

CTL & BTL

SOME DOES AND DON'TS OF CONVERTING COAL AND BIOMASS TO LIQUIDS

WORLD GTL CONGRESS, JANUARY 2013 DOHA

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SOLID FEEDSTOCKS FOR LIQUIDS PRODUCTION

■ COAL

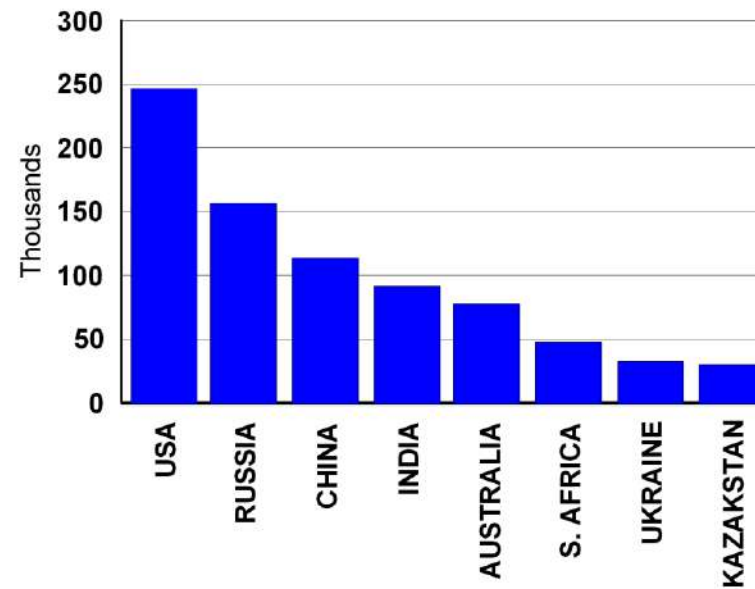
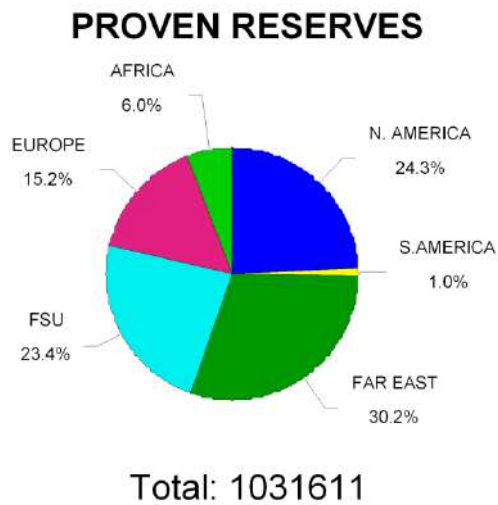
- ▶ BLACK COAL
- ▶ BROWN COAL/LIGNITES
- ▶ PEAT

■ BIOMASS

- ▶ ENERGY & FOOD CROPS - SUGAR CANE
- ▶ FOOD BYPRODUCT - CORN STOVER, STRAW
- ▶ FOREST RESIDUES
 - LIGNO-CELLULOSE

FEEDSTOCK - 1

WORLD COAL RESERVES (Millions of tonnes)

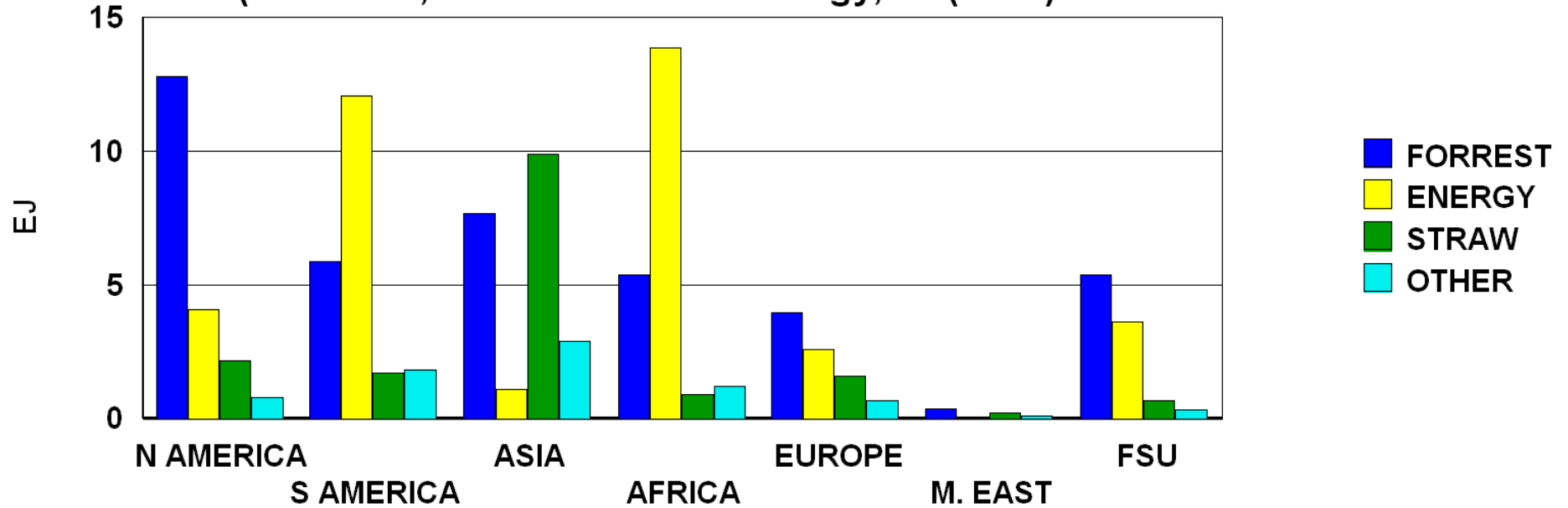


~ 20,000 EJ

SUSTAINABLE BIOMASS POTENTIAL (EJ)

WORLD TOTAL ca 100eEJ

(M Parrika, Biomass and Bioenergy, 27 (2004) 613)



BUT much already used:

	% USED
N. AMERICA	16%
S AMERICA	12%
ASIA	100%
AFRICA	39%
EUROPE	22%
M. EAST	7%
FSU	5%
WORLD	38%

FEEDSTOCK QUALITY

TYPE		Illinois No 6	PRB	Lignite	Loy Yang	WOOD	Prairie Grass
			Buckskin	Wilcox Tx	Lignite		
Ultimate Analysis (DAF)							
Carbon	wt.%	78.10%	74.44%	72.47%	69.40%	53.4%	50.06%
Hydrogen	wt%	5.50%	5.26%	6.09%	4.90%	6.4%	6.10%
Oxygen	wt%	10.90%	18.50%	19.28%	24.80%	40.1%	42.83%
Nitrogen	wt%	1.2%	1.20%	1.20%	0.51%	0.1%	0.92%
Sulphur	wt%	4.30%	0.60%	0.96%	0.31%		0.10%
		100.00%	100.00%	100.00%	99.92%	100.0%	100.00%
Ash (as received)	wt%	12.0%	5.5%		0.00%	1.0%	6.19%
Moistrure (as rec)	wt%	6.5%	28%		62.20%	40%	15.00%
As received Basis							
Carbon	wt.%	63.65%	49.5%	44.24%	26.23%	37.79%	39.45%
Hydrogen	wt%	4.48%	3.5%	3.72%	1.85%	4.5%	4.81%
Oxygen	wt%	8.88%	12.3%	11.77%	9.37%	28.36%	33.76%
Nitrogen	wt%	0.98%	0.8%	0.73%	0.19%	0.07%	0.72%
Sulphur	wt%	3.50%	0.4%	0.59%	0.12%	0%	0.08%
Ash (as received)	wt%	12.00%	5.5%	8.96%	0.00%	0.71%	6.19%
Moistrure (as rec)	wt%	6.50%	28.0%	30.00%	62.20%	28.57%	15.00%
		100.00%	100%	100.01%	99.97%	100.00%	100.00%
LHV (as received)	GJ/t	25.80		18.22			14.51
HHV (as received)	GJ/t	25.90	17.45	18.30		12.56	14.61
LHV (DAF)	GJ/t	30.57					17.58
HHV (DAF)	GJ/t	30.69		13.60			17.72

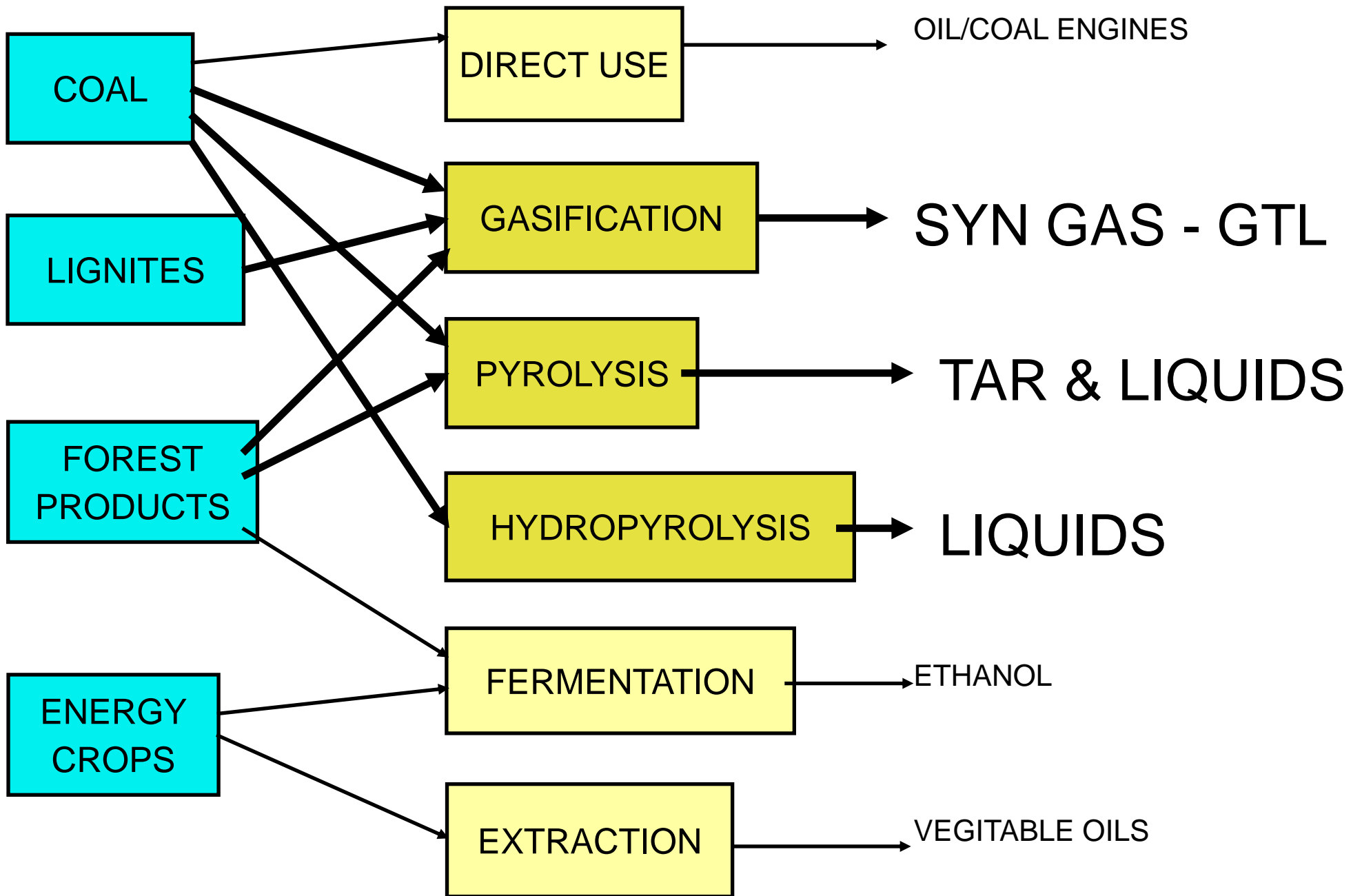
SUMMARY

▪ COAL

- ▶ LARGE WIDESPREAD DEPOSITS OF HIGH VALUE COAL
 - HIGH CALORIFIC VALUE > 25MJ/kg
 - LOW ASH < 15%
 - LOW MOISTURE < 10%
- ▶ LARGE AND WIDESPREAD DEPOSITS OF POORER QUALITY COAL
 - CALORIFIC VALUE 15 -20MJ/kg
 - HIGH ASH >25%
 - HIGH MOISTURE > 20%
- ▶ LARGE AND WIDESPREAD DEPOSITS OF LIGNITE
 - LOW CALORIFIC VALUE <10 MJ/kg
 - LOW ASH < 10%
 - VERY HIGH MOISTURE > 40%

▪ BIOMASS

- ▶ LOCALISED DEPOSITS (WOOD CHIPS)
- ▶ WIDESPREAD DEPOSITS (STRAW)
 - LOW CALORIFIC VALUE <12MJ/kg
 - HIGH OXYGEN CONTENT
 - MODERATE ASH >20%
 - HIGH MOISTURE >30%



PYROLYSIS

Pyrolysis is the conversion of heavy organic molecules at high temperature in the absence of oxygen.

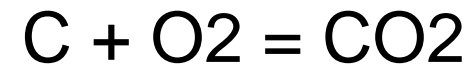
- **LARGE HYDROCARBON MOLECULES**
 - ▶ UNSTABLE RELATIVE TO THE ELEMENTS - CARBON, HYDROGEN
 - ▶ CONTAIN BONDS OF LOWER INTRINSIC ENERGY
 - CRACK AT LOW TEMPERATURES (300C)
- **SMALL HYDROCARBONS (< HEXANE)**
 - ▶ STABLE RELATIVE TO ELEMENTS AT TEMPERATURES < 600C
 - ▶ FOUND IN GASEOUS PHASE OF PRODUCT
- **OXYGENATES**
 - ▶ OXYGEN INCREASES STABILITY
 - ▶ WATER IN FEED CAN GENERATE OXYGENATES
 - ▶ OXYGENATES FOUND IN THE PRODUCTS
 - ▶ **OXYGENATES ARE WATER SOLUBLE**
 - TAR ACIDS, PHENOLS, CRESOLS

GASIFICATION AND PARTIAL OXIDATION

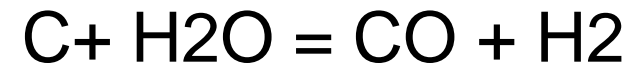
The principal chemical reactions are:

Solid - Gas Reactions:

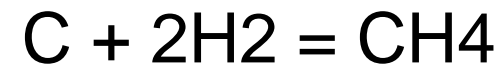
Combustion:



Steam Carbon:



Hydro-gasification:

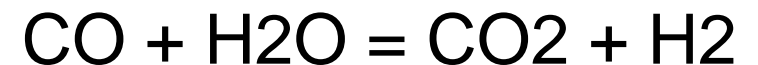


The Boudouard Reaction:

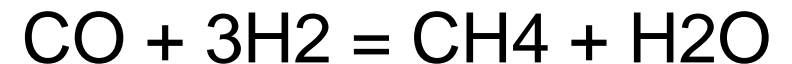


Gas Phase Reactions

Water-Gas-Shift:



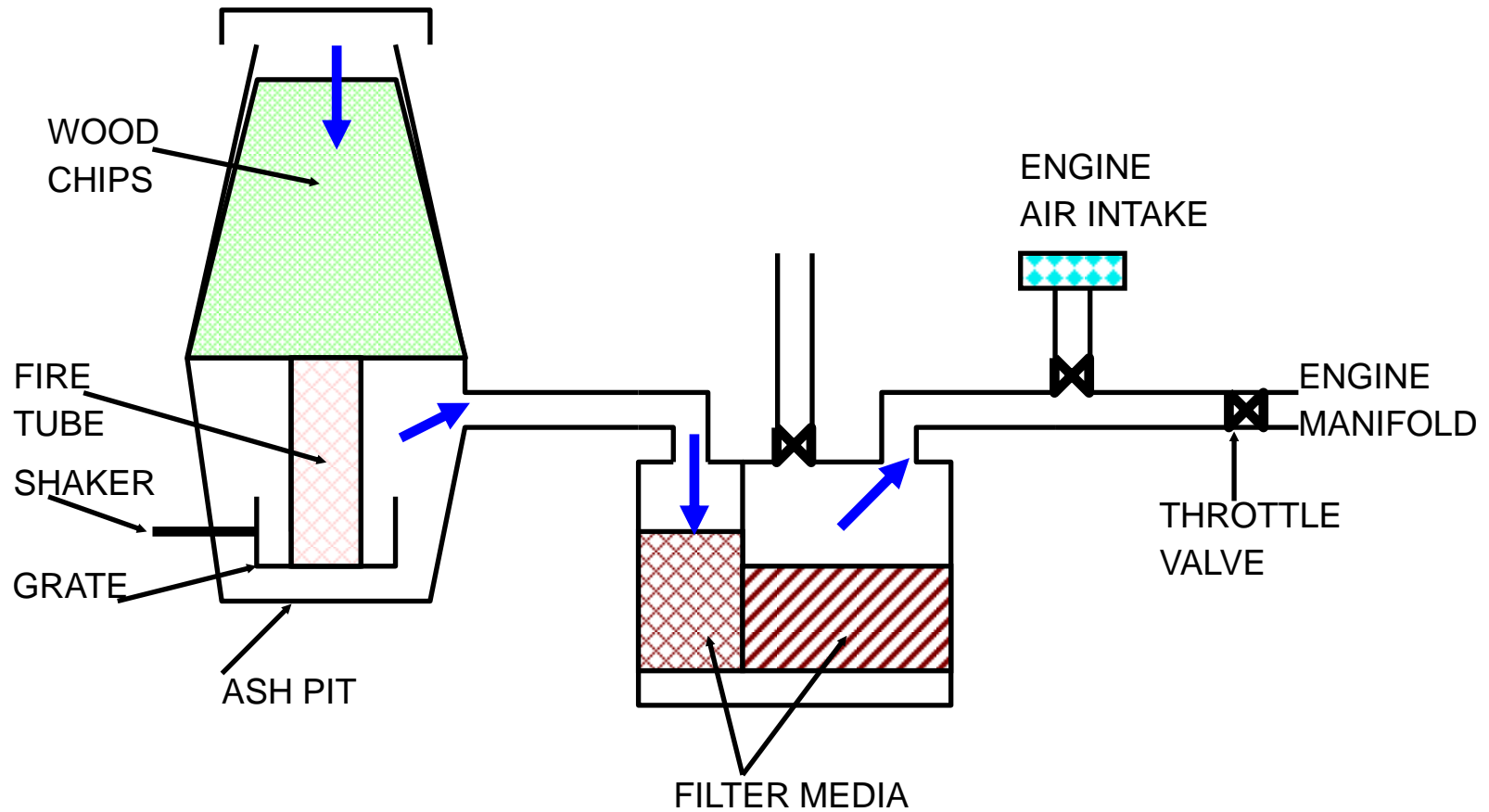
Methanation:



Pyrolysis

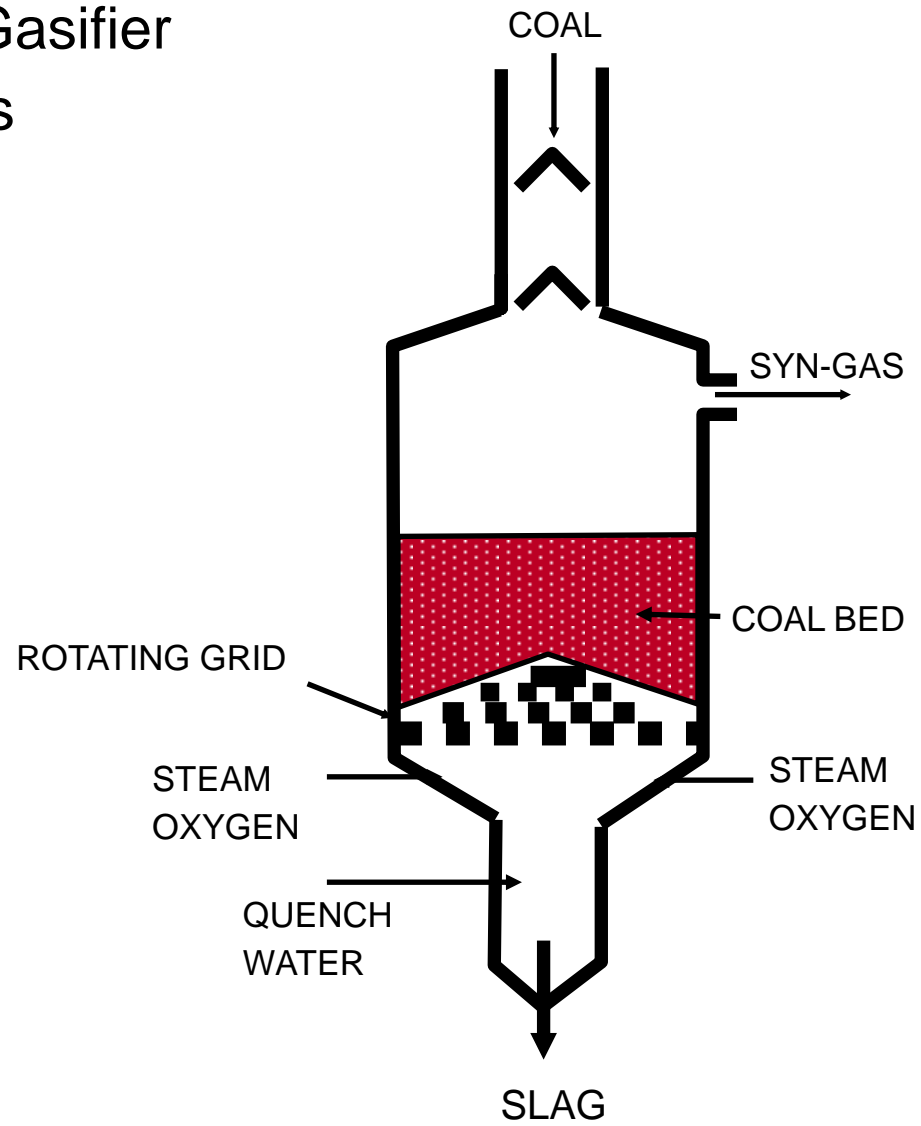
As well as these reactions, large molecules undergo pyrolysis and hydro-pyrolysis to small molecules.

STRATIFIED DOWNDRAFT GASIFIER



Moving Bed Gasifier

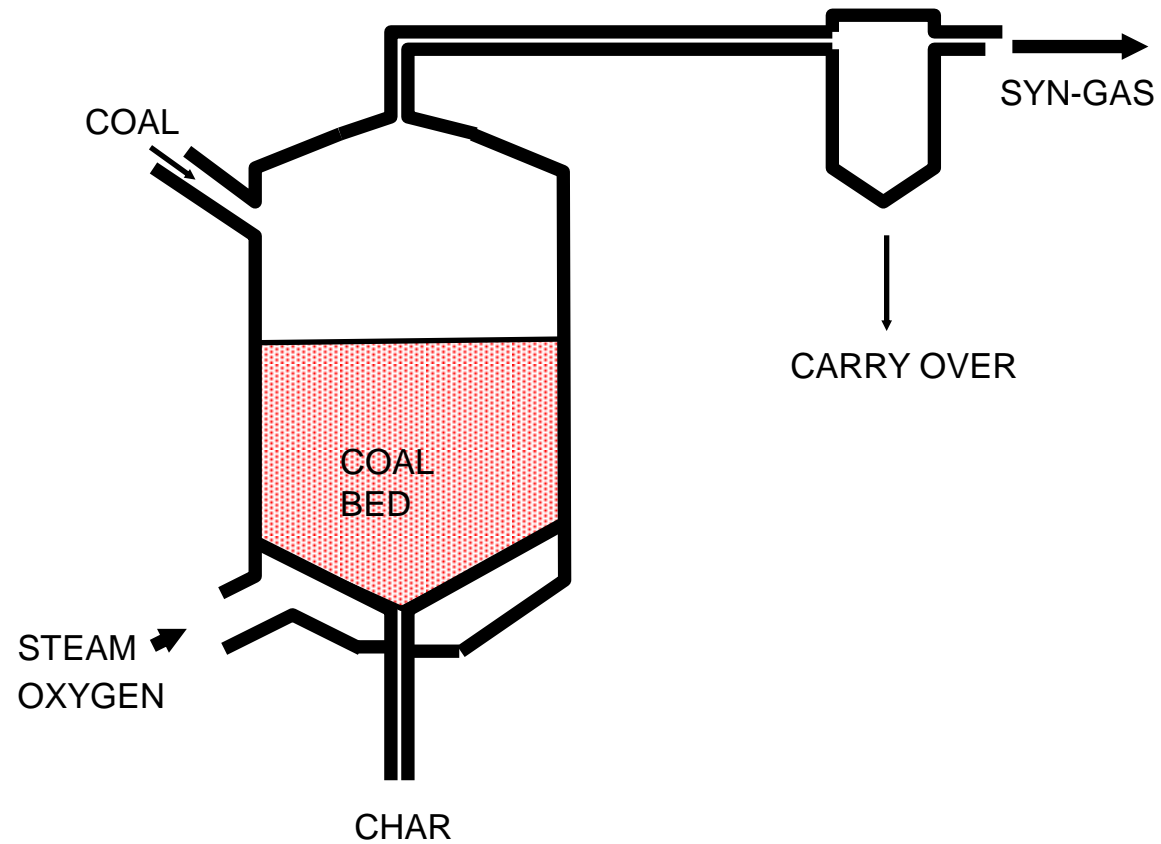
Coal as lumps



Fluidized Bed Gasifier

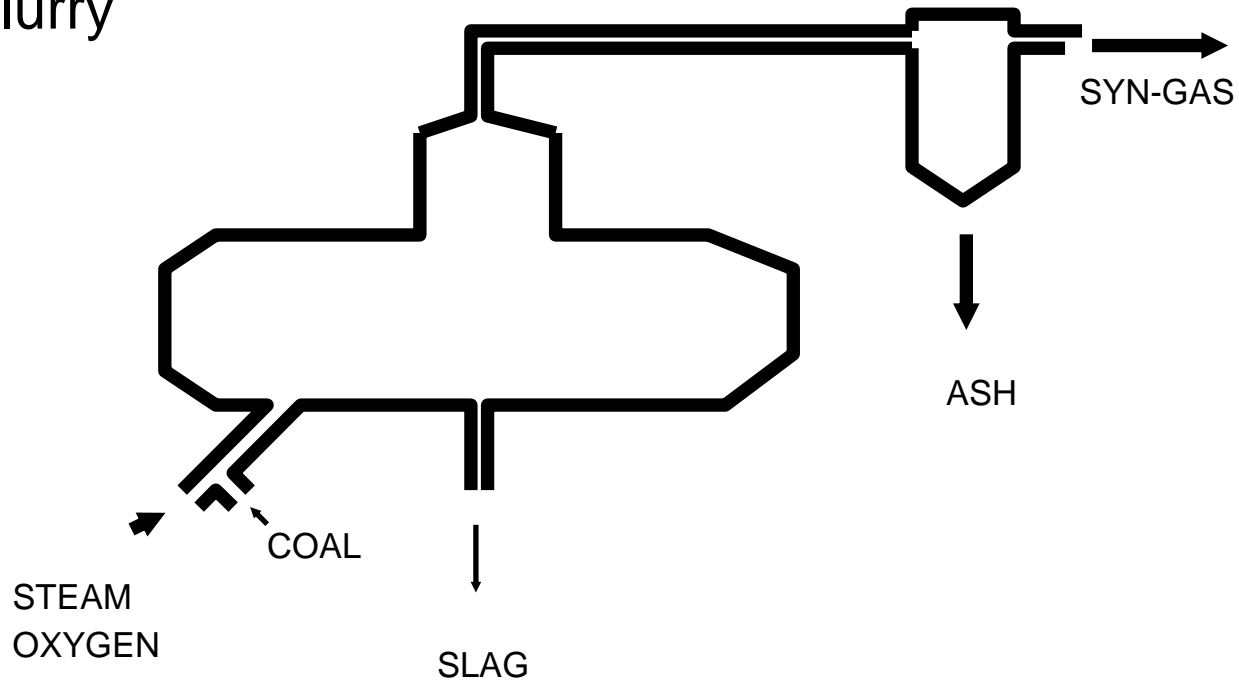
Coal as fines

WINKLER
U-GAS



Entrained Bed Gasifier

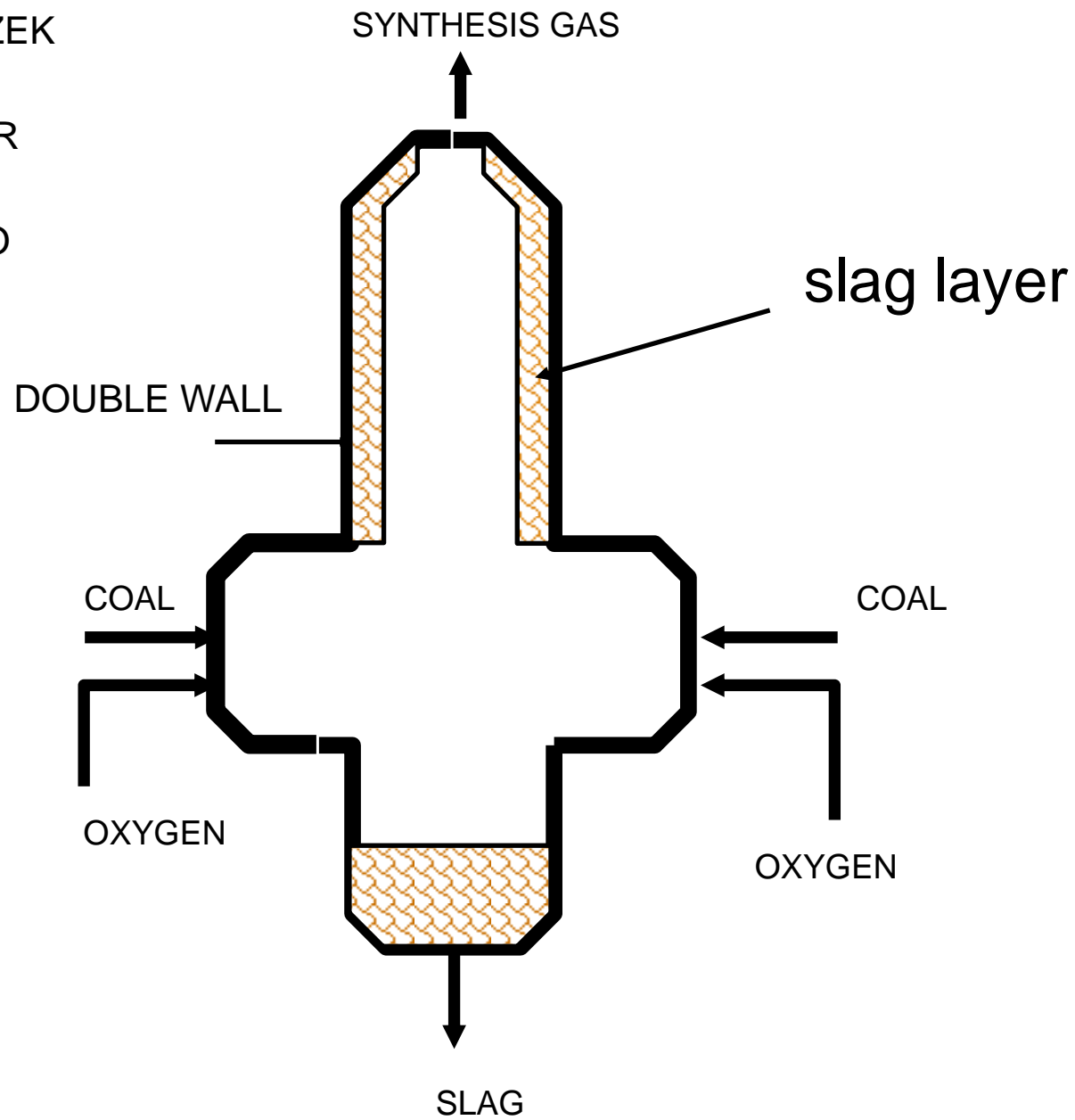
Coal as fines in gas or water slurry



KOPPERS - TOTZEK

SHELL - GASIFIER

UHDE - PRENFLO



CONOCOPHILLIPS

SYNTHESIS GAS

CHAR

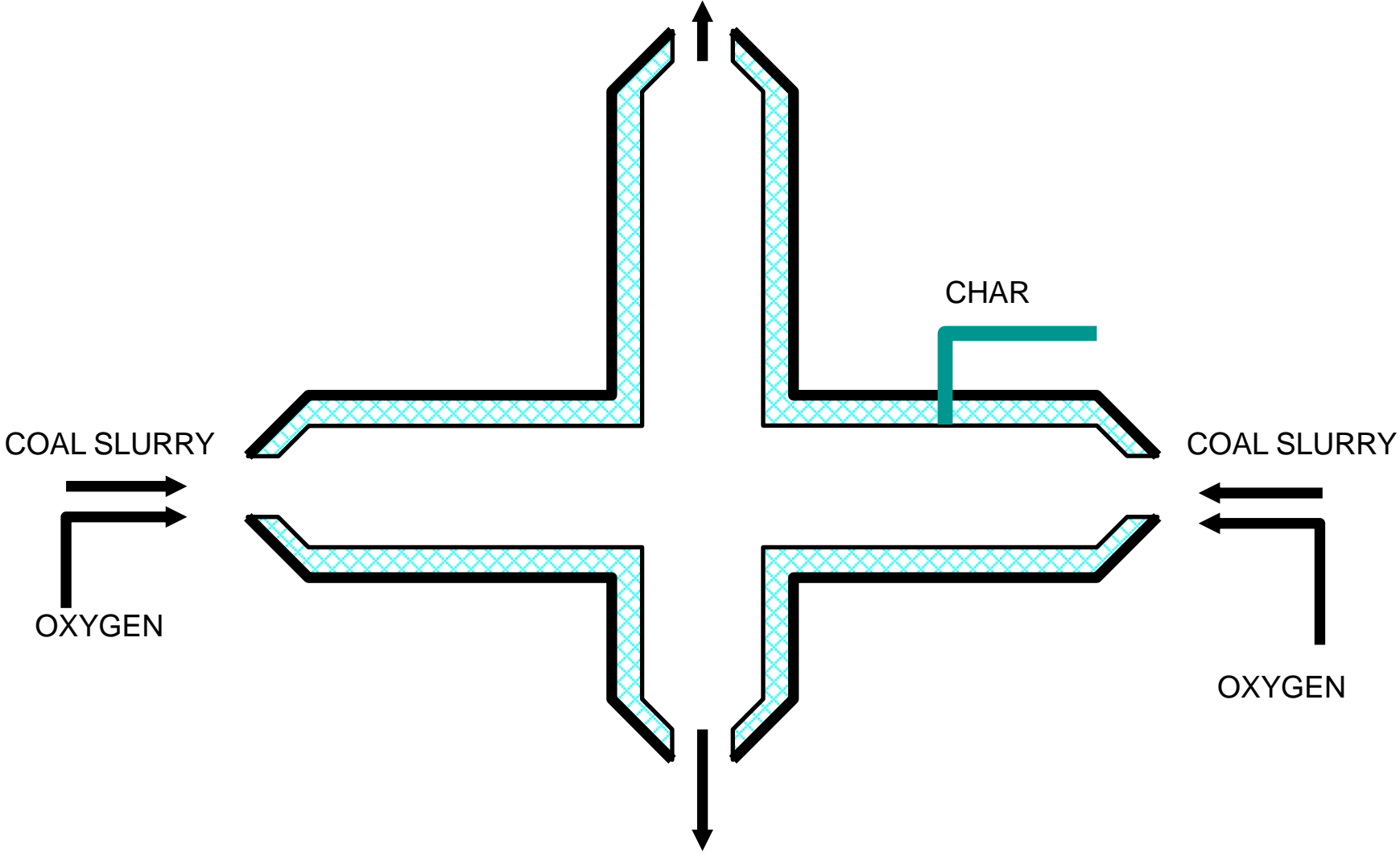
COAL SLURRY

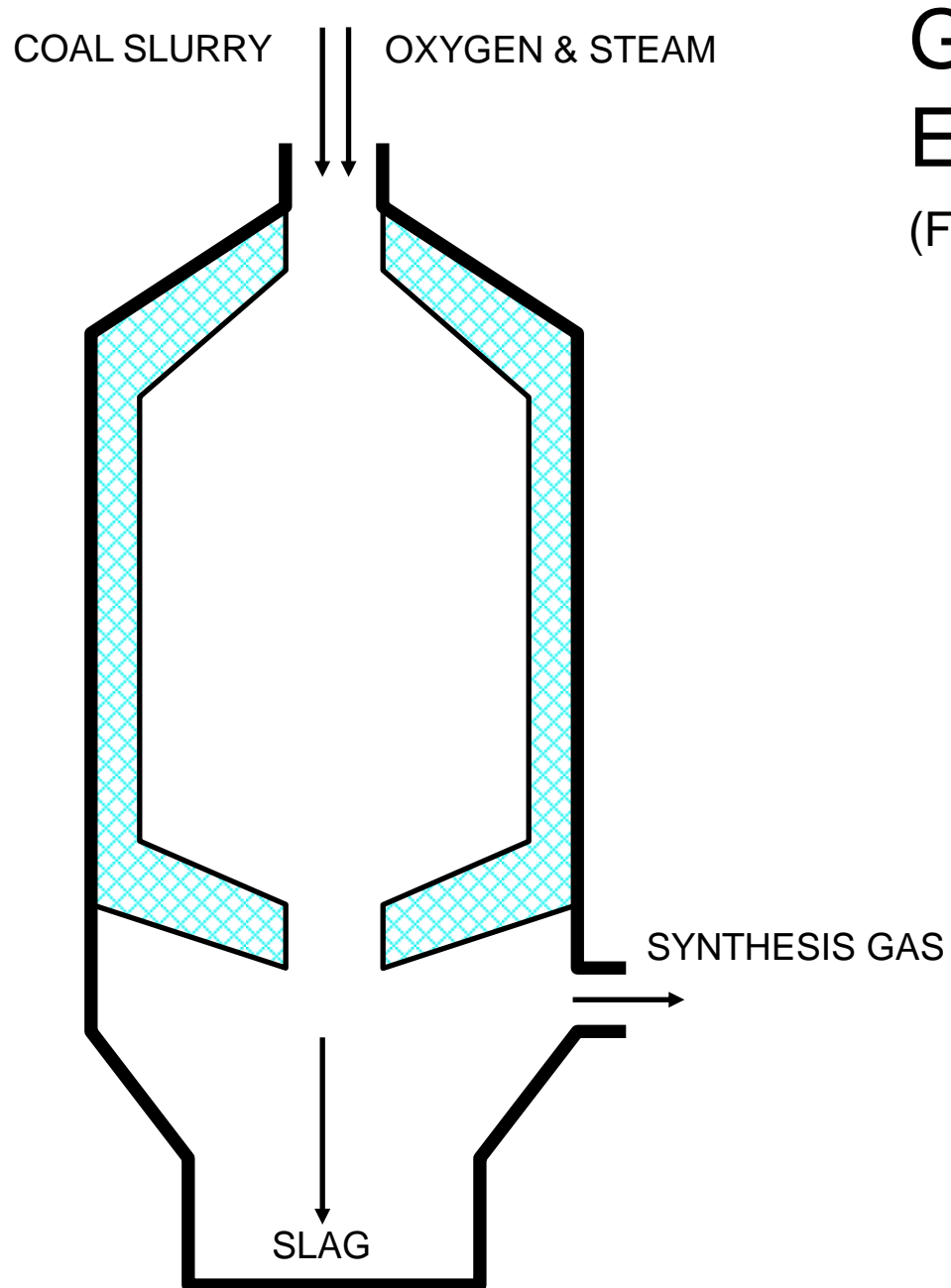
COAL SLURRY

OXYGEN

OXYGEN

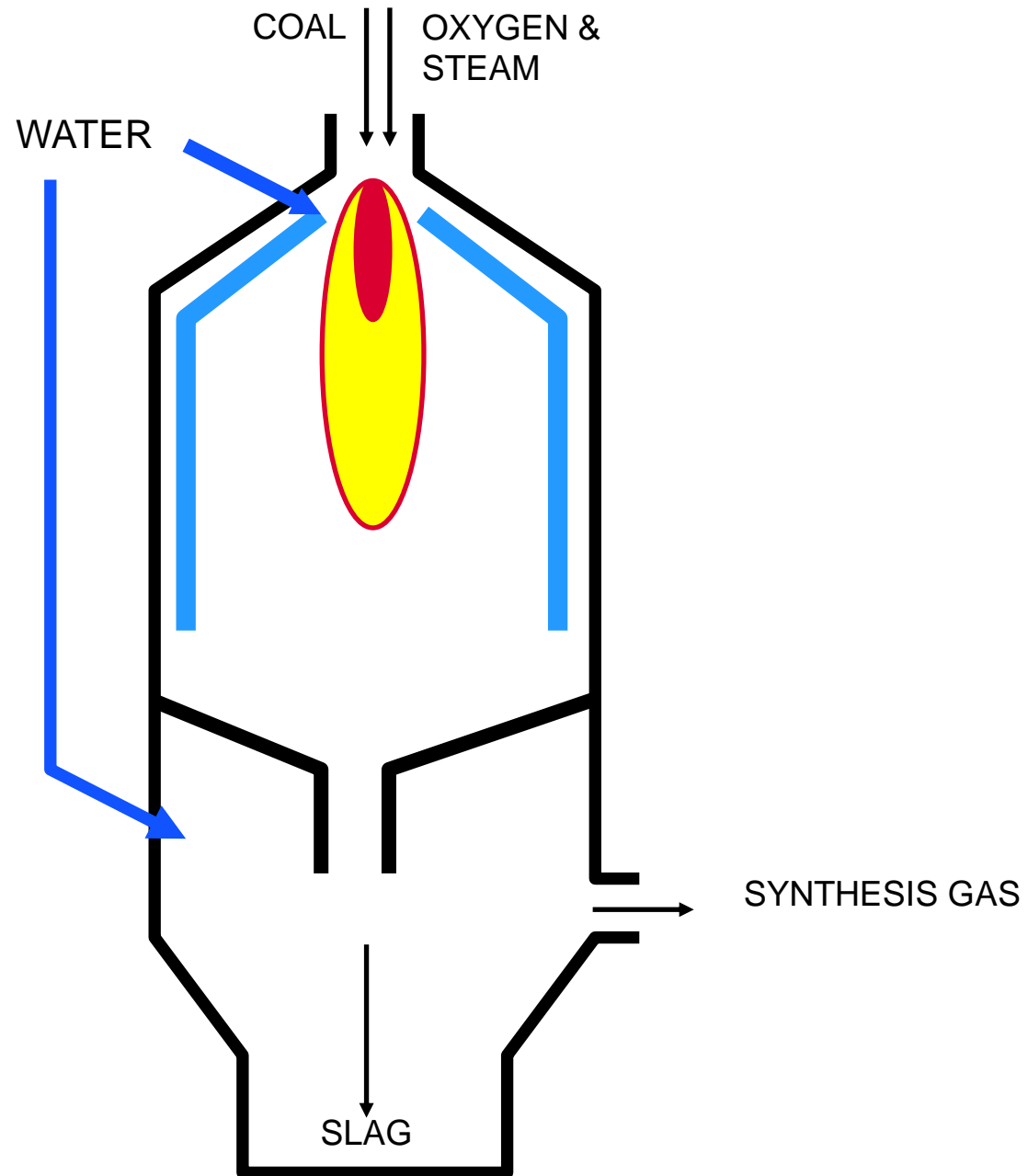
SLAG



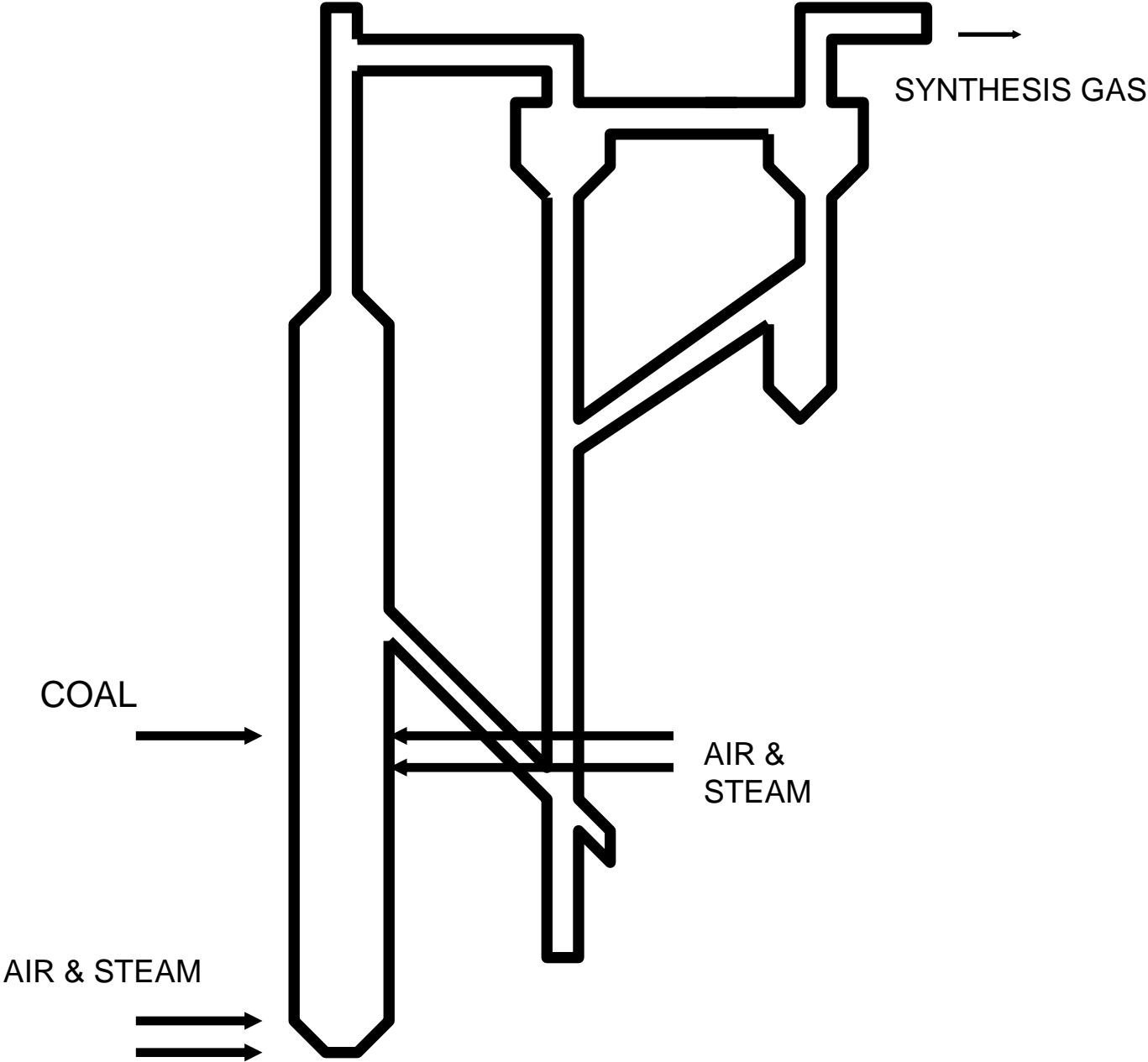


GE
ENERGY
(Formerly Texaco)

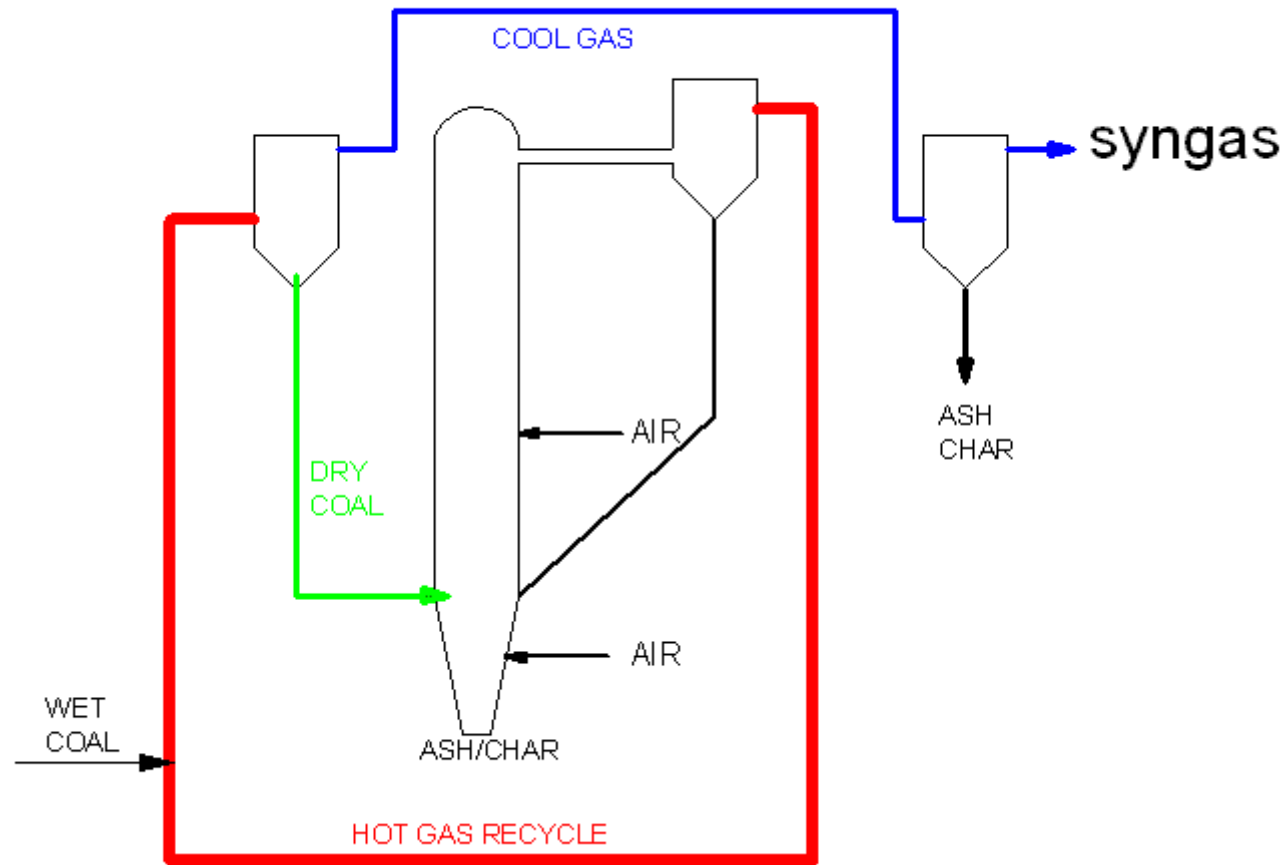
SIEMENS



KBR



HRL Integrated drying and gasification



GASIFIER PERFORMANCE DEPENDS ON:

1 GASIFIER TYPE

- SLAGGING
- NON SLAGGING

2 COAL PROPERTIES

- RANK
- WATER CONTENT
- ASH CONTENT
- SODIUM CONTENT

3 OXYGEN IN FEED

- OXYGEN IN COAL
- OXYGEN FEED
- WATER SLURRY

Performance of different gasifiers with Illinois No.6

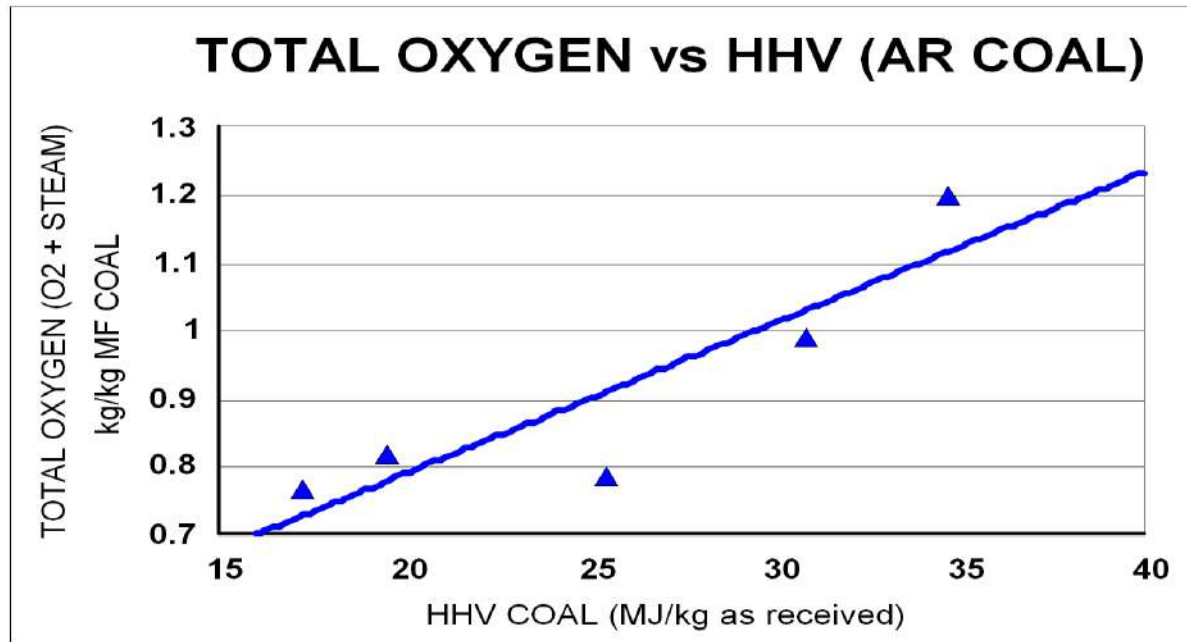
	Lurgi	BG/L	KRW	Texaco	Shell
Type of bed	Moving	Moving	Fluid	Entrained	Entrained
Pressure (MPa)	0.101	2.82	2.82	4.22	2.46
Ash Type	ash	Slag	Aglom.	Slag	slag
H ₂	52.2	26.4	27.7	30.3	26.7
CO	29.5	45.8	54.6	39.6	63.1
CO ₂	5.6	2.9	4.7	10.8	1.5
CH ₄	4.4	3.8	5.8	0.1	0.03
Other hydrocarbons	0.3	0.2	<0.01	Nil	Nil
H ₂ S	0.9	1.0	1.3	1.0	1.3
H ₂ S/COS	20/1	11/1	9/1	42/1	9/1
N ₂ + A	1.5	3.3	1.7	1.6	5.2
H ₂ O	5.1	16.3	4.4	16.5	2.0
NH ₃ + HCN	0.5	0.2	.08	0.1	0.02

Variation of Oxygen Demand with Coal Type

COAL	N. DAKOTA	WYOMING	ILLINOIS	UPPER	POCAHONTAS
	LIGNITE	PRB	No 6	FREEPORT	No 3
HHV (MJ/kg MF coal)	25.59	27.25	27.8	31.32	34.95
HHV (MJ/kg AR coal)	17.34	19.6	25.58	30.97	34.72
MOISTURE (kg/kg coal)	32.24%	28.09%	7.97%	1.13%	0.65%
OPERATING TEMP (C)	1400	1400	1450	1500	1550
DRIED TO 5% MOISTURE					
OXYGEN (kg/kg mf coal)	0.768	0.818	0.744	0.807	1.023
STEAM (kg/kg mf coal)	0	0	0.044	0.186	0.178

COMPARISON OF COAL AND WOOD GASIFICATION

	Lurgi	Shell	DDG
	COAL	COAL	WOOD
Type of bed	Moving	Entrained	
Pressure (MPa)	0.101	2.46	0.101
Ash Type	ash	slag	ash
H ₂	52.2	26.7	14.5
CO	29.5	63.1	14.7
CO ₂	5.6	1.5	15.5
CH ₄	4.4	0.03	2.5
Other hydrocarbons	0.3	Nil	0.37 +BTX
H ₂ S	0.9	1.3	
H ₂ S/COS	20/1	9/1	
N ₂ + A	1.5	5.2	52.3
H ₂ O	5.1	2.0	
NH ₃ + HCN	0.5	0.02	0.08



SYNTHESIS GAS CLEAN UP

– REMOVAL OF

▪ ASH AND DUST

- cyclones, bag filters, candle filters

▪ PYROLYSIS TARs

- wash columns

▪ HEAT

- waste heat boilers
- quench

– SHIFT OF CO TO H₂

Stoichiometric Ratio (SR) = H₂/CO (molar)

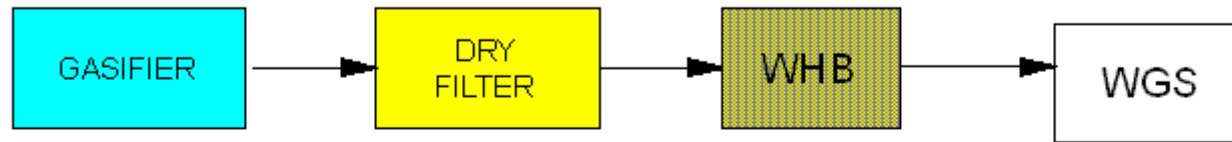
– REMOVAL OF

▪ CO₂

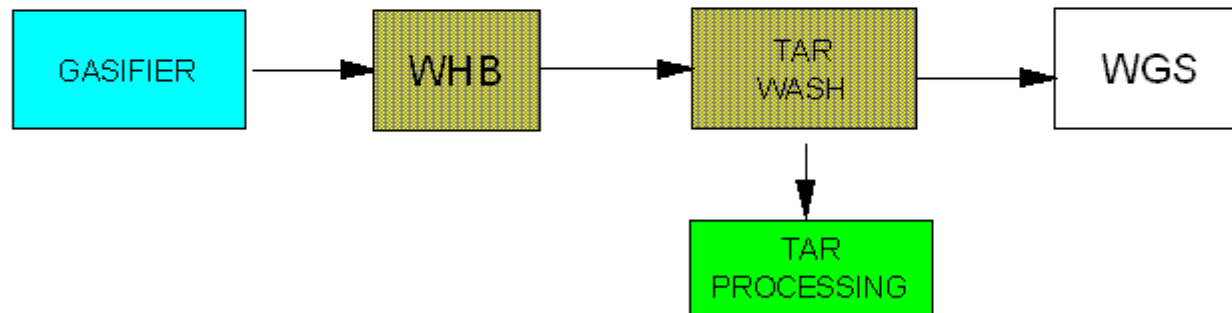
▪ H₂S (and other S compounds)

APPROACHES TO FIRST STAGE CLEANING

ENTRAINED BED



MOVING BED



BTL



SR REQUIREMENTS OF DIFFERENT TECHNOLOGY

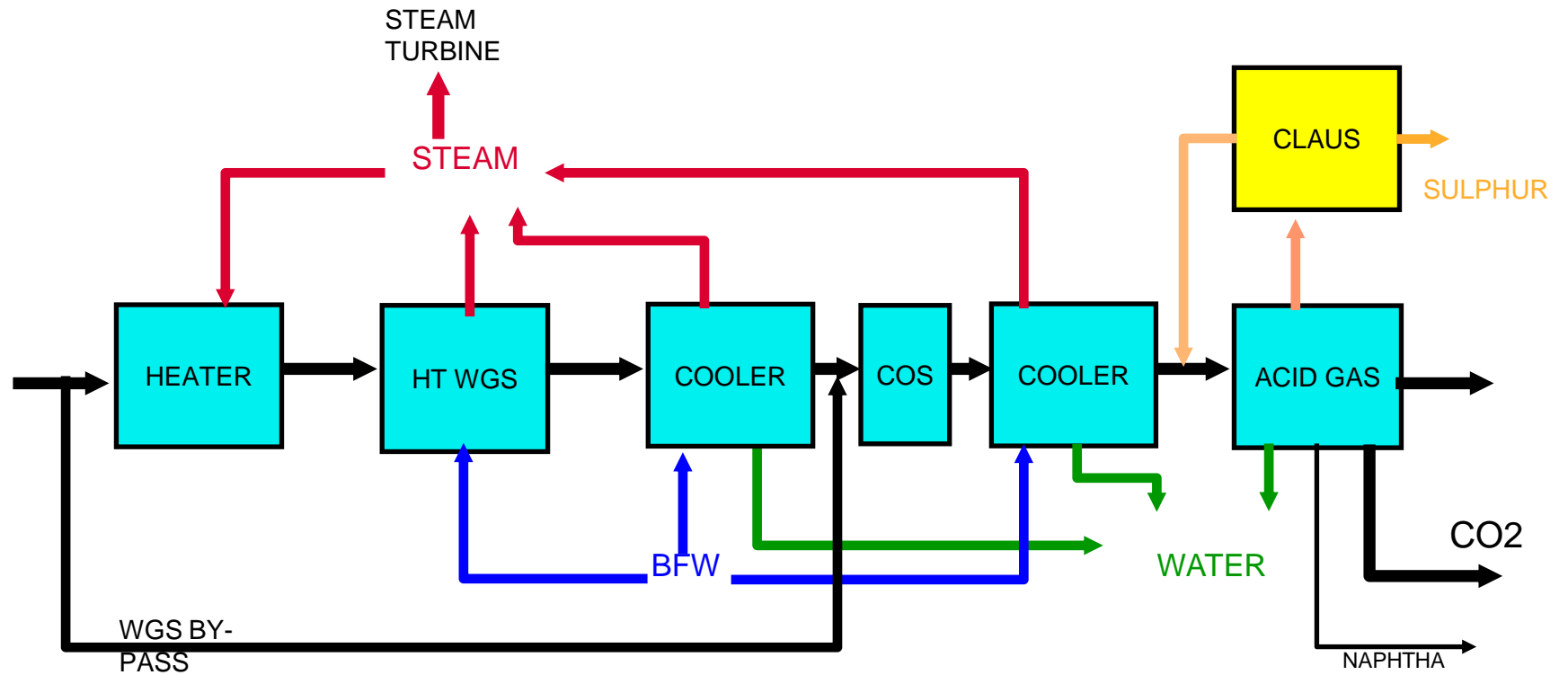
PRODUCT	H ₂ :CO	CAPACITY (000t/a)	SYNGAS (000Ncm/h)
Methanol	2:1	160 - 1,700	48 - 250
Fischer-Tropsch (Fe)	1.75:1	637 + (a)	48 - 250
Fischer-Tropsch (Co)	2:1	637 + (a)	48 - 250
Acetic Acid	0:1	275 - 545	18 - 36
Acetic Anydride	0:1	90	3.5
Oxo Alcohols	2:1	115 - 275	12 - 25
Phosgene (TDI)	0:1	45 - 160	3.5 - 12
Formic Acid	0:1	45	3.5
Methyl Formate	0:1	9	0.6
Propionic Acid	0:1	45 - 68	2.4 - 3.5
Methyl Methacrylate	1:1	45	4.7
1,4 - Butanediol	2:1	45	4.7

(a) 15,000bbl/d

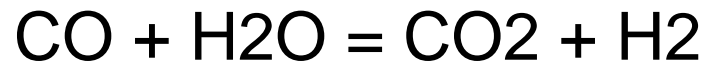
Impact of impurities in the synthesis gas on downstream processes

Component	Power	Ammonia	Methanol	Fuels
dust	No	No	No	No
H ₂	Yes	Yes	Yes	Yes
CO	Yes	Yes	Yes	Yes
CO ₂	Inert	No	Some	No
CH ₄	Yes	Inert	Inert	Inert
H ₂ O	Inert	No	Inert	No
H ₂ S + COS	No	No	No	No
N ₂	Inert	Yes	Inert	No
Cl	No	No	No	No

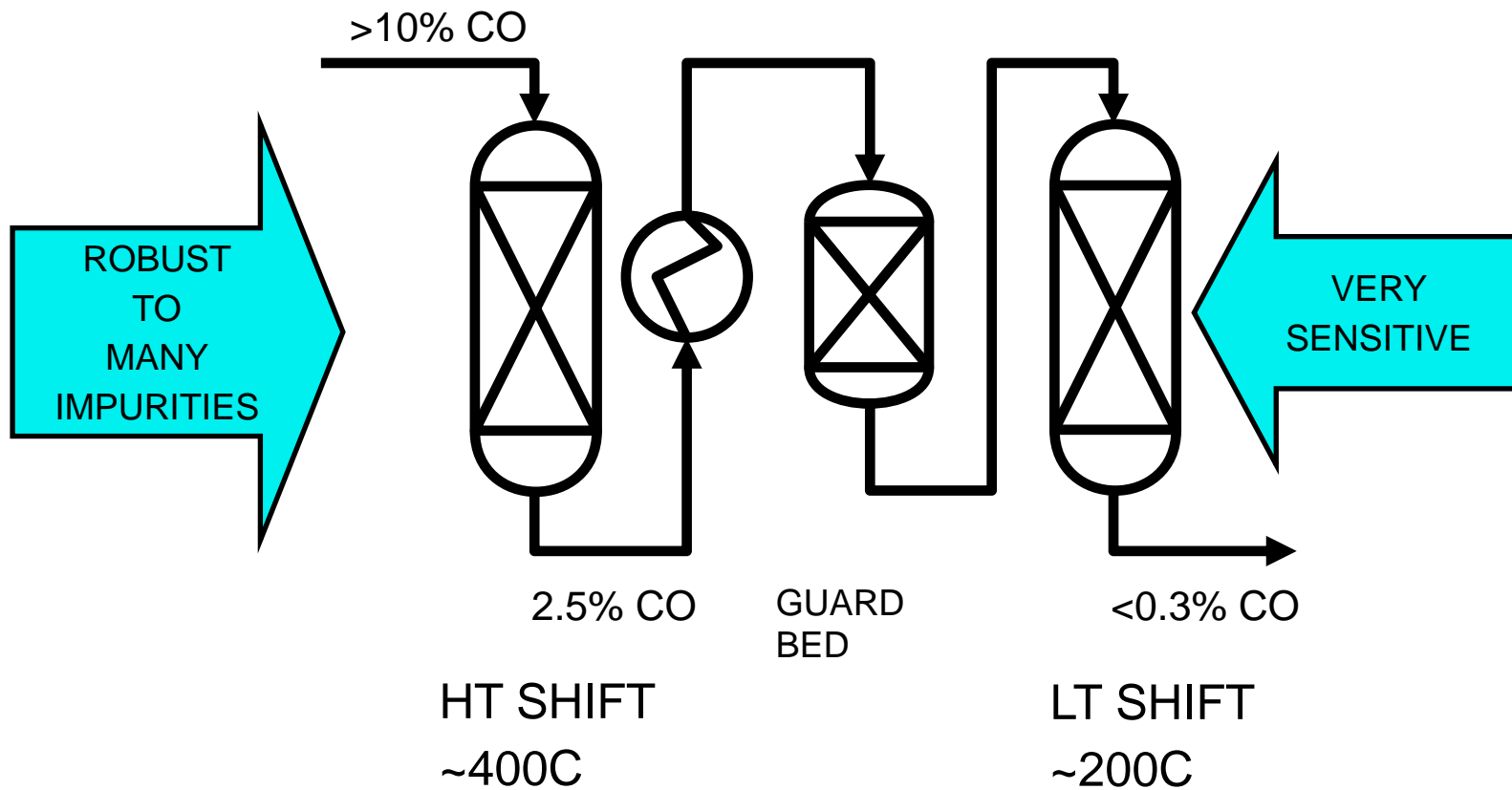
WGS SHIFT AND ACID GAS



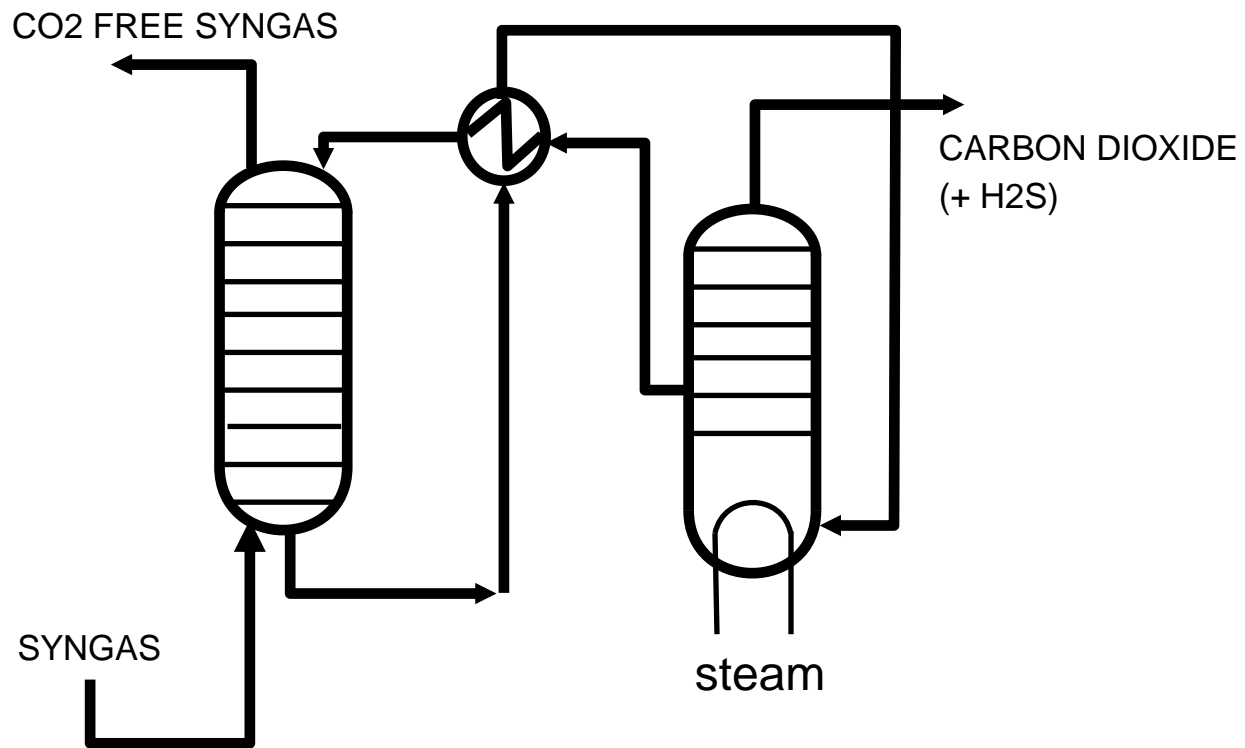
ANY SR CAN BE OBTAINED USING WGS



WATER-GAS-SHIFT



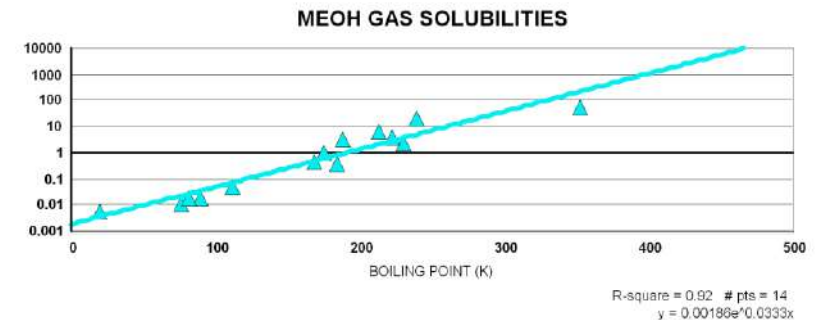
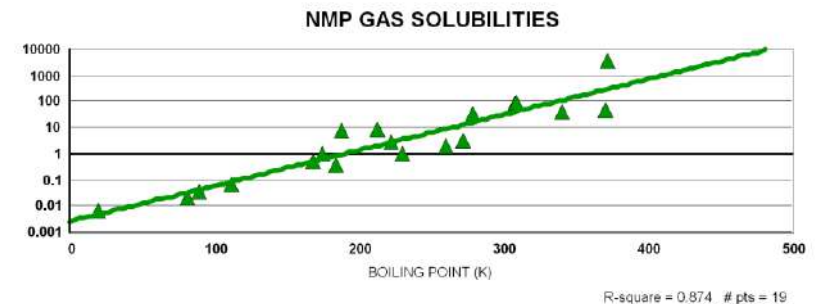
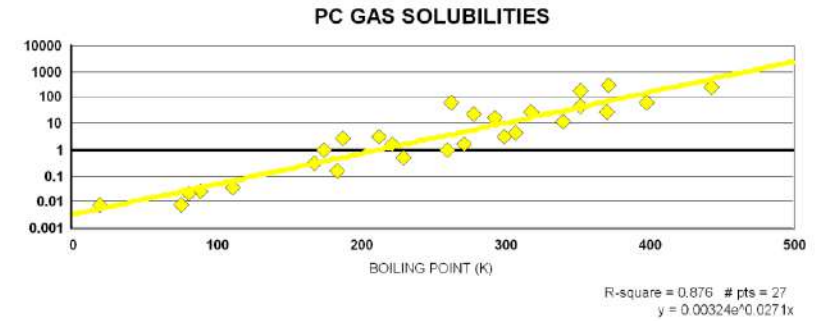
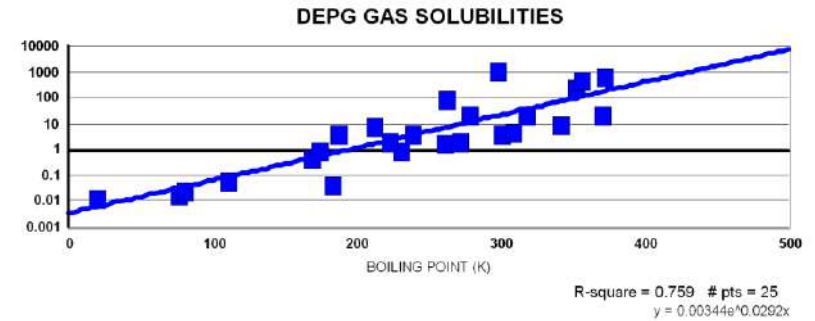
ACID GAS (CARBON DIOXIDE) STRIPPING



GAS SOLUBILITIES @25C

B.Burr, L. Lyddon, Hydrocarbon Processing, January 2009, p. 43

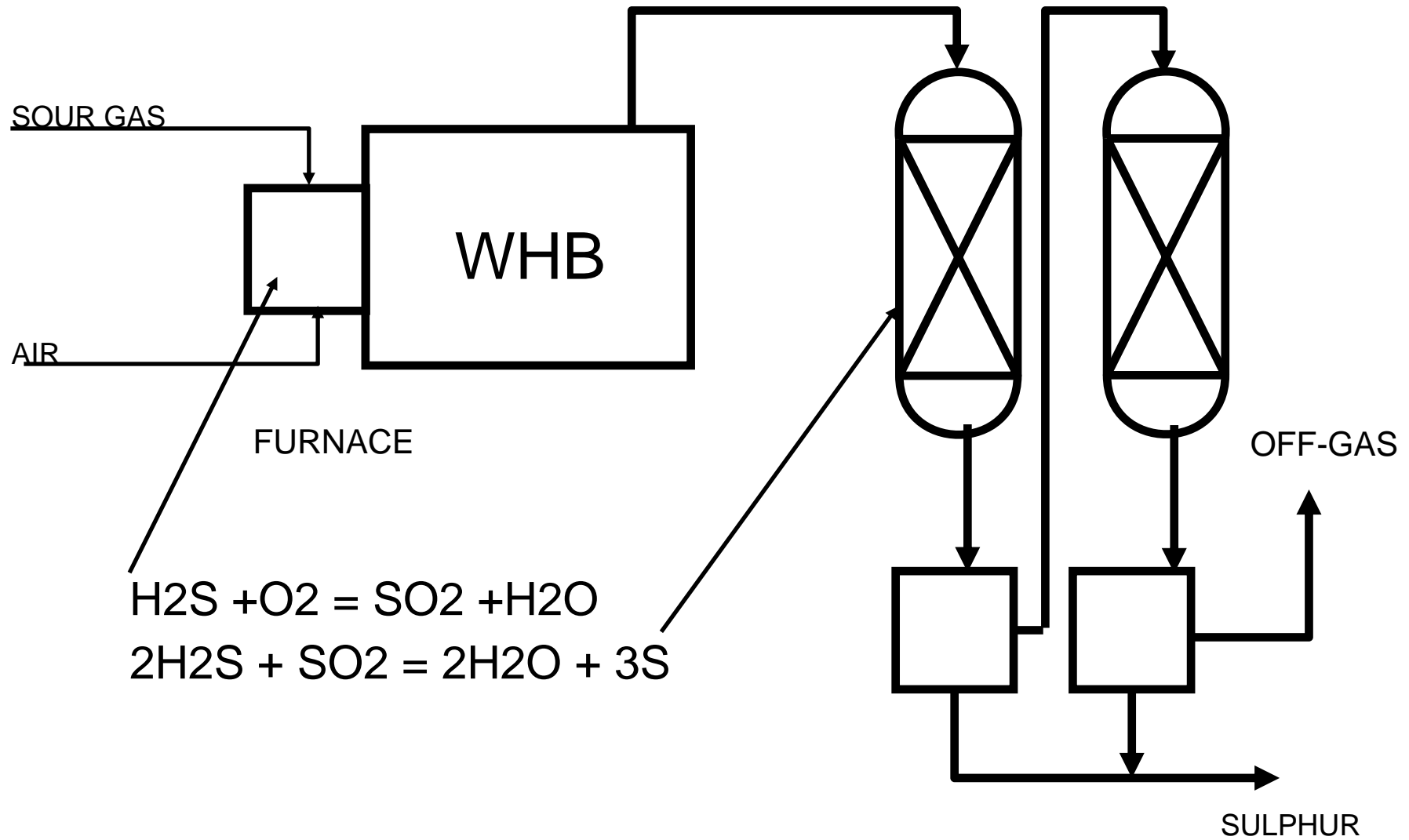
	density (kg/L)	bp (K)	DEPG	PC	NMP	MeOH
			1.03	1.195	1.027	0.785
H2		20.4	0.013	0.0078	0.0064	0.0054
N2		77.4	0.02	0.0084		0.012
O2		90.2		0.026	0.035	0.02
CO		81.7	0.028	0.021	0.021	0.02
CH4		112	0.066	0.038	0.072	0.051
C2H6		184.6	0.042	0.17	0.38	0.42
C4H4		169.3	0.47	0.35	0.55	0.46
CO2		175	1	1	1	1
C3H8		231.1	1.01	0.51	1.07	2.35
i-C4H10		261.4	1.84	1.13	2.21	
n-C4H10		272.7	2.37	1.75	3.48	
COS		223	2.3	1.88	2.72	3.92
i-C5H12		301	4.47	3.5		
C2H2		188.4	4.47	2.87	7.37	3.33
NH3		240	4.8			23.2
n-C5H10		309.2	5.46	5		
H2S		213.5	8.82	3.29	10.2	7.06
NO2		294.3		17.1		
n-C6H14		341.9	11	13.5	42.7	
CH3SH		279.1	22.4	27.2	34	
n-C7H16		371.6	23.7	29.2	50	
CS2		319	23.7	30.9		
c-C6H12		353.8		46.7		59.5
n-C8H18		398.8		65.6		
EtSH		308.2			78.8	
SO2		263.2	92.1	68.6		
CH3SCH3		310.5			91.9	
C6H6		353.2	250	200		
C10H22		444.7		284		
C4H4S		357.2	540			
H2O		373.2	730	300	4000	
HCN		299	1200			
CO2 SOLUBILITY						
	cuft/gal		0.485	0.455	0.477	0.425
	L/L		3.628	3.404	3.568	3.179
	L/kg		3.522	2.848	3.474	4.050



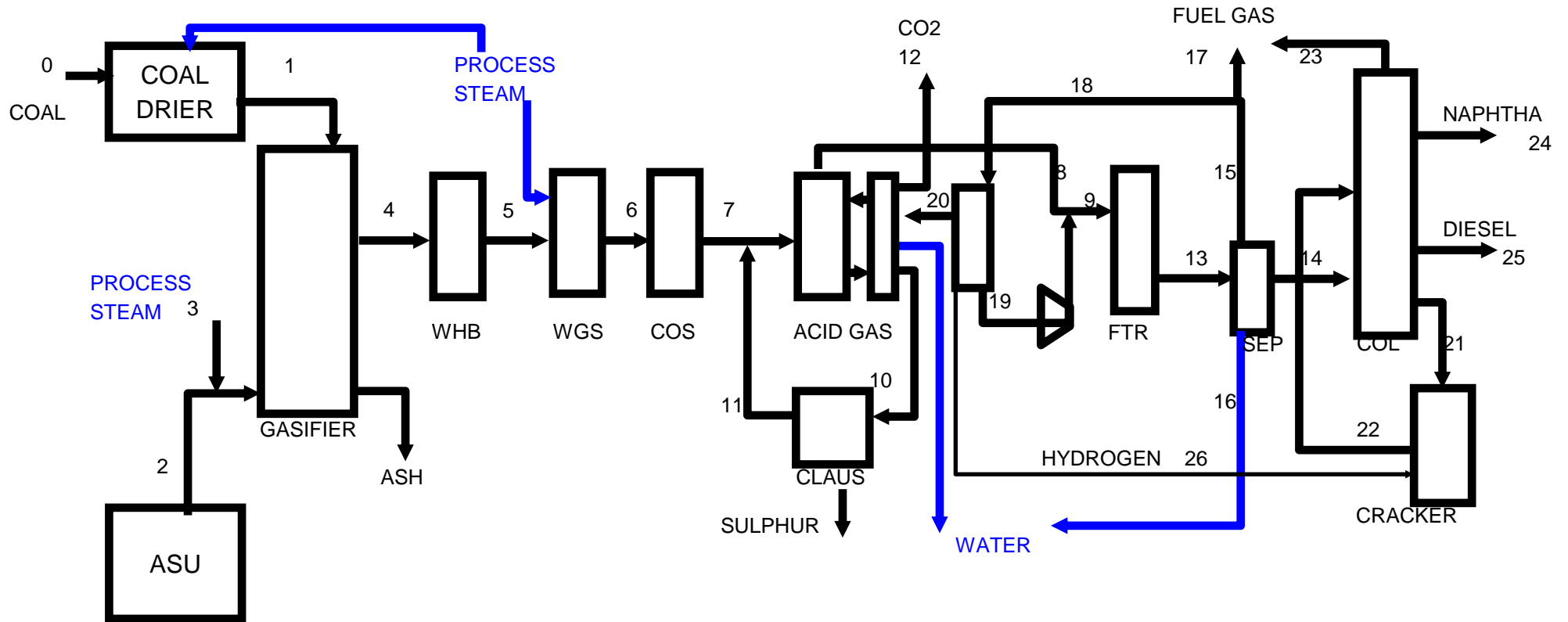
Boiling Point of Components of Interest

Gas	Boiling Point (T _b) Kelvins	Comments
H ₂	20	
N ₂	77	
CO	81	
A	87	
CH ₄	112	
(NO) ₂	122	mp. 112K
CO ₂	(175)	Sublimes at 195K, acidic
HCl	188	Acidic
H ₂ S	213	Acidic
COS	223	
NH ₃	240	
SO ₂	263	Acidic
HCN	299	Acidic
H ₂ O	373	mp. 273

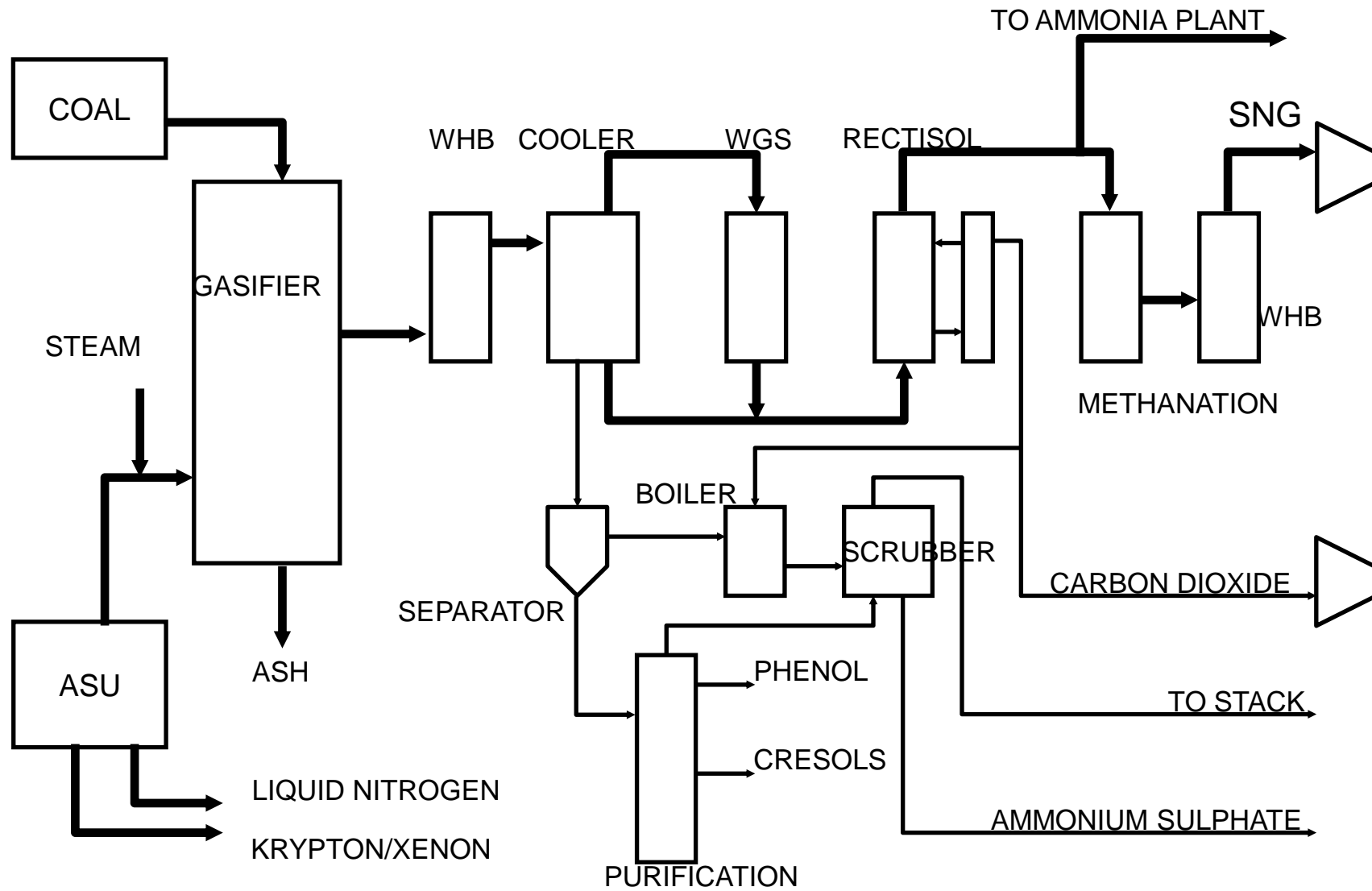
CLAUS PROCESS



COAL TO FT LIQUIDS - PROCESS FLOW



DAKOTA COAL GASIFICATION



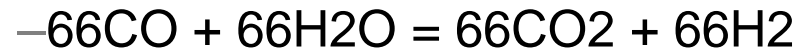
DIRECT ROUTE HAS HIGHER EFFICIENCY THAN FT ROUTE

■ FT ROUTE: 100 MOLES CARBON

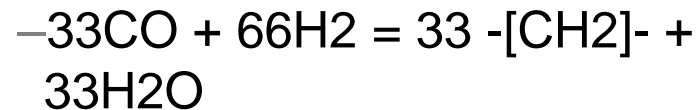
▶ GASIFIER



▶ WGS



▶ SYNTHESIS



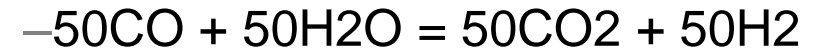
■ CARBON EFFICIENCY 33%

■ DIRECT ROUTE: 100 MOLES CARBON

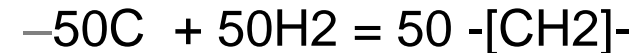
▶ GASIFIER



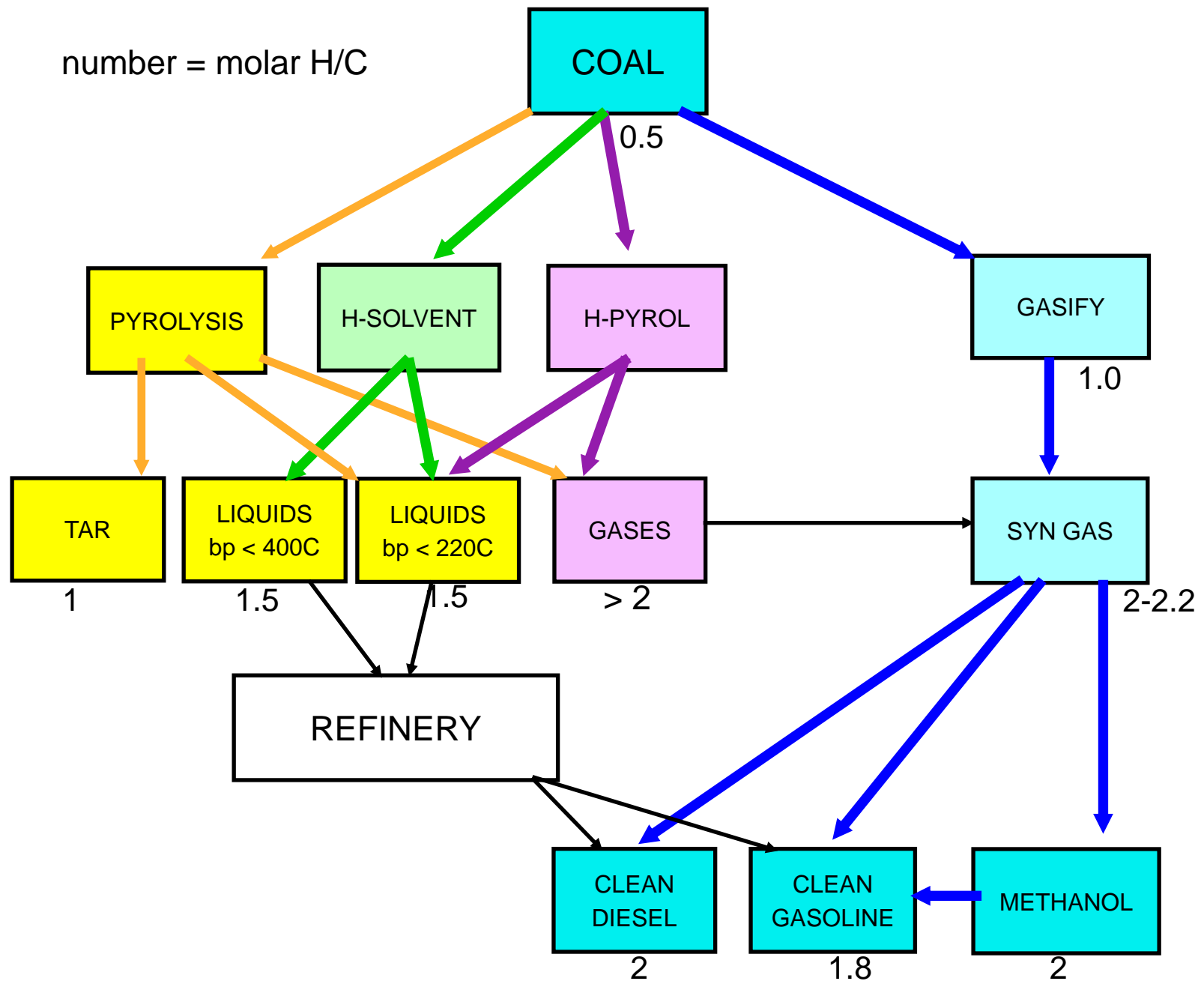
▶ WGS



▶ HYDROGENATION



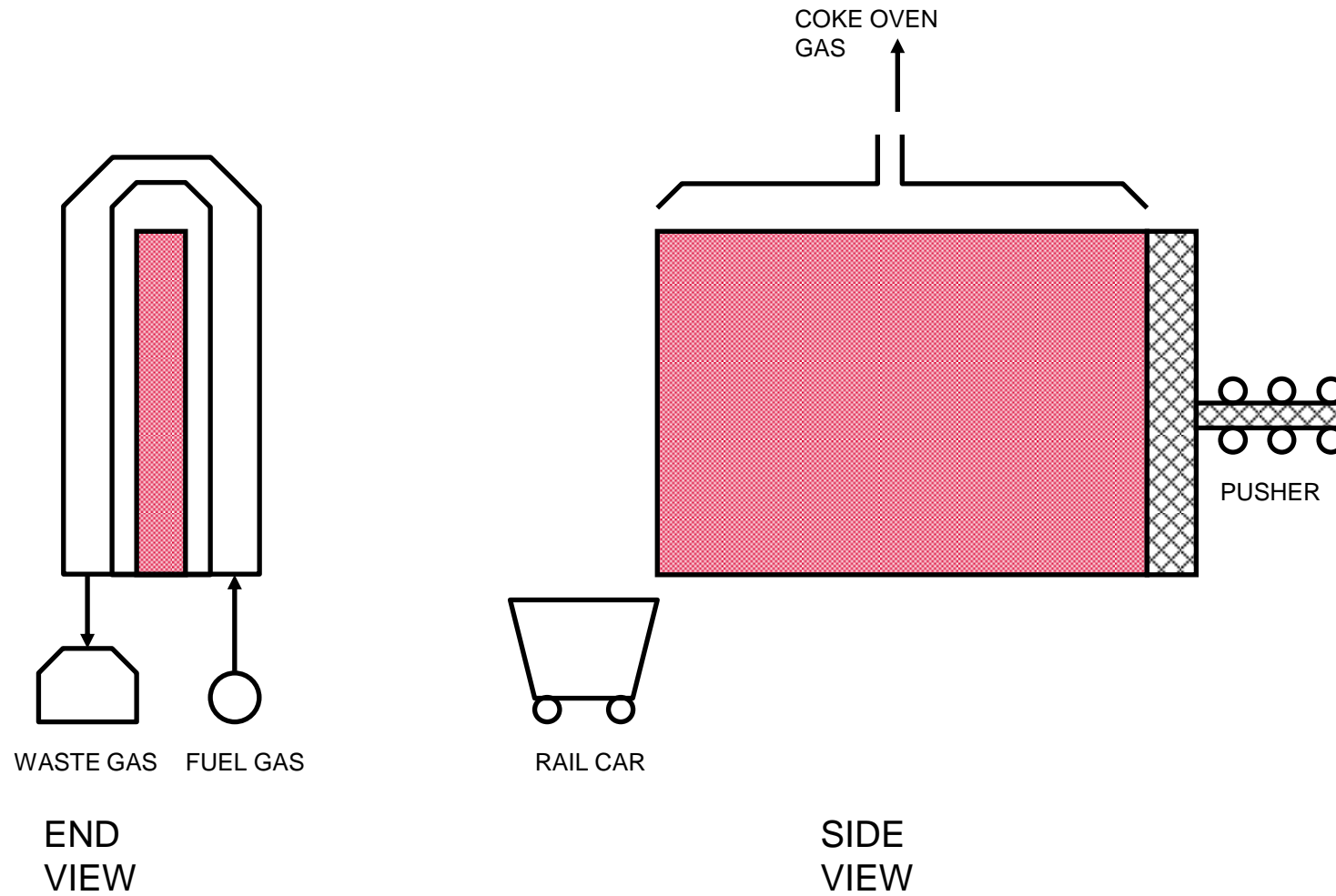
■ CARBON EFFICIENCY 50%



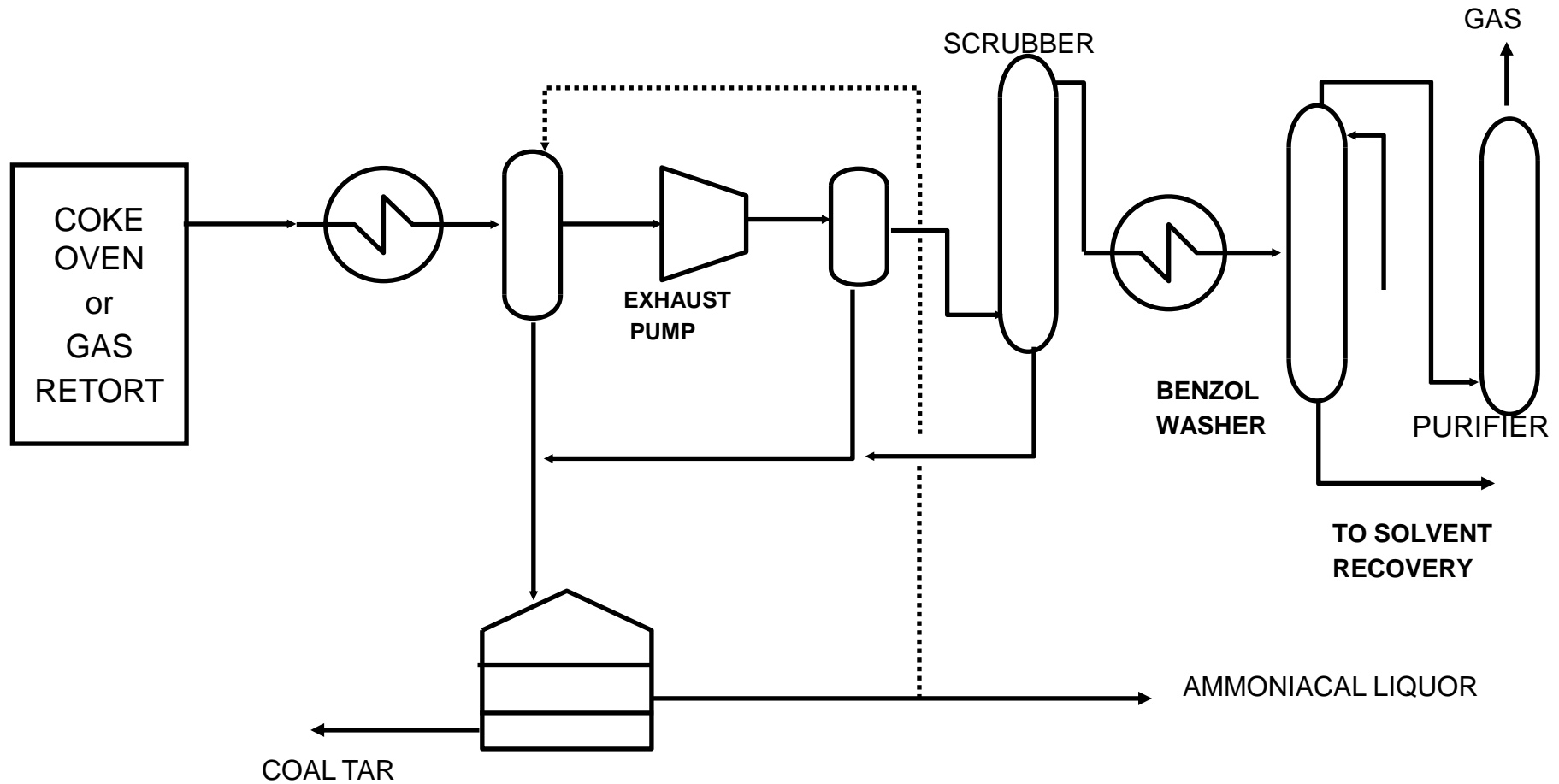
PYROLYSIS ROUTES

- Low temperature (450 - 600C) pyrolysis leads to higher liquid yields (15 - 20%).
- High temperature rapid (millisecond) pyrolysis can give higher liquid yields.
- Main product is char of lower hydrogen and heteroatom content
- Useful for upgrading lignites and the like to higher calorific value fuel
- Could potentially generate a large volume of liquids.
- Liquids need extensive further refining for transport fuel use.
- 3 technologies to pilot scale:
- 1992 (SGI International, Gillette Wyoming) Liquids from Coal (LFC) 1000 tpd sub bituminous coal with high moisture and sulphur content - low sulphur high HV solid and a liquid.

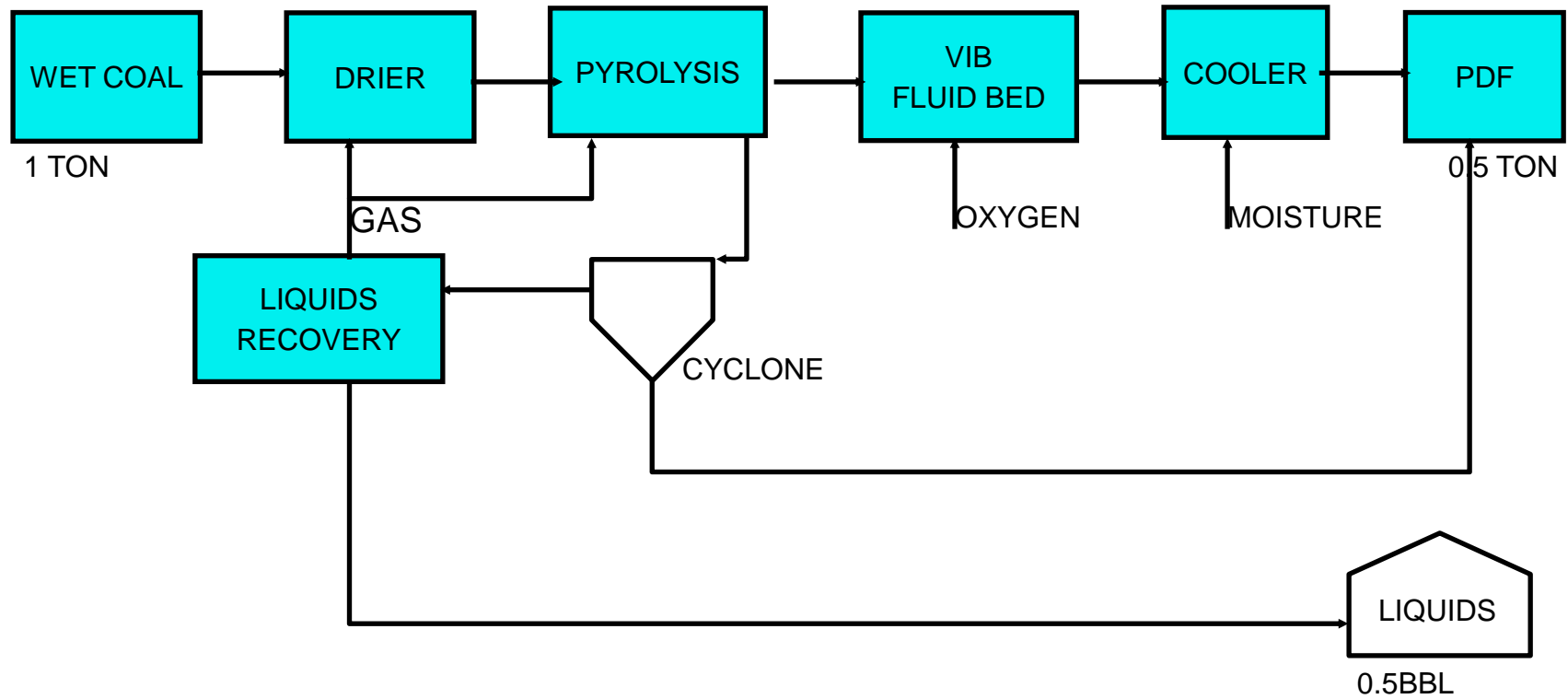
COKE OVEN



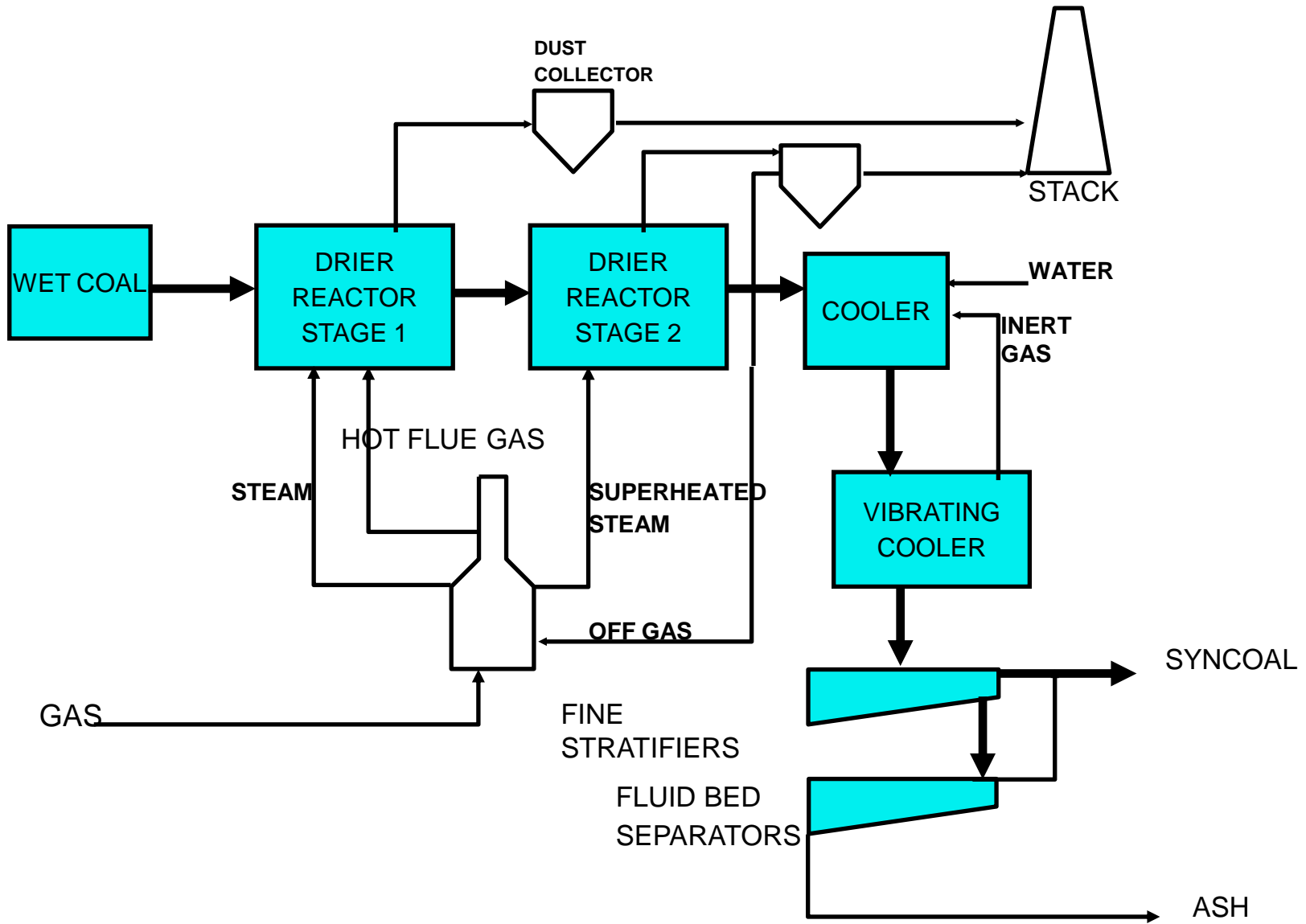
COKE AND TOWN GAS



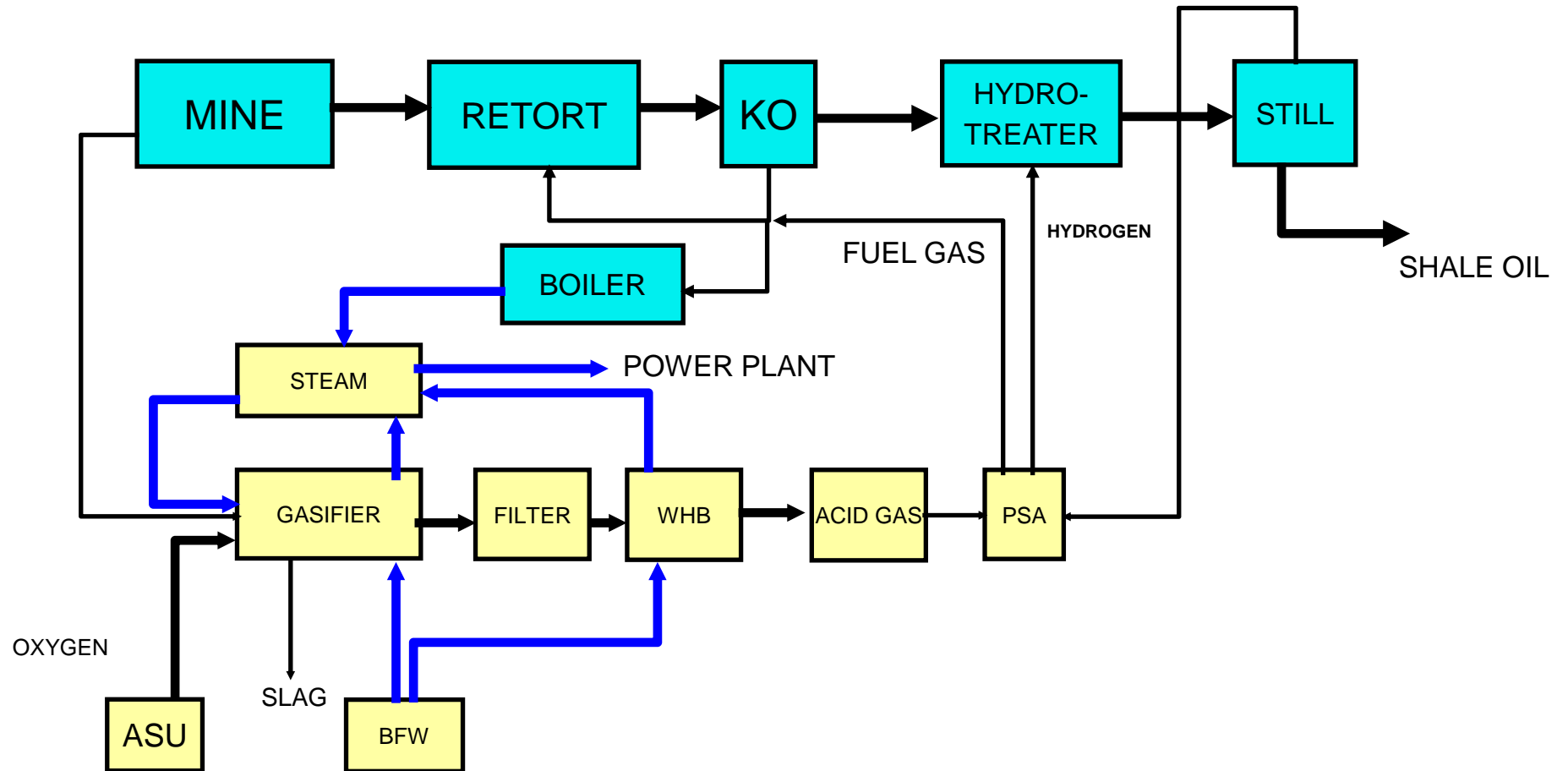
LFC (Encoal)



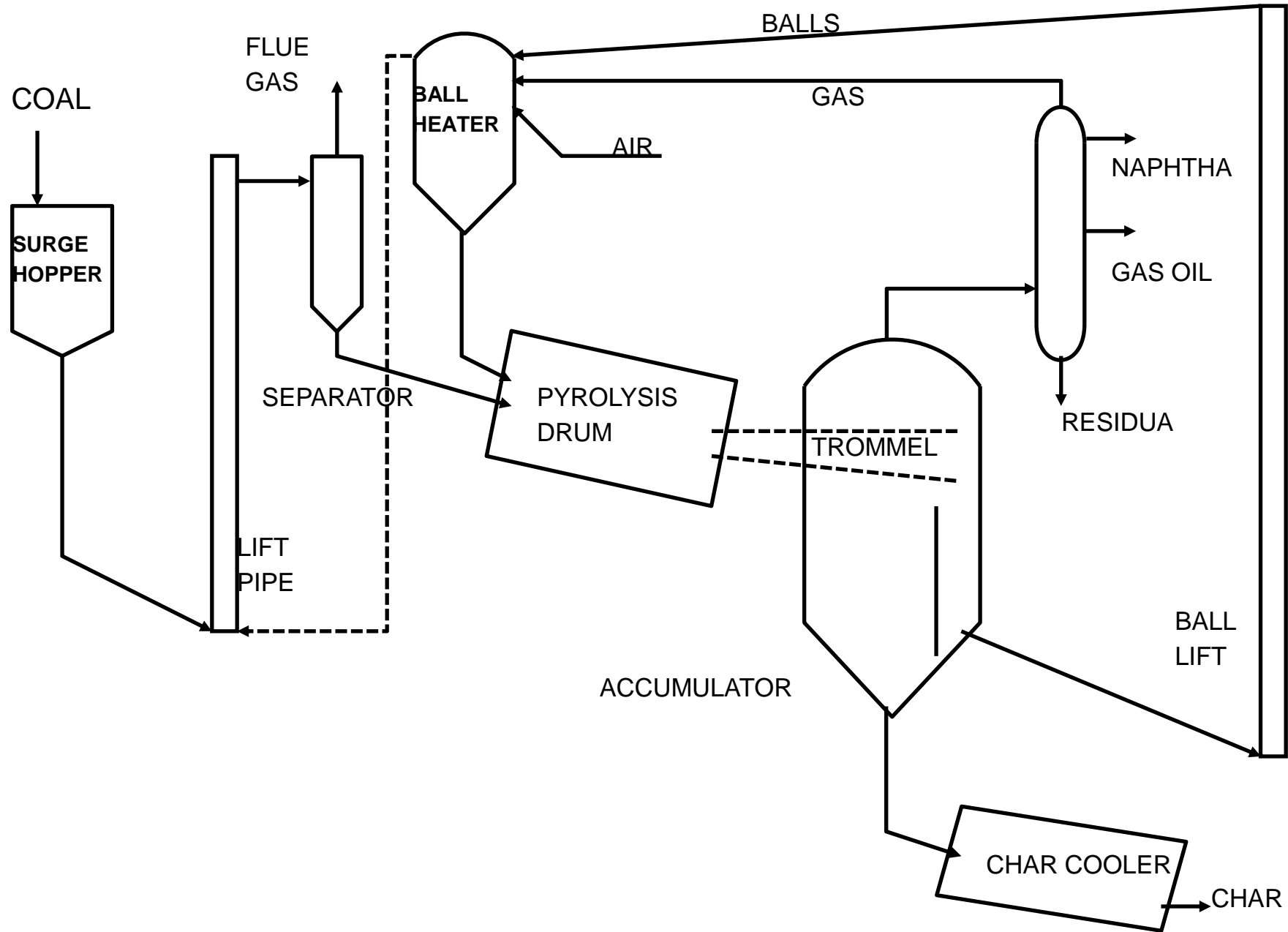
SYNCOAL



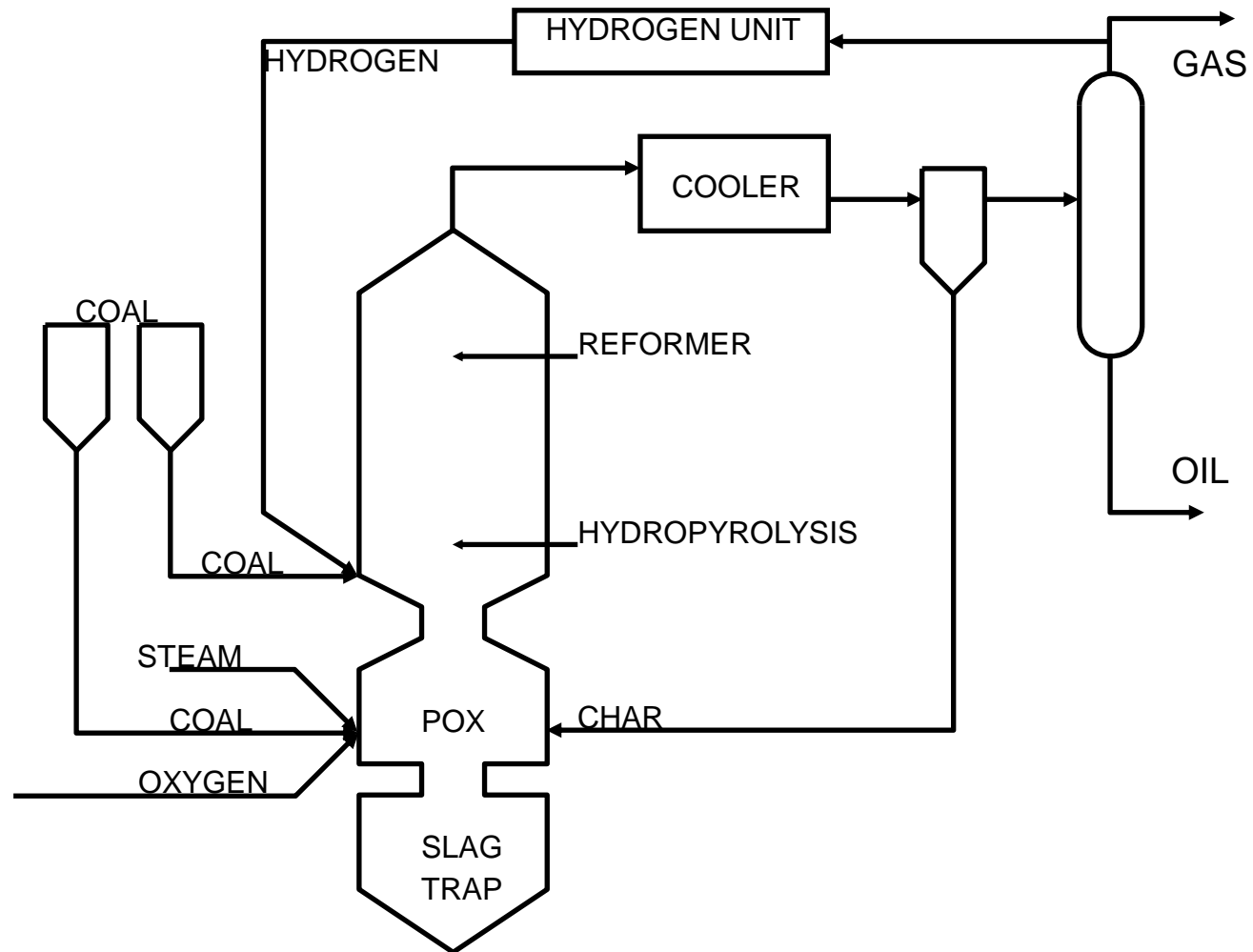
SHALE OIL PRODUCTION



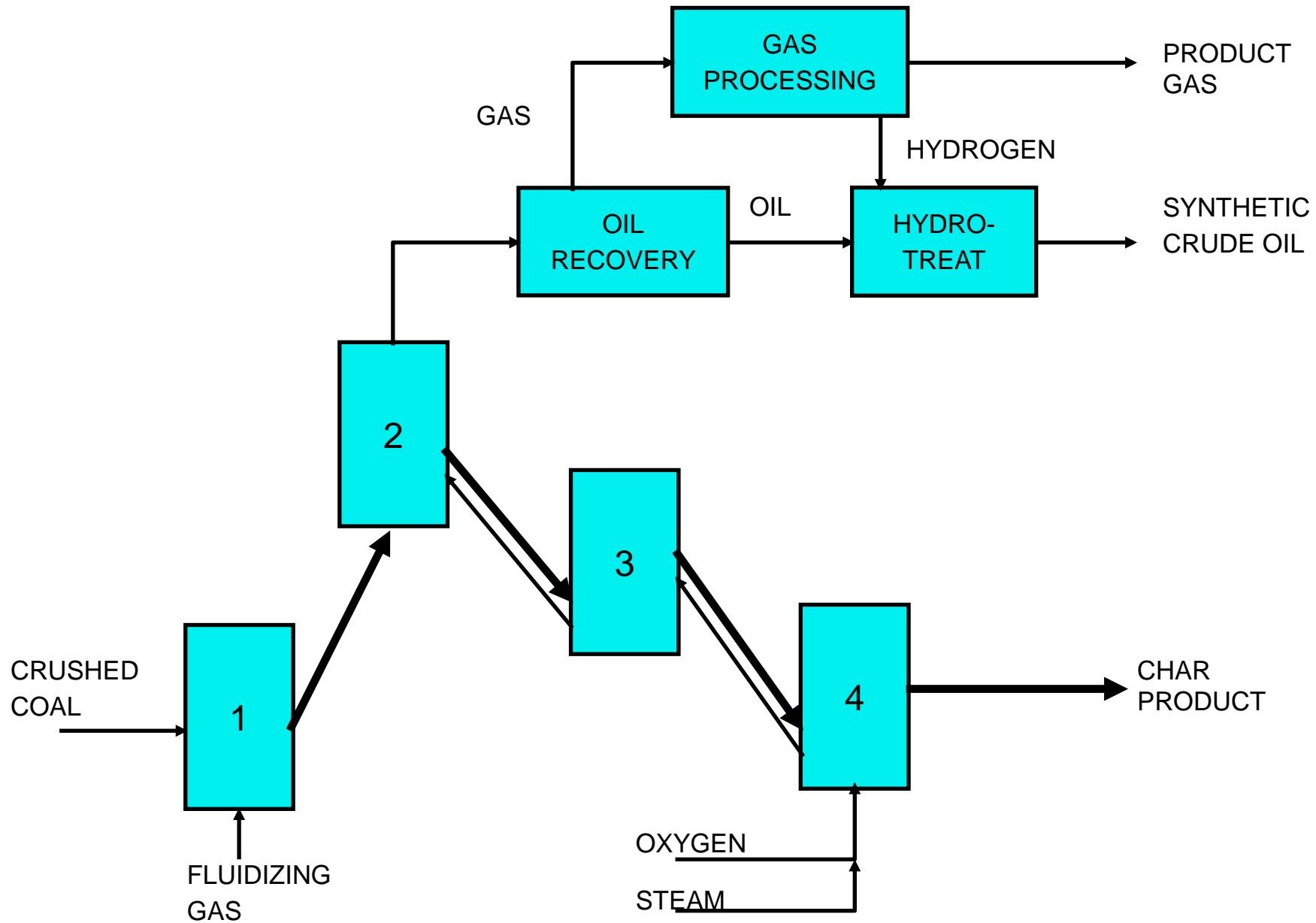
TOSCOAL



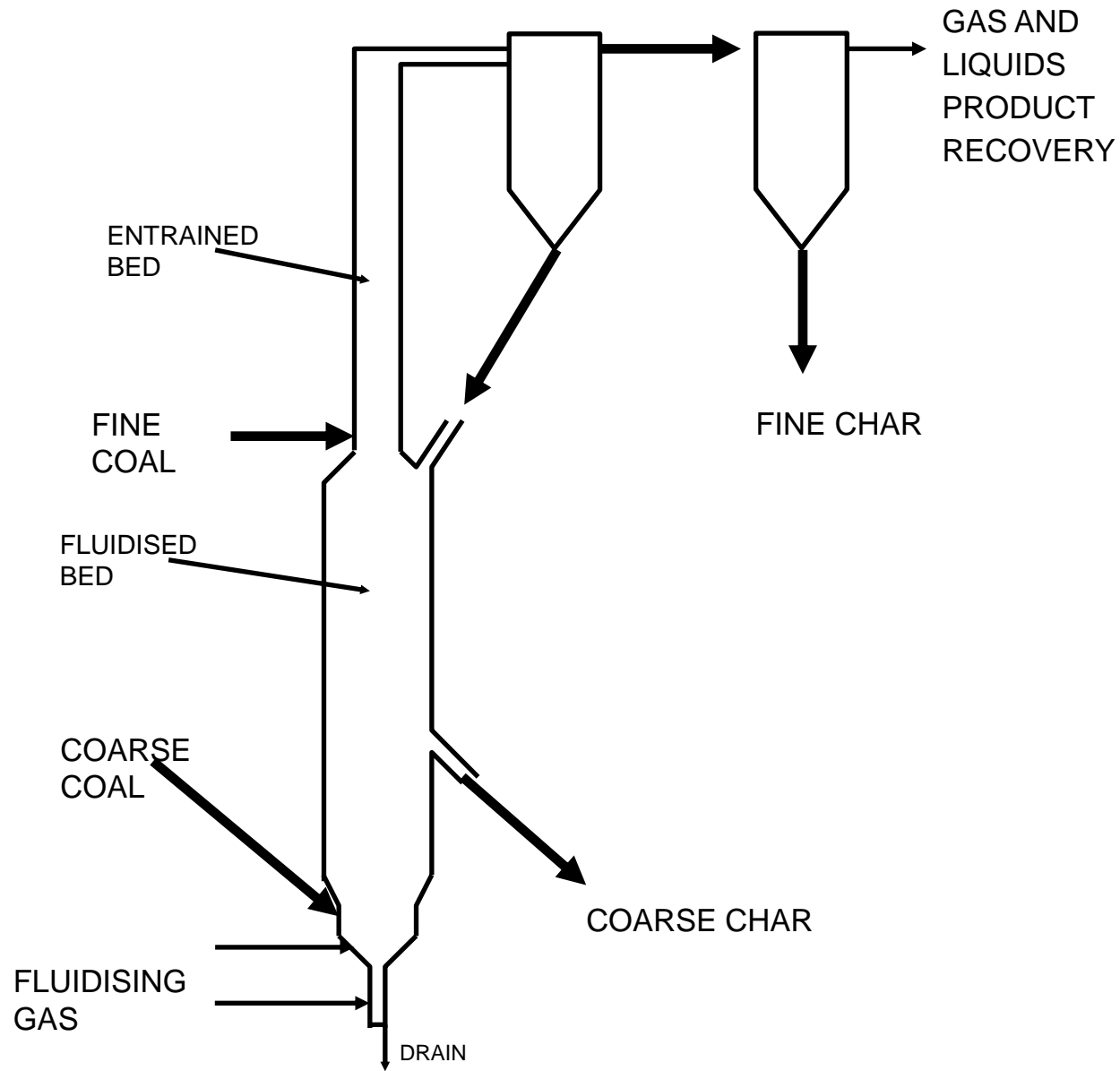
NIPPON HYDRO-PYROLYSIS

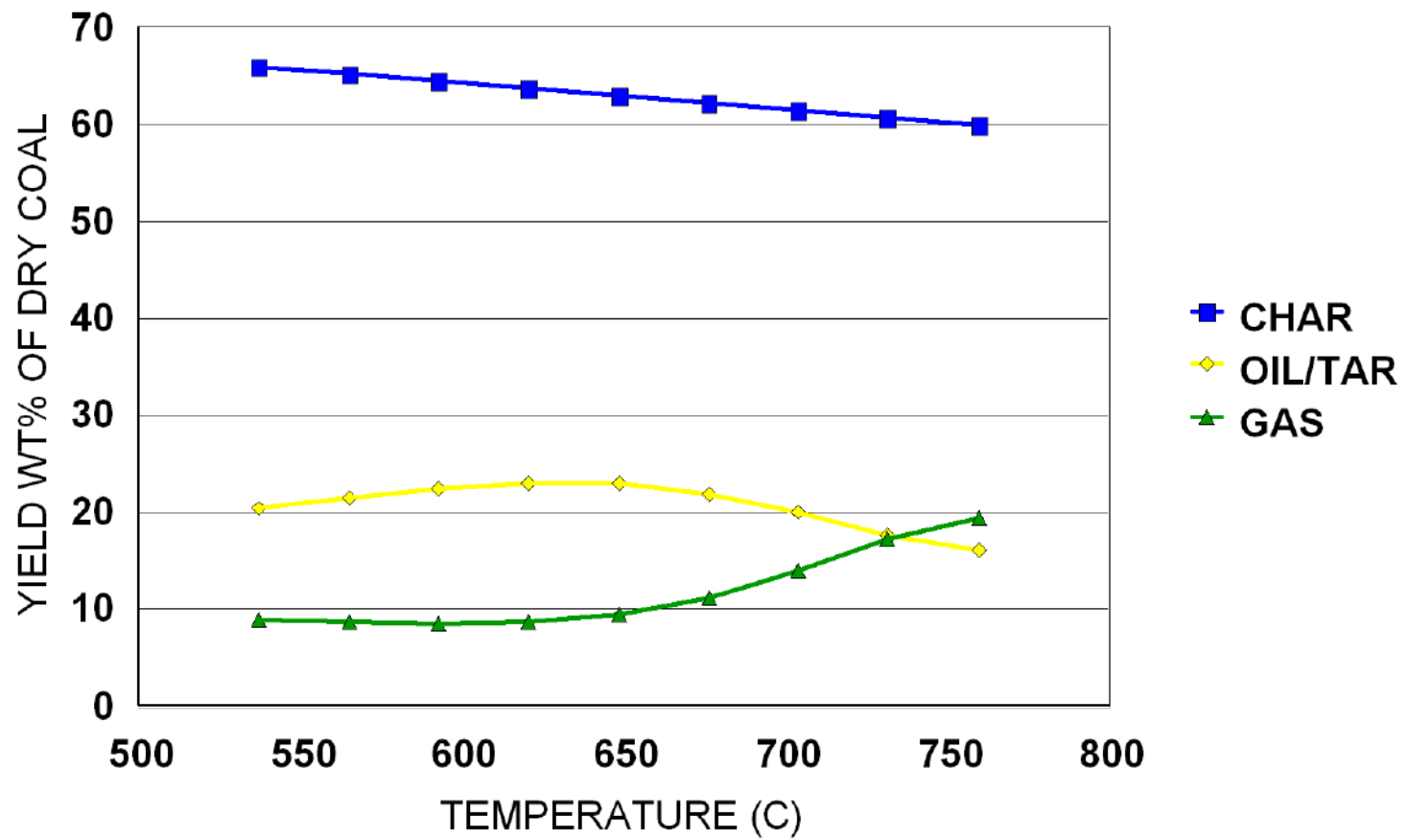


COED (FMC)



MILDGAS





CONCLUSIONS

1. COAL WIDESPREAD AND OF VARIABLE QUALITY
VAST QUANTITIES OF UNDEVELOPED RESERVES
LOW MINING COST FOR MANY RESERVES
2. BIOMASS HAS LIMITED AVAILABILITY
NOT FREE
3. COAL AND BIOMASS ARE NOT HYDROCARBONS
LOW TEMPERATURE CONVERSION PRODUCES OXYGENATES IN
THE PRODUCTS
4. BIOMASS IS A POOR FUEL
PRODUCT GAS CONTAMINATED
COSTLY CLEAN UP