

# 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

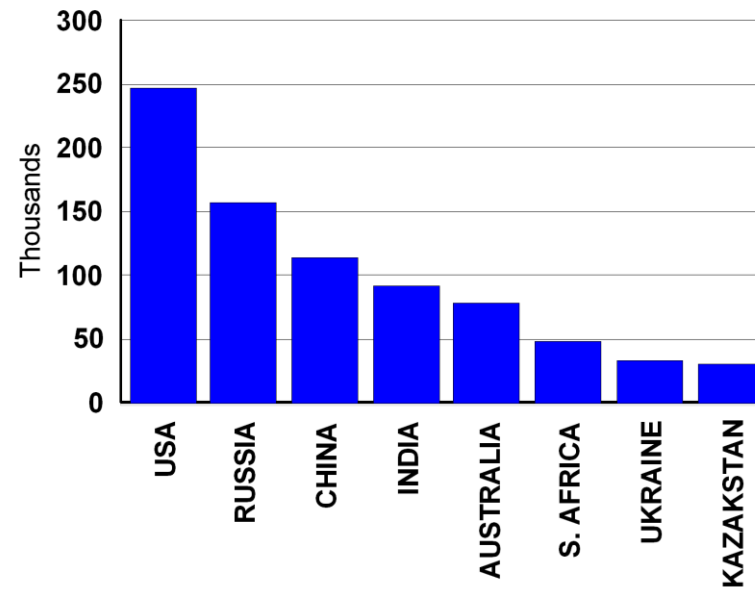
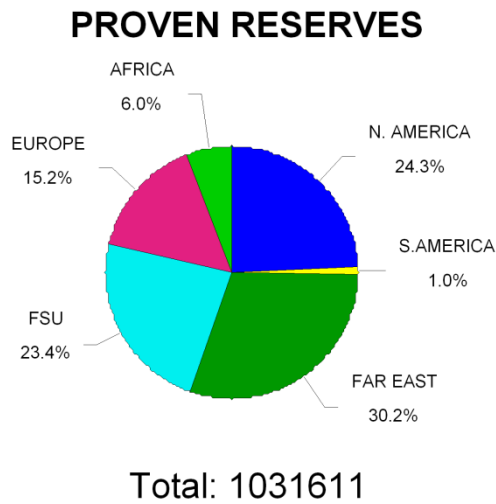
- ▶ BLACK COAL
- ▶ BROWN COAL/LIGNITES
- ▶ PEAT

## ■ BIOMASS

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

# FEEDSTOCK - 1

## WORLD COAL RESERVES (Millions of tonnes)

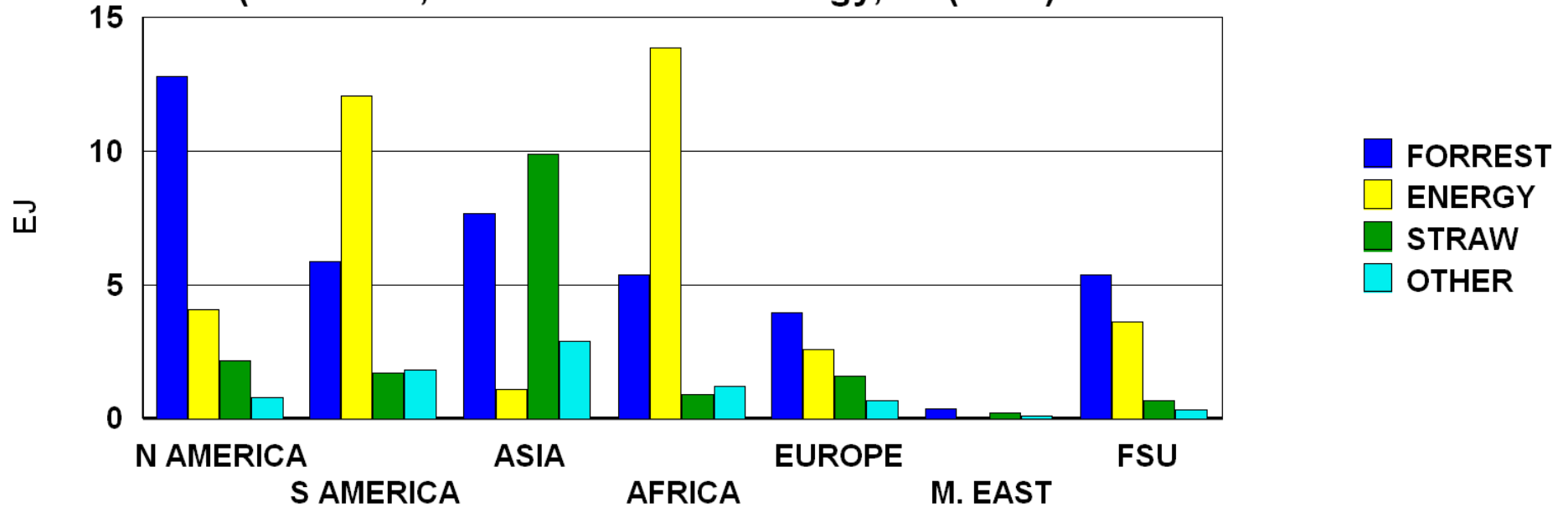


~ 20,000 EJ

# 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

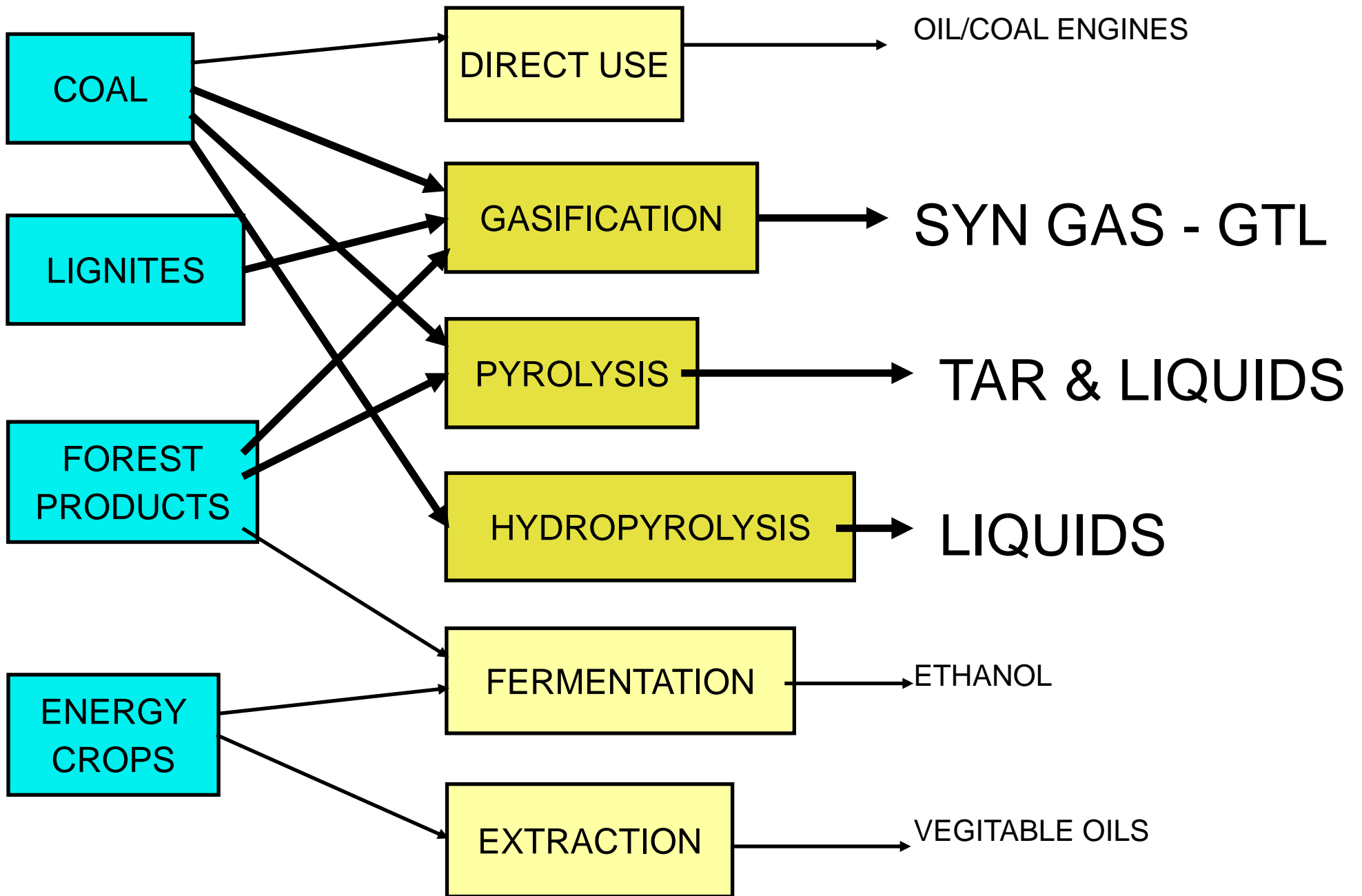
# SUMMARY

## ▪ 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**

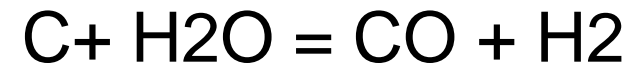
The principal chemical reactions are:

## Solid - Gas Reactions:

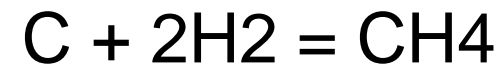
Combustion:



Steam Carbon:



Hydro-gasification:

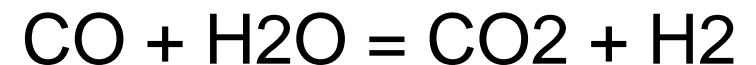


The Boudouard Reaction:

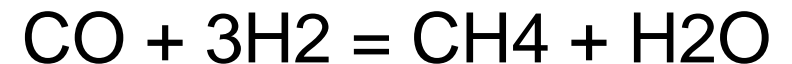


## Gas Phase Reactions

Water-Gas-Shift:



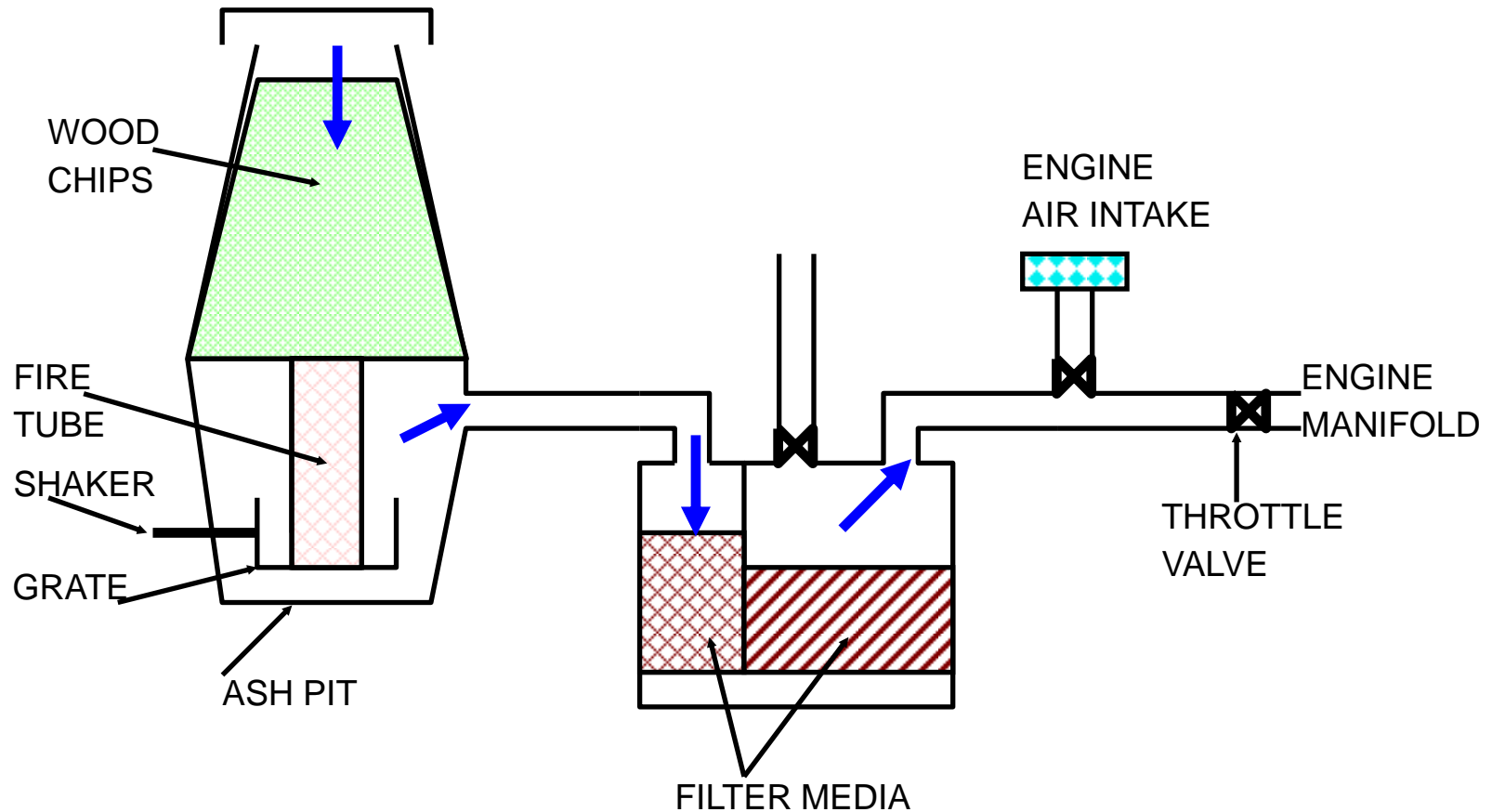
Methanation:



## Pyrolysis

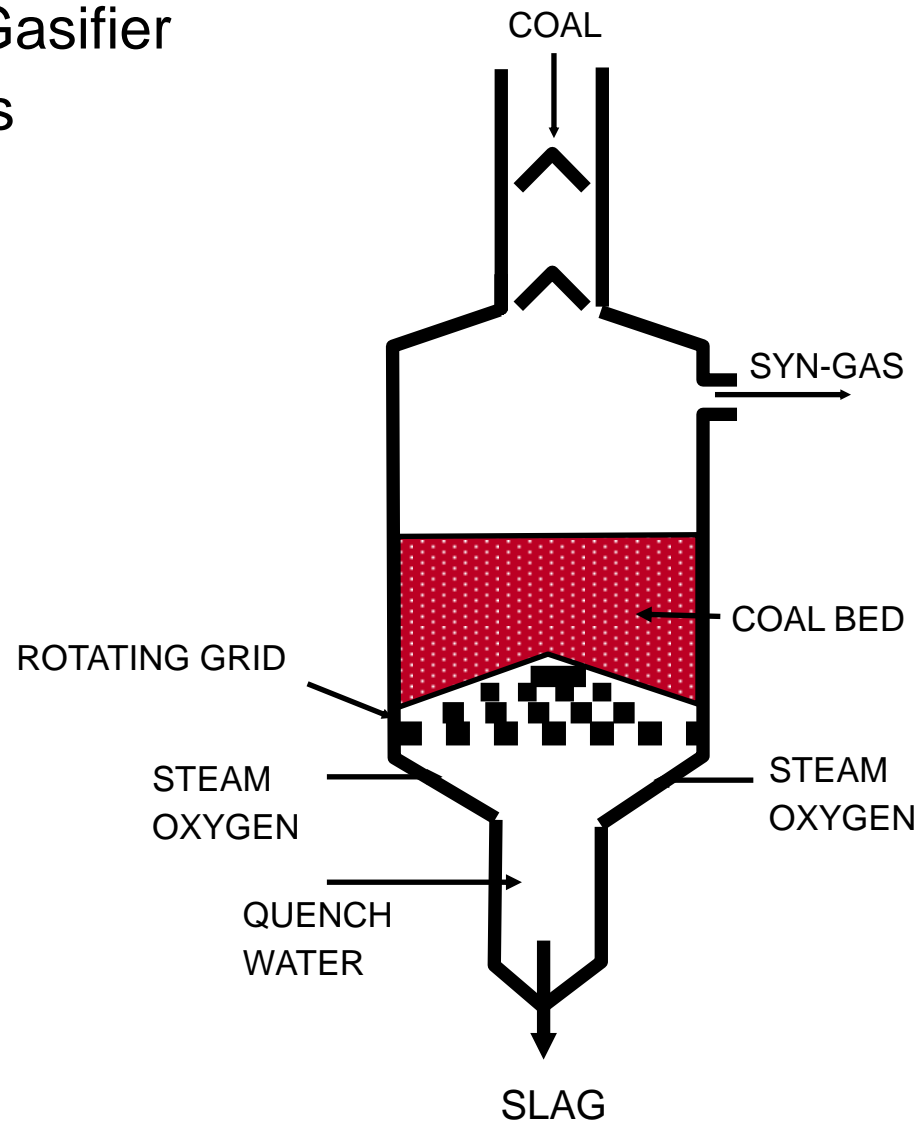
As well as these reactions, large molecules undergo pyrolysis and hydro-pyrolysis to small molecules.

# STRATIFIED DOWNDRAFT GASIFIER



# Moving Bed Gasifier

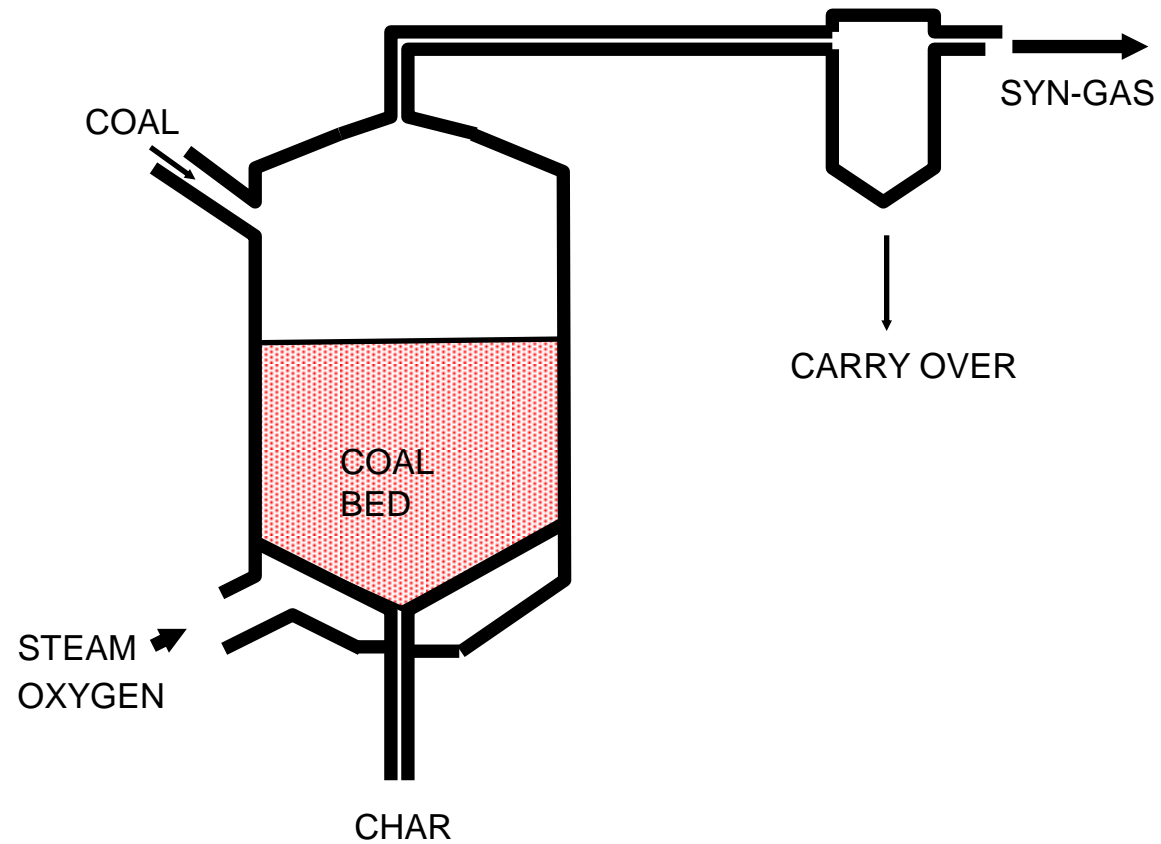
Coal as lumps



# Fluidized Bed Gasifier

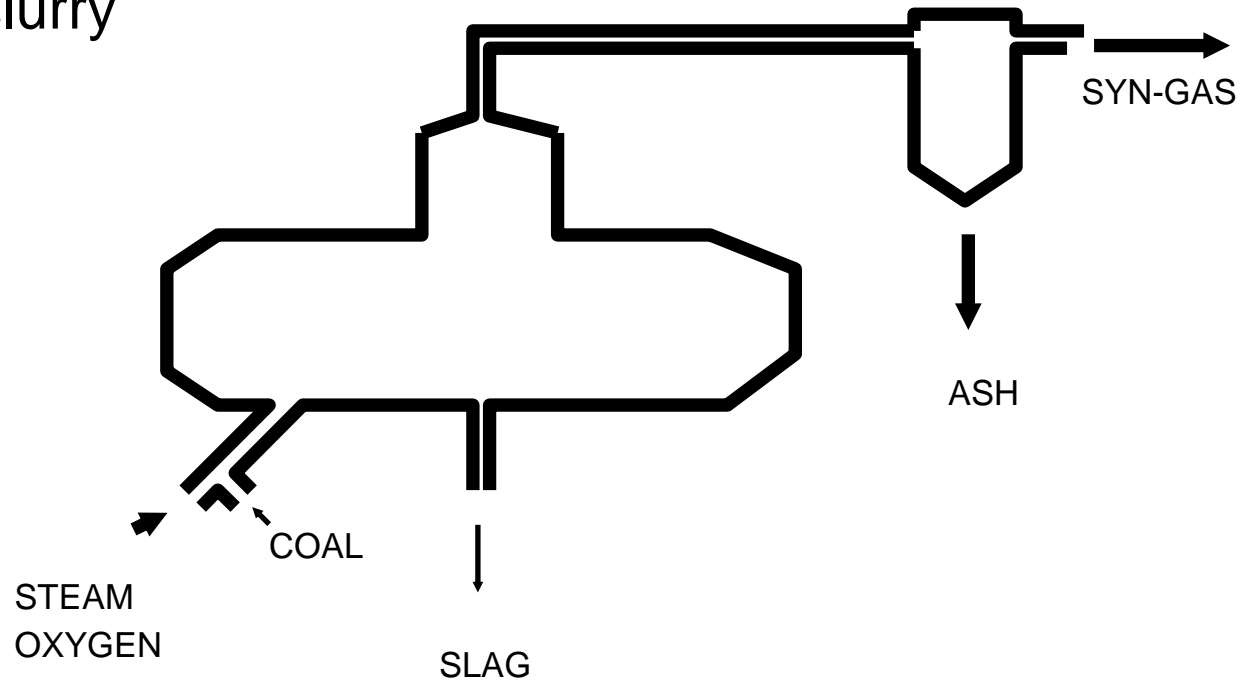
Coal as fines

WINKLER  
U-GAS



# Entrained Bed Gasifier

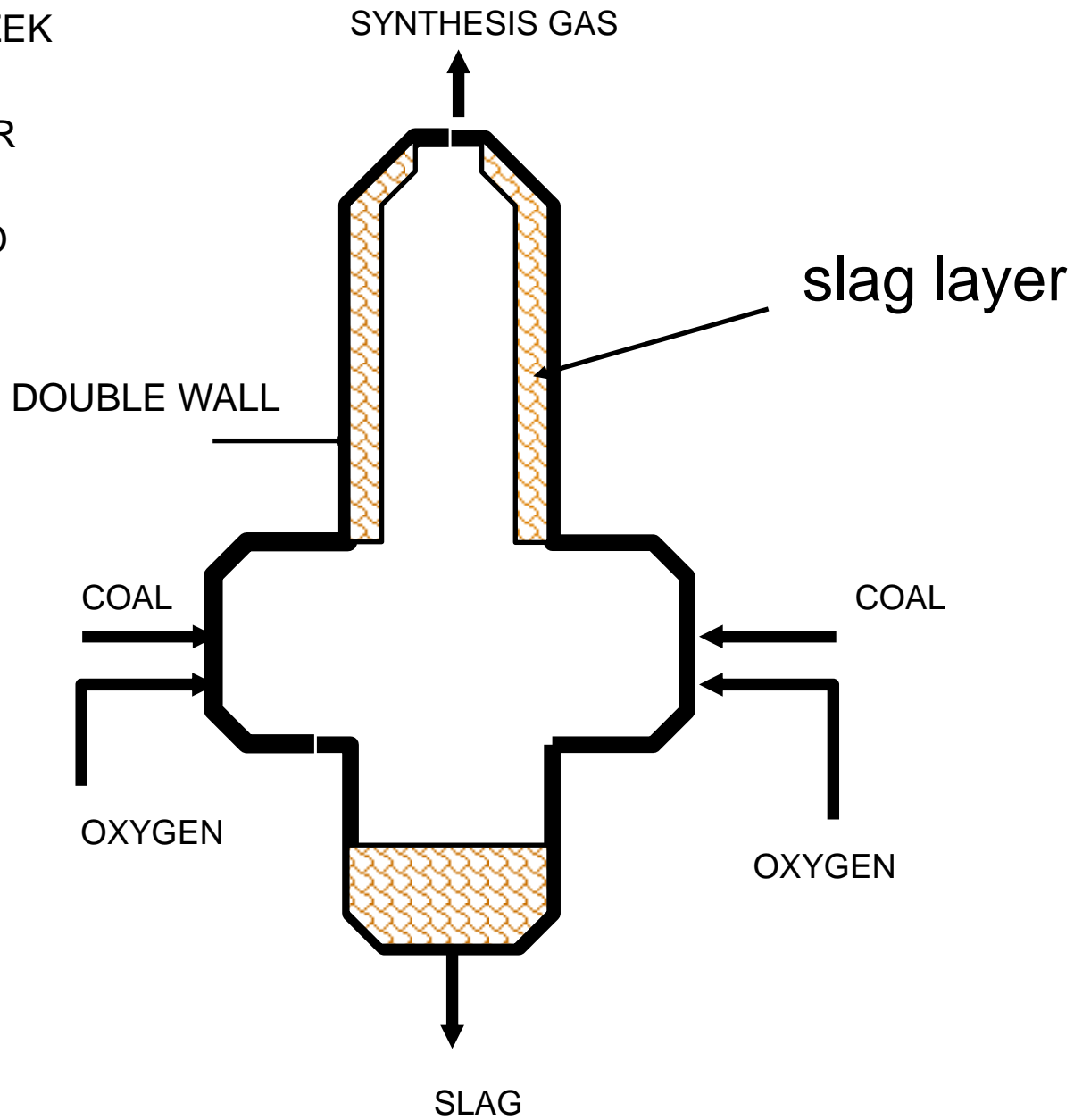
Coal as fines in gas or water slurry



KOPPERS - TOTZEK

SHELL - GASIFIER

UHDE - PRENFLO



CONOCOPHILLIPS

SYNTHESIS GAS

CHAR

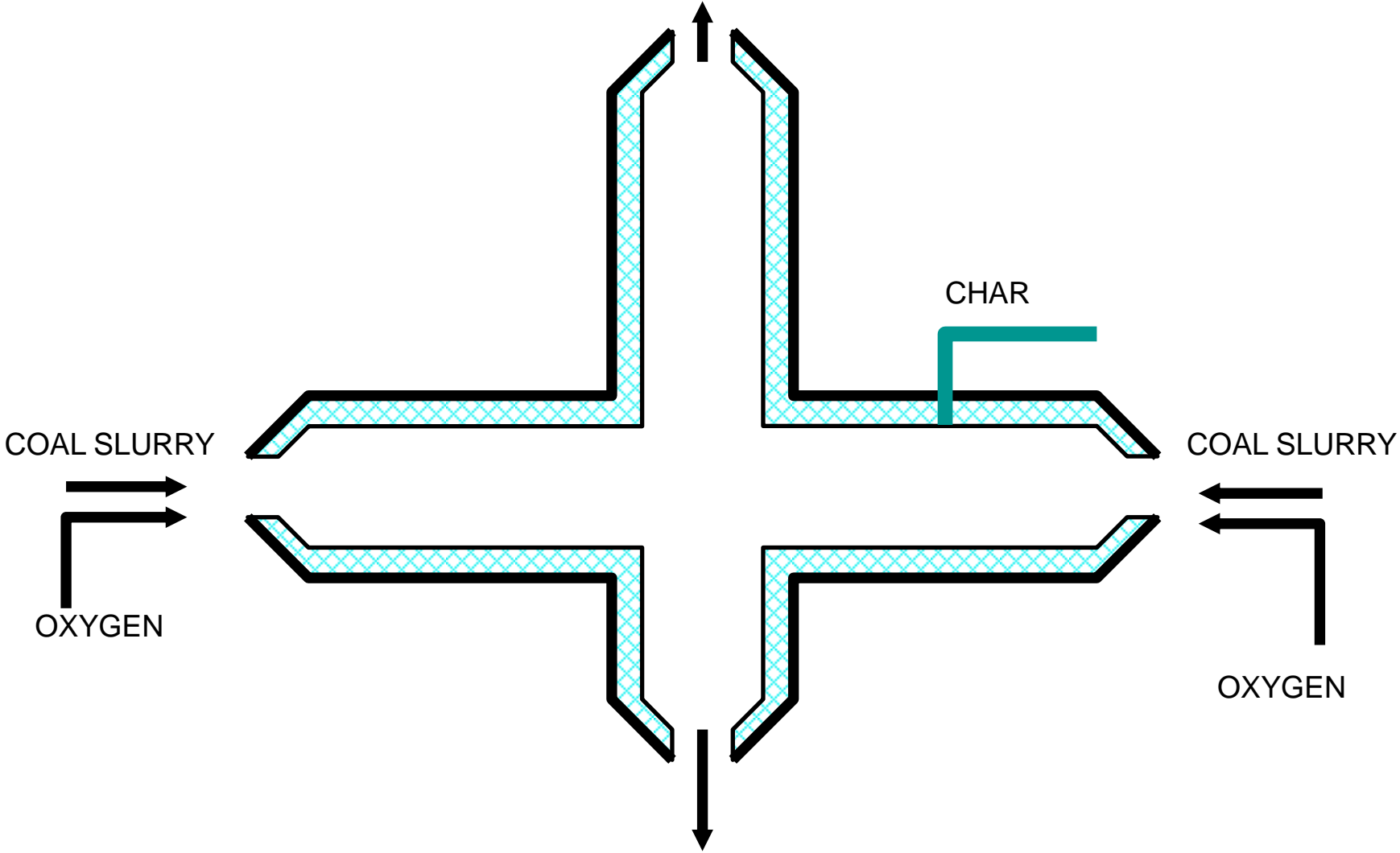
COAL SLURRY

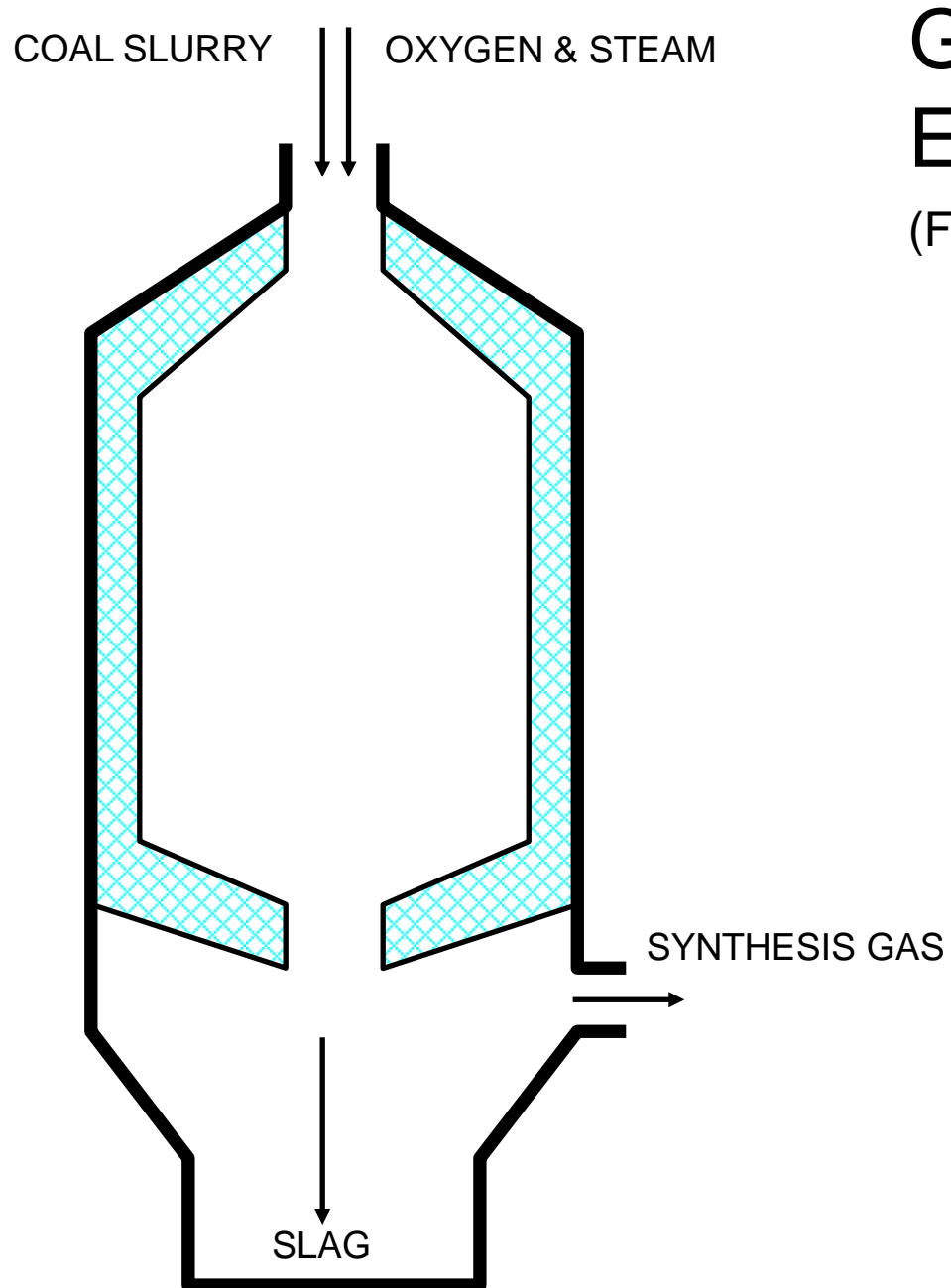
COAL SLURRY

OXYGEN

OXYGEN

SLAG

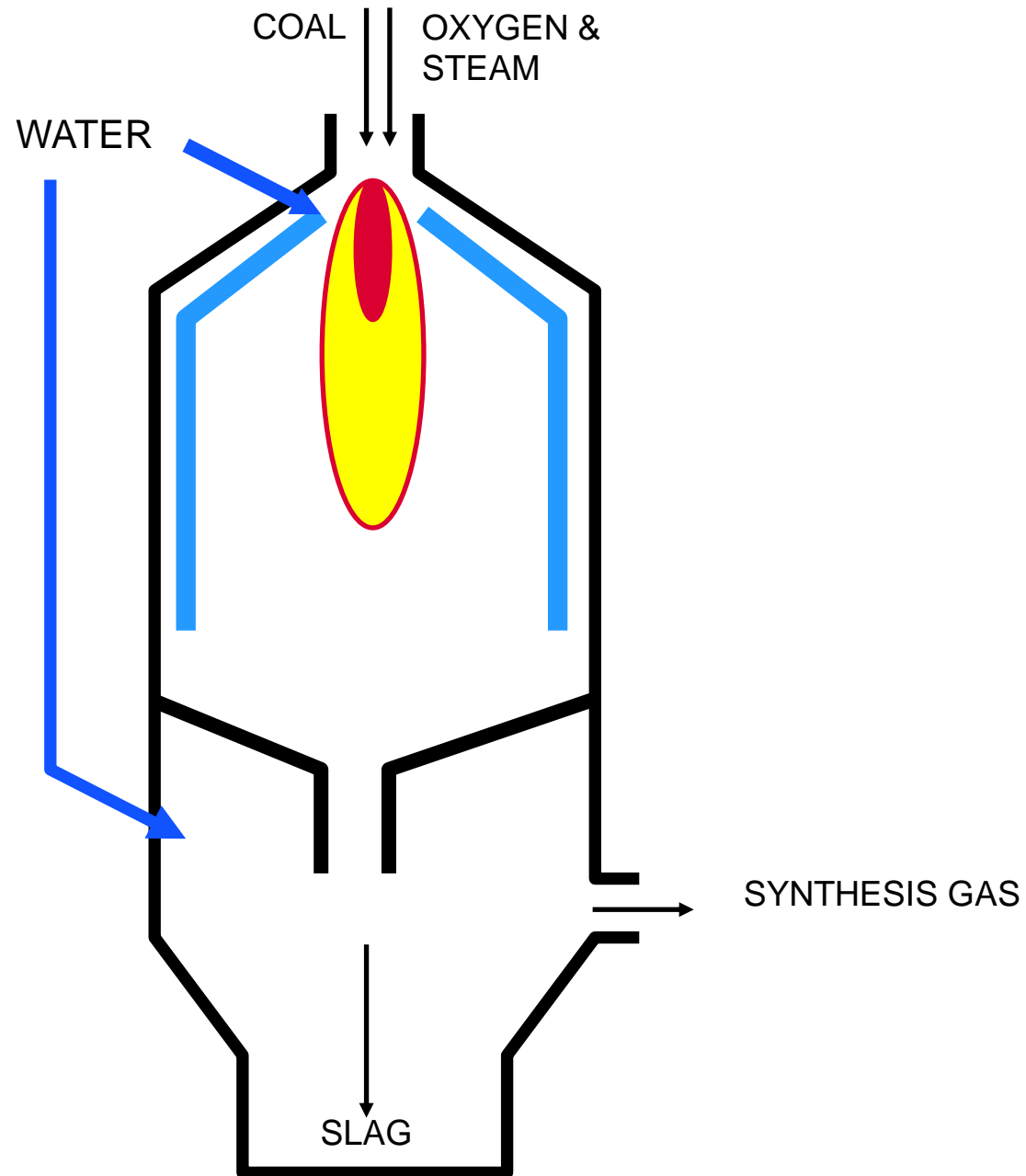




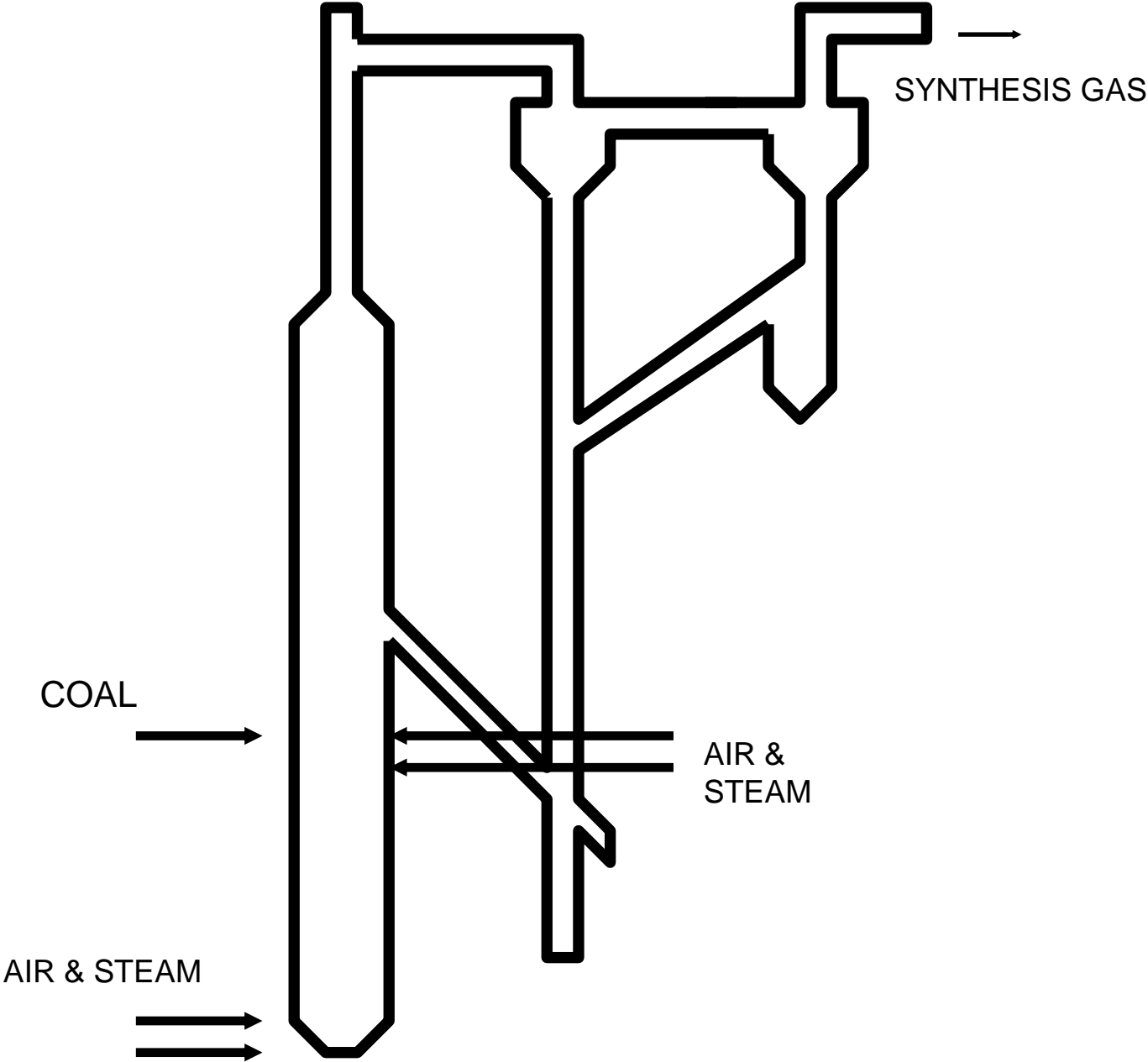
**GE**  
**ENERGY**  
(Formerly Texaco)



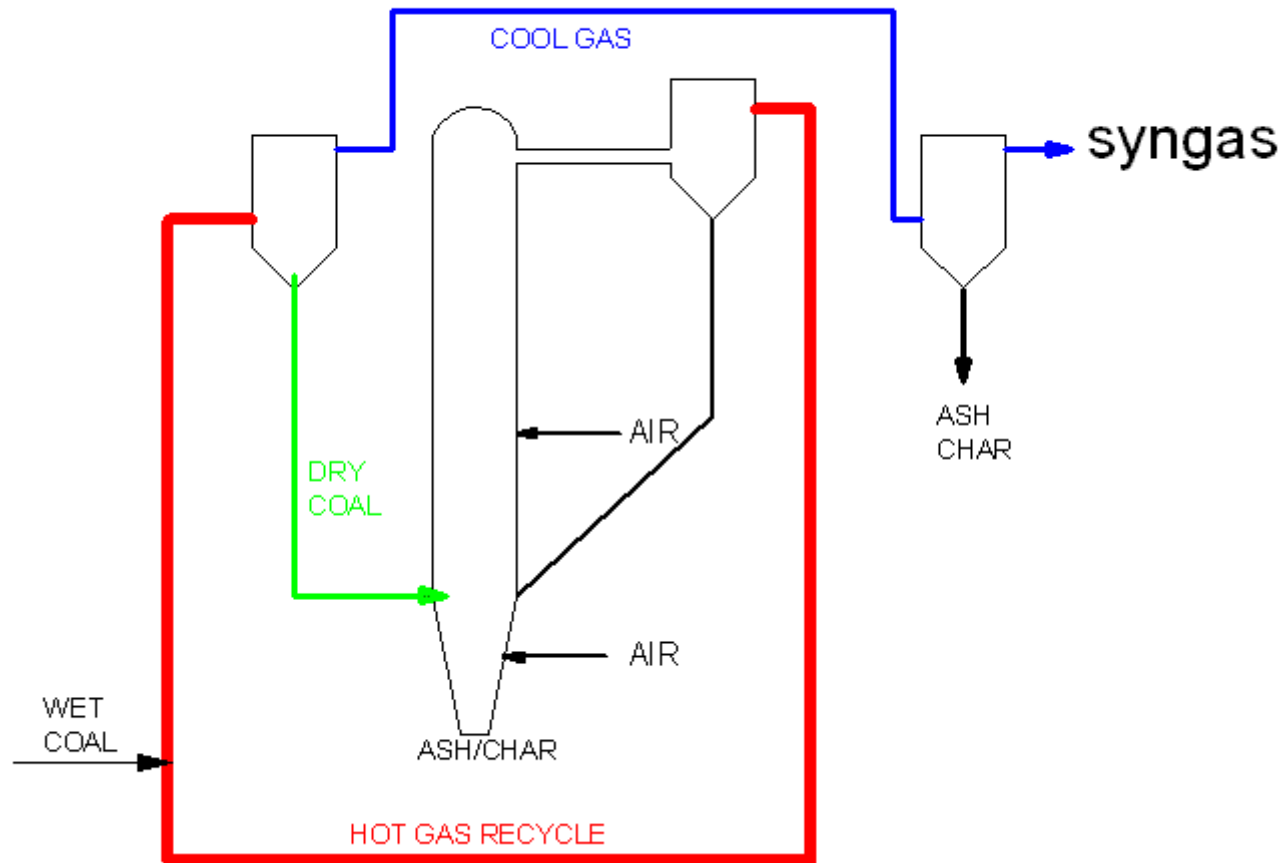
# SIEMENS



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

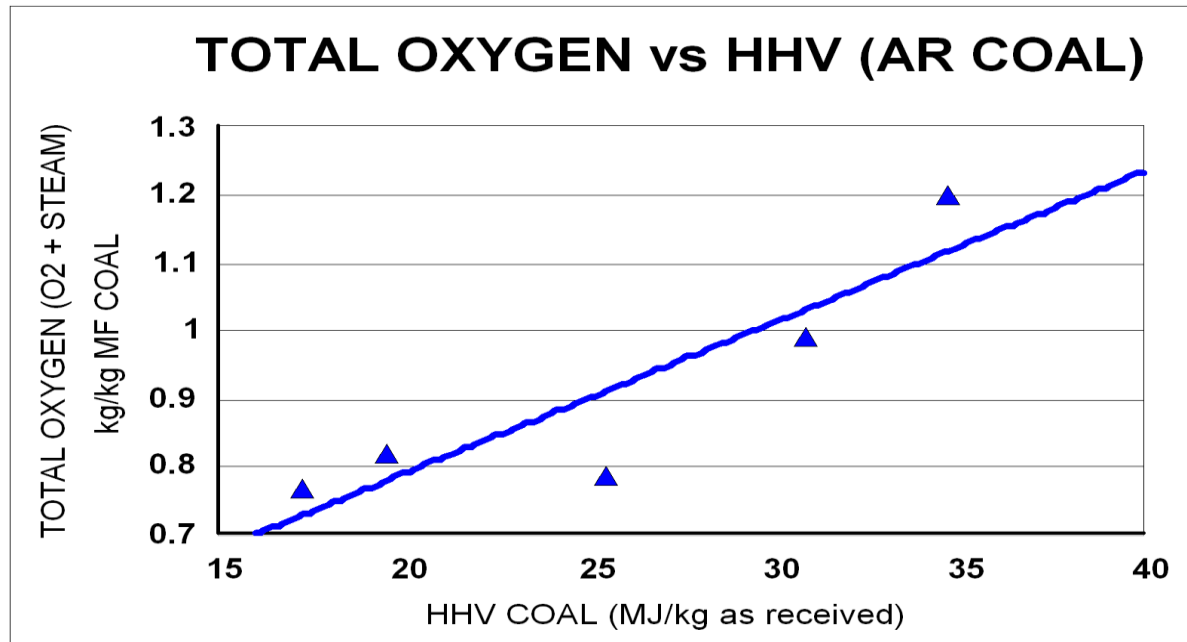
	Lurgi	BG/L	KRW	Texaco	Shell
Type of bed	Moving	Moving	Fluid	Entrained	Entrained
Pressure (MPa)	0.101	2.82	2.82	4.22	2.46
Ash Type	ash	Slag	Aglom.	Slag	slag
H <sub>2</sub>	52.2	26.4	27.7	30.3	26.7
CO	29.5	45.8	54.6	39.6	63.1
CO <sub>2</sub>	5.6	2.9	4.7	10.8	1.5
CH <sub>4</sub>	4.4	3.8	5.8	0.1	0.03
Other hydrocarbons	0.3	0.2	<0.01	Nil	Nil
H <sub>2</sub> S	0.9	1.0	1.3	1.0	1.3
H <sub>2</sub> S/COS	20/1	11/1	9/1	42/1	9/1
N <sub>2</sub> + A	1.5	3.3	1.7	1.6	5.2
H <sub>2</sub> O	5.1	16.3	4.4	16.5	2.0
NH <sub>3</sub> + 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 <sub>2</sub>	52.2	26.7	14.5
CO	29.5	63.1	14.7
CO <sub>2</sub>	5.6	1.5	15.5
CH <sub>4</sub>	4.4	0.03	2.5
Other hydrocarbons	0.3	Nil	0.37 +BTX
H <sub>2</sub> S	0.9	1.3	
H <sub>2</sub> S/COS	20/1	9/1	
N <sub>2</sub> + A	1.5	5.2	52.3
H <sub>2</sub> O	5.1	2.0	
NH <sub>3</sub> + 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 H<sub>2</sub>

Stoichiometric Ratio (SR) = H<sub>2</sub>/CO (molar)

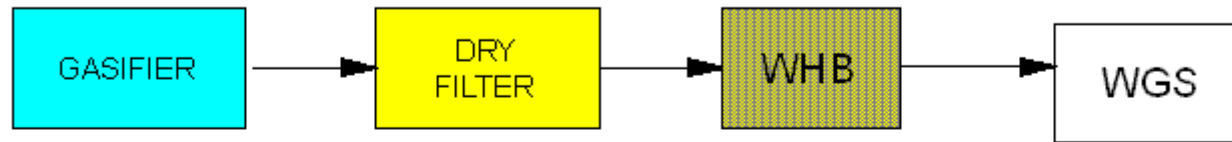
## – REMOVAL OF

### ▪ CO<sub>2</sub>

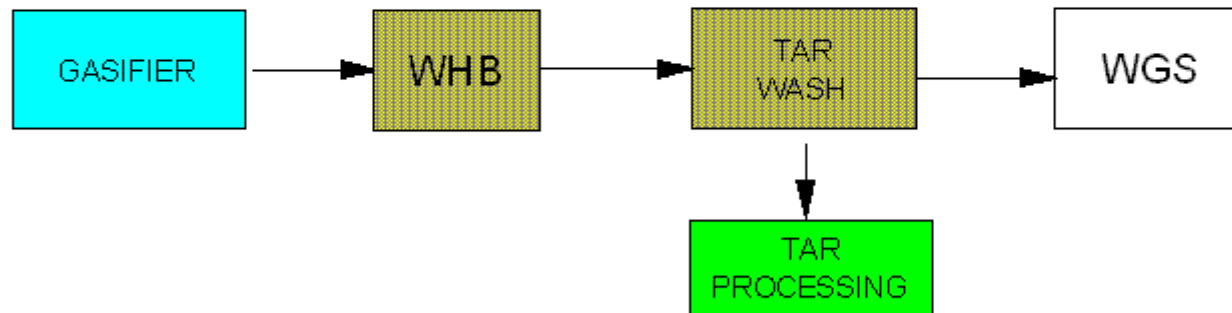
### ▪ H<sub>2</sub>S (and other S compounds)

## APPROACHES TO FIRST STAGE CLEANING

ENTRAINED BED



MOVING BED



BTL



## SR REQUIREMENTS OF DIFFERENT TECHNOLOGY

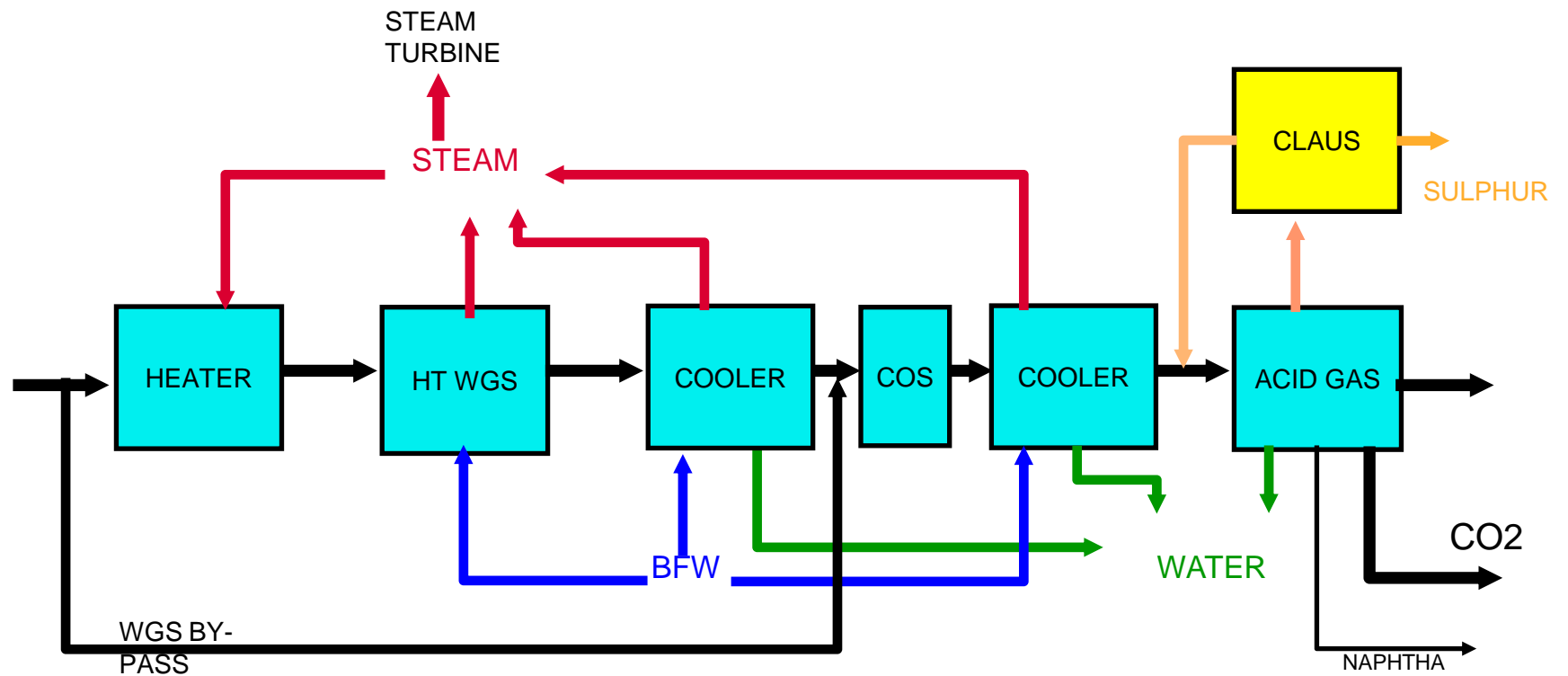
PRODUCT	H <sub>2</sub> :CO	CAPACITY (000t/a)	SYNGAS (000Ncm/h)
Methanol	2:1	160 - 1,700	48 - 250
Fischer-Tropsch (Fe)	1.75:1	637 + (a)	48 - 250
Fischer-Tropsch (Co)	2:1	637 + (a)	48 - 250
Acetic Acid	0:1	275 - 545	18 - 36
Acetic Anydride	0:1	90	3.5
Oxo Alcohols	2:1	115 - 275	12 - 25
Phosgene (TDI)	0:1	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

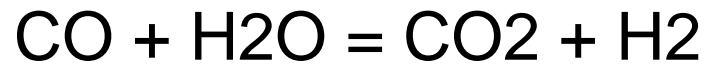
## Impact of impurities in the synthesis gas on downstream processes

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

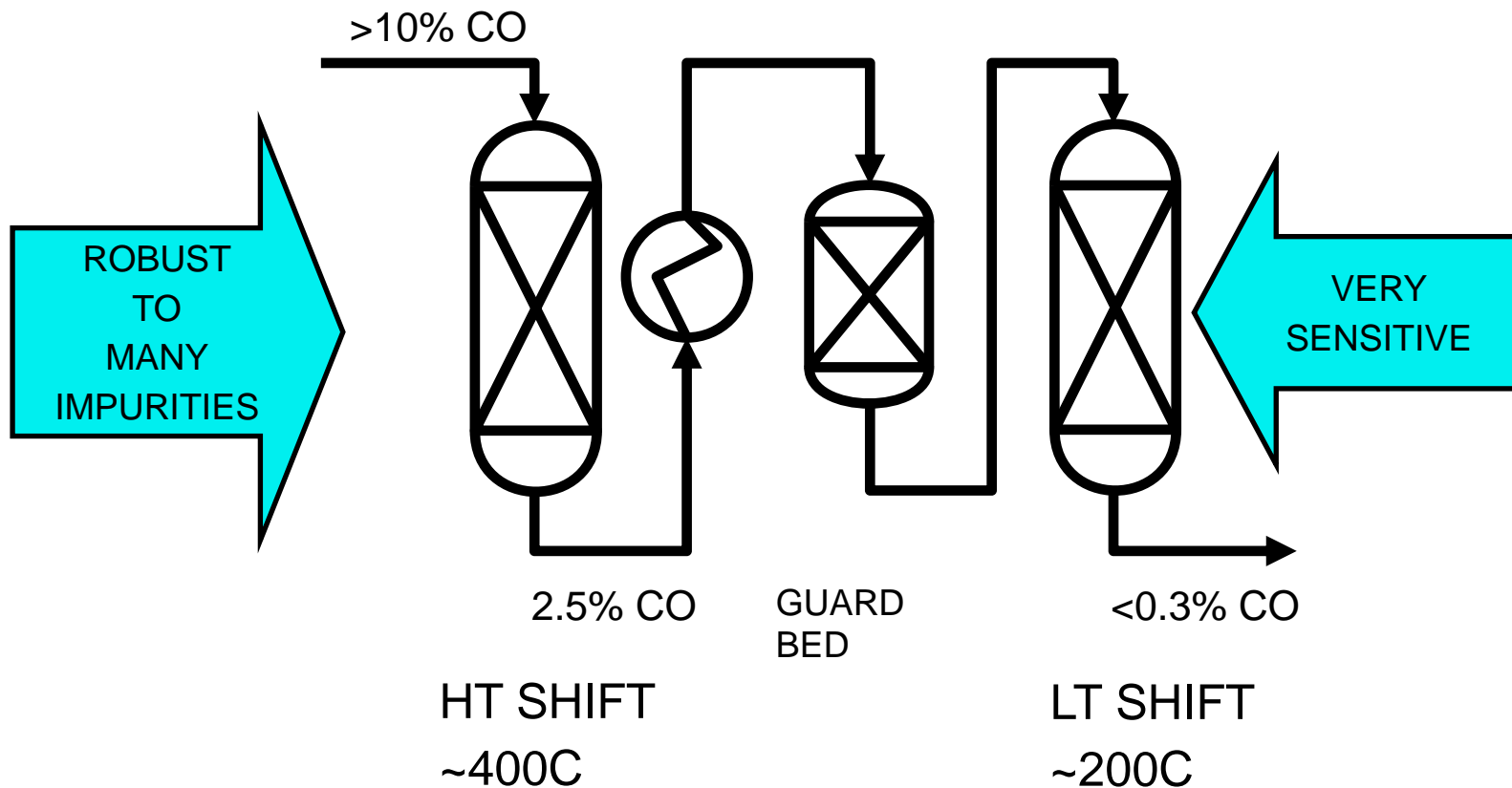
# WGS SHIFT AND ACID GAS



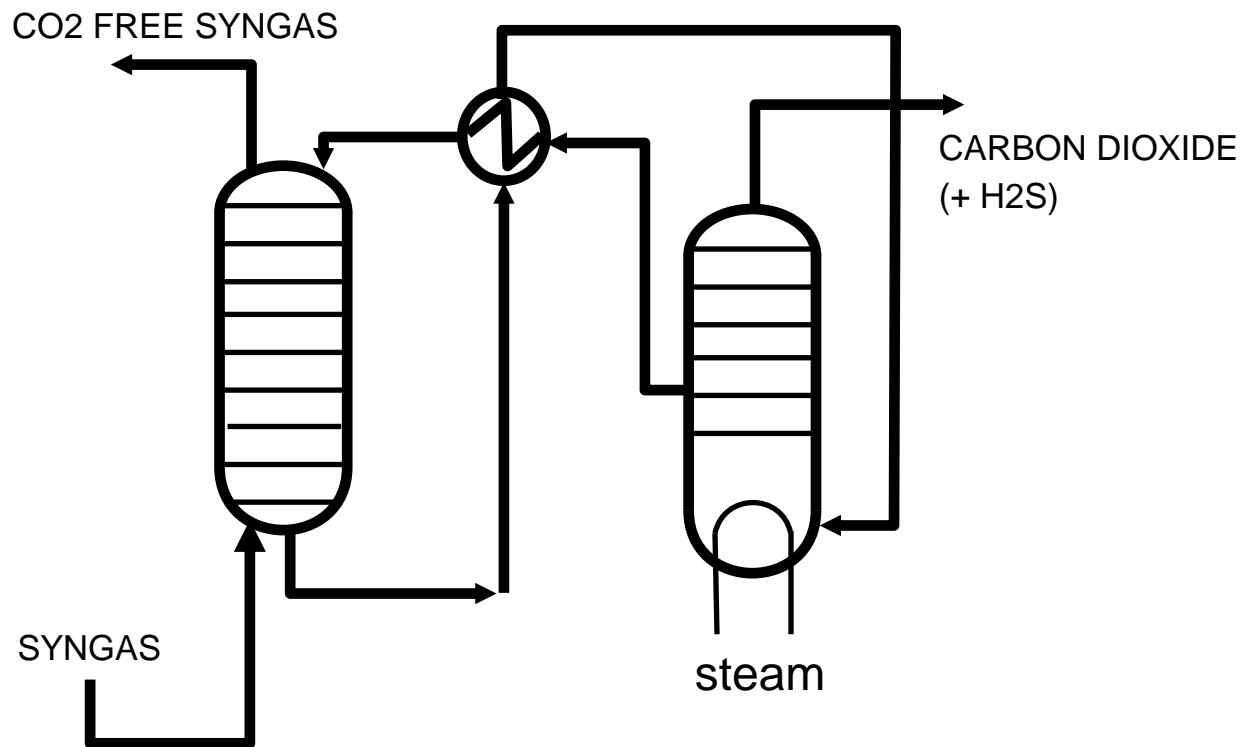
ANY SR CAN BE OBTAINED USING WGS



WATER-GAS-SHIFT



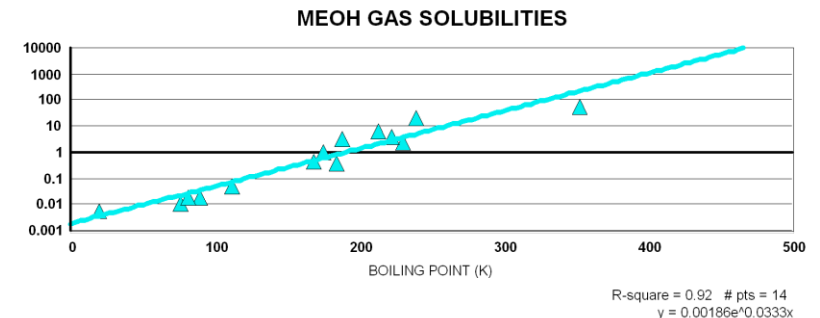
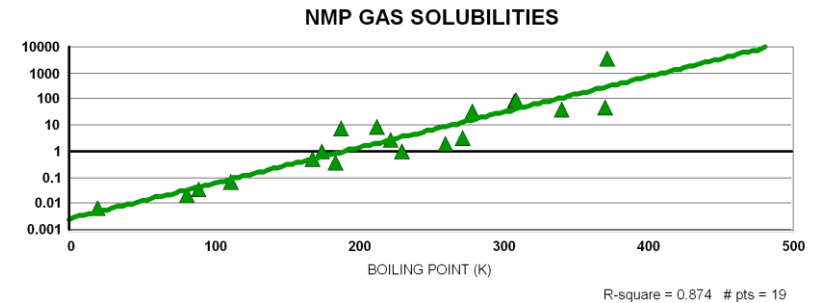
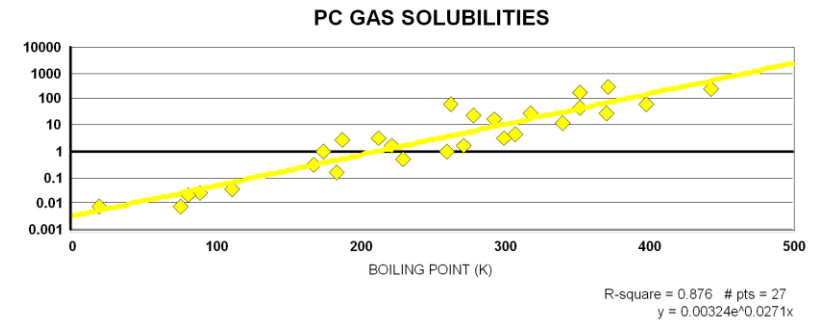
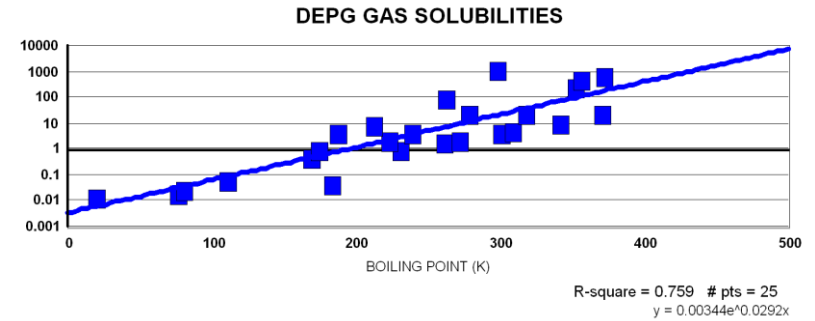
# ACID GAS (CARBON DIOXIDE) STRIPPING



# 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

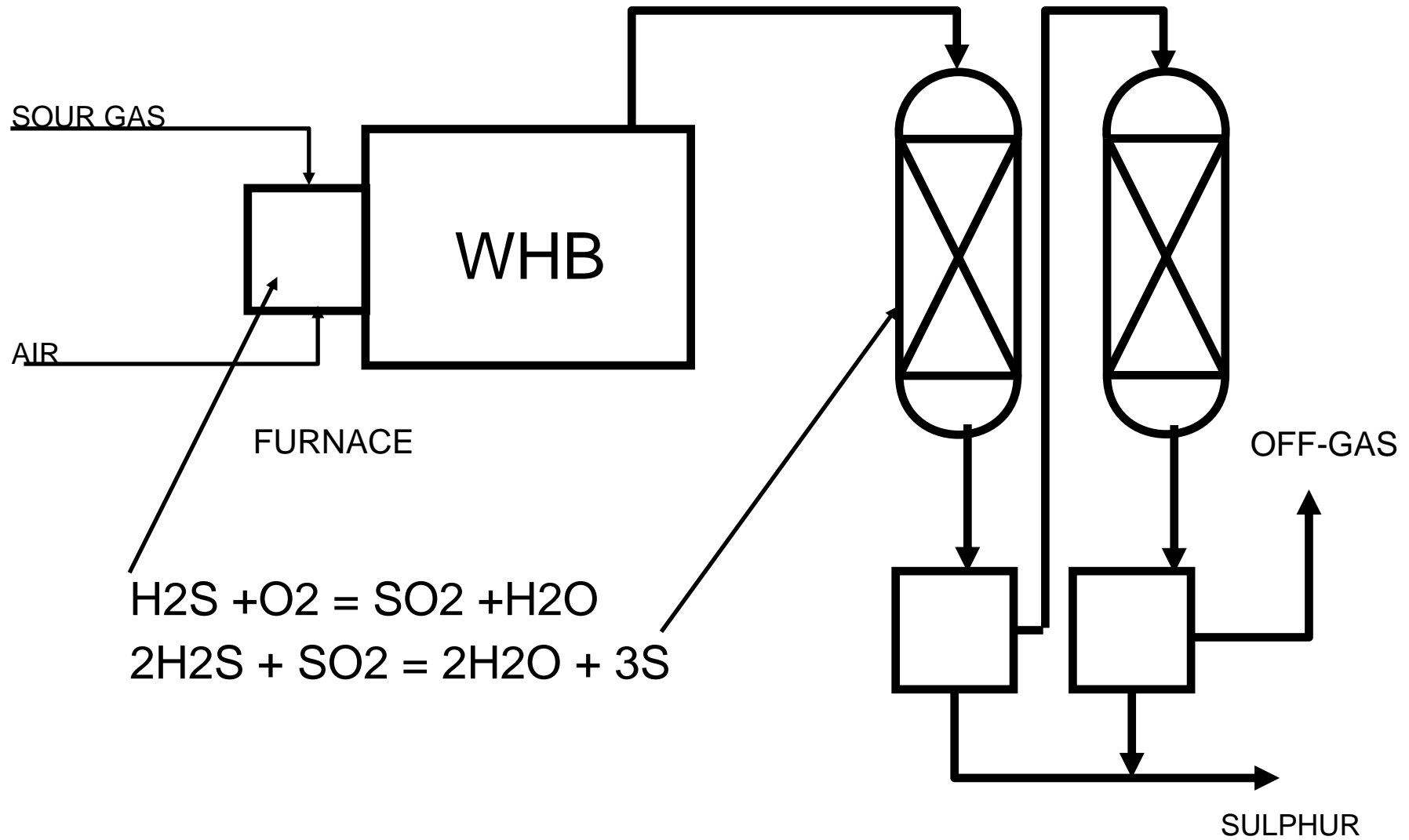




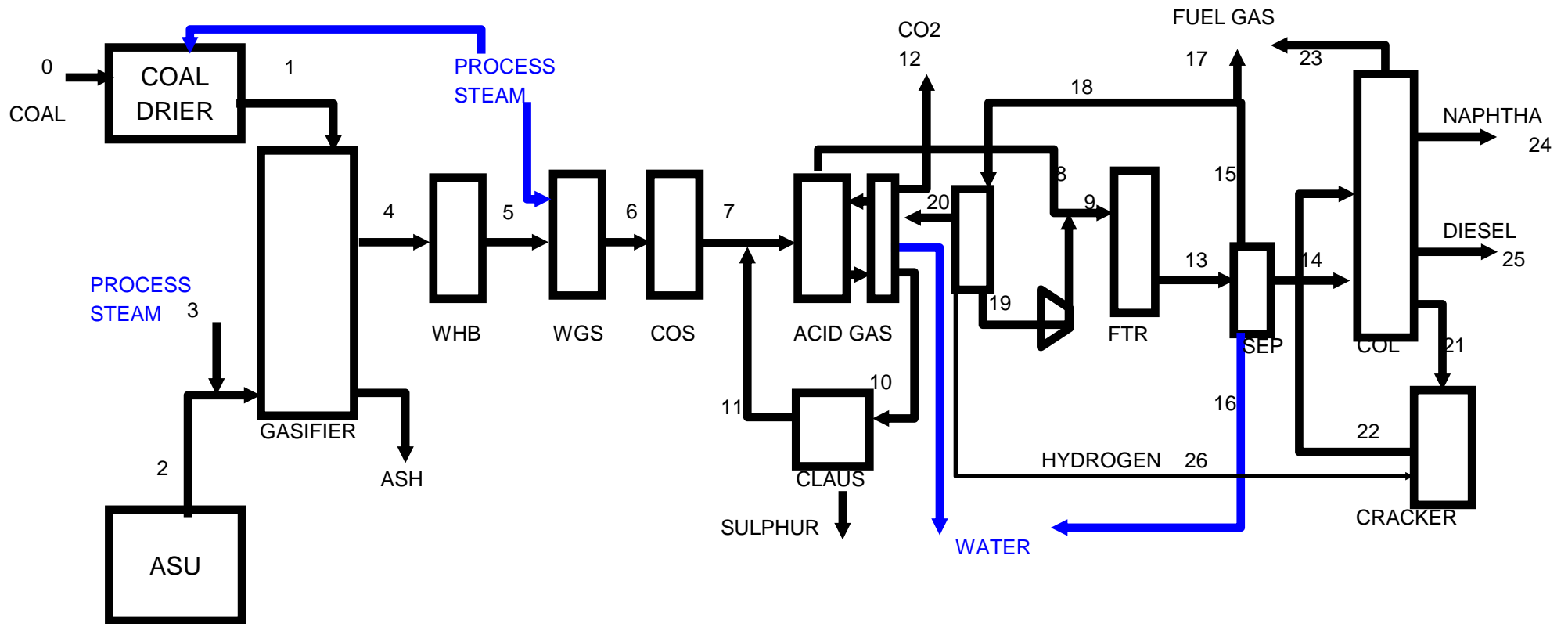
# Boiling Point of Components of Interest

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

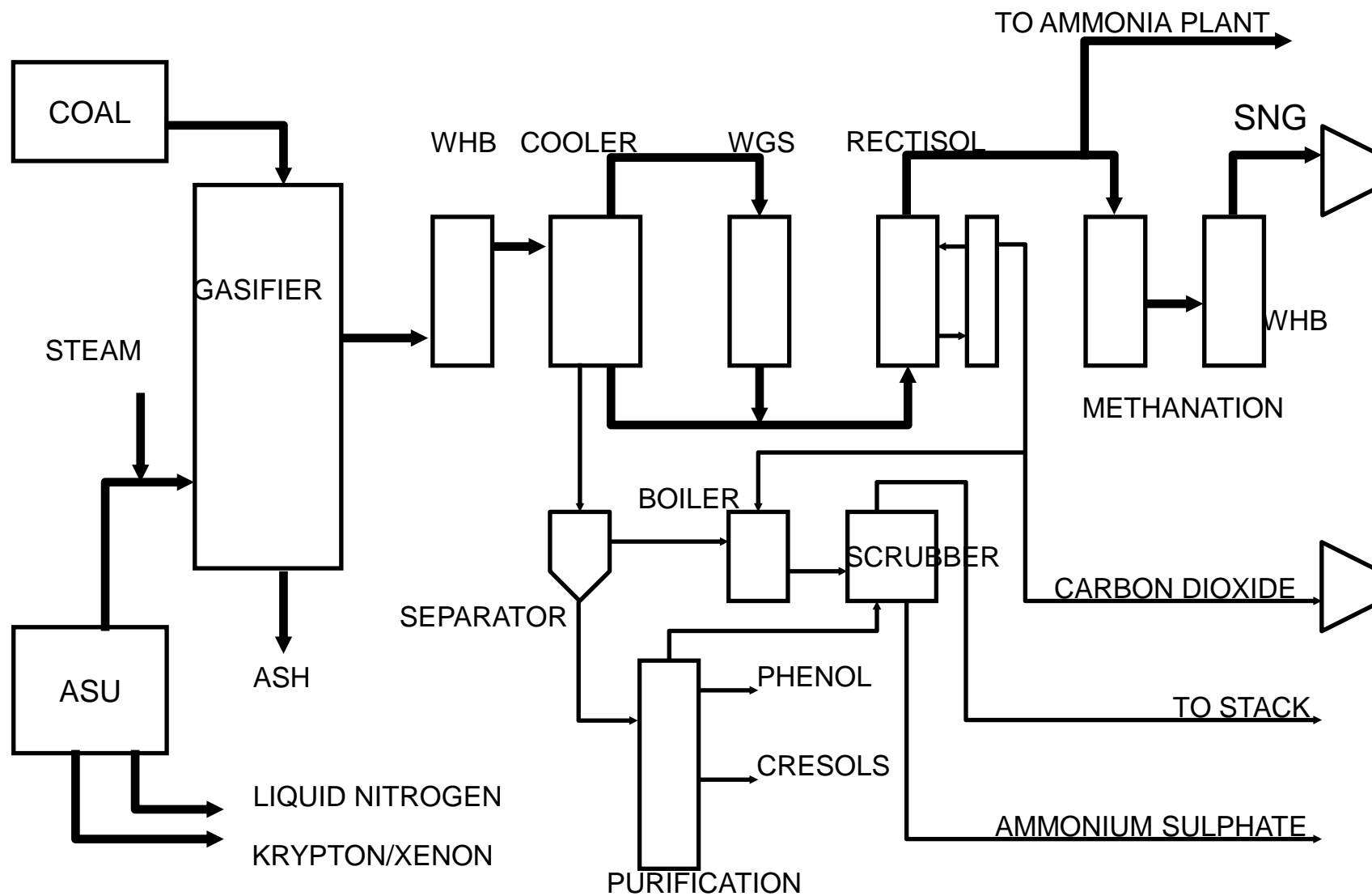
# CLAUS PROCESS



# COAL TO FT LIQUIDS - PROCESS FLOW



# DAKOTA COAL GASIFICATION



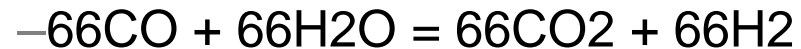
# DIRECT ROUTE HAS HIGHER EFFICIENCY THAN FT ROUTE

## ■ FT ROUTE: 100 MOLES CARBON

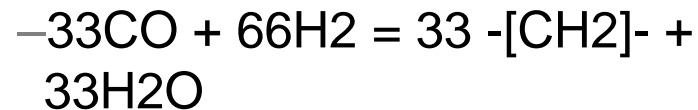
### ▶ GASIFIER



### ▶ WGS



### ▶ SYNTHESIS



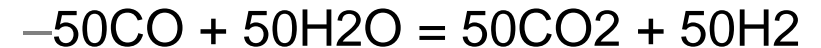
## ■ CARBON EFFICIENCY 33%

## ■ DIRECT ROUTE: 100 MOLES CARBON

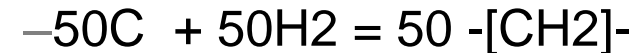
### ▶ GASIFIER



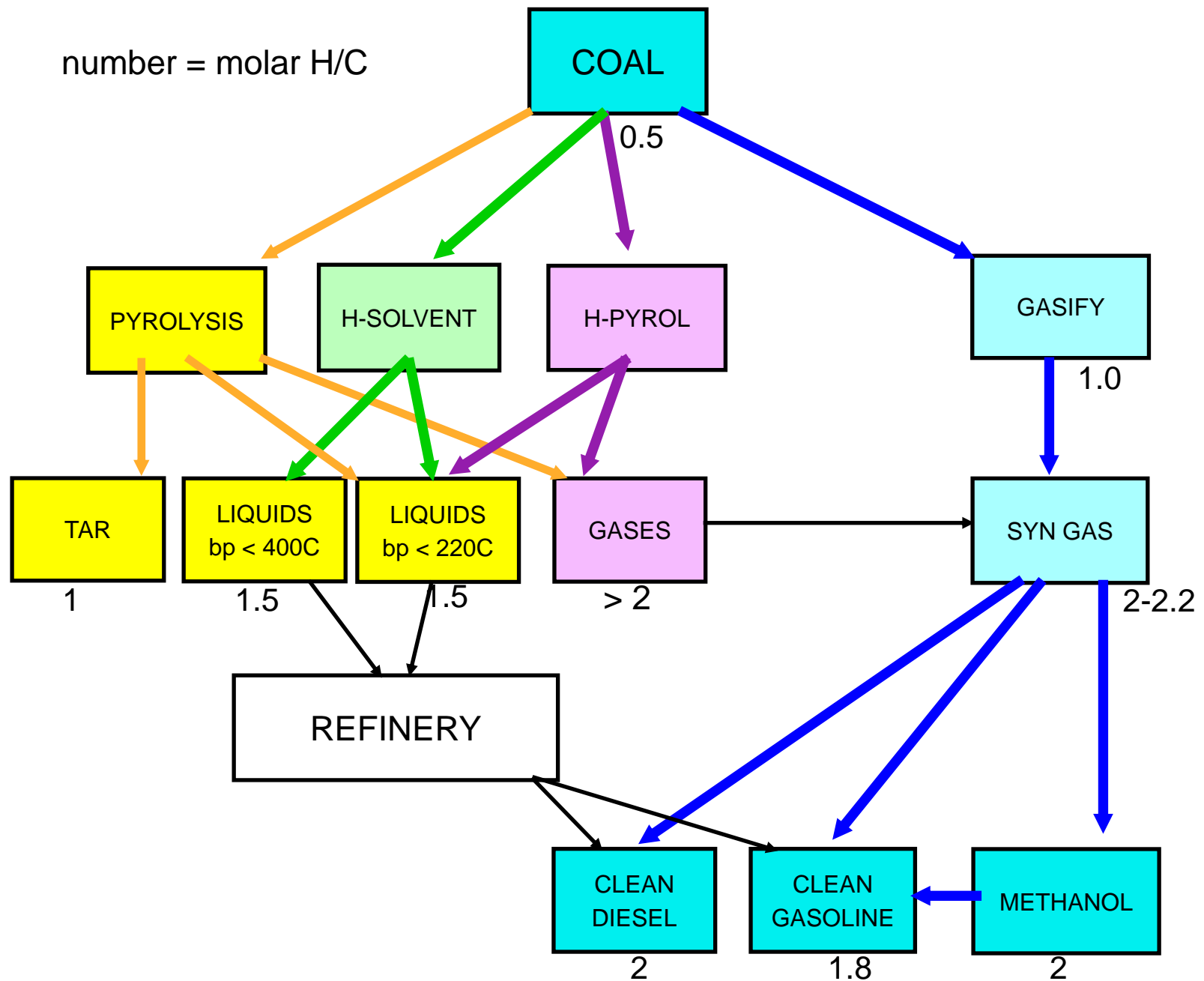
### ▶ WGS



### ▶ HYDROGENATION



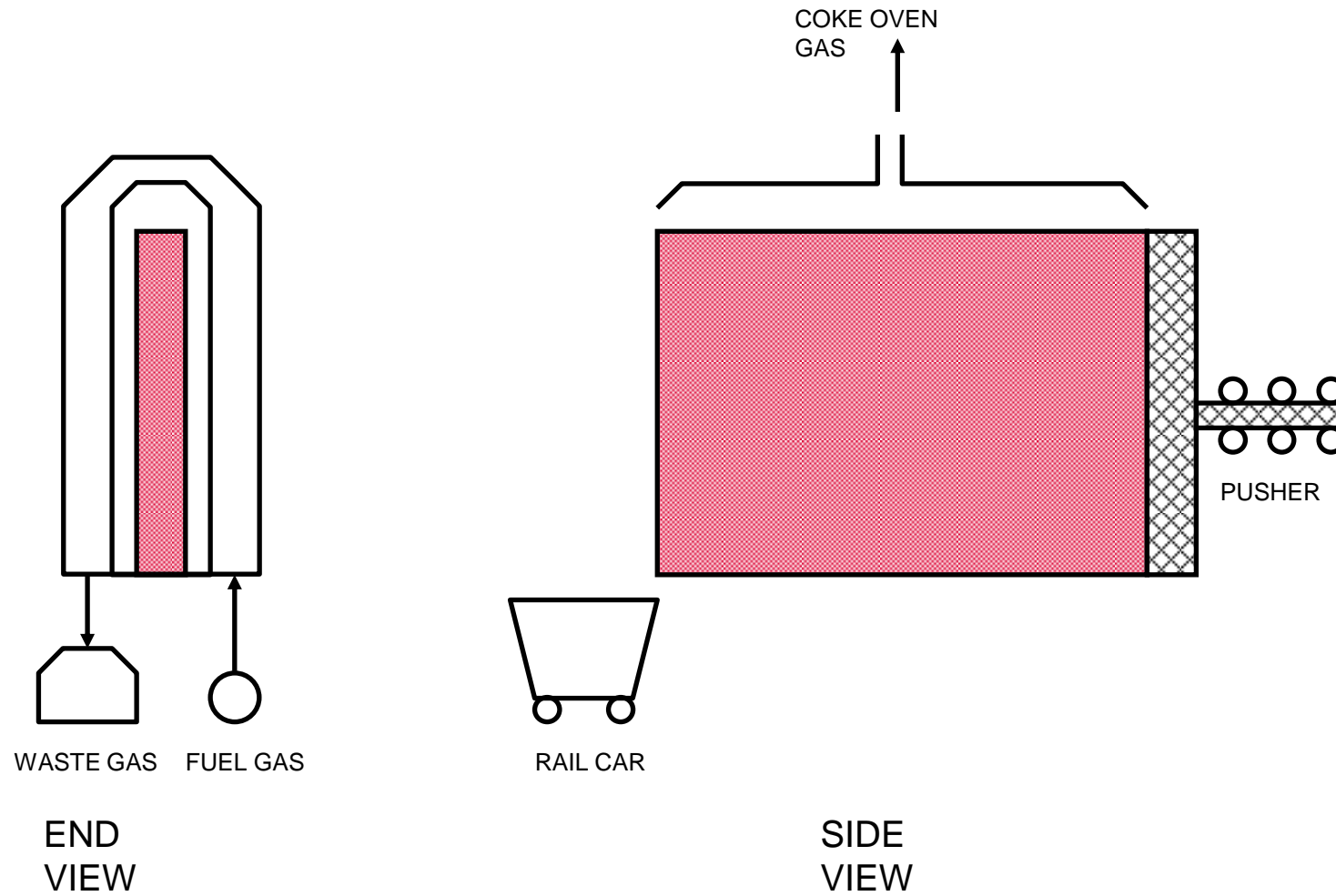
## ■ CARBON EFFICIENCY 50%



# PYROLYSIS ROUTES

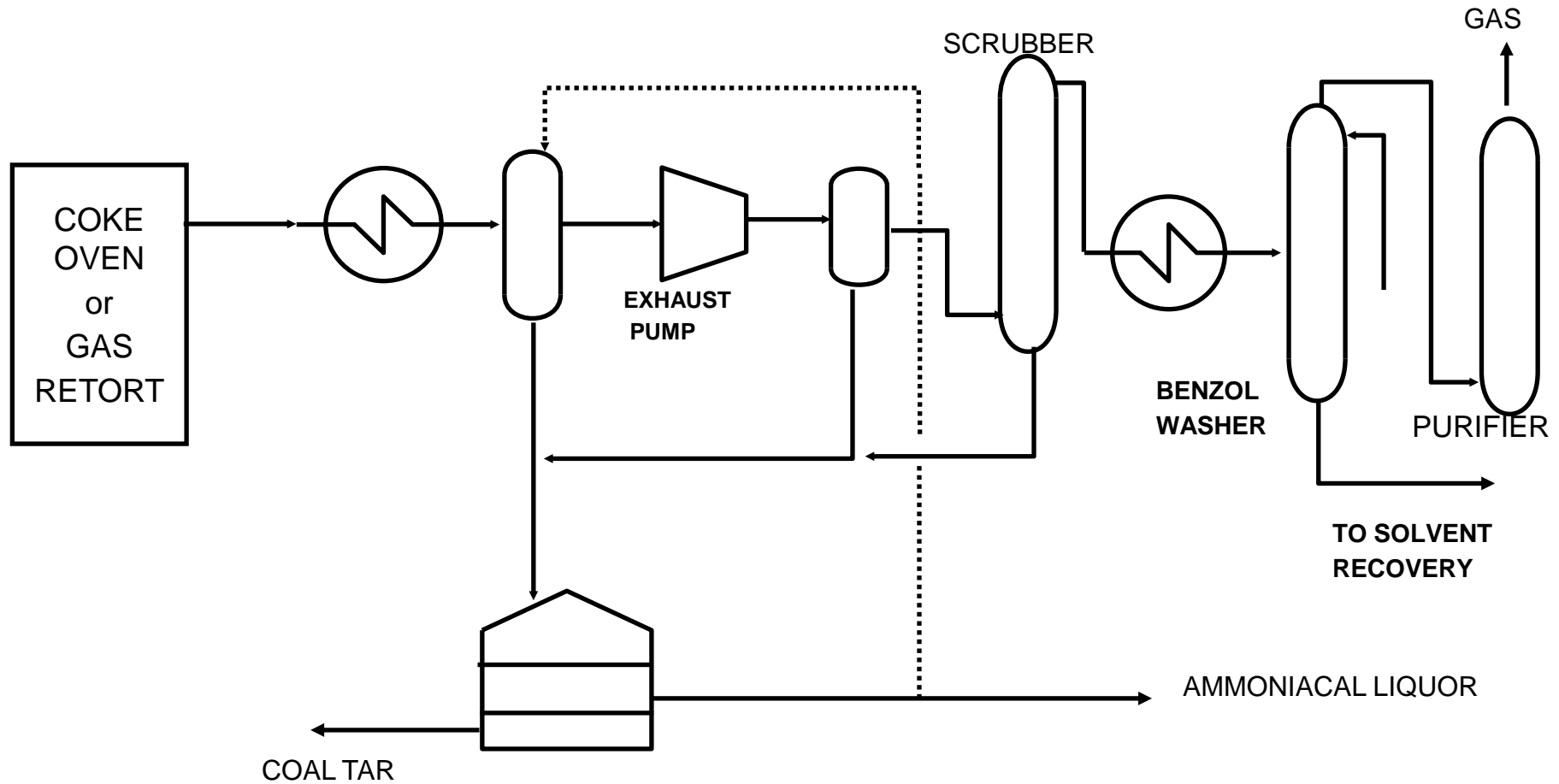
- Low temperature (450 - 600C) pyrolysis leads to higher liquid yields (15 - 20%).
- High temperature rapid (millisecond) pyrolysis can give higher liquid yields.
- Main product is char of lower hydrogen and heteroatom content
- Useful for upgrading lignites and the like to higher calorific value fuel
- 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

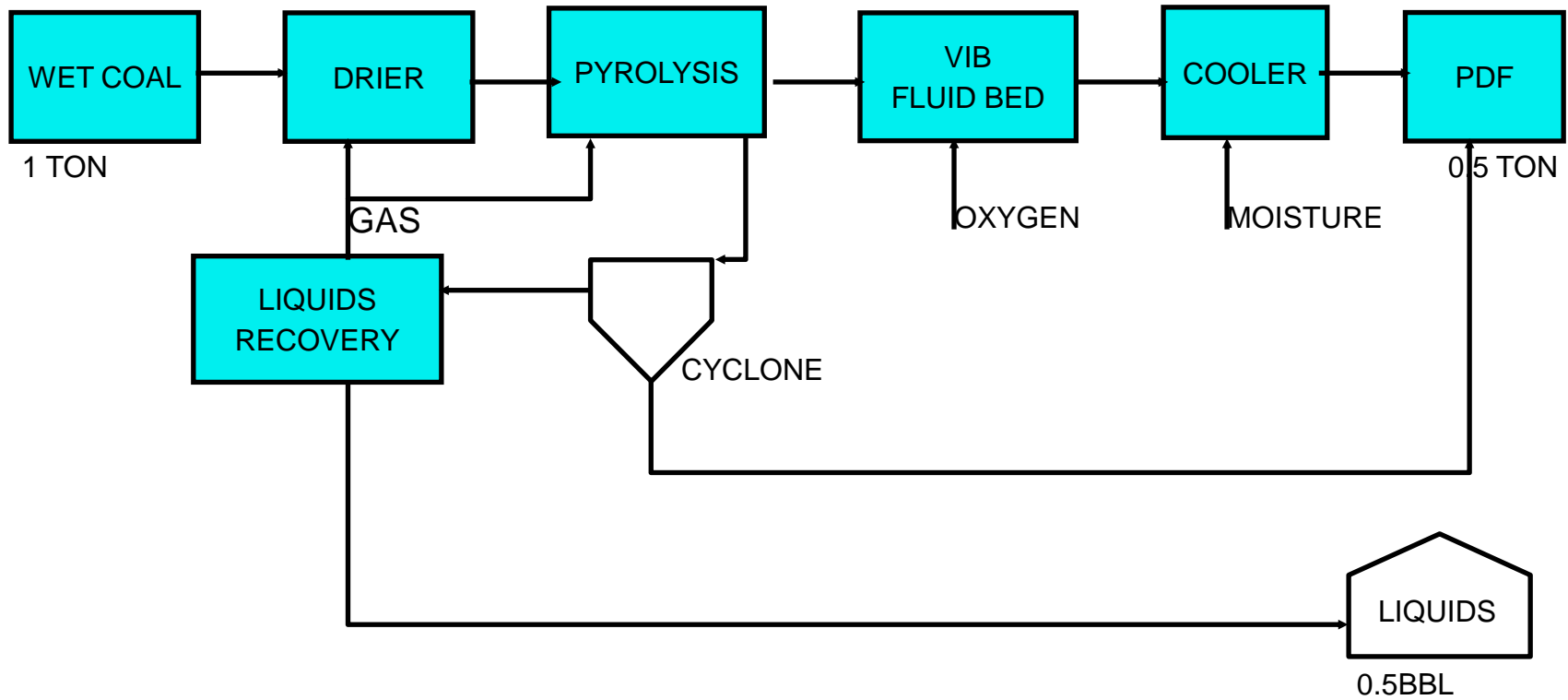




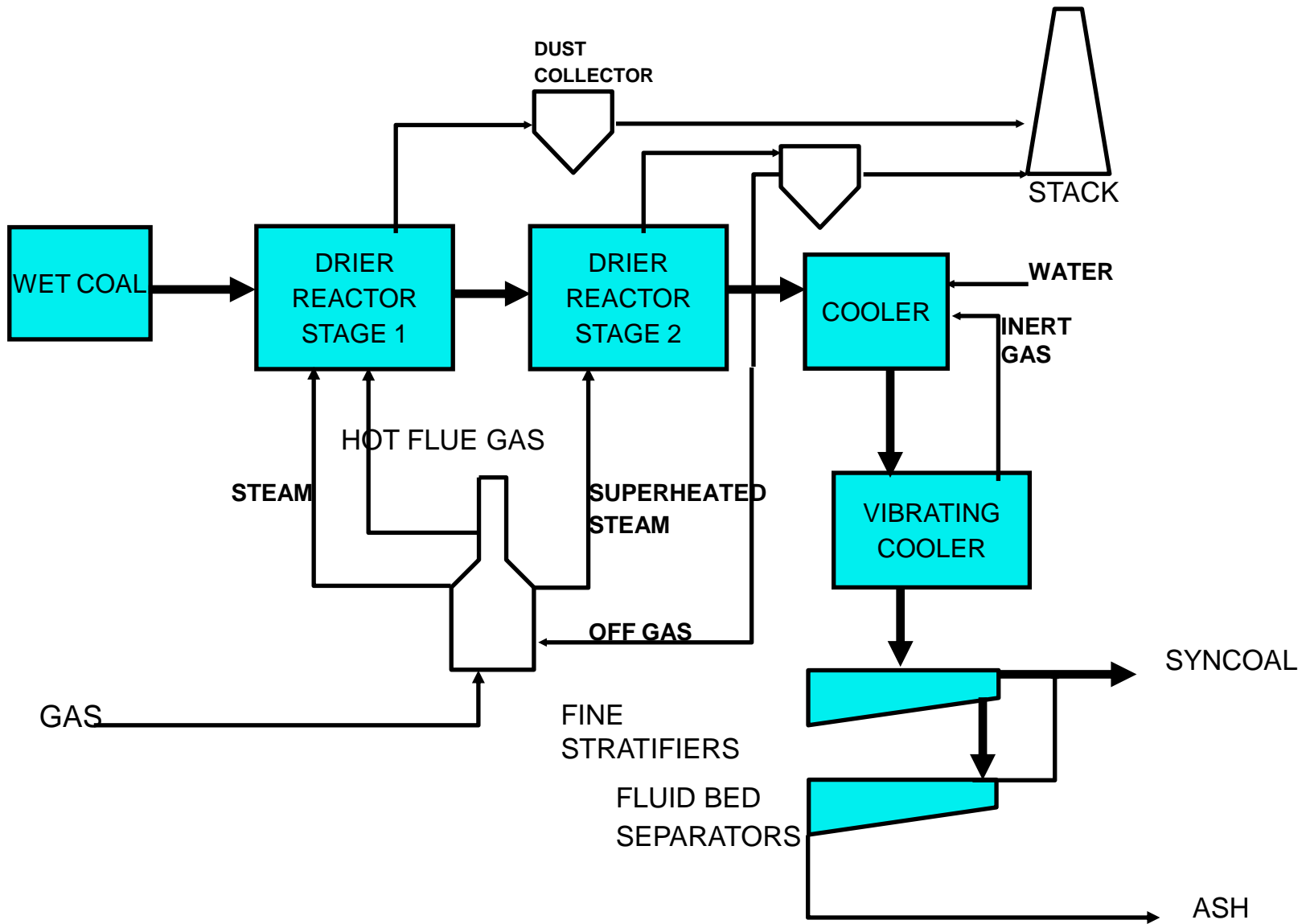
# COKE AND TOWN GAS



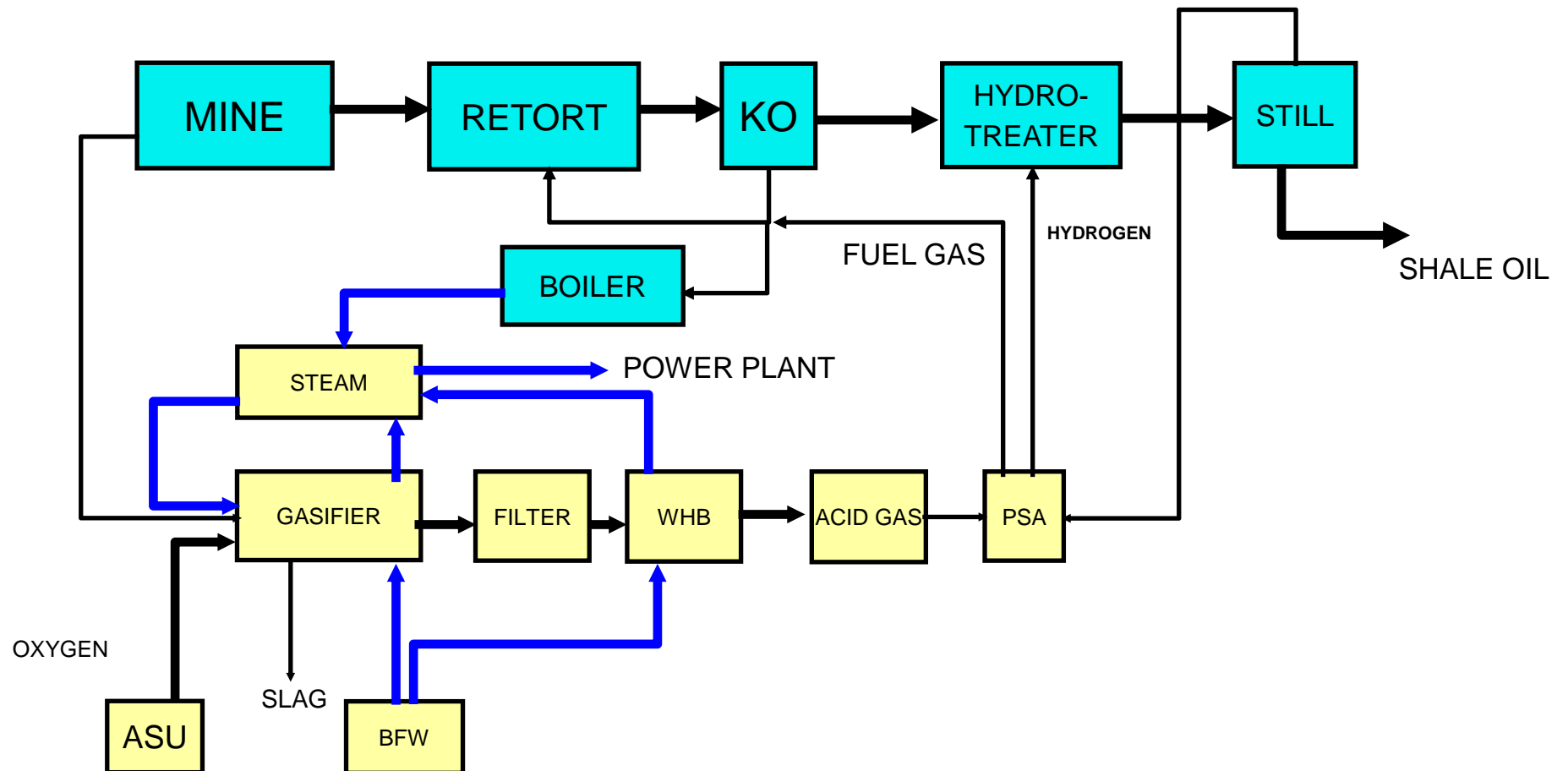
# LFC (Encoal)



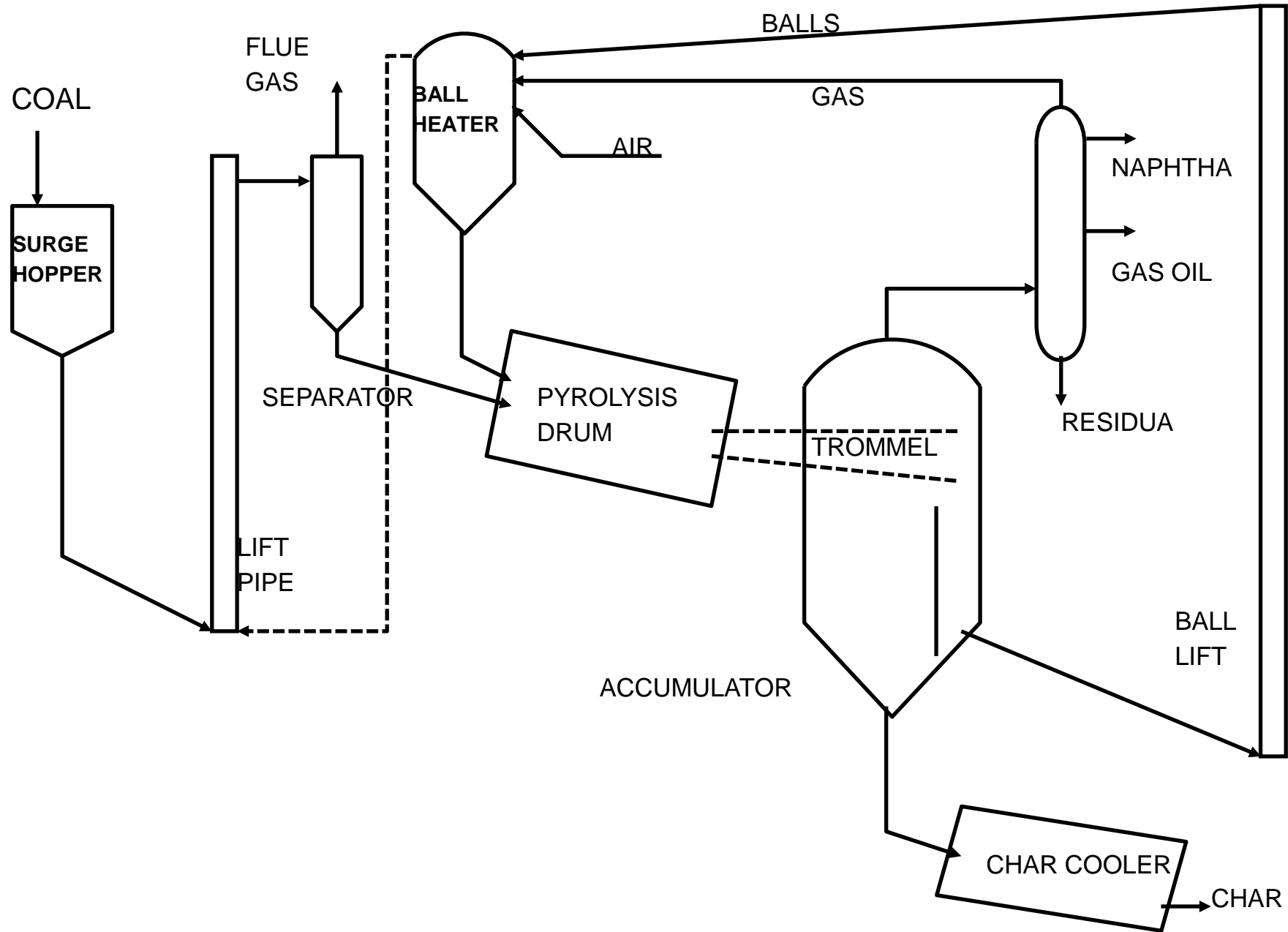
# SYNCOAL



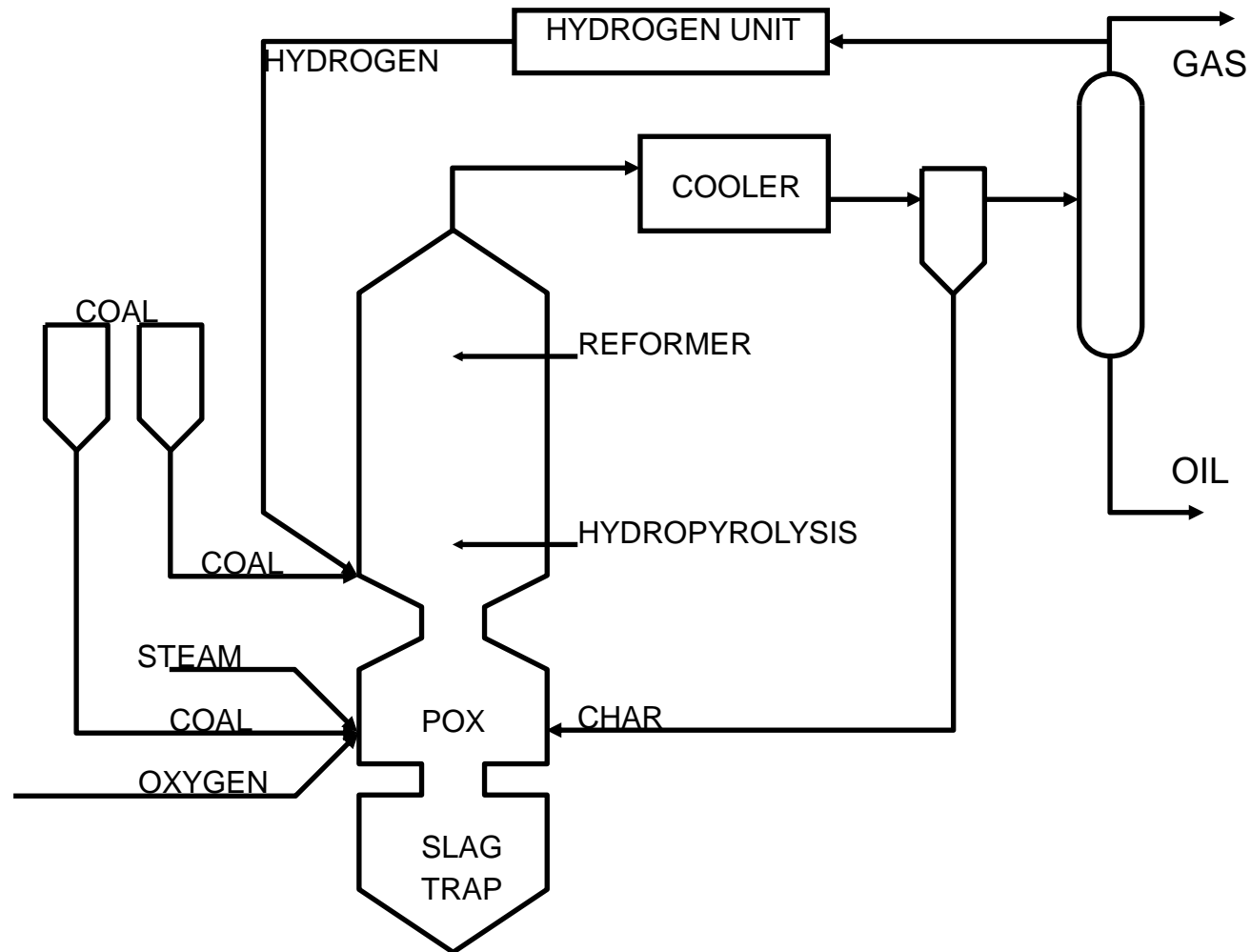
# SHALE OIL PRODUCTION



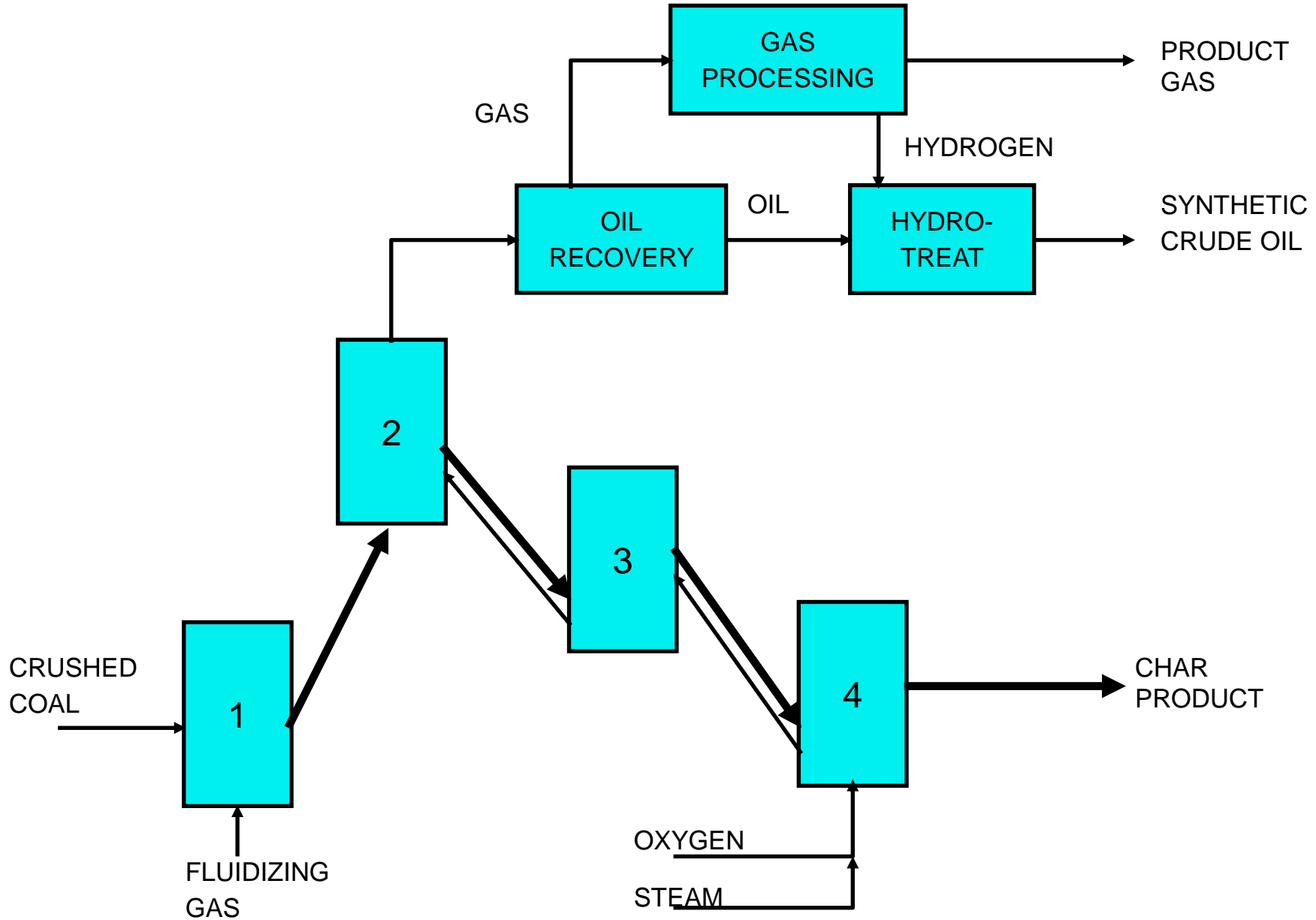
# TOSCOAL



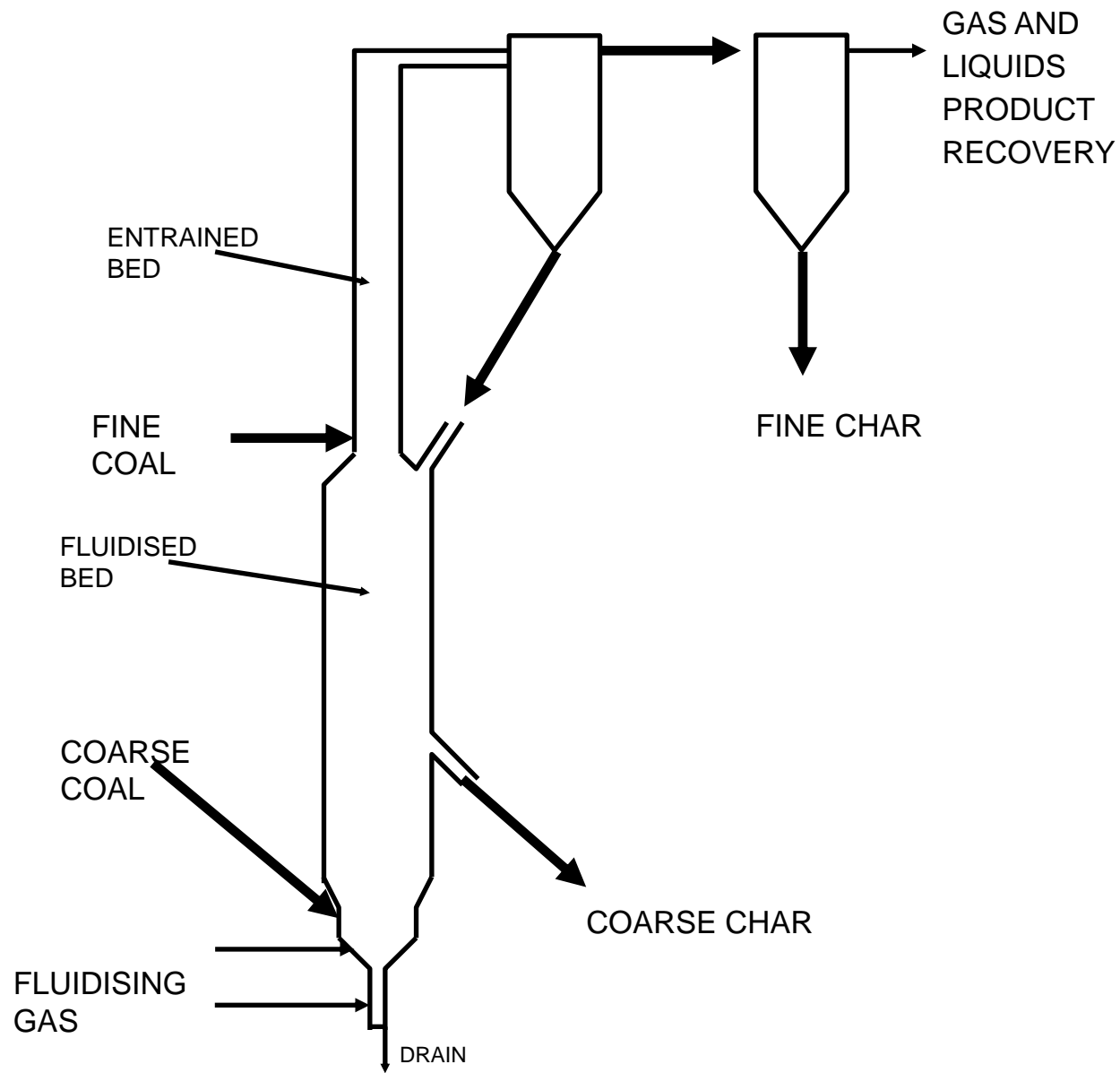
# NIPPON HYDRO-PYROLYSIS



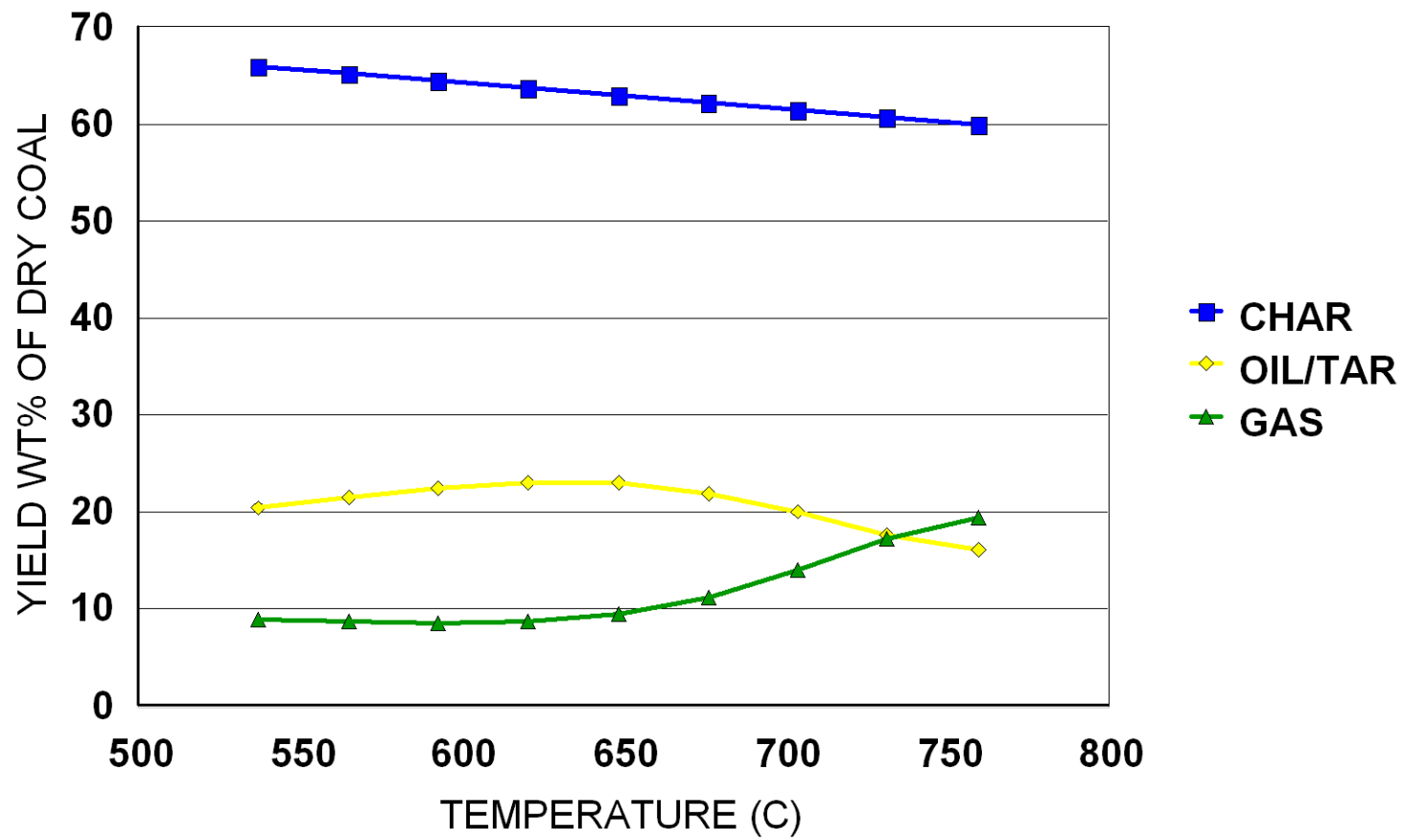
# COED (FMC)



# 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