GTI ENERGY
solutions that transform

tcbiomass2024

FUNDAMENTAL AND SCIENTIFIC UNDERSTANDING OF BIOMASS (and MSW / PLASTICS) PROPERTIES FOR GASIFICATION

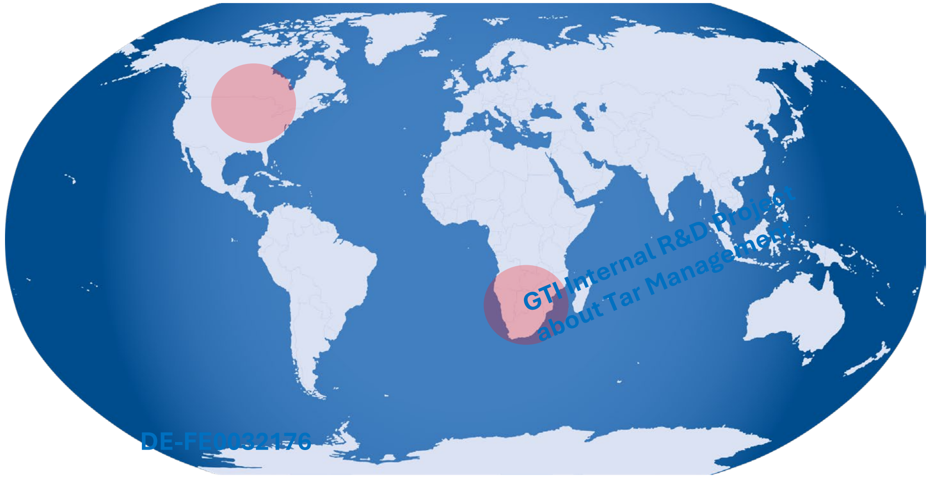
JC van Dyk (presenter), T Eastland, Zach El Zahab
GTI Energy, jvandyk@gti.energy

10-13 September 2024

ACKOWLEDGEMENT TO PROJECT PARTNERS AND SPONSORS

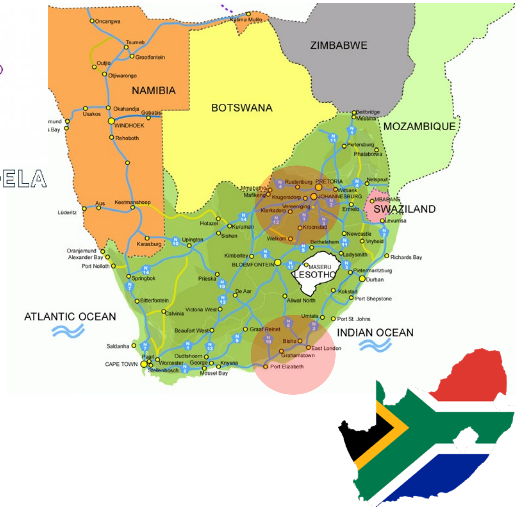
GTI ENERGY

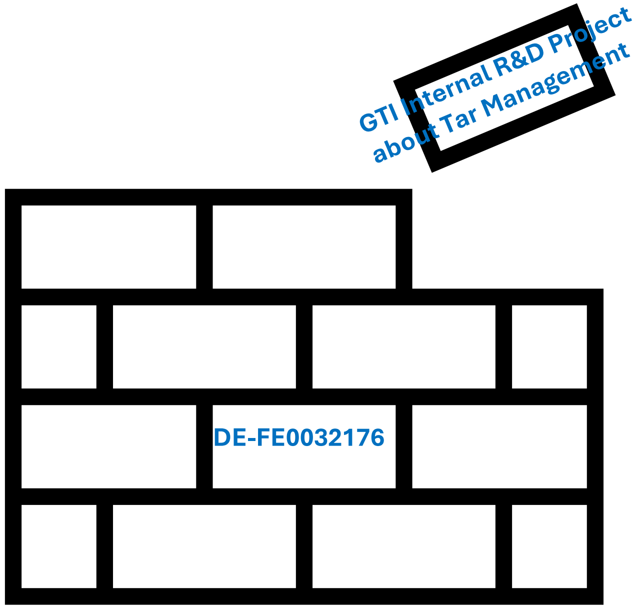
GTI ENERGY



NWU®

NELSON MANDELA UNIVERSITY





DE-FE0032176

- Feedstock sourcing (biomass, MSW, plastics)
- Kinetics data through TGA and bench scale
- Bubbling bed → MBU concept testing
- Syngas composition and temperature limits
- Temperature optimization to maintain below fouling
- Cost implications

GTI Internal R&D Project about Tar Management:

- Tar characterization
- Destructuring mechanism
- Influence of temperature and bed material

PROBLEM STATEMENT AND PURPOSE OF STUDY

1. Standard ISO or ASTM test methods are developed for coal, lignite, etc. specifically and statistically valid on properties within these ranks and variation. The need exists to develop procedures for standardized analyses on biomass, plastics and MSW.
2. Biomass, MSW and plastics are behaving similar with regards to conversion trends and in texture.
3. Some important factors affecting gasification are:
   1. **CO_2 Gasification Reactivity** and Fixed Carbon content (influence on gasification)
   2. Release of volatiles (**tar and oil formation**) and reduction parameters
      - ☐ The production of tar during gasification is one of the major problems affecting utilization efficiency, yields and CAPEX
      - ☐ Tar can also condense at reduced temperatures causing process related problems like clogging or blockage
      - ☐ Tar composition from some feedstocks may also be acidic and not suitable for downstream processing or blending
   3. **Inorganic speciation, slagging and fouling**

COMPOSITION OF ORIGINAL MATERIAL

GTI ENERGY

	Sample Identification		MSW	PLASTIC WASTE	BIOMASS	COAL
	Bulk density (Kg/m^3)	(as received)	183.25	145.75	228.25	
Proximate Analysis	% Inherent moisture content	(air-dried)	1.5	0.9	5.4	
	% Ash content	(air-dried)	12.7	7.8	1.0	
	% Ash content	(dry basis)	12.9	7.9	1.0	
	% Volatile Matter	(air-dried)	81.1	87.2	81.1	10-30(mass%)
	% Volatile Matter	(dry basis)	82.3	88.0	85.6	
	%Fixed carbon (by calculation)	(air-dried)	4.7	4.1	12.5	30-60(mass %)
Ash Flow Temperature	Initial Deformation Temperature	°C	1120	1140	1190	
	Hemispherical Temperature	°C	1180	1160	1250	
	Flow Temperature	°C	1210	1190	1310	
	Al_2O_3	%	10.1	10.4	31.9	
	SiO_2	%	48.2	45.8	48.6	
	CaO	%	17.6	20.6	5.1	
	MgO	%	1.9	4.3	2.0	
	Na_2O	%	7.2	5.7	0.2	
	Fe_2O_3	%	8.6	5.6	3.6	
	K_2O	%	0.4	0.6	0.6	
	SO_3	%	0.5	0.9	4.7	
	P_2O_5	%	0.4	0.3	0.9	
	TiO_2	%	2.3	0.0	1.5	
	MnO	%	0.2	0.1	0.0	
	LOI		2.6	5.7	0.9	

CO_2 Gasification Reactivity

TGA analysis @ 10ºC/min

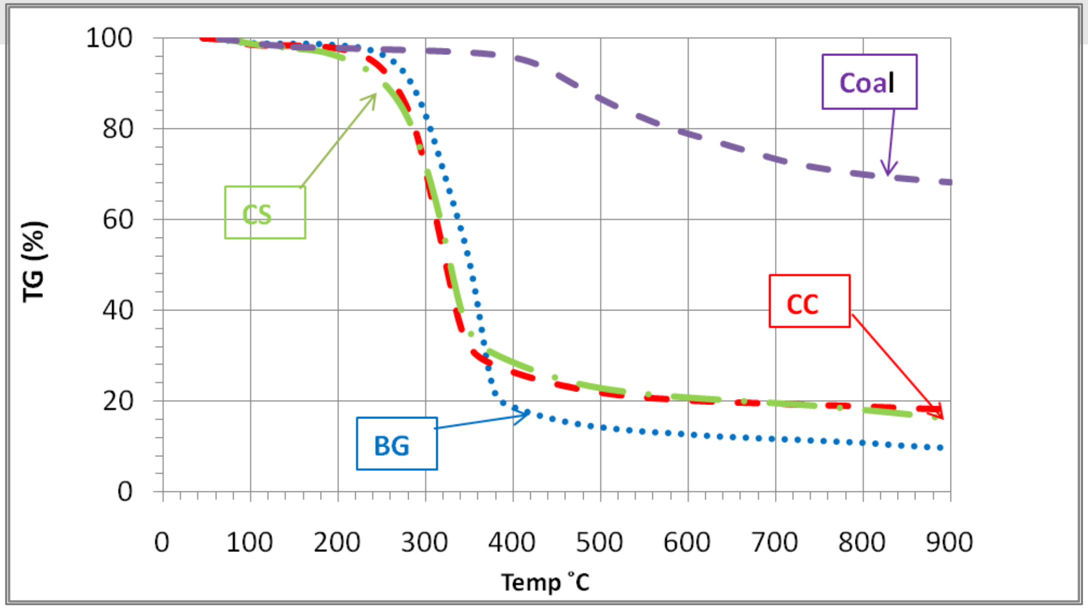
TGA conducted under inert (N_2) atmosphere

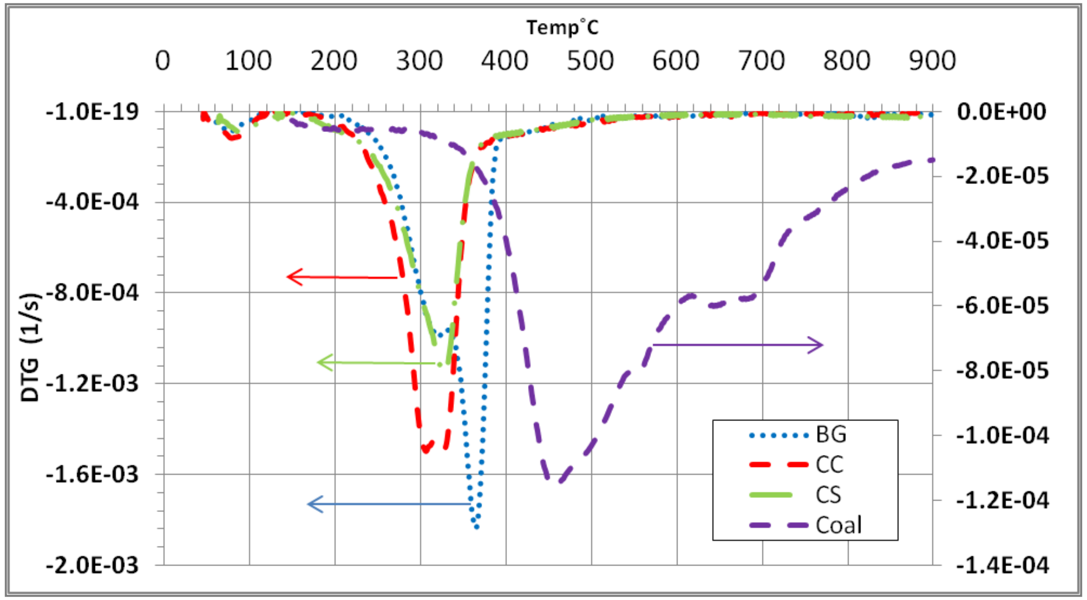
Coal weight loss is distributed over a larger temperature range (400-850°C) compared to biomass (200-400°C)

Biomass devolatilization rate nearly one order of magnitude greater than coal ($-1.2-1.8 \times 10^3\ s^{-1}$ compared to $-3\times10^4\ s^{-1}$)

Biomass peaks can be attributed to lignocellulosic content i.e. hemicellulose, cellulose and lignin

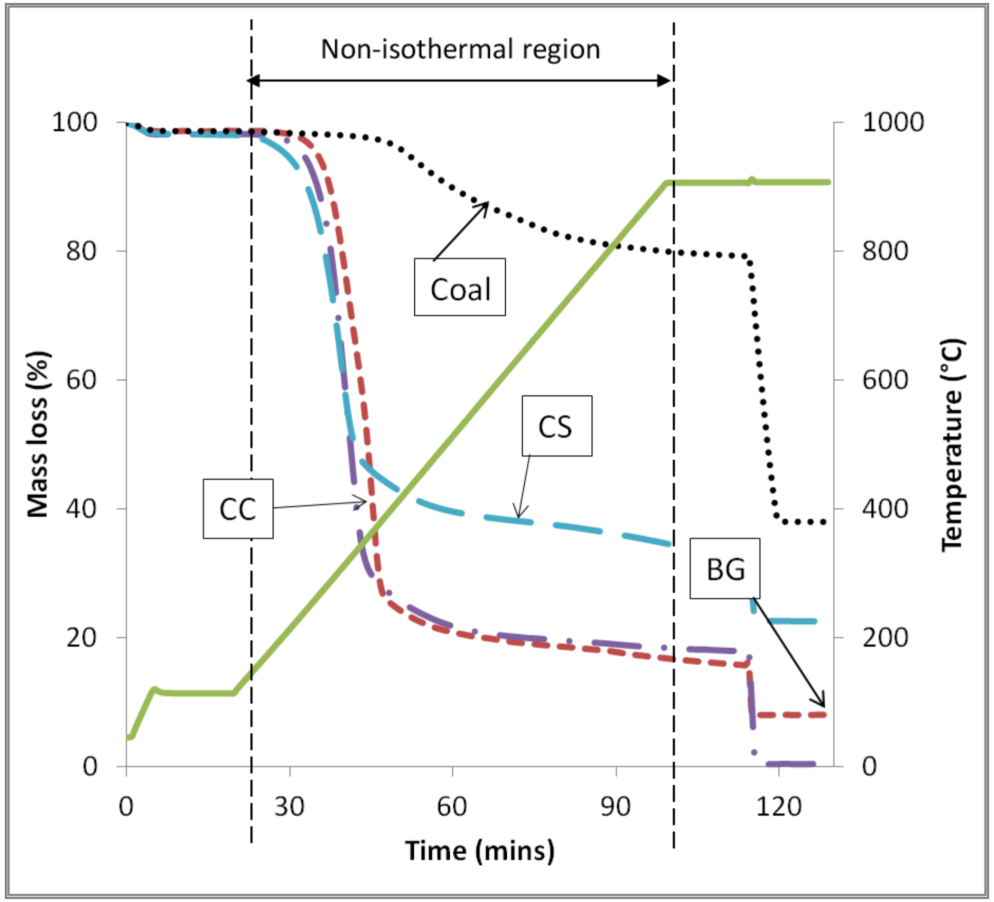
Coal peaks can be attributed to "regions of reactivity"





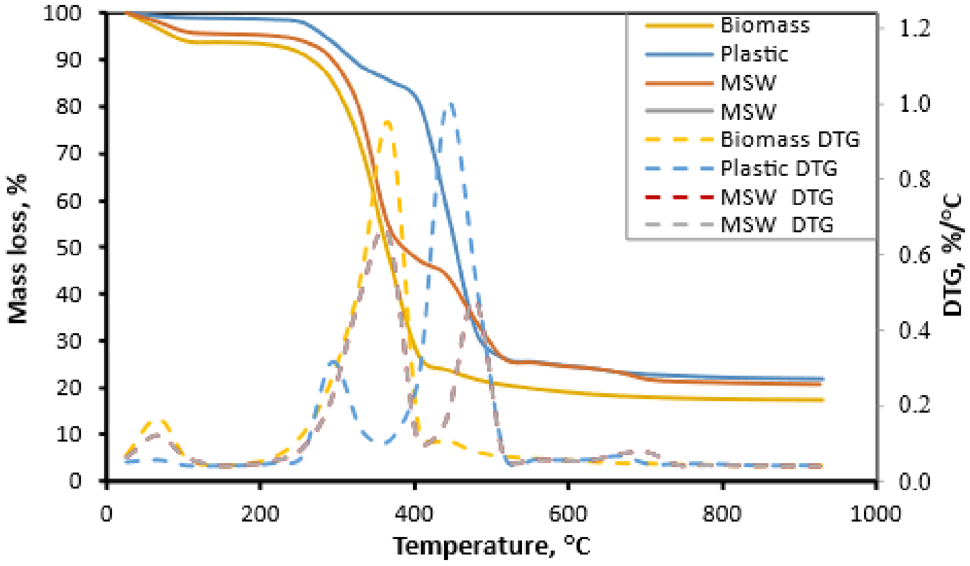
CO_2 Gasification Reactivity

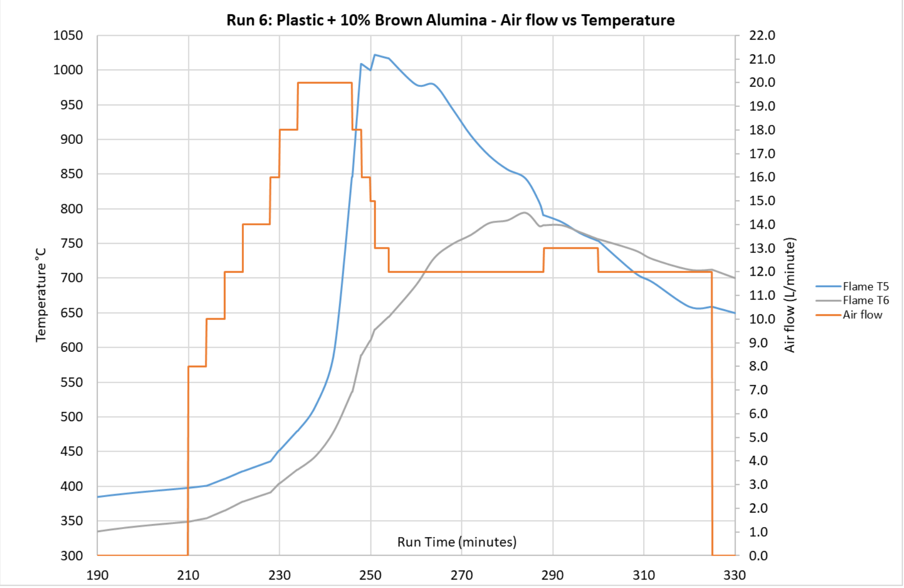
- Previous studies showed that pyrolysis kinetic parameters obtained under atmospheric conditions are also applicable to pressurized conditions of up to 40 bars
- Blends were analysed at 5, 10, and 50°C/min heating rates while single fuel samples were analysed at 5, 10, 20, 30, 40, 50 and 150°C/min
- Nitrogen was used as the purge gas, and was set to a flow rate of 150mL/min to ensure an inert atmosphere
- Sample masses of between 5-25 mg and particle size of less than 212µm limited the occurrence of secondary vapour–solid interactions, and the mass and heat transfer effects

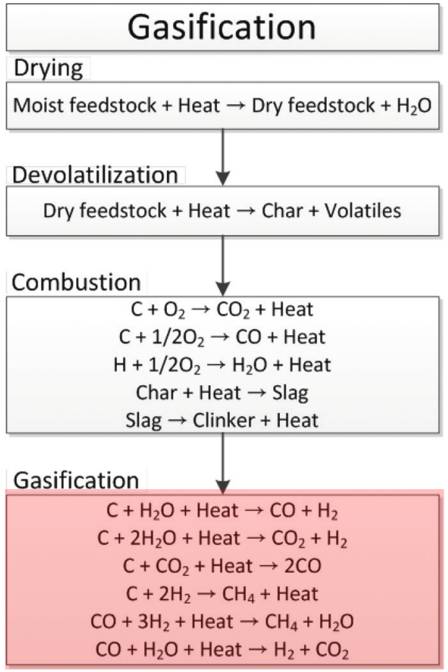


CO_2 Gasification Reactivity

1. Volatiles from Biomass, MSW and plastics are released at both a lower temperature and a faster rate compared to coal.
2. After the release of volatiles, the temperature inside the gasification zone has to be maintained in an endothermic environment controlled by the fixed carbon




Run 6: Plastic + 10% Brown Alumina - Air flow vs Temperature


Gasification

Drying

Moist feedstock + Heat → Dry feedstock + H_2O

Devolatilization

Dry feedstock + Heat → Char + Volatiles

Combustion

$C + O_2 \rightarrow CO_2$ + Heat
$C + 1/2O_2 \rightarrow CO$ + Heat
$H + 1/2O_2 \rightarrow H_2O$ + Heat
Char + Heat → Slag
Slag → Clinker + Heat

Gasification

$C + H_2O$ + Heat $\rightarrow CO + H_2$
$C + 2H_2O$ + Heat $\rightarrow CO_2 + H_2$
$C + CO_2$ + Heat $\rightarrow 2CO$
$C + 2H_2 \rightarrow CH_4$ + Heat
$CO + 3H_2$ + Heat $\rightarrow CH_4 + H_2O$
$CO + H_2O$ + Heat $\rightarrow H_2 + CO_2$

3. The problem with MSW and plastics, and to a lesser extent on biomass, are that the fixed carbon content is so low, that the temperature and heat inside the reactor are not maintained and a heat / energy sink observed.

EXAMPLE OF DETAIL UNDERSTANDING OF FEEDSTOCK REQUIRED (Lessons from 23302)

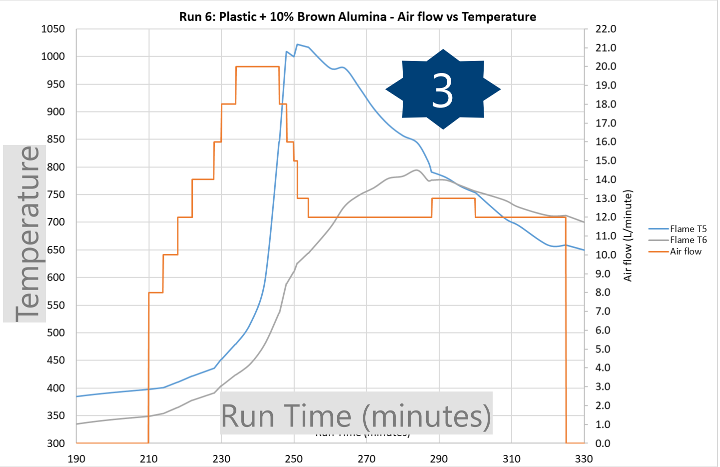
PROXIMATE ANALYSES		ULTIMATE ANALYSES		TO SYNGAS		TO PYR PRODUCTS (ALL)		TO ASH	
H2O	10	H2O	10	H2O	0	H2O	10	H2O	0
Mineral matter	11.1	Mineral matter	11.1	Mineral matter	0.0111	Mineral matter	0	Mineral matter	11.09
Volatile matter	71.1	C	44.5	C in FC Matrix	7.8	C	36.7	C	0.0
Fixed Carbon	7.8	H	6.4	H in FC Matrix	1.1	H	5.3	H	0
	100	N	0.8	N in FC Matrix	0.1	N	0.7	N	0
		S	0.4	S in FC Matrix	0.1	S	0.3	S	0.0
		O	26.5	O in FC Matrix	4.6	O	21.9	O	0
			99.7	C from vol gas	6.2	CHNSO TOTAL	64.8		
				H from vol gas	0.9				
PROXIMATE ANALYSES		**VOLATILE MATTER**		N from vol gas	0.1				
H2O	10	H2O	10	S from vol gas	0.1				
Mineral matter	11.1	Mineral matter	11.1	O from vol gas	3.7				
Volatile matter	71.1	Tar	47.0	C from tar crackin	0.0				
Fixed Carbon	7.8	Volatile H2O	11.9	H from tar crackin	0.0				
	100	Gas	11.9	N from tar crackin	0.0				
		Fixed Carbon	7.8	S from tar crackin	0.0				
			99.7	O from tar crackin	0.0				
TAR CRACKING	0	% volatile matter							
CARBON CONVERSION	100	% of fixed carbon			**24.7**		**74.8**		
SULPHUR TO ASH	10	% of total sulphur							

2

PYRGAS COMP (tar excl)		PYRGAS ALL
H2O	10	64.8
CH4	1.7	See file
H2	2.2	
CO2	0.5	
CO	2.4	
C2H6	0.1	
>C2s others	5.0	

	Sample Identification		MSW	PLASTIC WASTE	BIOMASS
	Bulk density (Kg/m³)	(as received)	183.25	145.75	228.25
Proximate Analysis	% Inherent moisture content	(air-dried)	1.5	0.9	5.4
	% Ash content	(air-dried)	12.7	7.8	1.0
	% Ash content	(dry basis)	12.9	7.9	1.0
	% Volatile Matter	(air-dried)	81.1	87.2	81.1
	% Volatile Matter	(dry basis)	82.3	88.0	85.6
	%Fixed carbon (by calculation)	(air-dried)	4.7	4.1	12.5
	Initial Deformation Temperature	ºC	1120	1140	1190
	Hemispherical Temperature	ºC	1180	1160	1250
	Flow Temperature	ºC	1210	1190	1310
	Al2O3	%	10.1	10.4	31.9
	SiO2	%	48.2	45.8	48.6
	CaO	%	17.6	20.6	5.1
	MgO	%	1.9	4.3	2.0
	Na2O	%	7.2	5.7	0.2
	Fe2O3	%	8.6	5.6	3.6
	K2O	%	0.4	0.6	0.6
	SO3	%	0.5	0.9	4.7
	P2O5	%	0.4	0.3	0.9
	TiO2	%	2.3	0.0	1.5
	MnO	%	0.2	0.1	0.0
	LOI		2.6	5.7	0.9

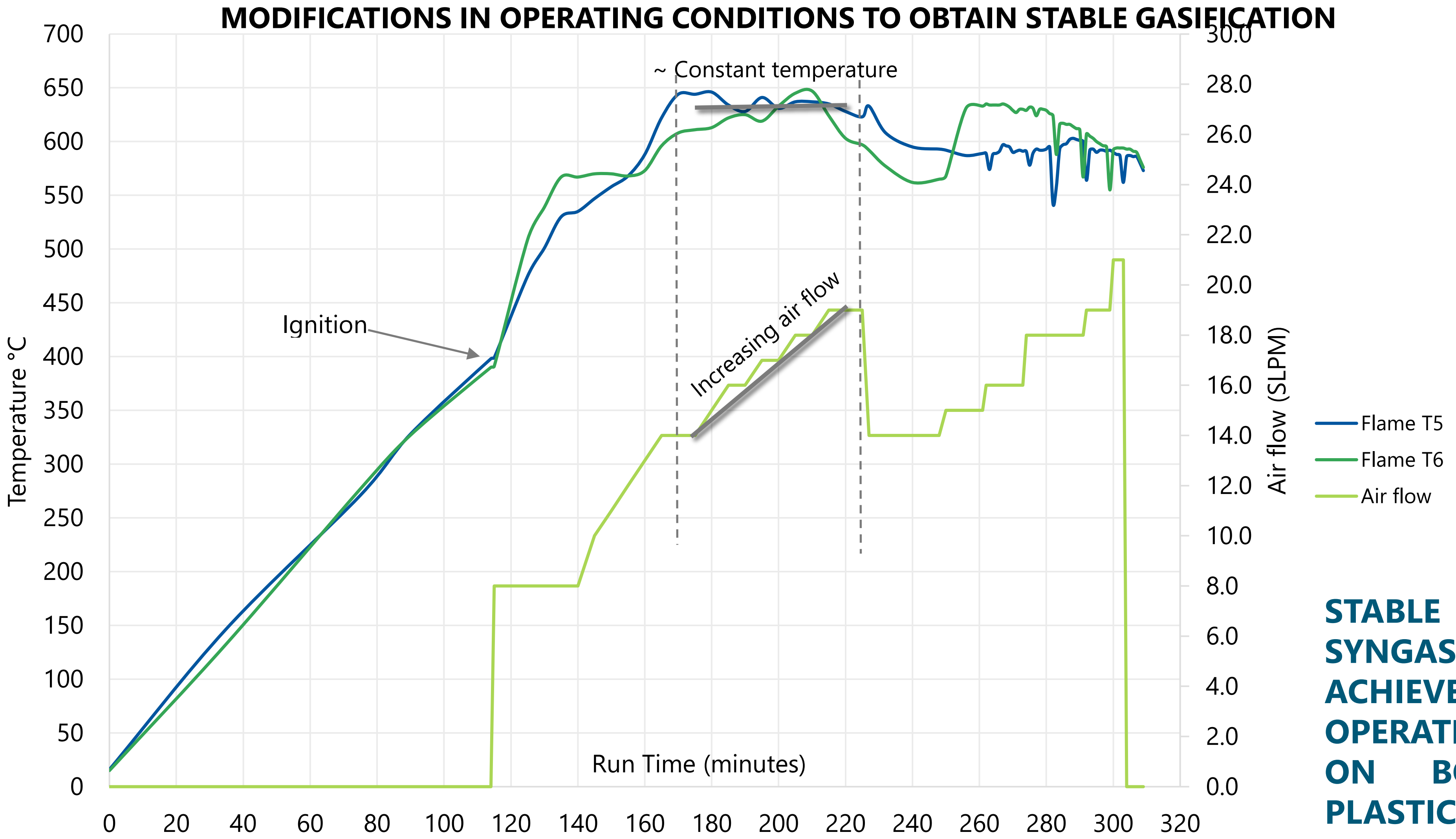
1



WHY DETAIL UNDERSTANDING OF FEEDSTOCK IS NEEDED:

1. **FIXED CARBON plays a role in both gasification (syngas production) and kinetics / reactivity.**
2. **TOTAL C speciation reflects C → tar and C → syngas.....ultimate analyses not the full picture**
    - **FTA REQUIRE from specialized labs (i.e. NWU and Sasol)**
3. **Low FIXED CARBON caused temperature run-away after devolatilization and 2-step operating is required**

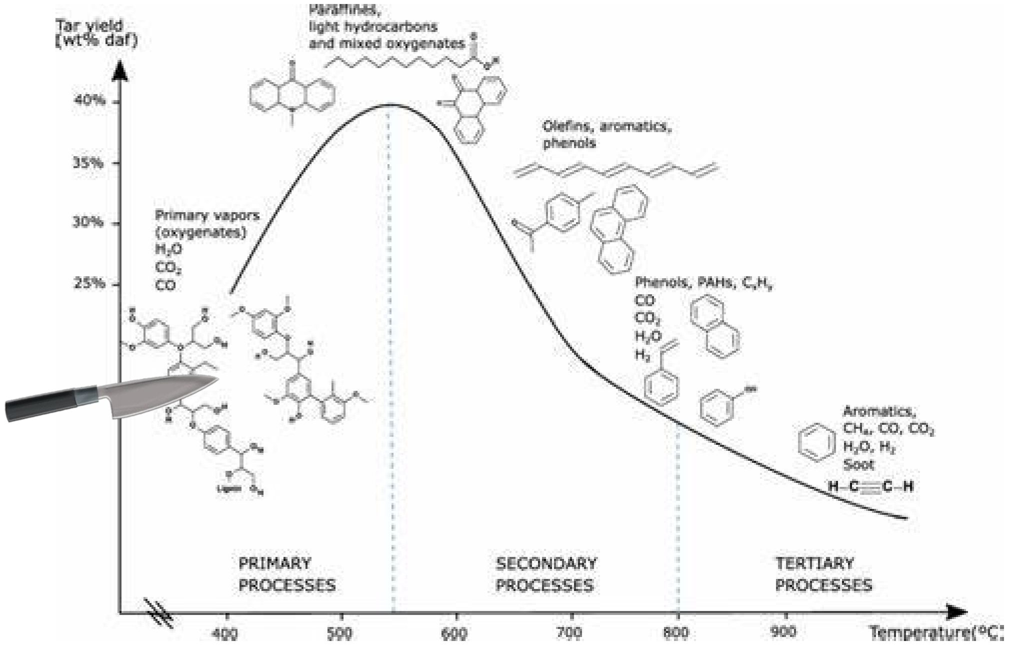
STABLE OPERATION ACHIEVED

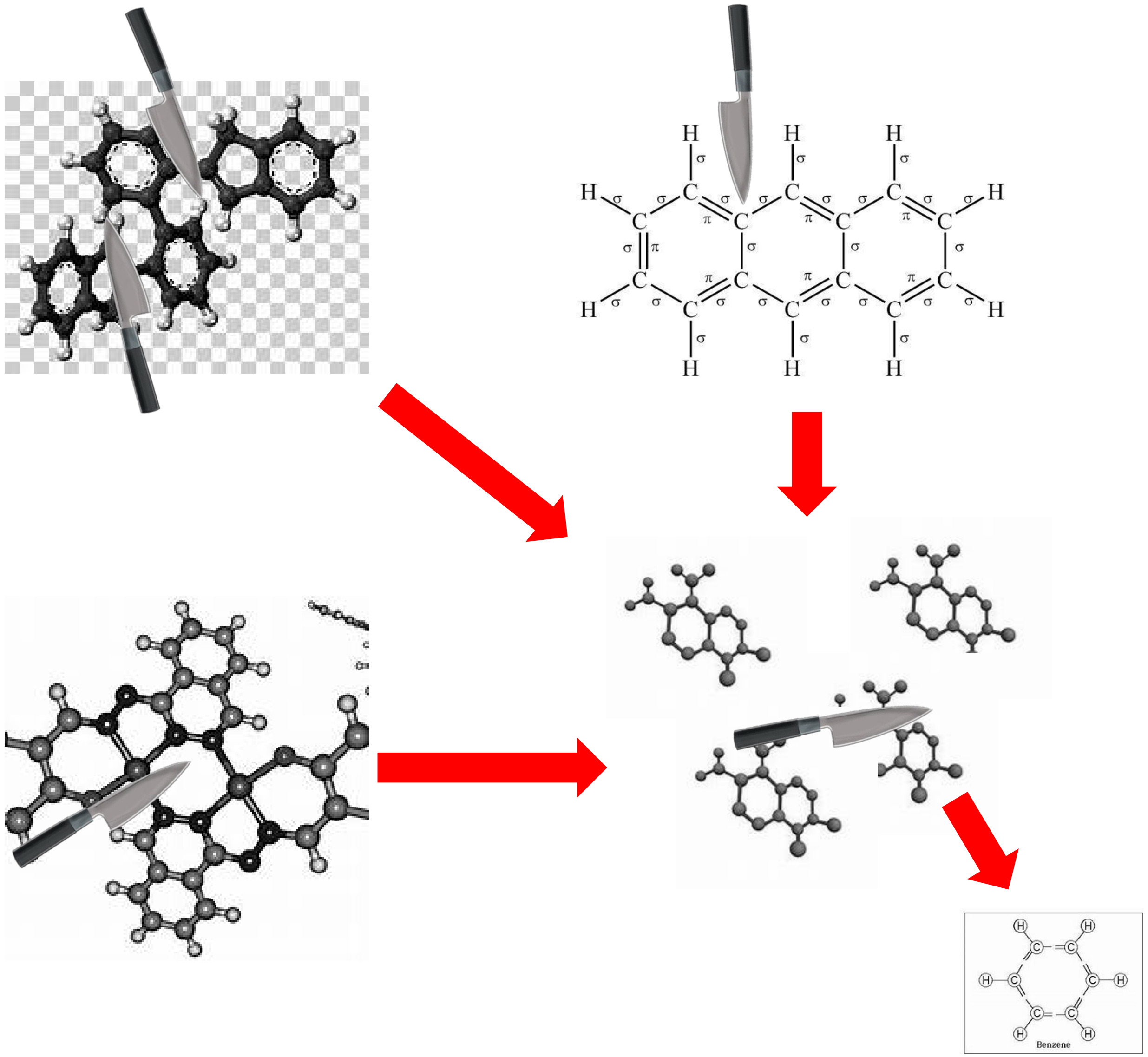


STABLE GASIFICATION AND SYNGAS PRODUCTION ARE ACHIEVED WITH ADJUSTED OPERATING CONDITIONS ON BOTH MSW AND PLASTICS

WHAT IS TAR CRACKING?

(Thermal versus chemical – and the combination)

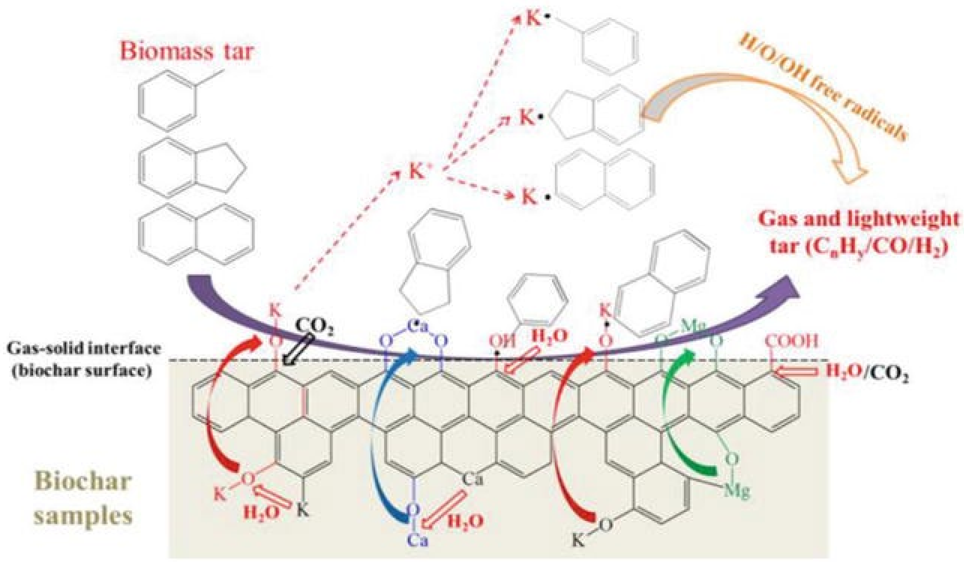




THERMAL =

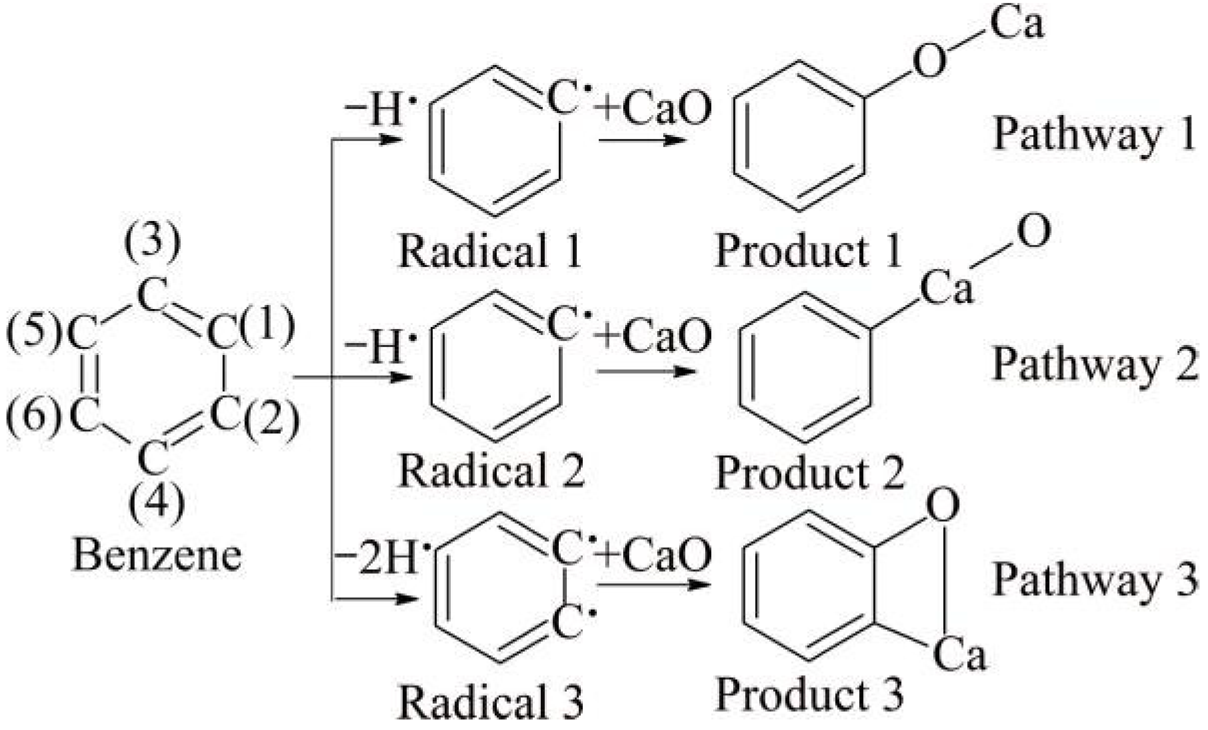
- cutting the carbon molecules (1 to >1)
- Smaller C-chains
- C6 stable
- Gas release

WHAT IS TAR CRACKING?



“K or Ca as an example, as a cheap and naturally abundant material, has been demonstrated as an effective catalyst for the catalytic cracking of tar. The basic sites of CaO can enhance the cleavage of C–H, C_{aryl}-C and aromatic C -C bonds of tar molecules to form active carbon and help for H_2O dissociation to form OH∗ and H∗ free radicals, the OH∗ radical reacts with active carbon to generate other oxygenate intermediates, and are subsequently decomposed to produce gaseous products and remove coke.

Bin Li, Christian Fabrice Magoua Mbeugang, Yong Huang, Dongjing Liu, Qian Wang, Shu Zhang,
A review of CaO based catalysts for tar removal during biomass gasification,
Energy,
Volume 244, Part B,
2022



CATALYTIC =

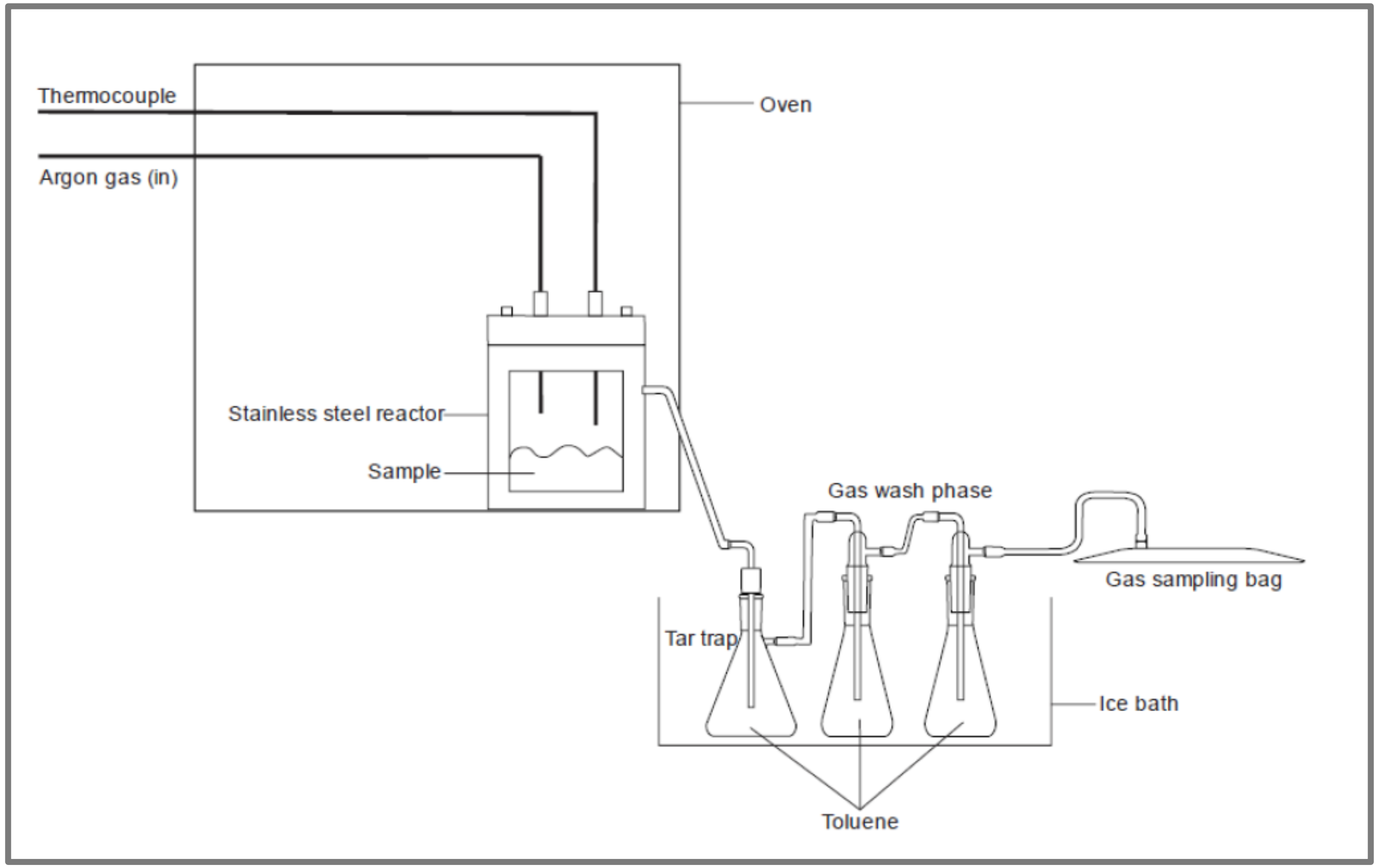
- Forming free radicals
- Weakening of bonds
- Easier to break chain and C6’s
- Higher gas-make

Modified Fisher Assay analysis

- Pyrolysis in Argon or N_2
- Wt. % of char, tar, gas and water
- Temperatures up to 1000 °C
- Max P = 30 bar
- Collect products for further analyses/tests
- 50 g sample per test

Examples of studies:

- Influence of additives/mineral matter on coal pyrolysis products[a,b]
- Possible catalysts to promote tar cracking during pyrolysis (Al_2O_3 ,K_2CO_3 , potassium acetate (CH_3COOK), and KOH)[b]
- Influence of temperature (520, 720 and 920 °C) and coal rank (ranging from lignite B to bituminous C) on pyrolysis product yields. Tars characterised[c]



---

[a] Bean, N. C., Bunt, J. R., Strydom, C. A., Neomagus, H. W. J. P., Van Niekerk, D., & Hattingh, B. B. (2018). Influence of additives on the devolatilization product yield of typical South African coals, and effect on tar composition. *Journal of the Southern African Institute of Mining and Metallurgy*, *118*(4), 395-407.

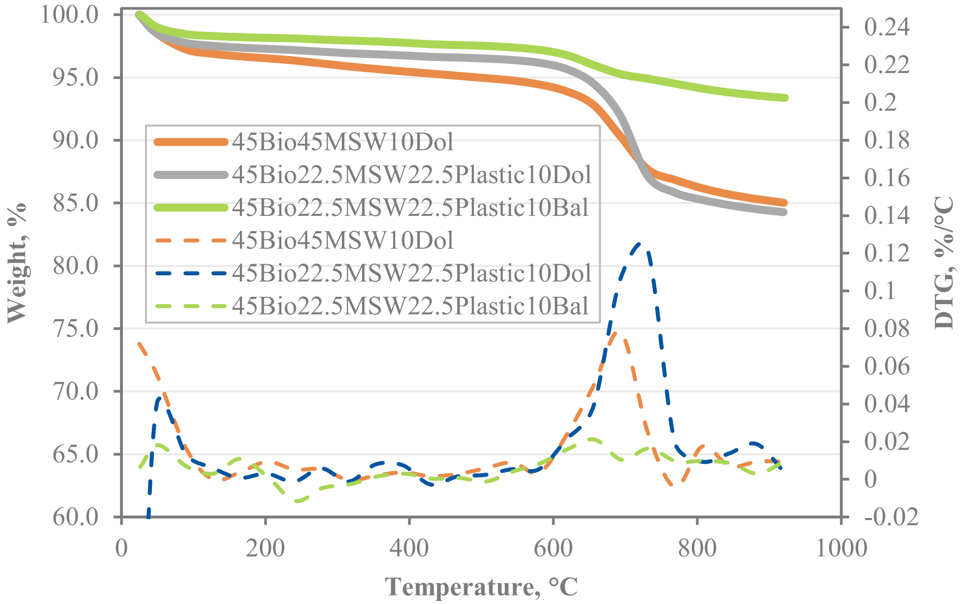
[b] Roets, L., Bunt, J. R., Neomagus, H. W., Strydom, C. A., & Van Niekerk, D. (2016). The effect of added minerals on the pyrolysis products derived from a vitrinite-rich demineralised South African coal. *Journal of analytical and applied pyrolysis*, *121*, 41-49.

[c] Pretorius, G. N., Bunt, J. R., Gräbner, M., Neomagus, H., Waanders, F. B., Everson, R. C., & Strydom, C. A. (2017). Evaluation and prediction of slow pyrolysis products derived from coals of different rank. *Journal of Analytical and Applied Pyrolysis*, *128*, 156-167.

SUMMARY OF NORTH-WEST UNIVERSITY STUDY

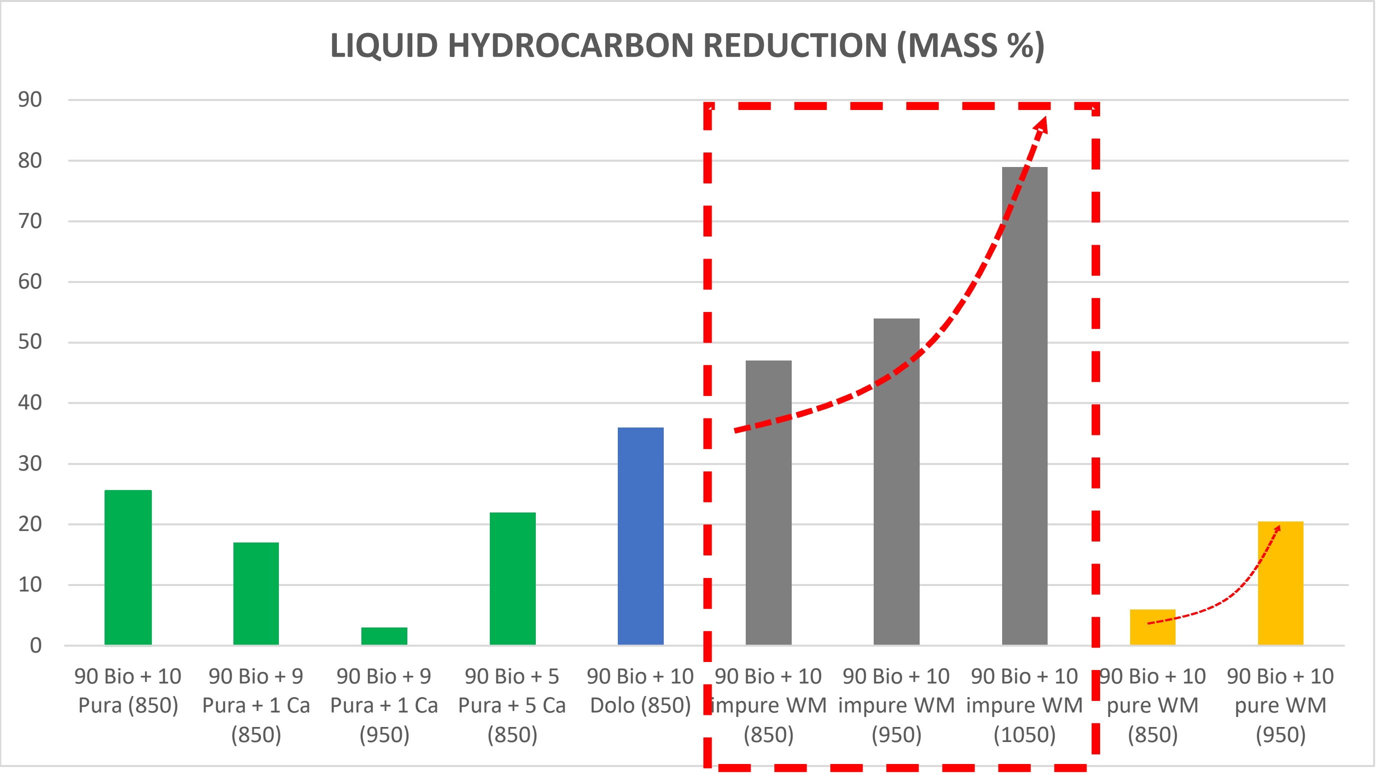
1. The tar samples from the blends with higher percentages biomass produced more phenolic type compounds than the tar from the blends with the higher amounts of paper and plastic waste. The tar from the blends with the highest amounts of MSW contained hydrocarbon compounds as the main group of compounds that formed. The main crude oil fraction of the tar samples was heavy vacuum oil. See below

Sample ID / crude fractions	Kerosene	Light gas oil	Heavy gas oil	Light vacuum oil	Heavy vacuum oil
45Bio45MSW10Dol (Run10)	19	26	7	10	37
45Bio22.5MSW22.5Plas10Dol-1 (Run12)	28	30	6	6	31
45Bio22.5MSW22.5Plas10Dol-2 (Run15)	25	33	5	6	31
45Bio22.5MSW22.5Plas10BAl (Run18)	27	32	5	6	29
100MSW (Run20)	14	26	10	10	41
10Bio10MSW80Dol (Run22)	15	23	21	9	32
10Bio10Plas80Dol (Run23)	18	26	17	11	28
10Bio5MSW5Plas80Dol (Run23)	17	28	13	9	33
45Bio45Plas10Dol (Run25)	26	32	6	8	29
90Bio10Dol (Run26)	32	21	8	11	28
90MSW10Dol (Run27)	14	29	10	10	37
18Bio72Plas10Dol (Run29)	23	32	8	8	29
72Bio18Plas10Dol (Run30)	32	29	4	6	28



2. Char from the paper waste showed the highest gasification reactivity in comparison to the chars formed from the biomass and plastic waste materials. Dolomite increases the gasification reactivity more than Brown Alumina does.

CHANGE IN ORGANIC CONTENT (mass%)



Sasol Puralox partical size <125µm
Biomass average size was 1mm
Unstable runs due to void and flow dynamics inside reactor

Washington Mills brown Al contains Ca, Fe and K
Particle size 1mm

Sasol Puralox and Washington Mills pure Al composition similar.
Particle size 1mm.

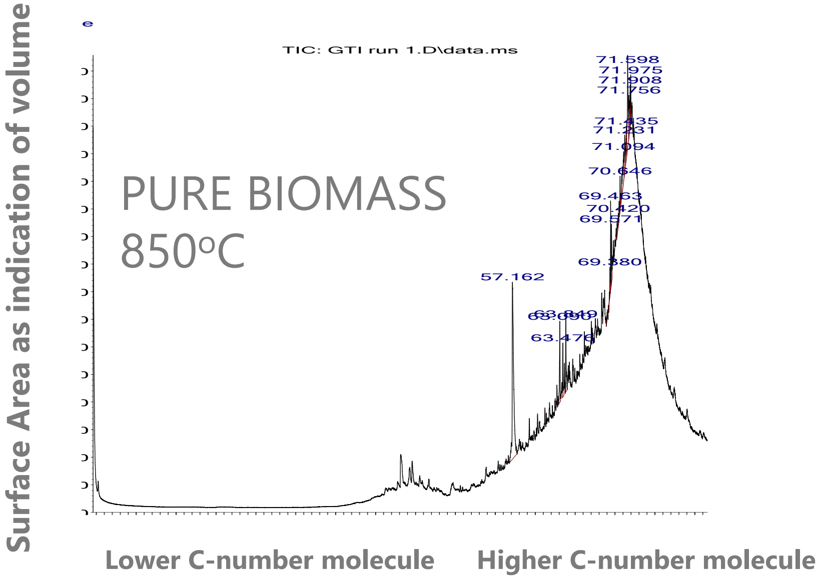
Mass loss calculated as % change from total mass of 100% biomass run

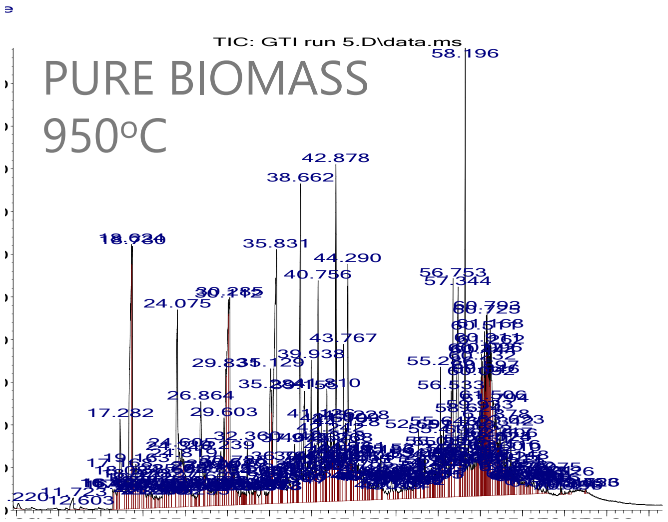
1. Sasol Puralox runs unstable and no specific conclusion on runs, caused by ultra fine PSD of catalyst.
2. Washington Mills "white Al" runs were stable. Influence of T observed. Average tar decreased in comparison with Sasol Puralox despite unstable runs with the Sasol catalyst.
3. Washington Mills "brown Al" runs resulted in most promising trends. Influence of temperature and catalyst observed.

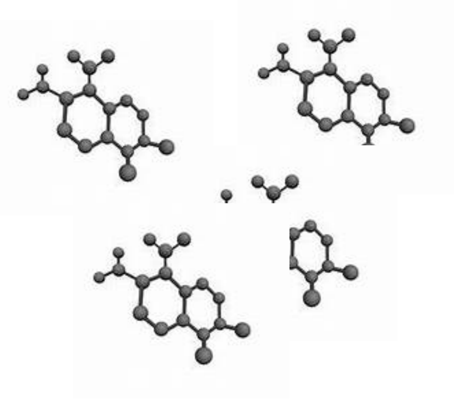
CHANGE IN ORGANIC COMPOSITION (SEMI-QUANTITATIVE DISTILLATION)

GTI ENERGY

Temperature change ONLY



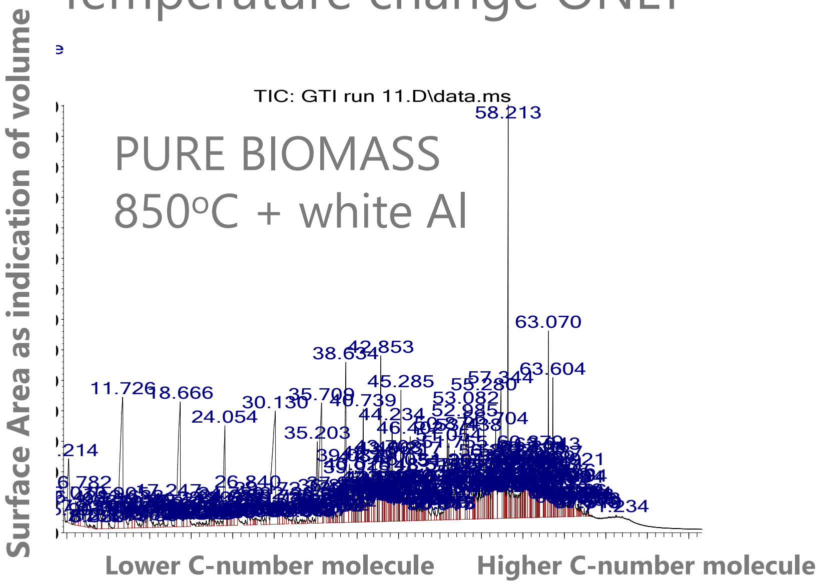




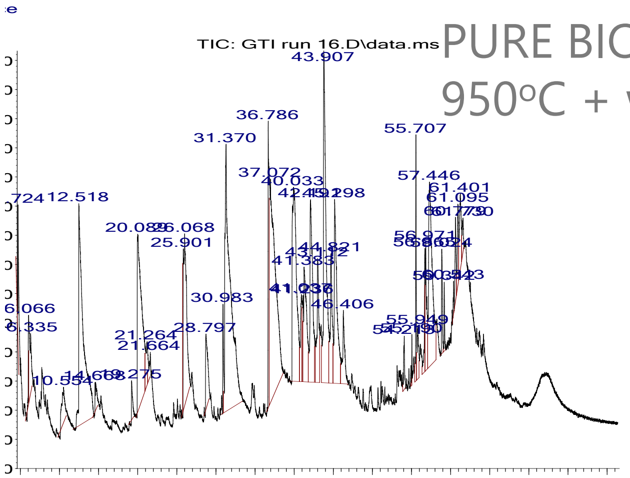
CHANGE IN ORGANIC COMPOSITION (SEMI-QUANTITATIVE DISTILLATION)

GTI ENERGY

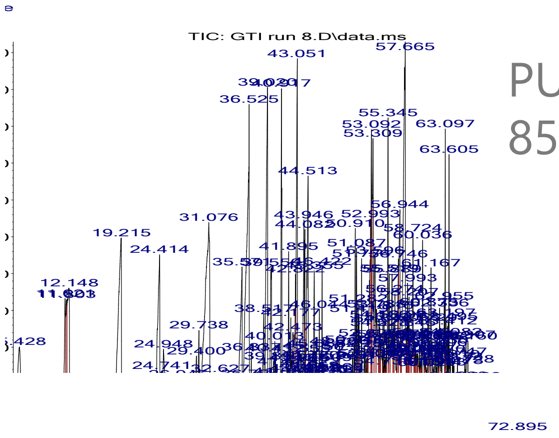
Temperature change ONLY



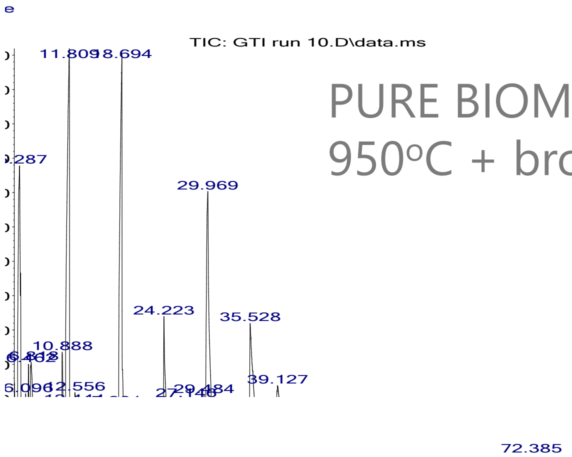
PURE BIOMASS
850ºC + white Al



PURE BIOMASS
950ºC + white Al



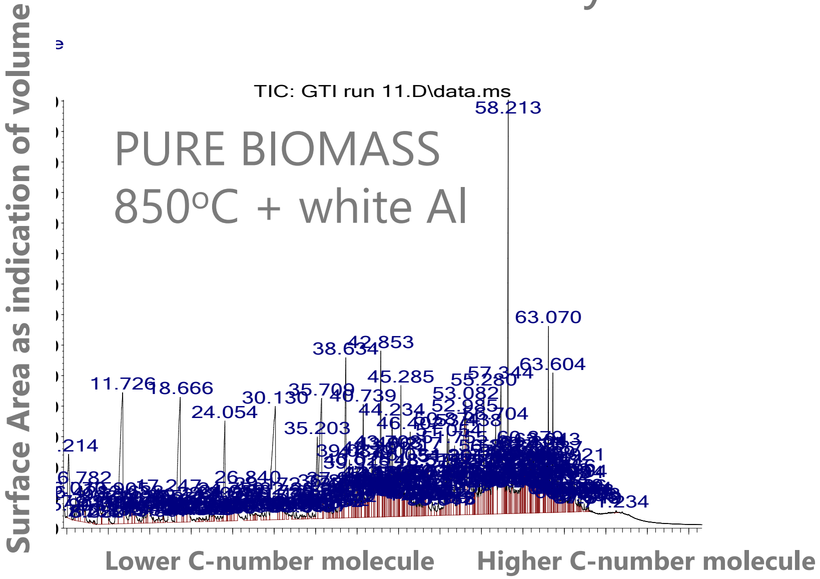
PURE BIOMASS
850ºC + brown Al



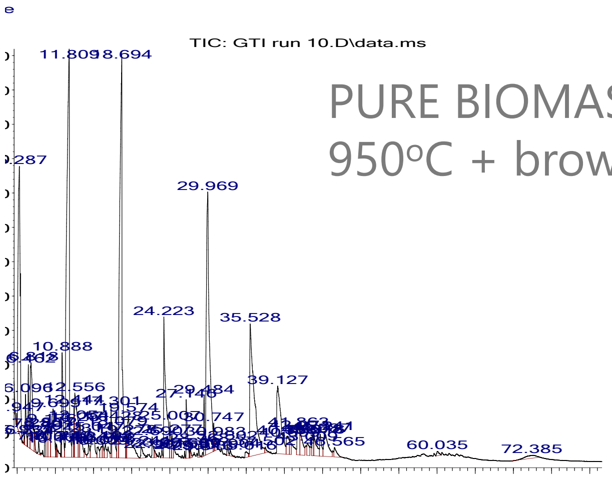
PURE BIOMASS
950ºC + brown Al

CHANGE IN ORGANIC COMPOSITION (SEMI-QUANTITATIVE DISTILLATION)

Influence of both catalyst and temperature

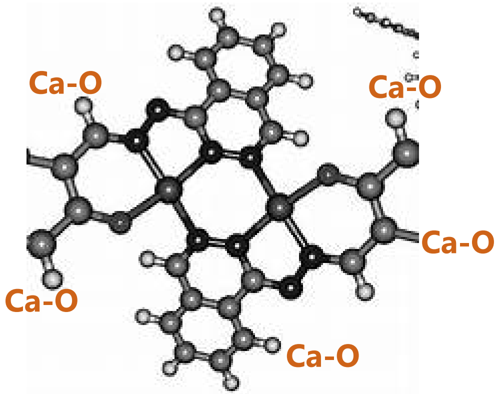


PURE BIOMASS
850°C + white Al

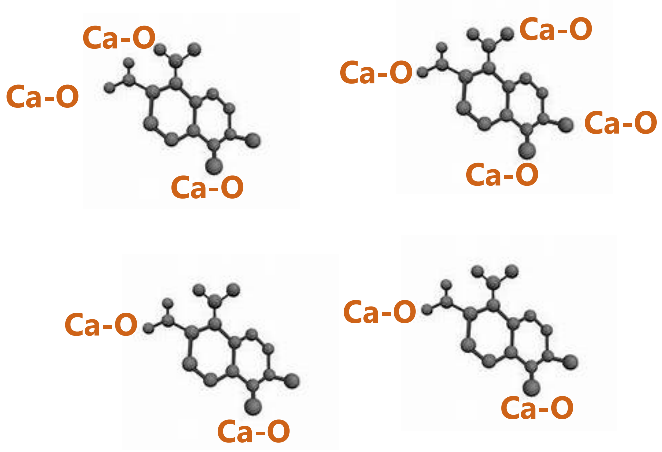


PURE BIOMASS
950°C + brown Al

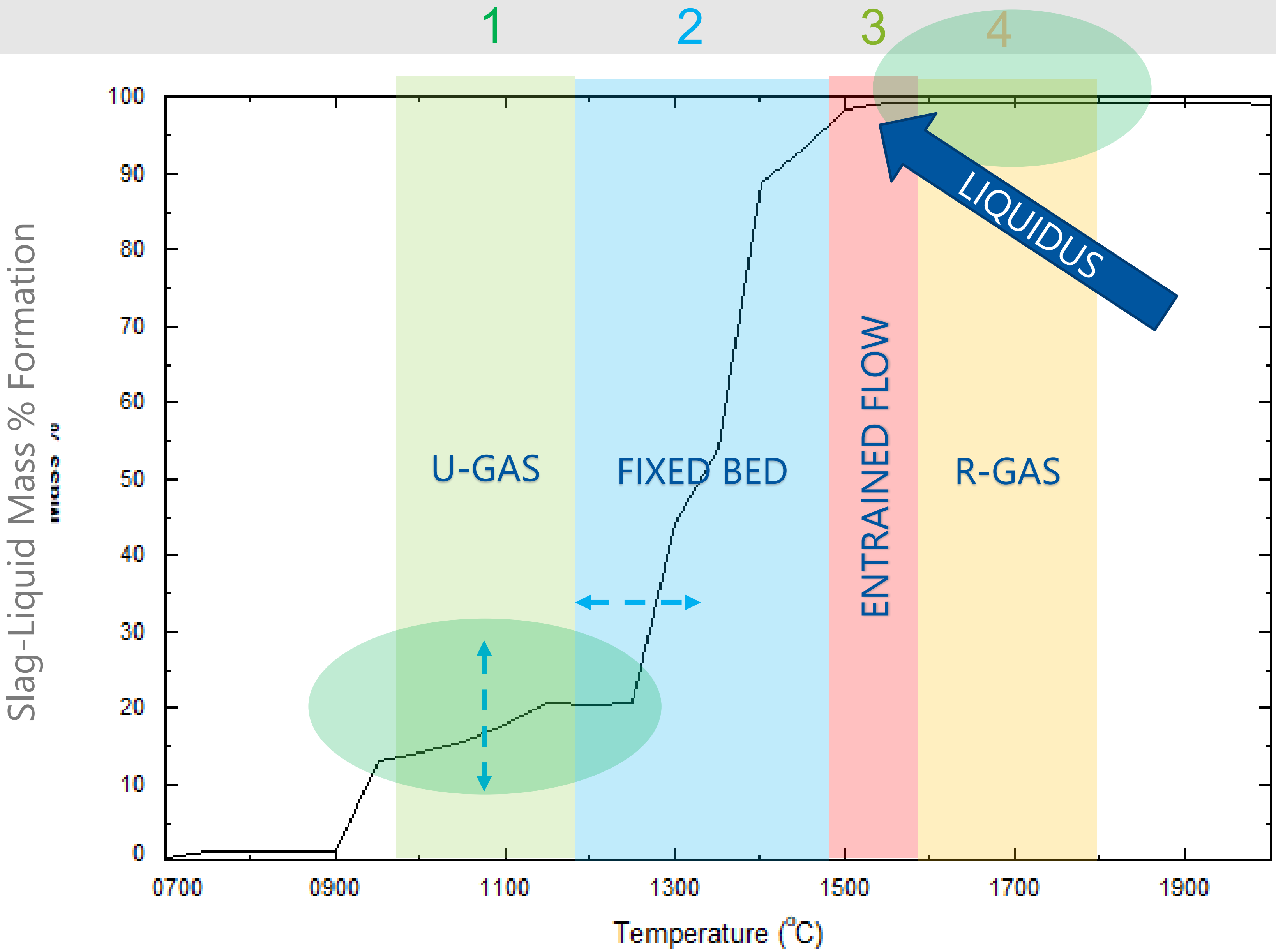
Influence of both catalyst and temperature



Catalyst ALONE only have limited radical atom connections



INORGANIC SPECIATION, SLAG FORMATION AND LIQUID PROFILE



FactSage 8.3

This product is licensed to:
GTI - Gas Technology Institute
Customer ID: 5819

Developers:
C.W. Bale, A.D. Pelton, W.T. Thompson -- G. Eriksson, K. Hack
P. Chartrand, S. Decterov, I-H. Jung, J. Melançon -- S. Petersen

Associates:
M.toBaben, E.Bélisle, A.Gheribi, J-P.Harvey, Y-B.Kang, C.Robelin, P.Spencer, M-A.VanEnde

Collaborators:
Z. Cao, X. Du, D. Fukayama, E. Jak, L. Jin, W.M. Khan, O. Kidari, J. Korb, N. Kumar,
D. Lindberg, Y. Nagano, P. Ouzilleau, M-K. Paek, M. Paliwal, S. Panda, A.-T. Phan,
V. Prostakova, B. Reis, D. Shishin, E. Sokolenko, F. Tang, J. Wang, Z. You, Z. Zhu

FactSage(TM) - Copyright (C) 1976-2023 Thermfact and GTT-Technologies

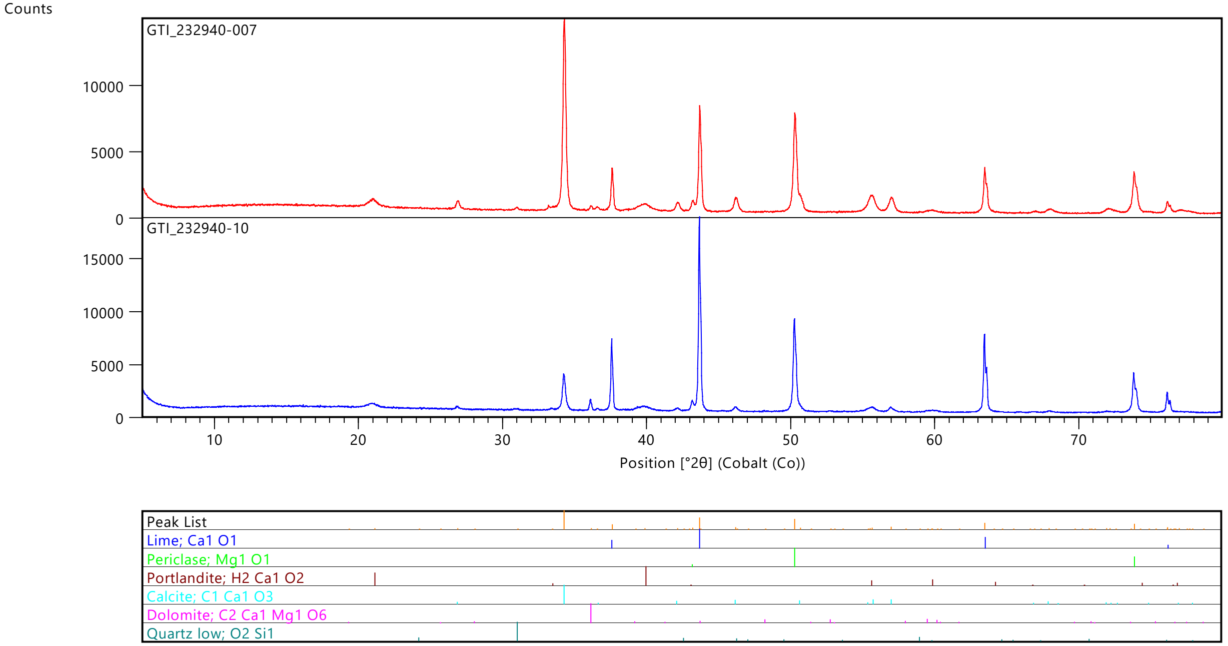
www.crct.polymtl.ca
www.gtt-technologies.de
www.factsage.com

Warning: This program and its databases are protected by copyright laws.
Unauthorized reproduction of the program or data is not permitted and is illegal.

XRD AND SEM ANALYSES

Two samples from the MBU Gasification run were submitted for full XRD and SEM Analyses:

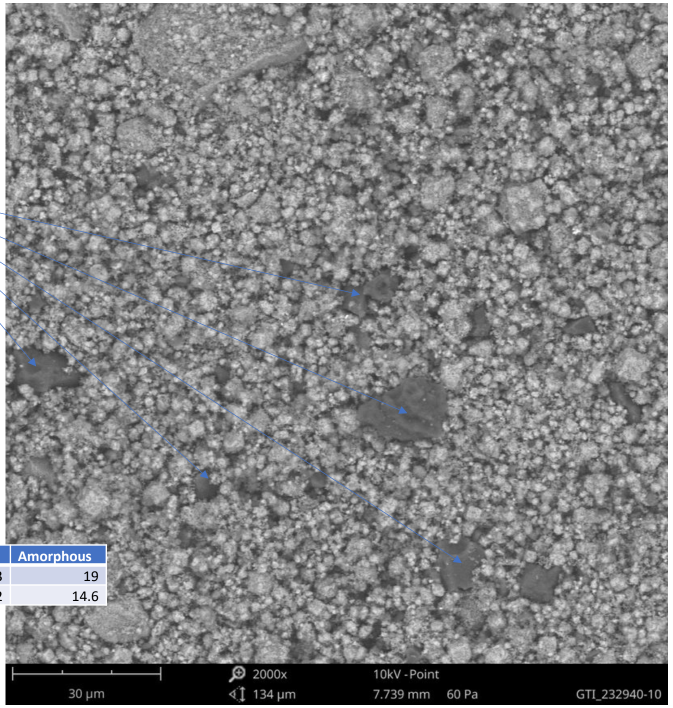
	Lime	Periclase	Portlandite	Calcite	Dolomite	Quartz	Amorphous
GTI_232940-007	17.3	32.5	3.8	26.2	0.8	0.3	19
GTI_232940-10	35	36.5	1.6	9.4	2.6	0.2	14.6



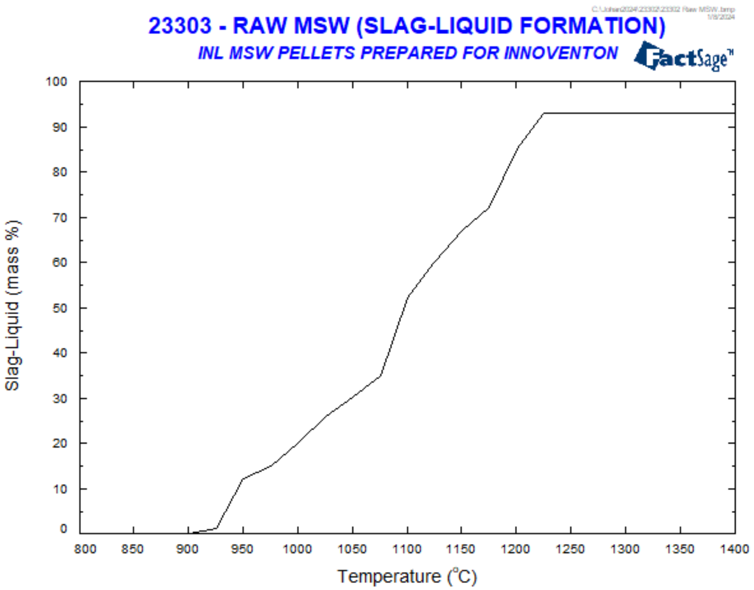
Bulk of structure mineral / crystalline

Localized slag and amorphous droplets

	Lime	Periclase	Portlandite	Calcite	Dolomite	Quartz	Amorphous
GTI_232940-007	17.3	32.5	3.8	26.2	0.8	0.3	19
GTI_232940-10	35	36.5	1.6	9.4	2.6	0.2	14.6



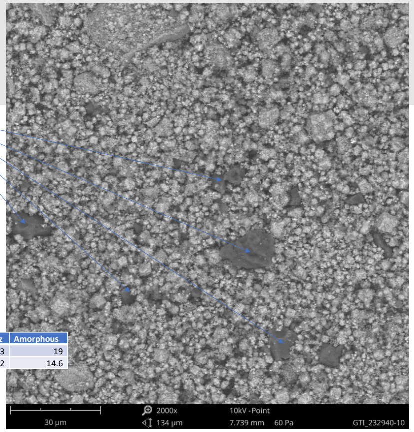
FACT™ EQUILIB SIMULATION ON FEED AND BED MATERIAL



23303 - RAW MSW (SLAG-LIQUID FORMATION)

INL MSW PELLETS PREPARED FOR INNOVENTON

- Similar profile as plastics, as expected
- First melt around 925°C
- Liquidus temperature 1225°C, the AFT (ISO) at 1210°C
- 7-8 hours run to reach equilibrium…..no reason for this long run, however, result as expected.

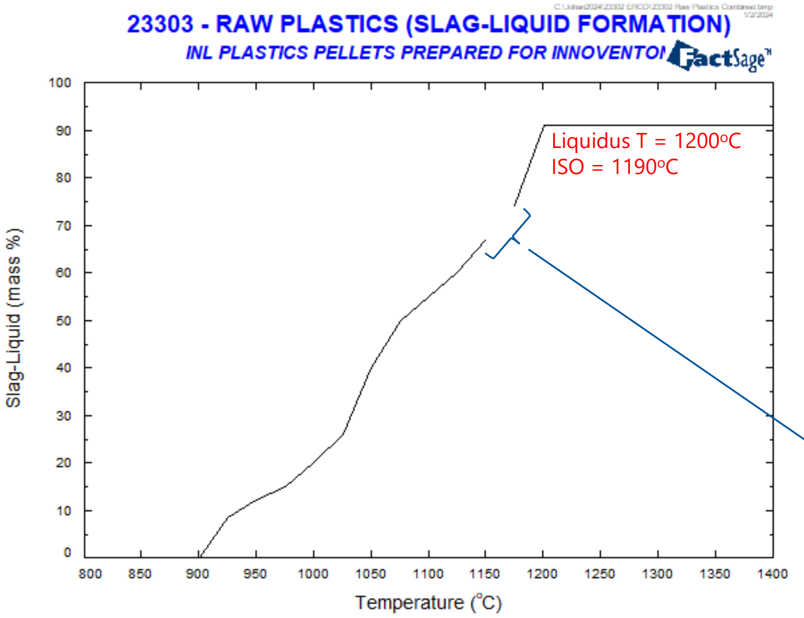


Bulk of structure mineral / crystalline

Localized slag and amorphous droplets

	Lime	Periclase	Portlandite	Calcite	Dolomite	Quartz	Amorphous
GTI_232940-007	17.3	32.5	3.8	26.2	0.8	0.3	19
GTI_232940-10	35	36.5	1.6	9.4	2.6	0.2	14.6

- The slag-liquid profile of all 3 feedstocks is as expected with liquidus temperatures comparable with the AFT as conducted by the ISO Standards.
- Localized droplets of slag from the feed may be formed.

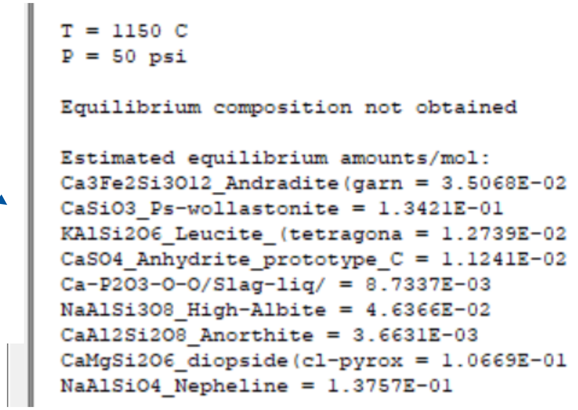


23303 - RAW PLASTICS (SLAG-LIQUID FORMATION)

INL PLASTICS PELLETS PREPARED FOR INNOVENTON

Liquidus T = 1200°C
ISO = 1190°C

- Si:Al ratio for this specific blend resulted in a miscibility gap around 1150°C.
- Caused by a ratio data point where no experimental validated data points are in databases.
- In this case not a concern as interpolation can be done.



```
T = 1150 C
P = 50 psi

Equilibrium composition not obtained

Estimated equilibrium amounts/mol:
Ca3Fe2Si3O12_Andradite(garn = 3.5068E-02
CaSiO3_Ps-wollastonite = 1.3421E-01
KAlSi2O6_Leucite_(tetragona = 1.2739E-02
CaSO4_Anhydrite_prototype_C = 1.1241E-02
Ca-P2O3-O-O/Slag-liq/ = 8.7337E-03
NaAlSi3O8_High-Albite = 4.6366E-02
CaAl2Si2O8_Anorthite = 3.6631E-03
CaMgSi2O6_diopside(cl-pyrox = 1.0669E-01
NaAlSiO4_Nepheline = 1.3757E-01
```

IN SUMMARY

GTI ENERGY

1. The characteristics discussed in this presentation are not the only properties affecting gasifier performance and stability.

2. Interpretation of these results gives an indication of expected gasifier performance, and also the suitability of a specific feedstock for a gasification technology.

3. **Gasification is not complex…..it how to convert the feedstock AND understand the feedstock.**