MINERAL MATTER TRANSFORMATIONS DURING SASOL-LURGI FIXED BED DRY BOTTOM GASIFICATION

GTT Workshop – June 2007

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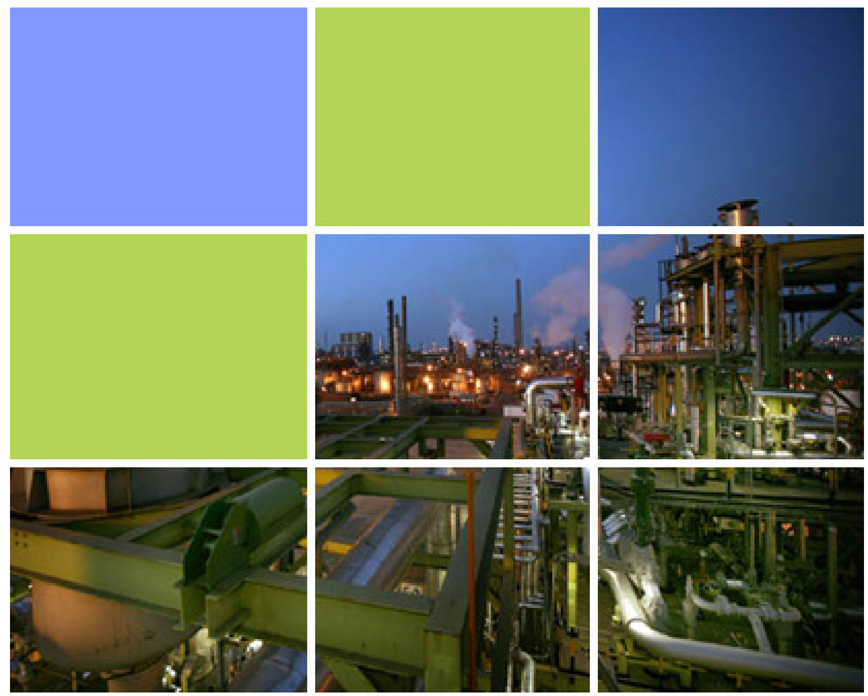
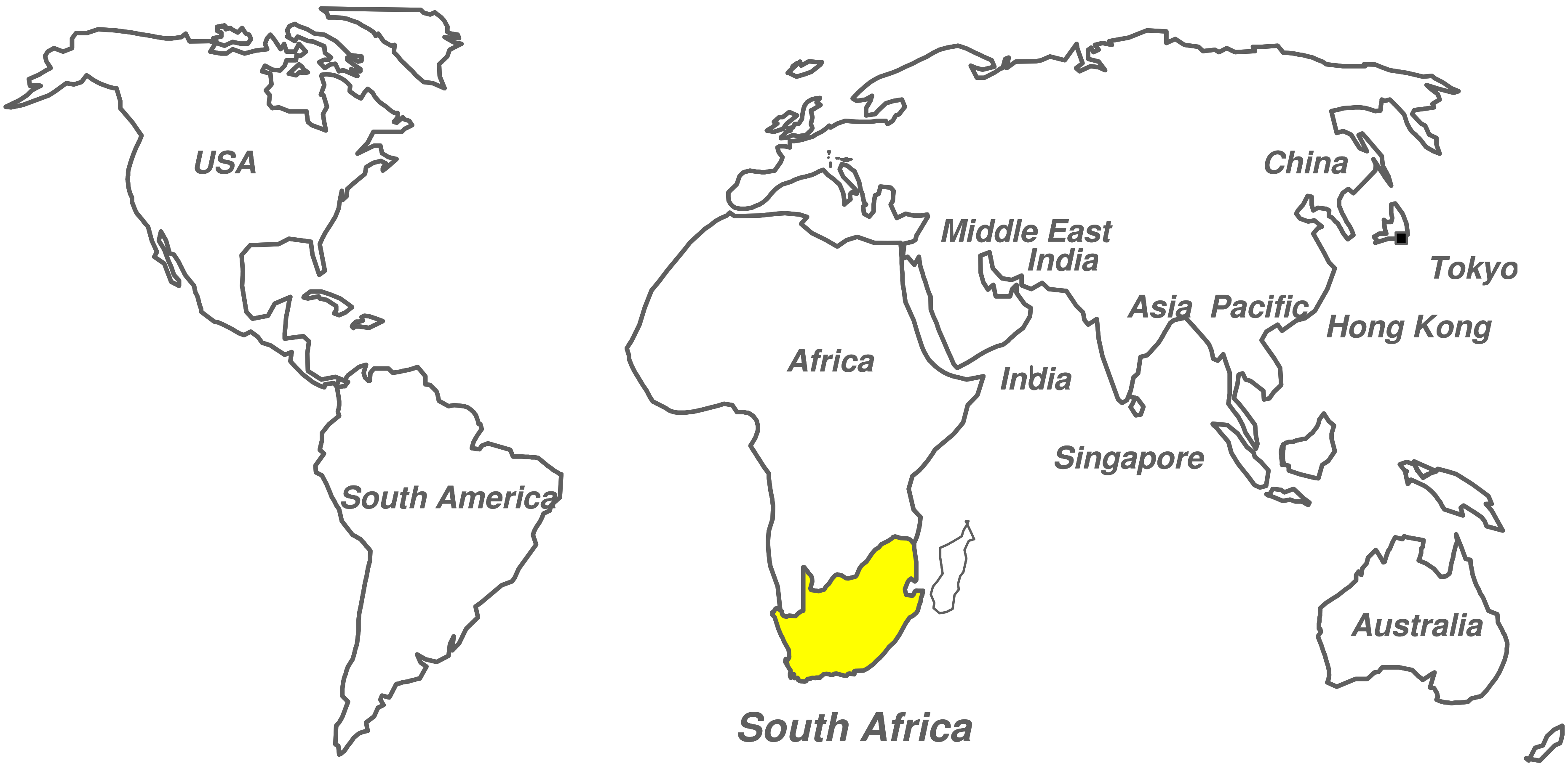


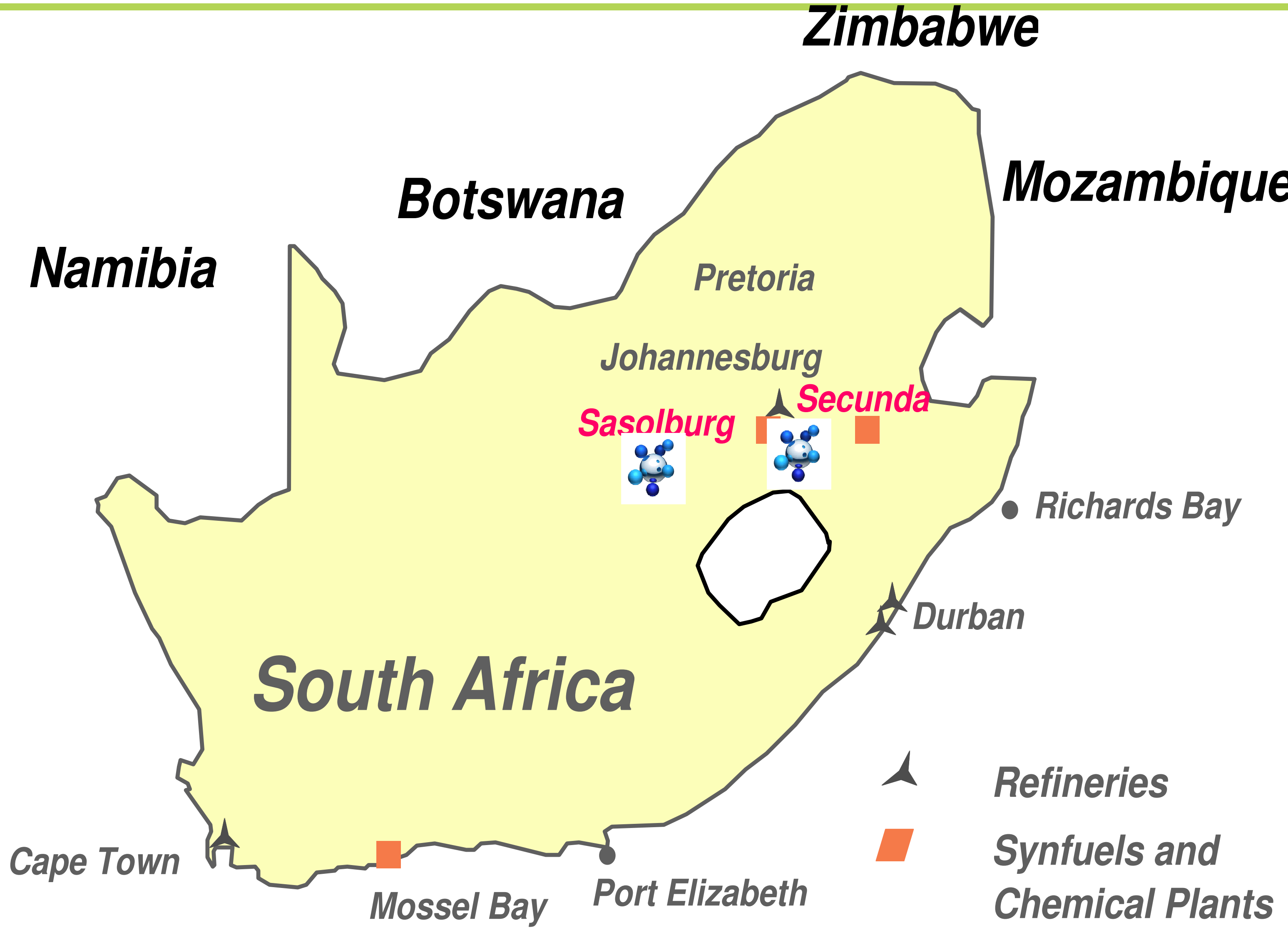
Roadmap of presentation

- Background of Sasol
- Sasol-Lurgi Fixed Bed Dry Bottom Gasification
- Understanding mineral matter transformations - WHY?
- Applications of FactSage
  - *Utilizing HT-XRD and FACTSAGE modelling as characterization tool (IP Approval PP0017)*
  - *Manipulation of gasification coal feed in order to increase the ash fusion temperature of the coal to operate the gasifiers at higher temperatures (IP Approval PP0090 and Patent PCT/IB2006/050277)*

Where is South Africa?



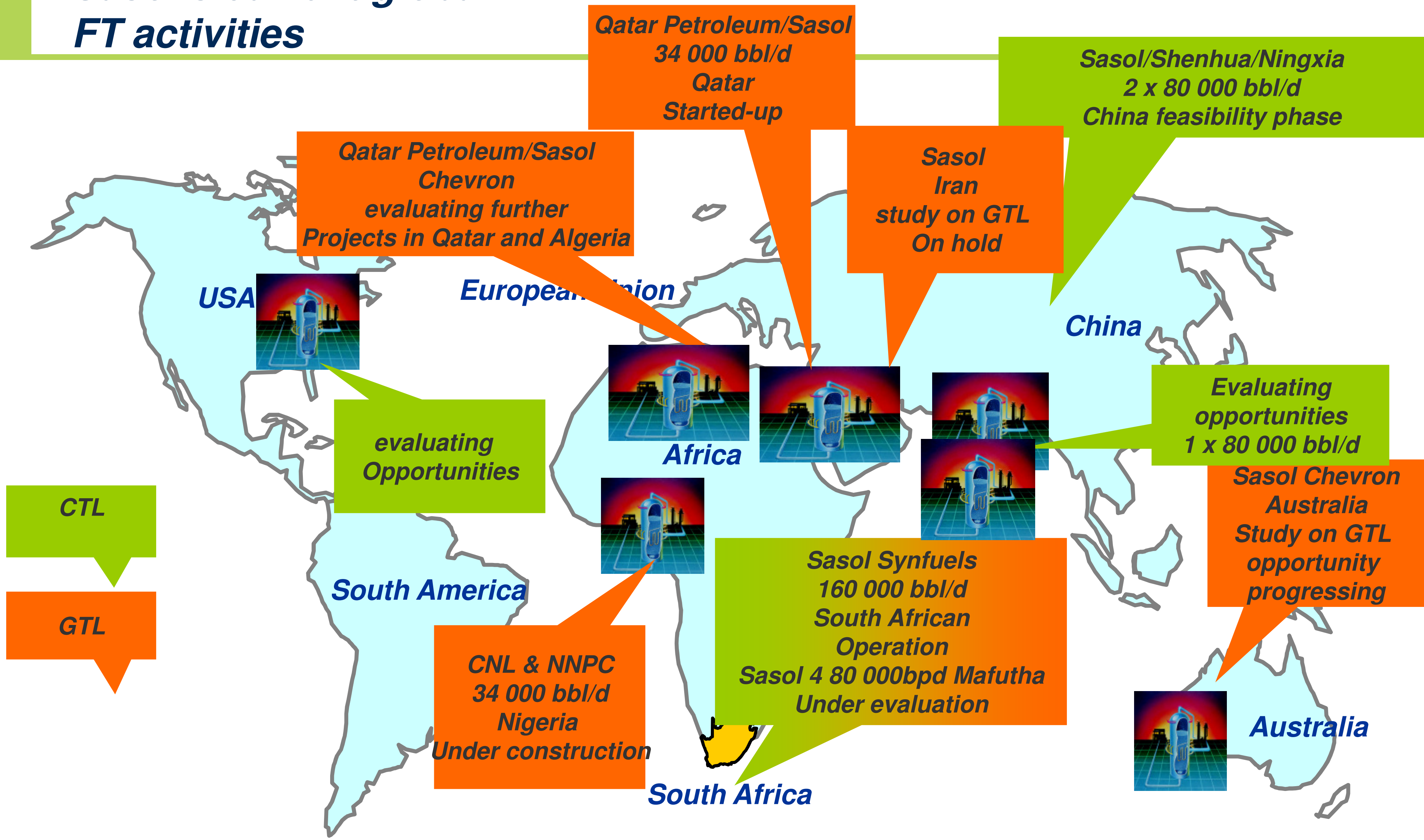
Where are the Sasol operations based in South Africa?



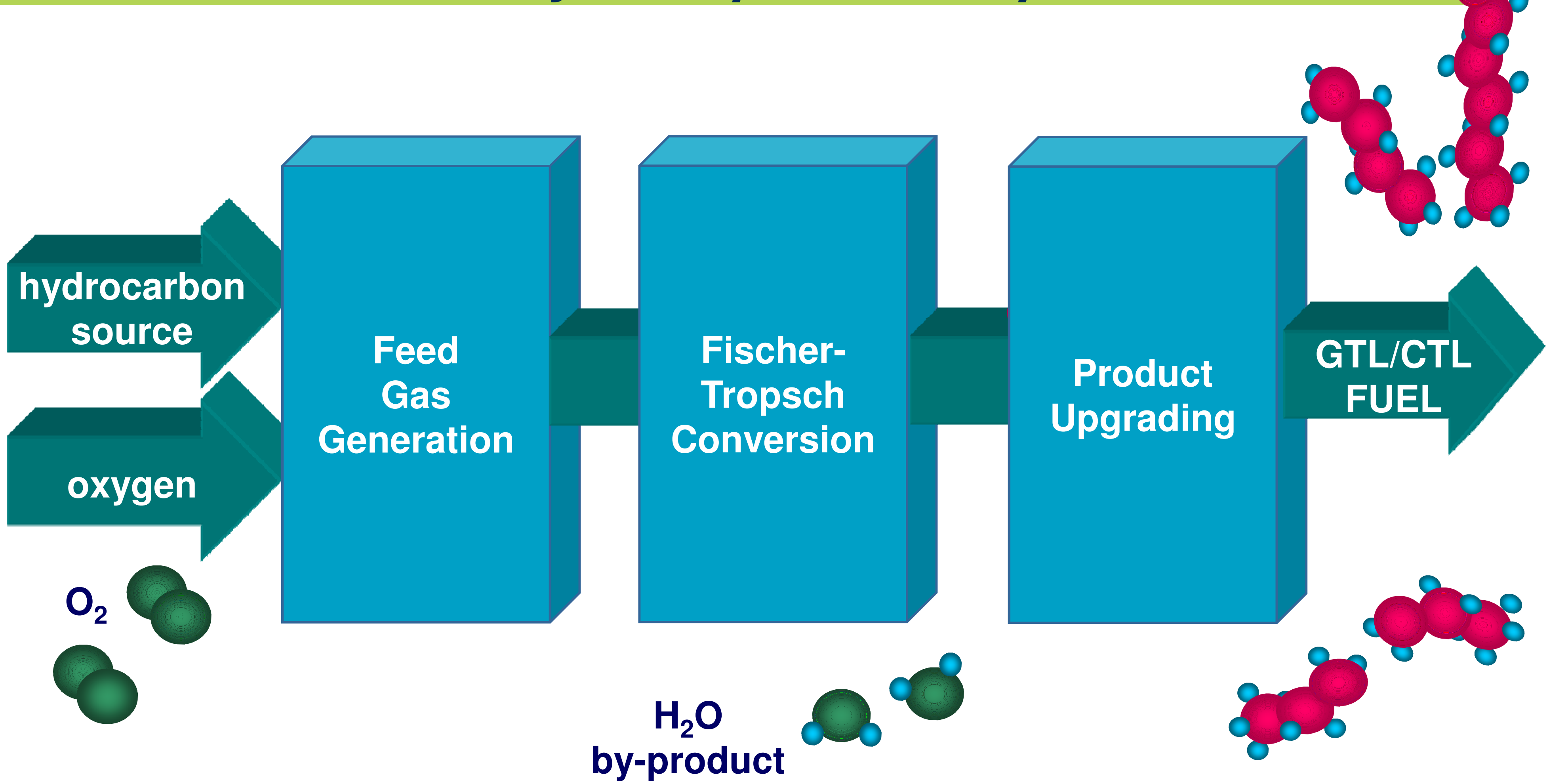
Sasol Facts

- *Initial driver to commercialize CTL in RSA...fuel independence on crude imports*
- *Secondary objective to convert low grade coal to petroleum products and chemical feedstocks*
- *Today Sasol produces >150 000 barrels per day*
- *Manufactures >200 fuel and chemical products*
- *Syngas production increased ±15% over the last 10 years*
  - *60% due to increased gasifier throughput*
  - *20% due to the reduction of CO_2 produced in gasification*
  - *10% due to the recovery of coal lock off gas*
  - *10% due to increased gasifier availability / reliability*

Sasol's current global FT activities



Sasol's FT Processes Convert "Locked-in" resources to easily transportable liquid fuels



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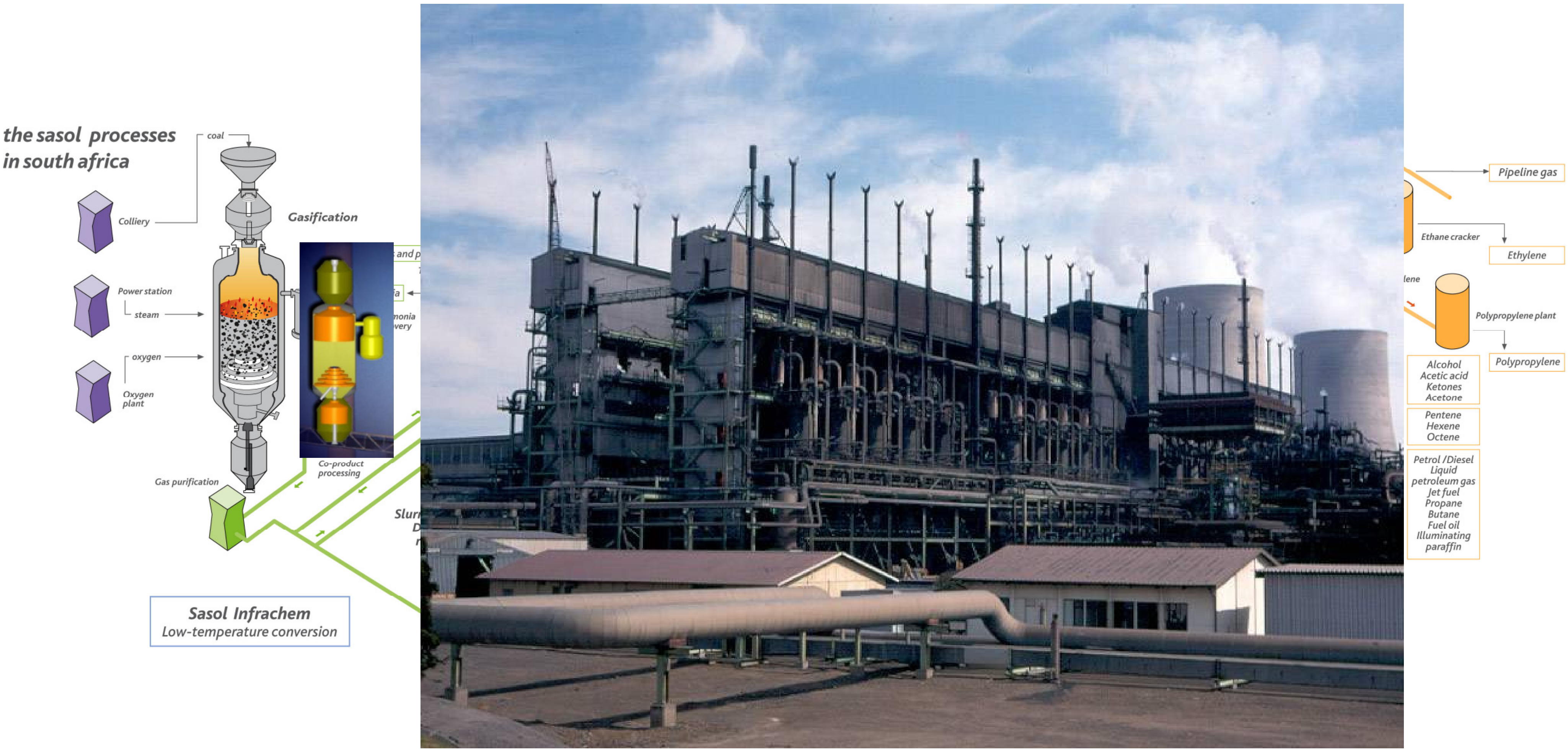
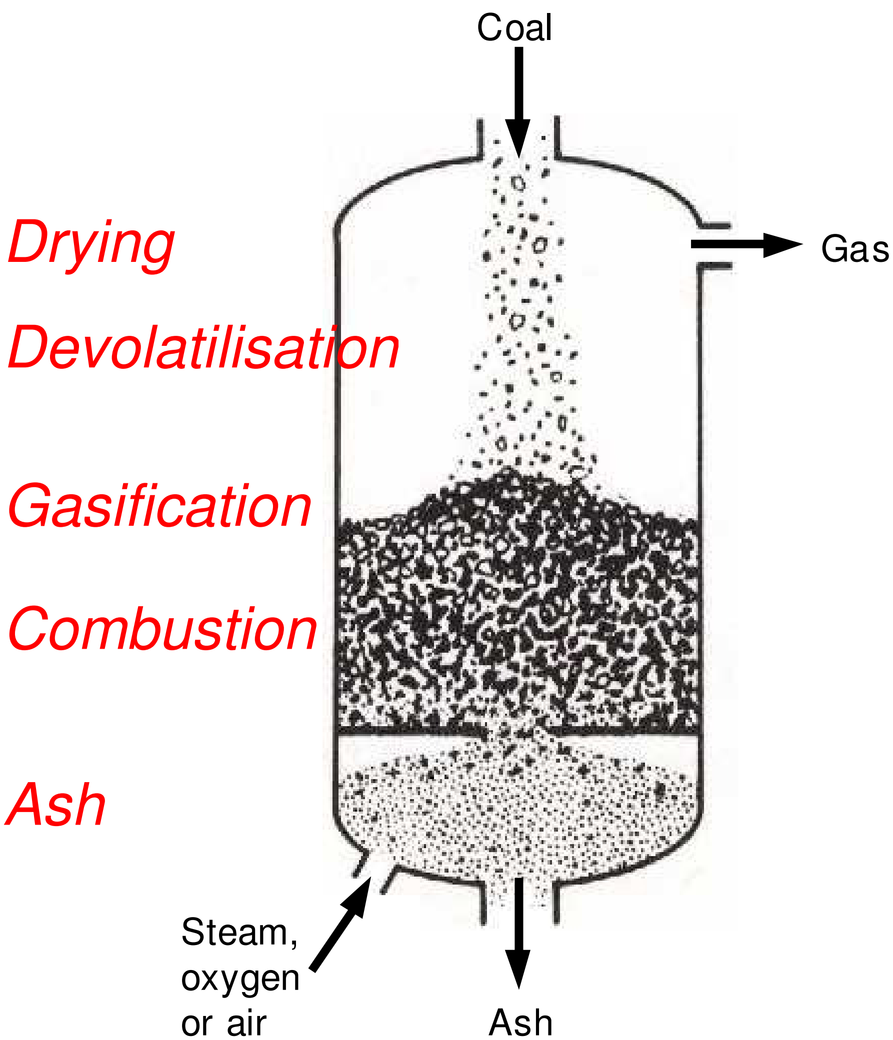
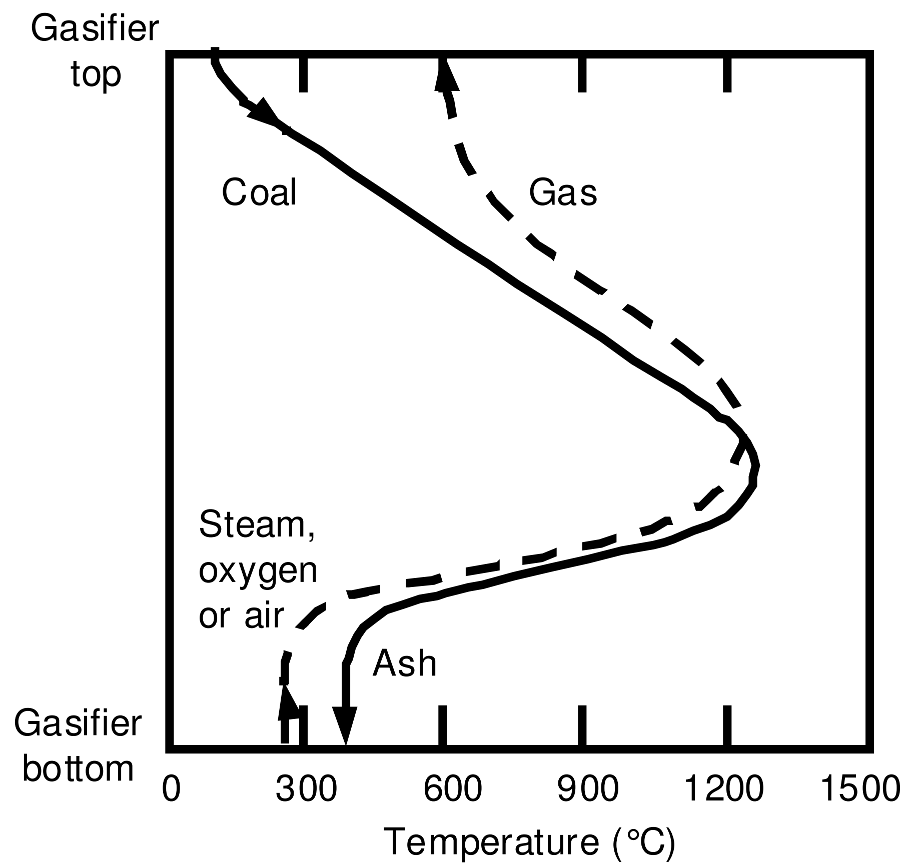
Sasol-Lurgi fixed bed dry bottom (FBDB) gasification



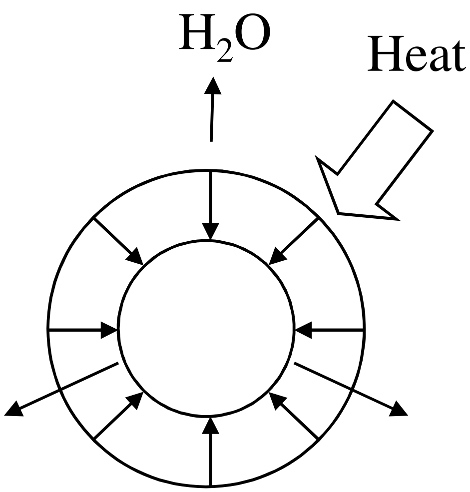
Sasol-Lurgi (FBDB) gasification (cont.)





Sasol-Lurgi (FBDB) gasification (cont.)

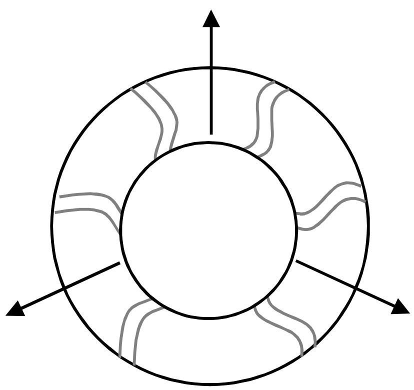
Heating and Drying



Thermal front penetrates particle

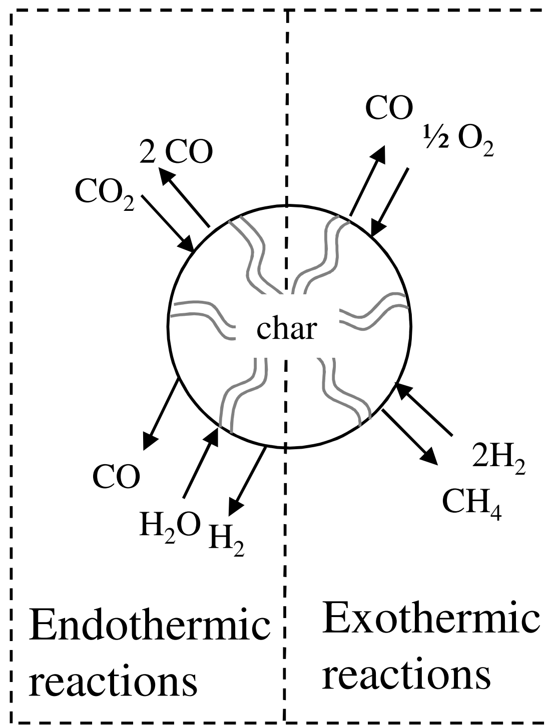
Pyrolysis

Volatile gases:
CO, CO_2, H_2, H_2O,
Light hydrocarbons, tar



Porosity increases

Gas-Solid Reactions



Gas-phase Reactions

$CO + H_2O \rightarrow CO_2 + H_2$

$CO + 3H_2 \rightarrow CH_4 + H_2O$

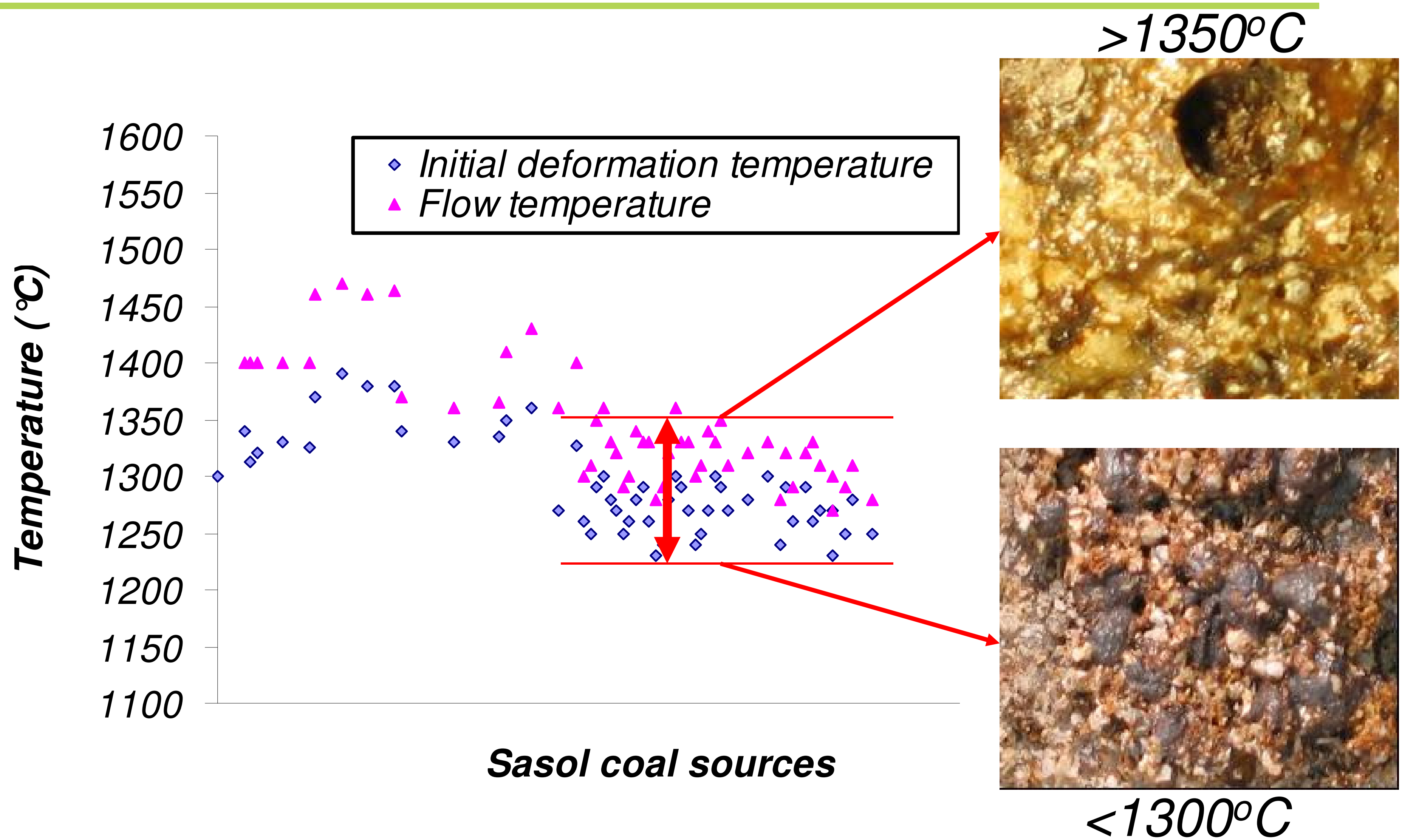
Understanding mineral matter transformations – WHY?

- **Ash fusion temperature (AFT)** is one property of coal that gives an indication of suitability for Sasol-Lurgi Fixed Bed Dry Bottom Gasification purposes

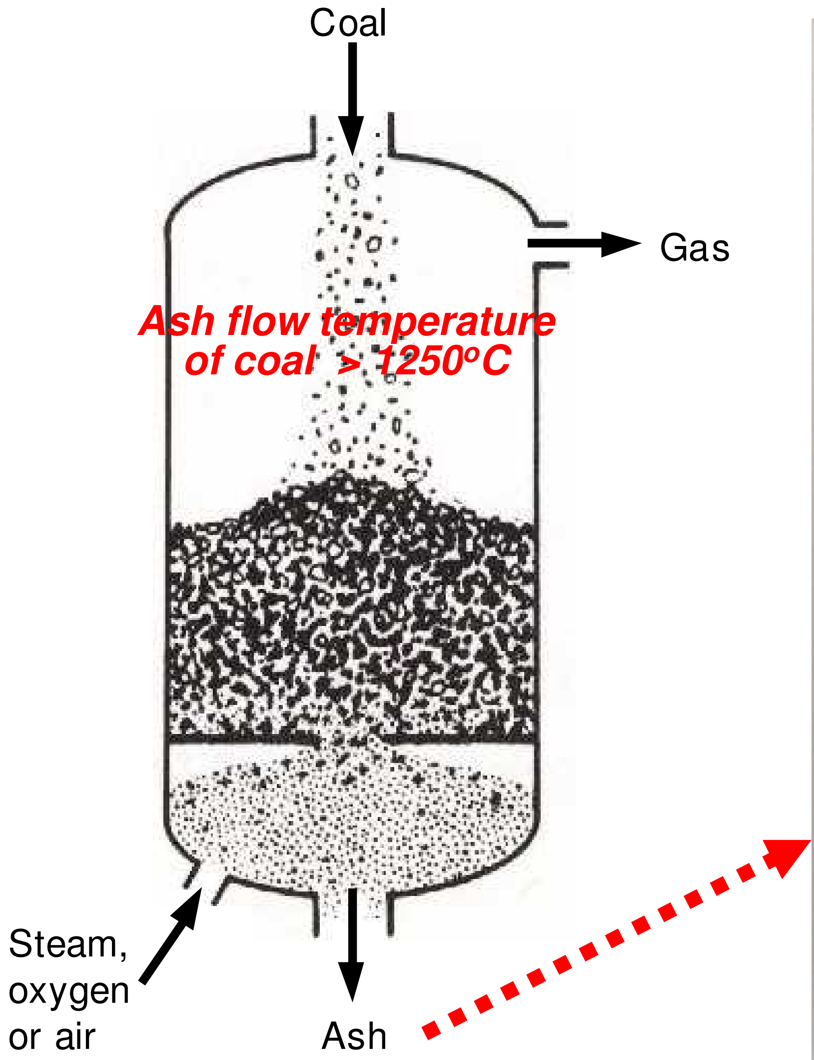
- Ash fusion temperature
  - *results in an average temperature where bulk mineral composition starts to become soft and melt*
  - *is an indication to what extent agglomeration / clinkering is likely to occur within the gasifier*
  - *is currently used to predict average slagging properties of coal sources and not at what temperature the first melt/sinter occurs*

- Ash clinkering can cause channel burning, pressure drop problems, unstable gasifier operation, etc

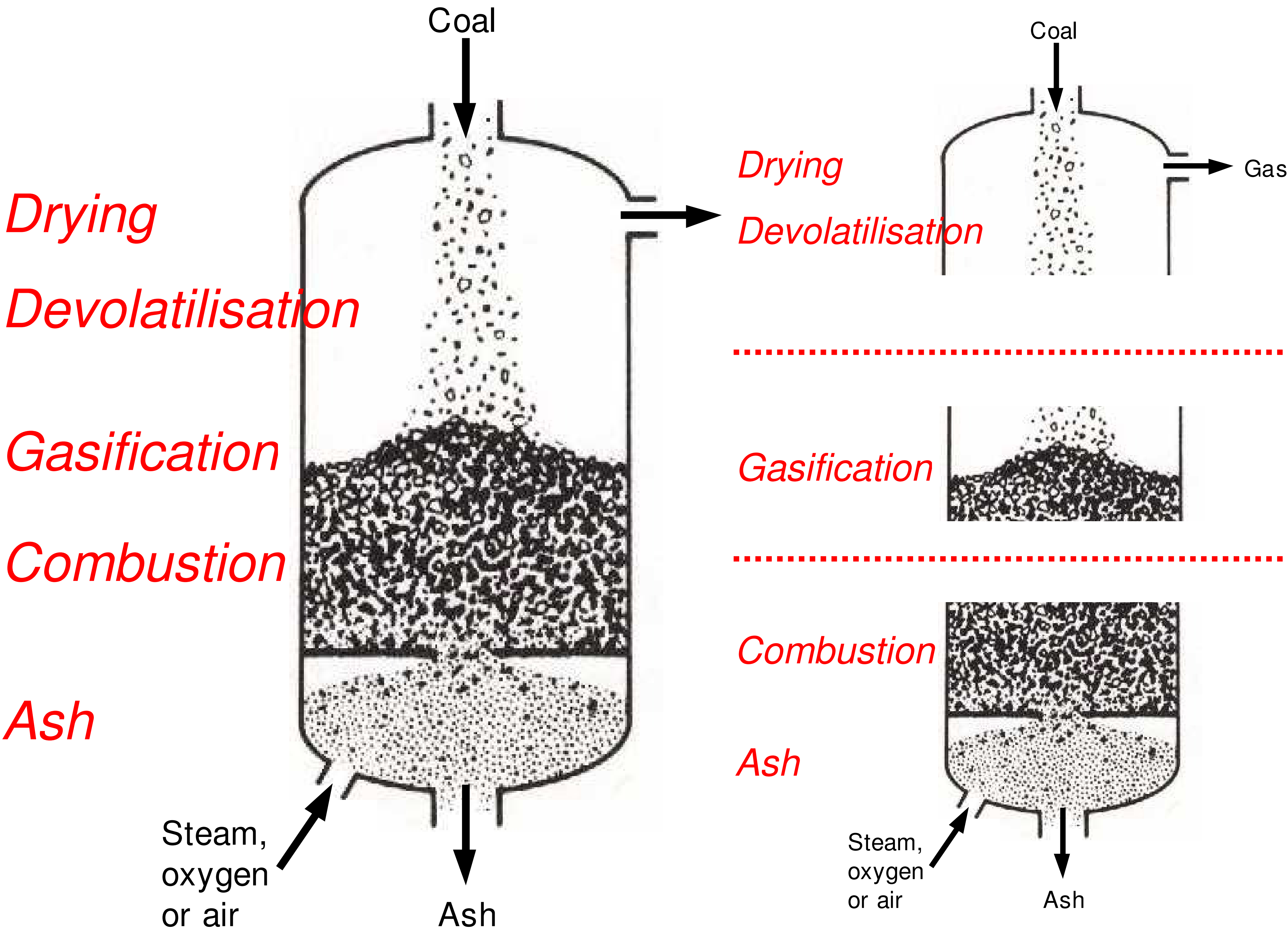
Window of operation between sintering and slagging



Syngas and ash producer

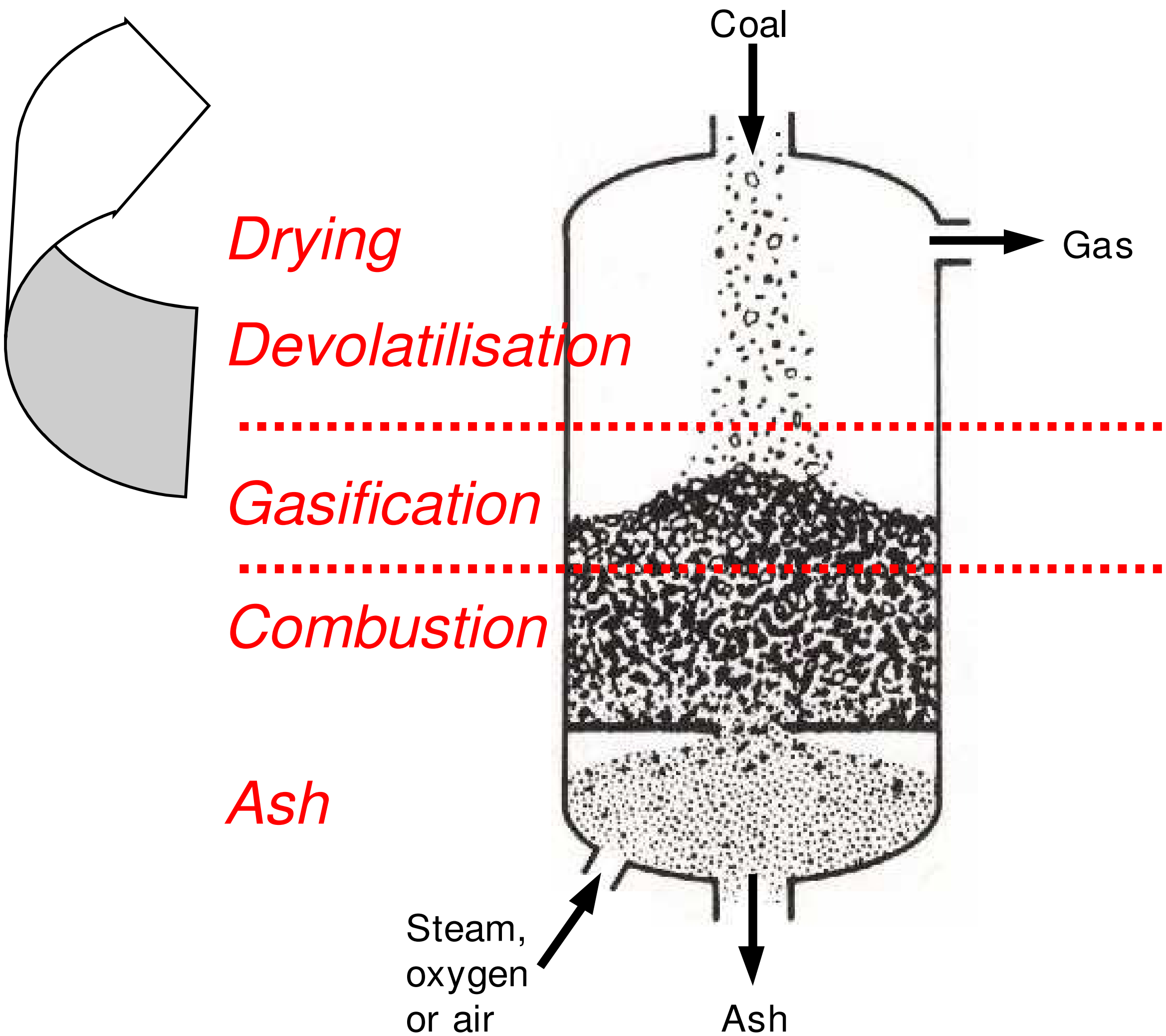


Courtesy of RH Matjie



Coal
Drying
Devolatilisation
Gasification
Combustion
Ash
Steam,
oxygen
or air
Ash
Coal
Gas
Drying
Devolatilisation
Gasification
Combustion
Ash
Steam,
oxygen
or air
Ash

FACTSAGE modelling approach



FACTSAGE input w.r.t. coal properties

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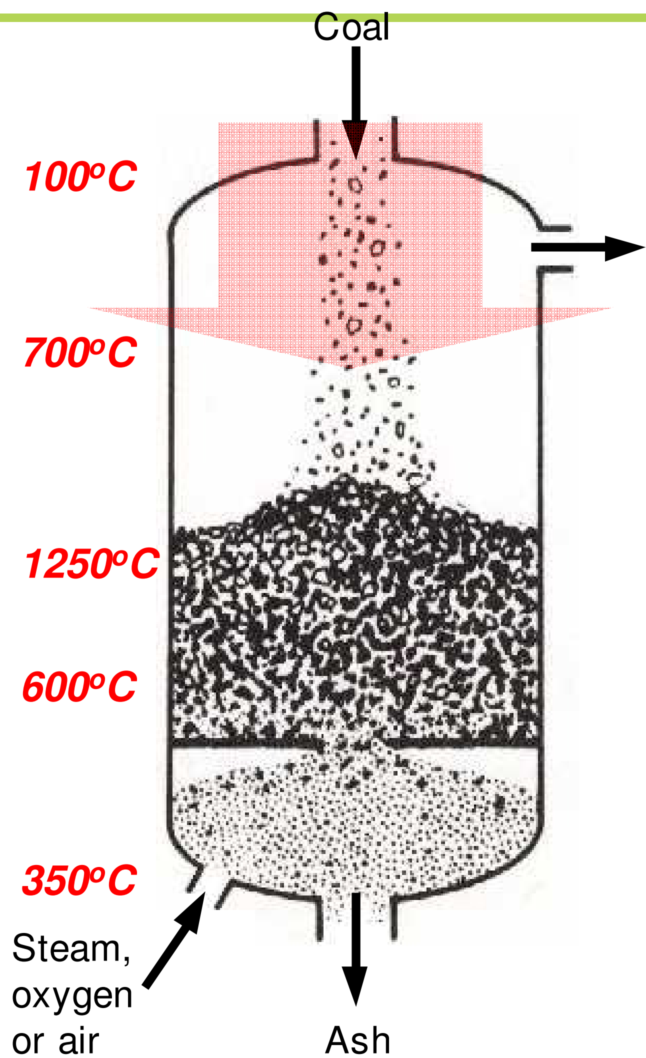
Component	Mass %	Mass flow (kg/hr)
Moisture	5.0	2550
Fixed carbon	46.3	23613
Volatile matter	22.9	11679
Ash	25.8	13158
TOTAL	100	51000

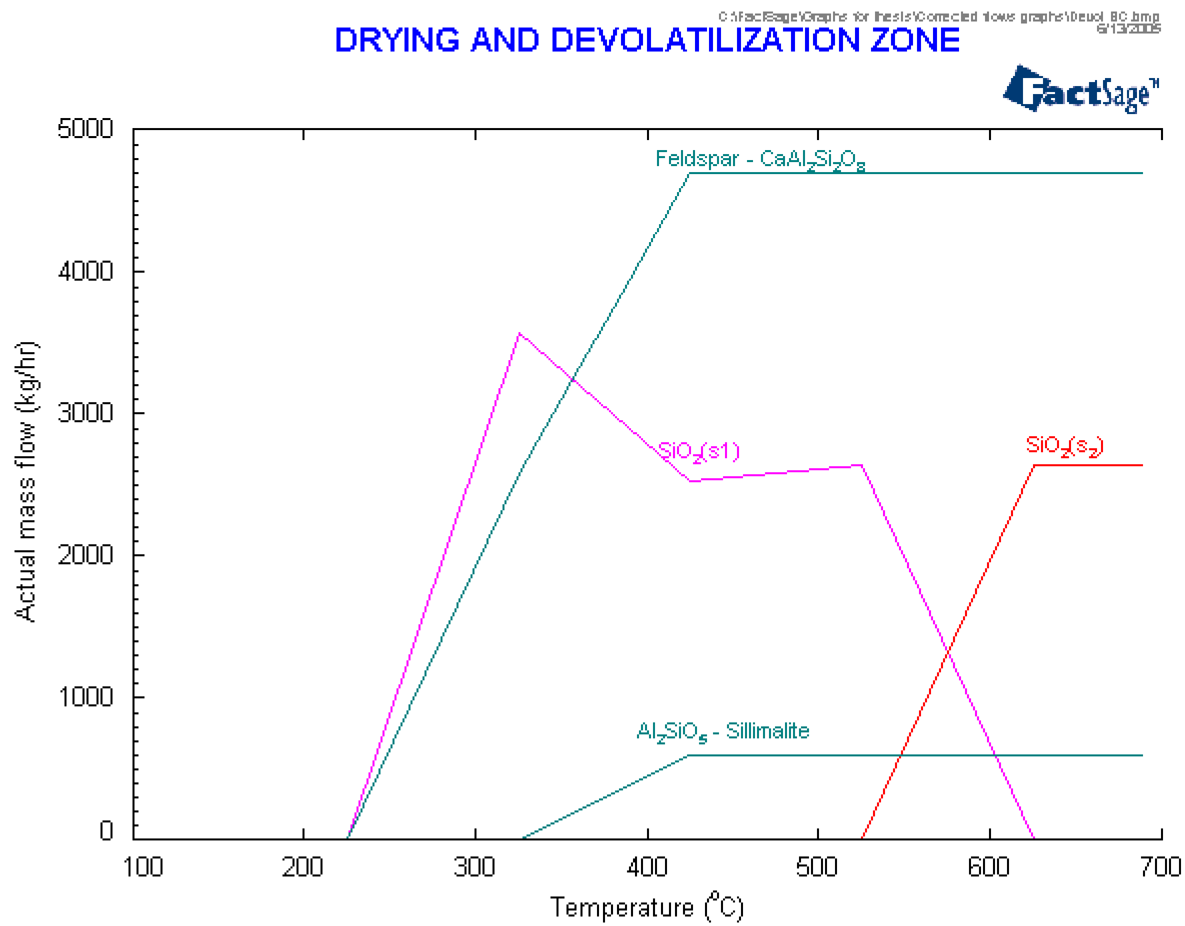
Property	Mass %	Mass flow (kg/hr)
H_2O	2.9	1479
H_2	0.15	76
CH_4	4.01	2045
CO	0.98	499
CO_2	7.2	3672
N_2	2.1	1050
Tar and oils	5.6	2858
TOTAL	22.9	11679

Mineral	Formula	Mass %	Mass flow (kg/hr)
Pyrite	FeS_2	4.0	526
Quartz	SiO_2	20.0	2631
Microline	$KalSi_3O_8$	1.9	250
Muscovite / Illite	$Kal_3Si_3O_{10}(OH)_2$	2.9	381
Kaolinite	$(Al_2O_3)(SiO_2)_2(H_2O)_2$	52.5	6913
Anatase	TiO_2	0.3	39
Calcite	$CaCO_3$	6.7	881
Dolomite	$CaMg(CO_3)_2$	10.1	1328
Apatite	$Ca_3(PO_4)_3(FOH)$	0.5	65
Gypsum	$CaSO_4(H_2O)_2$	1.1	144
TOTAL		100	13158

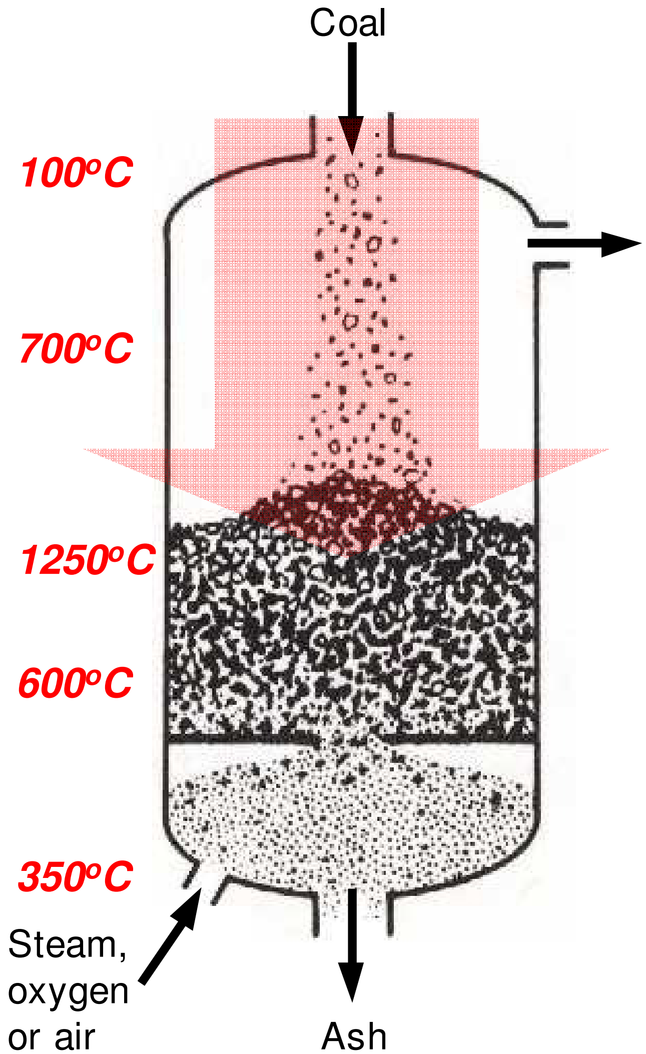
Property	Mass %	Mass flow (kg/hr)
Carbon (C)	78.8	25557
Hydrogen (H)	4.1	1329
Nitrogen (N)	2.2	713
Sulphur (S)	2.1	681
Oxygen (O) by difference	13.0	4154
TOTAL	100	32434

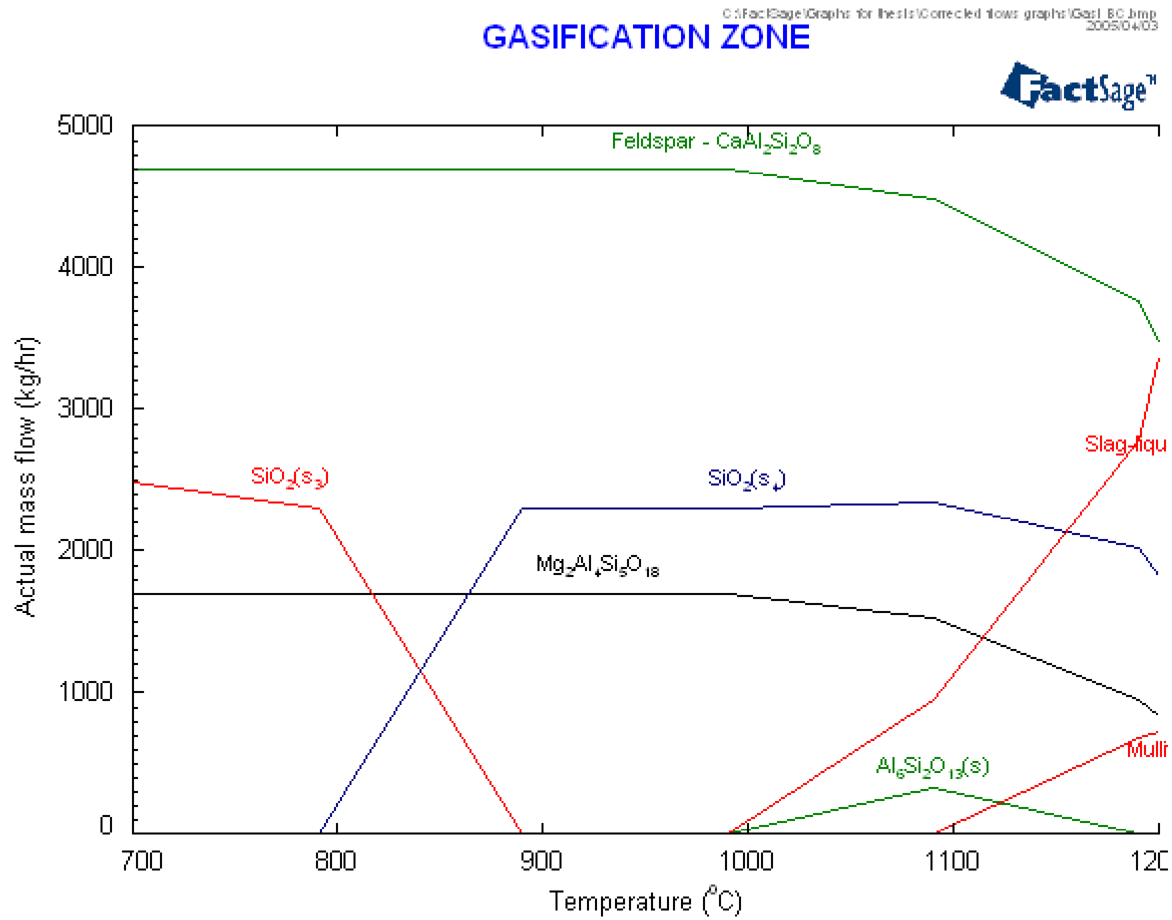
Drying and devolitilization zone





Gasification zone

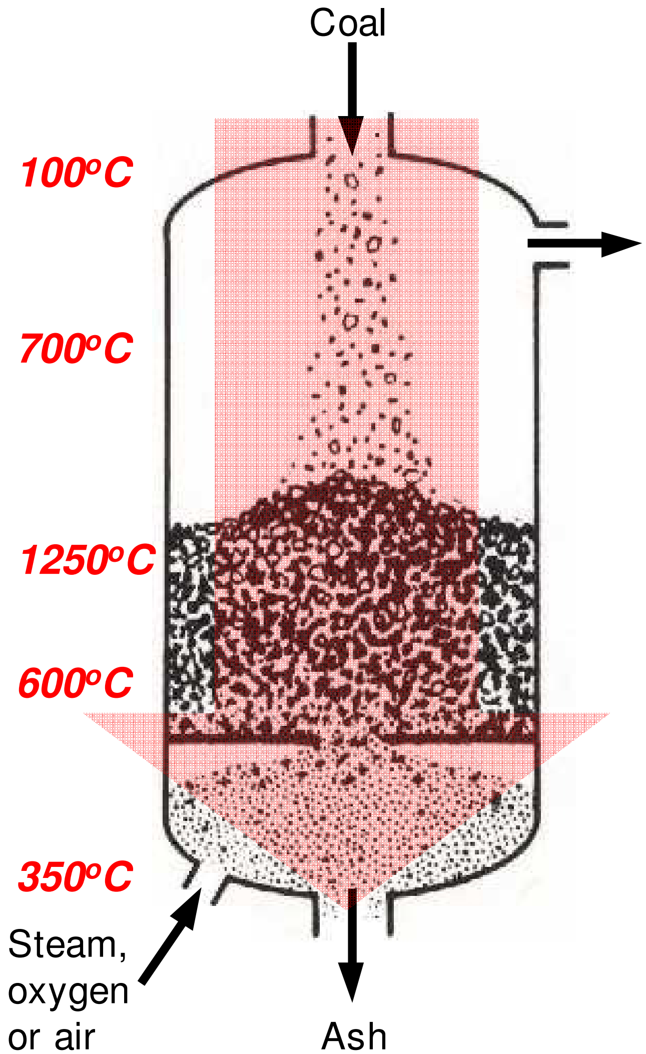


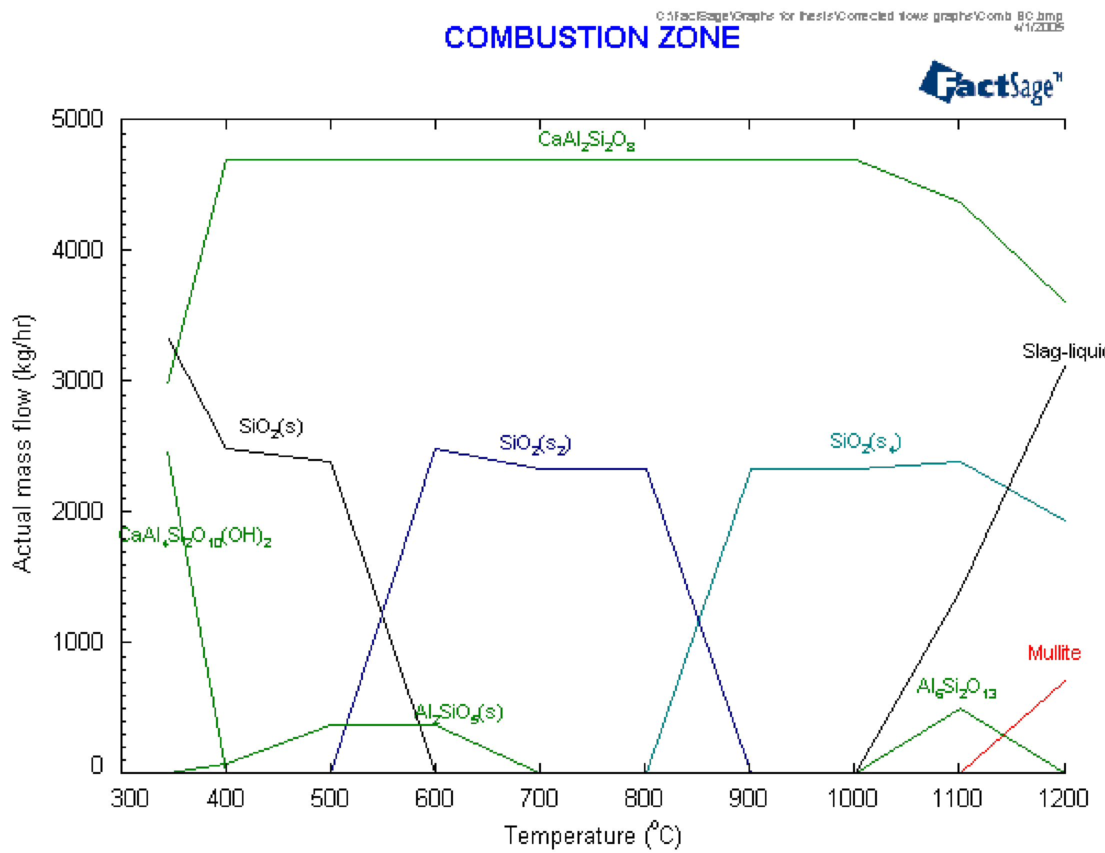


Gasification zone (cont.)

Slag-liquid composition (mass kg/hr)	Base case
MgO	150
FeO	315
SiO_2	1766
TiO_2	37
Ti_2O_3	0.001
CaO	219
Al_2O_3	635
K_2O	3
MgS	0.001
CaS	0.001
FeS	0.001
K_2S	0.001

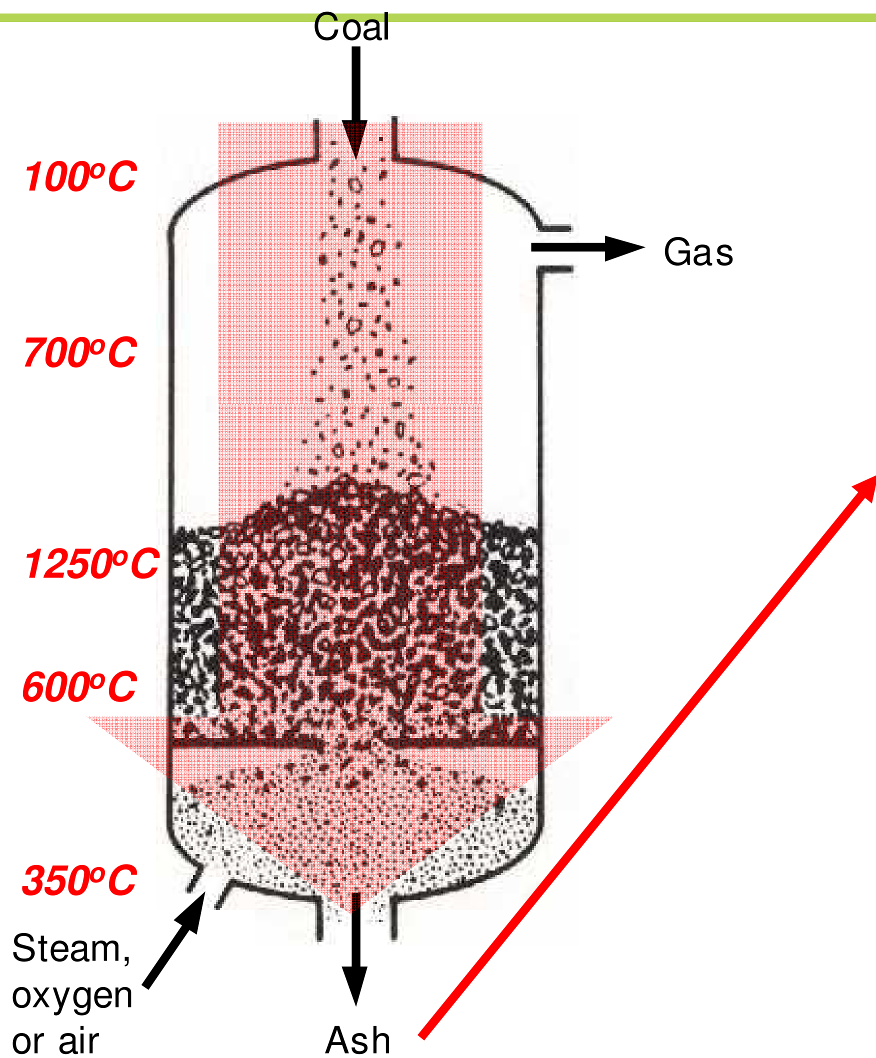
Combustion zone





Flow of material in gasifier…cooling process in combustion zone

Combustion zone (cont.)



Mineral composition of ash (crystalline material)
SiO_2 quartz
$CaAl_2Si_2O_8$ anorthite
$CaAl_4Si_2O_{10}(OH)_2$ margarite
$Mg_5Al_2Si_3O_{10}(OH)_8$
$KaI_3Si_3O_{10}(OH)_2$ muscovite
$Fe_3Al_2Si_3O_{12}$ almandine
$(FeO)(TiO_2)$ ilmenite

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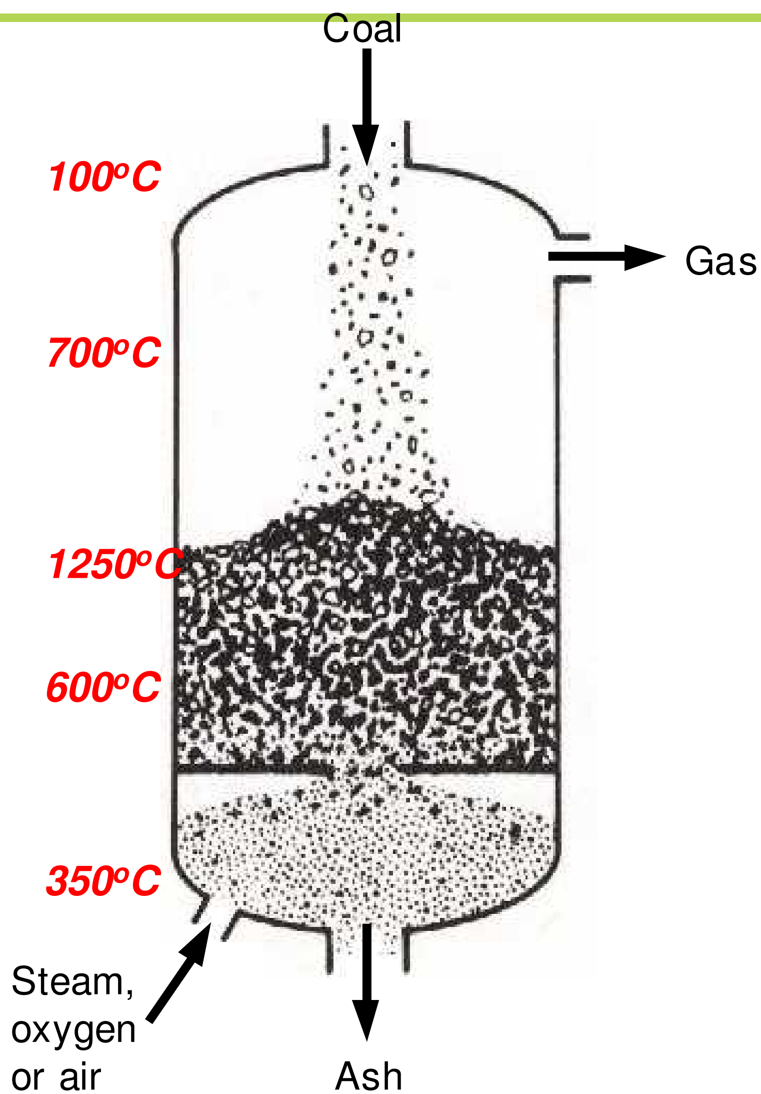
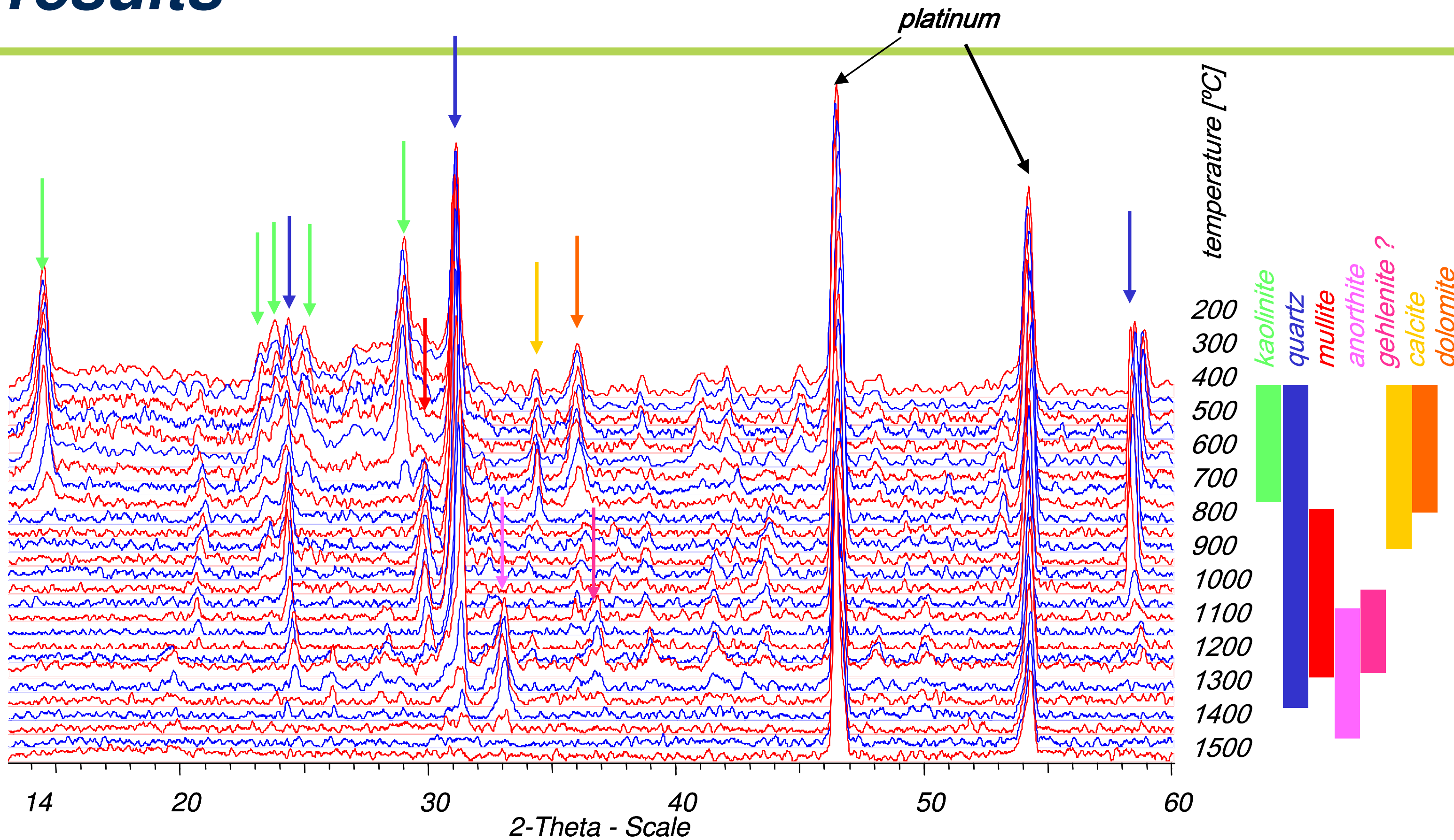
Summary of FACTSAGE results



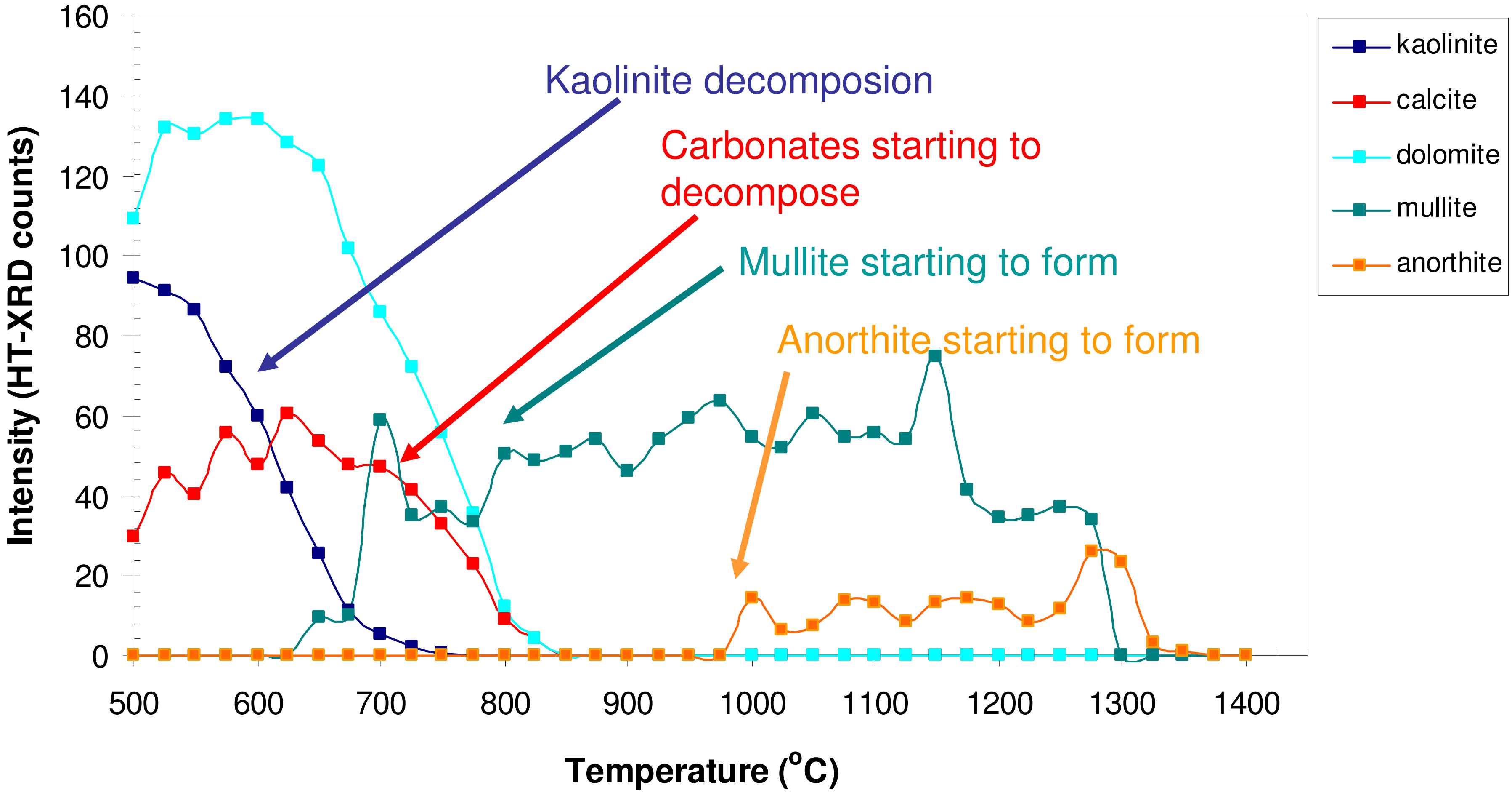
- *Kaolonite disappeared between 600^{o}C and 650^{o}C*
- *>650^{o}C meta-kaolonite forms from kaolonite*
- *Carbonates, calcite and dolomite decompose*
- *Mullite starts to form*
- *Intensities of mullite and quartz reflections decrease as a result of melt formation*
- *Anorthite crystallizes between 1000^{o}C - 1100^{o}C*
- *Above 1200^{o}C only quartz and anorthite remain stable in the liquidus*

HT-XRD results



- Recorded X-ray spectra with crystalline phase…50°C and 100°C intervals.
- Bars on right illustrate the temperature range during which the various crystalline phases are present.

Summary of HT-XRD results



Conclusions

Taken into account the results obtained from HT-XRD that

- *<500°C the starting material mainly composed of kaolonite ($Al_2SiO_5(OH)_4$), calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$), while quartz (SiO_2) remained unchanged*

- *between 500°C and 700°C kaolonite decomposes first, followed by calcite and dolomite*

- *around 1000°C anorthite ($CaAl_2Si_2O_8$) becomes stable due to partial melting of the phase assemblage*

- *above 1350°C the whole phase assemblage of the coal was molten*

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Conclusions (cont.)

it can be concluded that

- *HT-XRD does supply insight into specific mineral reactions and slag formation at temperatures below the average flow temperature obtained by AFT analyses*
- *Results are supported with phase diagrams on the SiO_2-CaO-Al_2O_3-MgO system*
- *Although the amount of melt was fairly low at 1000^oC, a percentage of melt is definitely present, which is not reflected by AFT analyses*

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Manipulation of coal feed to gasification

- *A method of increasing the AFT of a coal blend (decreasing the amount of slag propensity), in order to operate the gasifiers at higher temperatures*
- *Current operating philosophy to add excess steam to control the H_2/CO ratio and control operating temperature below the AFT*
- *However, when oxygen load is decreased, gas production is also decreased, thus, the preferred way in controlling the gasifier and temperature, is by varying the steam consumption, thereby having a direct effect on carbon utilization*

$$H_2O + CO \rightarrow CO_2 + H_2$$

Proposed solution to increase AFT

- *Additives (e.g. Ca and Fe) added to decrease the AFT for slagging gasifiers*
- *In fixed bed gasifiers slagging of ash is undesirable and has to be operated at a temperature below the AFT of the coal*
- *Addition of AFT increasing agent such as kaolonite ($Al_2Si_2O_5(OH)_4$), alumina (Al_2O_3), silica (SiO_2) or titania (TiO_2)*
- *The observed effects to be explained by considering the reactive chemical species*

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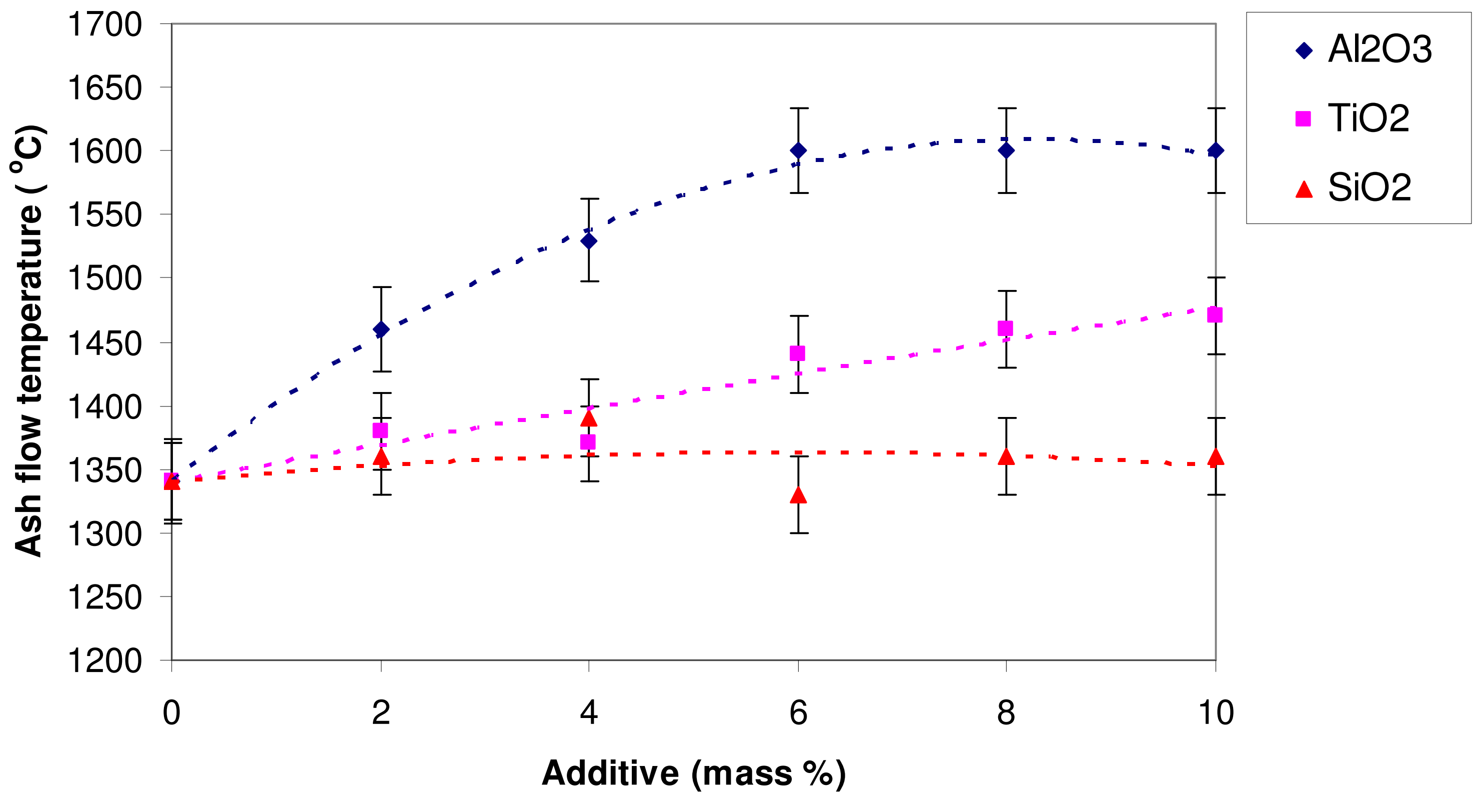
Coal used in this study

ELEMENT	Result of coal sample used in this study (mass %)	Coal characteristic as used during previous base case tests	
		Average (mass %)	Variation (minimum and maximum) (mass %)
SiO_2	50.1	48.7	40.0-51.9
Al_2O_3	23.3	24.1	20.9-30.2
Fe_2O_3	6.4	4.8	2.5-9.3
P_2O_5	0.7	0.7	0.5-2.2
TiO_2	1.0	1.4	1.0-1.6
CaO	8.1	7.9	6.1-11.6
MgO	2.7	2.5	1.9-3.2
K_2O	0.8	1.0	0.6-4.1
Na_2O	0.4	0.7	0.2-0.9
SO_3	6.1	7.3	5.3-9.5

Effect of silica, alumina and titania as pure components on AFT



- *Confirmed results as found on northern hemisphere coal sources by Vassilev, et. al., 1995*

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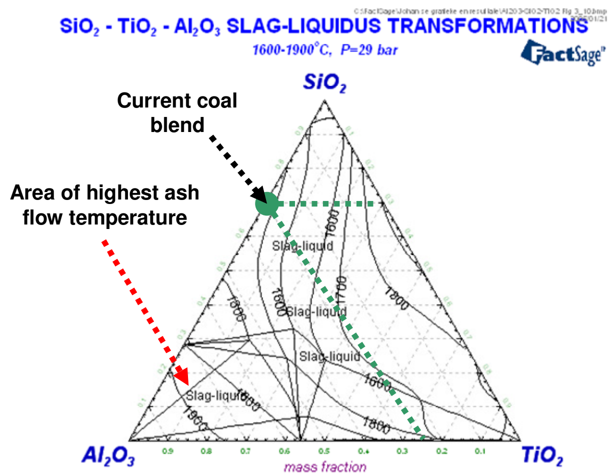
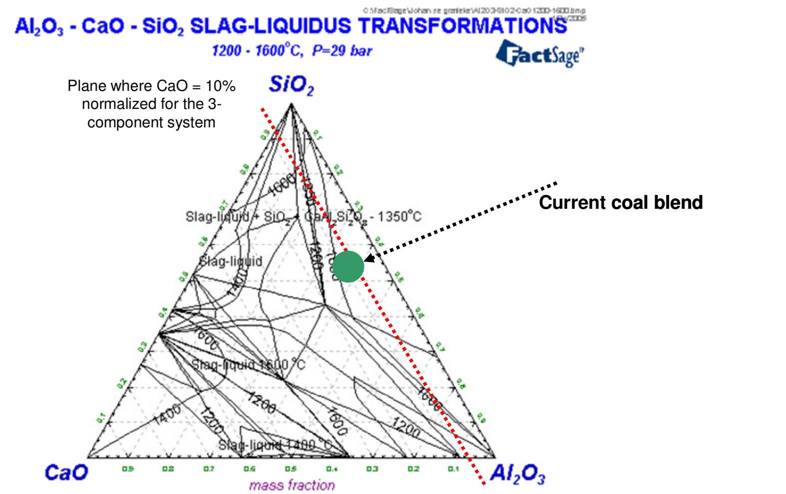
Effect of silica, alumina and titania as pure components on AFT

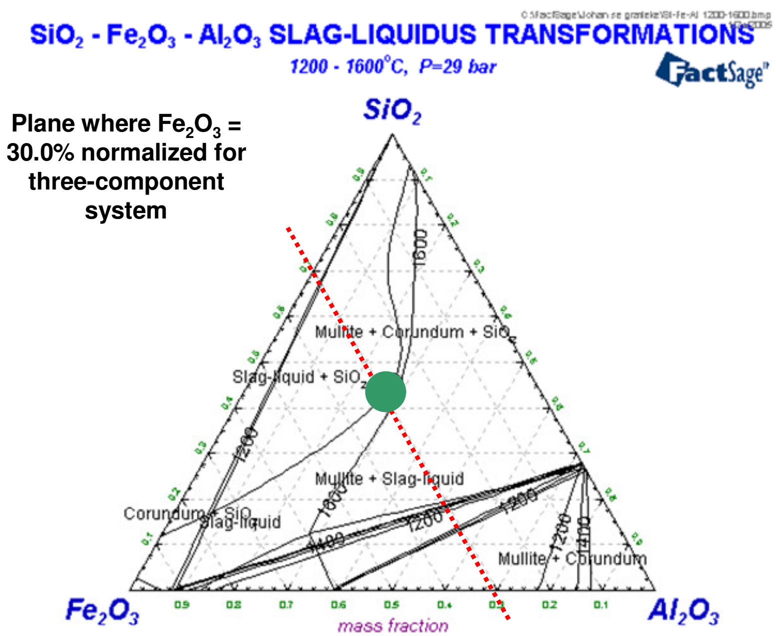
$$3(Al_2O_3.2SiO_2.2H_2O) \rightarrow 3(Al_2O_3.2SiO_2) + 6H_2O \rightarrow Al_6O_5(SiO_4)_2 + 6H_2O$$

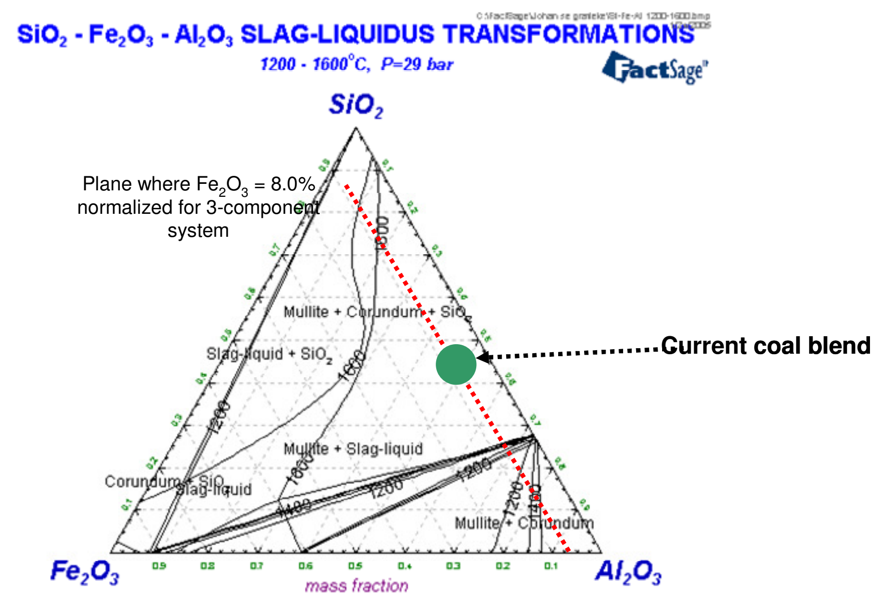
- *With the addition of free Al_2O_3 to the coal, the free SiO_2 (quartz) in the coal can react with the Al_2O_3 to directly form mullite ($Al_6O_5(SiO_4)_2$).*
- *Around 1000°C anorthite ($CaAl_2Si_2O_8$) becomes stable. Less SiO_2 now available, which implies less anorthite.*

Discussion of results by means of 3-component systems

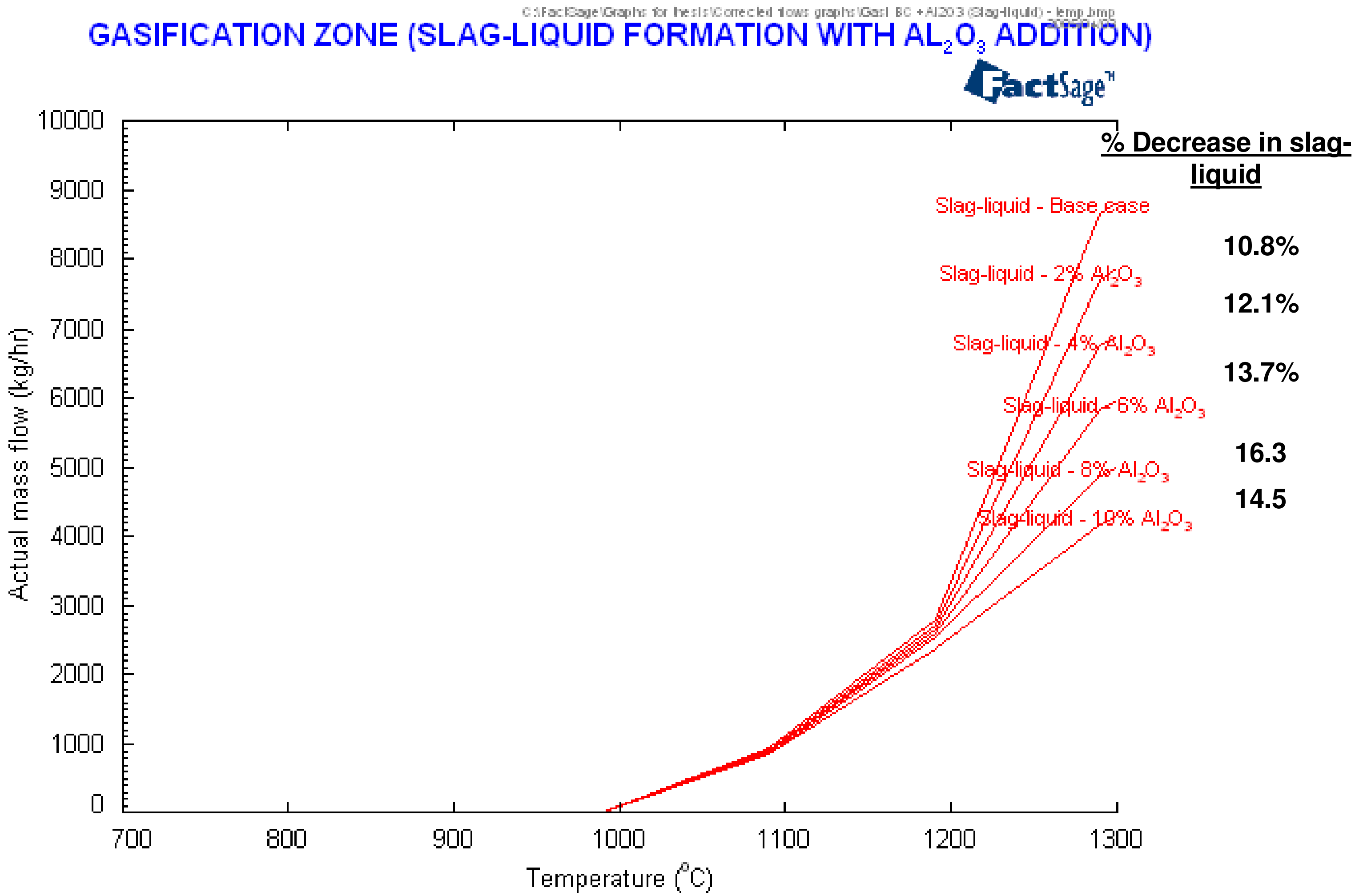




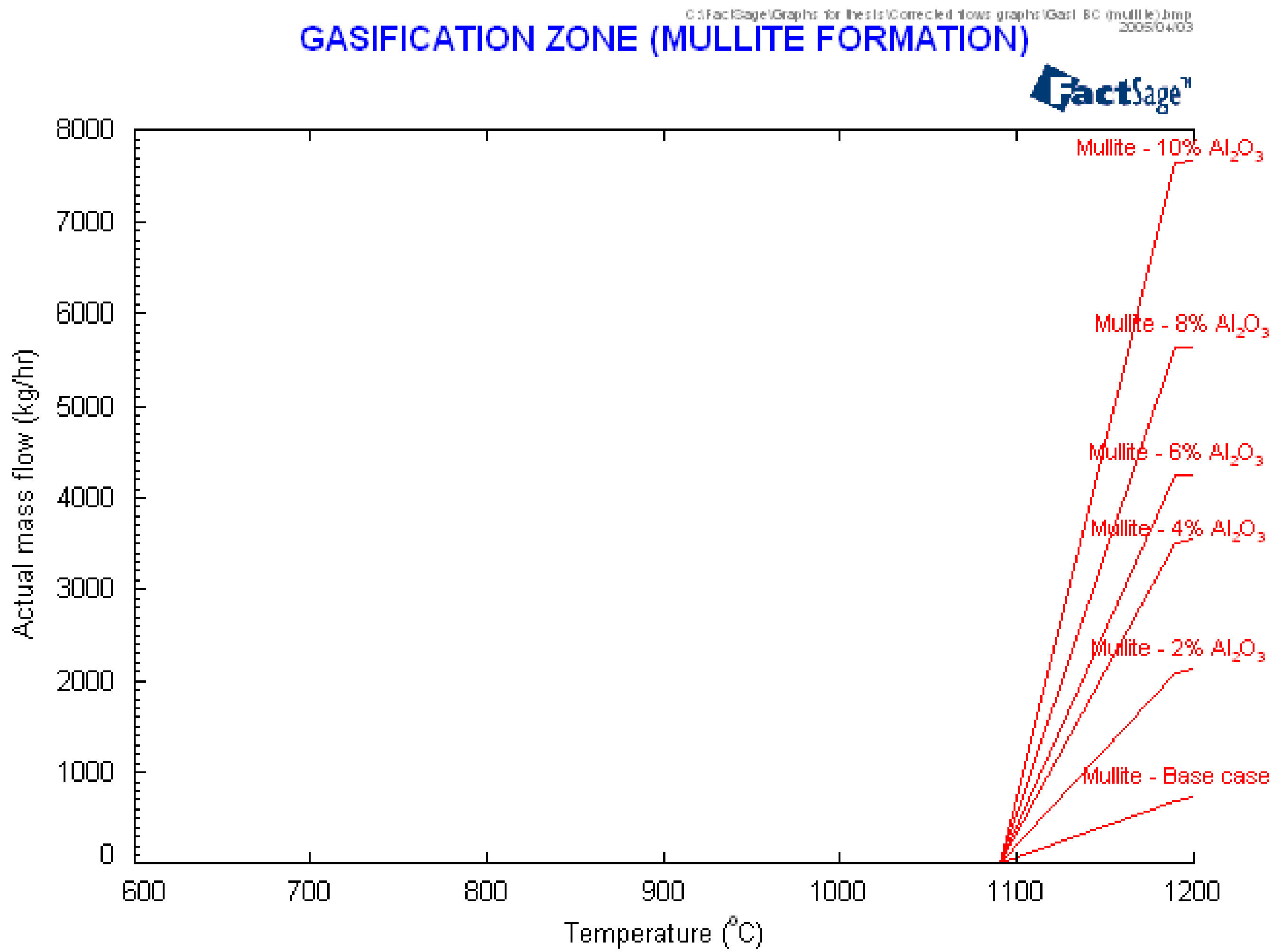




FACTSAGE results



FACTSAGE results (cont.)



Conclusions

- Al_2O_3 has the biggest / significant effect on AFT, with the effect of SiO_2 and TiO_2 very similar with regards to the effect on AFT
- Less Al_2O_3 was needed to increase the AFT to a similar AFT level in comparison to the SiO_2 and TiO_2
- Al_2O_3 keeps the oxygen molecules stronger bound to the structure. When the element becomes “free”, with free electrons, a different mineral phase can form with a different flow property
- AFT is non-additive (not a linear weighted calculated average) as was expected for the other coal properties such as the ash content, and therefore difficult to predict

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Conclusions (cont.)

- *Decrease in slag (anorthite) formation can be obtained by physical (DILUTION)) or chemical (NEW PRODUCT) formation…result of dilution is the worst case scenario*
- *Increase in crystalline material decreases slag formation*
- *Chemical reactions in the gasifier are taking place on micron scale…irrespective of feed particle size distribution*
- *Reaction of sillimalite towards mullite formation takes place in advance of anorthite formation…mullite formation thus limits anorthite formation*


THANK YOU