Fischer-Tropsch synthesis from laboratory to engineering scale up

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Introduction：

- Government need
- International technology situations

  Sasol: high temperature FTS

  Low temperature FTS

  Shell: SMDS
- Technology development in China

  Synfuels China® : HFPT ICC-IA

  LFPT ICC-IIA

CTL process:

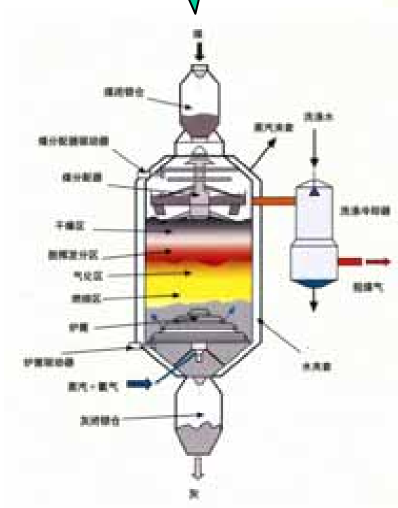
Coal gasification

- **Fixed-bed or moving bed gasifier**
- **Fluid-bed gasifier**
- **Entrained flow gasifier**

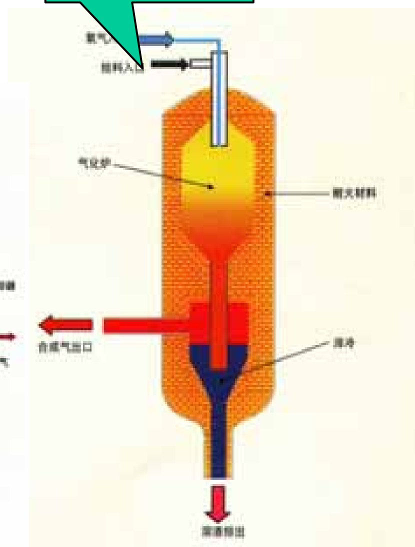
shift reaction
Acidic gas removal
Slurry FTS
Product upgrading

Coal gasification

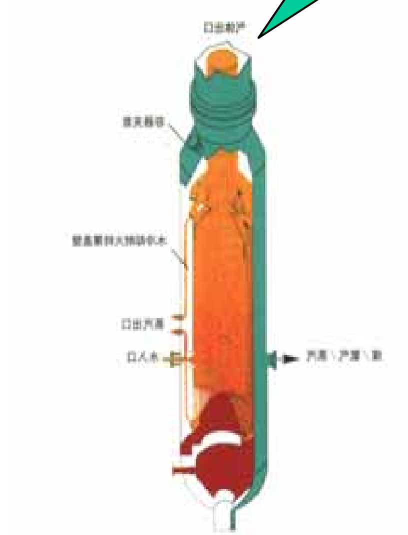
Lurgi



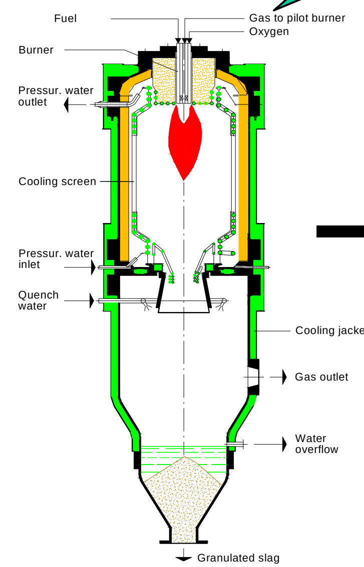
Texaco



Shell



GSP



→ **GSP**

Cheap in construction
Methane rich syngas
Coal adaptability
Tar recovery
Water treatment

Expensive in construction
High quality Syngas
Coal adaptability *
Short time on stream
High O_2 consumption

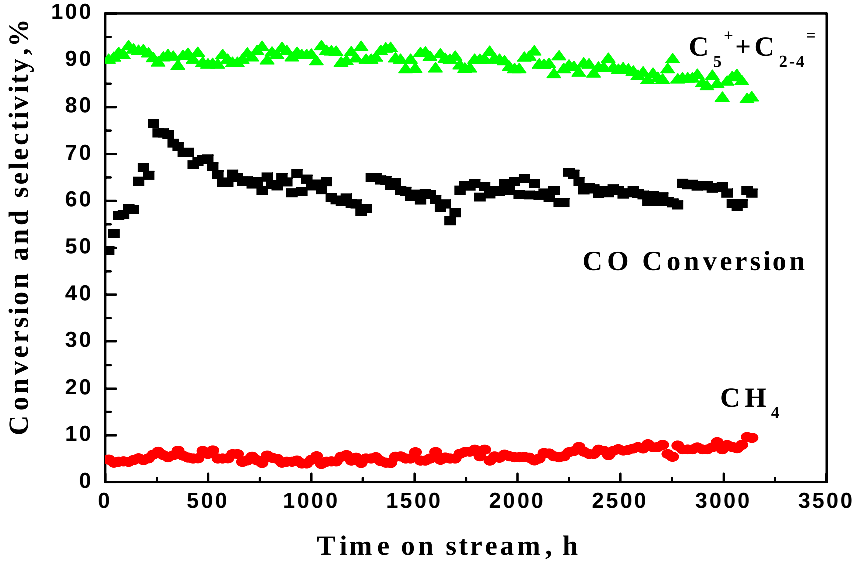
Expensive in construction
High quality Syngas
Coal adaptability**
Hot stream quenching
Large boiler size

Cheap in construction
High quality Syngas
Coal adaptability***
Quenching type and heat recovery
BDI SVP
FUTURE ENERGY
CHOREN

Laboratory research：

catalyst development and research

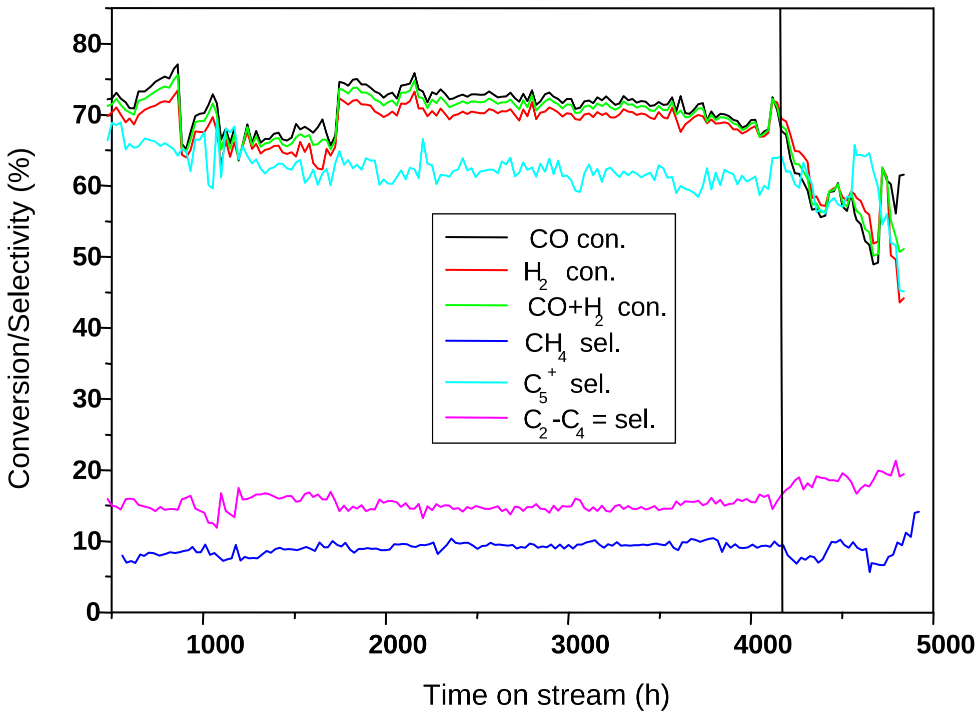
ICC-IA catalyst



Changes of conversions and selectivity with time-on-stream in slurry phase reactor (240 -270℃, 1.5-2.0 MPa, 2.0 NL/g-cat./h, H2/CO=0.67)

Laboratory research：

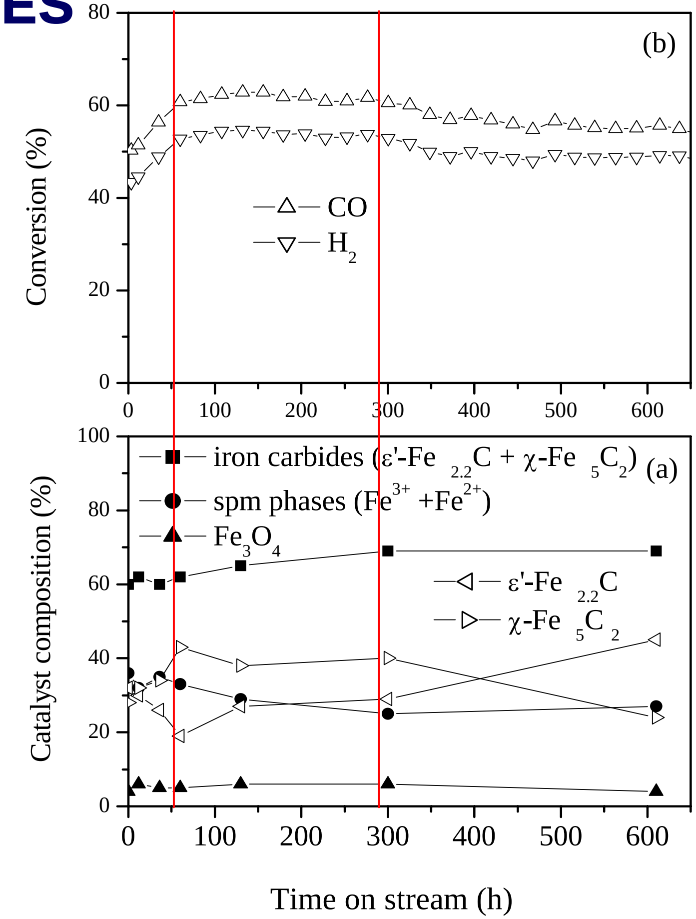
ICC-IIA catalyst



Changes of conversions and selectivity with time-on-stream in slurry phase reactor (240 -270℃, 1.5-2.0 MPa, 2.0 NL/g-cat./h, H2/CO=0.67)

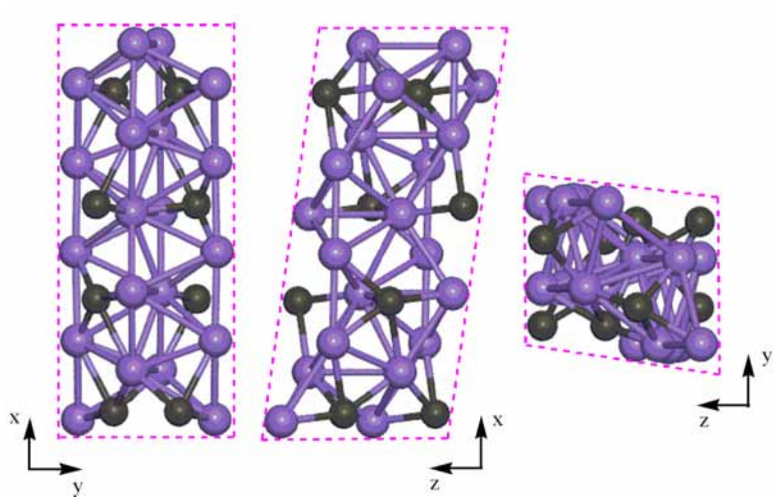
Catalyst characteristization

XRD,SEM,MES

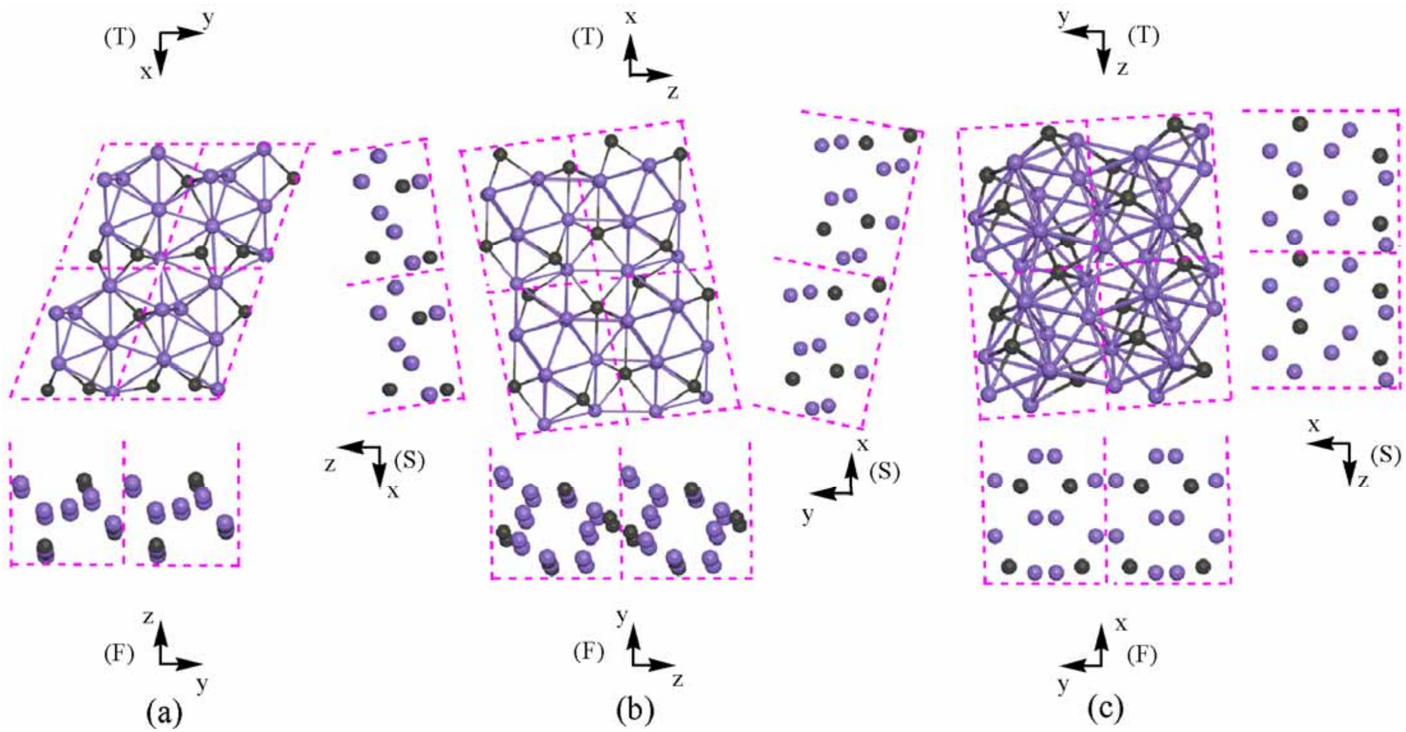


Correlative studies of phase transfer and activities of an ICC-IA model catalyst during FTS reaction. (240 -270℃, 1.5-2.0 MPa, 2.0 NL/g-cat./h, H2/CO=0.67)

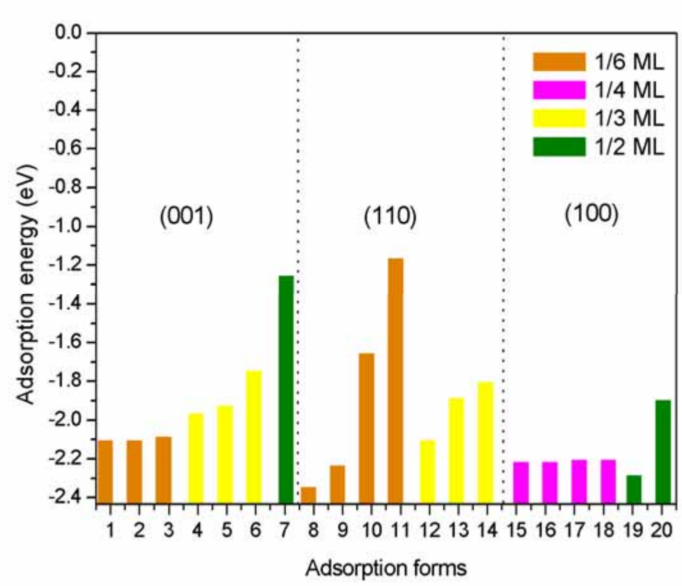
Quantum chemistry calculation

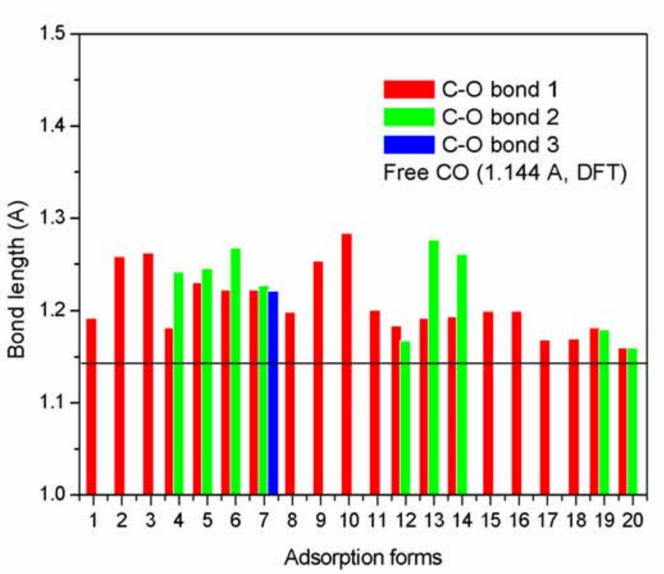


Schematic unit cell of Fe_5C_2. (Fe: light gray; C: deep gray.)
（1）CO adsorption on the surface of Fe_5C_2（001）、（110）、（100）



Schematic top and front views of Fe5C2(001) (a); top and side views of (110) (b); and top and front views of (100) (c) in a p(1×1) unit cell.

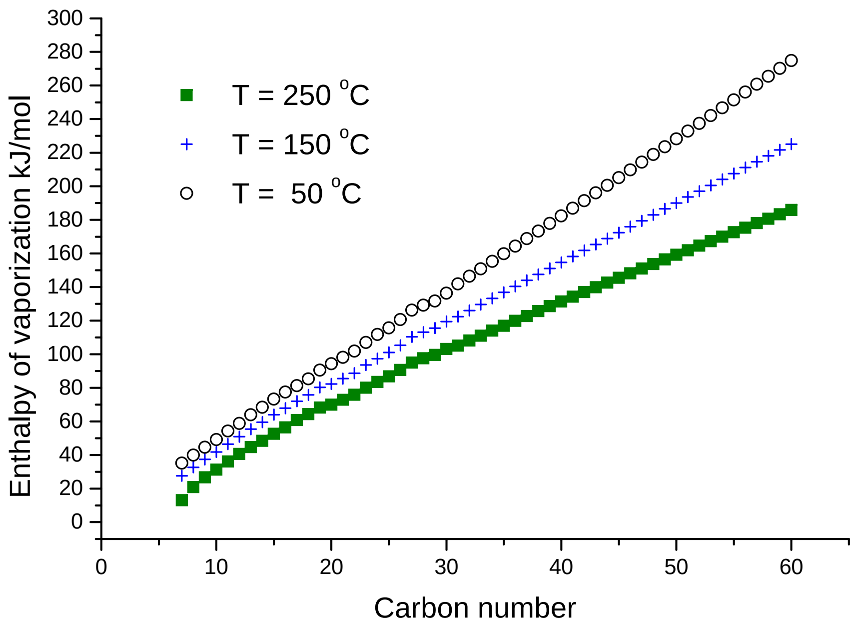




Adsorption energetics (left) and C-O bond activation (right) of CO adsorption on Fe5C2 surfaces

Kinetic and slurry reactor model research

Develop user databank for FTS



Enthalpy of vaporization at different temperature for n-paraffins, C7 ~ C30 data are from Aspen Plus, C31 - C60 data are fromthis work

FTS Kinetic research：

Kinetic research for Fe-Cu-K catalyst

Ma Wen-pin's model

Wang Yi-ning's Model

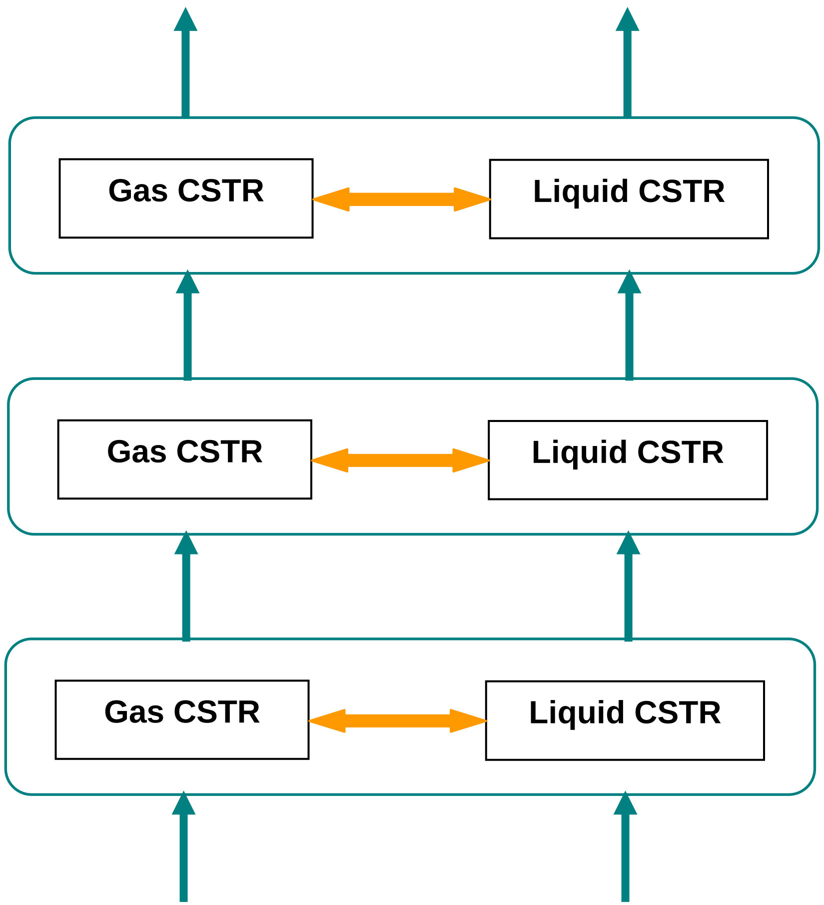
Zhang rong-le's model

FTS Kinetic research :

Kinetic research for Fe-Cu-K catalyst

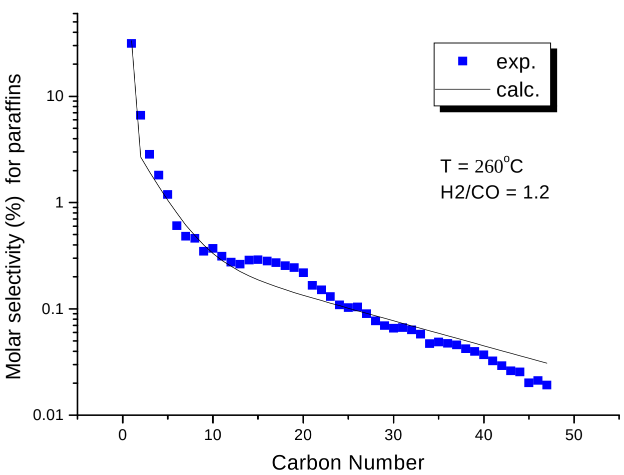
Ji Yuan-yuan's model
Yang Jun's Model
Teng Bo-tao's model

Develop slurry bubble reactor



$$\varepsilon_g \frac{dC_{g,i}}{dt} = \frac{u_{g0}C_{g0,i} - u_g C_{g,i}}{h} - (k_{L,i}a)(\frac{C_{g,i}}{m_i} - C_{L,i})$$

$$\varepsilon_L \frac{dC_{L,i}}{dt} = \frac{u_{L0}C_{L0,i} - u_L C_{L,i}}{h} + (k_{L,i}a)(\frac{C_{g,i}}{m_i} - C_{L,i}) - \frac{W_{cat}}{hS}\sum_j \alpha_{i,j}R_j$$



Pilot plant research

- **Construction began in 2001**
- **First run in 2002, 25 days**
- **Modifications in winter of 2002**
- **Three runs in 2003,**
- **Two runs in 2004, 1500 hours**
- **Catalyst, kinetic model and slurry bubble reactor were tested in the pilot plant.**

Develop product upgrading technology

- **Cooperate with industrial partner to Develop hydrogenation and hydrocracking technology**

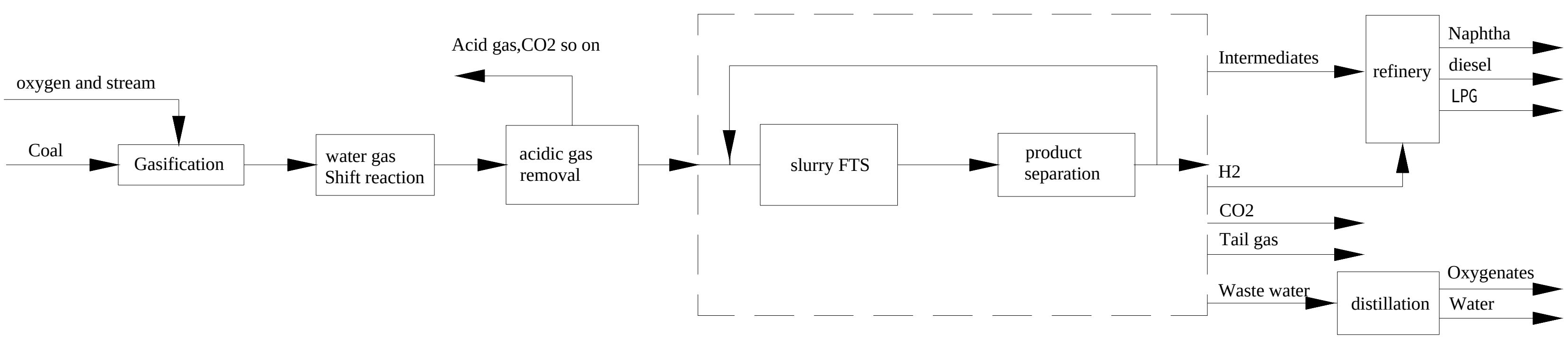
- **Developing hydrogenation and hydrocracking technology in laboratory**

CTL diesel properties (Synfuels China®)

Indexes	Hydrogenated Fraction Refinery Co-MoS2 catalyst	Hydrocracked Co-MoS2 catalyst	Hydrogenated Fraction S-free catalyst
Density kg/L	0.7684	0.7782	0.7664
Viscosity /mm2/s, 20 ^{o}C	3.172	3.957	3.276
Initial boiling point / ^{o}C	150	130	185
Final boiling point /^{o}C	370	385	330
Disti. Range / ^{o}C			
5%			185-206.2
10%	154-188	138-184	213.7
30%	257	231	232.7
50%	278	272	252.7
70%	293	305	278.2
90%	323	332	310.2
95%	330	341	322
dried	337	349	331.8
Flash point /^{o}C	64	66	>70
Cetane number	74.1	66	75-90
Total aromatics %	0.4	0.7	-
Olefin /%	0.5	-	
Sulfur / ppm	< 4	<5	<0.5
CFPP / ^{o}C	-3	-34	-2

Process integration research

- Coal gasification
- Water gas shift reaction
- Acidic gas removal
- Slurry FTS
- Product upgrading



Comparison between simulation and industrial results

	Coal slurry coal gasification		GSP coal gasification	
	Industrial value	simulation	Industrial value	simulation
Gasification temperature ℃	1400		1500	
Gasification pressure （Mpa）	4.0		3.0	
Coal slurry concentration(wt%)	63.96%		—	
Coal conversion %	98		99.6	
syngas %(dry base)				
H2	44.080	45.0227	27.06	27.06
CO	35.102	34.0537	68.36	68.28
CO2	19.970	20.0943	4.06	4.18
N2	0.374	0.5195	0.395	0.39
NH3	0.134	0.0034	0.00	0.00
H2S	0.150	0.1526	0.04	0.04
others	0.08	0.0994	0	0

	SHELL gasification Illinois 6# coal		SHELL gasification Texas Lignite	
	literature	calculation	literature	calculation
Gasification temperature ℃	1699.85		1644.25	
Gasification pressure（Mpa）	2.308		2.7	
Coal conversion %	99.5		99.32	
syngas %(dry base)				
CO	64.38	65.57	62.69	63.80
H2	27.31	27.23	28.50	28.28
CO2	1.52	1.32	2.86	3.04
CH4	0.03	0.06	0.03	0.07
Ar	1.12	0.09	1.06	0.09
N2	4.17	3.11	4.49	4.27
H2S	1.33	1.26	0.33	0.41
COS	0.14	0.13	0.03	0.04

Poly-generation：
the future of CTL in China

- **Poly-generation based on coal gasification is a promising sustainable strategy**
- **Poly-generation of CTL and co-produce electricity by combined cycle is an efficient way.**
- **The optimization of the poly-generation system should be carefully evaluated.**

Summary

- **CTL in china can be a feasible way from viewpoint of technology,resource,economics, and environment**

- **CTL technology developed in Synfuels China has been tested in pilot plant, can be scaled up to demonstration plant scale. The demonstration plant is been design.**

- **Poly-generation of oil and electricity,and chemicals is the future of Large CTL**

Thank you