THE MANUFACTURING OF CHARCOAL IN SEALED VESSELS

(Constant Volume Carbonization)

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Introduction

"Norway is funding a study of wood carbonization for metallurgical and fuel applications based on a collaboration of HNEI with the Norwegian University of Science and Technology (NTNU) and SINTEF (Norway)"

http://www.hnei.hawaii.edu/project/biocarb-research

Charcoal Uses

- Charcoals have different physical and chemical properties depending on the feedstock and reaction conditions used in their production.
- Charcoals with certain properties are an important source of clean burning fuel (smoke free) widely used for heating and cooking.
- Charcoal has potential uses as a renewable and clean replacement for coal in power generation (heat, power, & electricity production).
  - Most coal fired power stations cannot easily burn wood (or biomass in general) due to differences in fuel properties (grindability, volatile content, ignition temperature).
  - Charcoal can be co-fired with coal, reducing harmful emissions.
  - Security of supply & Sustainable.
  - Economic benefits to local economy.

Charcoal Uses:

HNEI

Coke for metallurgy

Charcoal for cooking/heat

Coke for silicon chip production

Soil amendment

Activated carbons for water or air purification, super-capacitors, etc.

Carbon Material Uses

Electric arc furnace
(graphite electrodes)

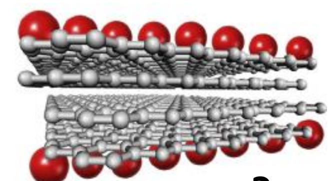
Refractory's
(i.e. ladles)

Aerospace industry

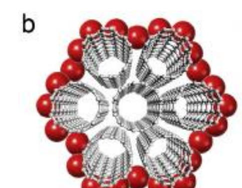
Aeronautic industry

Aluminium
(Carbon anodes)

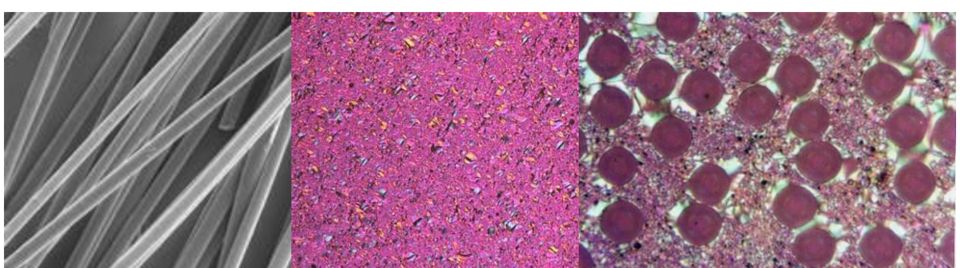
Competition



Graphene ?



Carbon Nanotubes ?



Properties:
- **Low weight**
- **High dimensional stability at high temperatures**
- **High thermal conductivity, ...**

Terminology: charcoal = bio-char = bio-carbon = bio-coke

Where can biocarbon be used (as a reductant)?

EYDE NETTVERKET

Quality requirements- Summary

teknova

Process	Al	SiMn and FeMn	Si and FeSi	SiC
Reactivity	Low	Low	High	High
Fix C	High(>95%?)	High(>95%?)	Med. (>70%)	Med. (>80%?)
Volatile matter	Low (<2,5%)	Low (<2,5%)	Med. 2,5-20%	Med. (8-12%)
Ash	Low (~2%)	-	3 qualities <4% <5% <10%	<3%
Ash elements	Low Fe, Mn, (K)	Low P, B	Low P, alkalies	Low Al, Fe
Strength	-	High	Low fines generation	-
Particle size	>1mm	(5) 10-25mm	10-100mm	<5mm
Density	High	-	-	-

Constant Volume Carbonization (CVC)

- CVC is a process where the feedstock is pyrolyzed in a sealed vessel.
- The first experimental research was performed by Violette (1850's)*
  - charcoal produced from wood in a sealed glass vial.
- Violette demonstrated that CVC produces a greater charcoal yield than traditional methods.
- However, the research was not continued and no data on the properties of the charcoal were reported.

** Violette M. Memoire sur les charbons de bois. Ann Chim Phy. 1853; (32) :304.*

Constant Volume Carbonization (CVC)

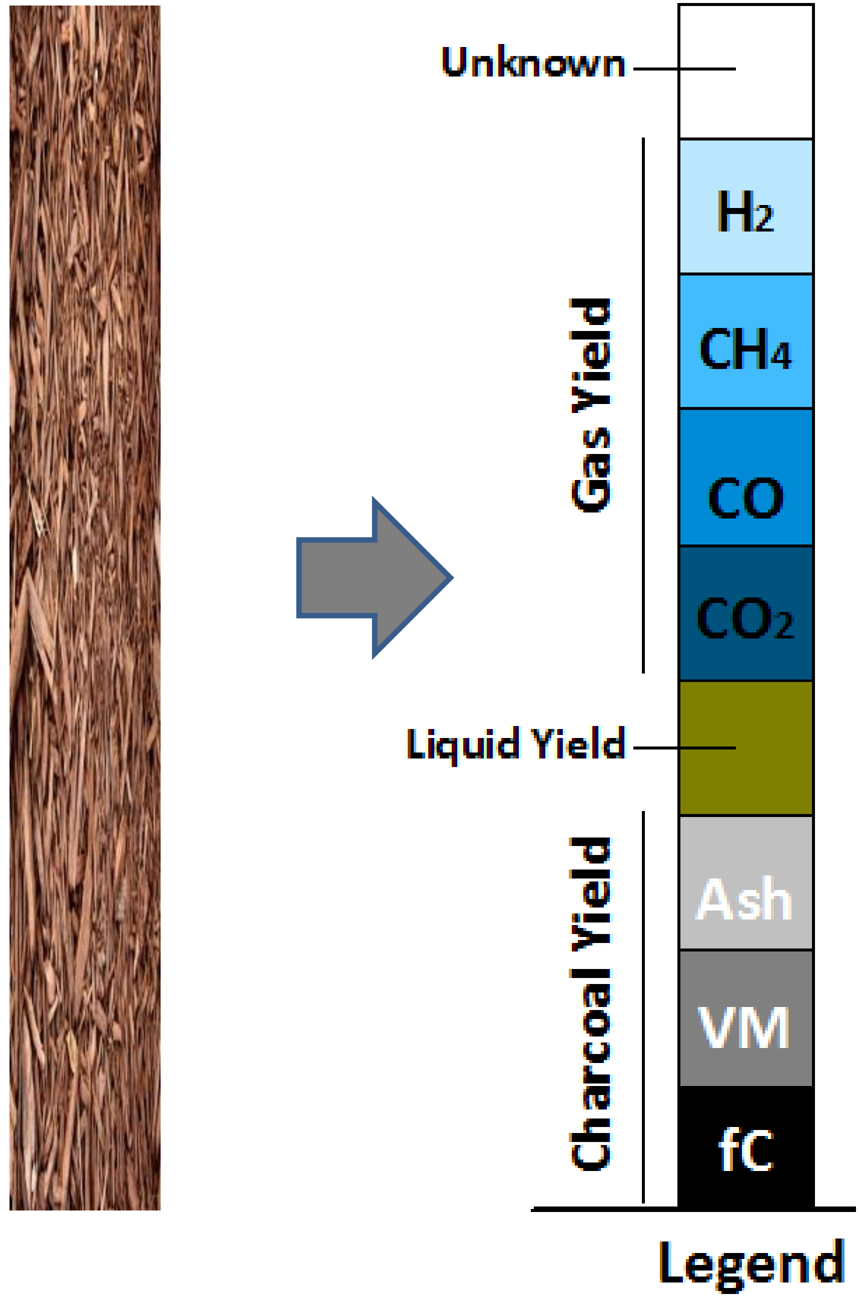
- Prof Antal and Dr Mok were the first to re-investigate Violette's, some 140 years after the initial research.
- This led to a detailed study of biomass pyrolysis:
  - Focusing on the effects of reaction pressure and reactor design.
  - The research resulted in the development of the patented "Flash Carbonization^{TM}" process by Prof Antal.
- Around 2011 Prof Antal started experimental research on CVC.
- Initial experimental results from CVC showed significant improvements in charcoal yield and quality compared to any other known process.

Current CVC Research

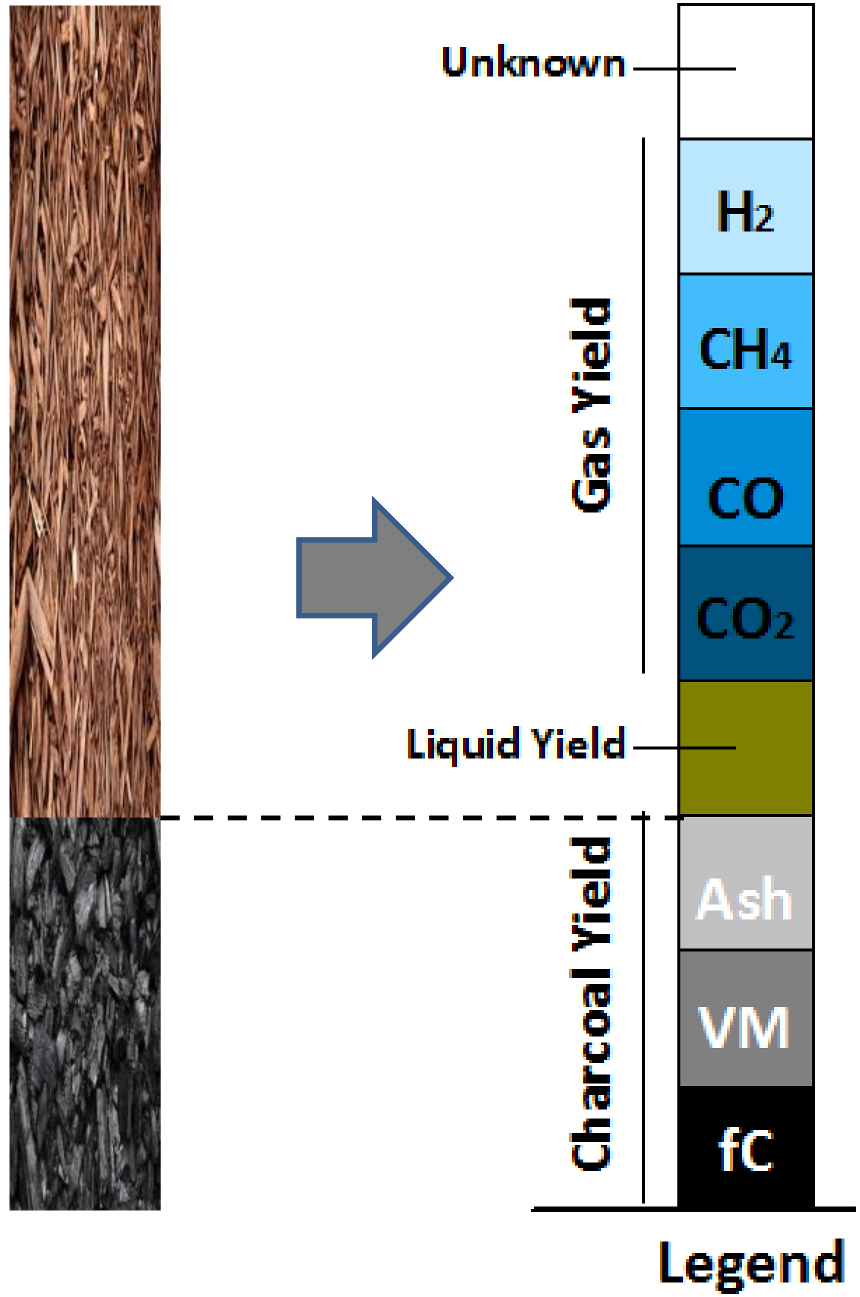
FACTORS	RESPONSE VARIABLES
Closed vessel vs Open vessel	Yields of the final products
Initial reactor pressure	Proximate analysis
Heat treatment temperature	Elemental composition
Particle size	Energy density
Biomass type	Surface area
Heating Rate	Reactivity

Feedstocks: cellulose, oak sawdust, spruce and birch woodchips.

Product Yields [wt.%]



Product Yields [wt.%]



$$y_{char} = \frac{m_{char}}{m_{bio}}$$

Solid product (after drying)

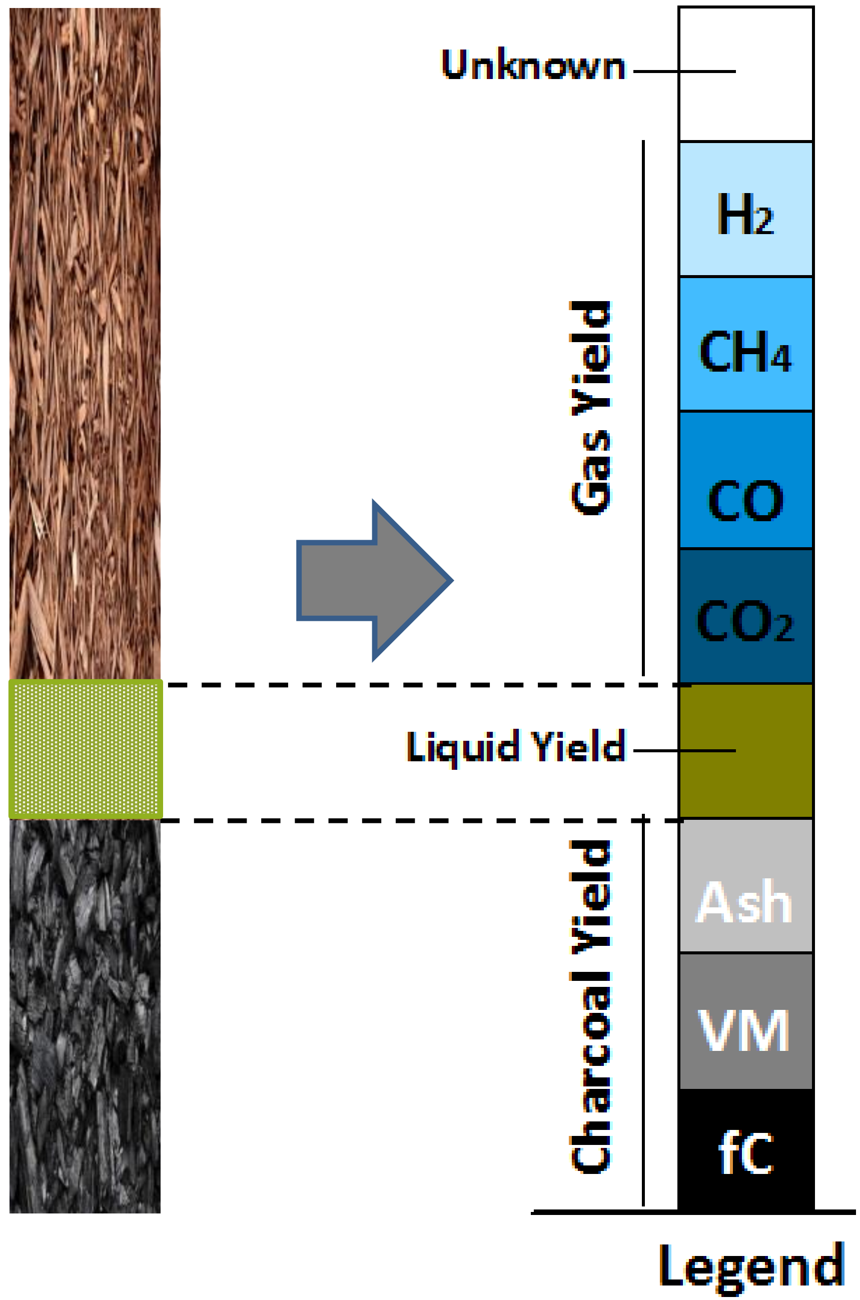
Product Yields [wt.%]

$$y_{liquid} = \frac{m_{liquid}}{m_{bio}}$$

Product driven off by heating in a vacuum oven at 105°C

$$y_{char} = \frac{m_{char}}{m_{bio}}$$

Solid product (after drying)



Product Yields [wt.%]

$$y_{gas} = \frac{m_{gas}}{m_{bio}}$$

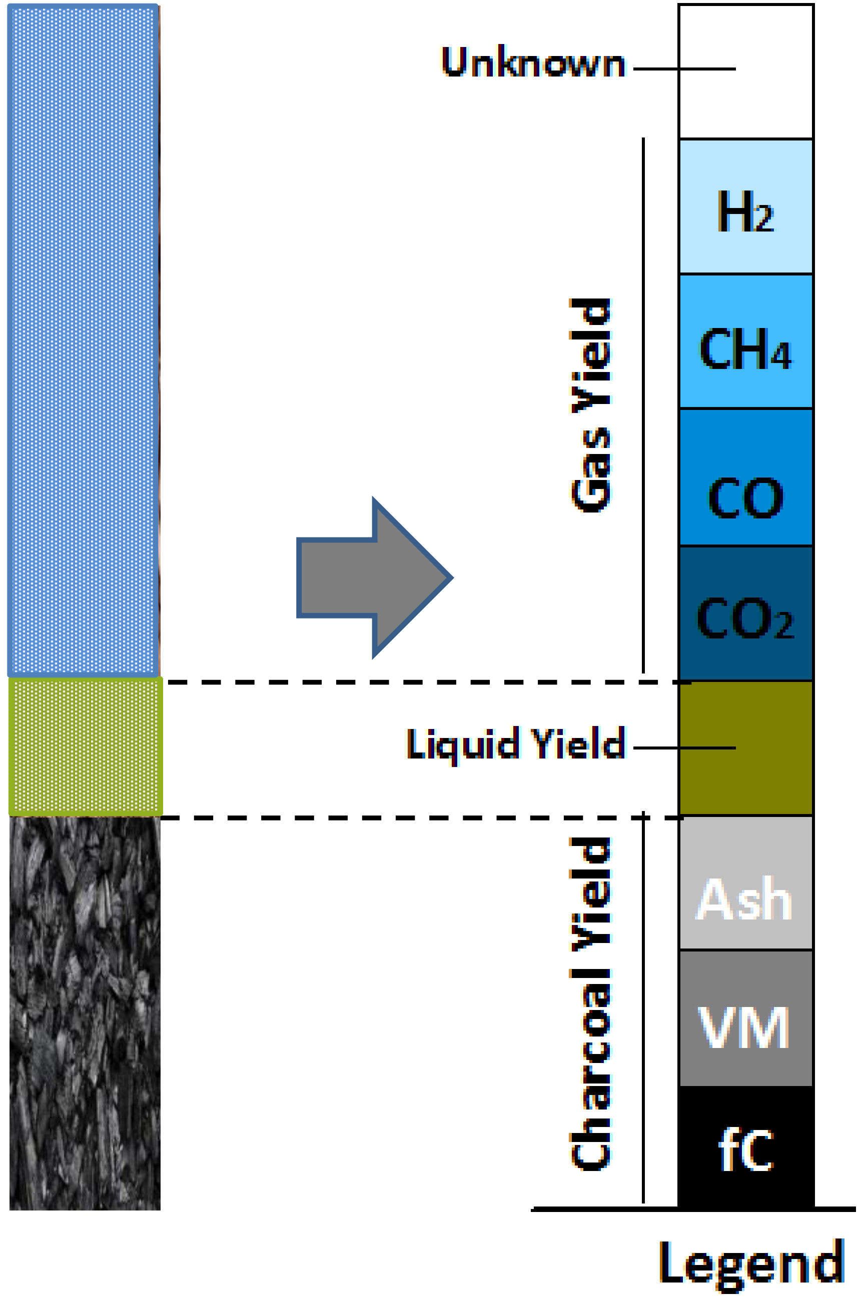
Gas product after cooling down the reactor to room T

$$y_{liquid} = \frac{m_{liquid}}{m_{bio}}$$

Product driven off by heating in a vacuum oven at 105°C

$$y_{char} = \frac{m_{char}}{m_{bio}}$$

Solid product (after drying)

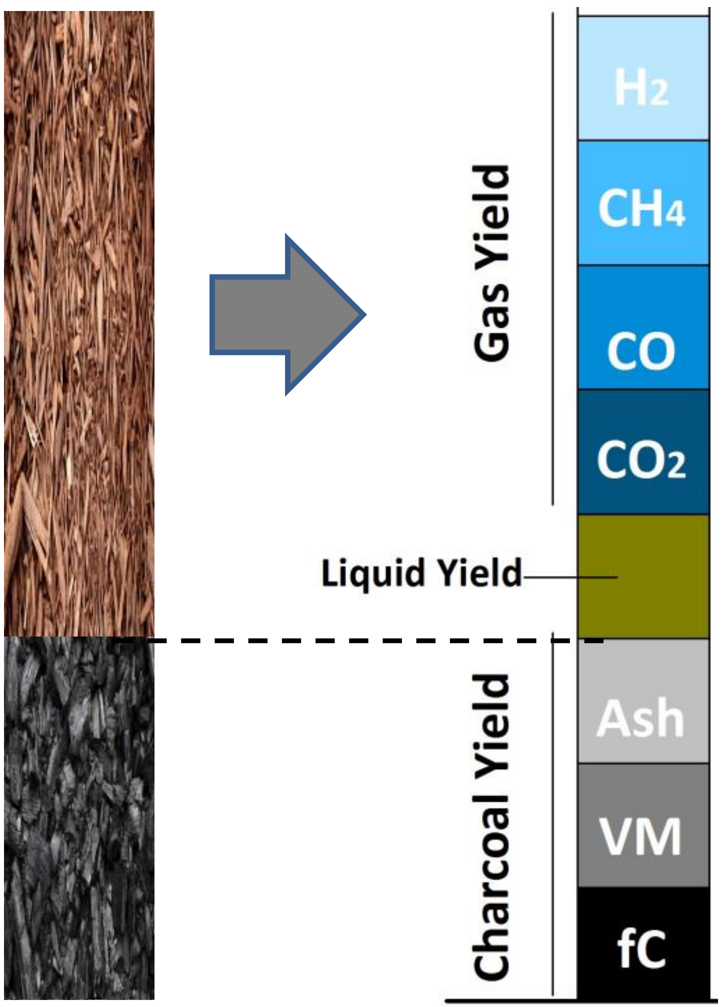


However, not all charcoal yields are the same!

[Proximate analysis, ASTM D1752-84]

$$100 = \%\,\mathrm{VM} + \%\,\mathrm{fC} + \%\,\mathrm{ash}$$

(volatile matter + fixed carbon + ash)



However, not all charcoal yields are the same!

[Proximate analysis, ASTM D1752-84]

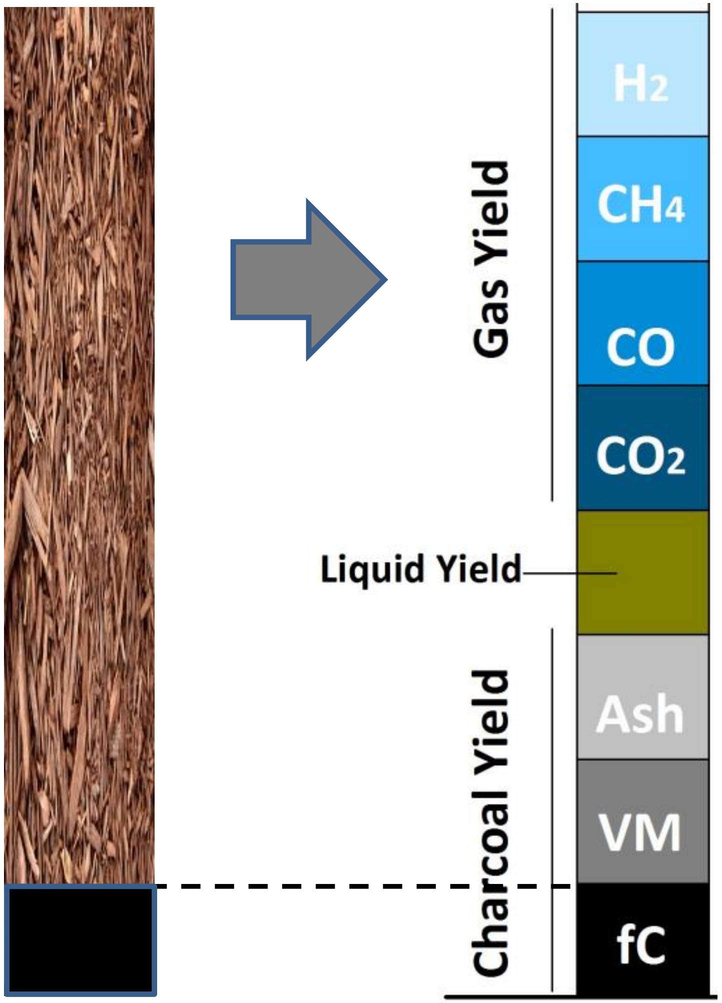
$$100 = \%\,VM + \%\,fC + \%\,ash$$

(volatile matter + fixed carbon + ash)

$$y_{fC} = y_{char} * \frac{\%\,fC}{(100 - \%\,feed\,ash)}$$

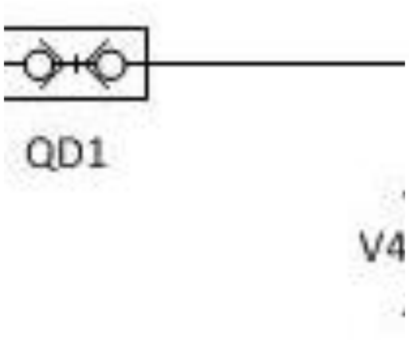
Fixed Carbon Yield

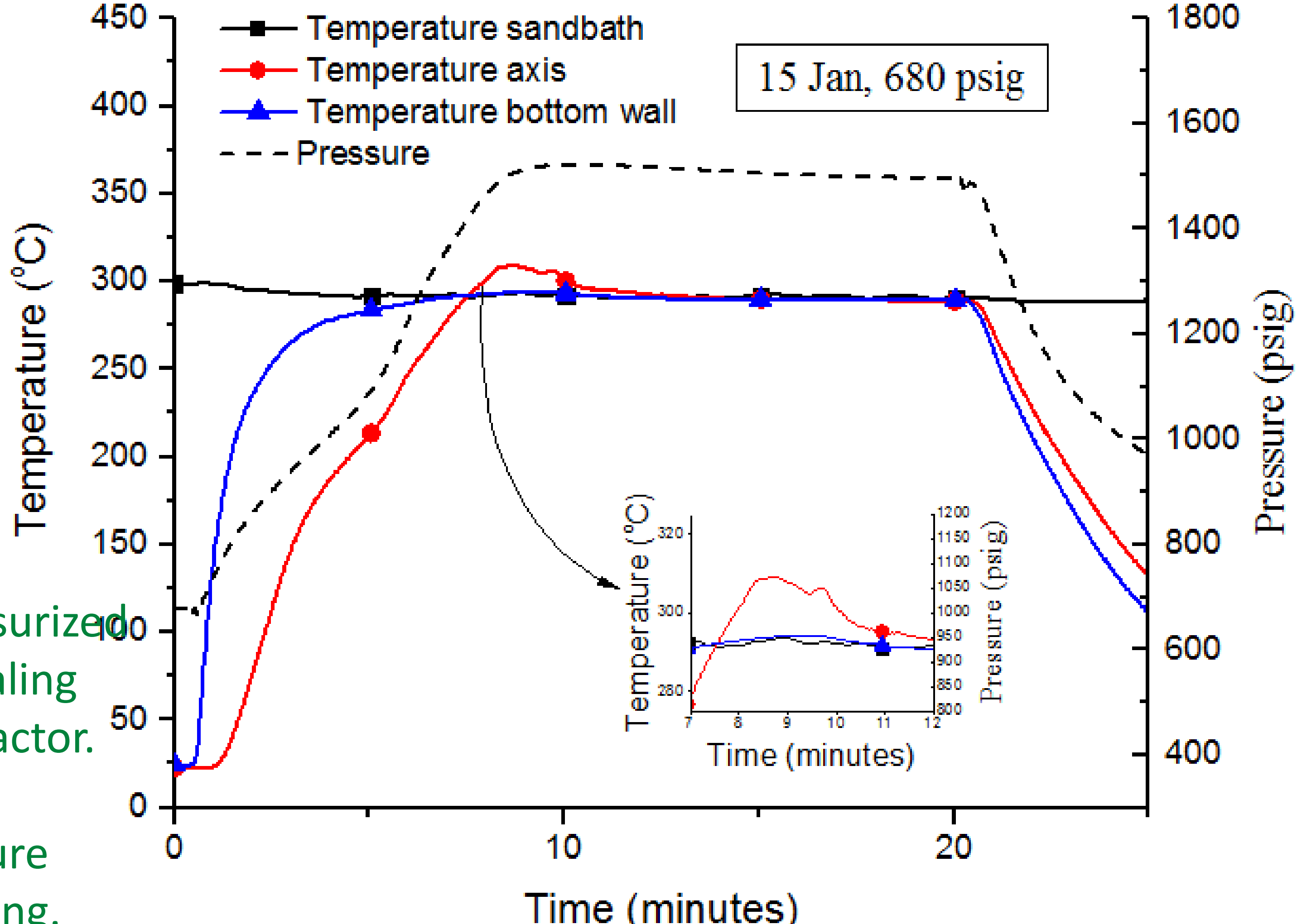
(defined by Prof Antal)



M. J. Antal, S.G. Allen, X. Dai, B. Shimizu, M.S. Tam, and M.G. Grønli. Attainment of the theoretical yield of carbon from biomass. 2000

CVC Reactor at HNEI

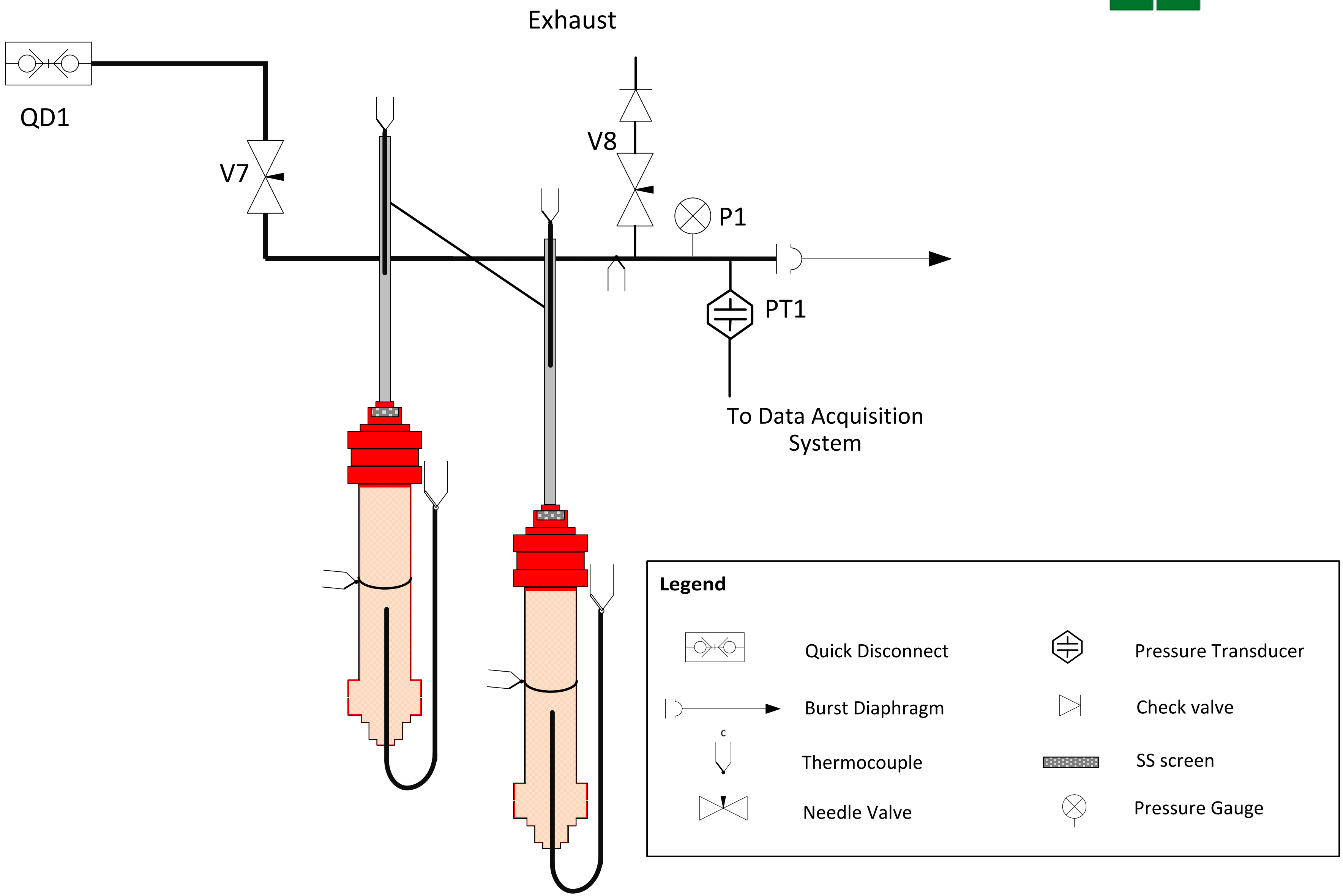




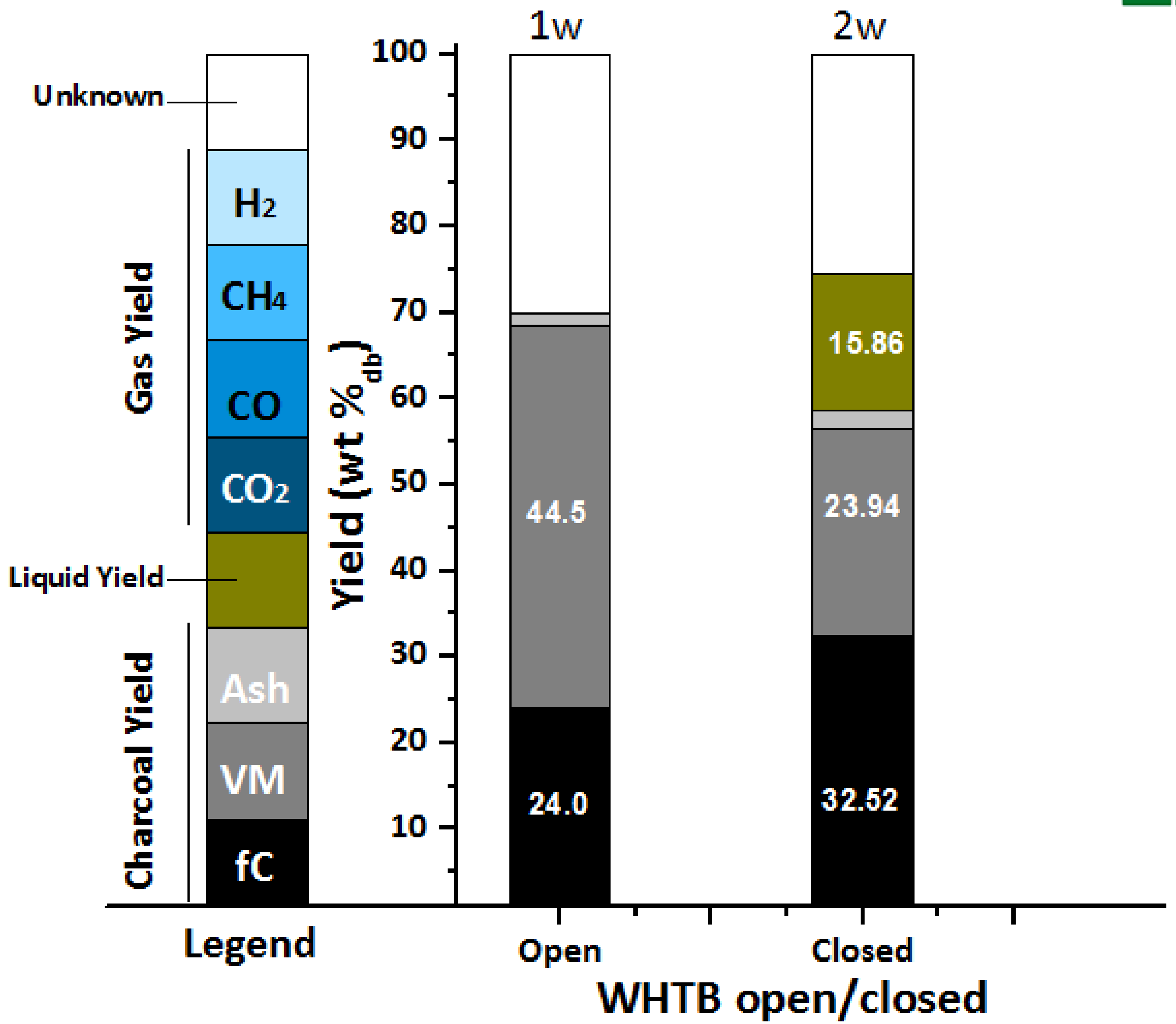
The reactor is pressurized with N_2 prior to sealing and heating the reactor.

I.e. the peak pressure occurs during heating.

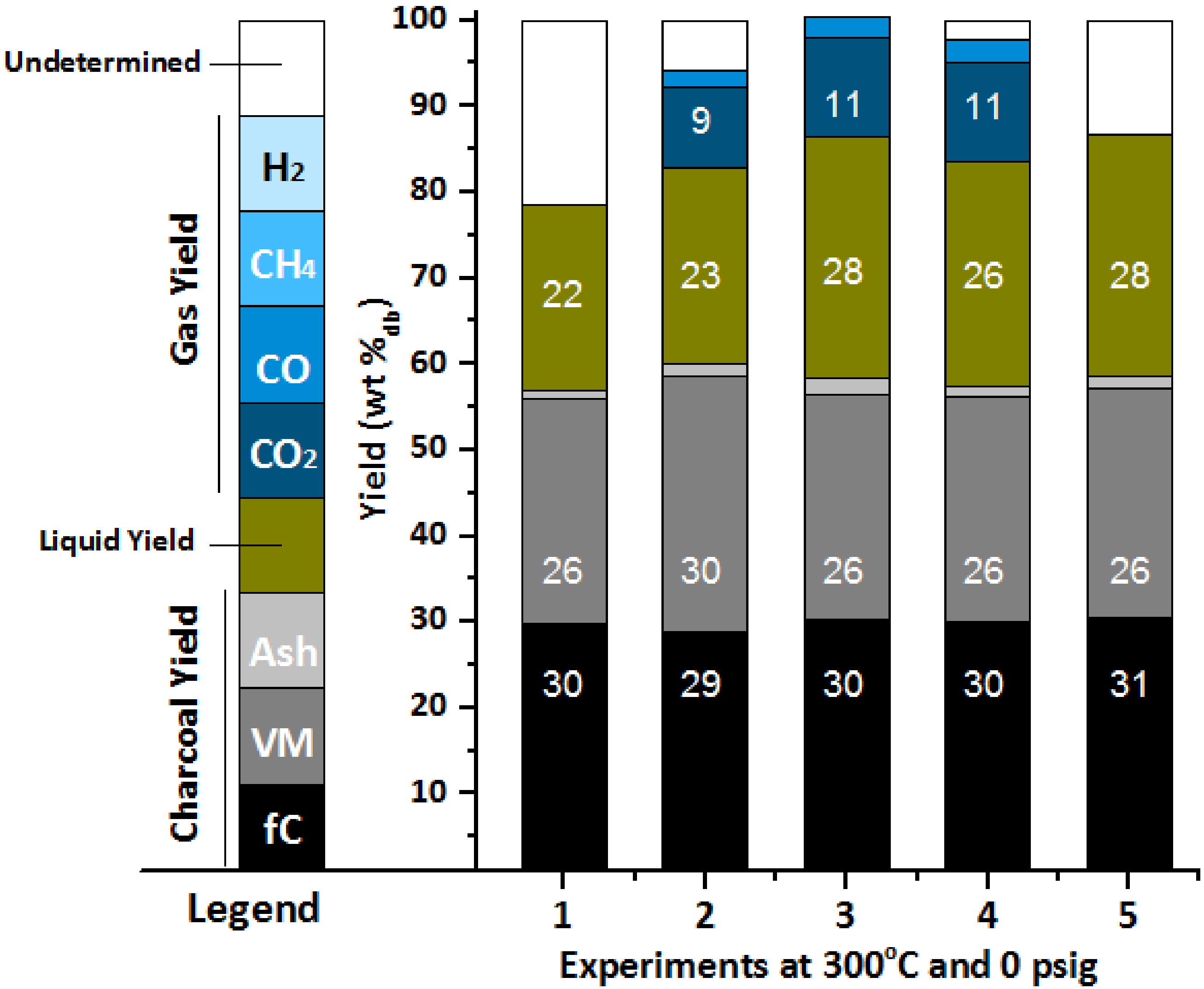
WHTB Dual Reactor



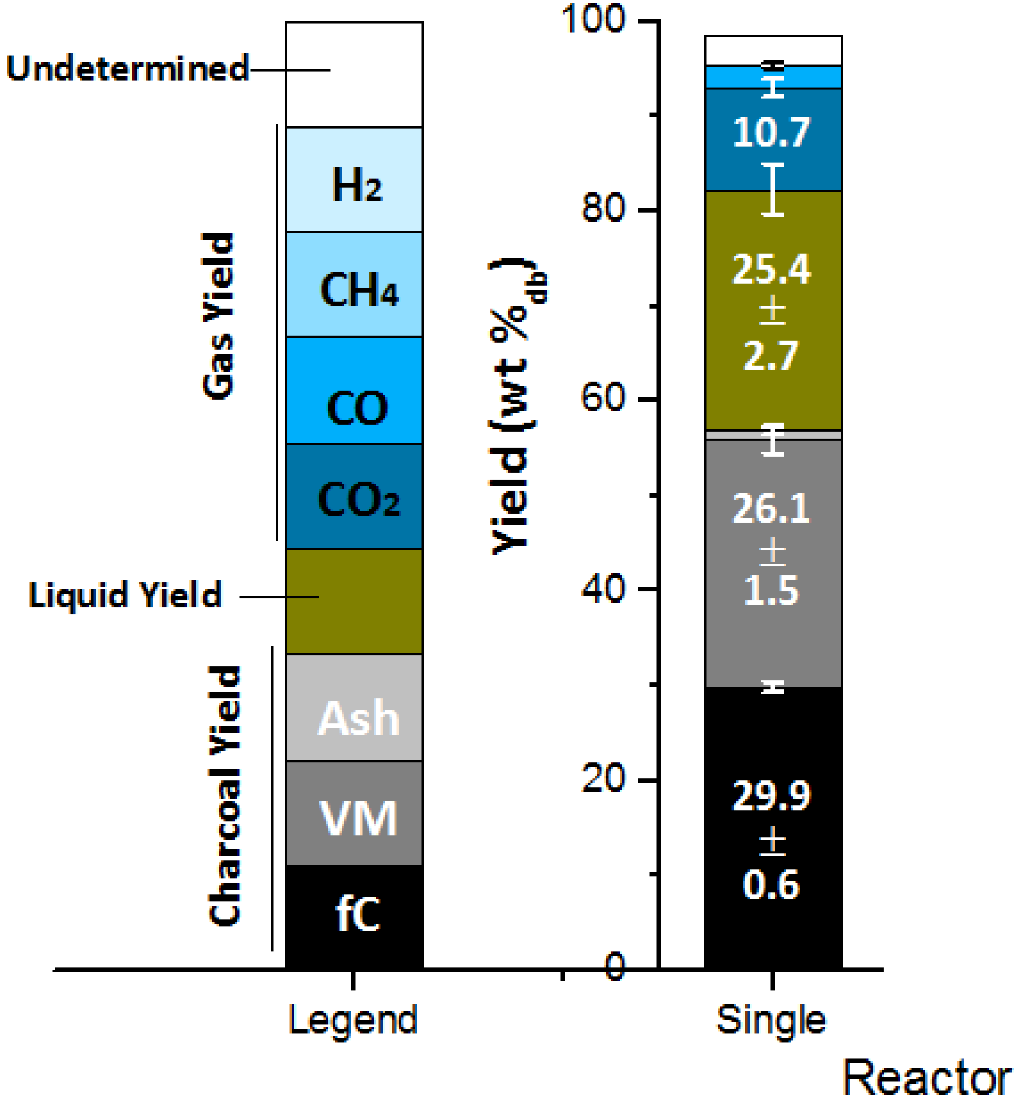
Open vessel vs Closed vessel



Uncertainty in the yields – 5 replicate experiments



Error bars in the yields

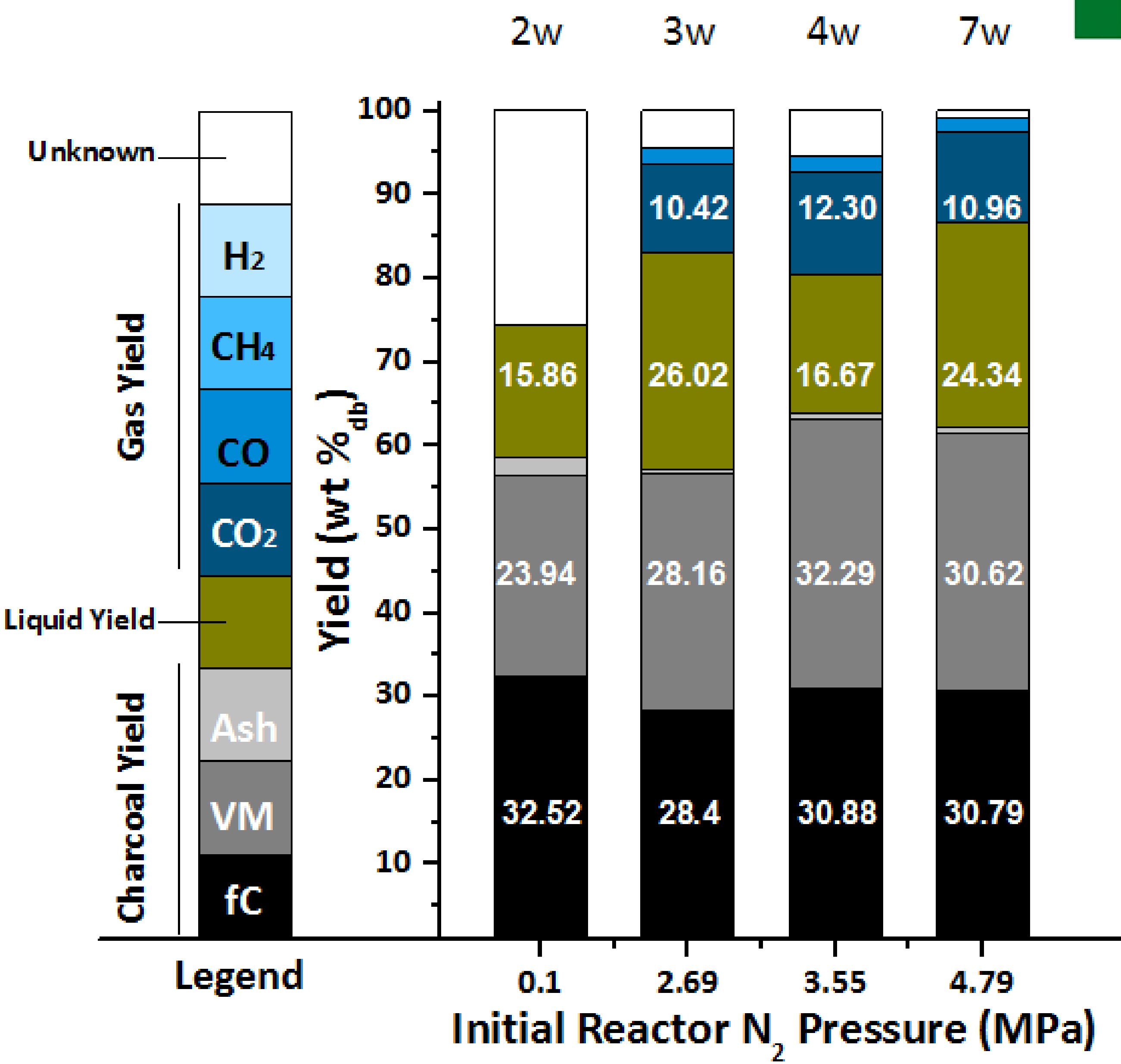


Effect of a closed vessel versus an open vessel:

Higher partial pressure and longer residence time of the tarry vapors promote secondary charring reactions.

Greater fixed-carbon yields are achieved when using a sealed vessel.

Effect of pressure – oak sawdust

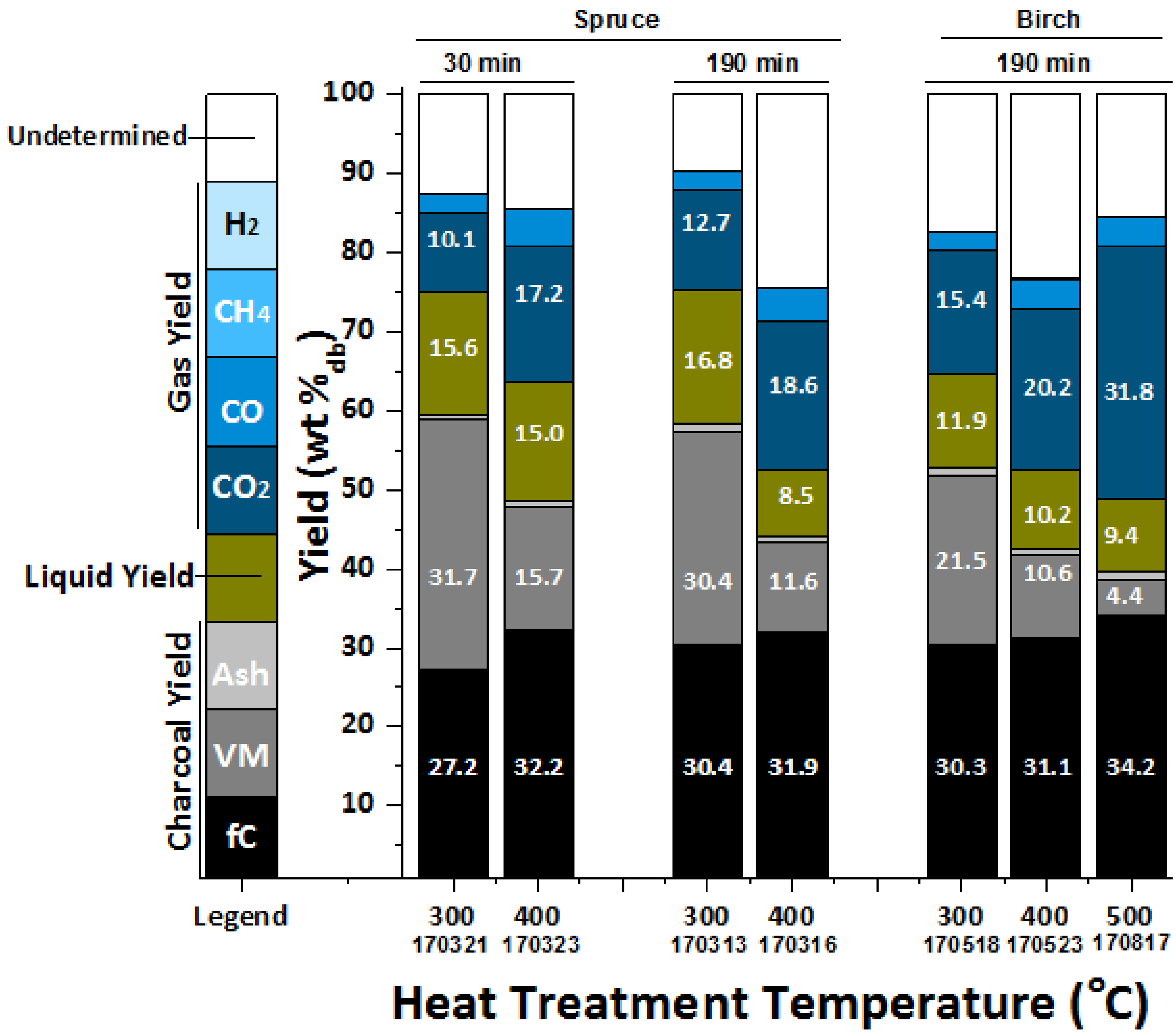


Effect of pressure

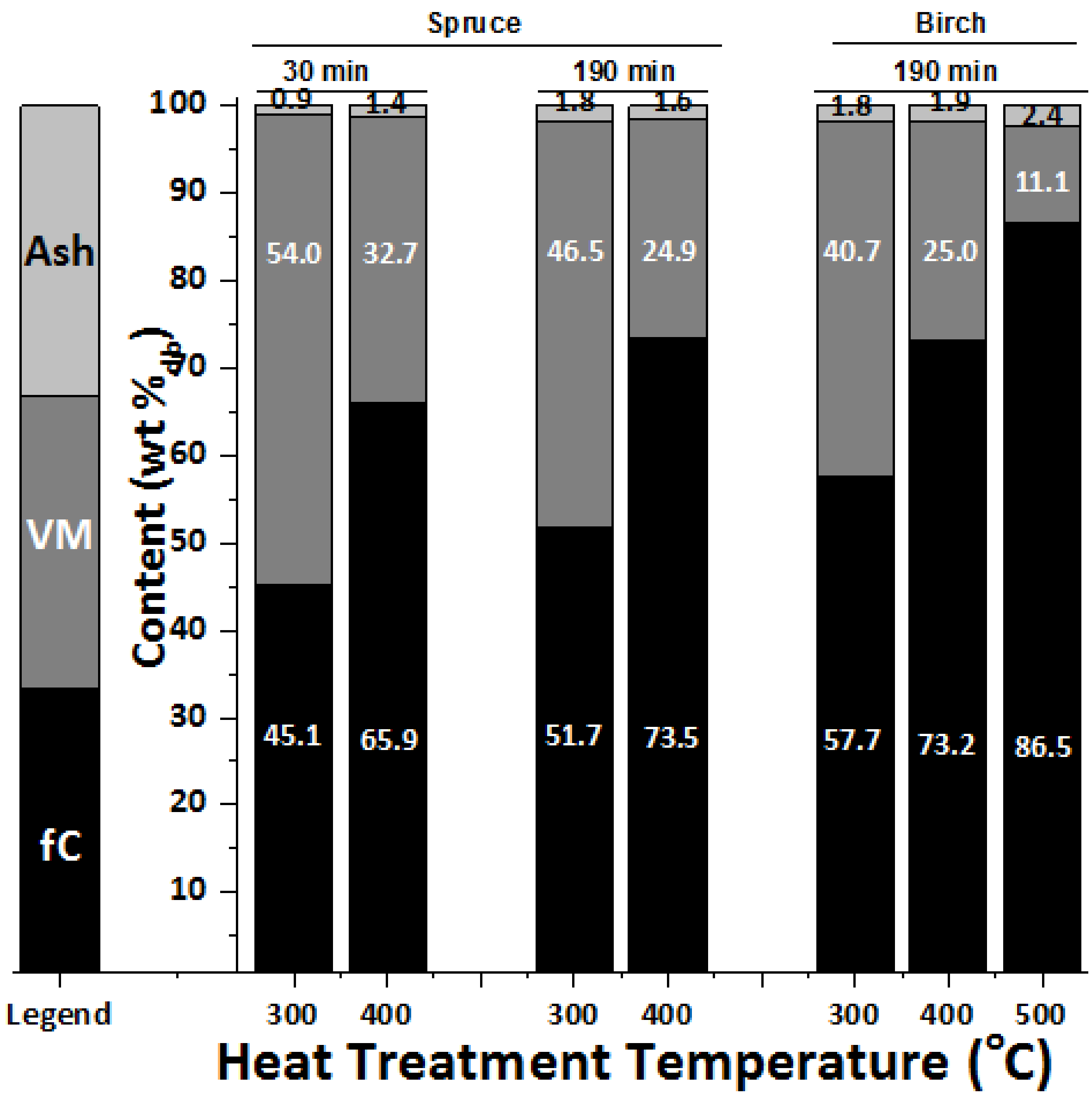
Higher partial pressure and longer residence time of the tarry vapors promote secondary charring reactions.

Increasing the pressure by using inert gas increased charcoal yield but does NOT significant effect the fixed-carbon content.

Effect of Temperature – Spruce & Birch



Effect Temperature – Spruce & Birch



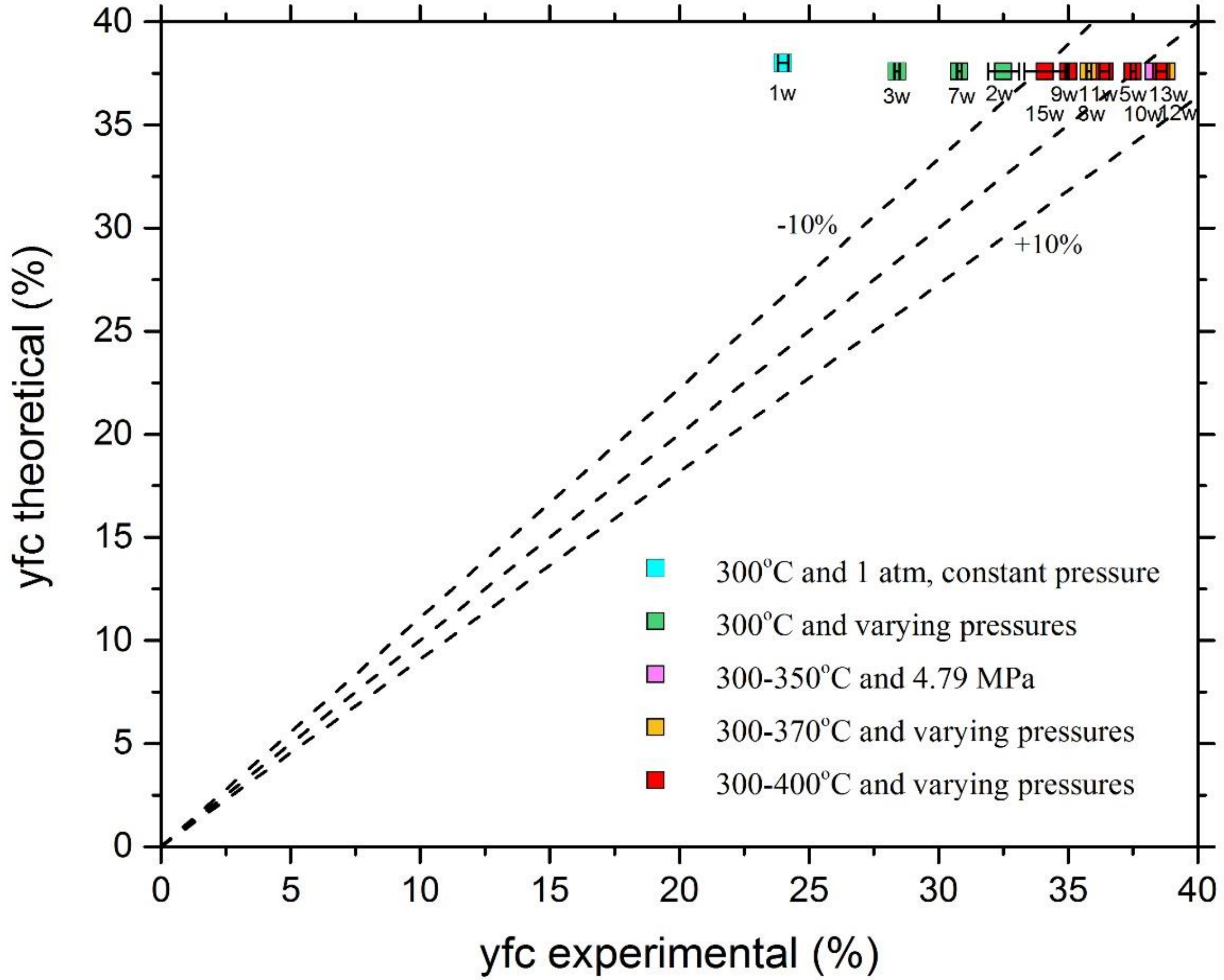
Effect of Temperature

An increase in the carbonization temperature (in a range from 300 to 500°C) produces a higher quality charcoal.

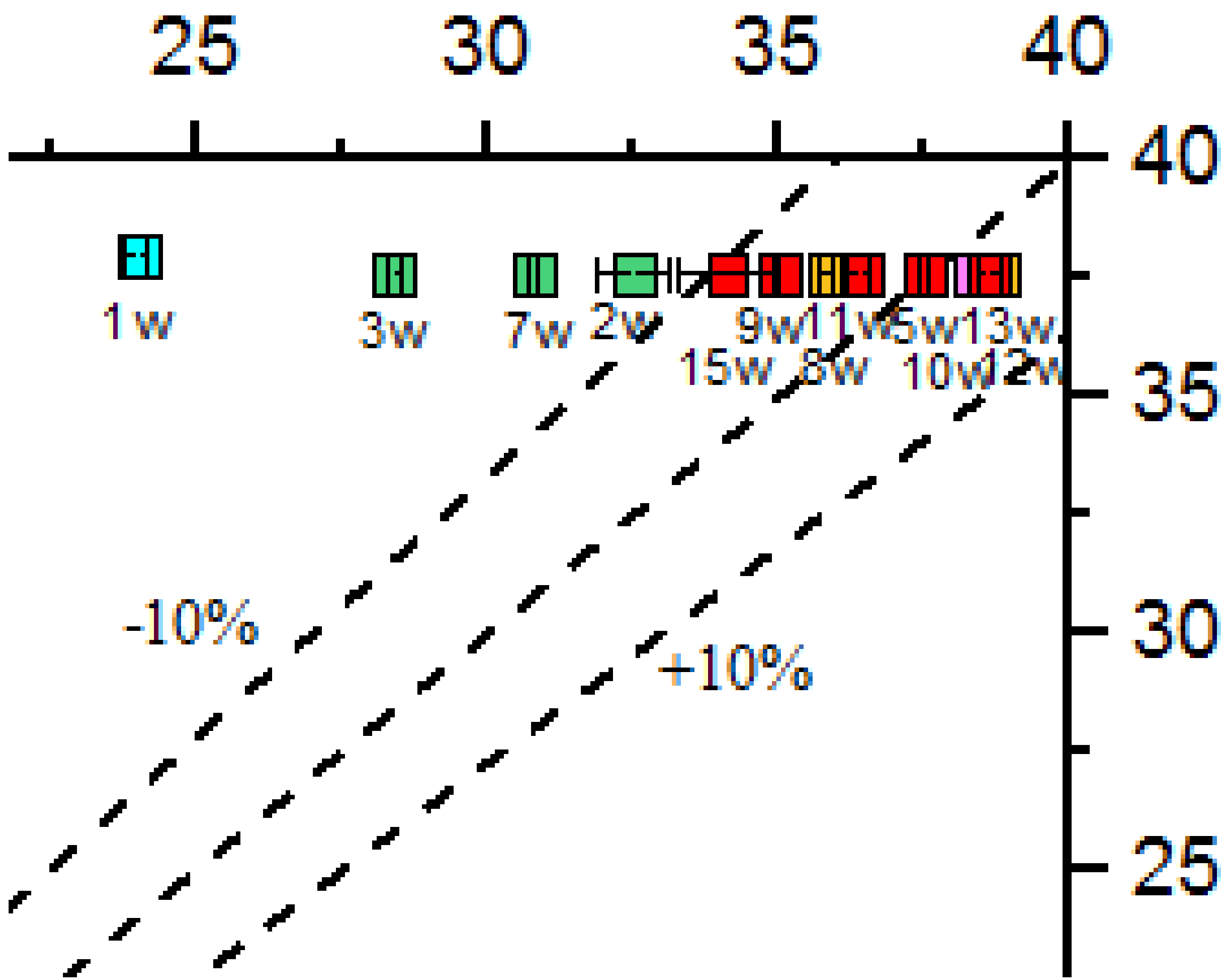
A lower charcoal yield but with higher fixed-carbon content, and/or reduced volatile matter (VM) content.

Being able to tune the VM content of the final charcoal is very important for industrial applications - especially if it can be done in a single step.

“Thermochemical equilibrium predictions set meaningful limits on the maximum (theoretical) yield of carbon that can be obtained from a particular biomass feedstock.”



Michael Antal and Morten Grønli. The art, science, and technology of charcoal production. Industrial & Engineering Chemistry Research, 42(8):1619-1640, 2003.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11w
8w
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13w
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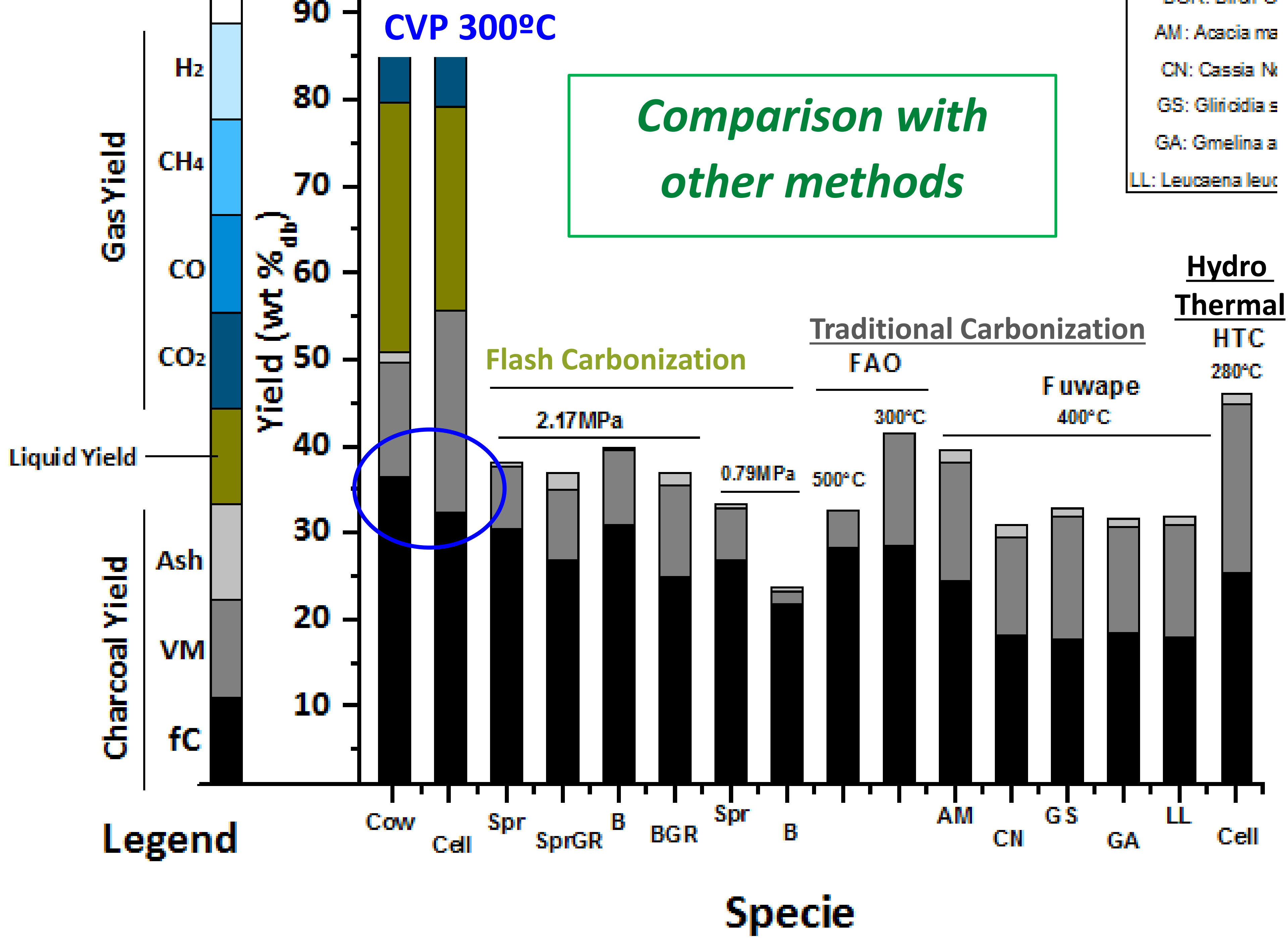
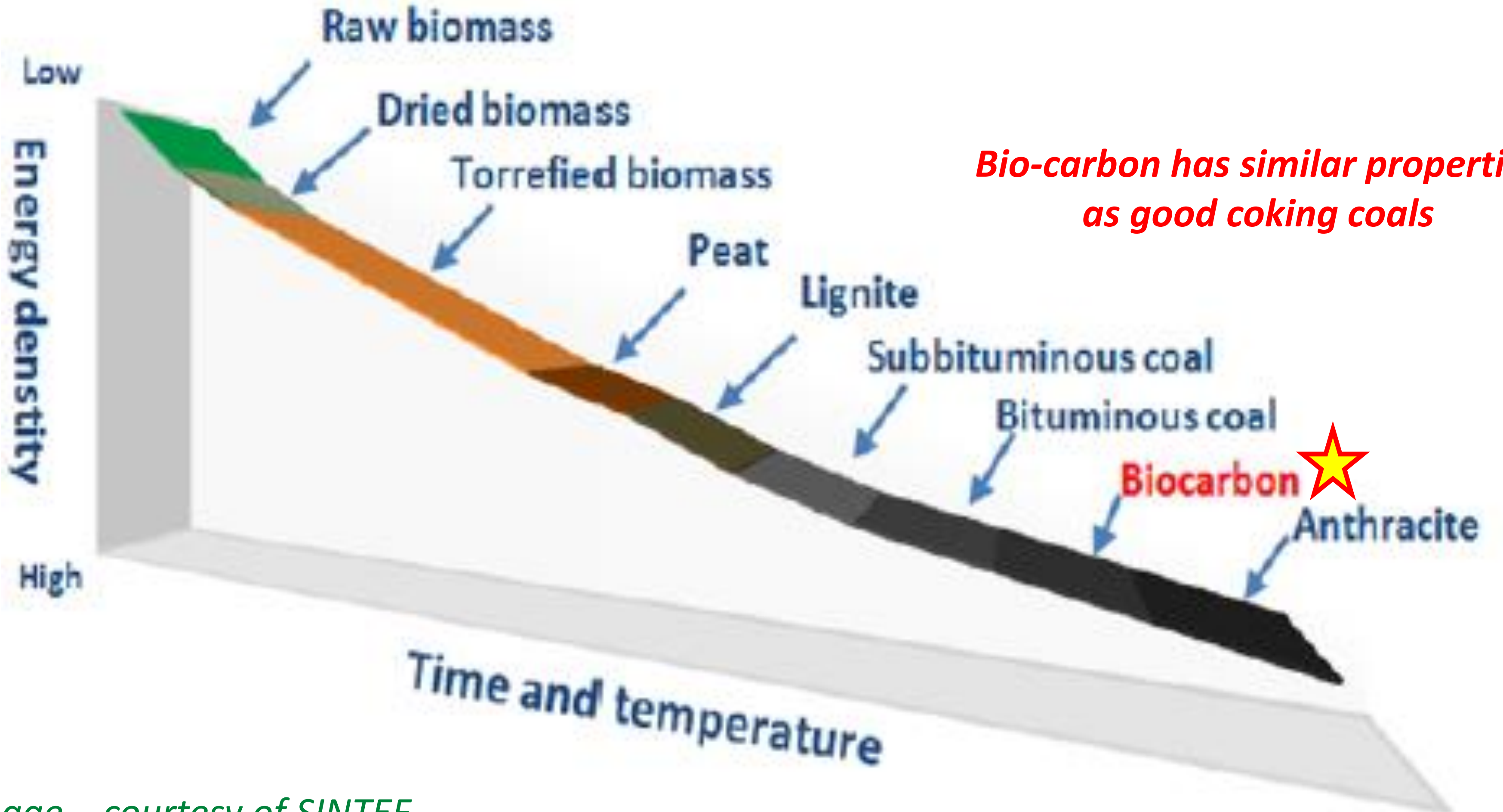
12w
-10%
+10%



CVP 300ºC
Comparison with other methods
AM: Acacia ma
CN: Cassia N
GS: Gliricidia s
GA: Gmelina a
LL: Leucaena leu
Gas Yield
H2
CH4
CO
CO2
Liquid Yield
Charcoal Yield
Ash
VM
fC
Legend
Yield (wt %db)
90
80
70
60
50
40
30
20
10
Flash Carbonization
2.17MPa
0.79MPa
Traditional Carbonization
FAO
500°C
300°C
Fuwape
400°C
Hydro Thermal
HTC
280°C
Cow
Cell
Spr
SprGR
B
BGR
Spr
B
AM
CN
GS
GA
LL
Cell
Specie

CVC Research

- Charcoal (bio-carbon) produced via CVC has a significantly improved energy density compared to raw biomass…
  - *Comparison with chars produced by other methods is on-going.*

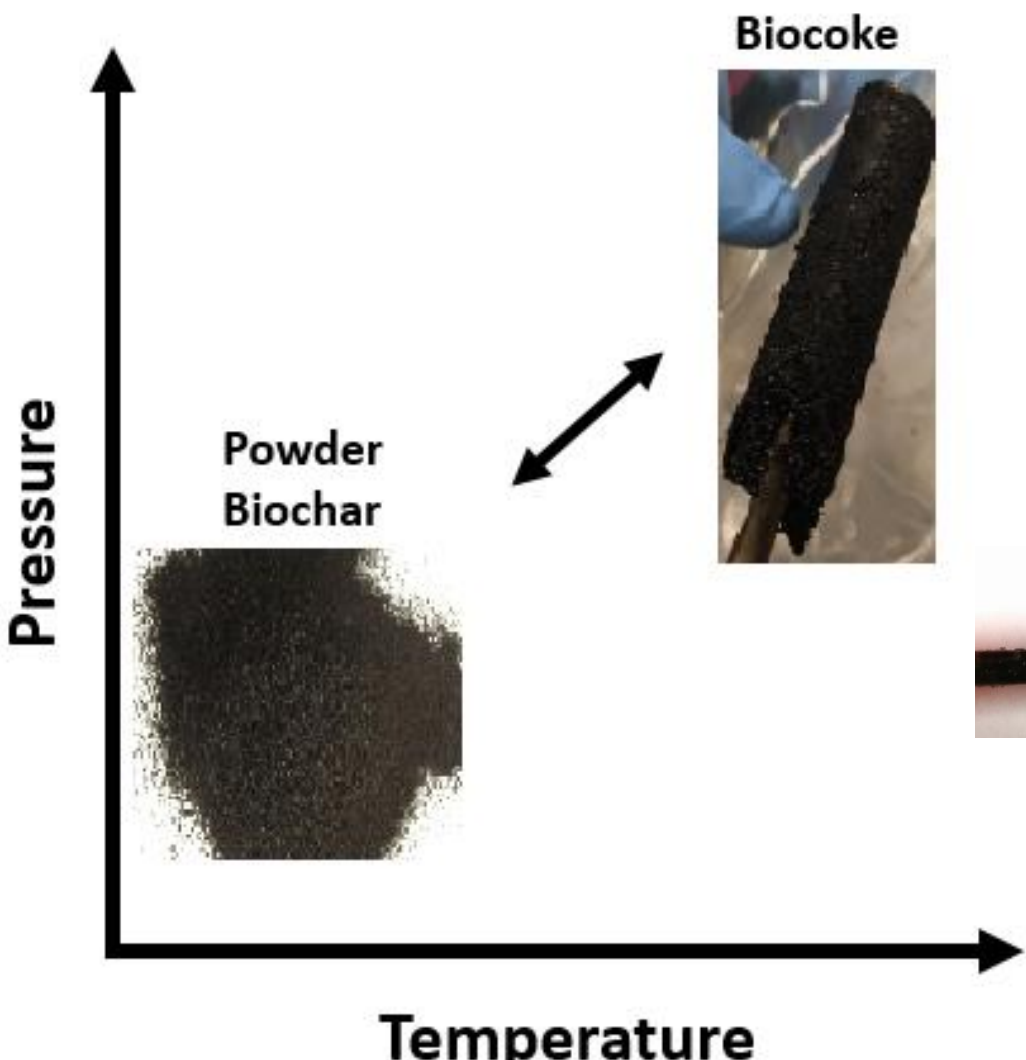


Bio-carbon has similar properties as good coking coals

Image – courtesy of SINTEF

Transient Plastic Phase (TPP)

Novel finding from the CVC research at HNEI: a TPP is observed when the temperature and initial pressure are greater than ~300°C and ~2.3 MPa.



Coarse sawdust, 300-400°C,2.69 MPa

Cellulose, 300-400°C, 2.28 MPa

Transient Plastic Phase (TPP)

An Effect of Particle Size

Literature:

Greater particle size→ Greater fixed carbon yields

"An increase in particle size delays the escape of volatiles from the carbon matrix. This delay offers additional opportunities for residual tarry vapors to suffer secondary reactions with the solid carbon and increases the yield of fixed carbon."

What if … a sealed reactor is used?

- An important finding from this research is that high charcoal yields can be obtained from sawdust - also high fixed-carbon yields.
- Confirmed using Spruce & Birch: >2.0 mm & <0.2 mm particle sizes

Michael Jerry Antal and Morten Gronli. The art, science, and technology of charcoal production. Industrial & Engineering Chemistry Research, 42(8):1619-1640, 2003.

An Effect of Heating Rate

Literature:

Lower heating rate→ Higher char yields

"If initially formed tar molecules do not vaporize quickly enough, they will have a tendency to crosslink and form thermally stable larger tar molecules which in turn can eventually form char."

What if … a sealed reactor is used?

This aspect of the research is ongoing.

J.P. Diebold T.B. Reed and R. Desrosiers. Perspectives in heat transfer requirements and mechanisms for fast pyrolysis. 1980

Higher heating value:

Charcoal[1] = 28-33 MJ/kg

Coal[2] = 13-34 MJ/kg

	Energy Content [MJ/kg]	Energy Yield [%]
Birch	18.5	
300°C	30.1	85.7
400°C	33.0	75.7
500°C	34.5	73.8
300°C, d<0.2mm,	29.7	86.3
300°C, d<0.2mm, high loading	31.0, 31.2	84.2, 85.9
300°C, 10 min, d<0.2mm, high loading	29.5	88.3
300°C, high P	31.3	89.5

1. Foley, G., *Charcoal making in developing countries*. 1986: Earthscan, International Institute for Environment and Development. Page 214.

2. *Solid Fuels*, in *Applied Combustion, Second Edition*. 2007, CRC Press. Pages 203-250.

Elemental analysis:

	C (wt%)	N (wt%)	H (wt%)	S (wt%)
Birch	47.4	0.2	6.3	0.02
300°C	74.3	0.4	5.1	0.01
400°C	83.2	0.5	4.4	0.01
500°C	90.4	0.4	3.3	0.01
300°C, d<0.2mm,	72.8	0.3	4.9	0.01
300°C, d<0.2mm, high loading	76.2, 77.2	0.4, 0.3	4.8, 5.0	0.01
300°C, 10 min, d<0.2mm, high loading	73.0	0.2	5.2	0.01
300°C, high P	76.4	0.2	5.2	0.01

Conclusions

- The fixed-carbon yield of sawdust pyrolysis in sealed vessels quickly attains (minutes) its theoretical limiting value set by thermodynamics.

- The initial N_2 pressure did not show any significant effect on the fixed-carbon yields.

  Vapor-phase partial pressures of the volatile products, rather than the total system pressure, appears to exert the dominant effect on increasing the fixed-carbon yield.

- An increase in the carbonization temperature produces a higher quality charcoal, i.e. charcoal with a greater fixed-carbon content.

Conclusions

- An increase in pressure and temperature transforms the final charcoal product from particulate to a transient plastic phase (TPP) that solidifies into a single piece.

- The final thesis will further explore the effects of reaction temperature and initial pressure on different feedstocks, as well as the roles of:

  1) Particle Size
  2) Heating Rate
  3) Mass Loading
  4) Reaction Time

Conclusions

- On-going research at HNEI is revealing unique findings important to furthering our understanding of carbonization.

- Current Accepted Mechanism (open vessel carbonization):
  - Char yield increases with feedstock particle size.
  - High quality wood (low ash content, high density) produces greater char yields and improves physical and chemical properties of the char.

- Novel CVC Results:
  - Char yield appears to increase with decreasing particle size.
  - High fixed carbon yield (>30 wt%) from low quality biomass.
  - Transient plastic phase observed.

- These are unique and scientifically important findings from a practical and fundamental perspective.

Thank you for you attention

Questions ??

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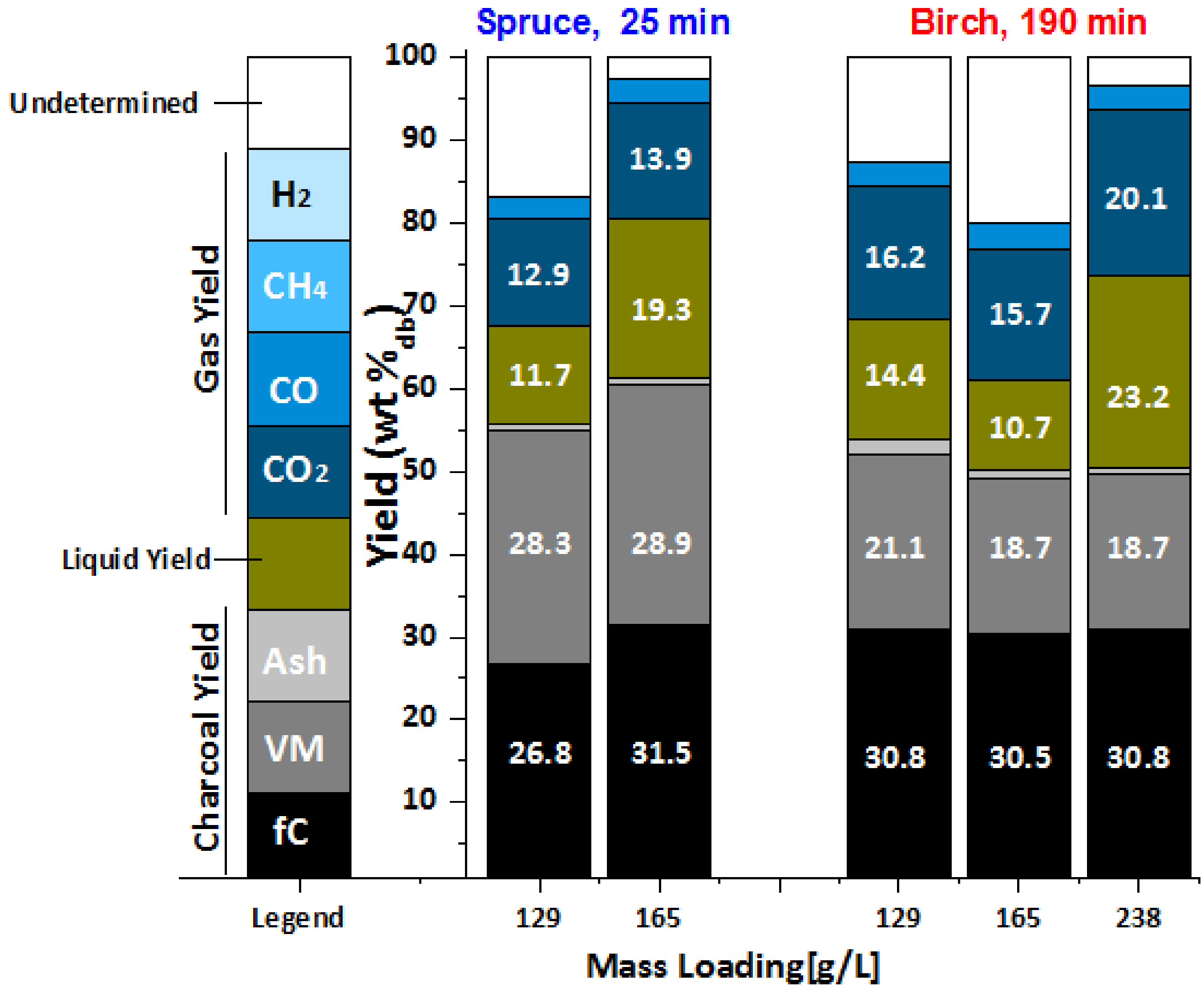
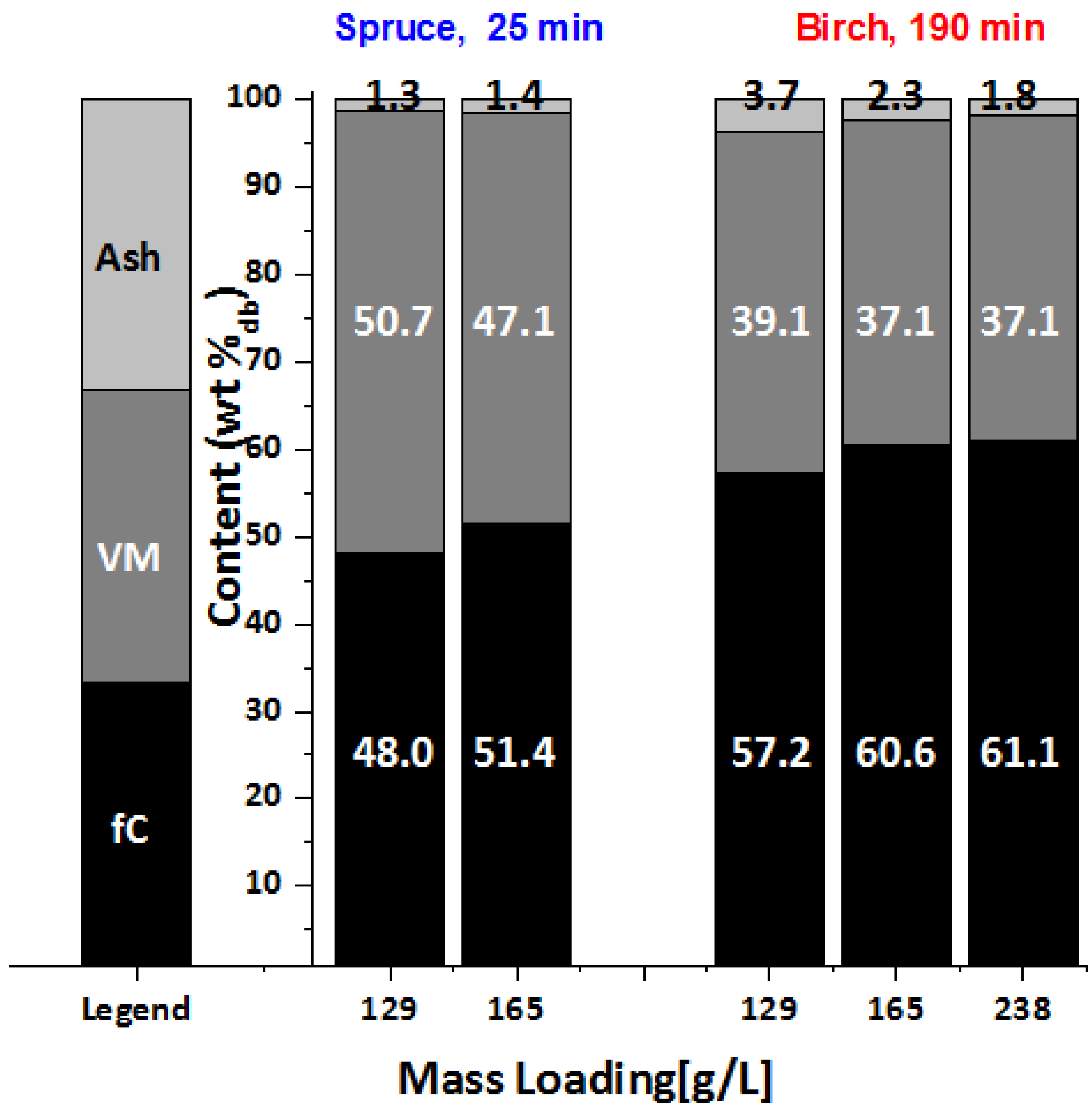
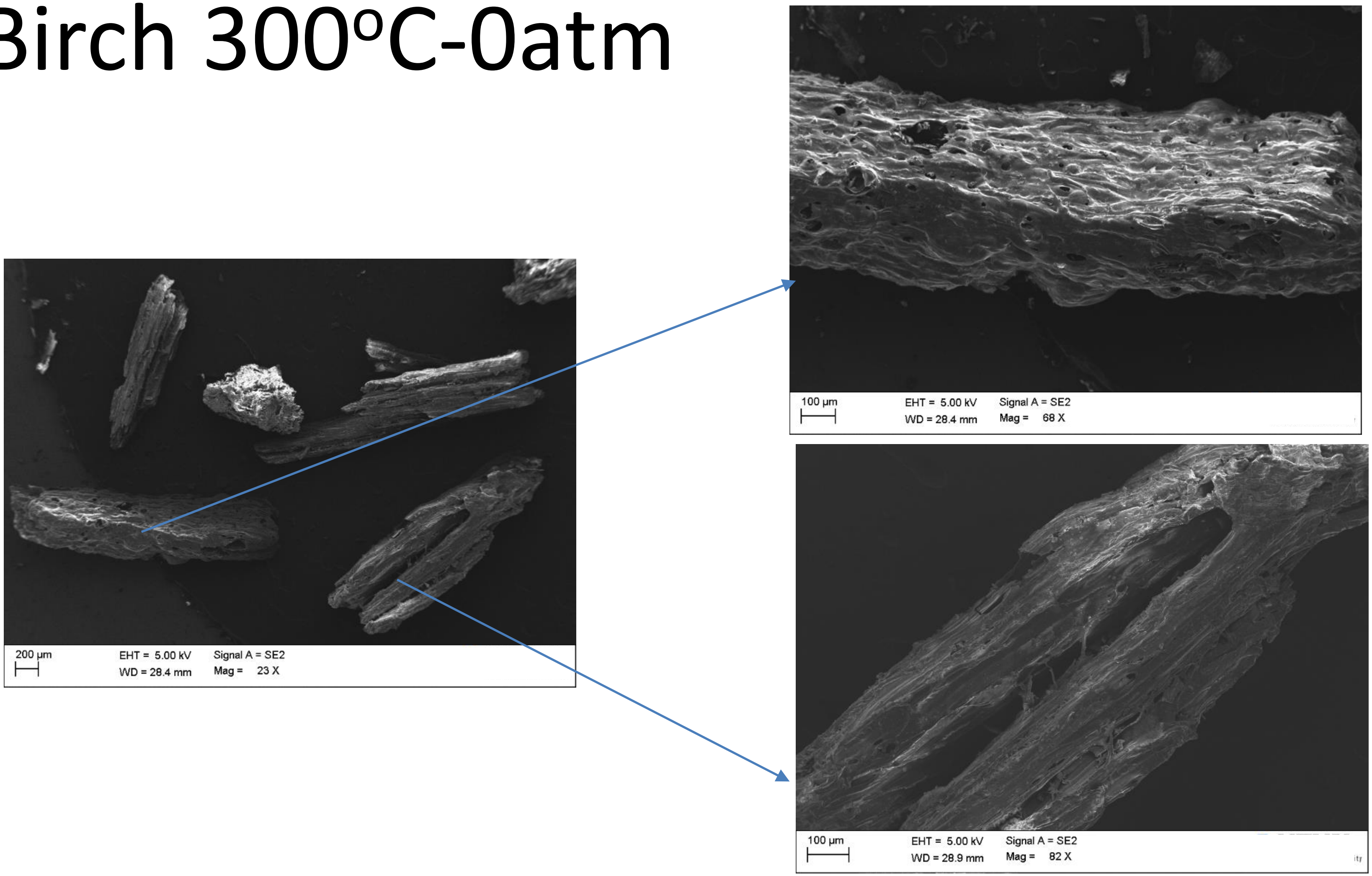
Effect of Mass Loading. 0 psig, 300ºC, <0.2mm



Effect of Mass Loading. 0 psig, 300ºC, <0.2mm

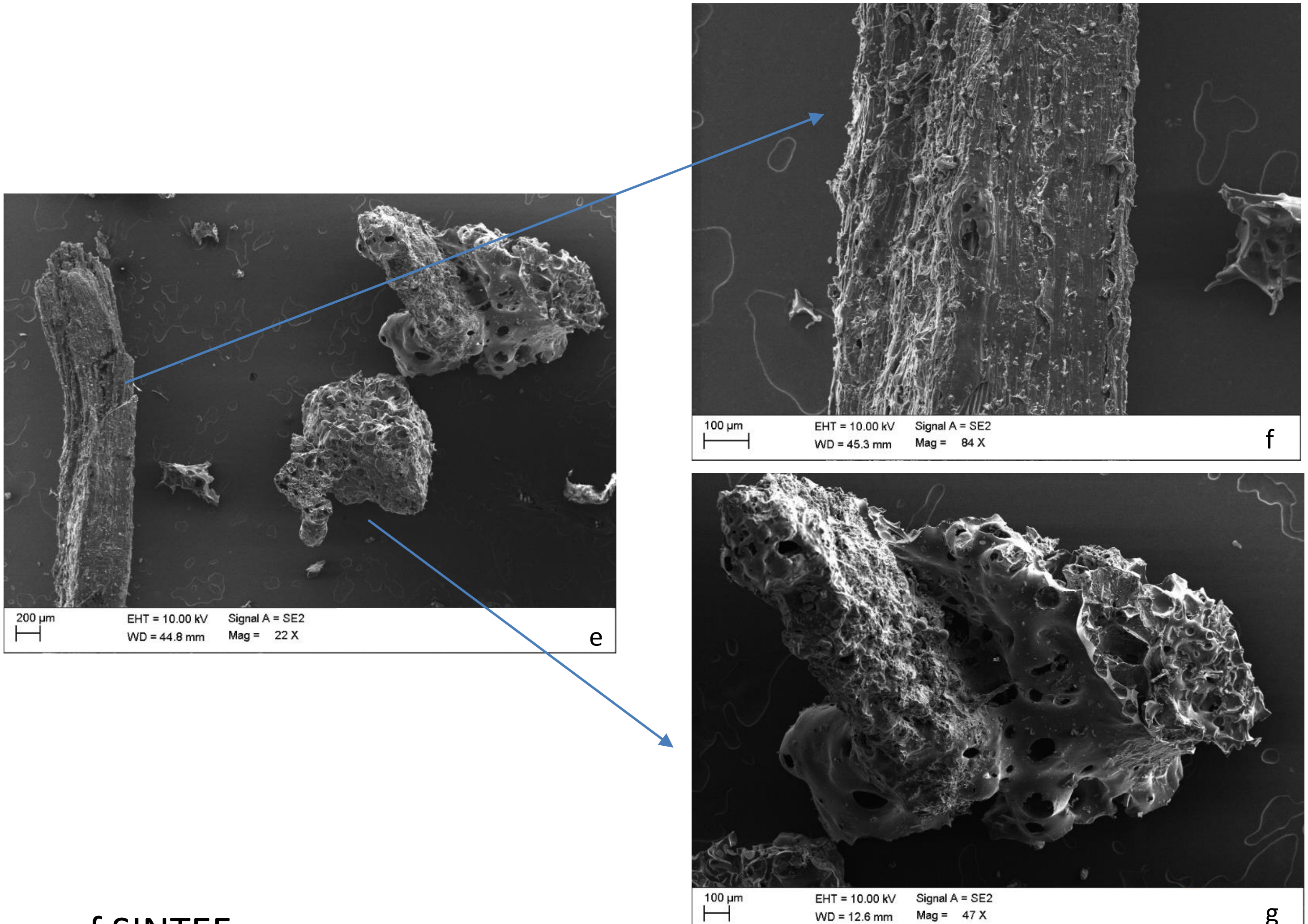


Birch 300ºC-0atm



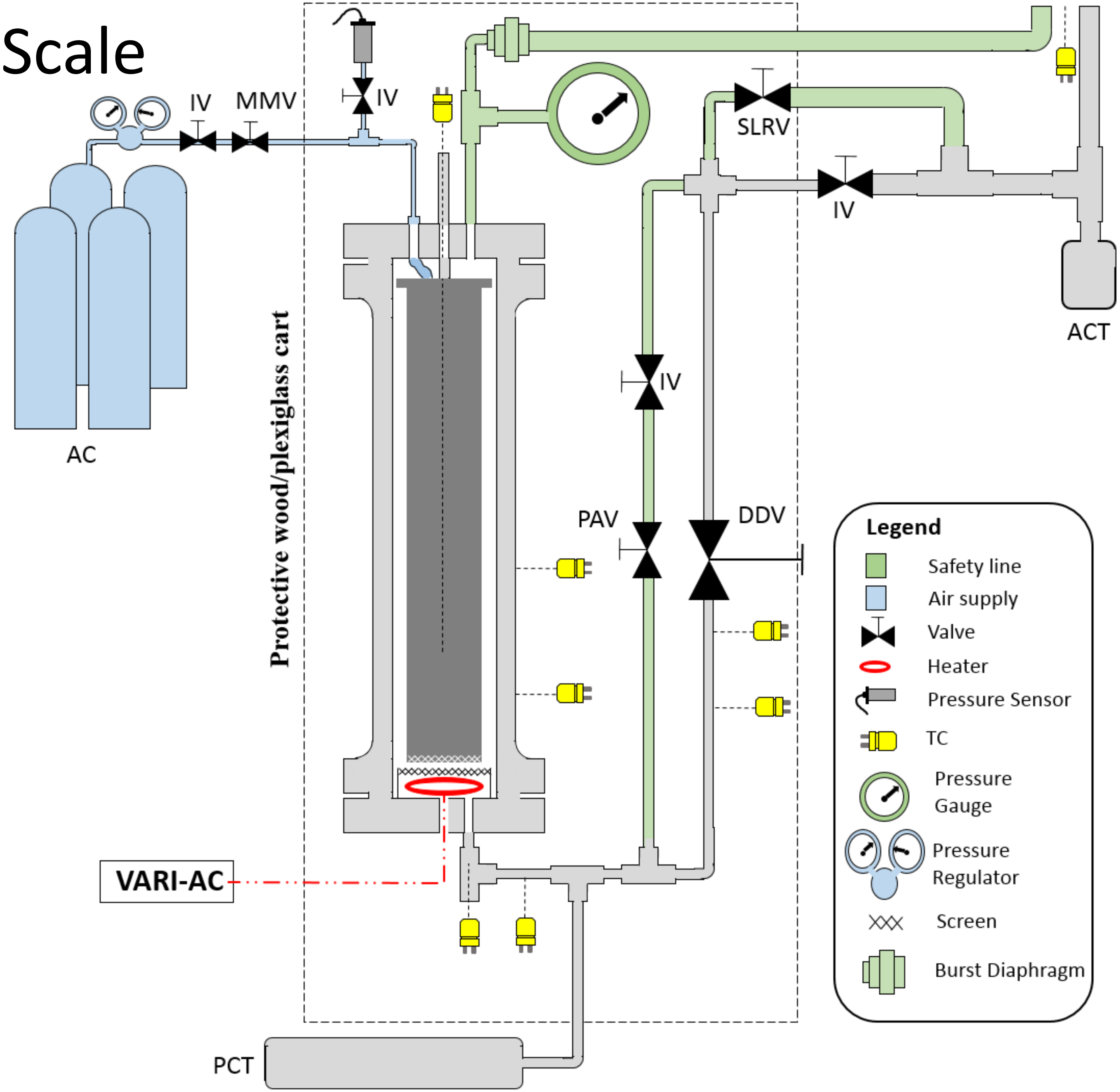
Courtesy of SINTEF

Birch 400ºC-0atm



Courtesy of SINTEF

FC Lab-Scale


IV
MMV
IV
SLRV
IV
ACT
AC
Protective wood/plexiglass cart
IV
PAV
DDV
VARI-AC
PCT
Legend
Safety line
Air supply
Valve
Heater
Pressure Sensor
TC
Pressure Gauge
Pressure Regulator
Screen
Burst Diaphragm