Biomass Torrefaction – A Promising Pretreatment Method for Thermo-Chemical Conversion Technologies

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Introduction

- Issues with biomass feedstock
  - Wide range of moisture content (60-15% wb)
  - Low bulk density (4 – 8 lbs/ft^3)
  - Low energy density (4,500-7,500 Btu/lb)
  - Uneven particle sizes (no flow)
  - Difficult to handle, store and transport
  - High transport and storage cost
  - Self heating and emission of off gases during storage

Introduction

- Issues with thermo-chemical conversion technologies
  - Combustion:
    - Difficult to co-fire with coal
    - Low energy density
    - High energy demand for grinding biomass
  - Gasification
    - Tar formation
    - Low C/H ratio for liquid fuel production
  - Pyrolysis:
    - Bio-oil instability & coke formation
  - Densification:
    - Low energy density & self heating

Biomass Pyrolysis to Liquid Fuels

Pyrolysis Unit

Bio-oil

- Critical Problems
  - Long-term storage and stability of biomass
  - High energy input for grinding to defined particle size
  - Formation of high molecular weight compounds
  - Bio-oil is unstable
    - Viscosity increases with time and temperature
    - Low pH, corrosive
  - Catalytic upgrading difficult
    - High oxygen content
    - Catalytic deactivation due to coke formation

What is Torrefaction?

- Solid-state thermal hydrolysis of biomass in an inert atmosphere (e.g.,N_2)
- Temperature range – 180 to 300°C
- Hemicellulose is hydrolyzed via release of acetic acid and subsequent hydrolysis reaction
- Moisture reduction, oxygen content reduced
- Some extractives volatilized, but 70-80% solids recovered
- Most familiar example – roasting coffee

Torrefaction History

- 1930's – heat treatment of wood for high durability, structural stability & fungal resistance (wood roasting), provides aesthetic value
- 1939 – US Patent (Bergstrom et al) on thermal heating of wood >220^{o}C
- 1976 – Pyrochar process for solid biomass into fuels
- 1980's – heat treatment of wood logs (180-220^{o}C), retifaction/torrefaction process (Yvan, 1985, Bourgeois et al, 1988), Torrefaction process development & reactor design (four patents)
- 2000 - Significant research & development on biomass torrefaction process

Mass & Energy Balance

Non-condensable:
H_2, CO, CO_2, CH_4,
Toluene, benzene

Condensable:
Water
Organic acids, alcohols
Furans, ketones
Terpenes, phenols
Waxes, tannins, lipids

Volatile off gases

0.3 m ~0.2 E

Biomass

1 m
1 E

Torrefaction Process

0.7 m
0.9 E

Torrefied biomass

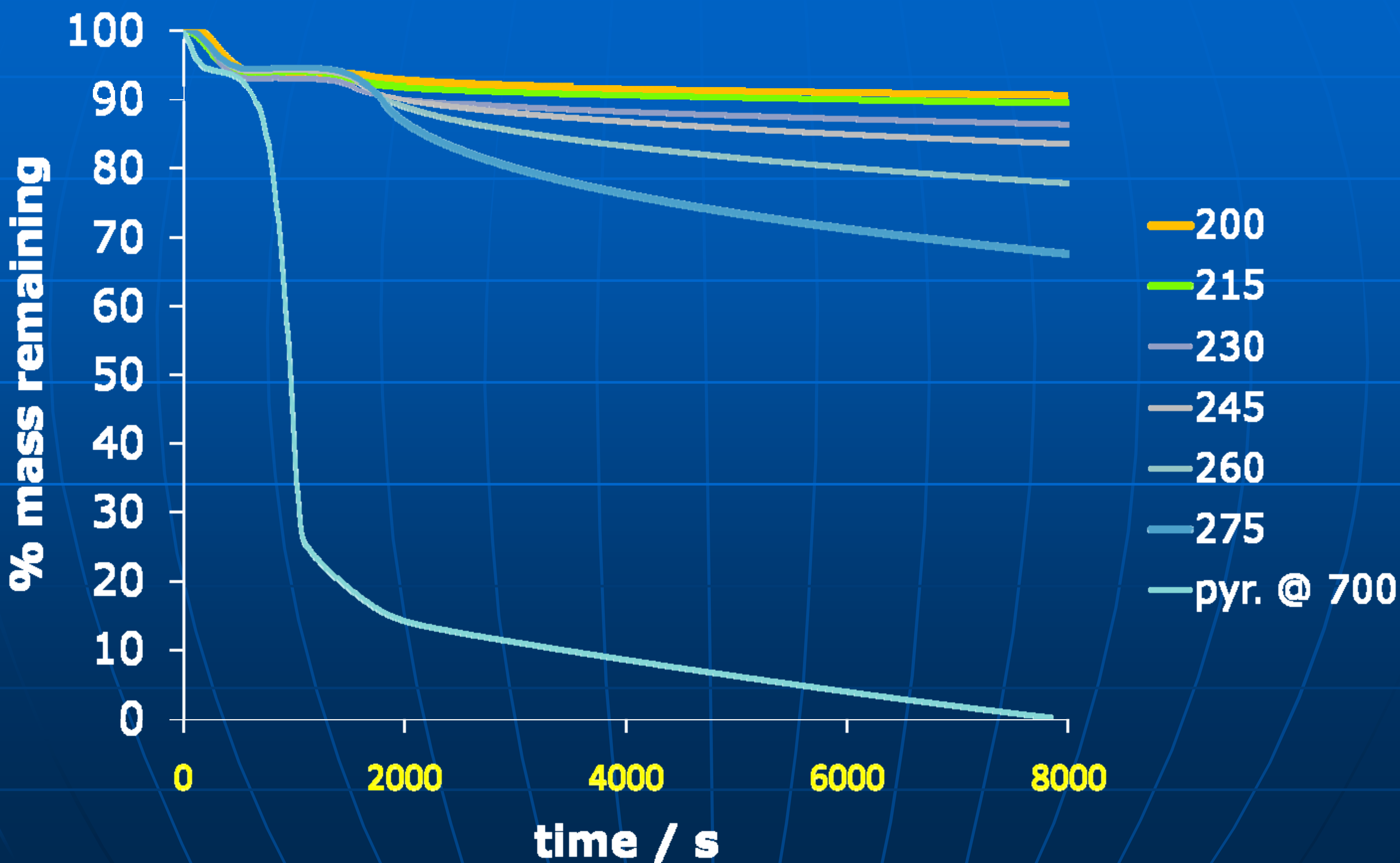
~0.1 E

External heat supply
Temp: 180-280^{o}C
Heating rate: <50^{o}C/min
Residence time: > mins

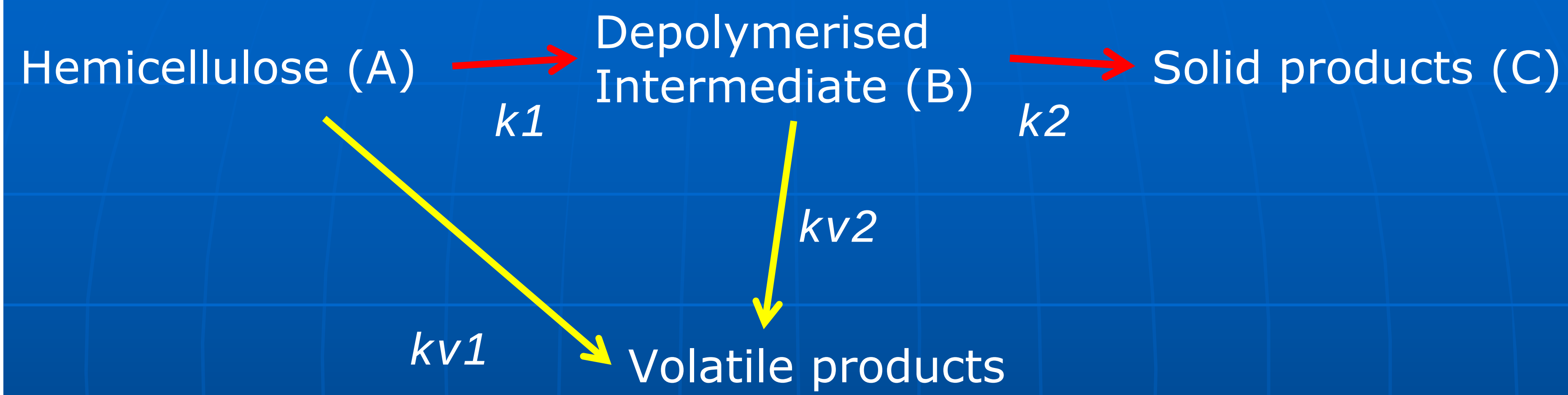
Research Objectives

- Biomass Torrefaction kinetics
  - Does it improve biomass storability and transportability?
  - Does it improve biomass grindability and reduce energy input?
  - Effect of torrefaction on,
    - bio-oil stability
    - Eliminate or reduce coke forming precursors and improve catalytic upgrading of bio-oil to fuels
    - Syngas quality and tar concentration during gasification
    - Pellet quality
    - Combustion behavior

Mass loss with time for a range of torrefaction conditions – TG-MS



Proposed Torrefaction Kinetics Model



- Model equations:

  For components a, b and c:

  $a'(t) = -(k1+kv1)*a(t)$, $a(0) = 1$ (normalized vs. starting mass)

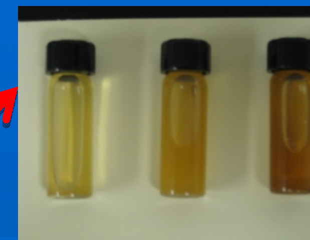
  $b'(t) = k1*a(t)-(k2+kv2)*b(t)$ $b(0) = 0$

  $c'(t) = k2*b(t)$ $c(0) = 0$

Torrefaction Experiment

Forest Residue chips

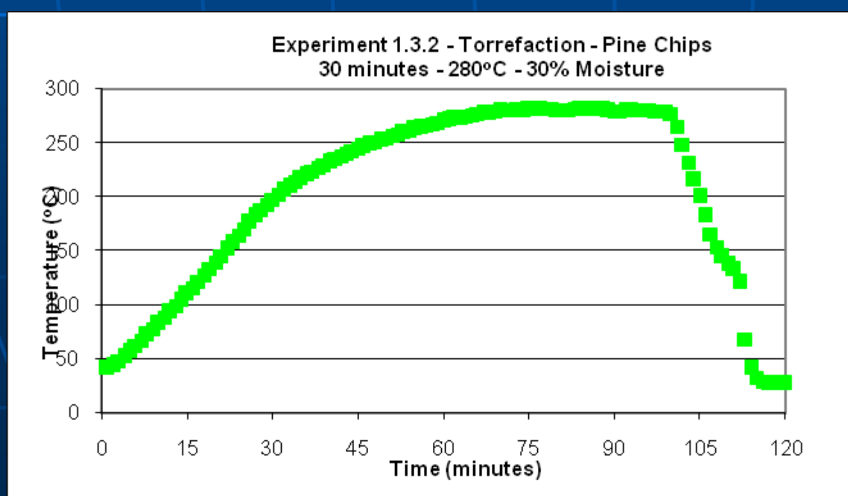
Torrefaction Reactor



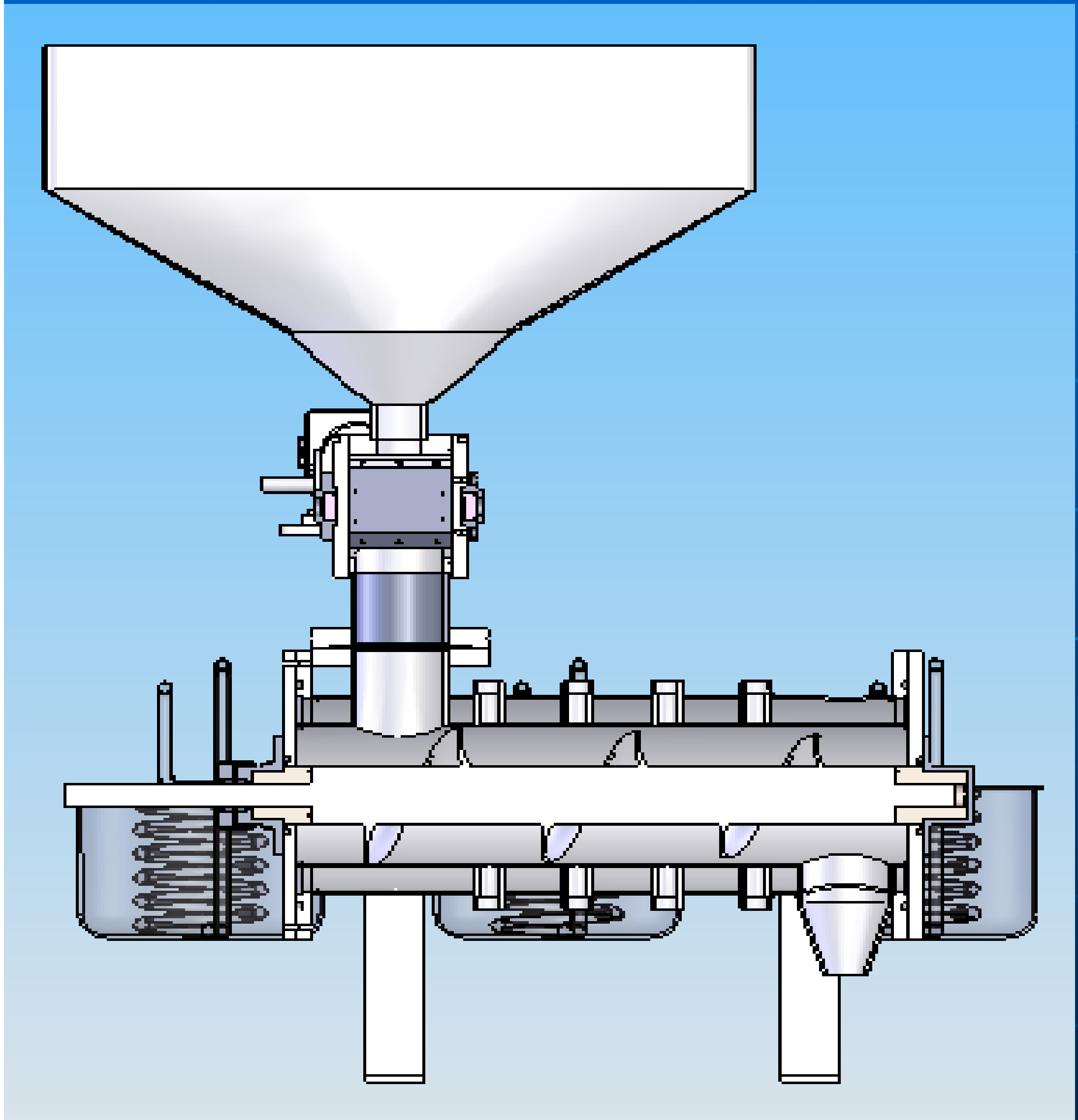
Condensed liquids

Non-condensable gases

Torrefied biomass



Torrefied Auger Reactor - UGA

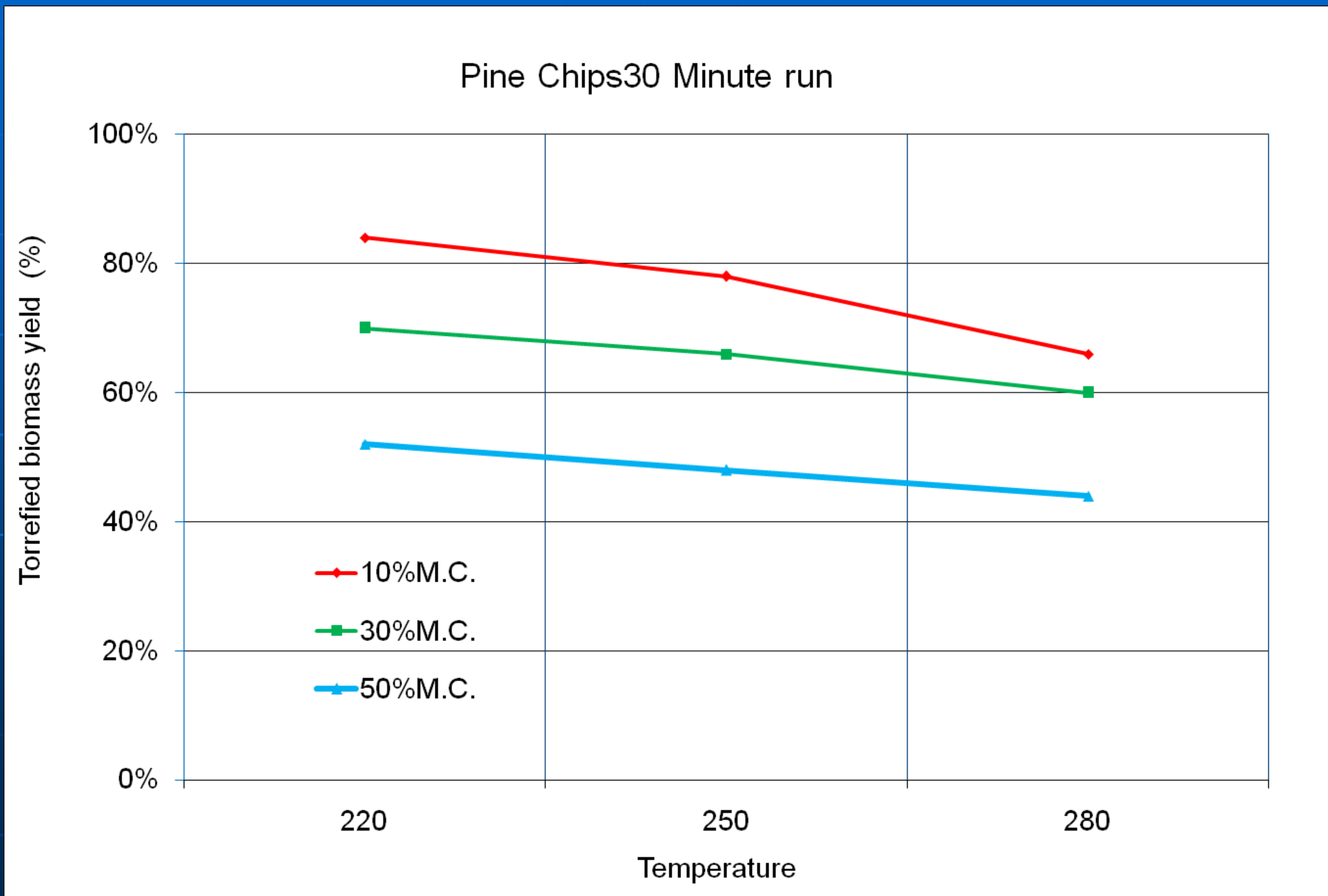


- Continuous Reactor
- Capacity – 5 to 10 kg/h
- Capability to collect condensable
- Non-condensables gases can be recalculated in the auger

Rotary drum reactor – UGA

(indirect heating)

Results – Torrefied biomass yield

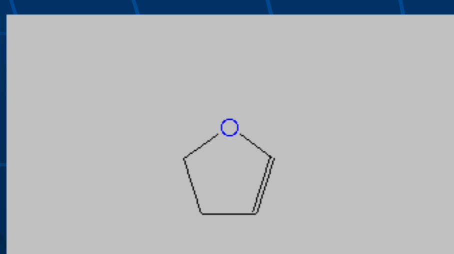


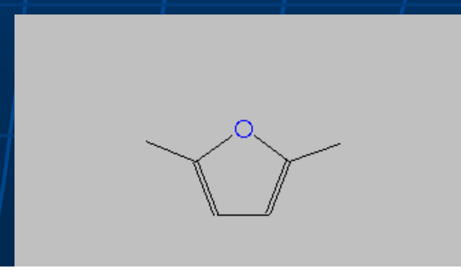
Torrefaction of Pine Chips

Torrefaction Process

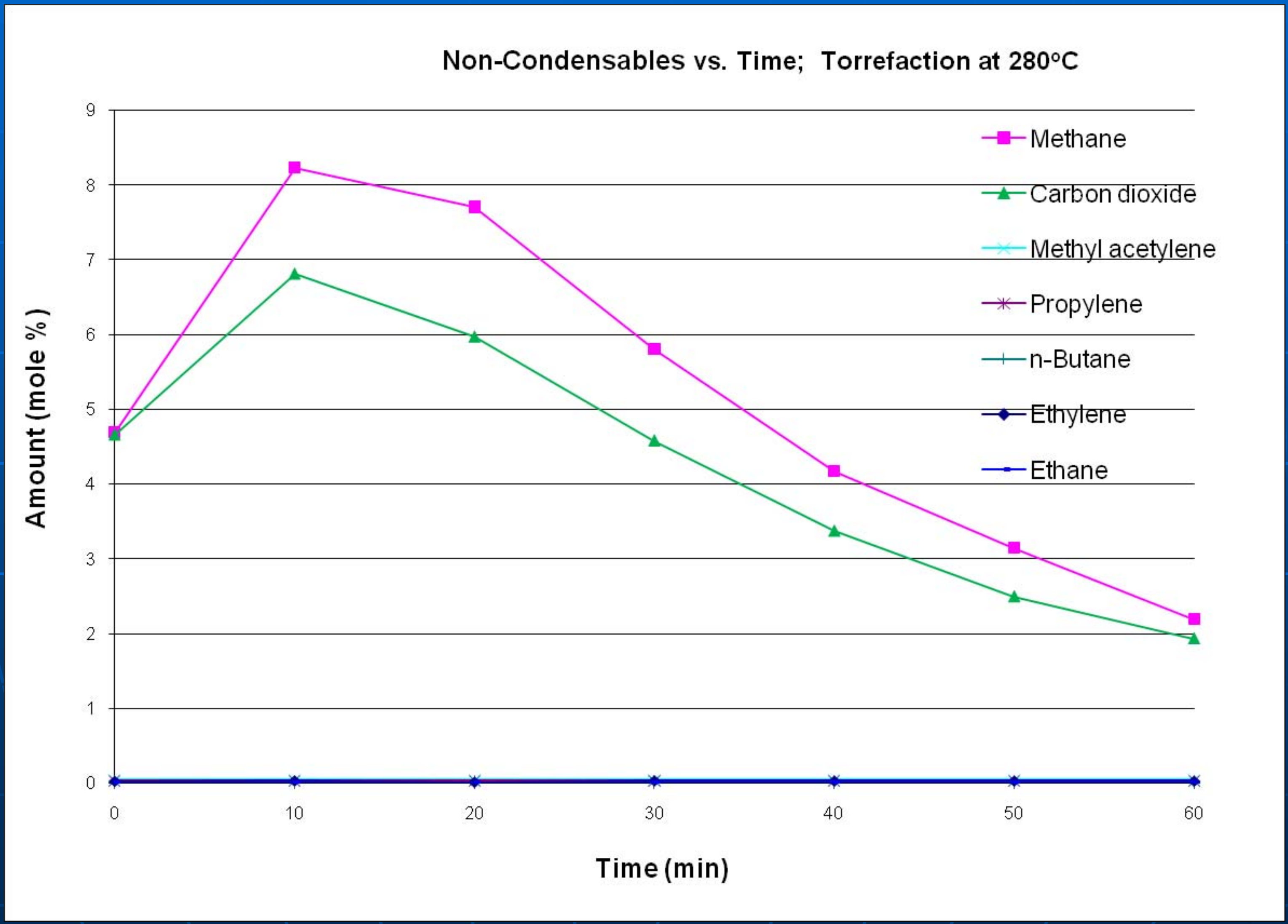
Torrefaction Results

- **GC/MS of Non-condensables (gas phase)**
  - Acetaldehyde, α-pinene, β-pinene, camphene, phellandrene observed at low temperatures (220C)
  - Acetaldehyde evolution increased with time
  - Pinenes decreased with holding time
  - As temperature increased, acetic acid, methylester and furans appeared (220 to 250C and above)
    - Furan, 2-methylfuran, 250C
    - 2,3-dihydrofuran and 2,5-dimethylfuran, 280C

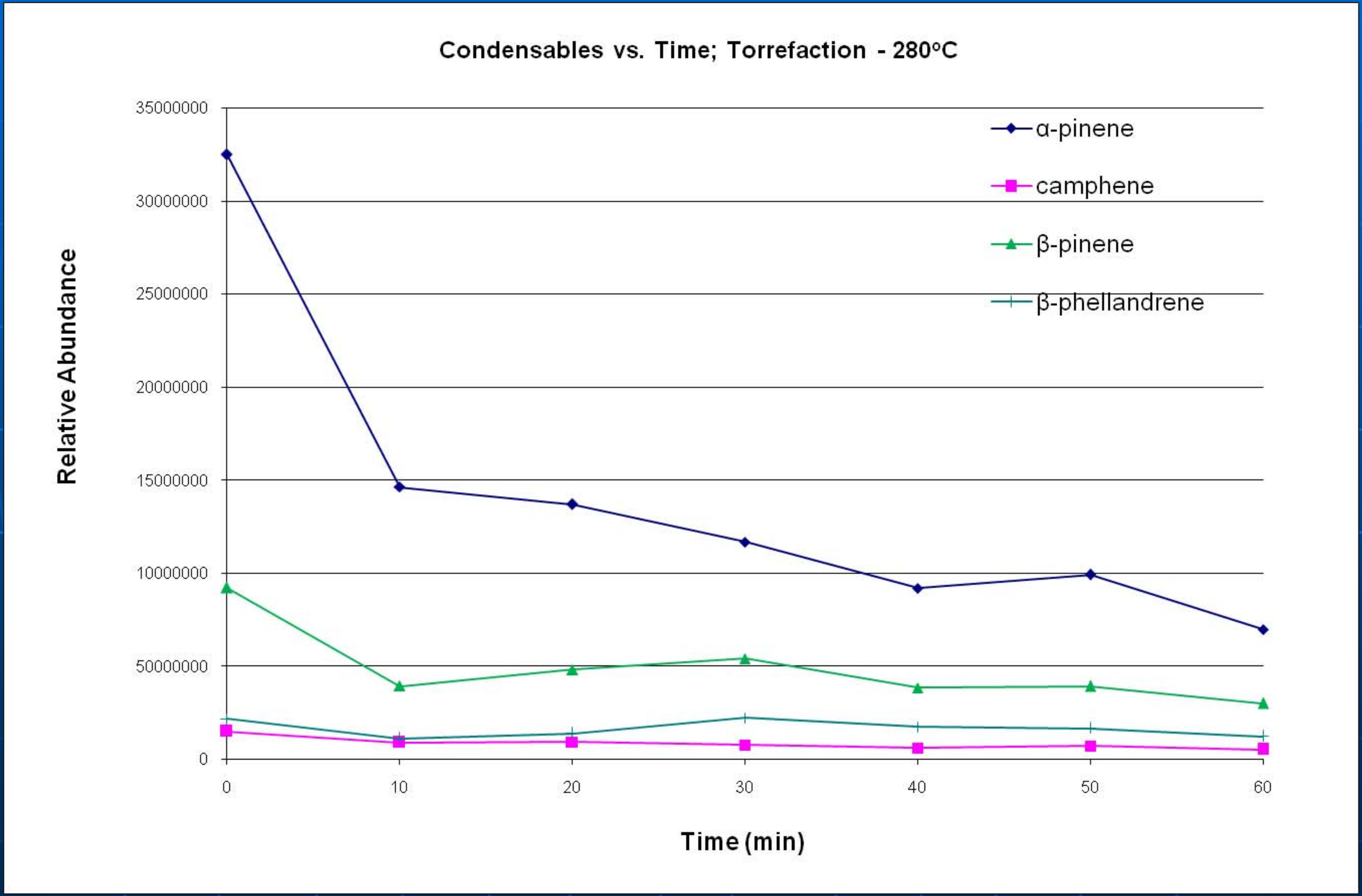




Results – Non-condensable at 280^oC



Results – Condensable at 280^{o}C



Results – Compositional changes

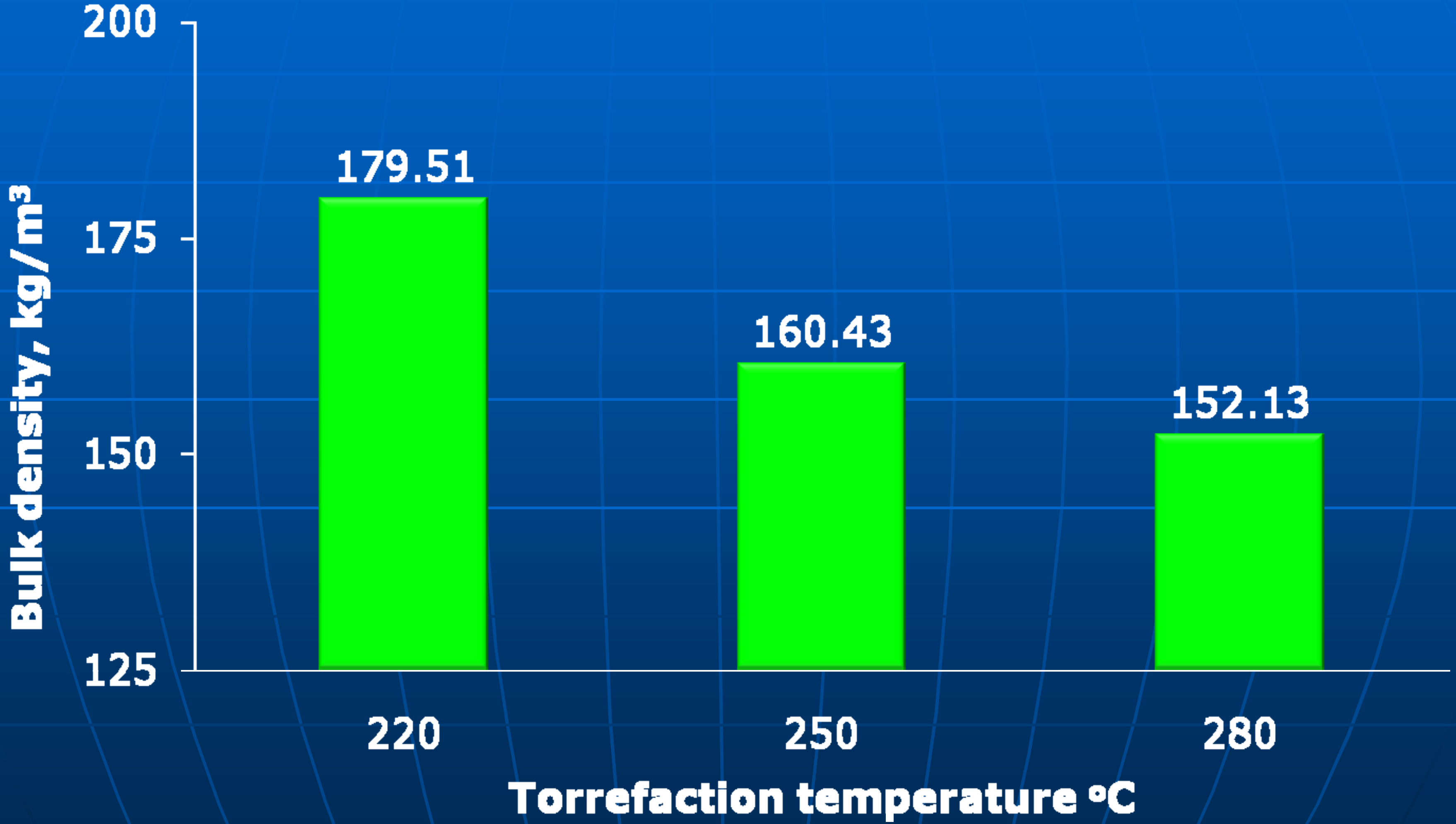
Forest residue chips	Cellulose (% wt)	Hemi-cellulose (% wt)	Lignin (% wt)	Heating value (Btu/lb)
Non-torrefied (10% m.c.)	43.1	18.4	20.9	7,774
Torrefied at 220°C	40.7	12.0	25.1	8,474
Torrefied at 250°C	37.3	5.0	31.8	9,376
Torrefied at 280°C	20.6	2.9	47.3	10,167

Forest residue chips	C	H	O	N	S	Ash (% wt)
Non-torrefied (10% m.c.)	45.3	5.9	48.5	0.3	0.1	0.6
Torrefied at 220°C	49.4	5.5	44.1	0.3	0.0	1.1
Torrefied at 250°C	50.5	5.4	41.8	0.4	0.0	1.2
Torrefied at 280°C	56.4	5.4	36.1	0.9	0.1	1.4

Results – Compositional changes

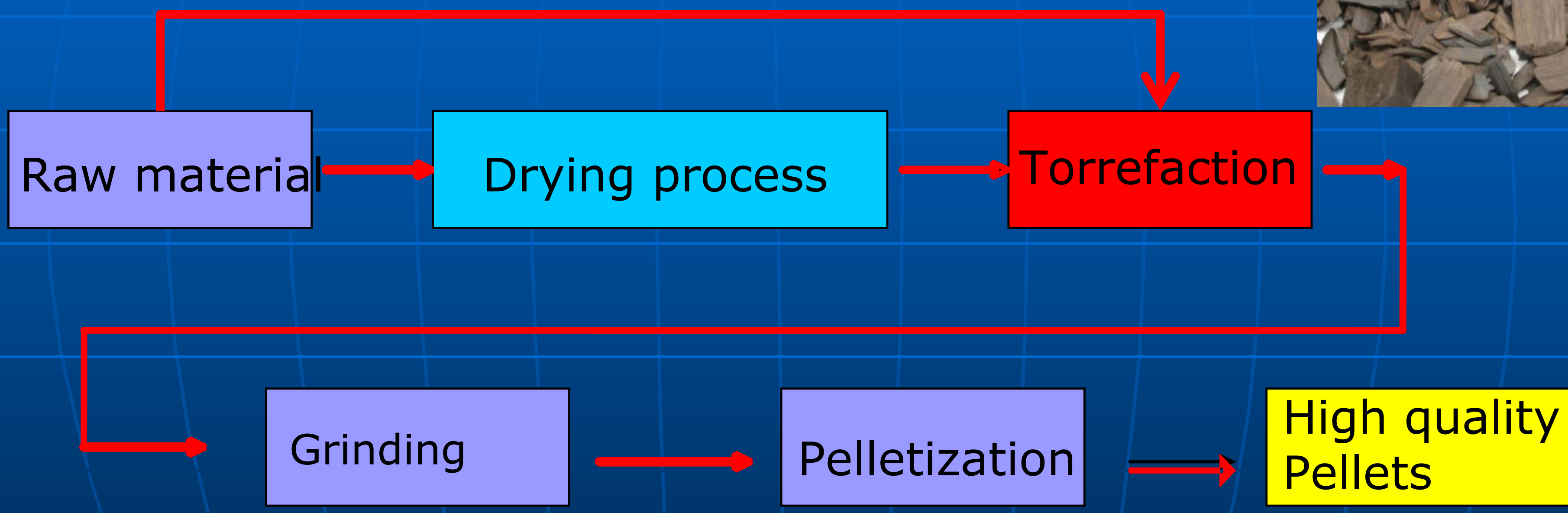
Forest residue chips	Moisture (%)	Volatile C (% wt)	Fixed C (% wt)	Ash (%)
Non-torrefied (10% m.c.)	10	75.3	16.3	0.4
Torrefied at 220^{o}C	3.2	76.8	19.1	1.1
Torrefied at 250^{o}C	2.3	74.9	20.6	1.2
Torrefied at 280^{o}C	2.1	70.8	25.6	1.4

Change in bulk density during Torrefaction

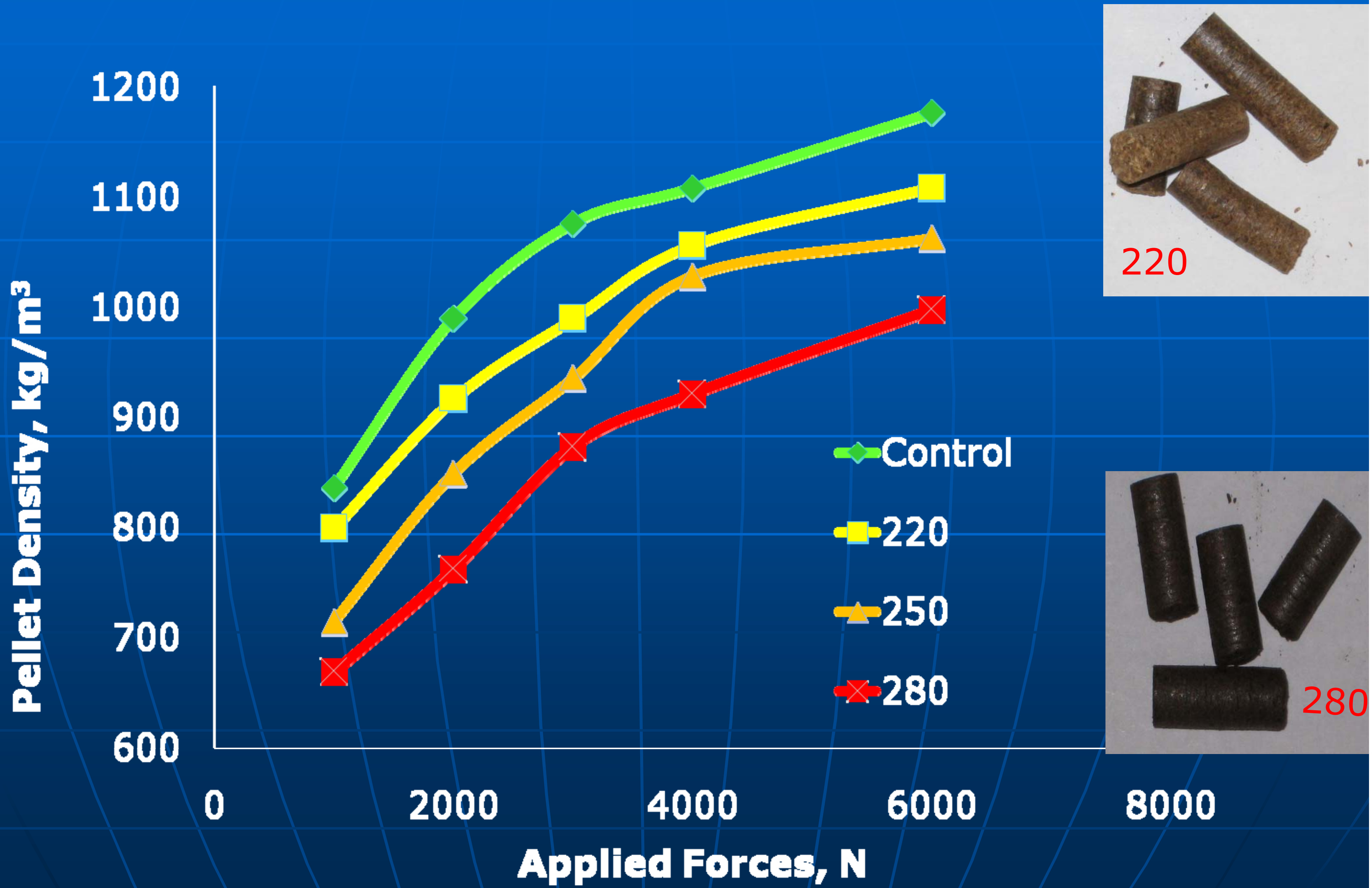


Forest biomass chips – 18% change

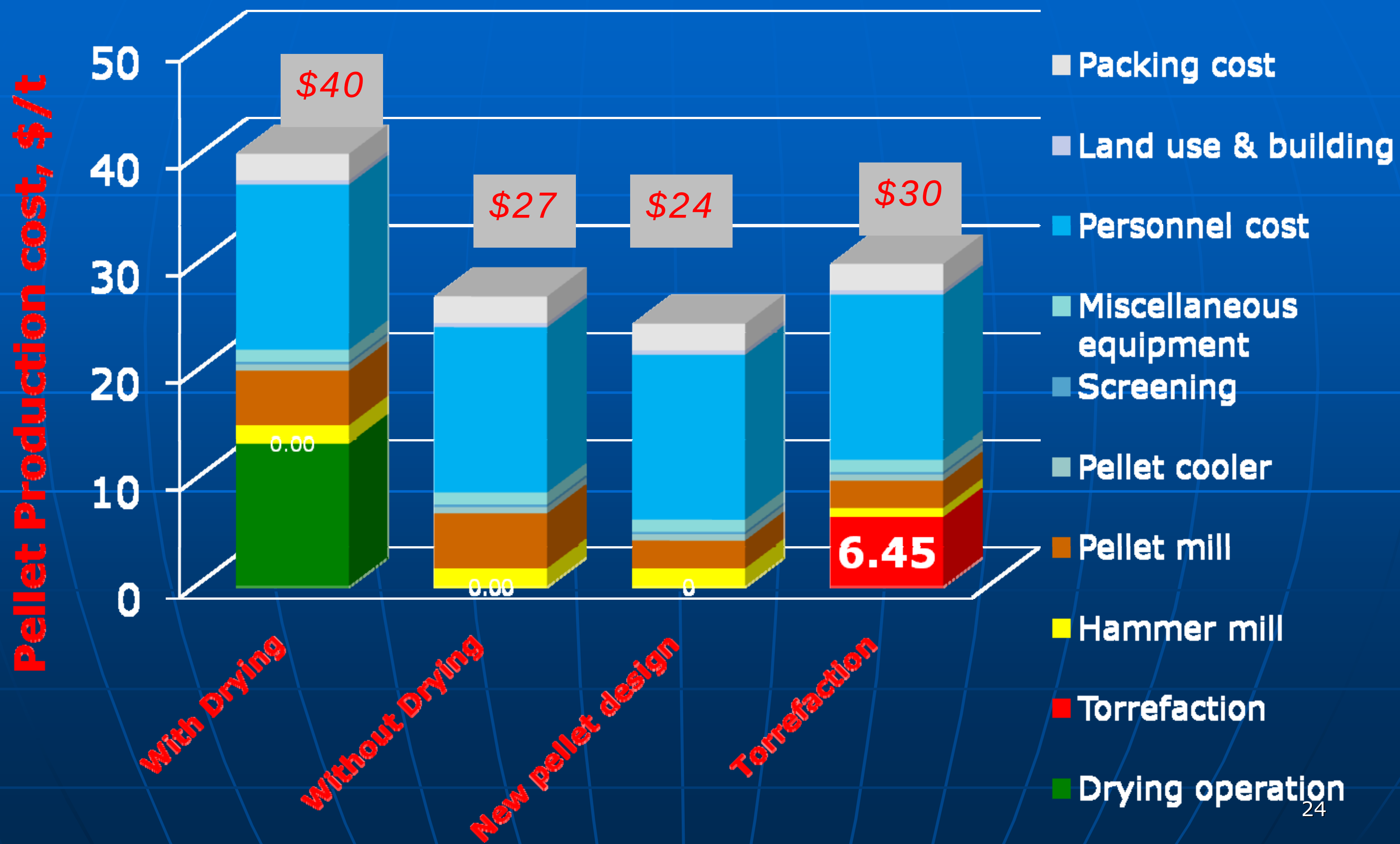
Improved Pelleting Process



Effect of Torrefaction on Pellet Density



Torrefaction- Pellet Production Cost



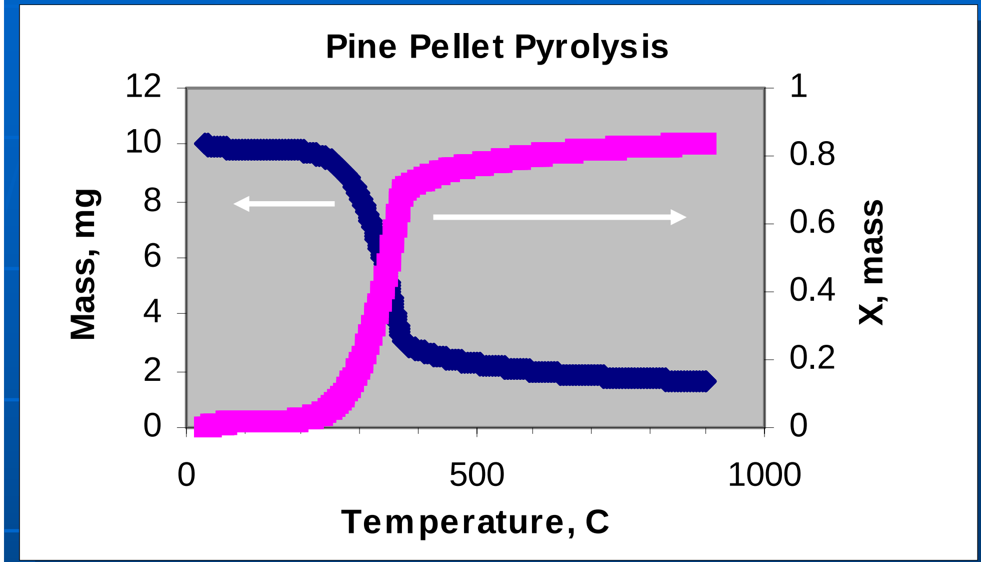
Torrefaction - Pyrolysis

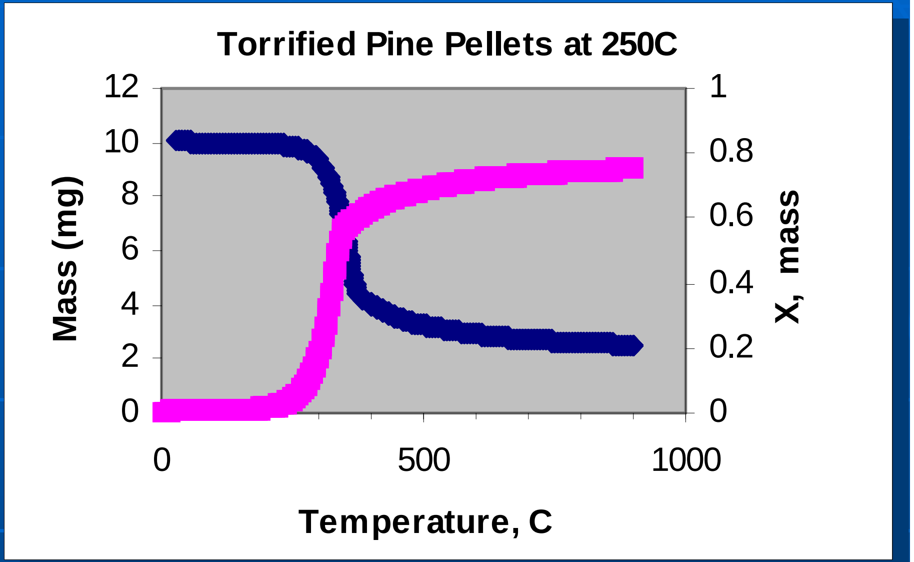
TG/MS Analysis of Torrefied Biomass

- TGA/MS (Mettler Toledo)
- Performed under pyrolytic conditions – N_2 or Ar carrier gas
- 10mg sample, 50 ml/min, 30-900°C at 10°C/min
- Monitored Off Gas in Selective Ion Mode (SIM)

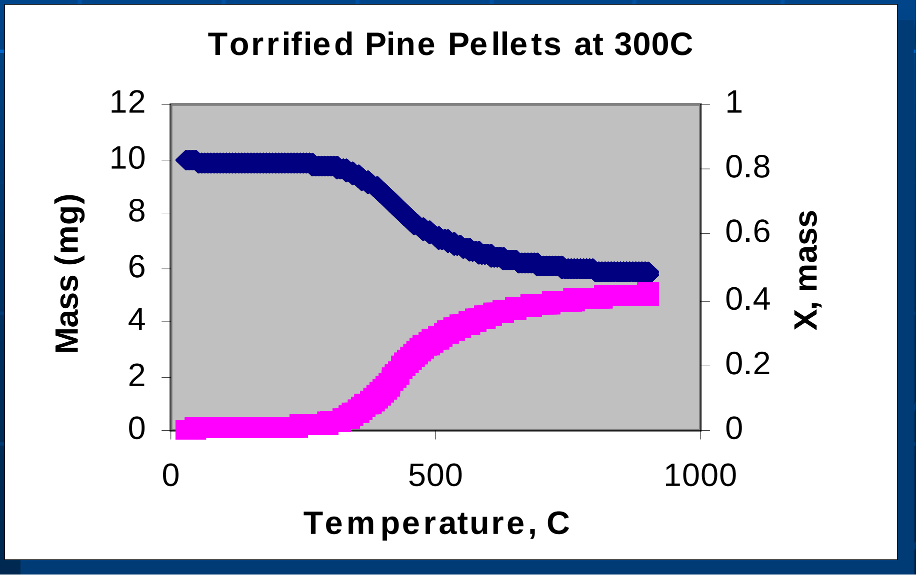
  - Non-condensables, CO-28, CO_2-44, H_2-2, H_2O-18
  - Potential tar compounds,
    - Benzene – 78
    - Guaiacol – 124
    - Naphthalene – 128
    - Phenol – 94
  - Potential hemicellulose breakdown products
    - Acetaldehyde – 29
    - Acetic acid – 60
    - Acetol – 45

Effect of Torrefaction on Pyrolysis Kinetics (TGA Analysis)





- X, fractional biomass conversion
- Higher temperature torrefaction (> 300°C) appears to reduce biomass thermal decomposition and alter pyrolysis kinetics
- More research needed to confirm effect



Torrefaction-Pyrolysis-Solids Properties

- Oxygen content reduced
- Fixed carbon increased

Characteristic	Material				
	PP BM	PP T250	PP T300	PP T350	PP P500
C	52.6	53.9	73.2	78.0	82.5
H	5.7	5.3	4.7	3.7	2.6
N	0.2	0.1	0.2	0.2	0.2
S	0.0	0.1	0.1	0.1	0.0
O	38.9	37.6	19.6	15.0	4.4
Moisture	7.2	0.0	1.0	2.0	3.2
Volatiles	79.8	71.2	42.4	32.2	28.1
Ash	0.5	3.0	2.2	2.9	2.8
Fixed Carbon	19.7	25.8	55.4	64.9	69.1
HHV (MJ/kg)	20.6	20.9	28.8	29.7	31.0

Parameter	Bio-Oil Characteristics			
	P[a]	PU[b]	TP[c]	TPU[d]
Ultimate analysis (wt % dry)				
C	69.6	73.1	71.3	73.9
H	7.65	8.1	7.97	7.93
N	0.74	0.4	0.19	0.17
S	0.05	0.0	0.01	0.02
O[e]	22.0	18.4	20.5	18.0
HHV (MJ/kg, wet basis)	29.1	30.9	28.6	30.7
H_2O (wt. %)	2.4	4.0	9.3	6.7
pH	3.1	3.2	3.7	3.5

[a]P: Pyrolysis (catalytic upgrading feedstock, no torrefaction)

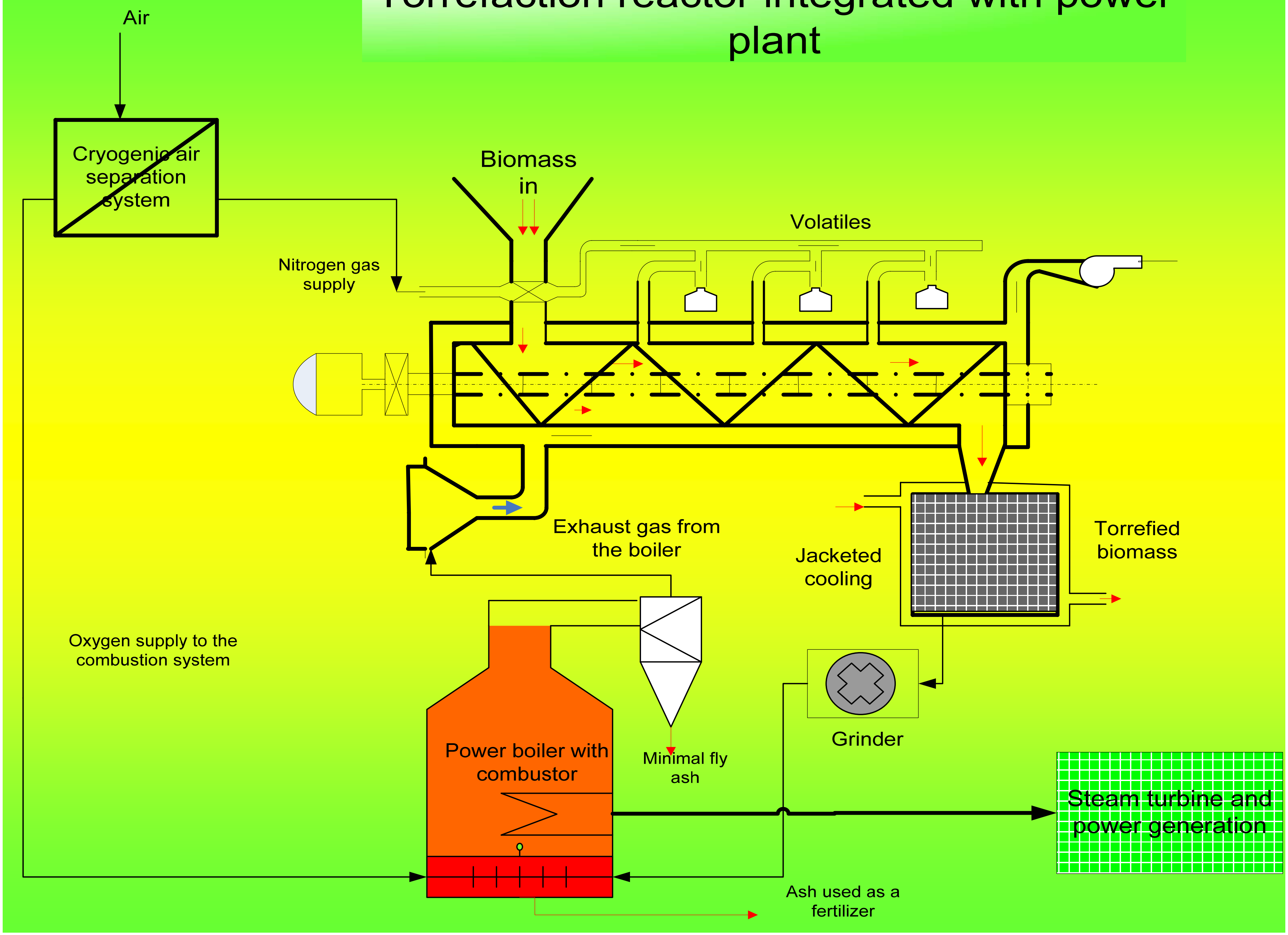
[b]PU: Pyrolysis + catalytic Upgrading (no torrefaction)

[c]TP: Torrefaction + Pyrolysis (catalytic upgrading feedstock)

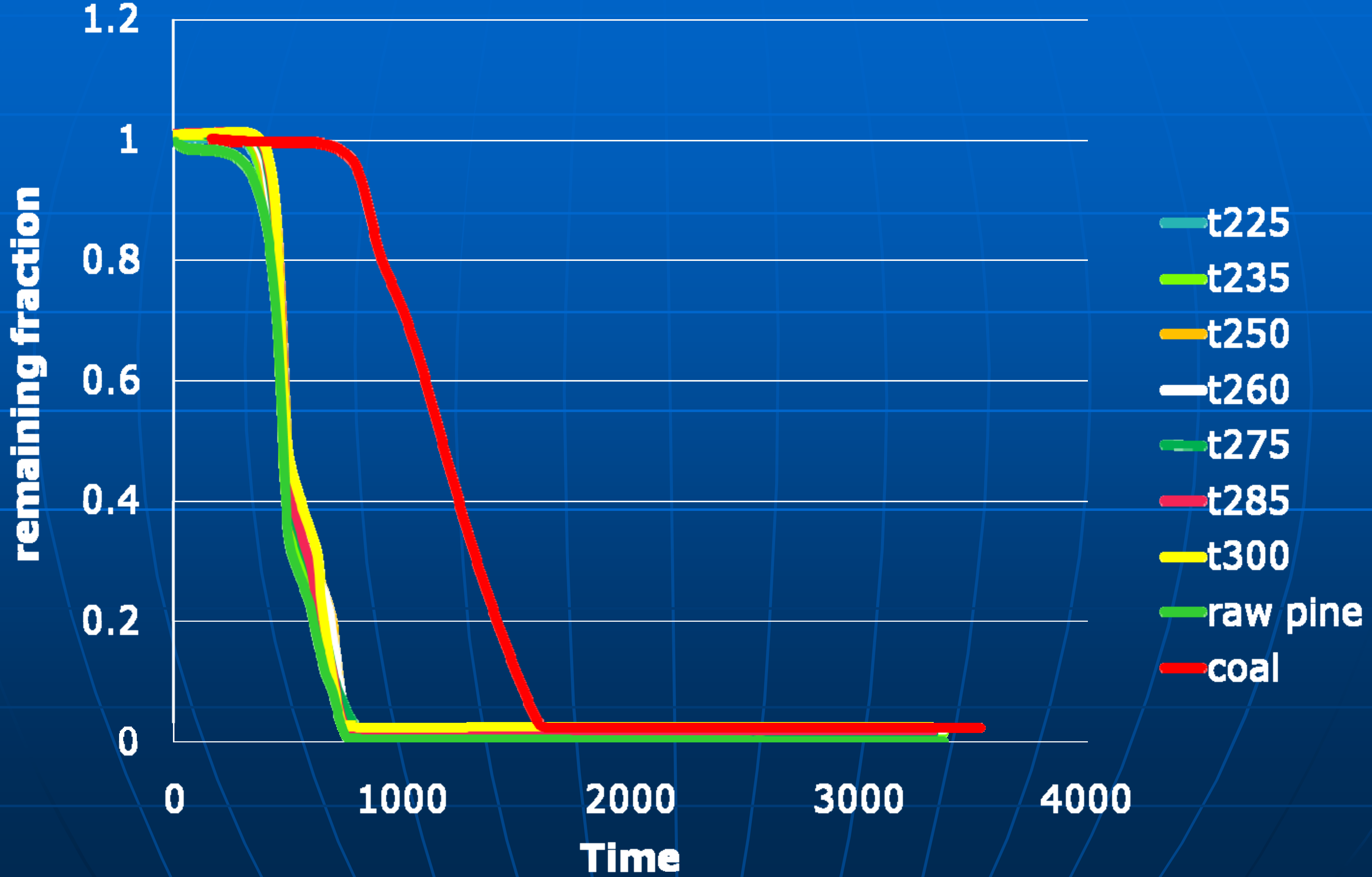
[d]TPU: Torrefaction + Pyrolysis + catalytic Upgrading

Torrefaction - Combustion

Torrefaction reactor integrated with power plant



Comparison of combustion of torrefied biomass, untreated biomass and coal



Conclusions

- Condensable compounds are mainly released from extractives in the biomass as α, β-pinene, camphene etc. These compounds can be redirected to supply heat energy during torrefaction
- During torrefaction, hemi-cellulose is almost removed and results in higher energy density product with a heating value of 10,000 Btu/lb. Torrefaction temperature plays a major role in defining the energy density of biomass and can be optimized for any specific applications.
- Torrefaction followed by pelleting costs about $30/t of pellets. Torrefaction process alone costs about $6.5/t.

Conclusions

- Biomass torrefaction process can produce high energy density and consistent feedstock for thermal conversion technologies (gasification, co-firing & pyrolysis)
- Pelleting of Torrefaction of biomass may be difficult due to hydrophobic nature of the material and require additional binders to increase the bulk density
- Future research at UGA is focused on optimizing the best reactor configuration for a torrefaction process and promote its application to co-firing, gasification and pyrolysis processes

Acknowledgement

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  - University of Georgia Research Foundation
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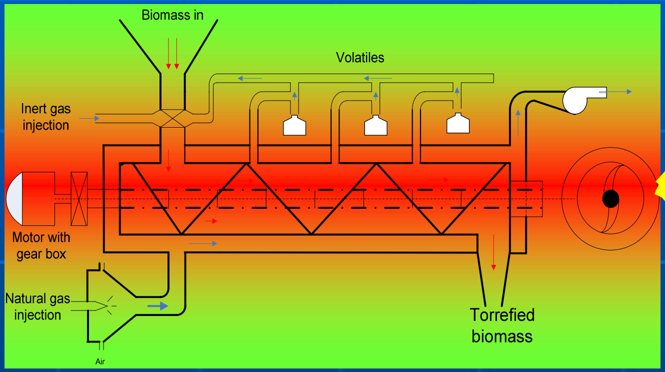
  - Georgia Power – Southern Company

Thank you



Biocoal

Densification

Direct combustion

Gasification

Co-firing with coal

Biomass Torrefaction Technology