8 th Korea-China clean Energy workshop, Nov. 23-27, 2010

R&D Activities of Coal to Fuel/Chemicals Technology in China

Wen Li

State Key Lab of Coal Conversion

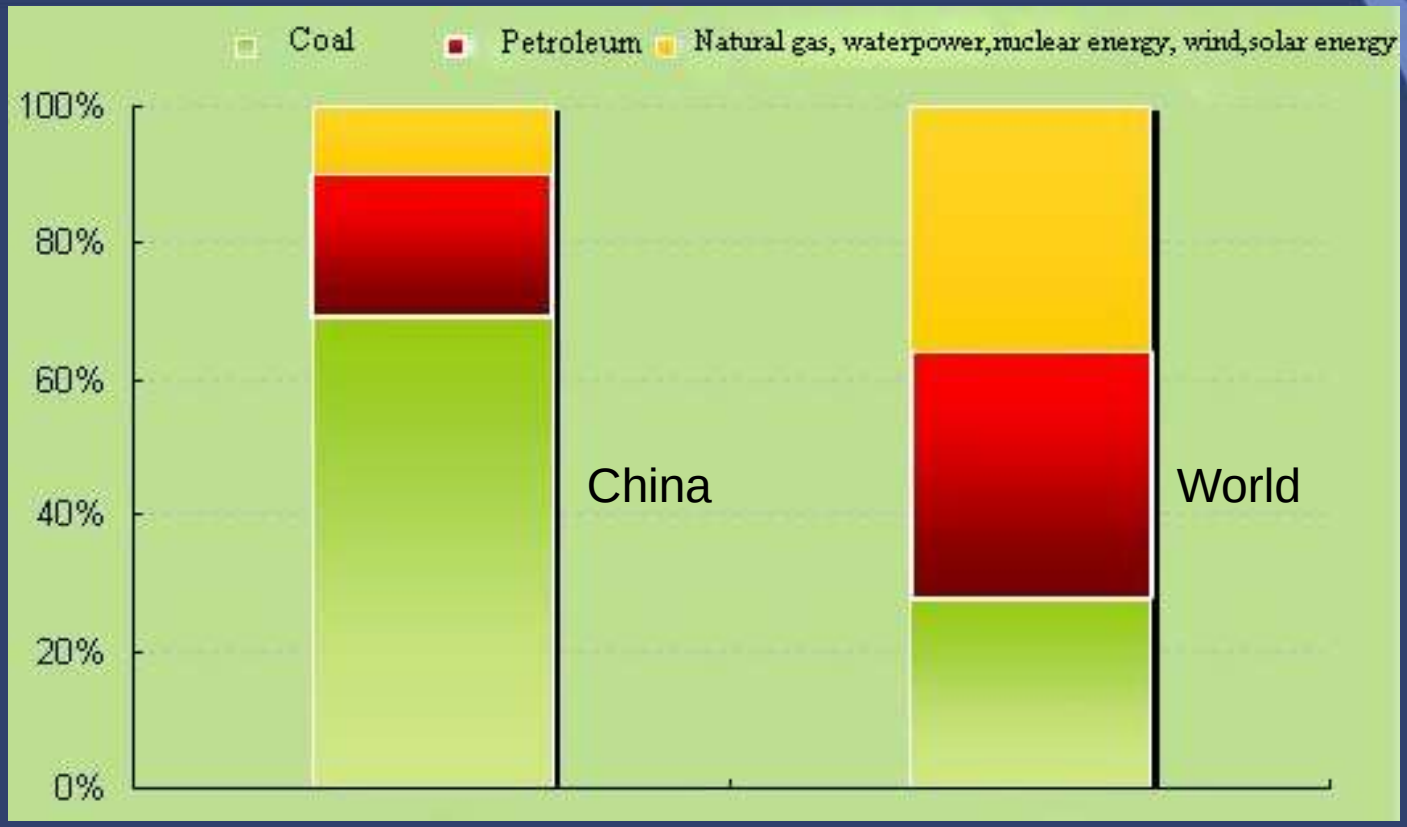
Institute of Coal Chemistry, CAS

liwen@sxicc.ac.cn

In this presentation…

- **Coal Utilization in China**
- **Direct Coal Conversion**
  - Pyrolysis
  - Direct liquefaction
- **Indirect coal conversion**
  - Coal Gasification
  - Fischer-Tropsch Synthesis
  - Higher Alcohols Synthesis
  - Down-stream product of methanol
- **Integrated liquefaction for low rank coal**

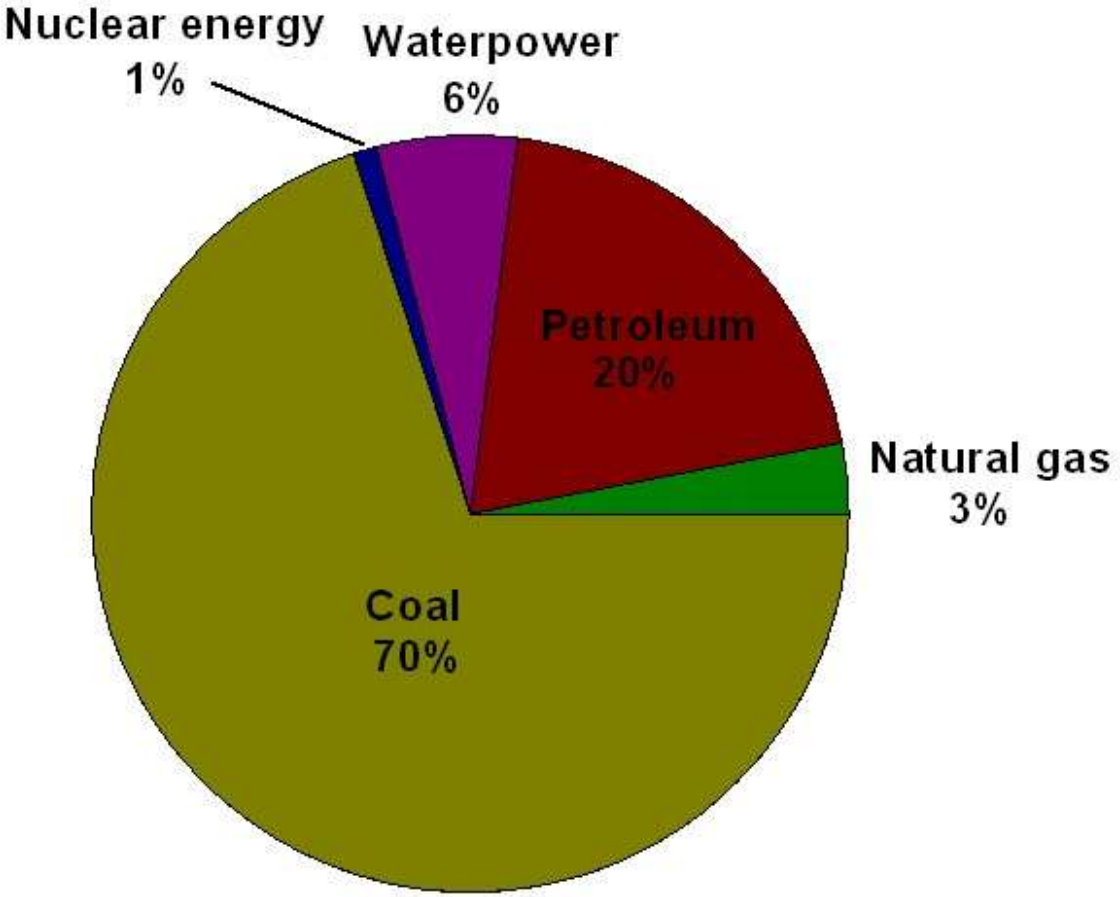
Structure of primary energy consumption



Source: world bank report -world development index, 2008

Coal is the most important energy source in China

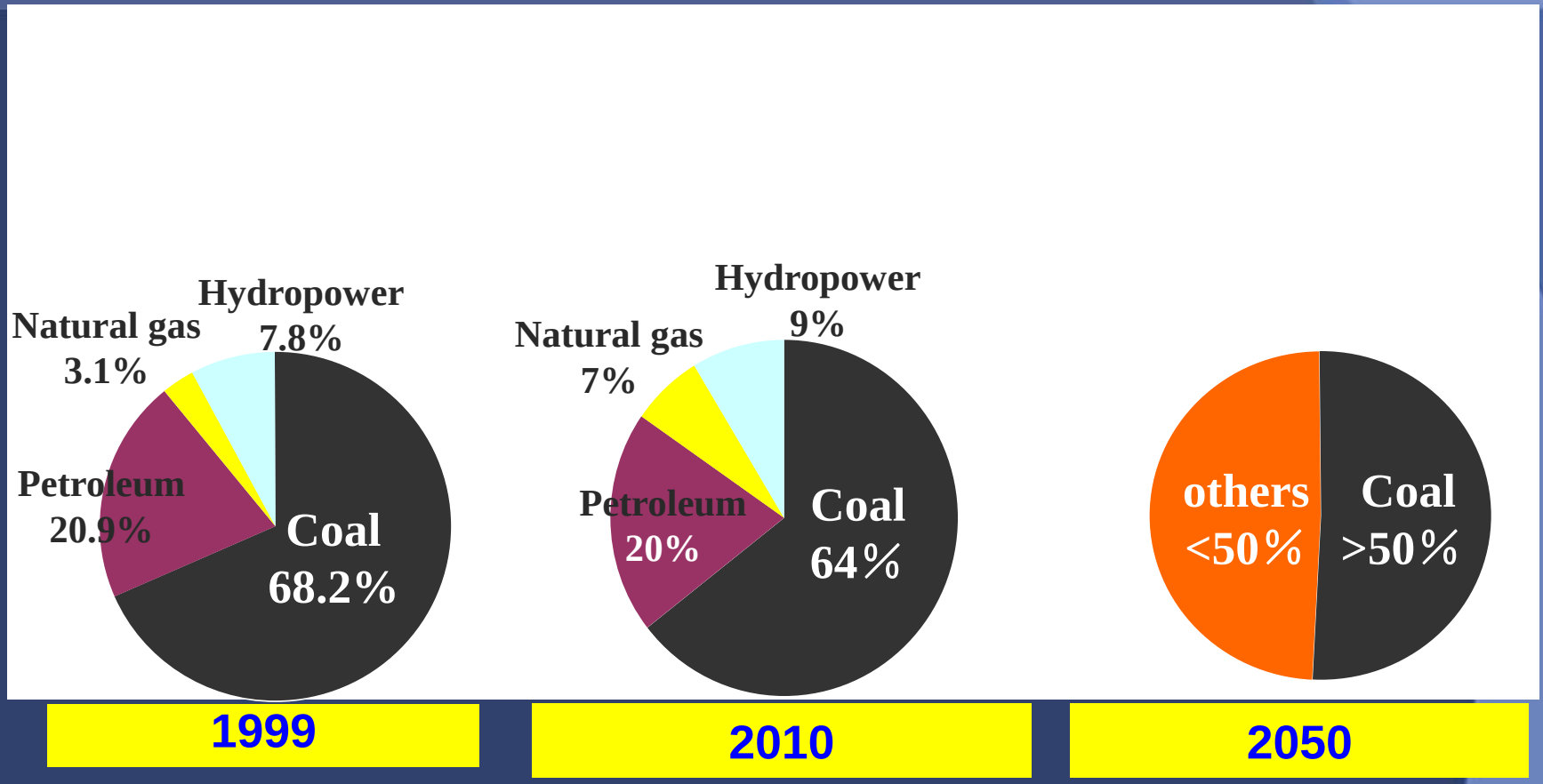
Structure of energy consumption in China



Source: BP energy statistics, 2008

About 70% of the primary energy was supplied by the coal in China

Predicted primary energy structure of China



Coal will be the predominant energy in China for a long time.

currently ～70%; 2050 > 50%

Coal Utilization in China

Annual Production of Coal in China:

over 2.2 billion Tons

Coal Utilization in China

power generation	56%
metallurgy	16%
building materials	13%
domestic fuel	10%
chemicals	5%

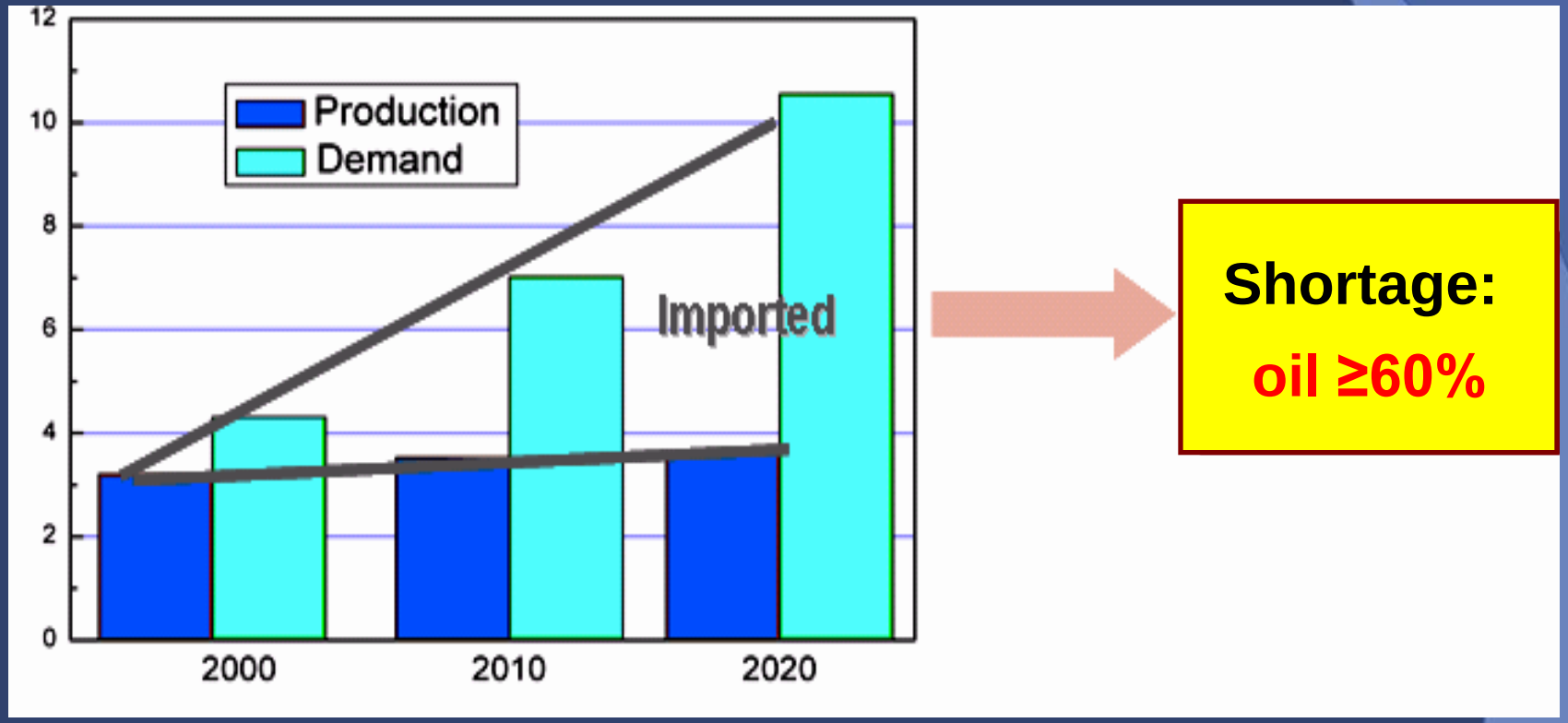
combustion ≈80%

Coal Utilization in China

Status of coal utilization in China

- **predominant in combustion**
- **huge amount, low efficiency, heavy pollution**

Supply and demand of petroleum in China



Over 50% of oil is imported in 2009, and will increase with time.

Only coal to liquid (CTL) can compensate such big deficiency.

3 problems must be solved concerning coal utilization in China

- efficiency improvement
- pollutant and CO_2 emission control
- coal to liquid fuel

R&D Activities in China

Clean Coal Technology

Route 1 Direct conversion

Route 2 Indirect conversion

Direct conversion

- Pyrolysis: tar, gas, char
- Direct coal liquefaction: oil

Pyrolysis

Combined with CFB

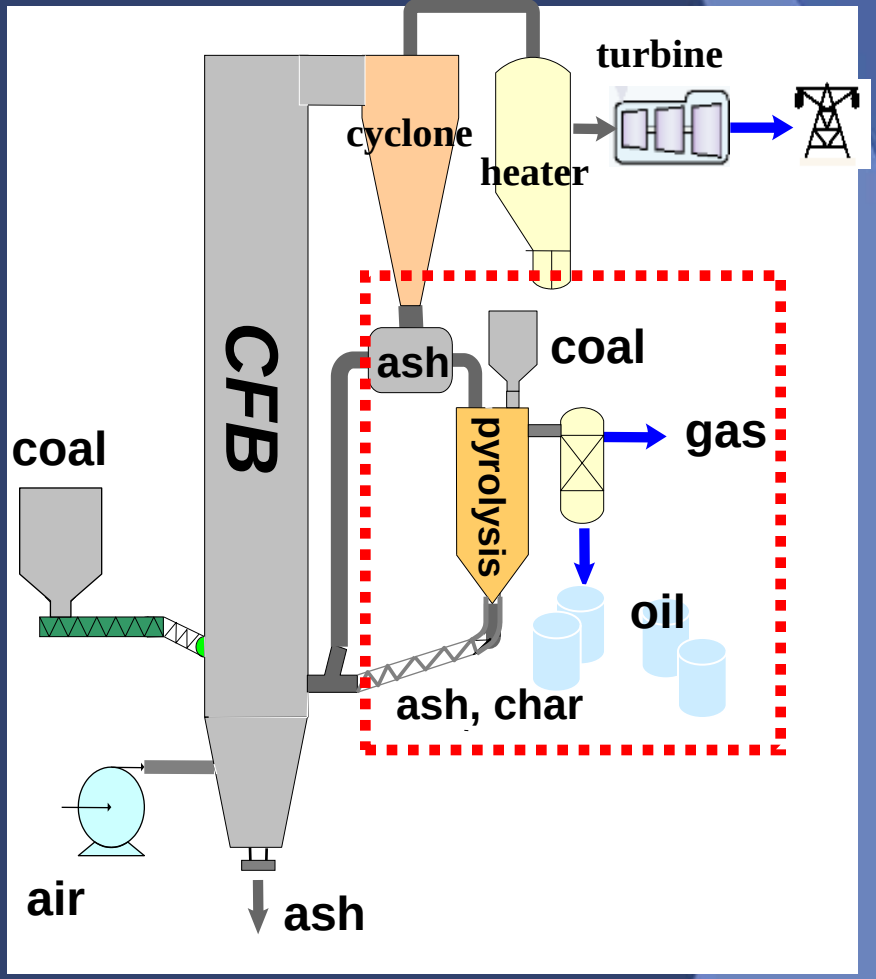
Results in demo scale

75 t/h CFB

- **Oil 10%**
- **Gas 5%**

} Coal price

- **S removal 40%**



Direct Liquefaction Project in Shenhua Group

Overall Status

Approved scale: 5 Mt/a (constructed in two phase)

Demon. scale: 1 Mt/a (first train of phase)

Construction site: Erdos, Inner Mongolia

Direct Liquefaction Project in Shenhua Group

May-Jul., 2008

Gasifier for H_2 supply performed successfully

Shell Technology

2000 t/day

Direct Liquefaction Project in Shenhua Group

Dec., 2008

Coal liquefaction reactor performed successfully

After 24 h, target product

13 days stable operation

Direct Liquefaction Project in Shenhua Group

Full View of Coal Liquefaction Plant in Operation

Direct Liquefaction Project in Shenhua Group

- Current problems-equipments

  failure of let-down valve & recycling pump system

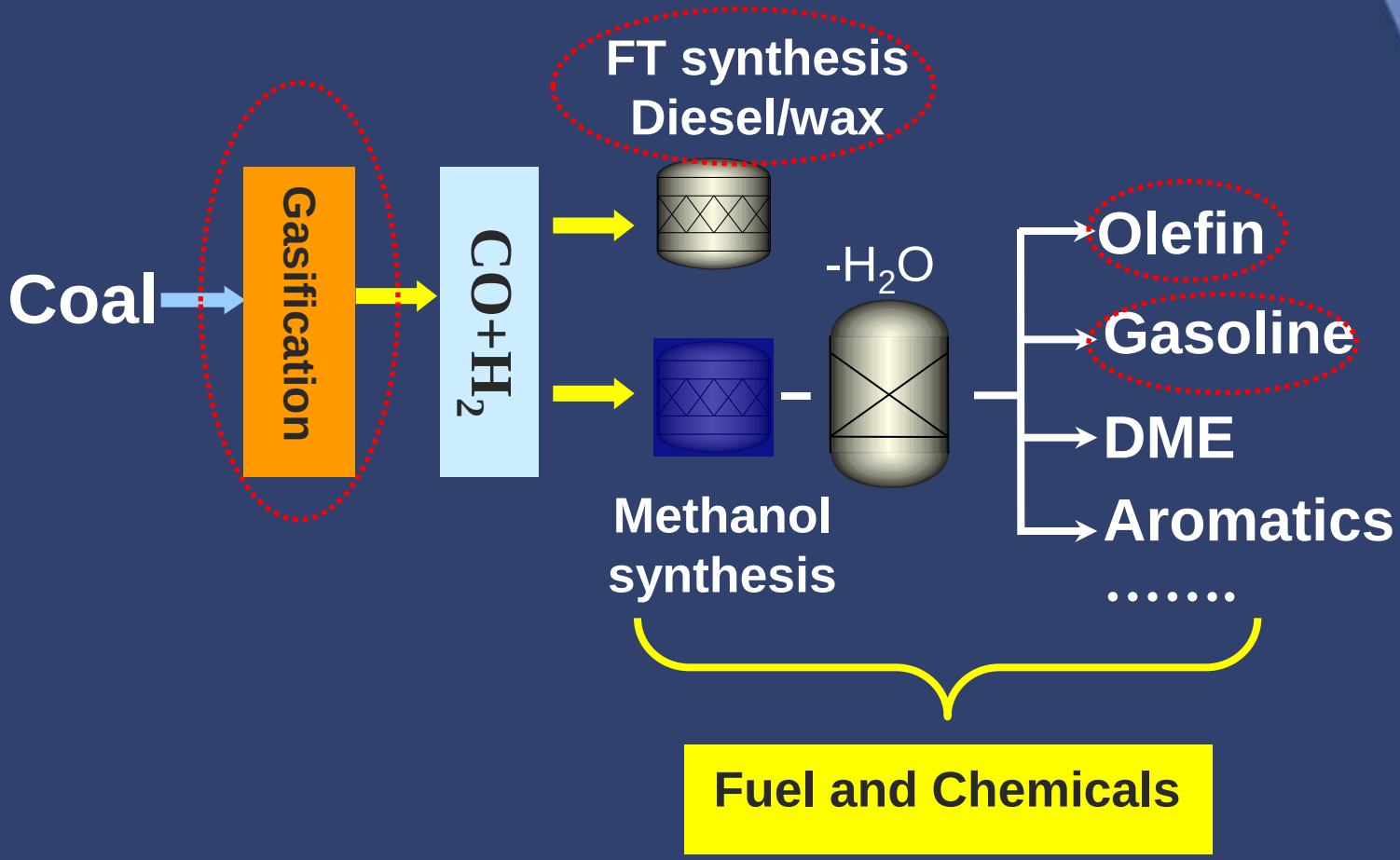
  unstable vacuum level of vacuum tower

- Short-term targets

  To operate the unit > 4000 hrs accumulatively

  To keep the load of the unit over 80%

Indirect Coal Conversion



Coal Gasification Status in China

- **Fixed-bed Gasifier**

  Lurgi, 2.6 MPa, 480 t/d Lump coal

- **Fluidized-bed Gasifier**

  HTW, 1.0～2.5 MPa, 800-950°C, 720 t/d

  Coal with high reactivity

- **Entrained-bed Gasifier**

  Texaco (30), Shell (20), GSP (7)

  3.0 MPa, 500- 2000 t/d

  High quality coal （low ash, low ash fusion temp.）

Most technology is imported; Costly;

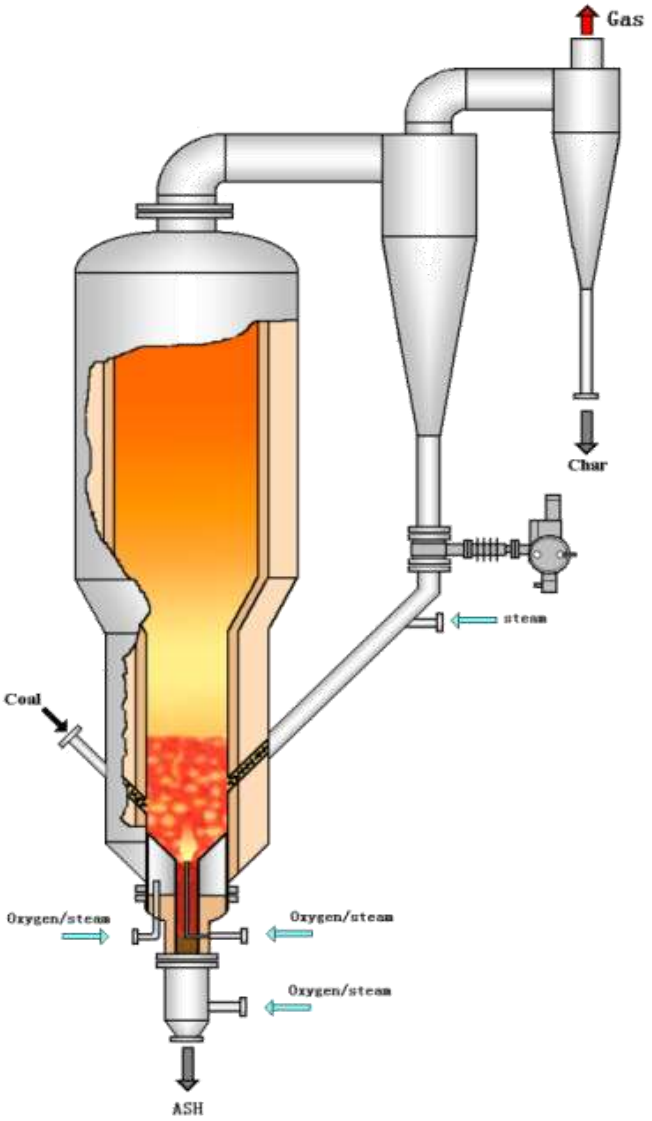
Difficult to gasify “3 high” coal in China

Target Coal for the Conversion

3 “high” coal

- high S, high ash, high ash fusion temp. >1500℃
- 30 - 40% of the total coal reserve in China

Ash Agglomerating Fluidized Bed Coal Gasification Process-ICC



- **Gas-solid fluidization**
  - **Fast heat and mass transfer**
  - **High gasification capacity**
- **Central HT jetting region**
  - **Improve coal conversion**
  - **Promote Ash agglomerating**
- **Selective ash separation**
  - **Lower carbon content in ash**
  - **Improve operation reliability**

Ash agglomerating fluidized bed (AFB)-ICC

Superior coal adaptability

Different kinds coals, Petro coke, biomass + coal

Wide ash content ：1%～38%

High ash fusion point：1160～1500 °C +

“3 high” coal

Carbon conversion: ~90%

Efficient gas ($CO+H_2$): ~70%

Lower O_2 consump.: ~300 Nm^3 O_2/km^3 ($CO+H_2$)

Ash agglomerating fluidized bed (AFB)-ICC

AFB pilot plant-2007

1.0-3.0 MPa

D=0.8 m

50～100 t /d

Ash agglomerating fluidized bed (AFB)-ICC

0.6 MPa

D=2.4 m

300 t /d
Anthracite
~30% ash

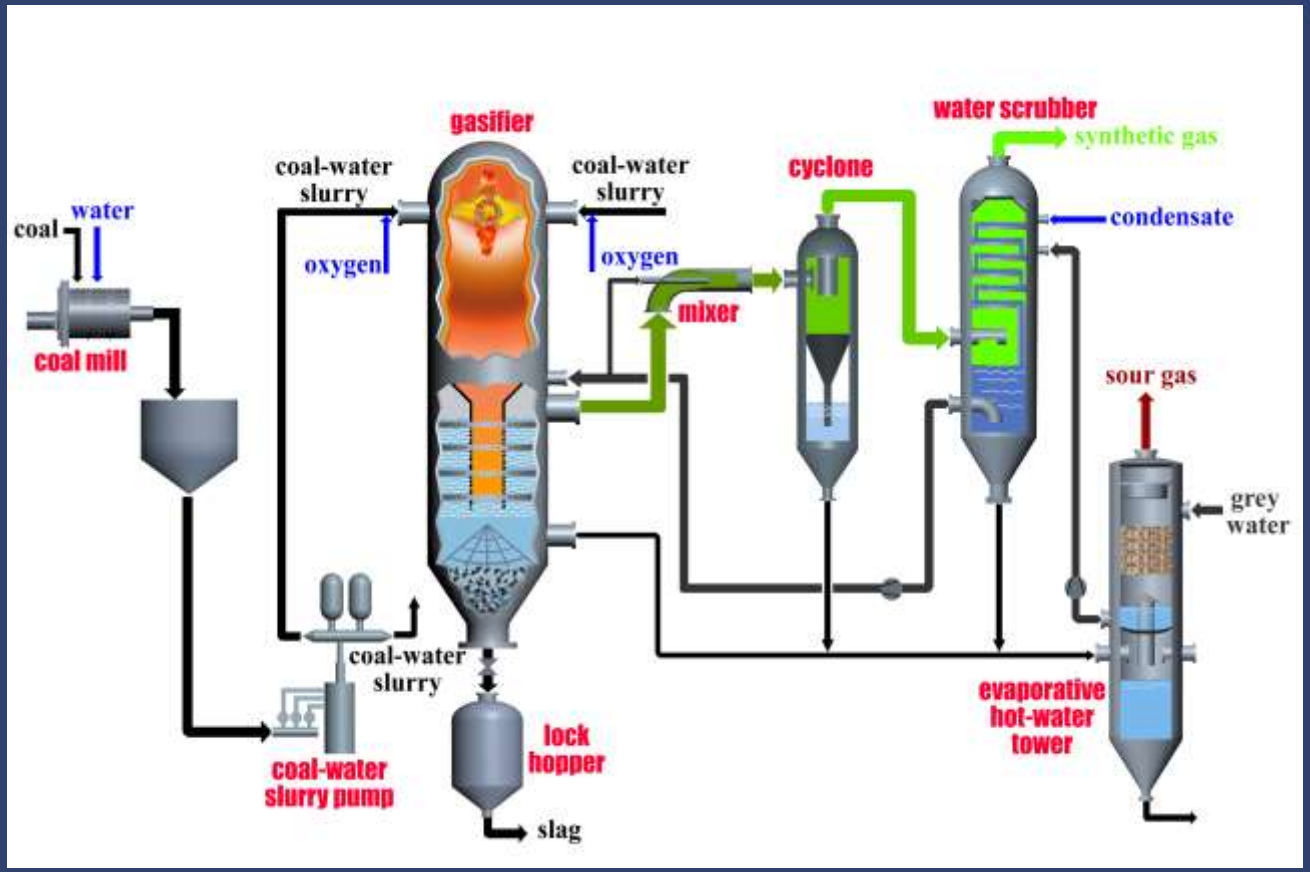
AFB used for 50 kt/a Ammonia, 2009

Ash agglomerating fluidized bed (AFB)-ICC

AFB Process used for 100 kt/a MTG Plant, 2010

Jincheng Anthracite Group

Multi-nozzle-opposed entrained flow gasifier-ECUST



China-owned Independent Tech.: 4 nozzles opposed enhanced heat transfer, improved C conversion

Multi-nozzle-opposed entrained flow gasifier-ECUST

Comparison of Multi-nozzle Gasifier with Texaco for Beisu coal

Item	Multi-nozzle	Texaco
C conversion,%	>98	95
$CO + H_2$	85	82-83
O_2 consum.*Nm^3/km^3	309	336
Coal consum.*kg/km^3	535	547

* Based on the volume of $CO + H_2$

Multi-nozzle-opposed entrained flow gasifier-ECUST

1150 TPD gasifier for NH_3 production in Yanzhou coal Group

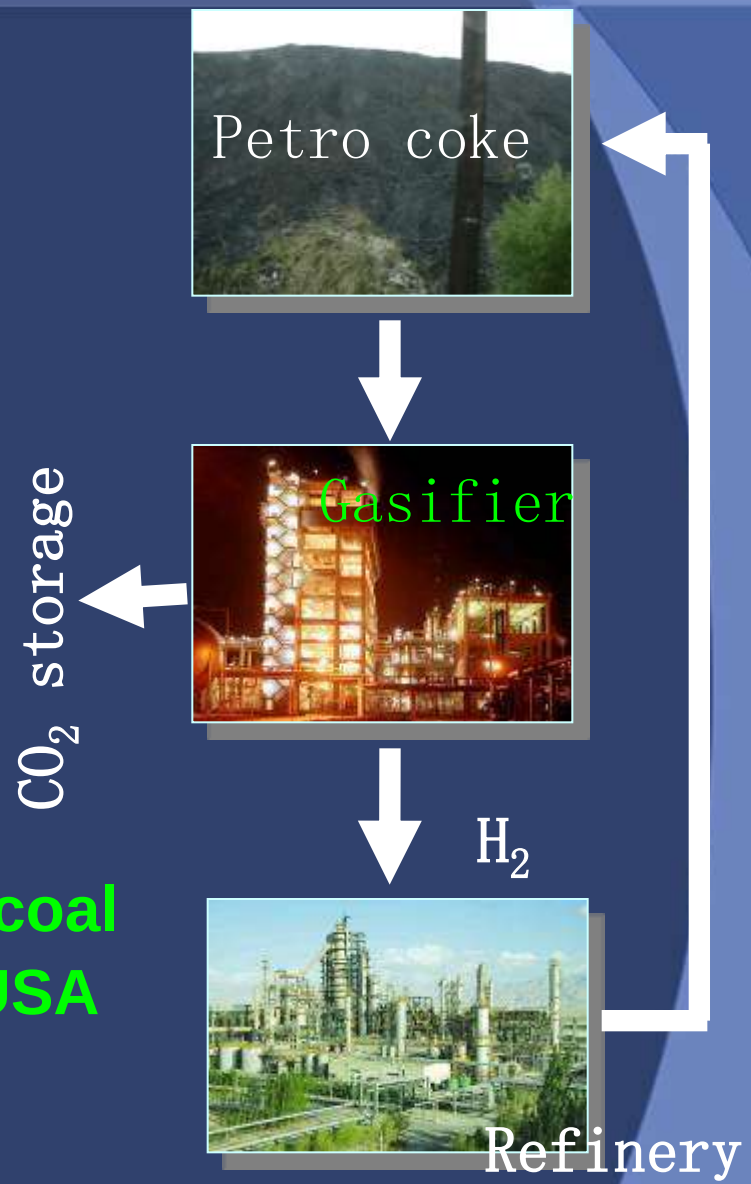
Multi-nozzle-opposed entrained flow gasifier-ECUST

2000 TPD gasifier for methanol production in Shenhua Group

Multi-nozzle-opposed entrained flow gasifier-ECUST

2008, exported to Valero Energy Co. USA, H_2 production from petro coke

~2300 t/d，4 run,1 spare



China firstly export large-scale coal chemical engineering tech. to USA

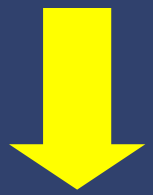
Multi-nozzle-opposed entrained flow gasifier-ECUST

Application:18 enterprises, 50 sets gasifier

Scale, t/d	Product	status
2000	methanol	6 run, 11 in construction
1800	ammonia	4 run, 2 in construction
1500	methanol, NH_3	4 run, 3 in construction
2300	methanol, DME	8 in construction
1500	Methanol, power	3 run

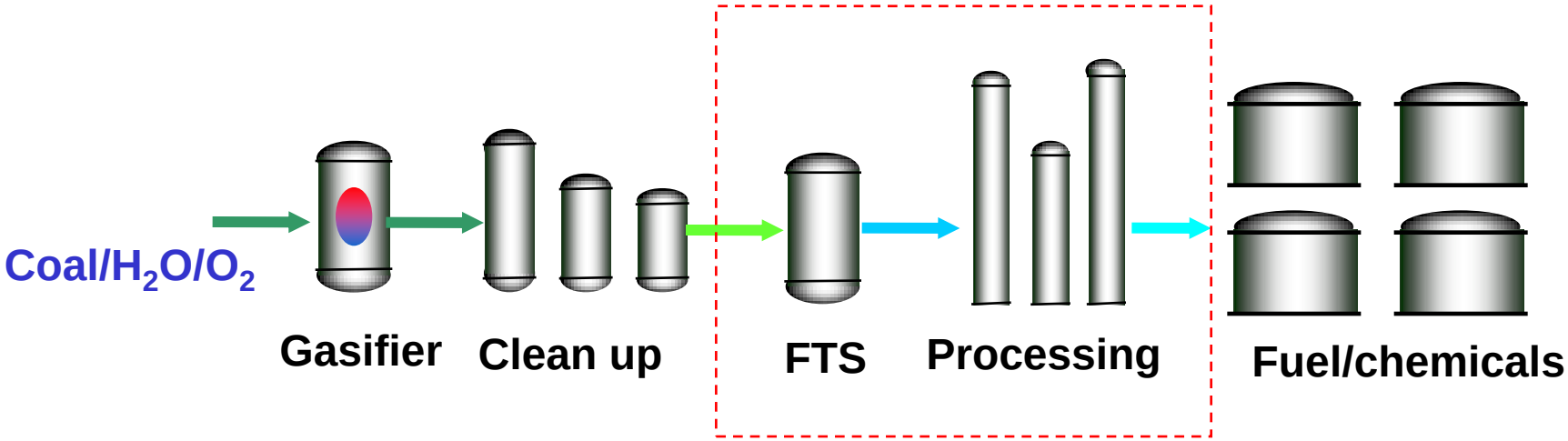
Indirect coal Conversion

Fuel/chemicals from coal



- F-T synthesis to diesel and higher hydrocarbons
- Higher alcohols synthesis
- Methanol down stream product

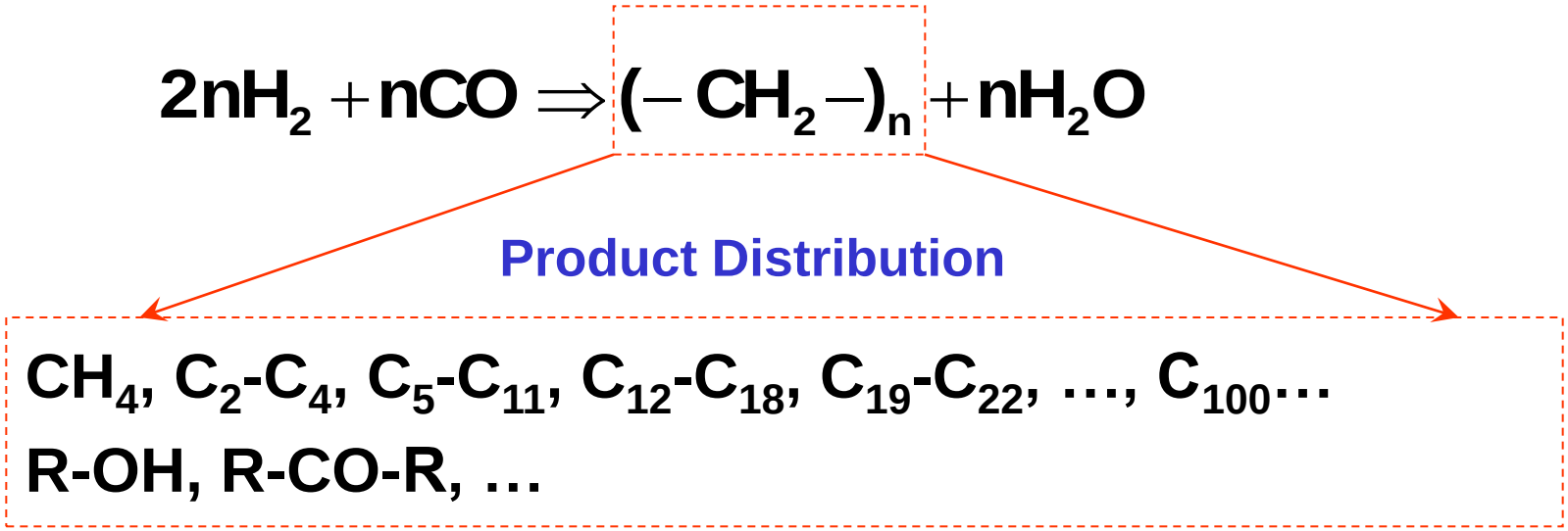
Fischer-Tropsch Synthesis (FTS)



Two kinds of Process

- Fe-based Cat. Slurry-bed, syngas low H/C
- Co-based Cat. Fixed-bed, syngas high H/C

F-T Synthesis: Fundamentals



Catalyst: selectivity, stability

Reactor: heat transfer (exothermic reaction)

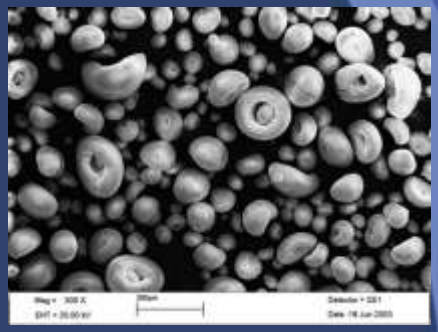
Fe-based catalyst for FT Synthesis

- **Low Temperature Process**

  temperature 250 ^{o}C

  productivity 0.25 kg/ kg h

  efficiency 40%

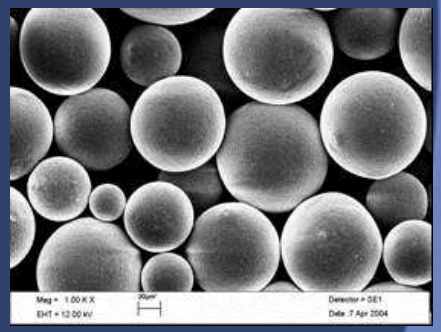


- **High Temperature Process**

  temperature 270 ^{o}C

  productivity 0.80 kg/ kg h

  efficiency 44%



HT steam was used for power generation to improve efficiency

Fe-based catalyst for FT Synthesis

diesel

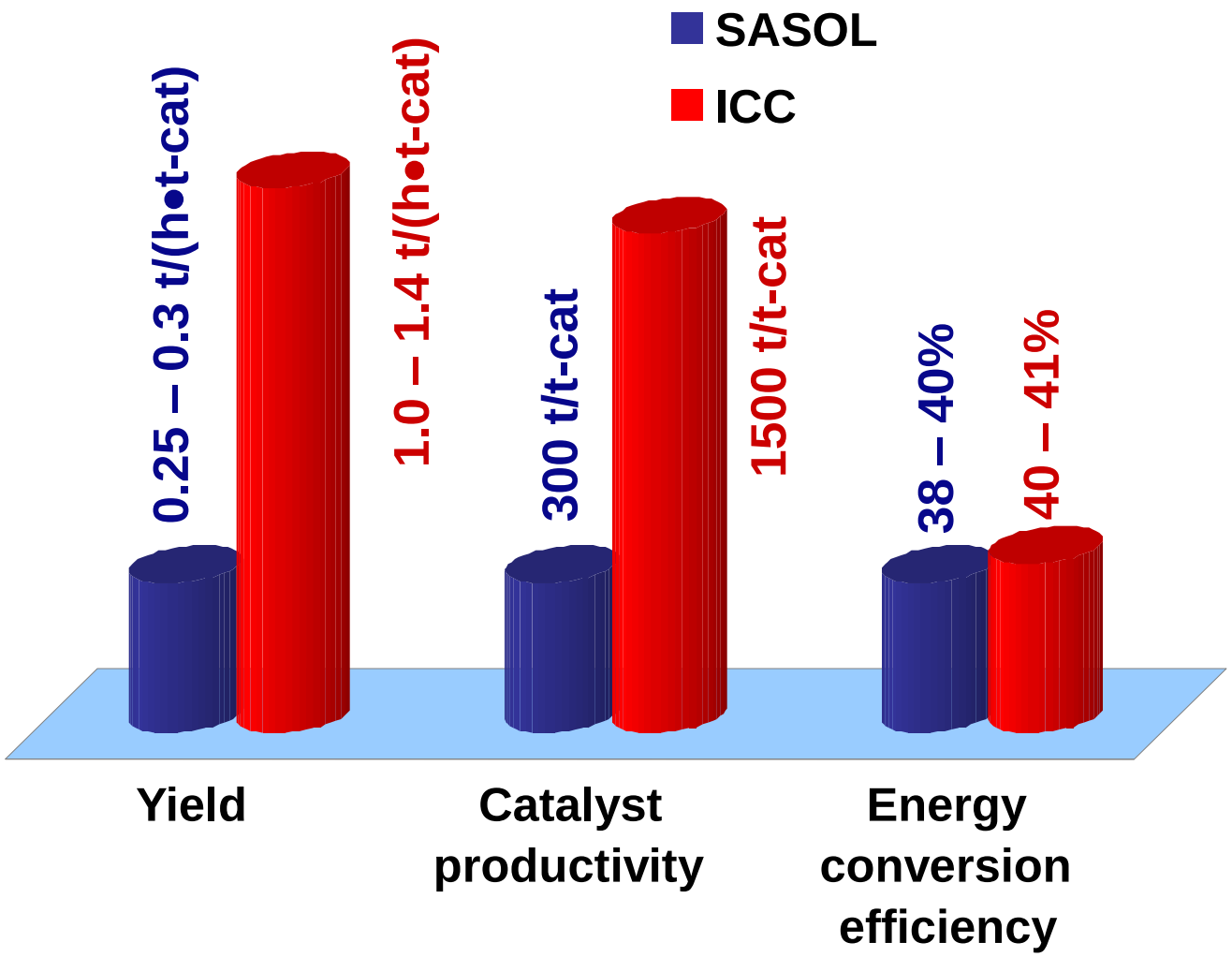
1,000 t/a pilot, 2006

Fe-based catalyst for FT Synthesis

160 kt-diesel /a demo plant run very well in full production in May, 2010 in Inner Mongolia

Another 2 demo plants are being operated

Fe-based catalyst for FT Synthesis

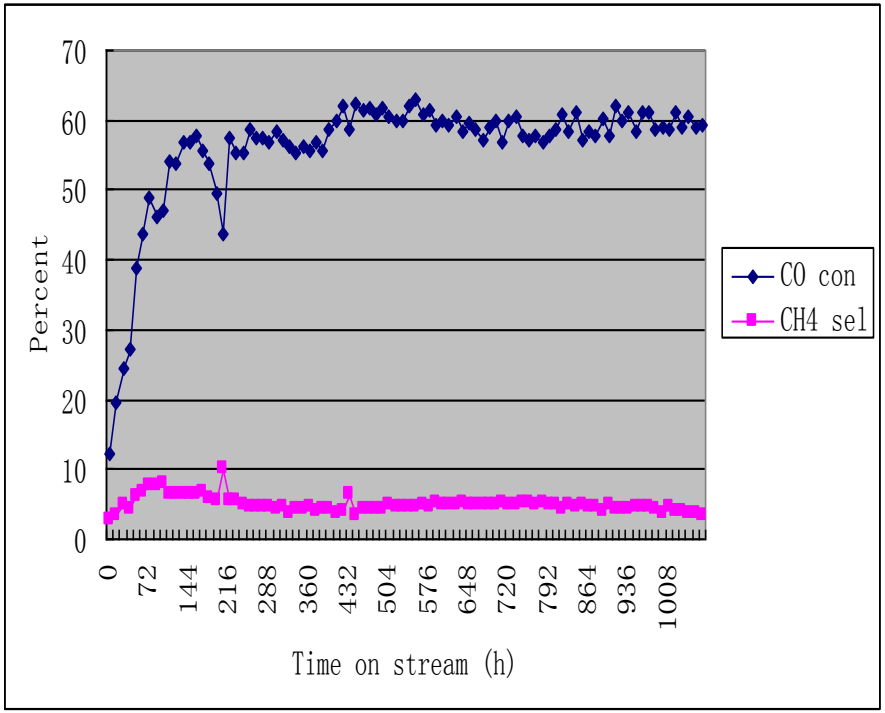


Co-based catalyst for FT Synthesis

fixed-bed reactor

Catalyst property

Time, h	25	80
T , ℃	180	190
CO conv.	54.1 %	78.9 %
C_5^+ selec.	89.4 %	90.9 %
C_5^+ produc. (gr/L/hr)	111	170
CH_4 selec.	3.8%	3.7%



It is featured by low CH_4 selectivity and good stability

Co-based catalyst for FT Synthesis

Wax

Run with 5 L catalysts

Conversion 63%

CH_4 < 6%, C_{5+} > 90%

500 h^{-1}

Co-based catalyst for FT Synthesis

Demo plant of 5000 t/a was run well in Lu'an Group

The 1st Co-based FT CTL demo plant in China

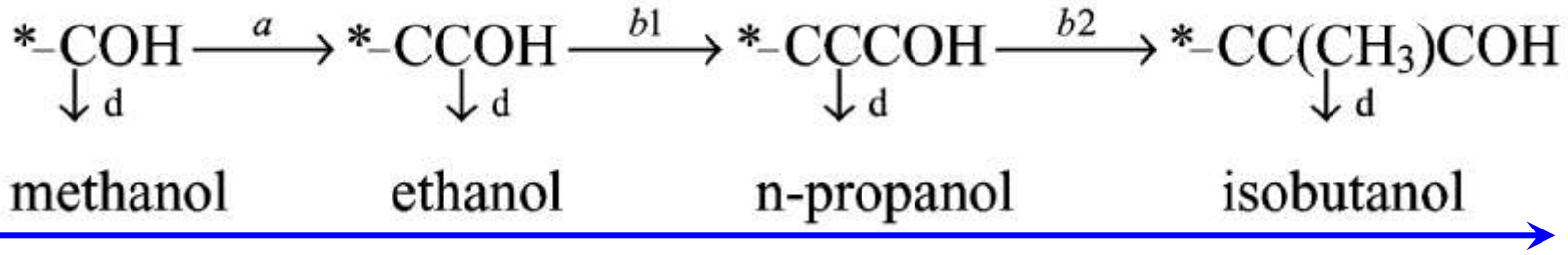
Higher Alcohols Synthesis (HAS)

$$C_nH_{2n+1}OH$$

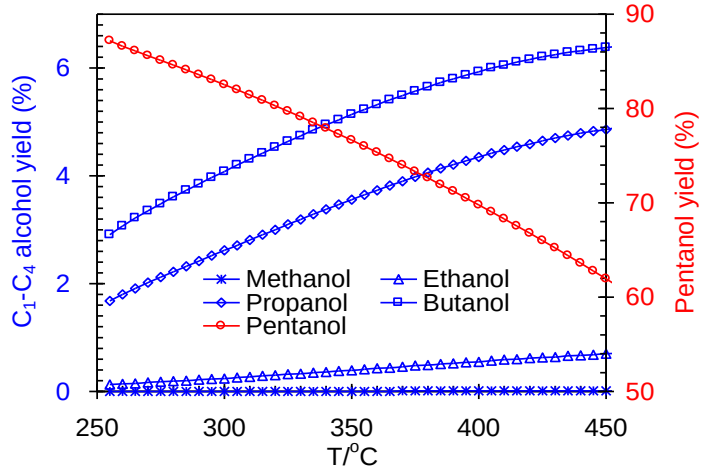
- **Fuel and Fuel Additives**
- **Chemicals and Intermediates for Synthesis**

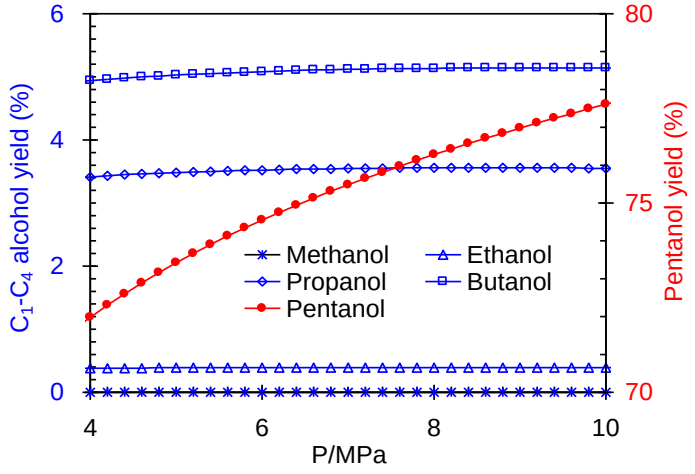
Higher Alcohols Synthesis: Thermodynamics

$$CO + H_2 = C_nH_{2n+1}OH$$

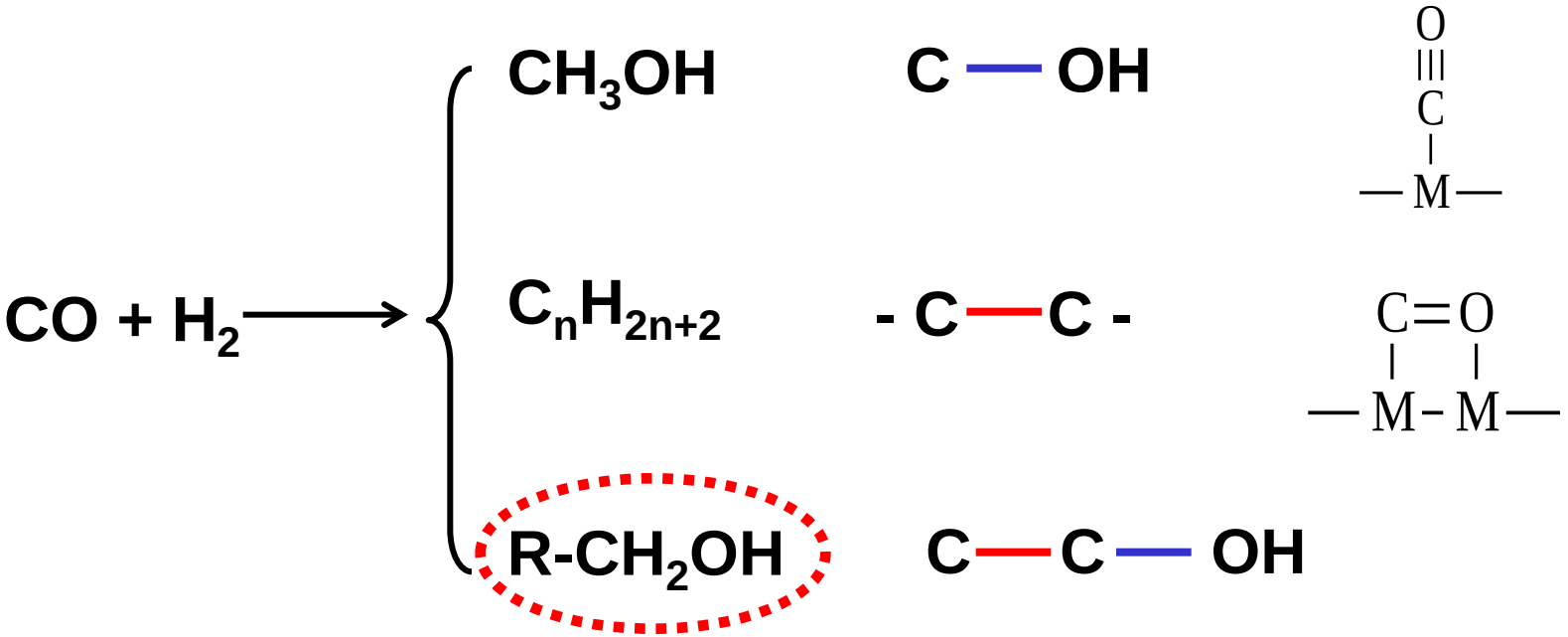


Higher alcohols synthesis is favored in thermodynamics.





Higher Alcohols Synthesis: mechanism



Difficulty: the synthesis of higher alcohols needs carbon chain growth and C-OH formation on the same catalyst simultaneously.

Higher Alcohols Synthesis: Selectivity

Challenge: **Selectivity of the catalyst**

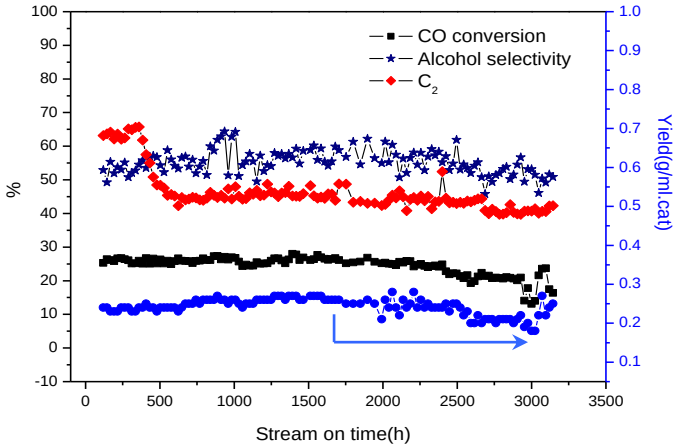
alcohols not hydrocarbons (FTS)

higher alcohols ($C2^{+}$) not methanol (MS)

Alcohols Synthesis: Progress at ICC

Basic properties of the Cu-Fe catalyst

Catalyst	I-type
Morphology	Black cylinder
Size/mm	Φ3.0×4.0
Particle density/g/mL	1.1-1.4
Surface area/m^2/g	130-180
Average pore size/nm	8-10
CO conversion/%	20-40
Selectivity of total alcohols/%	>50
C_2^+OH/total alcohol/%	>45
Space time yield/Kg/(Lcat·h)	>0.2
Productivity(oxygenates.g)/L(Syngass)	0.07-0.12



Alcohols Synthesis: Progress

20 Kg/d, 6～8MPa, 240～260℃, Cu-Fe Catalyst

Methanol Derivatives

Methanol Market in China

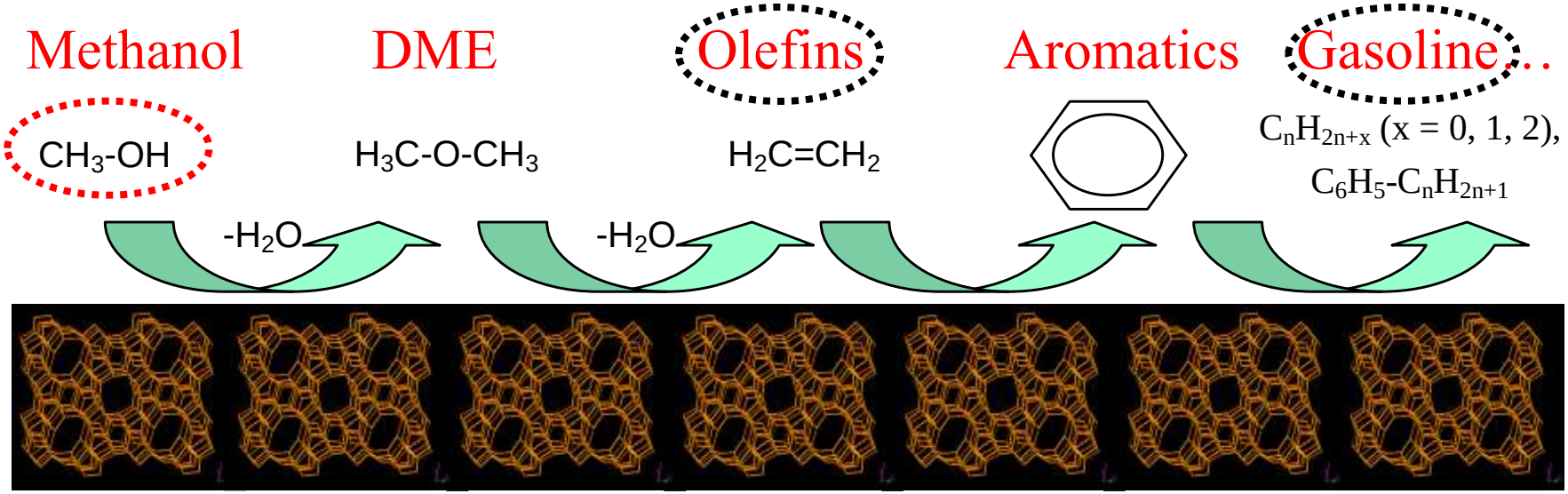
Feedstock	Plants	ratio%	Capacity	ratio%
	Number		Mt	
Coal	229	81.2	21	67
Natural Gas	32	11.3	7.4	23.9
Coke Oven Gas	21	7.5	2.8	9.1

2009，Capacity: 32 Mt，quantity demand:10 Mt.

2010，Capacity: 32.12 Mt，Quantity demand:18-21Mt.

Methanol capacity is badly surplus. Its down steam product is urgent.

Methanol Conversion Reactions



Different products could be obtained from controlled conversion of methanol in zeolite cat.

Down stream product of methanol-gasoline

MTG process-ICC

Small ZSM-5 crystals

3500 t/a DEMO plant

One step synthesis

Heat insulation reactor

Down stream product of methanol-gasoline

Results obtained in the DEMO Plant

Gasoline compositions:

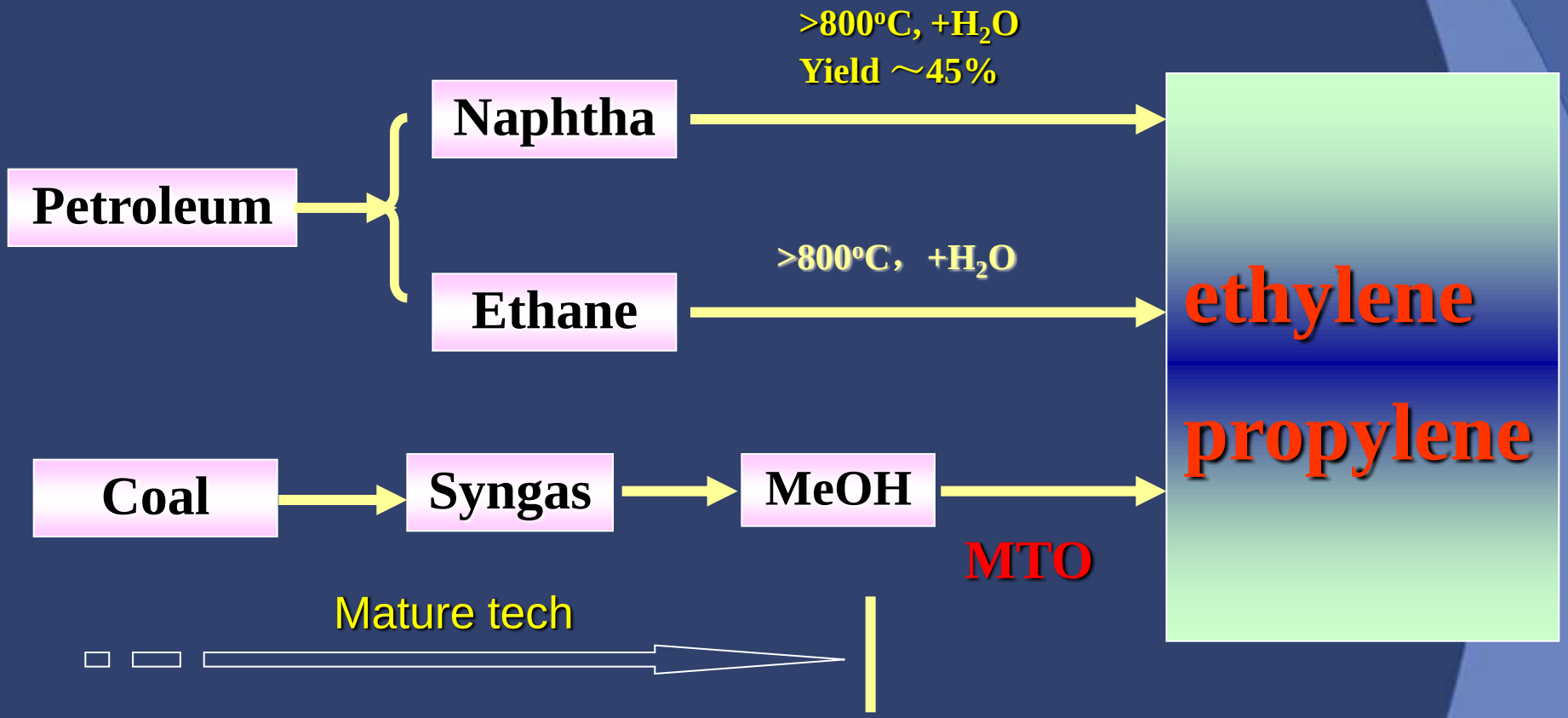
Isoparaffins	39.1%
Olefins	6.3%
Paraffins	6.8%
Cycloalkanes	7.3%
Aramatics	37.4%
Sulfur	0%

Qualified 93# gasoline was obtained.

Now a 200 kt/a MTG factory is under construction.

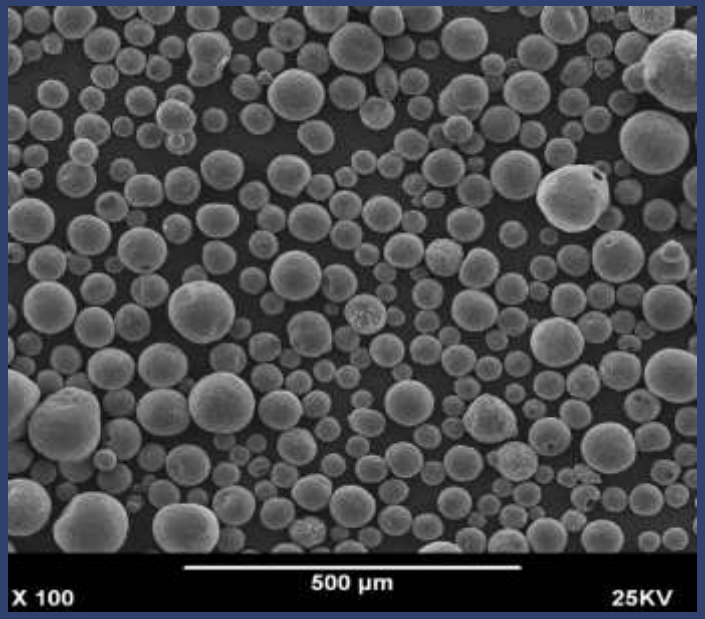
Down stream product of methanol-olefins

Route to olefins production



Down stream product of methanol-olefins

MTO developed by Dalian Institute of Chemical Physics



SAPO-34

Cat recovery	550°C 5 min	550°C 10 min	550°C 30 min	550°C 60 min
Residue C（wt%）	3.2	1.6	0.87	0.56
Conversion (%)	100	100	100	100
Product selec. (wt%)				
CH_4	1.39	1.43	1.49	1.82
$C_2^=$--$C_3^=$	93.60	93.41	92.99	90.55

The selectivity of olefin is over 90% with low formation of CH_4

600 Kt/a MTO in Shenhua Group

The first industrial apparatus for MTO in the world

MeOH conv.100%, Olefin Selectivity 80%

Aug, 2010, Qualified PP was produced

Effective utilization of low rank coal

Integrated liquefaction:

Combination of direct & indirect conversion

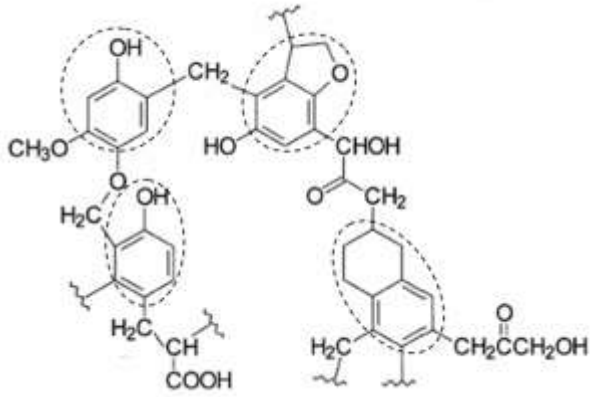
Low rank coal in China

	lignite	sub-bitu	bitu	anthara
water %	**20-50**	**10-20**	**10-15**	**2-10**
volatile %	**38-65**	**37-55**	**10-35**	**3-6**
heat kcal/kg	**2000-4000**	**~ 5000**	**5000-6000**	**~ 7000**
Oxygen %	**15-23**	**10-15**	**3-12**	**2-3**
H/C	**0.97**	**0.79**	**0.77**	**0.33**
utilization	**??**	**Power??**	**coke/power**	**sygas/power**

lignite **130 Bt**

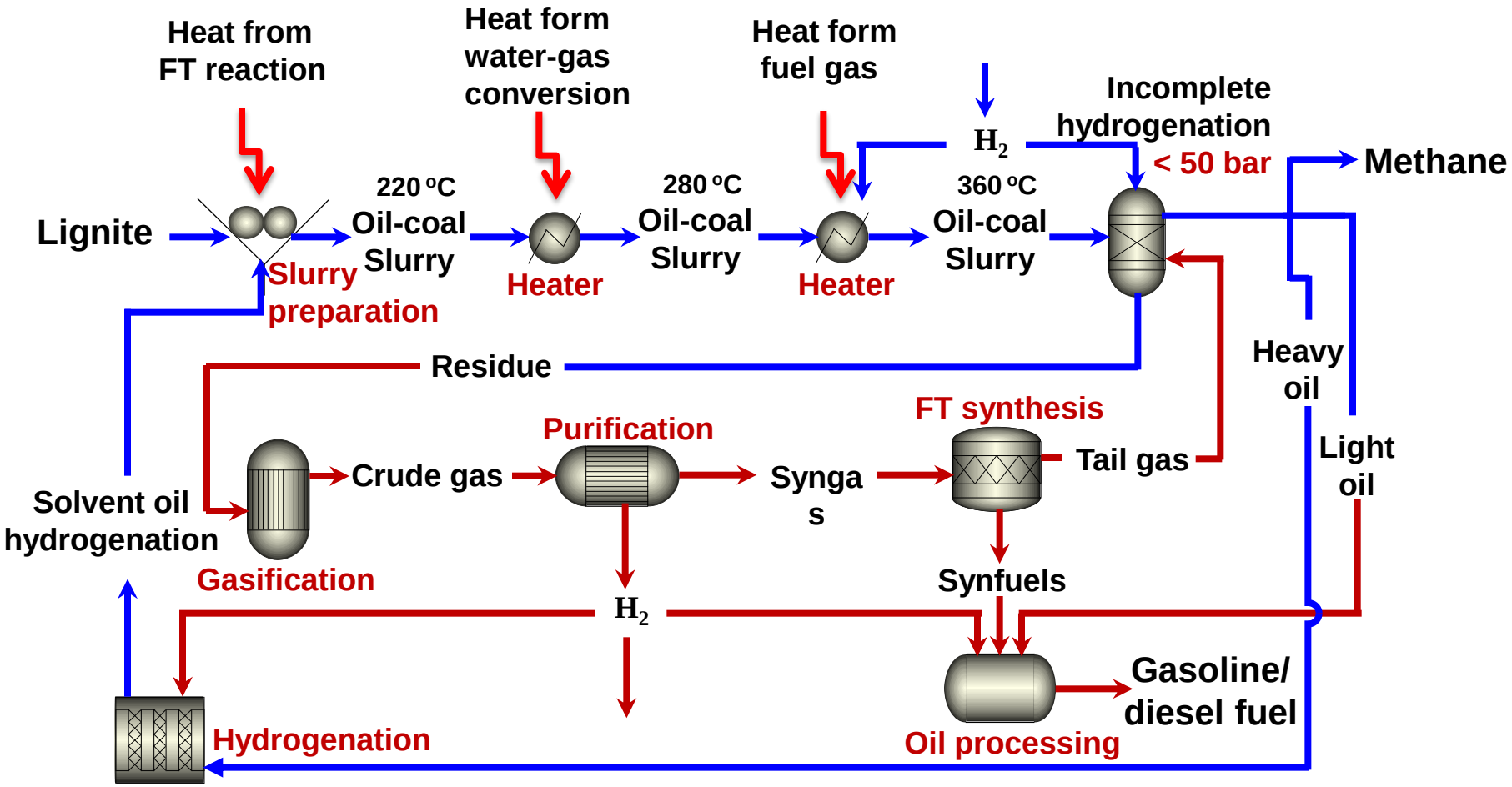
Sub-bitu **300 Bt**

} Low rank coal ~ **50%**



Ideal feedstocks for fuel/chemicals

Integrated liquefaction for low rank coal



Drying + Partial liquefac + FT; energy efficiency 35 → 40%

Integrated liquefaction for low rank coal

Demo plant processing lignite of 10 Kt/a, Inner Mongolia

CONCLUSIONS

- **Compared to conventional combustion in coal utilization, the routes to fuels and chemicals via coal gasification are recognized as the most advanced technology in clean coal utilization.**

- **Large amount of coal in China with high ash content (>25 wt%) and high ash fusion temperature (>1500 ^{o}C) can be used as the feedstock of AFB gasification.**

- **The new concept of integrated liquefaction is most suitable to convert low rank coal into fuel/chemicals with high energy efficiency.**

Acknowledgement

Chinese Academy of Sciences

Ministry of Science and Technology

National Science Foundation of China

Thanks for your attention