CTL & BTL

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

WORLD GTL CONGRESS, JANUARY 2013 DOHA

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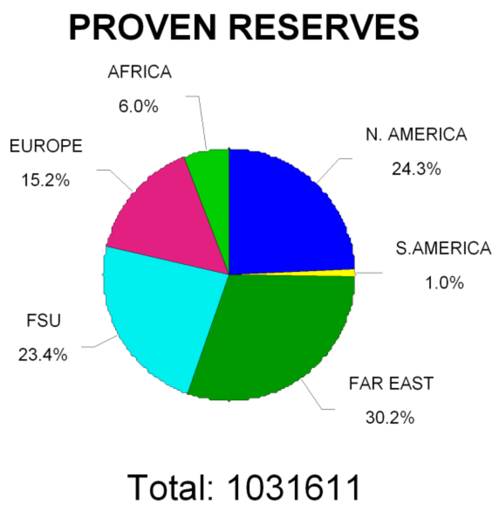
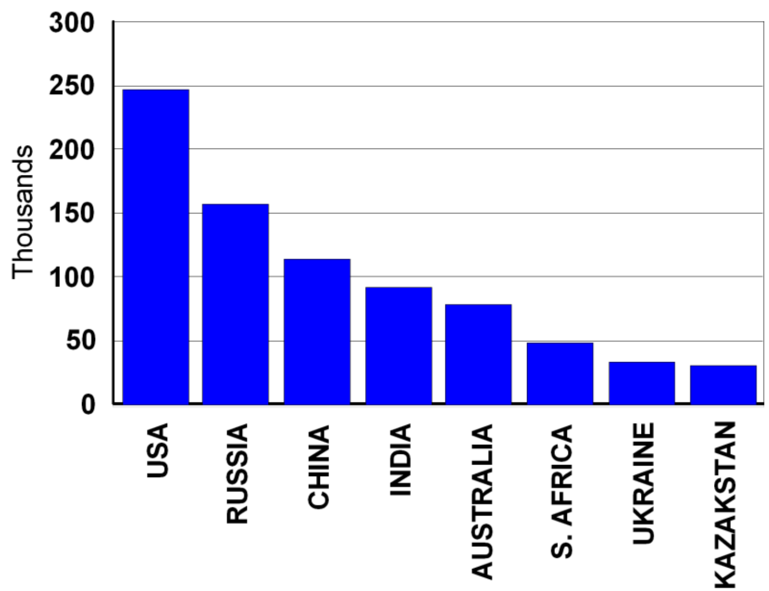
SOLID FEEDSTOCKS FOR LIQUIDS PRODUCTION

- COAL
  - BLACK COAL
  - BROWN COAL/LIGNITES
  - PEAT
- BIOMASS
  - ENERGY & FOOD CROPS - SUGAR CANE
  - FOOD BYPRODUCT - CORN STOVER, STRAW
  - FOREST RESIDUES
    - LIGNO-CELLULOSE

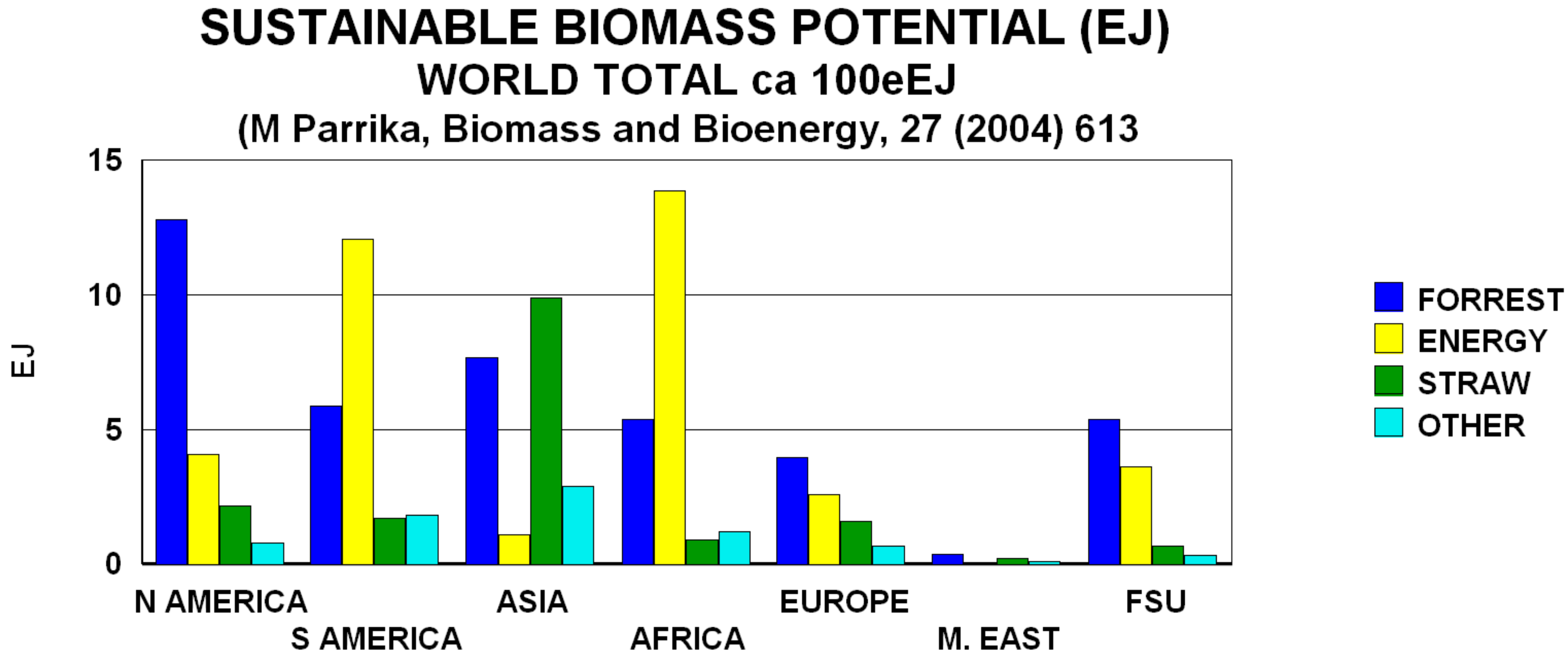
FEEDSTOCK - 1

WORLD COAL RESERVES
(Millions of tonnes)





~ 20,000 EJ



BUT much already used:

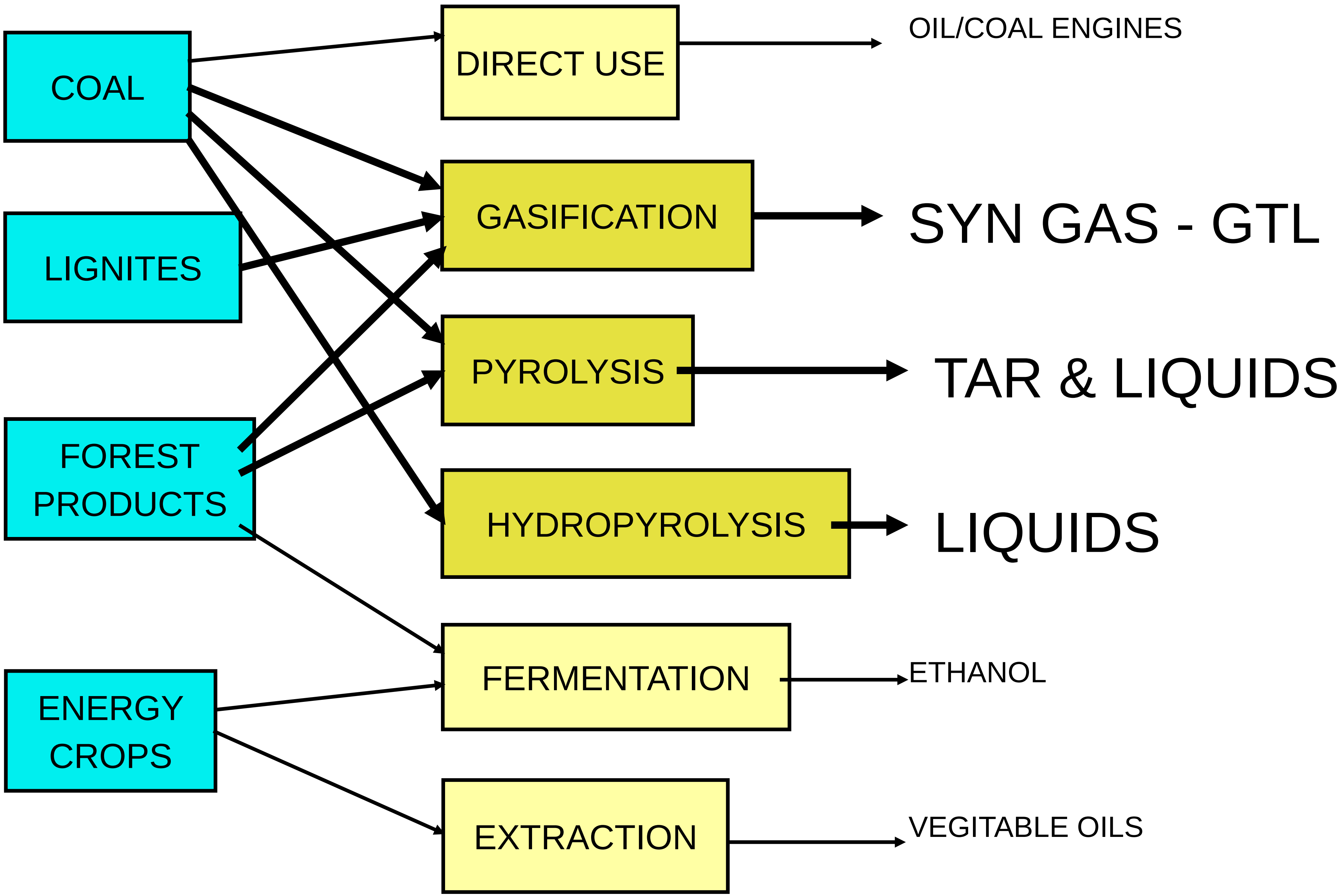
	% USED
N. AMERICA	16%
S AMERICA	12%
ASIA	100%
AFRICA	39%
EUROPE	22%
M. EAST	7%
FSU	5%
WORLD	38%

FEEDSTOCK QUALITY

TYPE		Illinois No 6	PRB	Lignite	Loy Yang	WOOD	Prairee 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%


COAL
LIGNITES
FOREST PRODUCTS
ENERGY CROPS
DIRECT USE
GASIFICATION
PYROLYSIS
HYDROPYROLYSIS
FERMENTATION
EXTRACTION
OIL/COAL ENGINES
SYN GAS - GTL
TAR & LIQUIDS
LIQUIDS
ETHANOL
VEGITABLE OILS

PYROLYSIS

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

- LARGE HYDROCARBON MOLECULES
  - ► UNSTABLE REALTIVE 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:	$C + O_2 = CO_2$
Steam Carbon:	$C + H_2O = CO + H_2$
Hydro-gasification:	$C + 2H_2 = CH_4$
The Boudouard Reaction:	$C + CO_2 = 2CO$

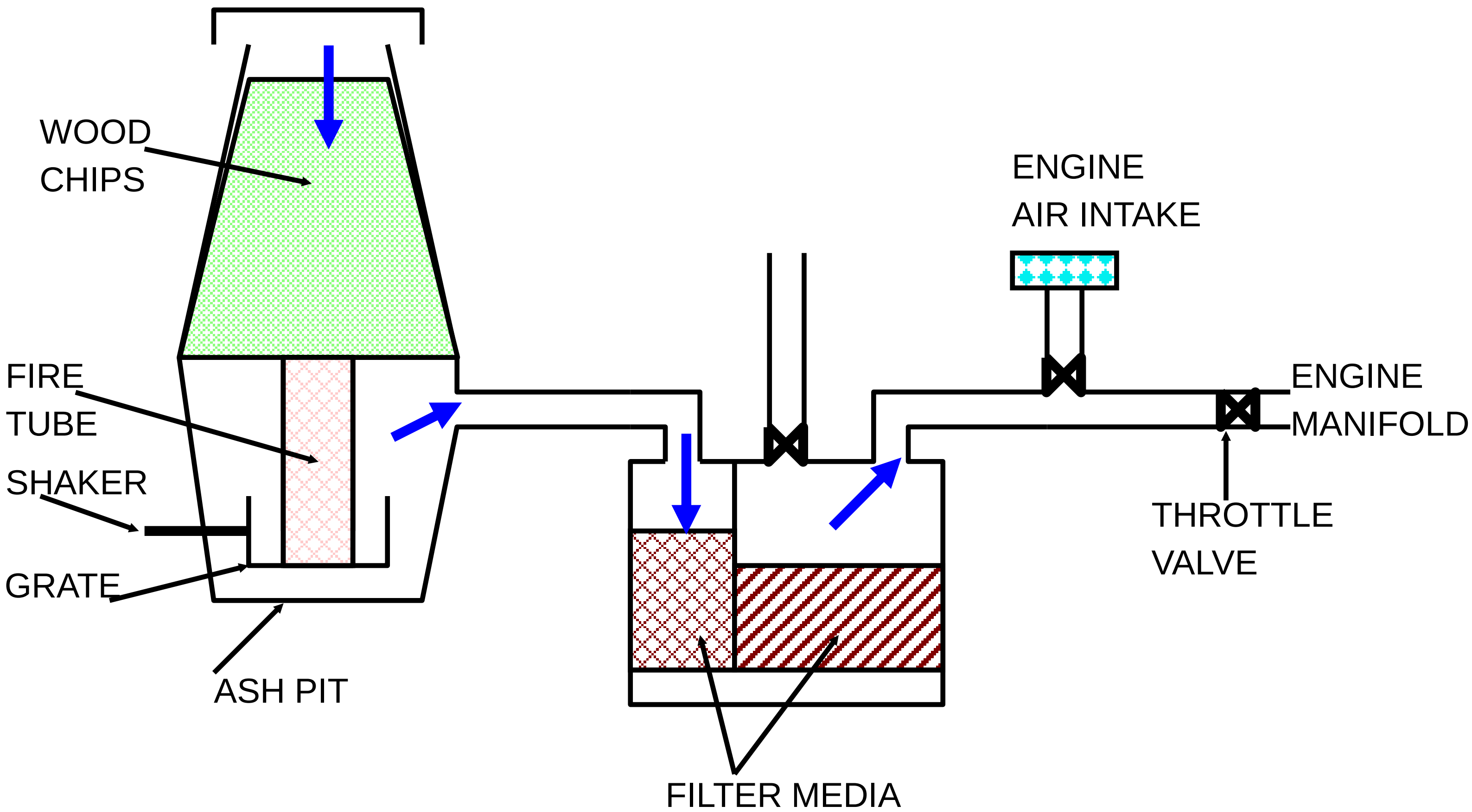
Gas Phase Reactions

Water-Gas-Shift:	$CO + H_2O = CO_2 + H_2$
Methanation:	$CO + 3H_2 = CH_4 + H_2O$

Pyrolysis

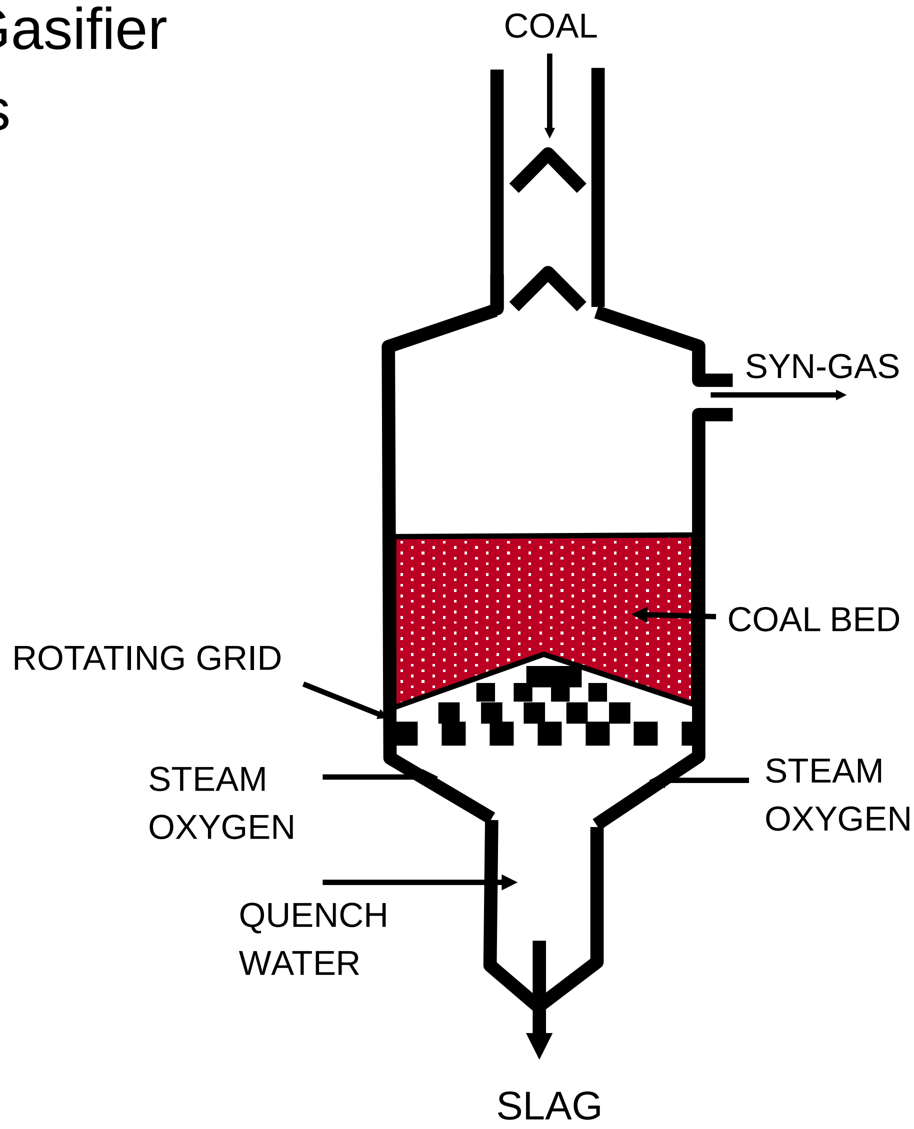
As well as these reactions, large molecules undergo pyrolysis and hydro-pyrolysis to small molecules.

STRATIFIED DOWNDRAFT GASIFIER



Moving Bed Gasifier

Coal as lumps

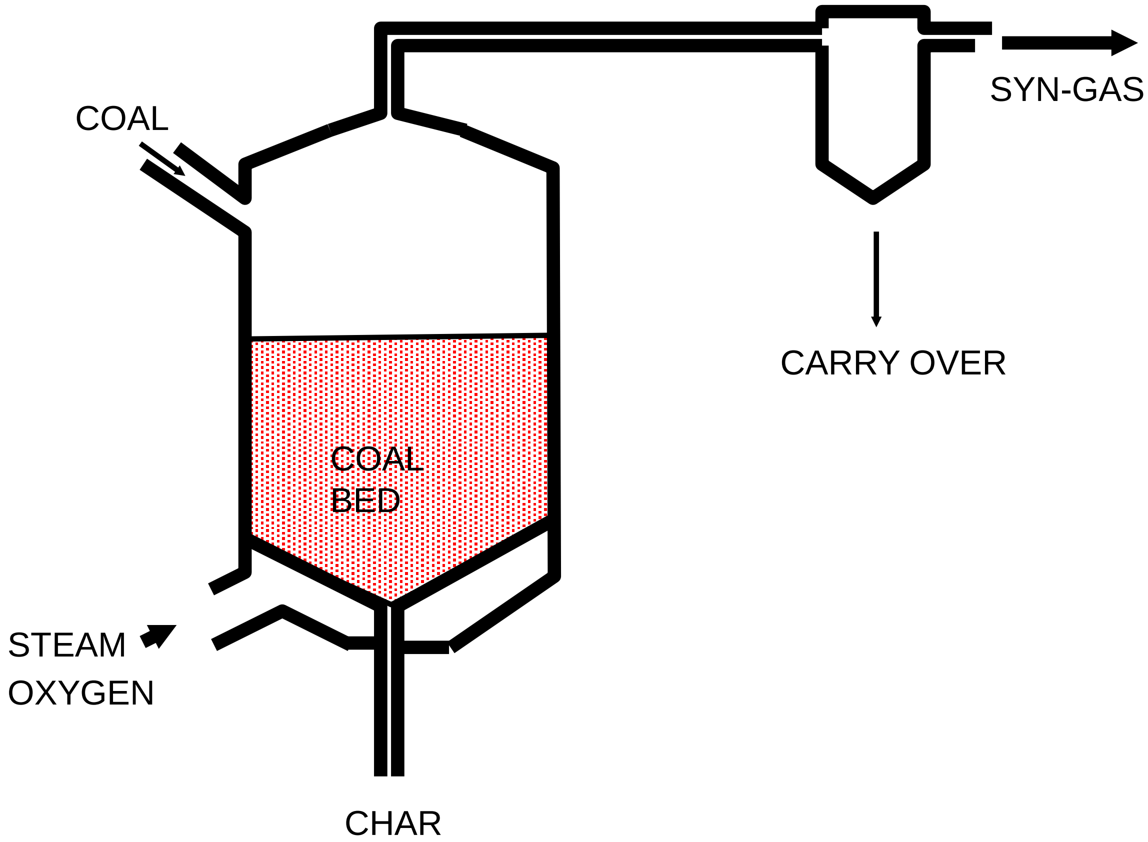


Fluidized Bed Gasifier

Coal as fines

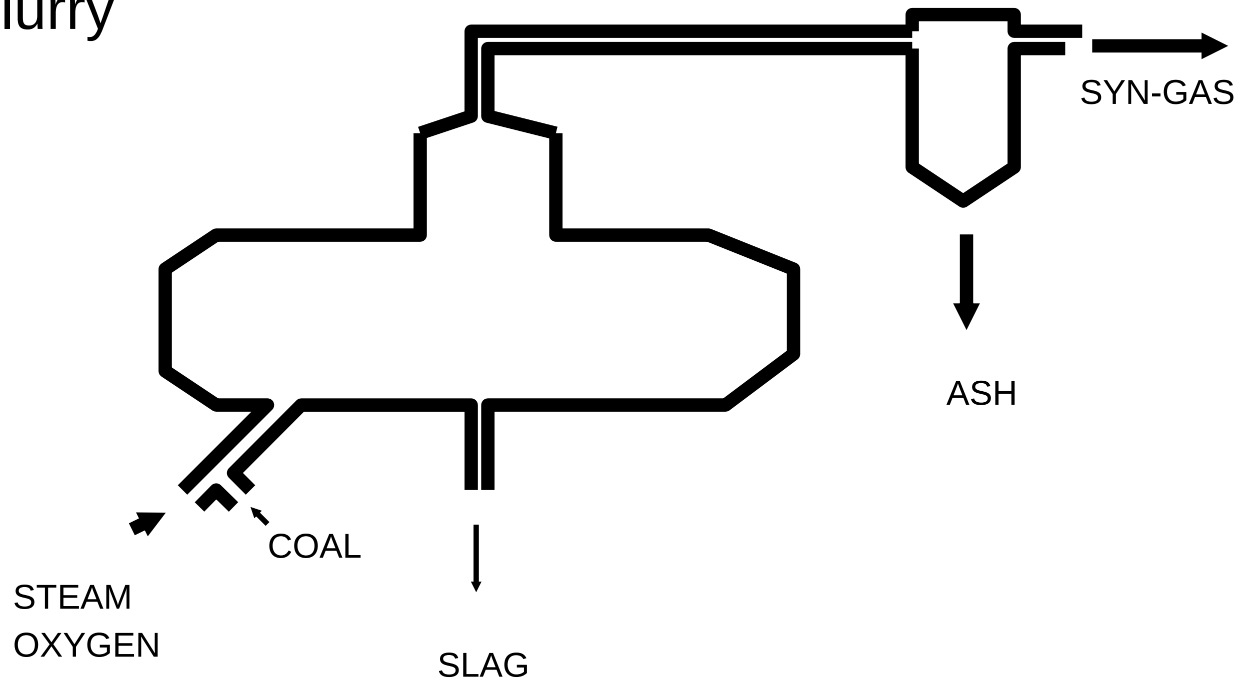
WINKLER

U-GAS



Entrained Bed Gasifier

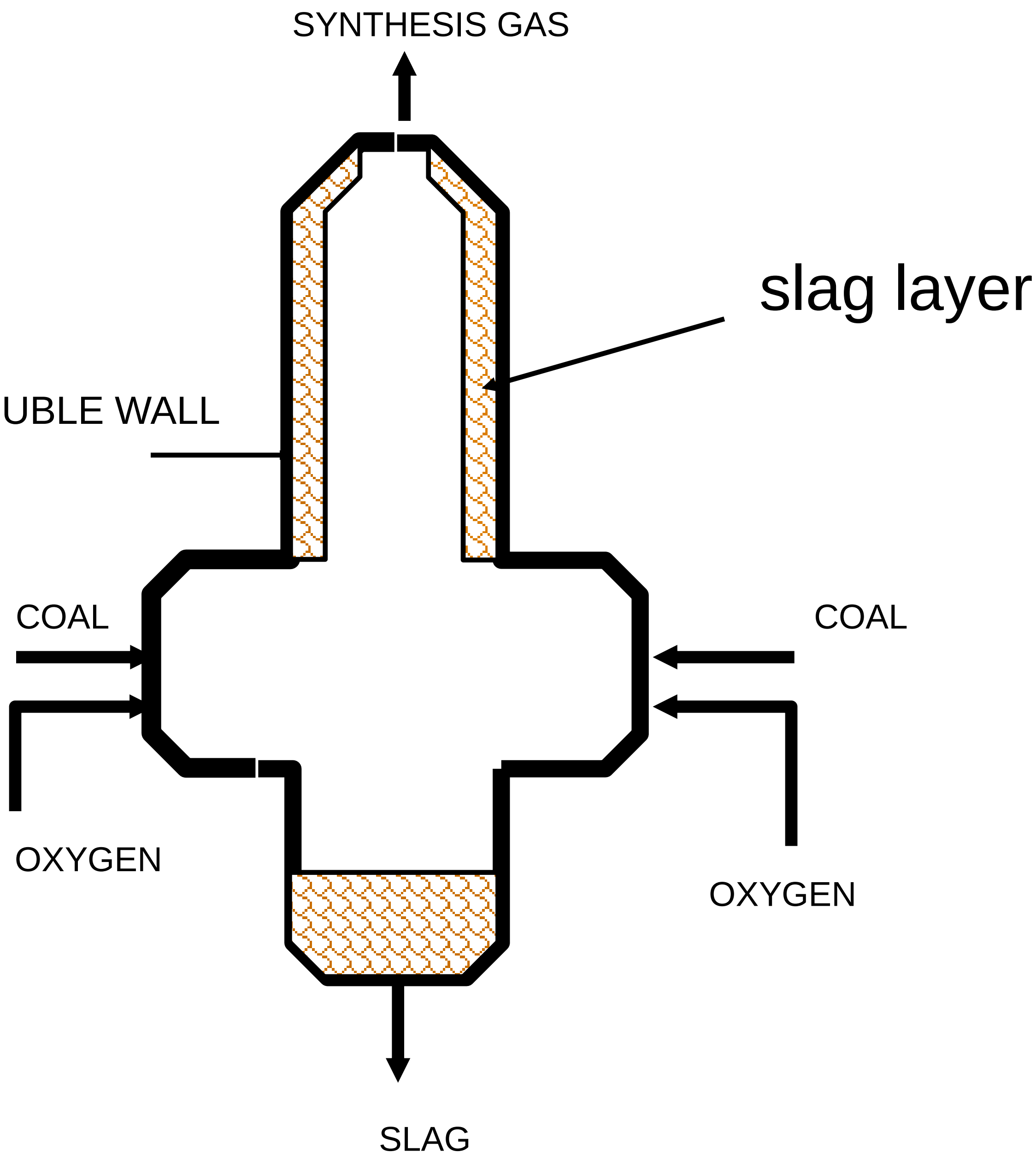
Coal as fines in gas or water slurry



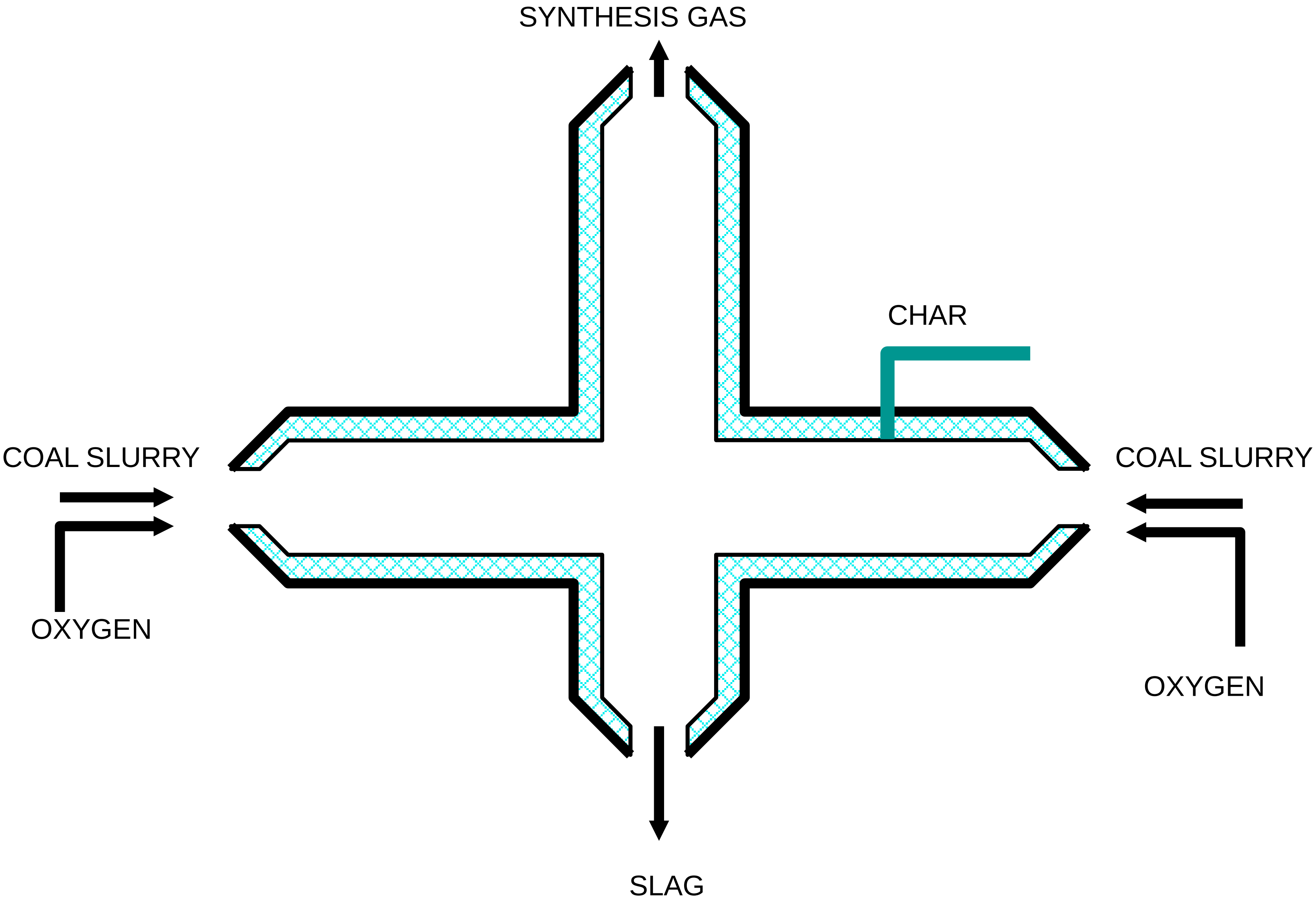
KOPPERS - TOTZEK

SHELL - GASIFIER

UHDE - PRENFLO

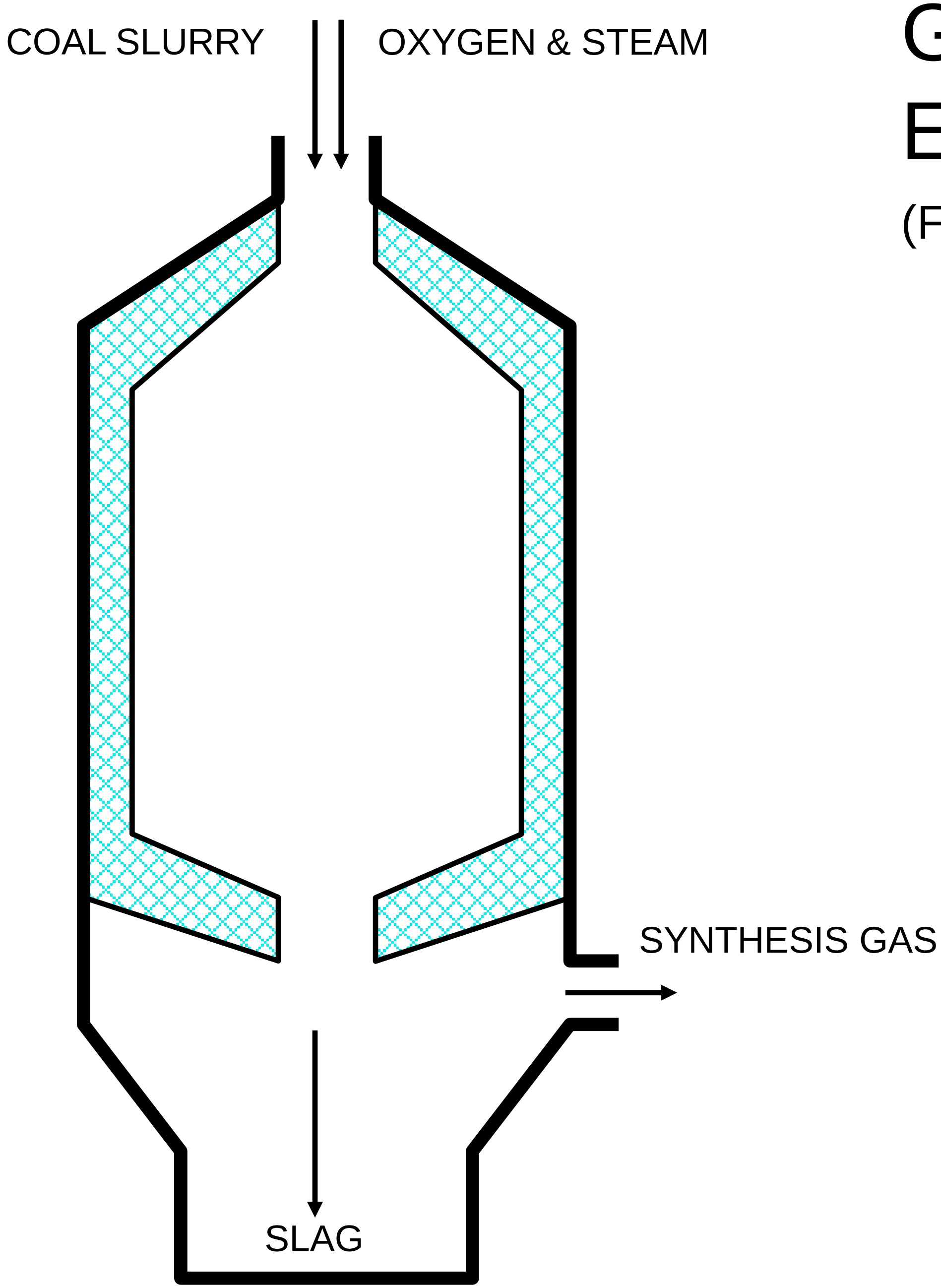


CONOCOPHILLIPS

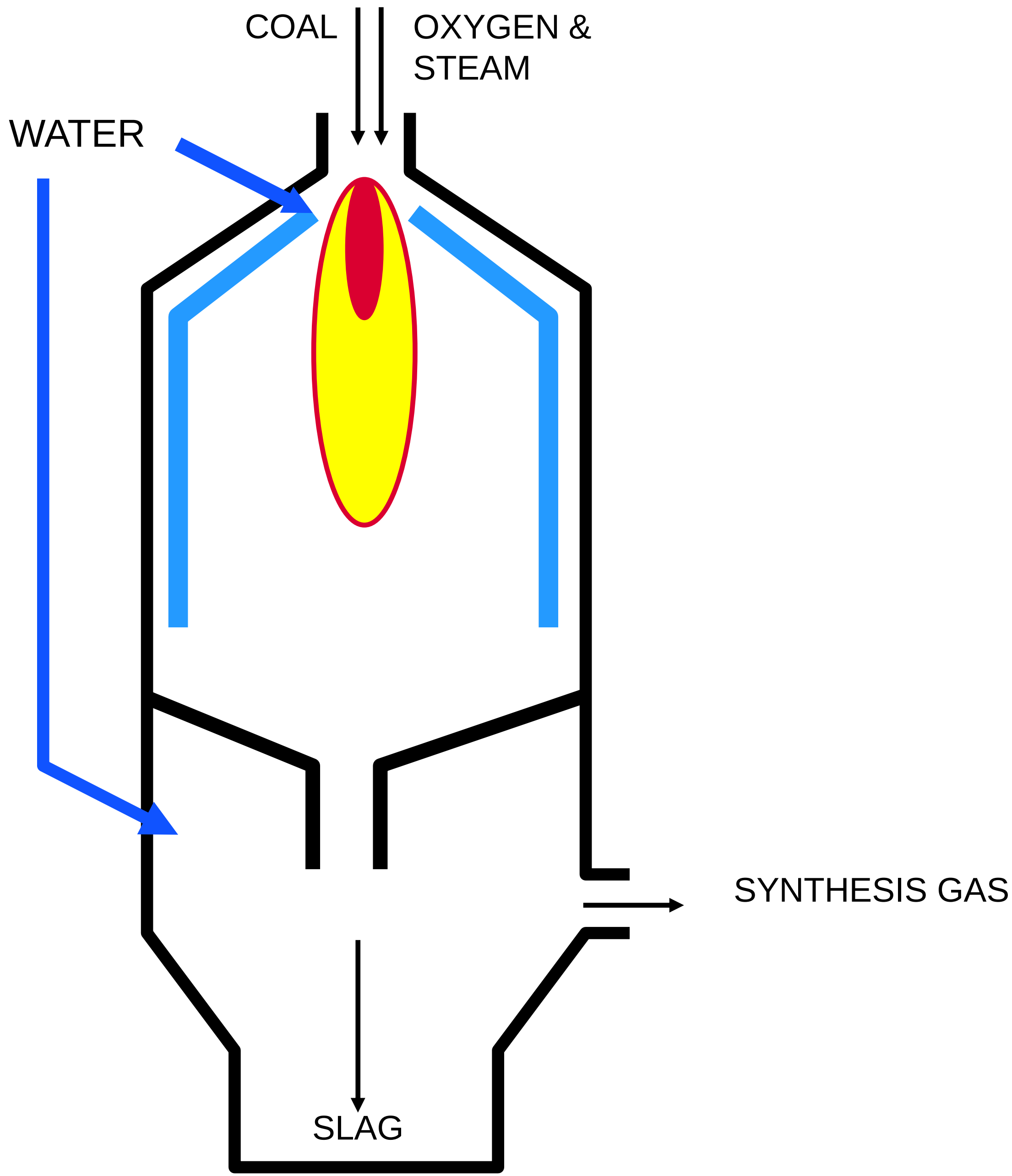


GE ENERGY

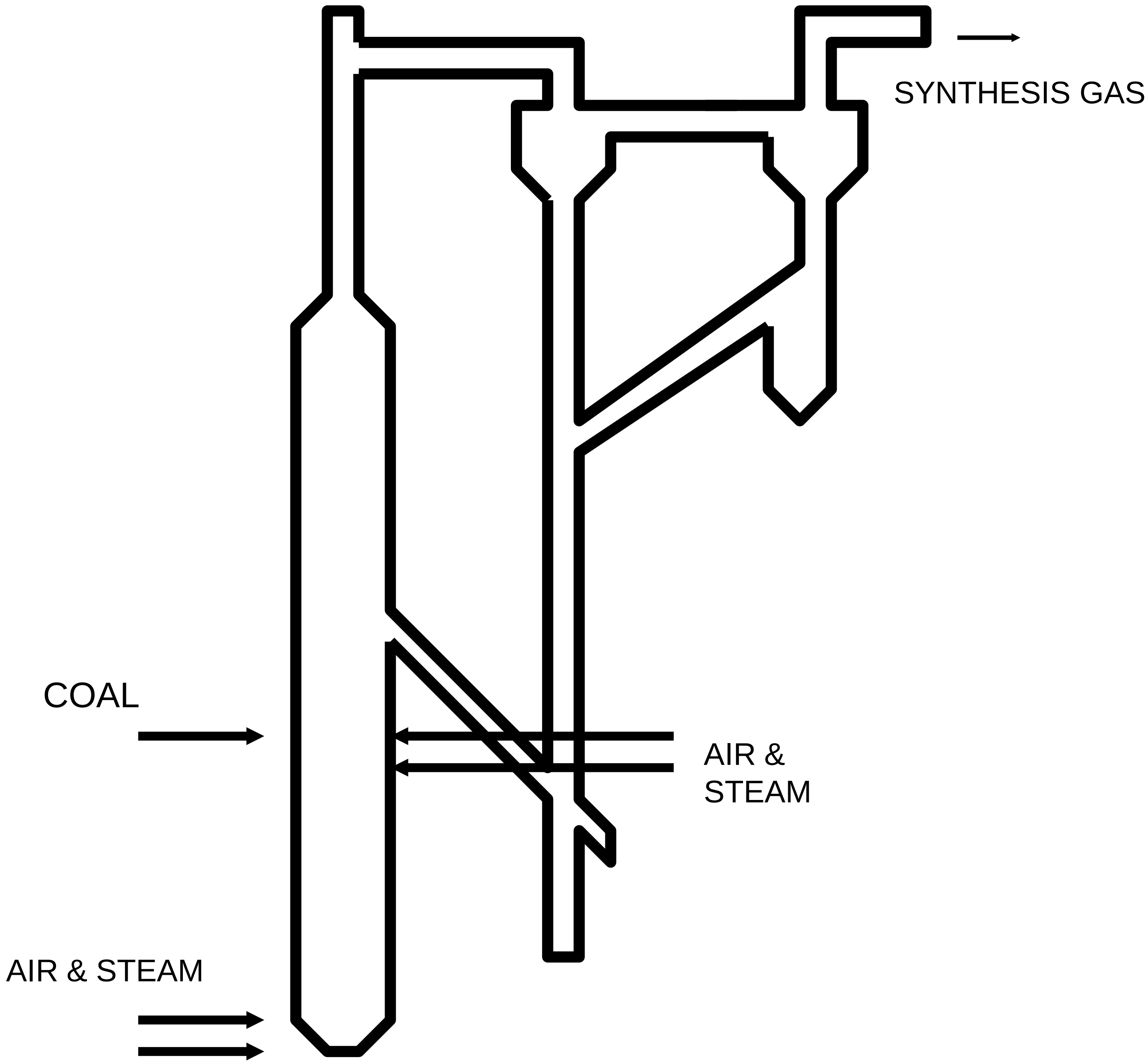
(Formerly Texaco)



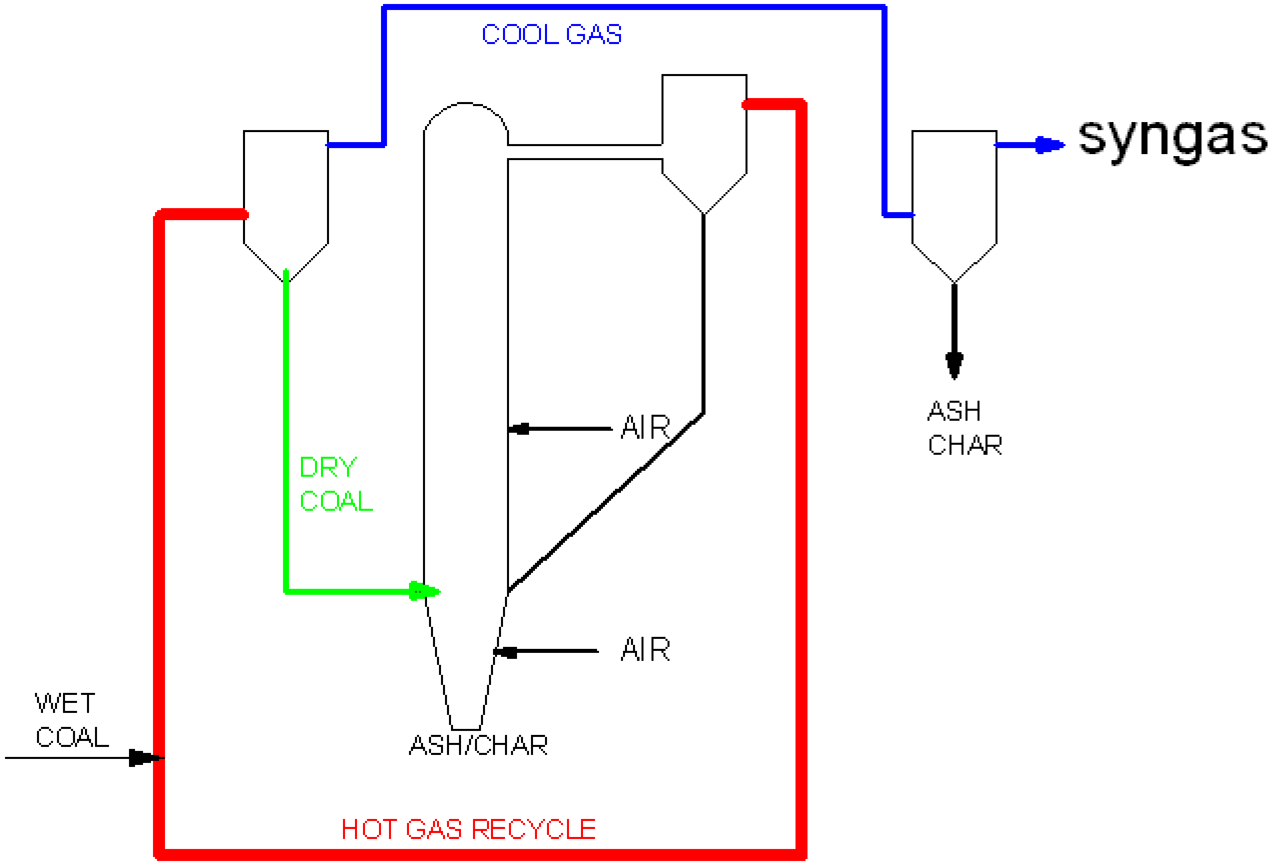
SIEMENS



KBR



HRL Integrated dying 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

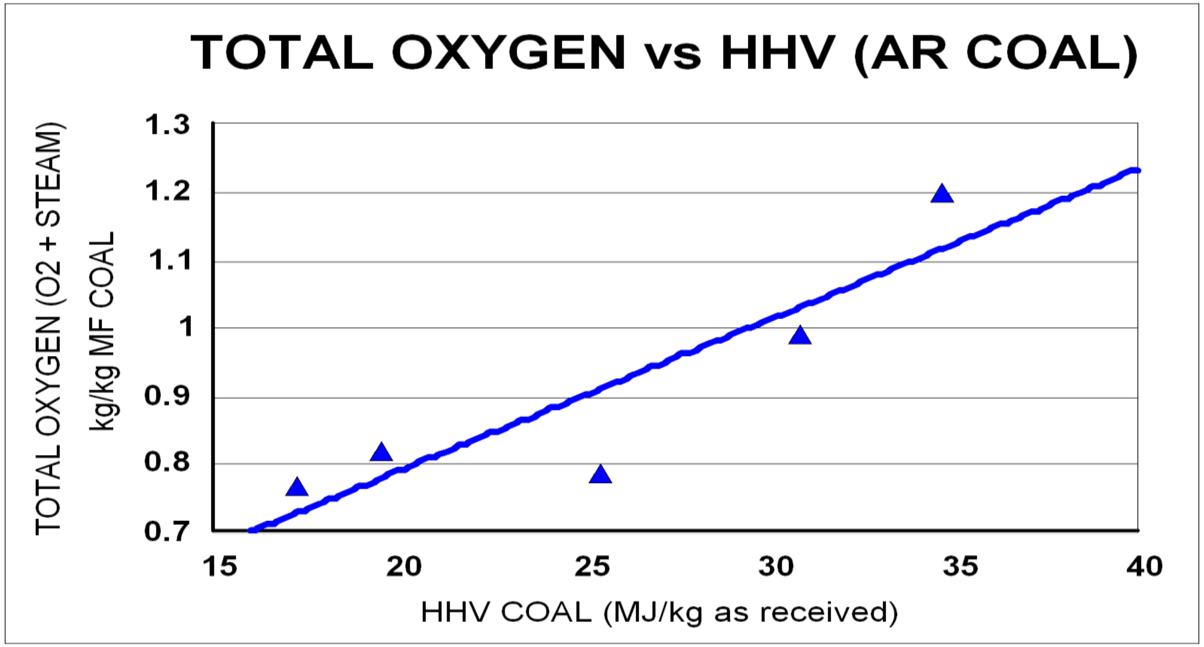
	Lurgi	BG/L	KRW	Texaco	Shell
Type of bed	Moving	Moving	Fluid	Entrained	Entrained
Pressure (MPa)	0.101	2.82	2.82	4.22	2.46
Ash Type	ash	Slag	Aglom.	Slag	slag
H_2	52.2	26.4	27.7	30.3	26.7
CO	29.5	45.8	54.6	39.6	63.1
CO_2	5.6	2.9	4.7	10.8	1.5
CH_4	4.4	3.8	5.8	0.1	0.03
Other hydrocarbons	0.3	0.2	<0.01	Nil	Nil
H_2S	0.9	1.0	1.3	1.0	1.3
H_2S/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_2O	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
H2	52.2	26.7	14.5
CO	29.5	63.1	14.7
CO2	5.6	1.5	15.5
CH4	4.4	0.03	2.5
Other hydrocarbons	0.3	Nil	0.37 +BTX
H2S	0.9	1.3	
H2S/COS	20/1	9/1	
N2 + A	1.5	5.2	52.3
H2O	5.1	2.0	
NH3 + HCN	0.5	0.02	0.08

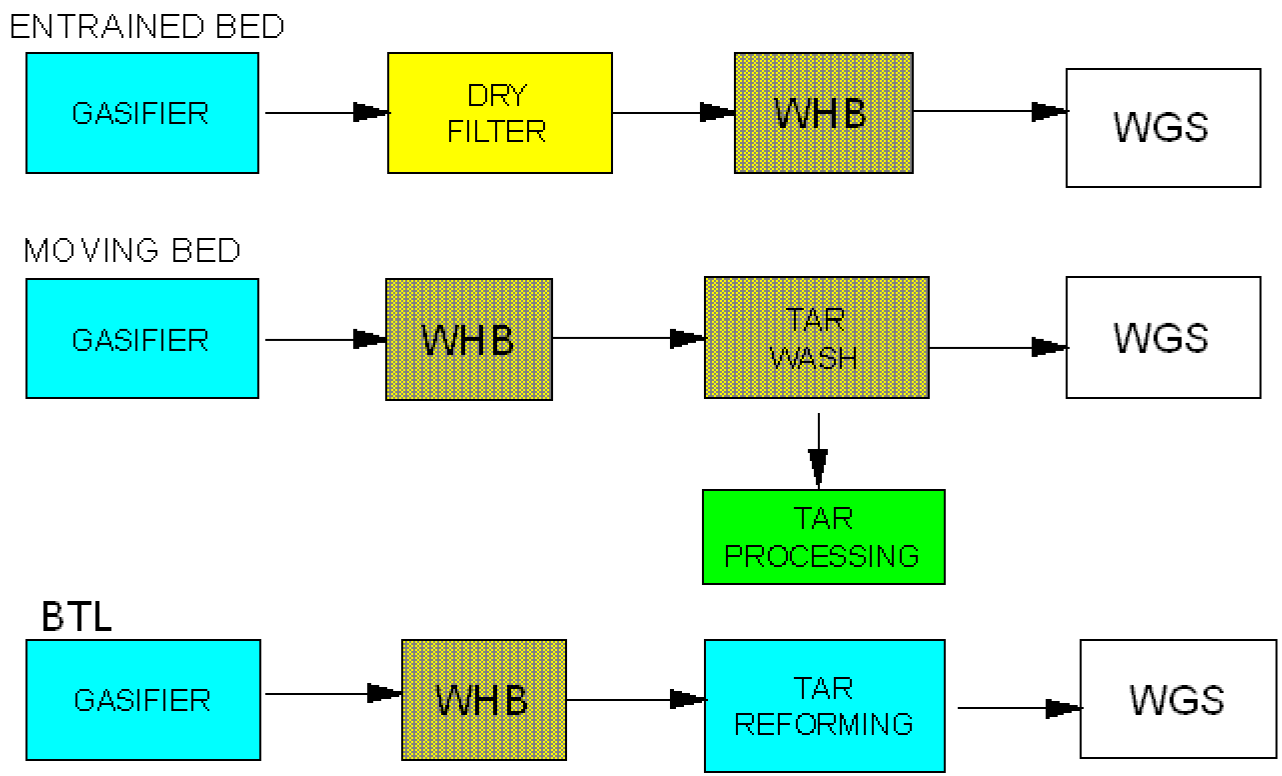

TOTAL OXYGEN vs HHV (AR COAL)
TOTAL OXYGEN (O2 + STEAM)
kg/kg MF COAL
1.3
1.2
1.1
1
0.9
0.8
0.7
15
20
25
30
35
40
HHV COAL (MJ/kg as received)

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



SR REQUIREMENTS OF DIFFERENT TECHNOLOGY

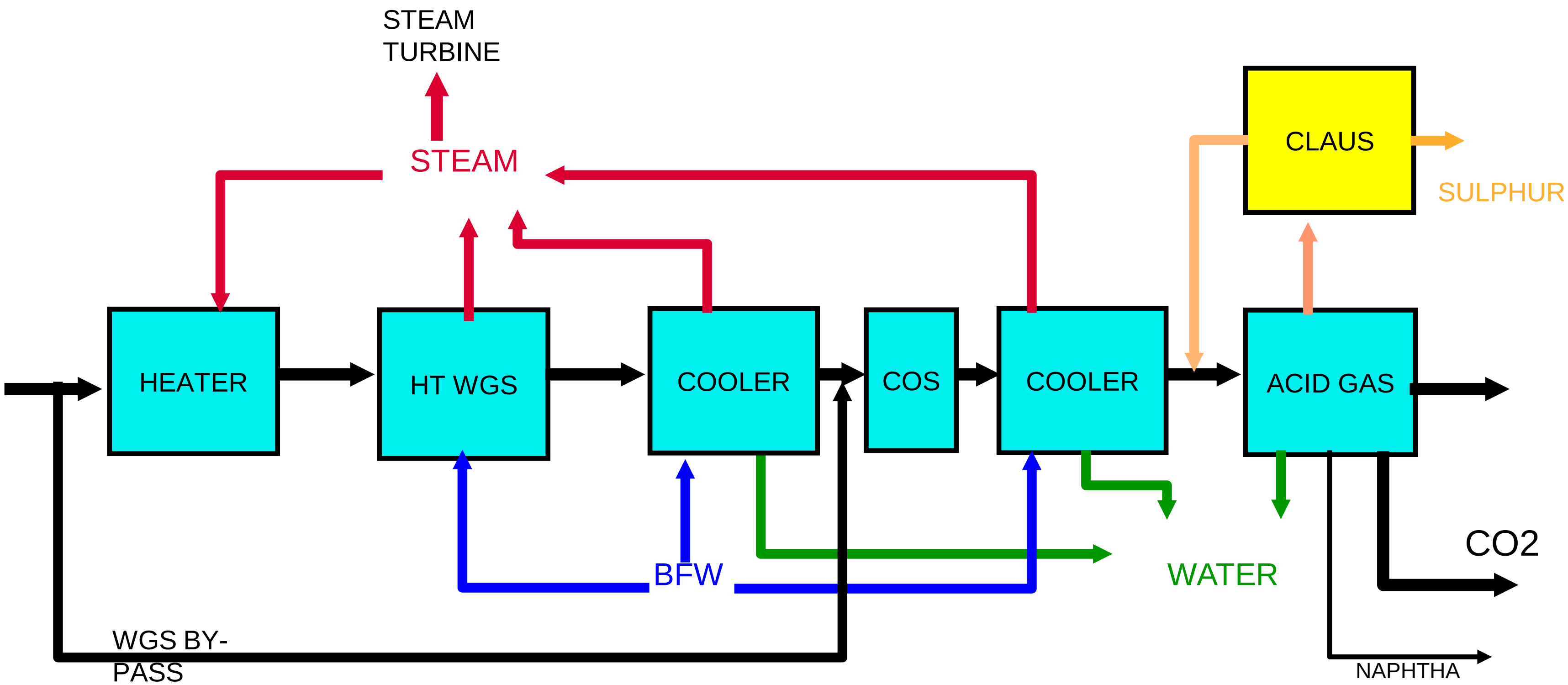
PRODUCT	H2:CO	CAPACITY (000t/a)	SYNGAS (000Ncm/h)
Methanol	2:1	160 - 1,700	48 - 250
Fischer-Tropsch (Fe)	1.75:1	637 + (a)	48 - 250
Fischer-Tropsch (Co)	2:1	637 + (a)	48 - 250
Acetic Acid	0:1	275 - 545	18 - 36
Acetic Anydride	0:1	90	3.5
Oxo Alcohols	2:1	115 - 275	12 - 25
Phosgene (TDI)	0:1	45 - 160	3.5 - 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_2O	Inert	No	Inert	No
H_2S + COS	No	No	No	No
N_2	Inert	Yes	Inert	No
Cl	No	No	No	No

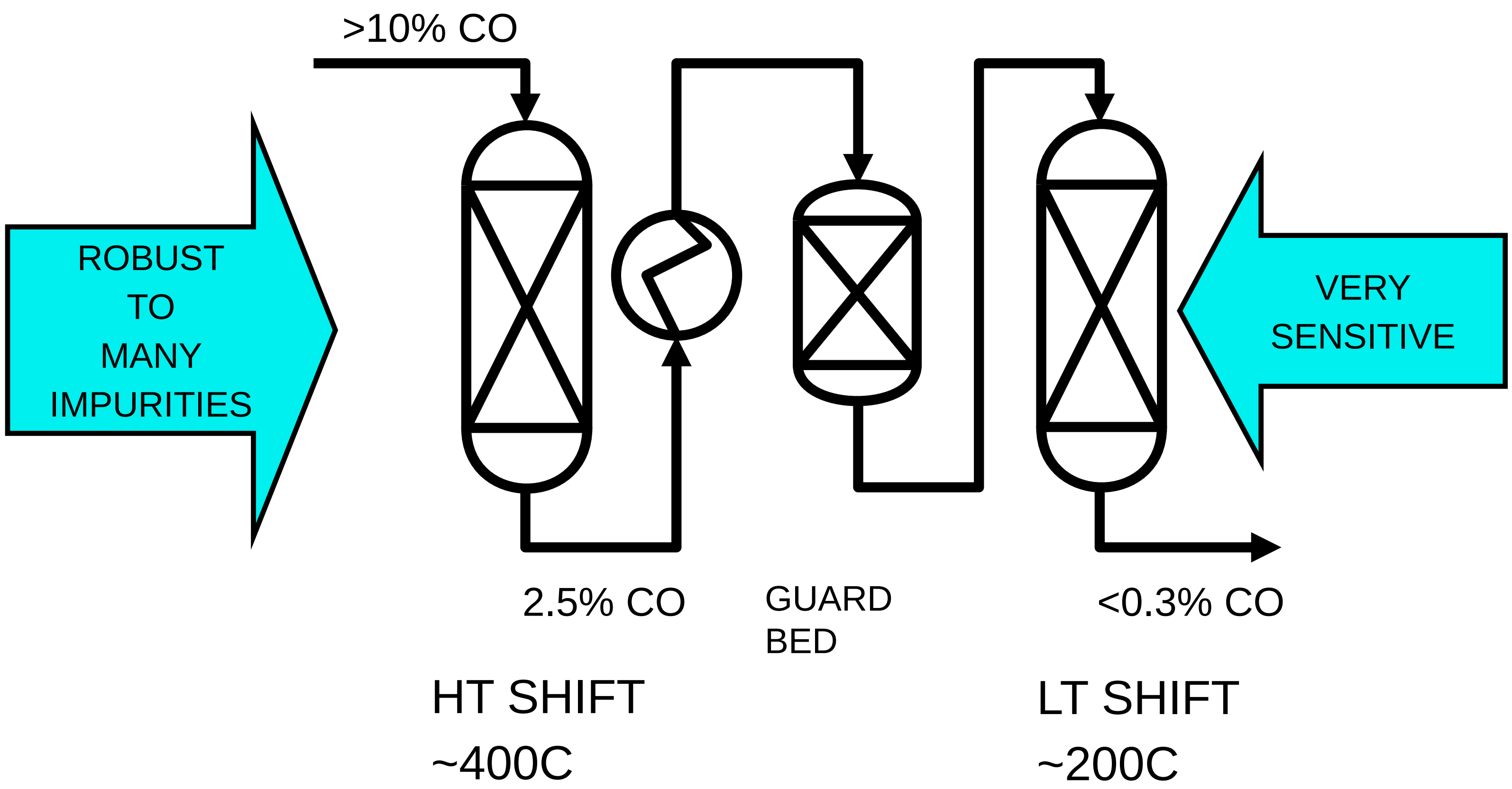
WGS SHIFT AND ACID GAS



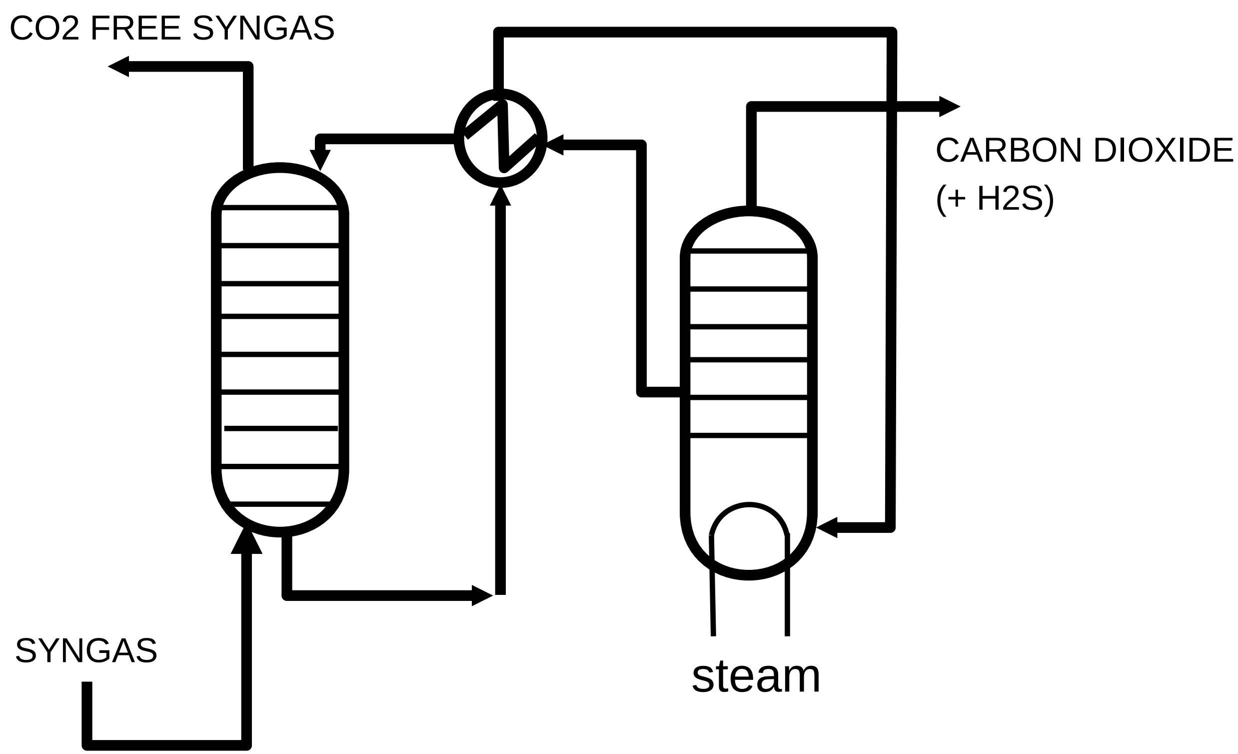
ANY SR CAN BE OBTAINED USING WGS

$$CO + H_2O = CO_2 + H_2$$

WATER-GAS-SHIFT



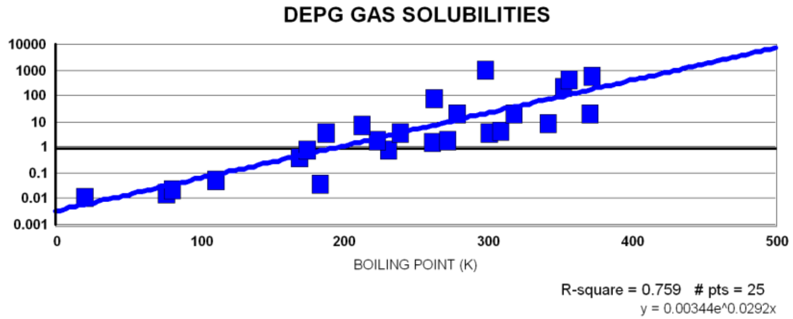
ACID GAS (CARBON DIOXIDE) STRIPPING

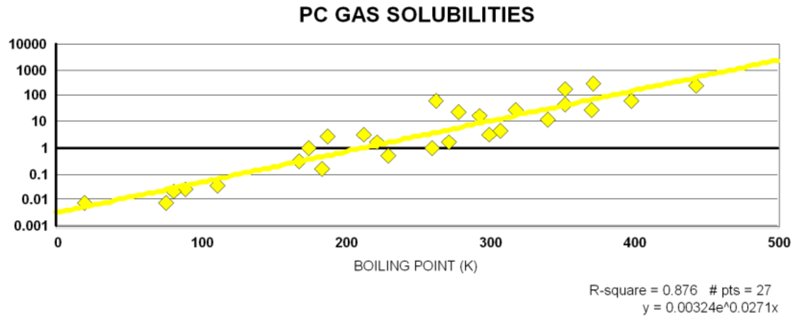


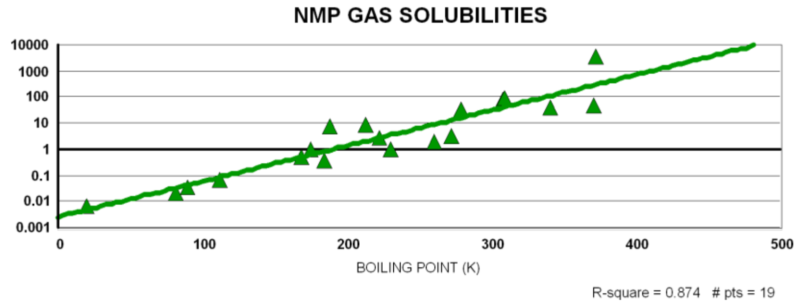
GAS SOLUBILITIES @25C

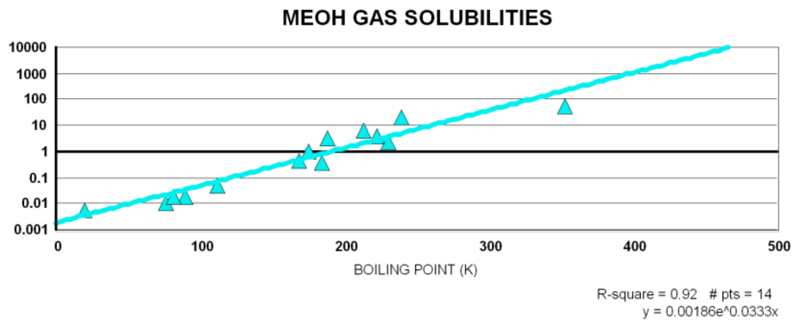
B.Burr, L. Lyddon, Hydrocarbon Processing, January 2009, p. 43

	density	bp (K)	DEPG	PC	NMP	MeOH
	(kg/L)		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





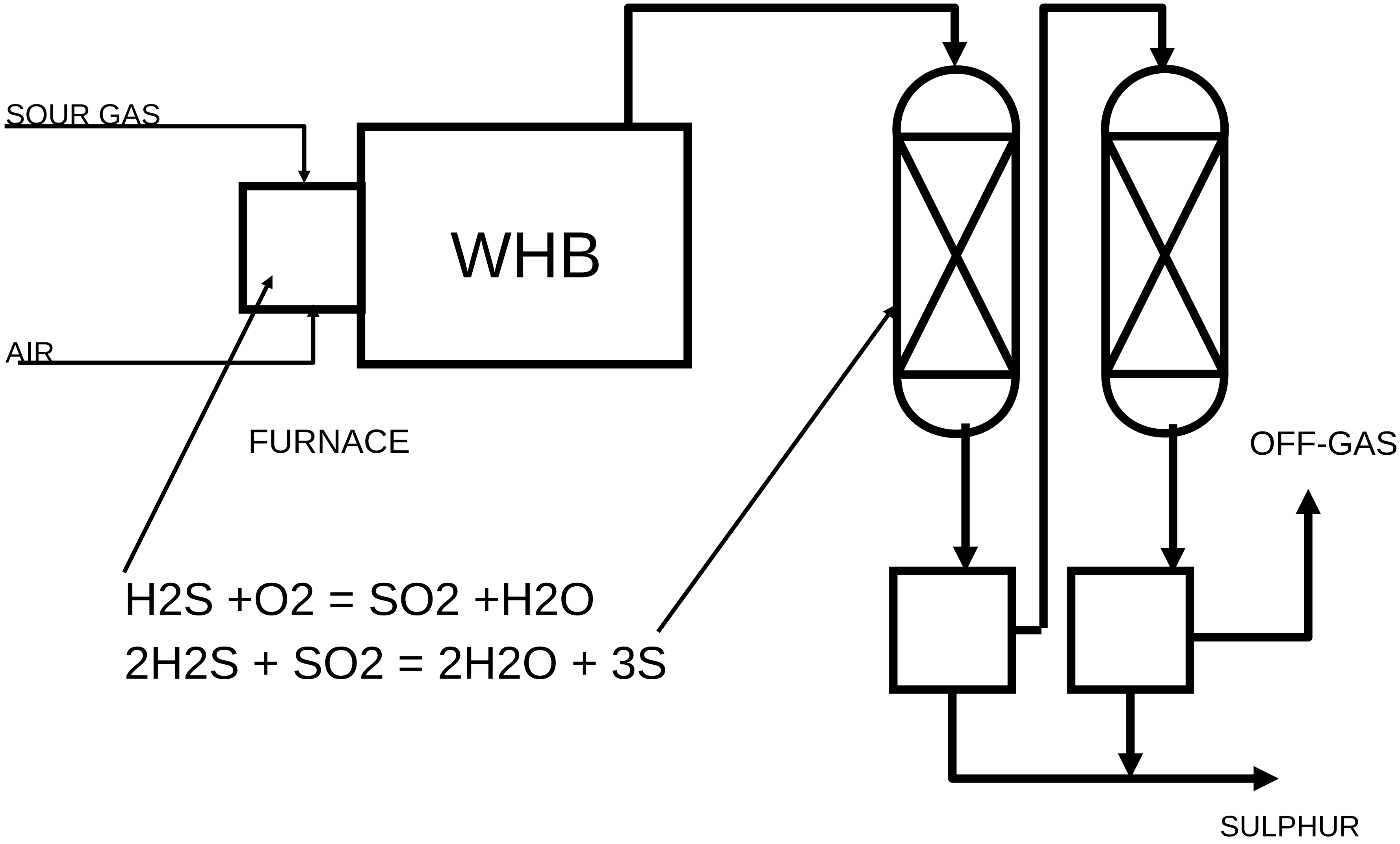




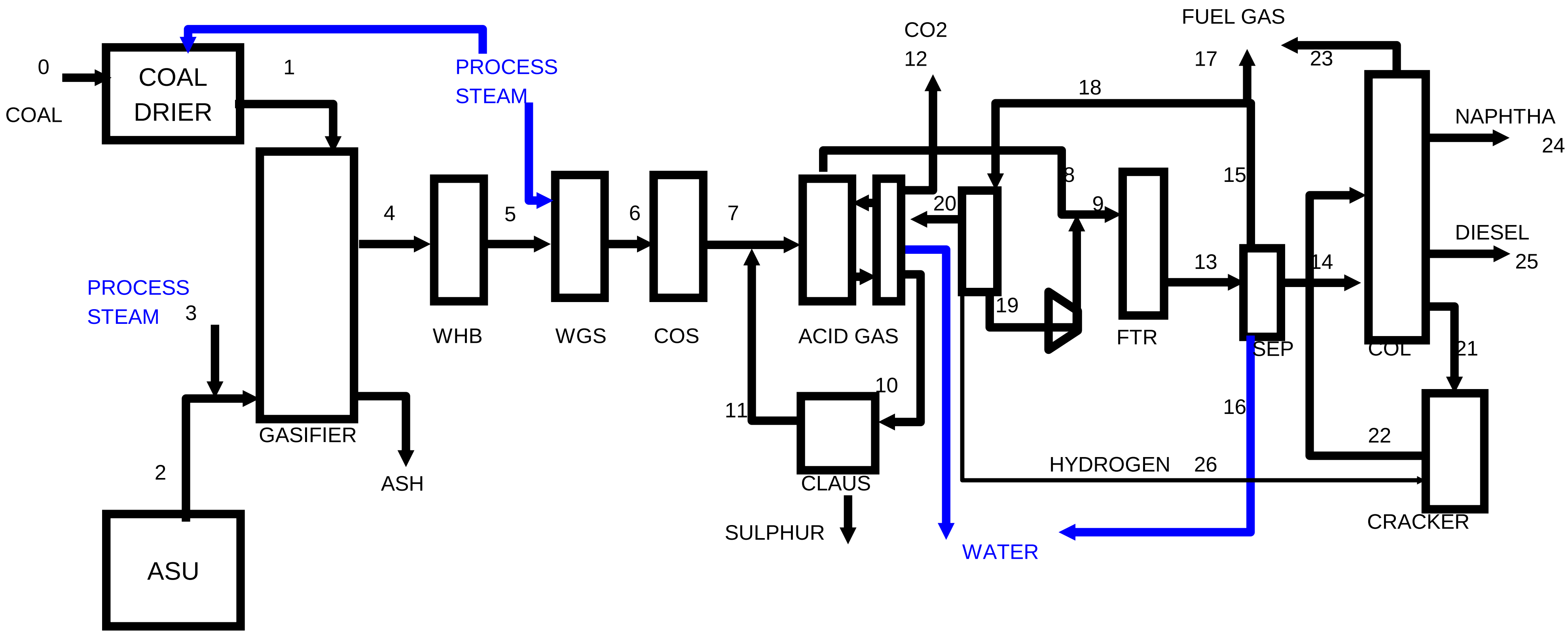
Boiling Point of Components of Interest

Gas	Boiling Point	
	(Tb) 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_2S	213	Acidic
COS	223	
NH_3	240	
SO_2	263	Acidic
HCN	299	Acidic
H_2O	373	mp. 273

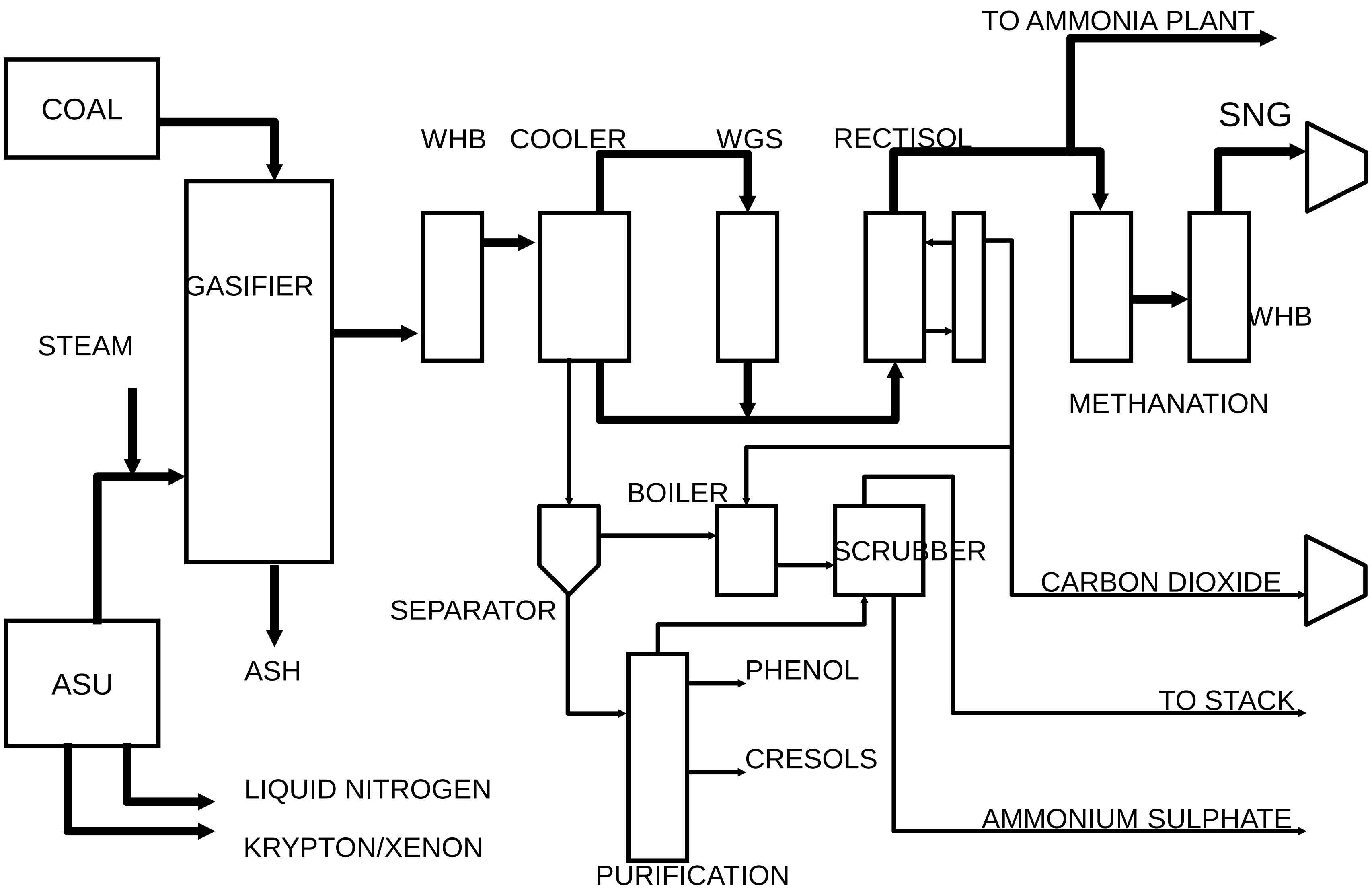
CLAUS PROCESS



COAL TO FT LIQUIDS - PROCESS FLOW



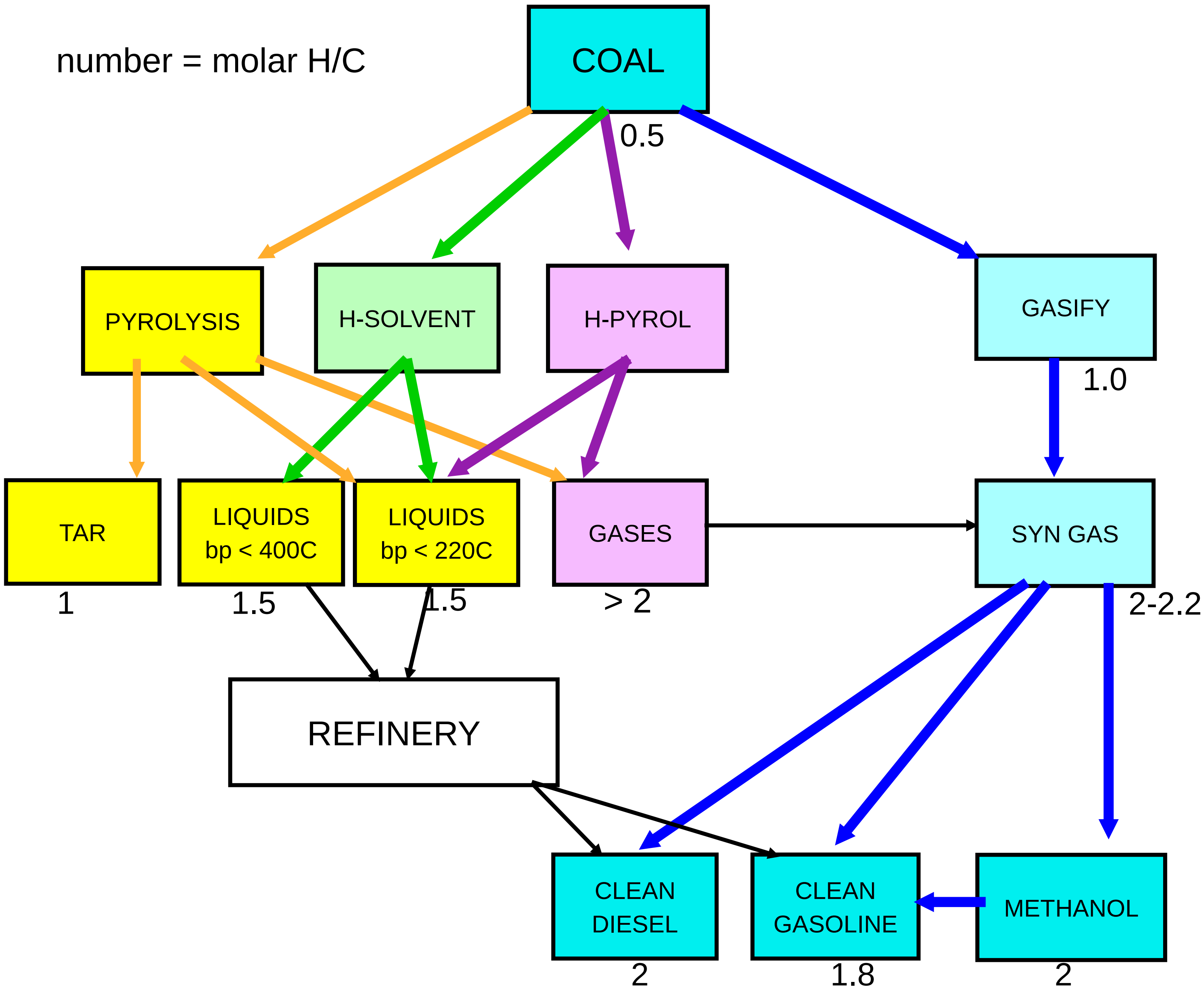
DAKOTA COAL GASIFICATION



DIRECT ROUTE HAS HIGHER EFFICIENCY THAN FT ROUTE

- FT ROUTE: 100 MOLES CARBON
  - GASIFIER
    - $100C + 50O_2 = 100CO$
  - WGS
    - $66CO + 66H_2O = 66CO_2 + 66H_2$
  - SYNTHESIS
    - $33CO + 66H_2 = 33\ \text{-}[CH_2]\text{-} + 33H_2O$
- CARBON EFFICIENCY 33%

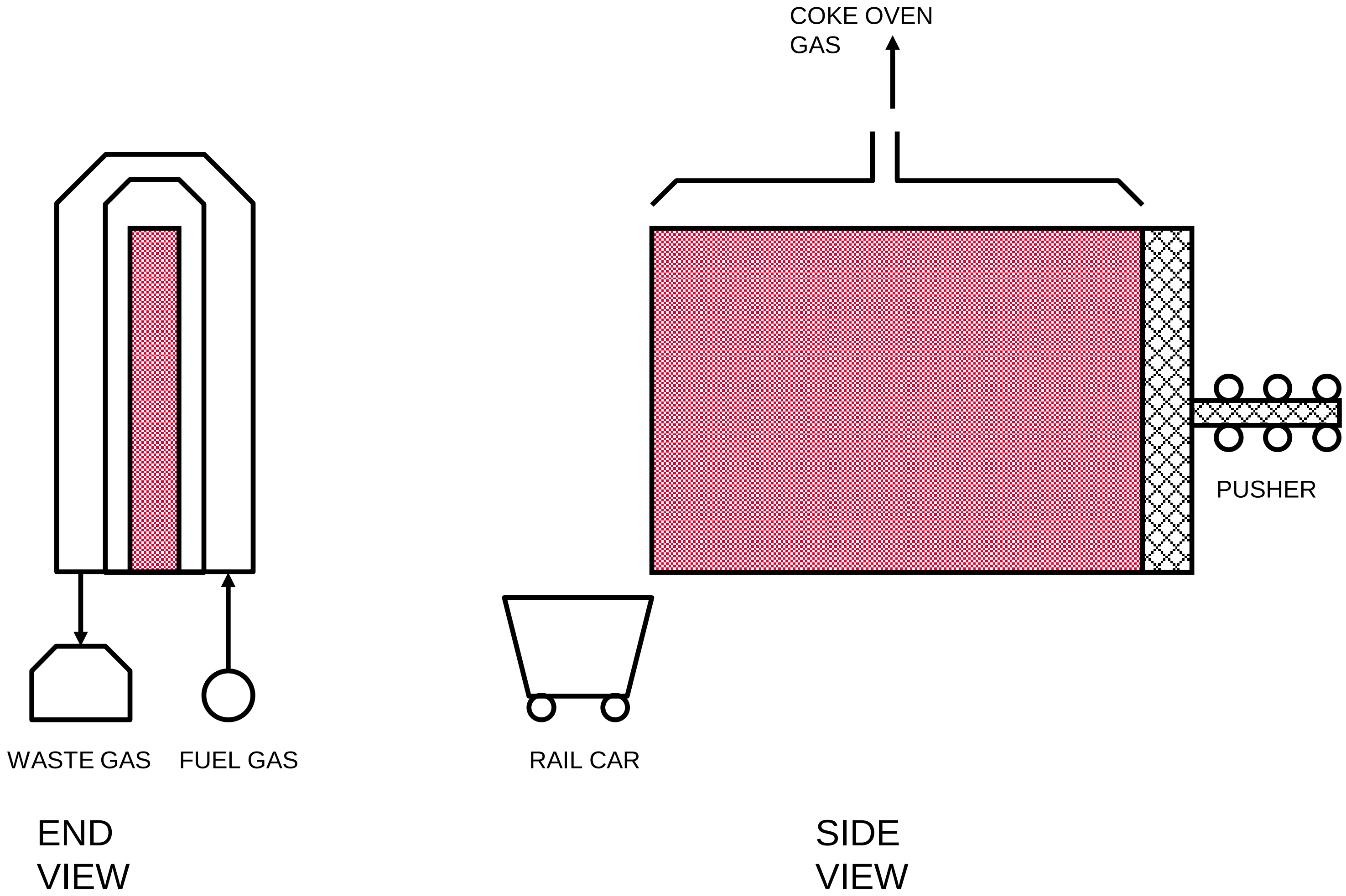
- DIRECT ROUTE: 100 MOLES CARBON
  - GASIFIER
    - $50C + 25O_2 = 50CO$
  - WGS
    - $50CO + 50H_2O = 50CO_2 + 50H_2$
  - HYDROGENATION
    - $50C + 50H_2 = 50\ \text{-}[CH_2]\text{-}$
- CARBON EFFICIENCY 50%


number = molar H/C
COAL
0.5
PYROLYSIS
H-SOLVENT
H-PYROL
GASIFY
1.0
TAR
LIQUIDS bp < 400C
LIQUIDS bp < 220C
GASES
SYN GAS
1
1.5
1.5
> 2
2-2.2
REFINERY
CLEAN DIESEL
CLEAN GASOLINE
METHANOL
2
1.8
2

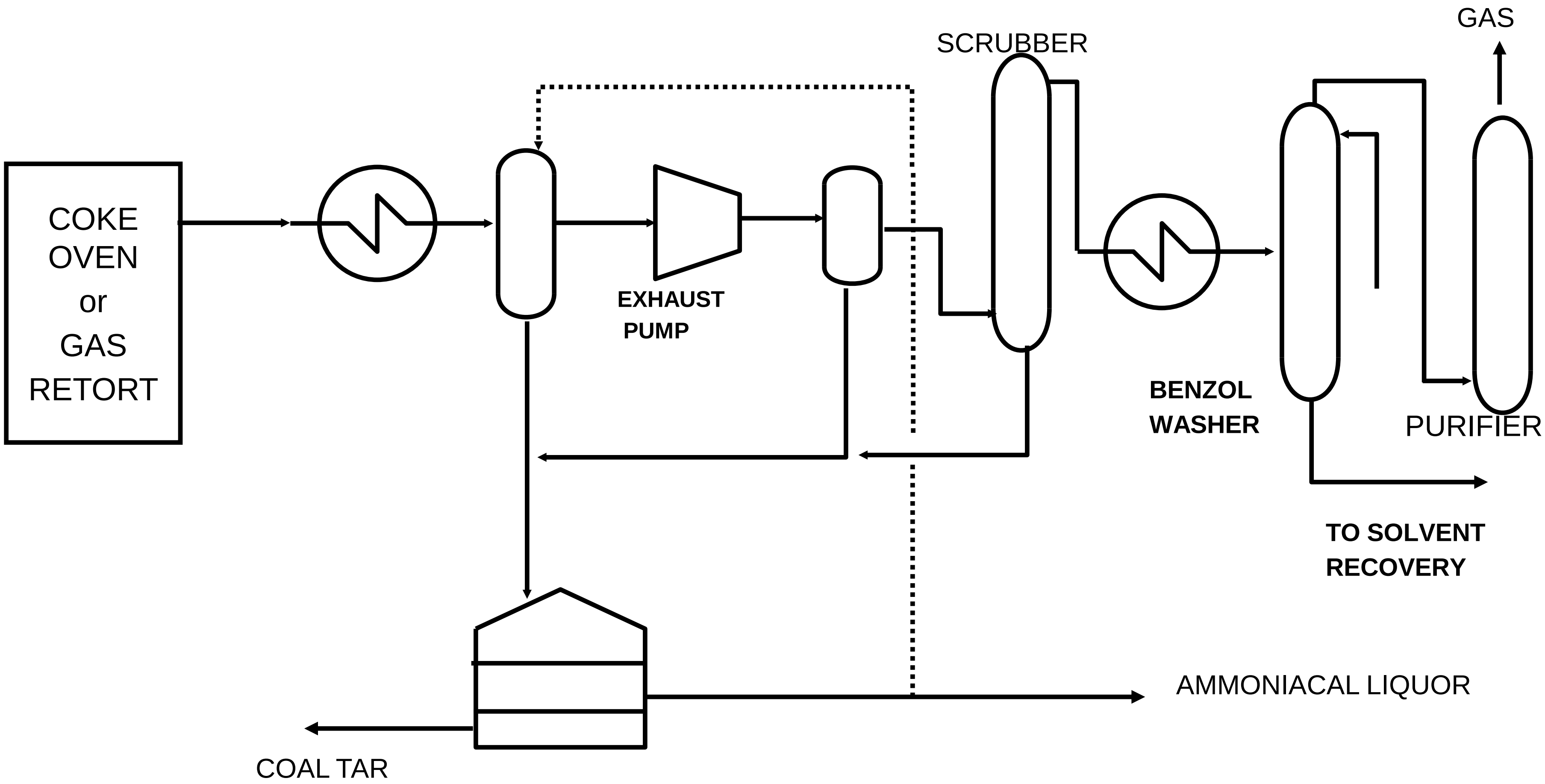
PYROLYSIS ROUTES

- 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 hetroatom 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.

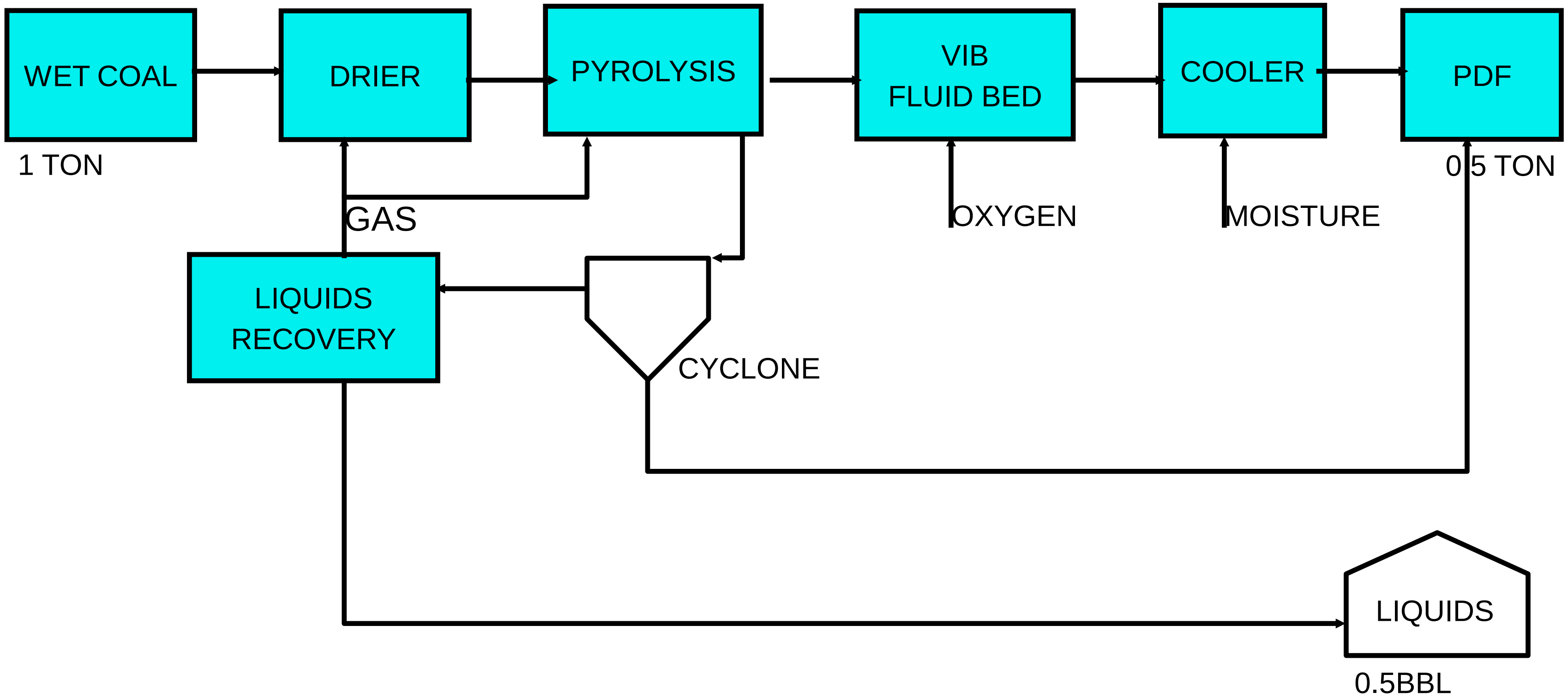
COKE OVEN


COKE OVEN
GAS
PUSHER
WASTE GAS
FUEL GAS
RAIL CAR
END
VIEW
SIDE
VIEW

COKE AND TOWN GAS

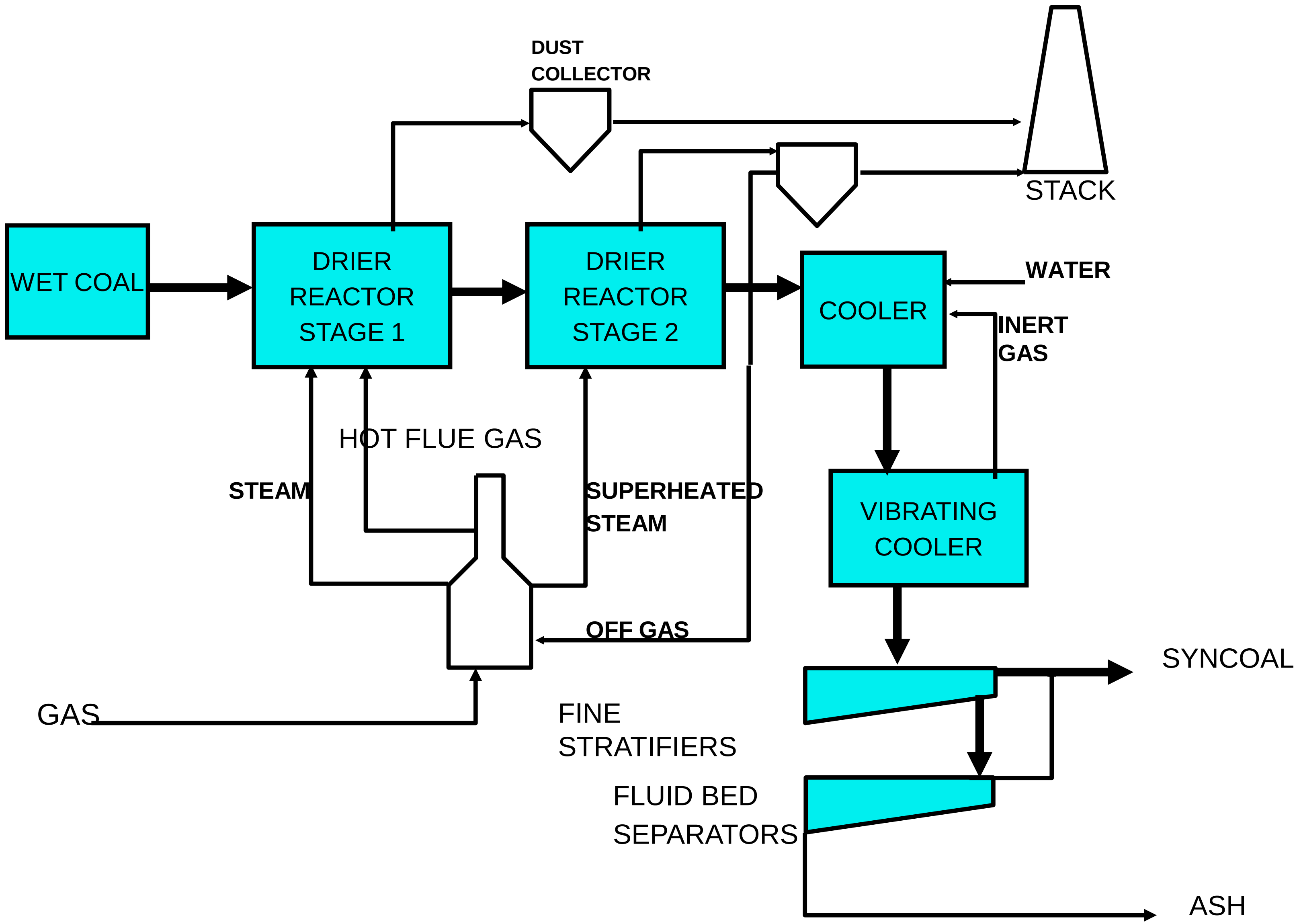


LFC (Encoal)

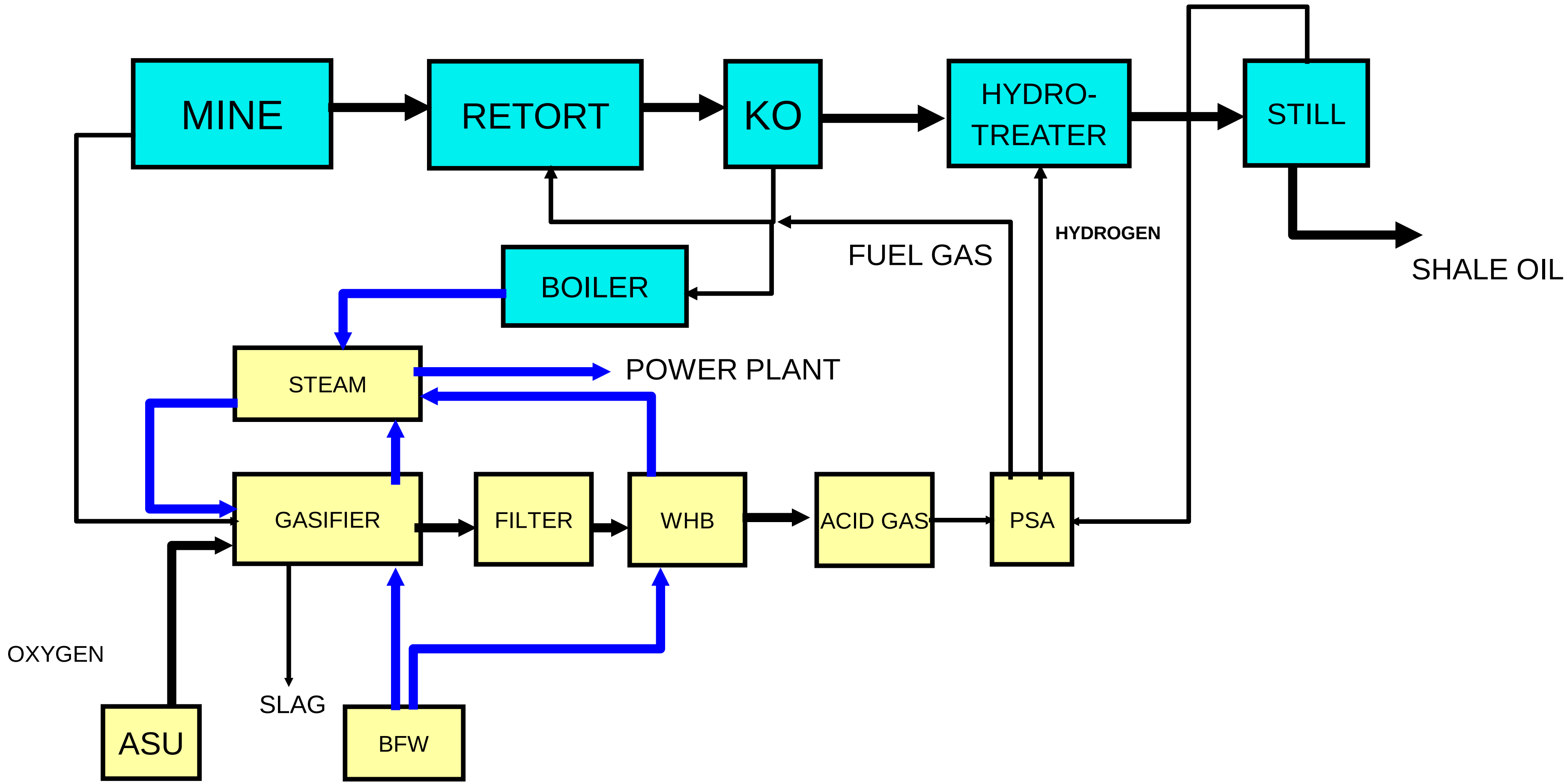


WET COAL
1 TON
DRIER
PYROLYSIS
VIB
FLUID BED
COOLER
PDF
0.5 TON
GAS
OXYGEN
MOISTURE
LIQUIDS
RECOVERY
CYCLONE
LIQUIDS
0.5BBL

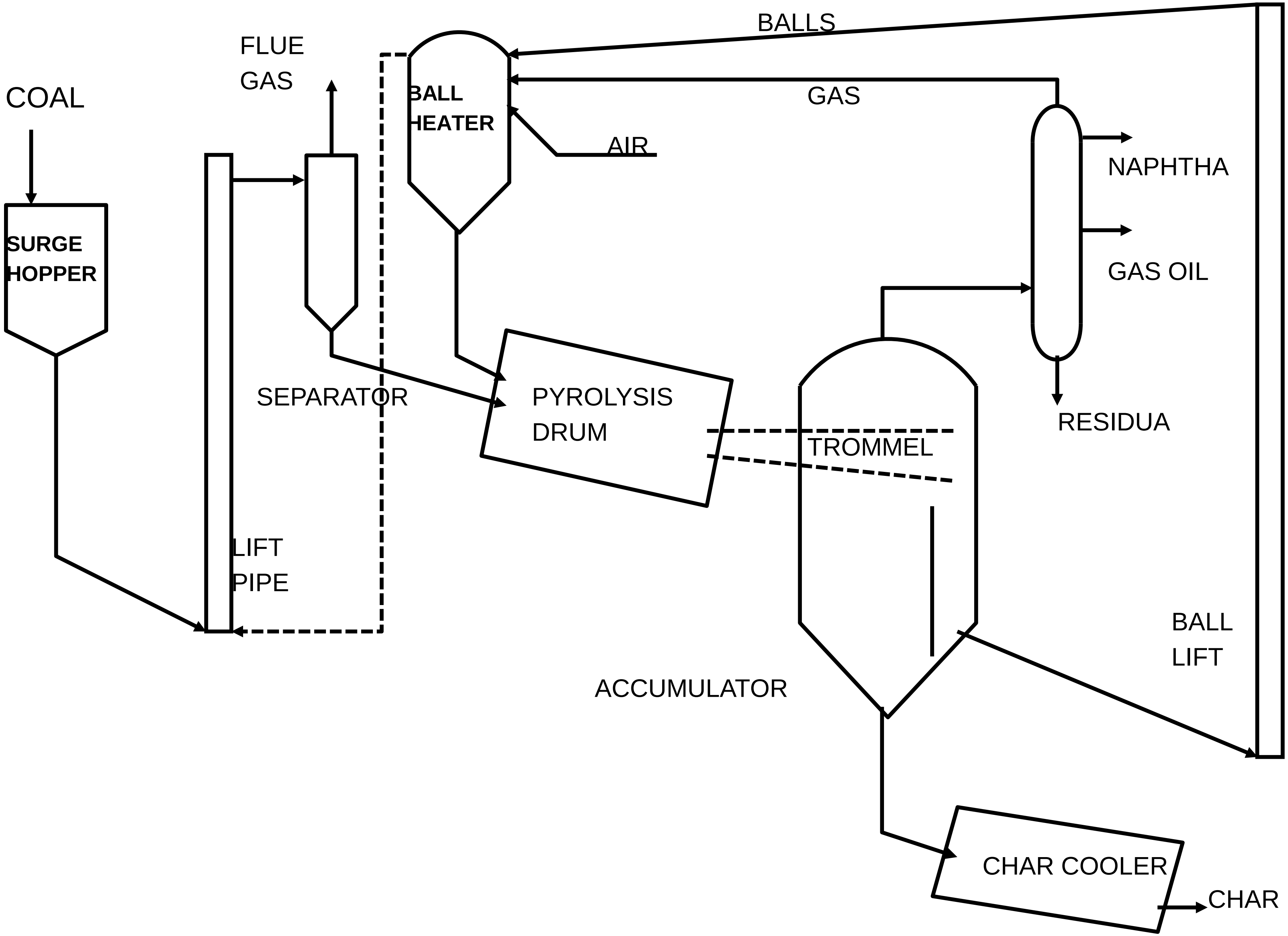
SYNCOAL


DUST
COLLECTOR
STACK
WET COAL
DRIER
REACTOR
STAGE 1
DRIER
REACTOR
STAGE 2
COOLER
WATER
INERT
GAS
HOT FLUE GAS
STEAM
SUPERHEATED
STEAM
VIBRATING
COOLER
OFF GAS
SYNCOAL
GAS
FINE
STRATIFIERS
FLUID BED
SEPARATORS
ASH

SHALE OIL PRODUCTION

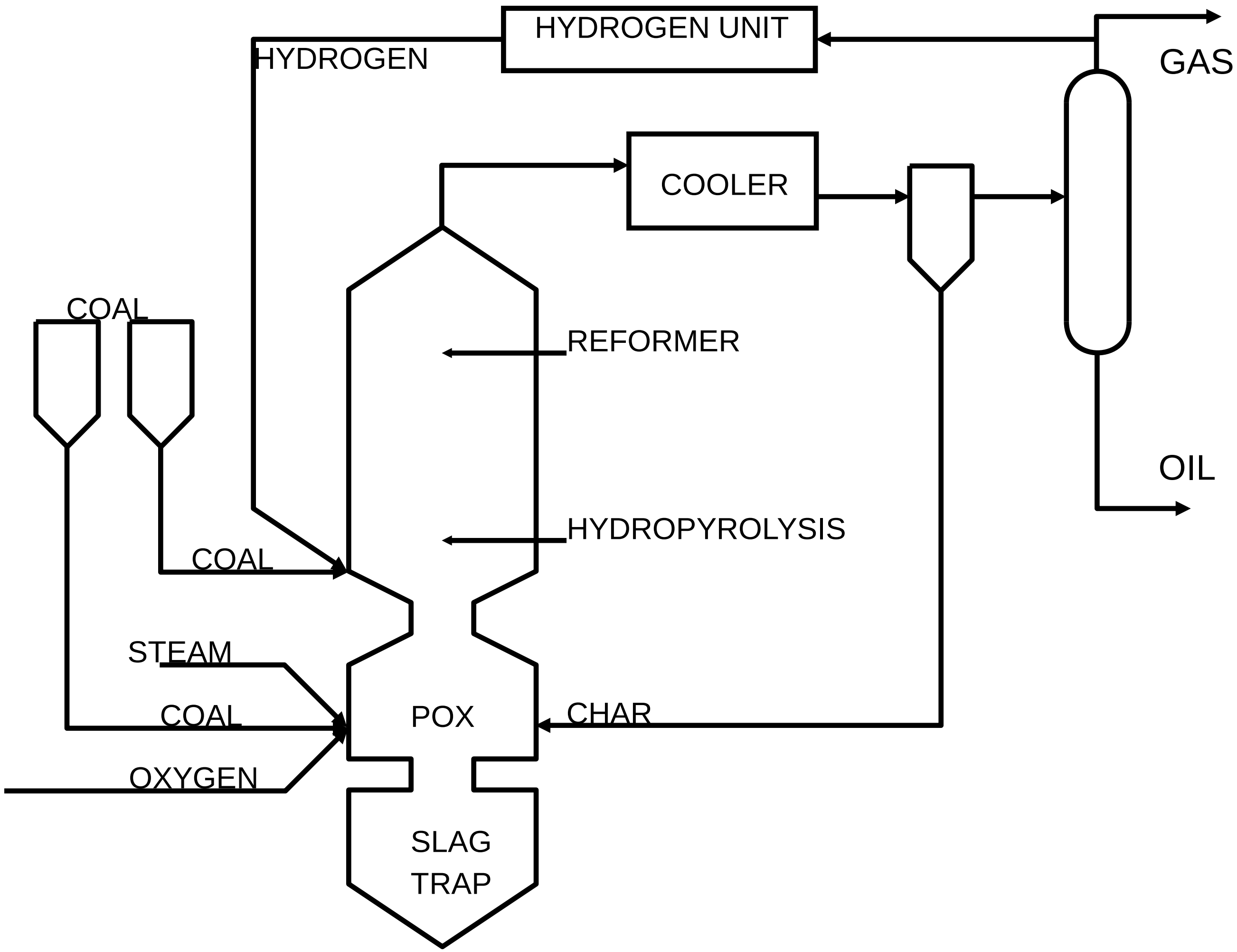


TOSCOAL

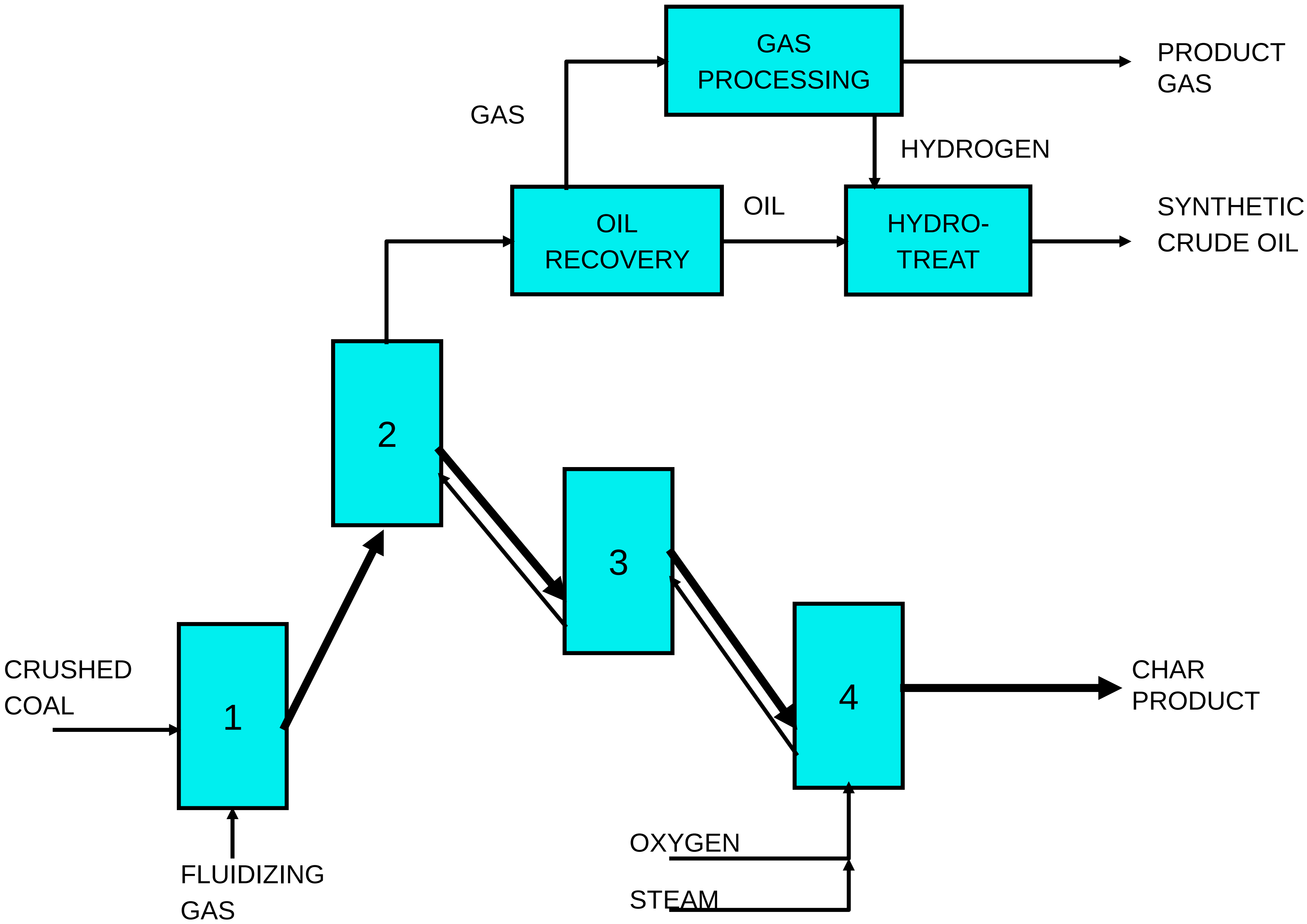


BALLS
FLUE
GAS
COAL
BALL
HEATER
GAS
AIR
NAPHTHA
SURGE
HOPPER
GAS OIL
SEPARATOR
PYROLYSIS
DRUM
RESIDUA
TROMMEL
LIFT
PIPE
BALL
LIFT
ACCUMULATOR
CHAR COOLER
CHAR

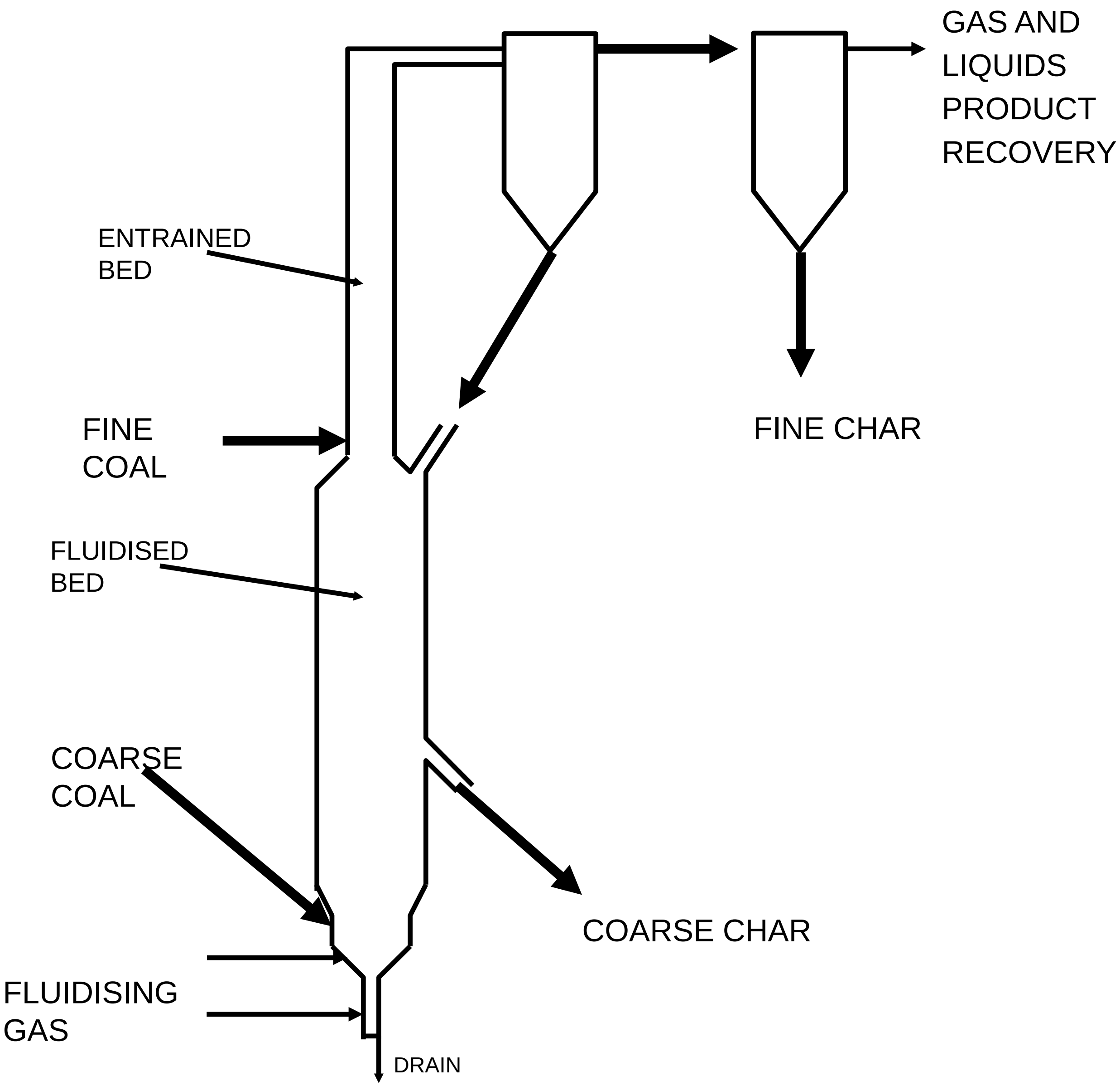
NIPPON HYDRO-PYROLYSIS

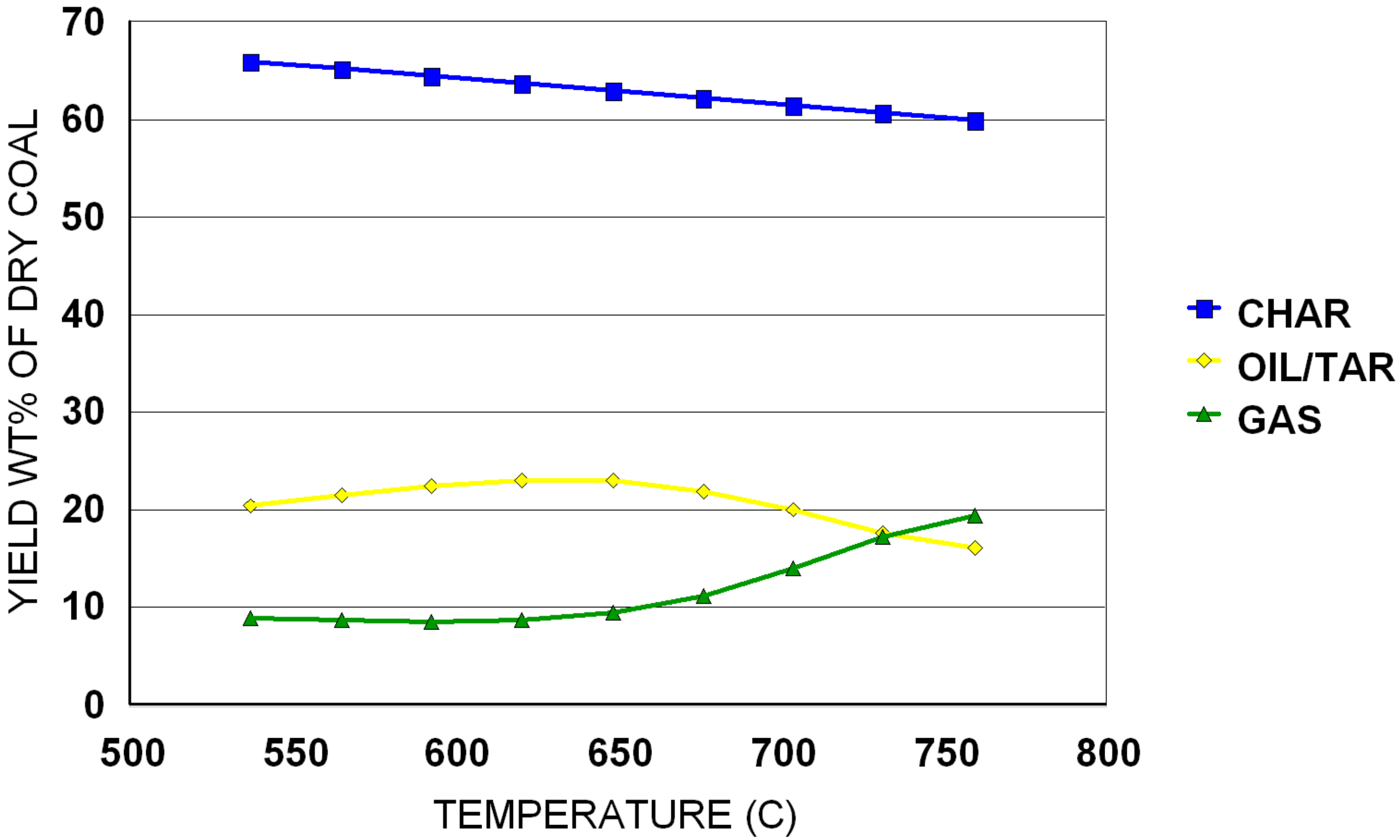


COED (FMC)


GAS PROCESSING
PRODUCT GAS
GAS
HYDROGEN
OIL RECOVERY
OIL
HYDRO-TREAT
SYNTHETIC CRUDE OIL
2
3
4
1
CRUSHED COAL
CHAR PRODUCT
FLUIDIZING GAS
OXYGEN
STEAM

MILDGAS


GAS AND
LIQUIDS
PRODUCT
RECOVERY
ENTRAINED
BED
FINE
COAL
FINE CHAR
FLUIDISED
BED
COARSE
COAL
COARSE CHAR
FLUIDISING
GAS
DRAIN



70
60
50
40
30
20
10
0
500
550
600
650
700
750
800
YIELD WT% OF DRY COAL
TEMPERATURE (C)
CHAR
OIL/TAR
GAS

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