal

- JFE DME synthesis process
- Coal quality and Gasification
- Synthesis gas preparation
- Total system

# Characteristics of JFE DME Synthesis Process

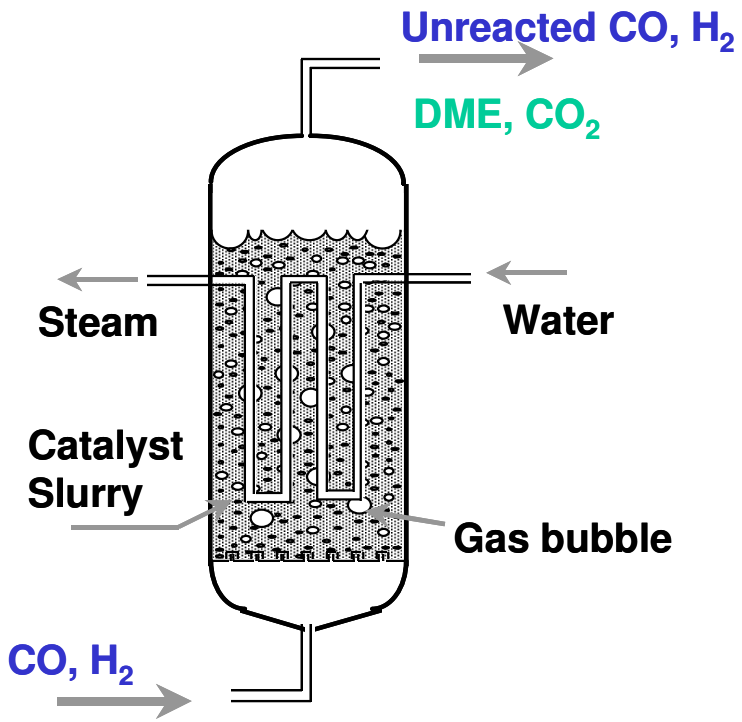
- DME ($CH_3OCH_3$) is synthesized from $H_2/CO=1.0$ synthesis gas.

$$3CO+3H_2 \rightarrow DME+CO_2$$

This reaction is highly exothermic, rather than Methanol synthesis, reaction temperature control is important to avoid catalyst degradation.

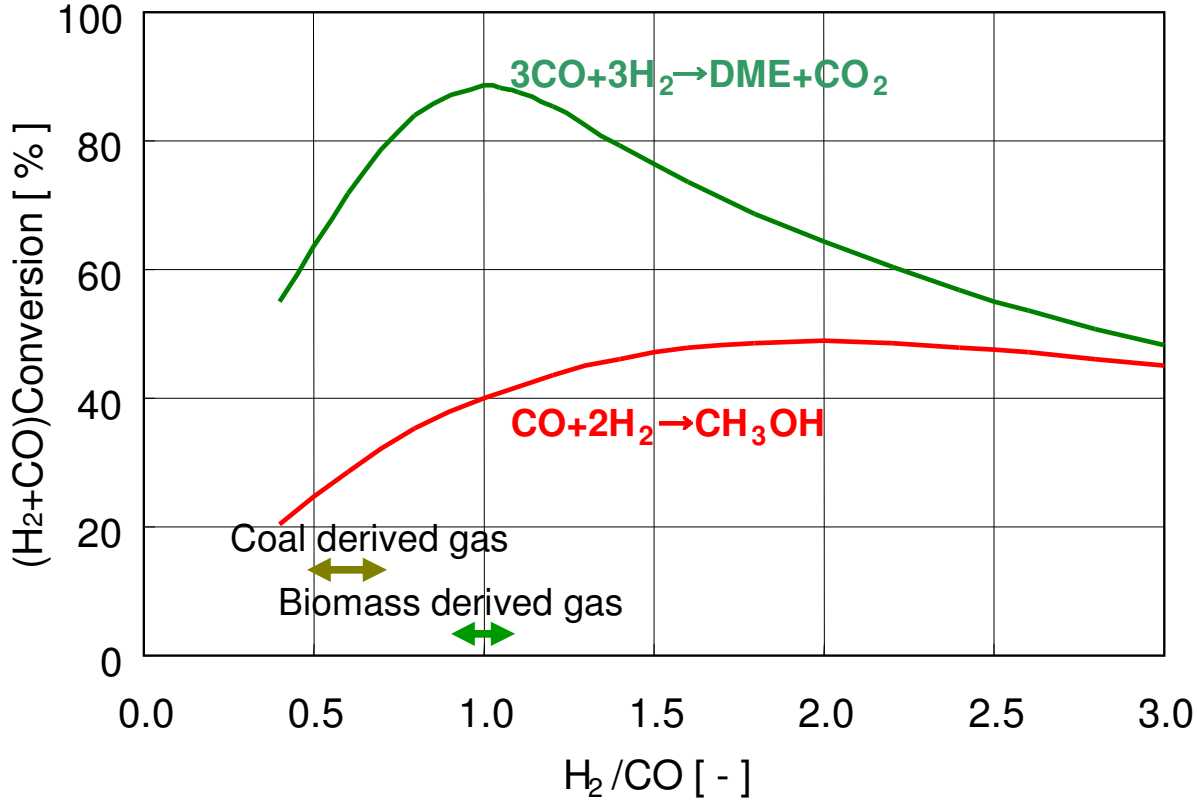
- Slurry Phase Reactor, in which Temperature is homogeneous. Reactor temperature can be controlled to the optimum point by steam pressure.

- JFE's proprietary catalyst system is adequate to slurry phase reaction.



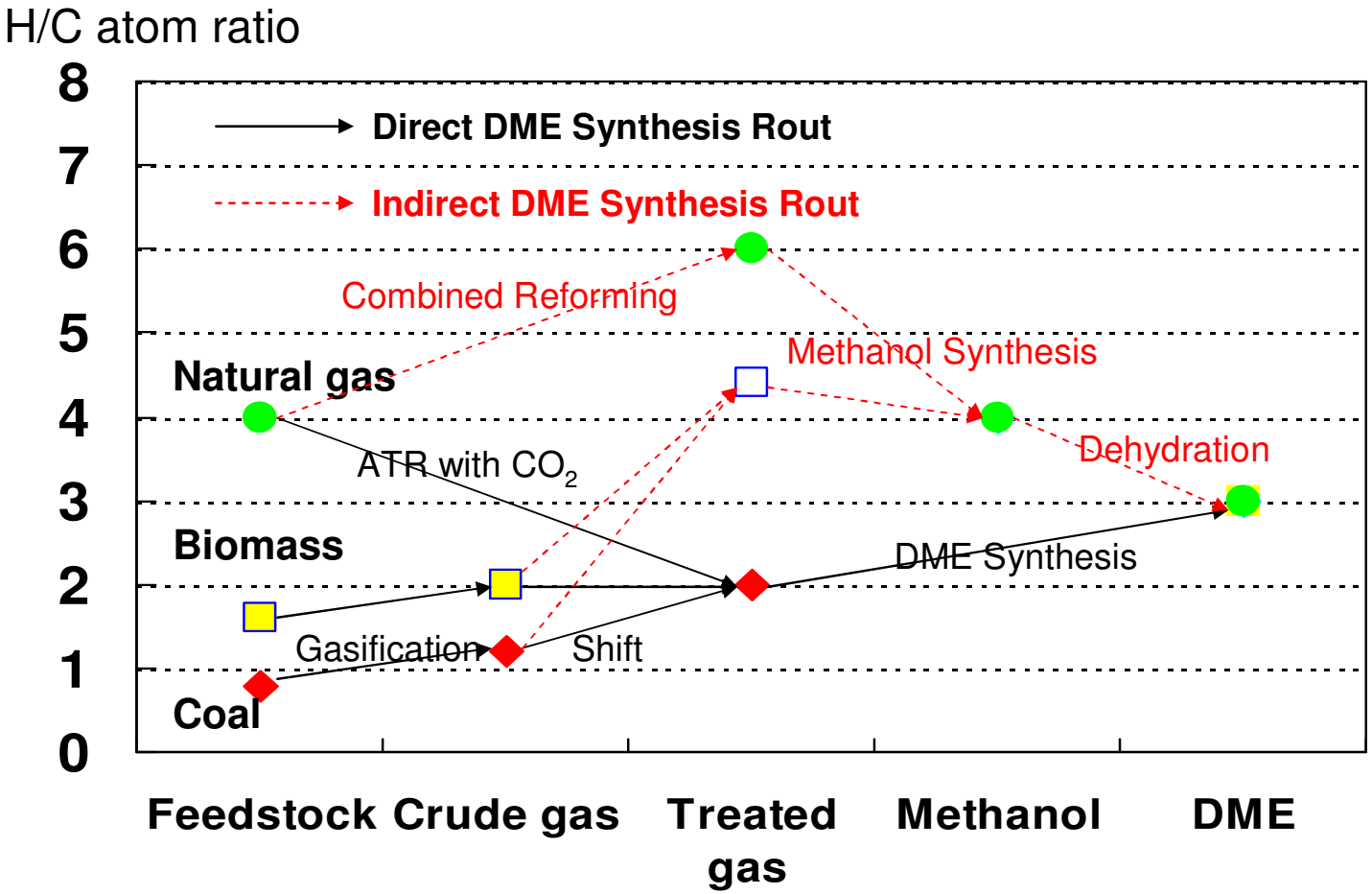
# Equilibrium Conversion (260ºC, 5MPa)

- DME synthesis is, having the maximum conversion at $H_2/CO=1.0$, advantageous to synthesis gas from Coal ($H_2/CO=0.5$-$0.7$) or Biomass ($H_2/CO\approx1$).



# H/C Change on Process Rout from Feedstock to DME

- On Direct DME synthesis rout, H/C change is smaller and Process efficiency is higher, especially starting from Coal and Biomass.



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# Coal Quality for Gasification

- Coal is classified by VM content : 65-7% (H/C: 1.2-0.5)

  Lignite, Sub-bituminous, Bituminous and Anthracite

  Proximate analysis (air-dried%) : VM,FC, Ash, Moisture

  Ultimate analysis (dry%) : C, H, N, O, S, Others

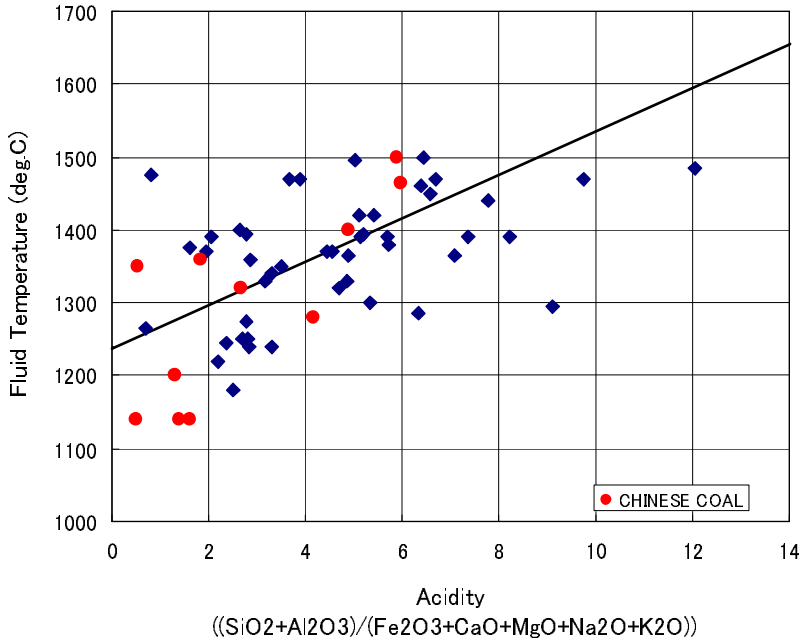
- Heating value HHV(MJ/kg) estimated using Ultimate analysis

  HHV =0.339C+1.433(H-O/8)+0.094S

HHV decreases with higher content of Ash, Moisture

- Fluid temperature of Ash Tf (ºC) correlated with Acidity of Ash

  Tf can be changed by Adding flux materials; Lime stone (CaO), Iron Oxide ($Fe_2O_3$ ), or by Mixing with low Tf coal.



# Coal Gasification Process

- Gasification Temperature should be sufficiently high to minimize residual $CH_4$ and tar and for stable slag discharge.

  Entrain bed (Pulverized coal) is suitable, rather than Fixed bed or Fluidized bed (Lump coal).

- Coal feed type to pressurized gasifier

  Dry feed is better than Slurry feed for higher gasification efficiency.

- Inert gas($CH_4$,$N_2$) content in synthesis gas should be minimum for higher efficiency in down stream synthesis.

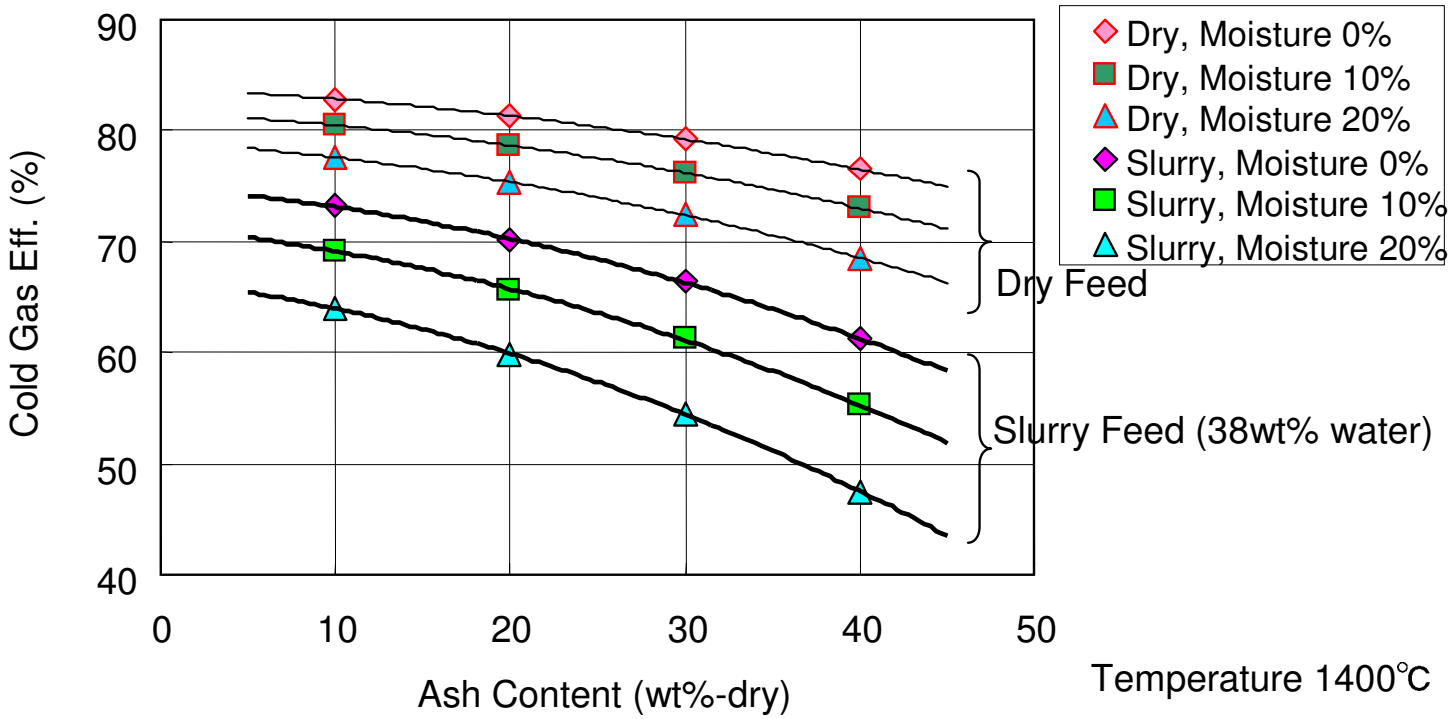
  $O_2$ concentration should be as high as possible.

  Dry $CO_2$ is used as carrier gas in place of $N_2$.

- Large scale coal gasifier such as 2000 ton/day is already available, equivalent to 1,000 ton/day of DME production.

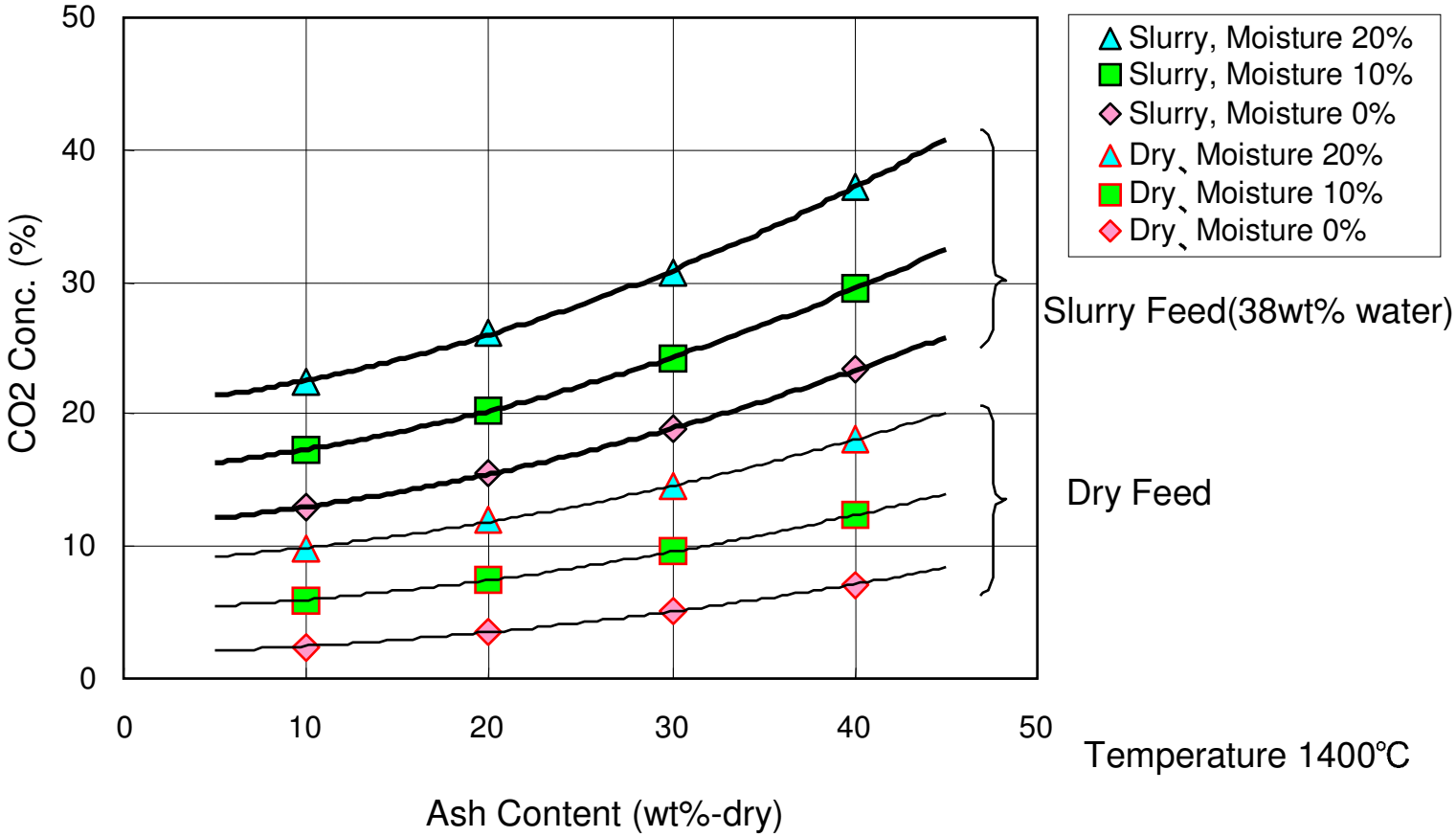
# Cold Gas Efficiency of Gasification

- High ash content, high moisture give lower cold efficiency.
- Dry feed gives higher cold gas efficiency by 10–20 % than Slurry feed for the same ash content and moisture.



# $CO_2$ Concentration of Crude Syngas

- Higher $CO_2$ concentration in synthesis gas results in more $CO_2$ removal and less efficient process.



# DME production from Coal

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# Synthesis Gas Preparation

- Removal of catalyst poisoning impurities

  $H_2S$,COS,$NH_3$,HCN,etc

  Required level is same for Methanol synthesis and DME synthesis.

- Adjustment of $H_2$/CO to stoichiometric ratio

  $H_2$/CO=2 for Methanol synthesis, $H_2$/CO=1 for DME synthesis

  by Shift reaction $CO+H_2O \rightarrow CO_2+H_2$

  Heating value of synthesis gas decreases with Shift reaction

  as it is exothermic. Steam is required as reactant for shift reaction.

- Removal of $CO_2$

  $CO_2$ is removed by solvent absorption.

  A part of $H_2$ and CO is absorbed by solvent and lost with $CO_2$.

  Steam is required to regenerate absorbent of $CO_2$.

# Effect of $CO_2$ on Methanol and DME synthesis

## Methanol synthesis in the fixed bed reactor

- For Methanol synthesis, $R=(H_2-CO_2)/(CO+CO_2)=2$ should be satisfied.

In coal derived gas, no excess $H_2$. $CO_2$ consumes $H_2$ and gives water, methanol production decreases and distillation load increases.

- $CO_2$ content at reactor inlet must be as low as possible.

## DME synthesis in the slurry phase reactor

- Slurry is saturated with $CO_2$ generated by DME synthesis reaction and $CO_2$ in synthesis gas has little effect on DME synthesis.

- Partial $CO_2$ removal is sufficient and Energy consumption for $CO_2$ removal is smaller.

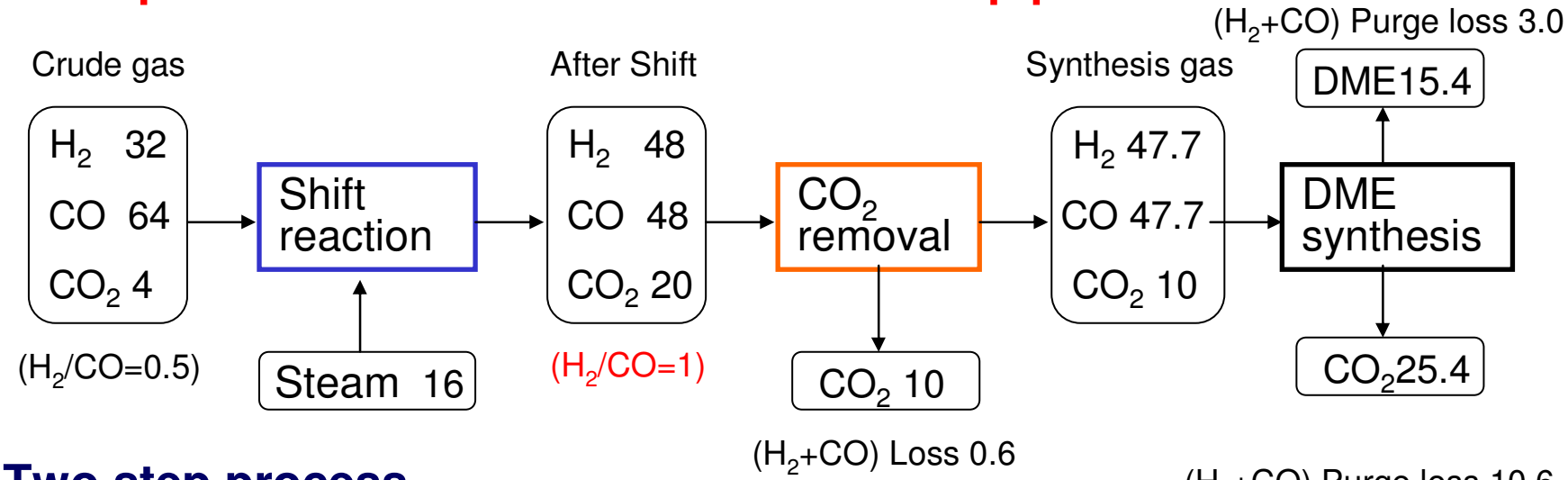
- Residual $CO_2$ goes out of reactor with by-produced $CO_2$.

# Comparison of Material balance of DME production

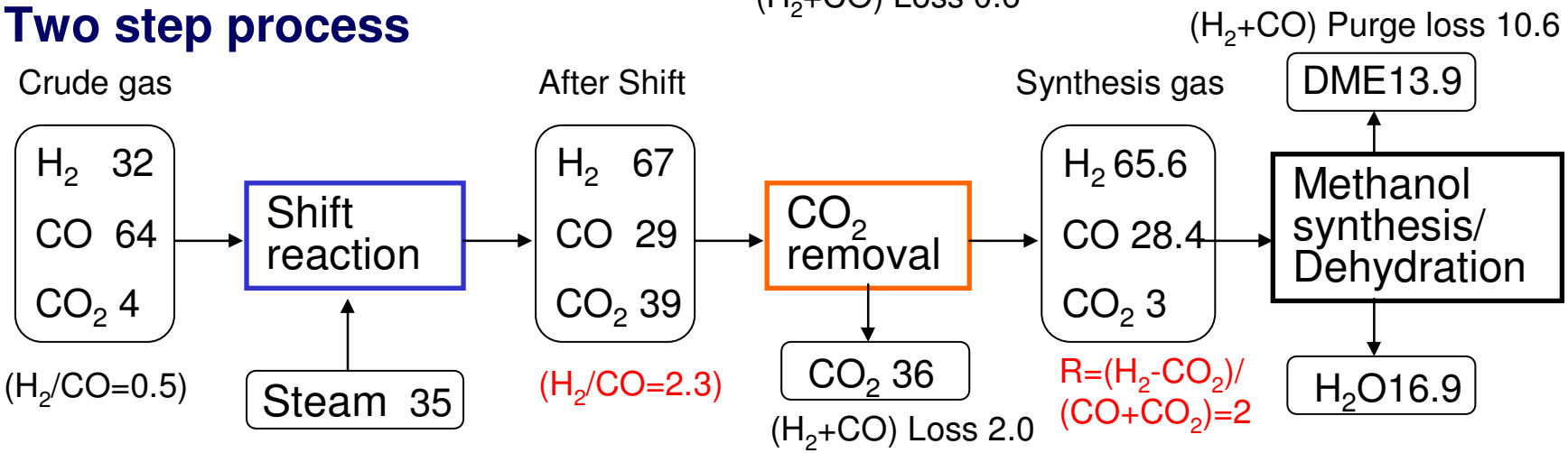
## JFE process

(Unit: kmol)

**DME production is 10% more than Two step process.**




## Two step process



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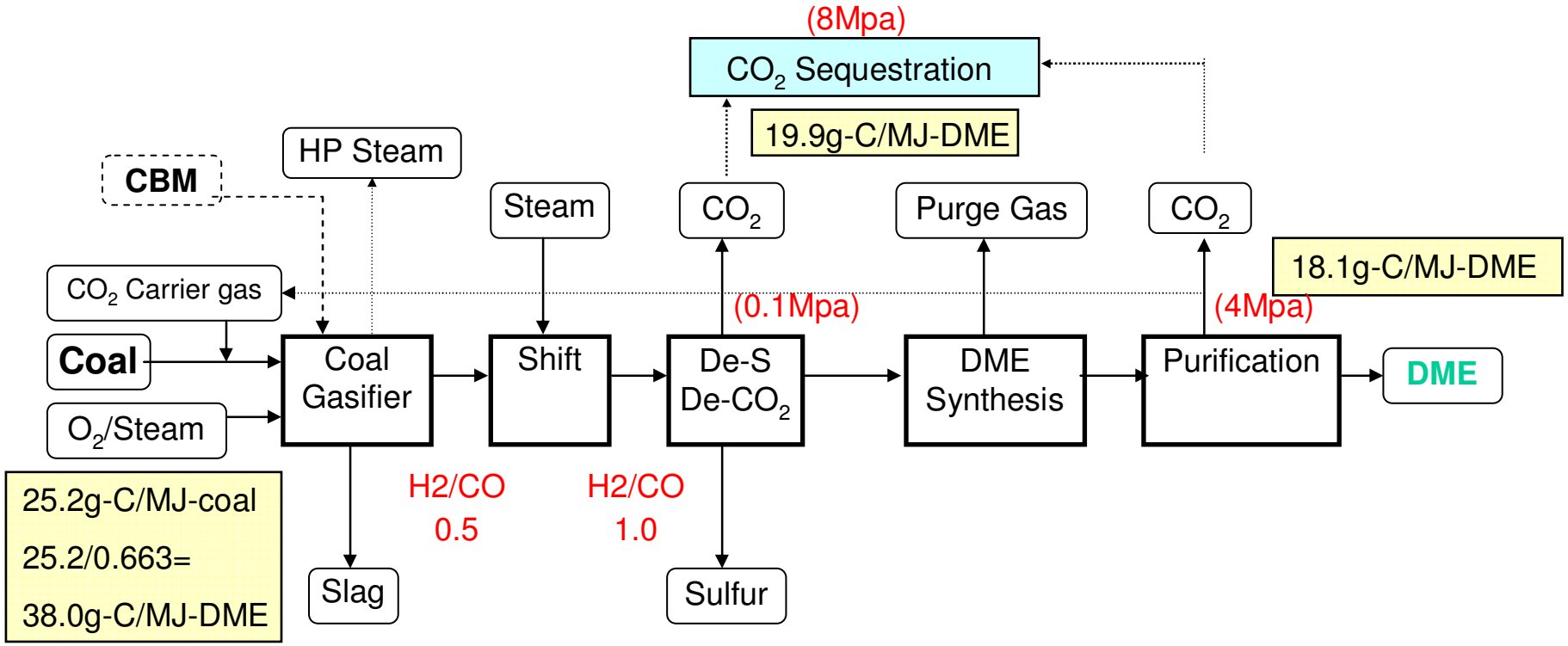
# Total System of DME Production from Coal




: CO2 Emission , Cold gas efficiency from Coal to DME : 66.3%

Coal consumption: 1.5 dry-t/t-DME, Oxygen consumption: 1.2 t/t-DME

# Total Cold Gas Efficiency of DME Production

- Total Cold gas efficiency of Dry feed/JFE process is 20% higher than Conventional process(Slurry feed/Two step).

| Gasification/Synthesis | Dry feed/ JFE process | Dry feed/ Two step | Slurry feed/ Two step |
|---|---|---|---|
| Cold gas efficiency of gasification | 83.3% | 83.3% | 76.9% |
| Cold gas efficiency from coal to synthesis gas | 81.2% | 78.3% | 73.2% |
| Cold gas efficiency from synthesis gas to DME | 81.7% | 74.9% (78X0.96)* | 74.9% (78X0.96)* |
| Total cold gas efficiency | 66.3% | 58.6% | 54.8% |
| CO2 emission at plant site (g-C/MJ-DME) | 19.9 | 24.9 | 27.9 |

* Assumption of Cold gas efficiency for Methanol synthesis: 78% and for Dehydration: 96%

# DME production from Biomass

- Characteristics of Biomass and Gasification
- Total system

# Characteristics of Biomass as Feedstock

- Terrestrial biomass actually used are of so many kinds, but non-edible aspect is very important.

Wood chip, Bark, Saw dust, Switch grass, Bermuda grass, Agricultural residues such as Rice husk, Bagasse, Cotton stalks, Corn stalks, Coconut shell

- Size and shape is various. Pulverizing biomass is not so easy as coal, biomass is generally used as sized lump. Biomass feeding technology should be adapted to specific feedstock.
- Chemical composition(dry%) is almost same:

C 45-50%, H 5-6%, O 44%, H/C(atom ratio)=1.6

Ash content is small 1%(wood)-10%(grass).

Moisture content is high 20-70%.

- Heating value HHV(MJ/dry-kg)=0.457C(dry% )-2.70

# Biomass Gasification Process-1

- Most of the gasification is conducted by Partial combustion with oxygen/air. With higher $O_2$ content, $N_2$ content in produced gas is lower.

  Fixed bed (down-draft or up-draft), Circulating fluidized bed,

  Fluidized bed with fluidizing media, Entrained bed

- The other type of gasification is Steam reforming in fluidized bed with indirect heating by circulating solid media or external heater.
- As sticking of fed materials and slagging of ash often happen at high temperature, Gasification temperature is relatively low at around 850 ºC and produced gas contains $CH_4$ and Tar.
- For stable operation of down-stream process, Tar should be removed, or reformed together with $CH_4$ by secondary reforming into $H_2$ and CO.
- Biomass contains more oxygen than Coal, $CO_2$ content in synthesis gas is higher.

# Biomass Gasification Process-2

- Sulfur content of biomass is very low, but crude gas from biomass contains around 10ppm of $H_2S$+COS, which is tolerable as fuel gas, but should be removed as synthesis gas to avoid catalyst degradation in down stream process.
- Ash is discharged as dry ash by mechanical device.
- So many types of Biomass gasifiers have been developed for fuel gas of power generation, but few for synthesis gas.

Reliable gasifier is the key for synthetic fuel production from biomass.

- Biomass gasification scale is small because of high cost of long distance transportation: Maximum scale could be of several 100 ton/day.
- With coal/biomass mixture feed, coal may compensate instability of biomass supply and increase thermal efficiency because plant scale can be bigger with it. Reactivity of coal is important.

Example of Biomass Gasifier 1

# IISc Fixed Bed Gasifier (Down-draft)

• 40 units of IISc' Gasifier are used mainly in India for power generation fuel gas, Maximum scale around 1200kWe (30 ton/day).

Gas composition(dry%) with Air blowing:

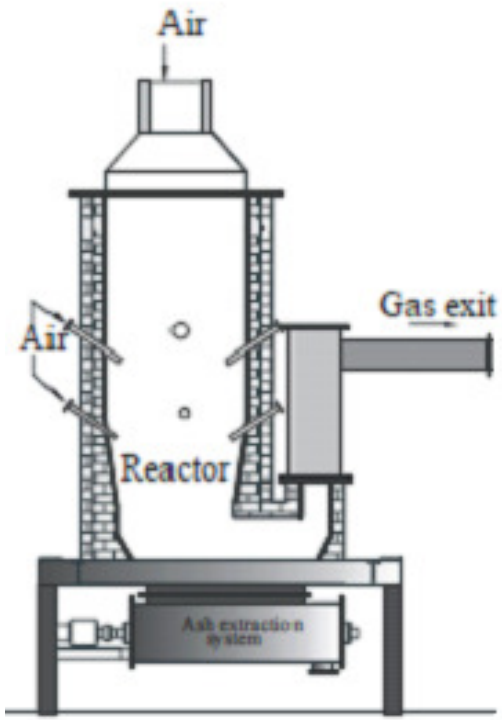
$H_2$ 20%,CO 20%, $CH_4$ 4%, $CO_2$ 8%,$N_2$ 48%

For synthesis gas production, N2 content should be reduced.

• AIST, Japan has conducted pilot test of similar type of gasifier. (0.1 ton/day)

With $O_2$ in blow increasing from 21 to 31.5%, $N_2$ in syngas decreases from 47 to 32% and Carbon conversion rises from 92 to 96%.

With syngas, bench scale tests were conducted for DME synthesis and FT synthesis. (www.aist.go.jp)




Ref: Technology of Biomass Gasification(IISc)

Example of Biomass Gasifier 2

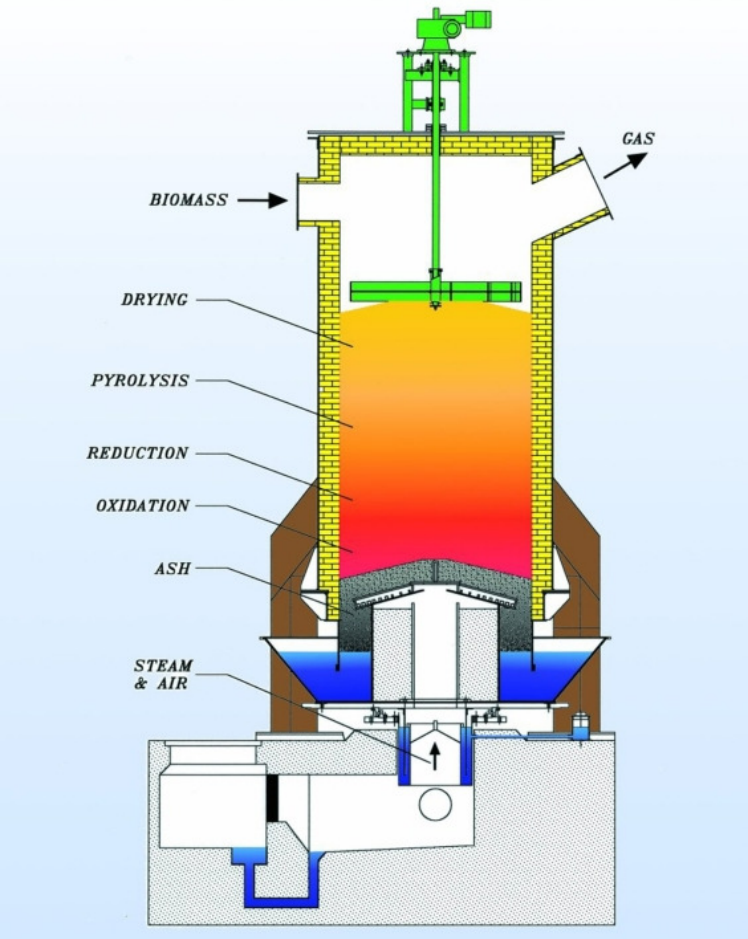
# Volund Fixed Bed Gasifier (Up-draft)

- Development had started in 1989 and a commercial plant of 41ton/day has been built in 1996 in Harboore in Denmark. Gas cleaning system has been improved until 2003.

Typical gas composition with Air/steam blowing: $H_2$ 19.0, CO 22.8, $CH_4$ 5.3, $CO_2$ 11.9, $N_2$ 40.7%.

Gas is used for gas engine power generation or boiler fuel. Power generation efficiency attains to 29%.

- JFE(Exclusive licensee in Asia) has constructed three commercial plant (60-100ton/day) in Japan.




Ref: www.volund.dk

Example of Biomass Gasifier 3

# VVBGC Pressurized Circulating fluidized bed

(VVBGC: Växjö Värnamo Biomass Gasification Center)

- Air blowing test conducted as IGCC system successfully for 8500 hours in 1994-2000 in Värnamo, Sweden.

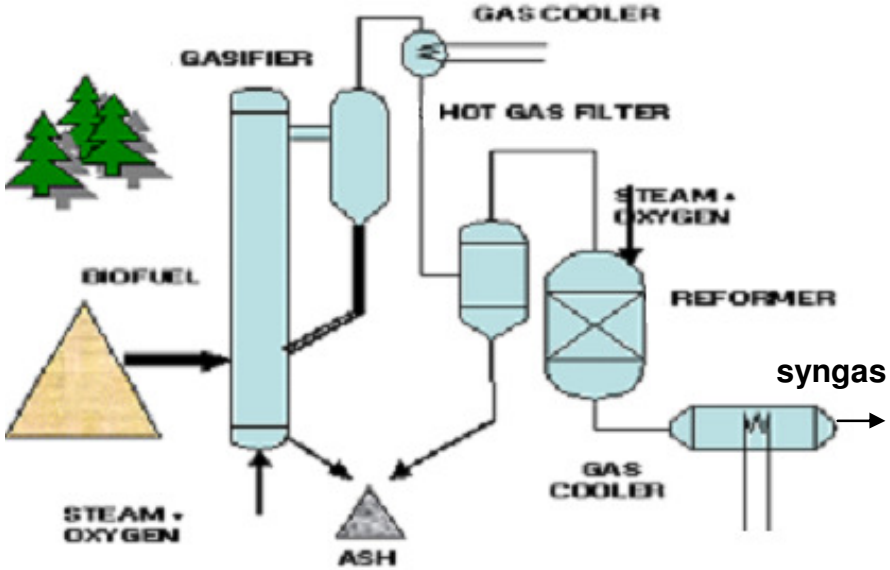
100ton-Ds/day,pressure:20 bar

- CHRISGAS Project (2005-)

(Clean Hydrogen Rich Gas)

Revamp of plant and hot test were completed in 2007.

Modification to Oxygen blowing with Secondary reforming of tar methane will start in 2009.




Ref: www.vvbgc.se

Example of Biomass Gasifier 4

# TRI Steam Reformer with External Pulse Heater

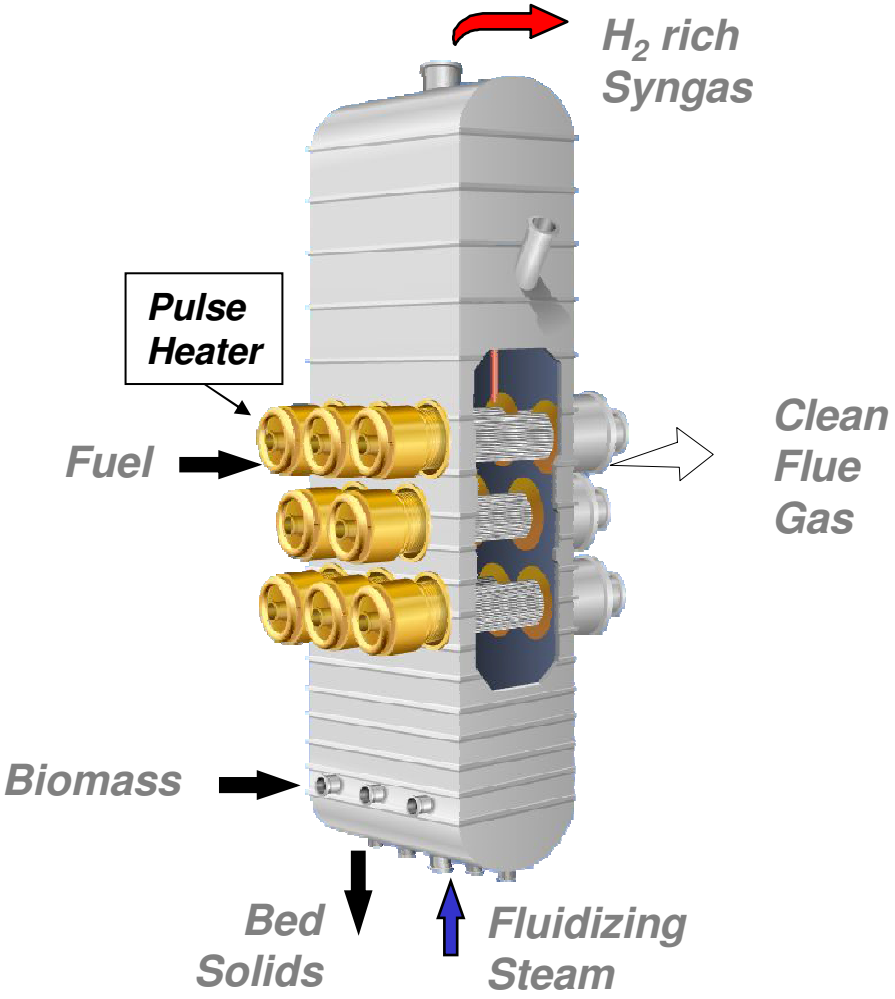
- Commercialized for Black liquor(115 ton/day) in Canada
- Proprietary indirectly-heated steam reforming process at medium temperature and low pressure
- Black liquor is gasified with high temperature steam in deep fluidized bed.

Chemicals in black liquor become small particles, which are bed solids, and discharged at bottom.

- Application to Solid (Wood chip, Rice hull, Saw dust,etc.) under Pilot test

Black liquor composition (%):

C 36.8, H 3.7, N 0.1, S 3.1, O 10.6, Ash (Na, K, Cl,etc.) 45.8



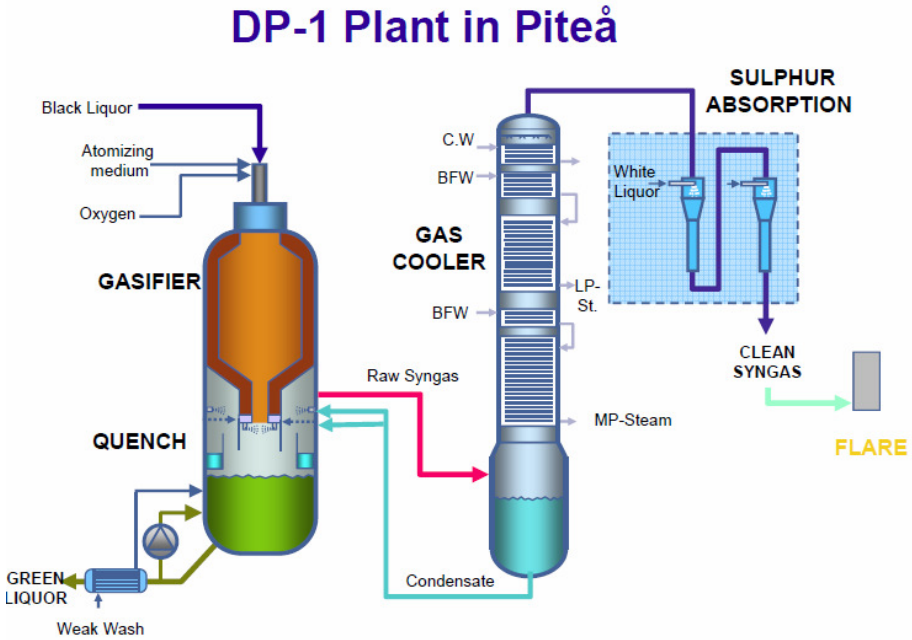

By courtesy of TRI (www.tri-inc.net)

Example of Biomass Gasifier 5

# Chemrec Black liquor entrained bed gasifier

- Similar to GE coal/heavy residue gasifier. Black liquor is gasified at high temperature with oxygen and produce synthesis gas without tar.
- Chemicals in black liquor is solved in quench water and recovered as green liquor.

- Pilot plant(20ton-Ds/day) has been now operated successfully for 9,900 hours in Sweden since 2005.
- DME pilot plant(4-5ton/day) is under construction and will start in2010.
- DME will be supplied to Volvo truck test.



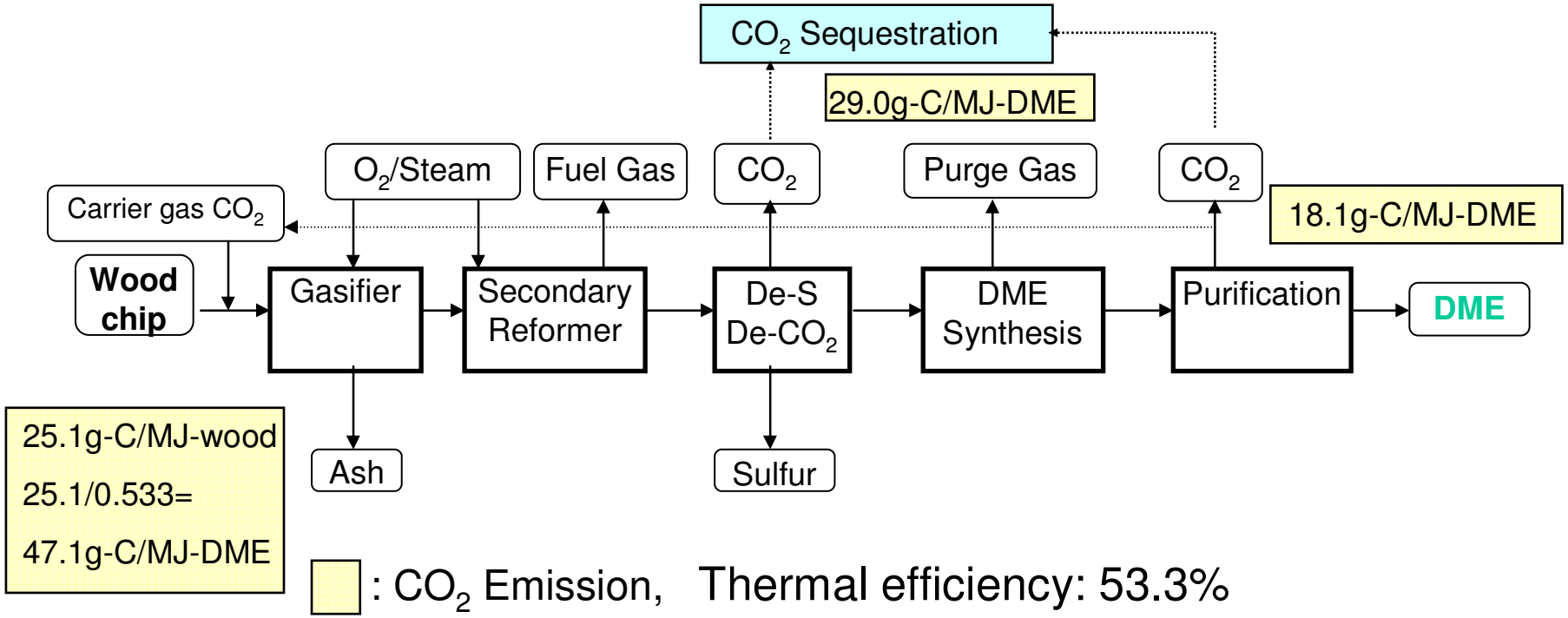

Ref: www.chemrec.se

# DME production from Biomass

- Characteristics of Biomass and Gasification
- Total system

# DME production from Biomass (Wood chip)

- DME production system of Oxygen blowing Pressurized CFB gasifier and JFE process




: $CO_2$ Emission, Thermal efficiency: 53.3%

- Unit consumption: Wood chip 3.0t-Ds/t-DME, Oxygen 1.5 t/t-DME
- Purge gas and a part of synthesis gas are used as fuel gas in DME production system.

# Synthesis gas composition and Cold gas efficiency

• Crude gas contains $CH_4$ and tar, which is reformed with $O_2$ and steam in Secondary reformer. $H_2S$ and a part of $CO_2$ are removed.

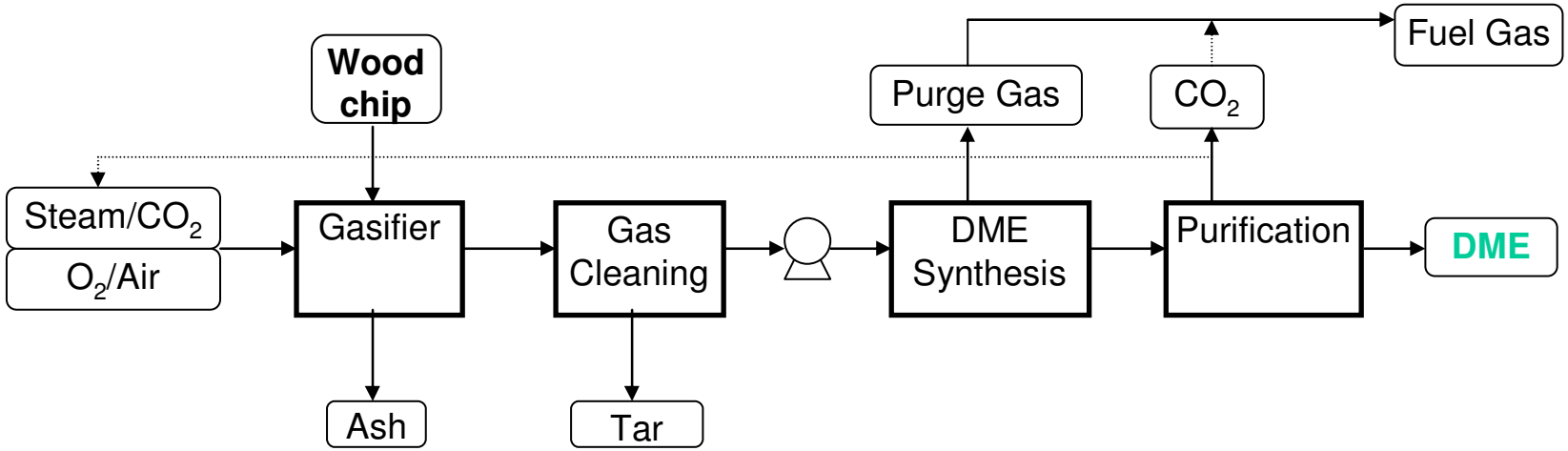
| Conc.(%) | Crude gas | Reformed gas | Synthesis gas |
|---|---|---|---|
| $H_2$ | 10-15 | 23.2 | 47.0 |
| CO | 10-15 | 22.8 | 46.0 |
| $CO_2$ | 20-25 | 19.5 | 6.5 |
| $N_2$ | | 0.20 | 0.4 |
| $CH_4$ | 10-12 | 0.05 | 0.1 |
| Tar | 2-5 | 0 | 0 |
| $H_2O$ | 40 | 34.25 | 0 |
| $H_2S$ | | 10ppm | <0.1ppm |

• Cold efficiency: 73% from Wood chip to Clean synthesis gas, 59.1% for Total system, Thermal efficiency including fuel gas: 53.3%

• Wood chip composition(dry-wt%): C 50.0, H 6.0, O 42.0,N 0.3, S 0.025, Ash 1.7, LHV 18.9MJ/dry-kg, Moisture(after dryer) 15.0%

# DME production with $O_2$ enriched air

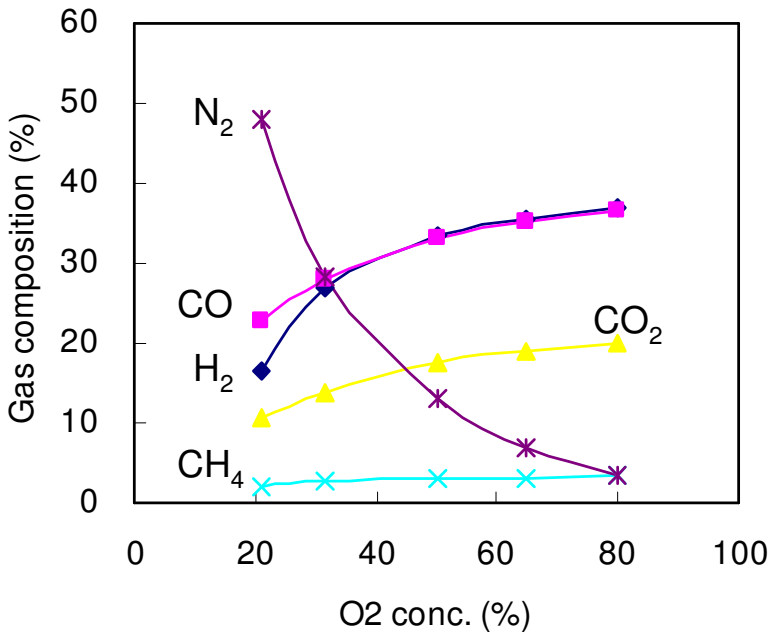
- Small scale DME production system of Down-draft Fixed bed gasifier with $O_2$ enriched air and JFE process

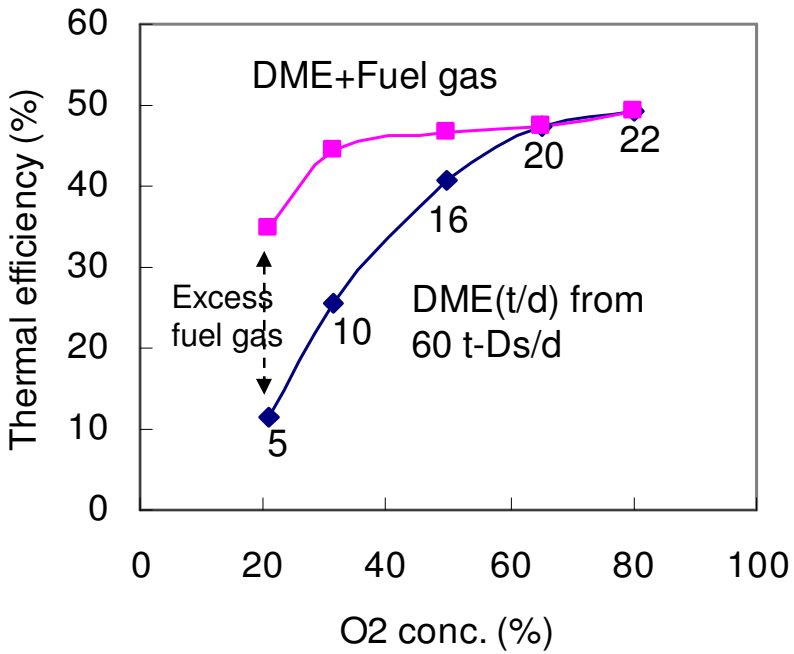



- Steam/$CO_2$ is added to keep gas temperature in front of blowing nozzle.
- Gasifier is operated at ambient pressure, after gas cleaning, synthesis gas is compressed to synthesis pressure.
- All utilities in this system are supplied by fuel gas and recovery heat.

# Oxygen enrichment and DME production

- $N_2$ content in synthesis gas goes down with $O_2$ content in Air+$O_2$ . $H_2$/CO is controlled with recycled $CO_2$.
- Over $O_2$= 50%, Thermal efficiency of DME production exceeds 40% and DME production gets closer to a full oxygen operation level.



# Conclusion

- Coal preparations such as Coal washing, Drying, Control of Ash fluid temperature is recommended to improve Gasification efficiency.
- With Dry feed, Cold gas efficiency of gasification is better than with Slurry feed. $O_2$ of high purity and Dry $CO_2$ as carrier gas should be used to minimize Inert content in synthesis gas.
- Total Cold gas efficiency of Dry feed/JFE process is 20% higher than Conventional process(Slurry feed/Two step).
- Biomass gasification process for synthesis gas should be developed more intensively to realize Feasible Biomass to DME and Secondary reforming is important to reduce tar and methane.
- For small scale DME production from biomass, oxygen enrichment blowing could be practical for less equipment cost and relatively high DME production capacity.

# Thank you very much

# for your attention !!