Effects of Biomass Source on the Composition and Reactivity of Thermochemical Reaction Products

[1]Carlos Aizpurua, [1]Lily Xiao, [1]Hoyong Kim, [2]Mark Davis
[1]Hasan Jamel, [1]Sunkyu Park, [1]Steve Kelley

[1]Department of Forest Biomaterials
North Carolina State University
Raleigh, NC

[2]National Renewable Energy Laboratory
Golden CO

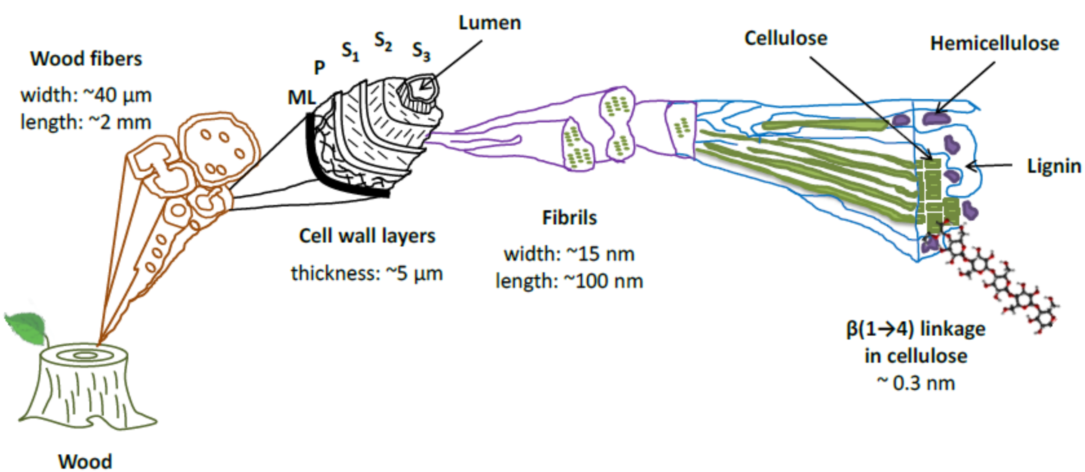
Outline - Context

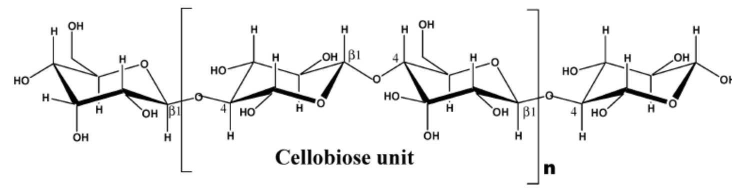
- Impacts of biomass source on Biochemical processes well known, hexose/pentose, lignin structure (S/G), cellulose recalcitrance

- Presume that biomass sources is not important for Thermochemical processes

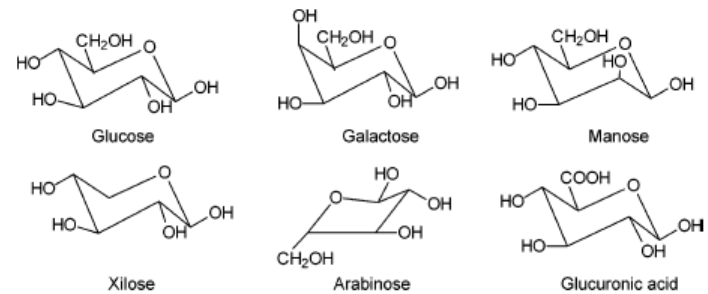
    - Chemical details of pyrolysis reactions
    - Bench scale samples and process modeling
    - Gasification reactions

Biomass cell wall constitution and composition



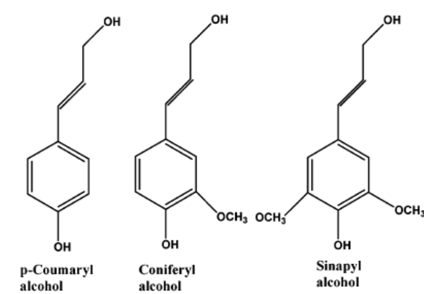


Cellulose polymer



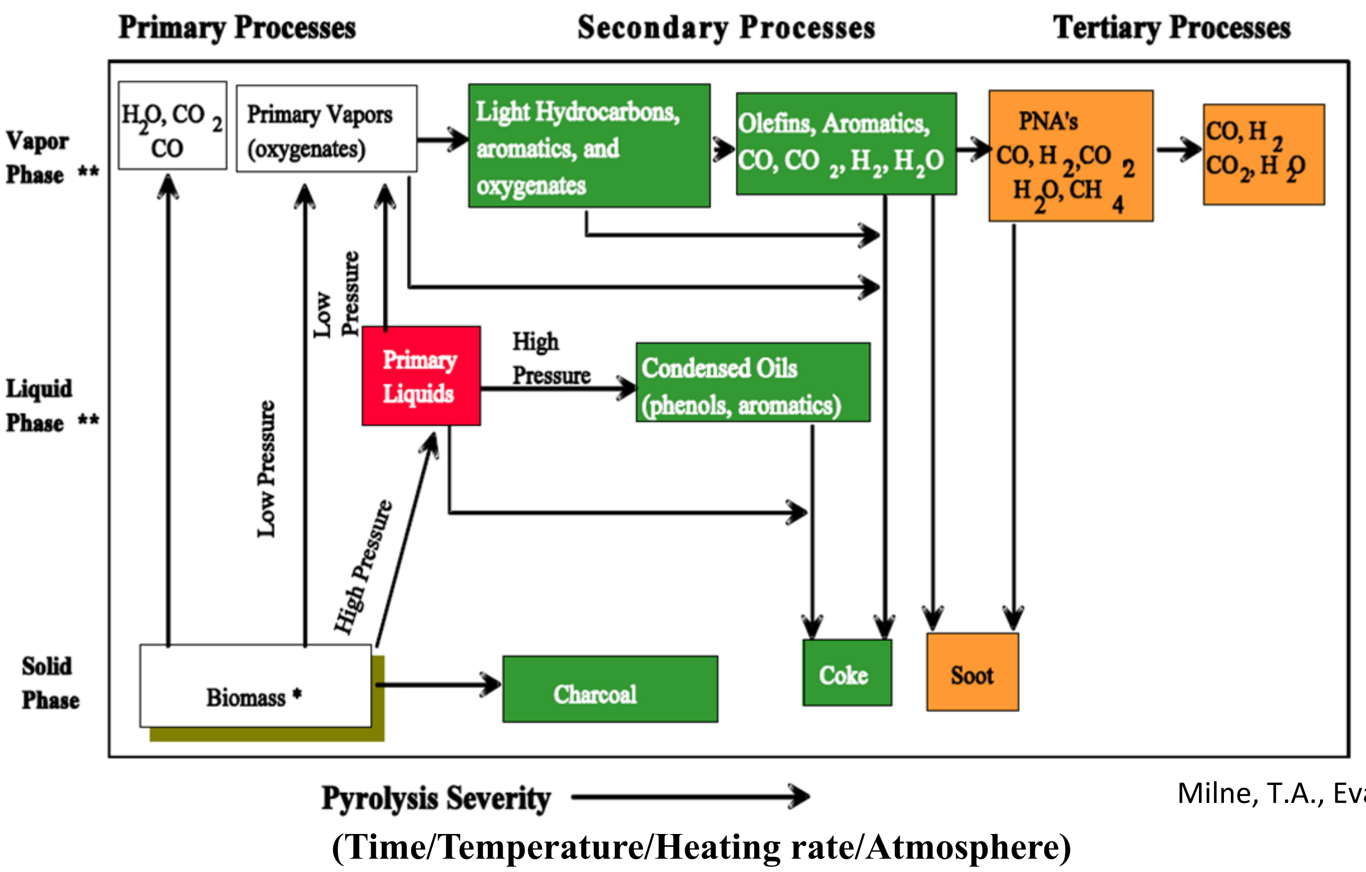
Hemicellulose components

- In thermal decomposition of biomass, cell wall structure and composition will impact:
  - ✓ Mass transfer, heat transfer, bond energy, thermal stability of initial products
  - ✓ The ash and specific mineral composition



Lignin monomer

Biomass pyrolysis and gasification



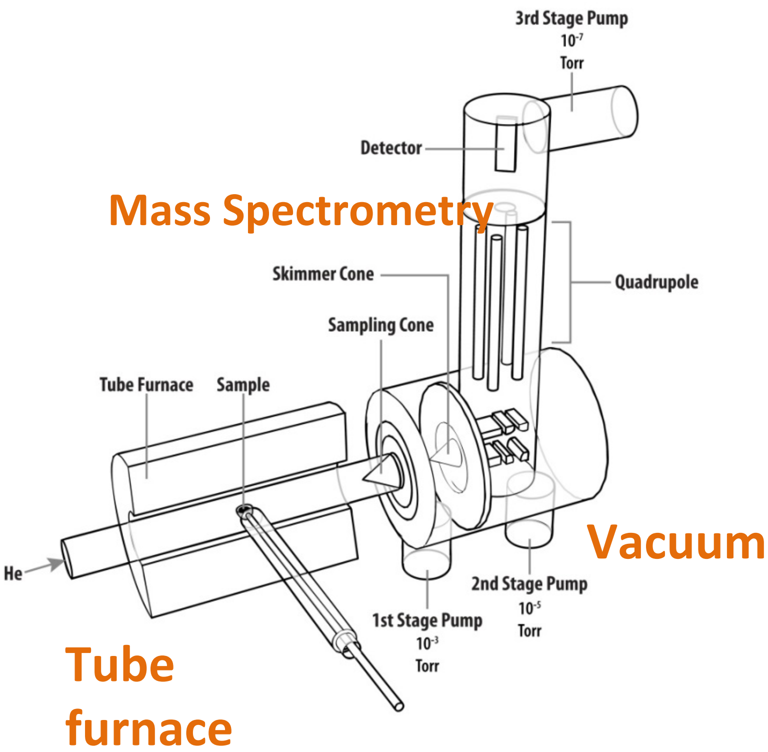
Milne, T.A., Evans, R.J. 1998.

- Biomass pyrolysis and gasification reaction regimes:
  - ✓ Biomass → Primary products → Secondary products → Tertiary products

Effects of Biomass Source in Pyrolysis Processes

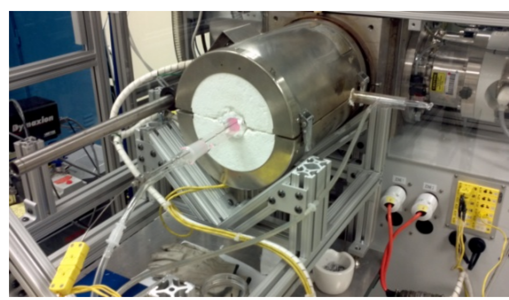
- Initial reaction products not the same things as the recovered products
- Interactions between biomass, inorganics and char
- Understanding will drive the selection and price of the feedstock, and dominate the properties and value of the initial products

Pyrolysis Molecular Beam Mass Spectrometry (Py-MBMS)



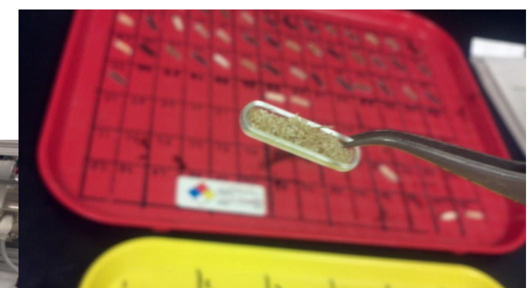
Pros

- Sampling can be coupled closely to the high-temperature reactor;
- Universal for volatiles
- Real time: 0.5s/scan
- High throughput
- Small Sample size: 10-20mg
- Well controlled condition



Cons

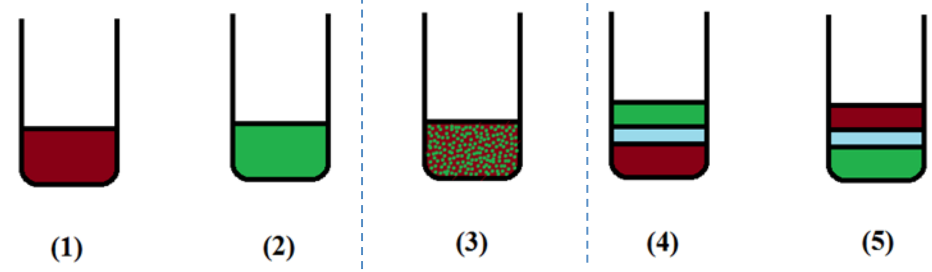
- instrument drift: internal standard - Ar &NIST SRM
- Semi-quantitative: calibration
- Isomer identification: high resolution mass spectrometry



Experimental and methods

- Pine + Switchgrass
- Pine + Leached switchgrass
- Pine + Switchgrass char
- Pine + Alfalfa
- Pine + Leached alfalfa
- Pine + Alfalfa char

(1), (2) Calculate mixing results | (3) Mixed | (4) (5) Separately position: phase separation



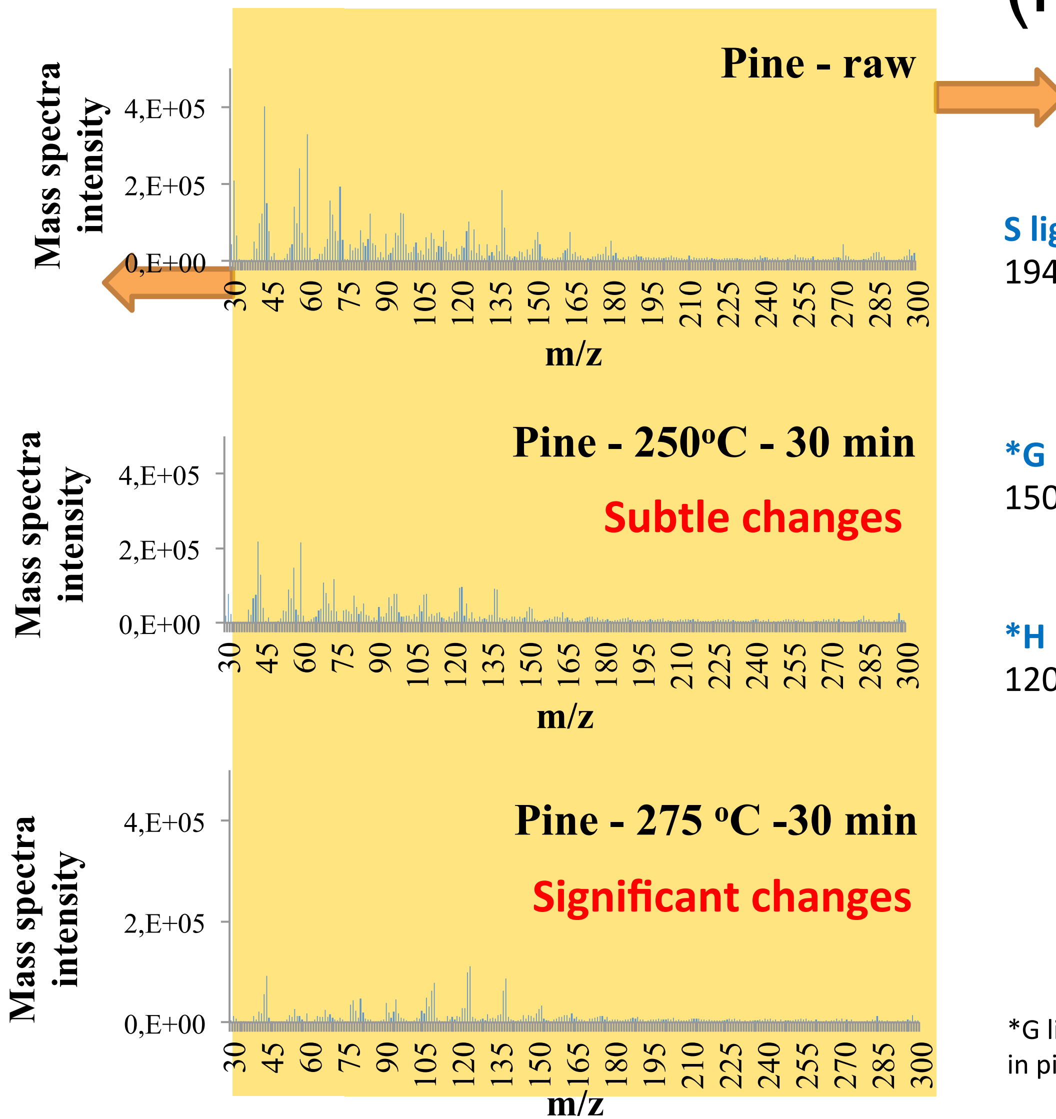
- ***Switchgrass:***
  - ✓ *High annual productivity, High adaptability to low soil quality*
  - ✓ *Easy integration into existing agriculture operations*
- ***Alfalfa:***
  - ✓ *High annual productivity (65 million metric tons production per year)*
  - ✓ *Widely grown (third most widely grown crop in US (2006))*
  - ✓ *Nutrition cycle: leaves can be sold as higher-value animal feed*

NREL Py-MBMS of torrefied wood (m/z 30-300)

Carbohydrate compounds (m/z 43, 60, 73, 85, 114, 126)

Levoglucosan and its fragments (m/z 163, 144, 57, 60, 73, 98)

Furfural derivatives (126, 100, 96)



S lignin (m/z 154, 167, 168, 182, 194, 208, 210)

***G lignin** (m/z 124, 137, 138, 150, 164, 178)

***H lignin** (m/z 94, 106, 108, 120, 150)

*G lignin and H lignin are not shown in pine.

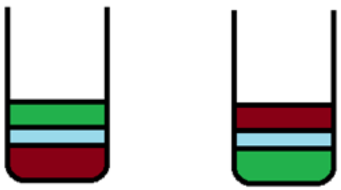
Feedstock properties

Sample	Ash wt%	C wt%	H wt%	N wt%	O wt%
Pine	0.7	48.8	6.6	0.3	43.6
Switchgrass	7.4	44.1	6.1	1.0	41.3
Water leached switchgrass	6.2	45.3	6.6	0.7	41.2
Switchgrass char made at 500°C	22.1	60.4	4.9	1.2	11.4
Alfalfa	10.5	42.1	6.3	3.1	37.9
Water leached alfalfa	4.2	47.4	5.8	3.0	43.8
Alfalfa char made at 500°C	18.5	56.0	4.9	3.2	17.4

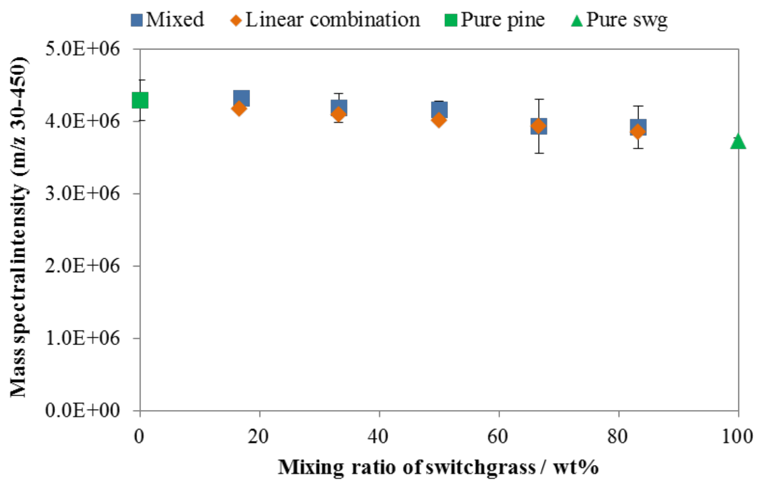
Switchgrass and alfalfa has higher ash content than pine.
Alfalfa has extremely high nitrogen content than the pine and switchgrass.

Pine - water leached switchgrass

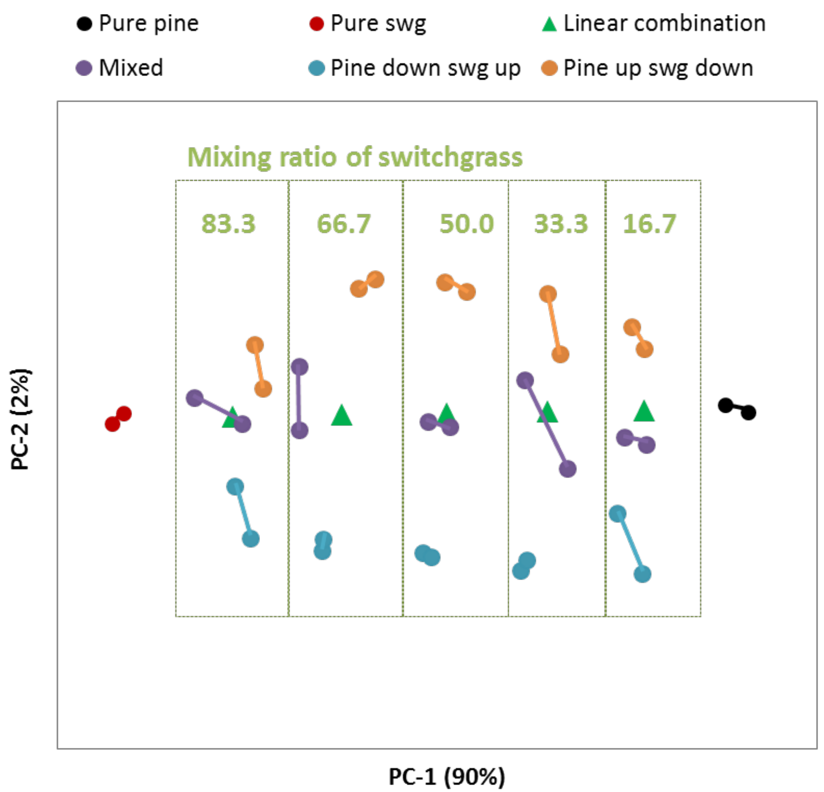
- Pine-switchgrass, No interaction



Vapor yield



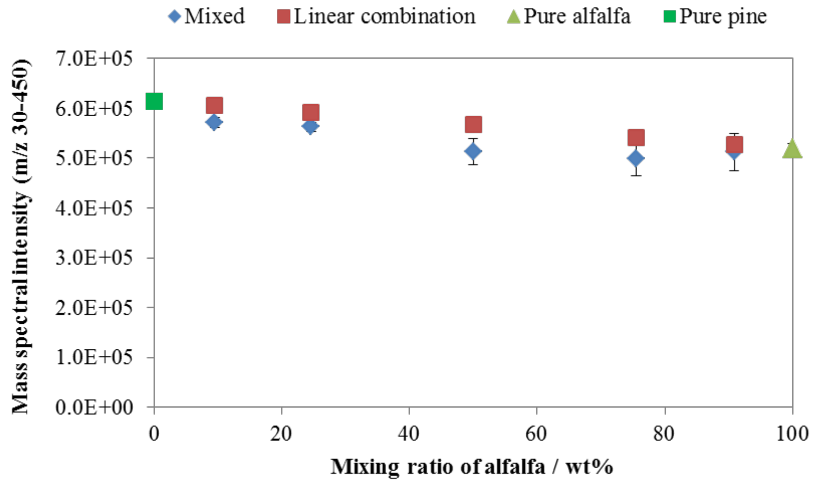
Vapor composition



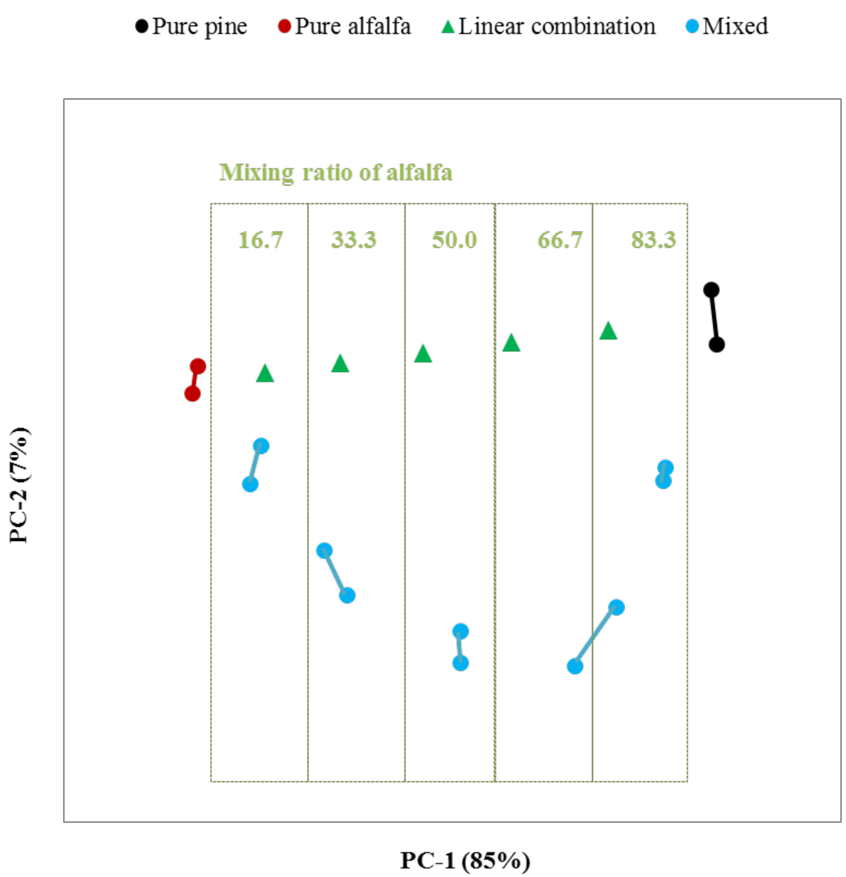
Pine - Non leached alfalfa

- Pine-alfalfa, Interactions due to inorganics

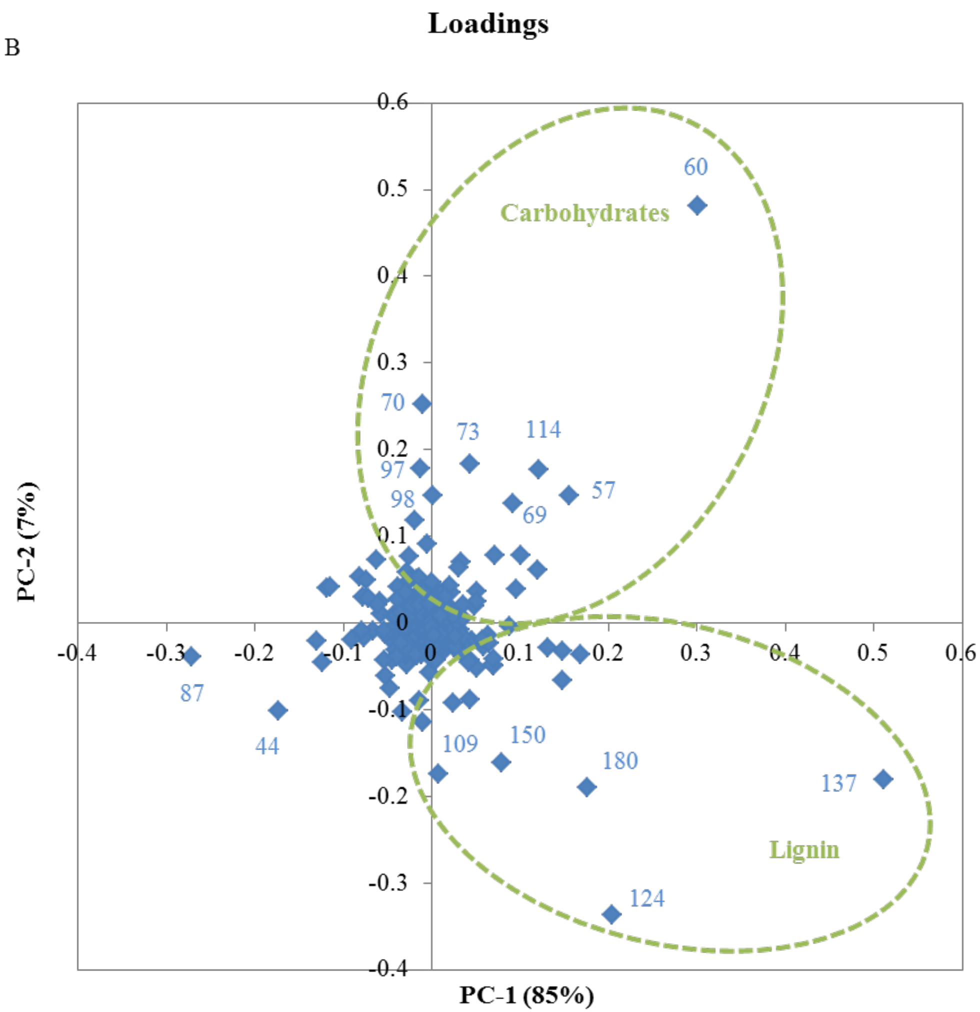
Vapor yield

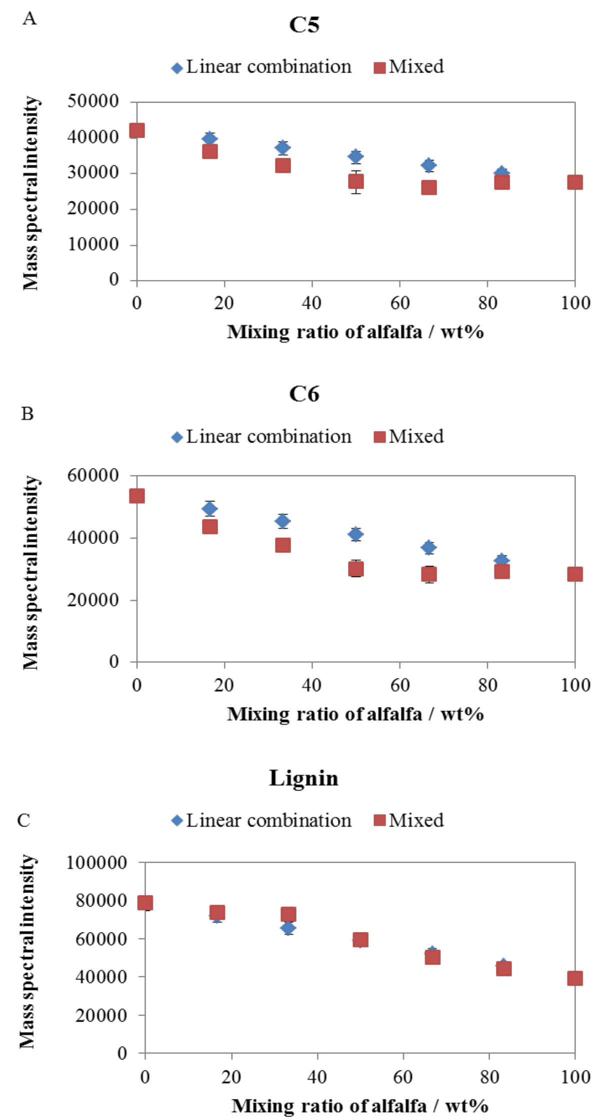


Vapor composition



Interaction due to inorganics
Which biomass component?

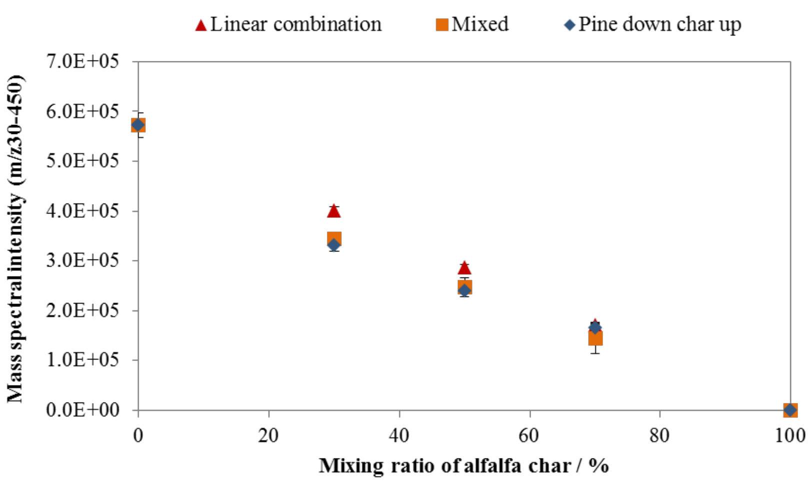




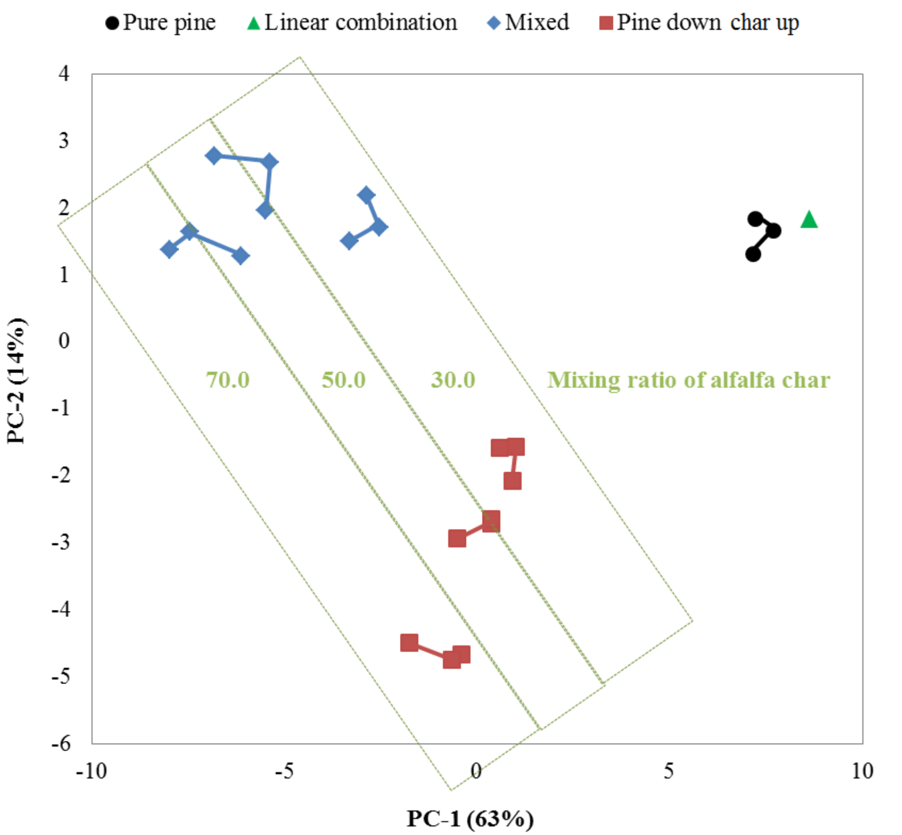
Pine - alfalfa char

Interactions due to inorganics AND char

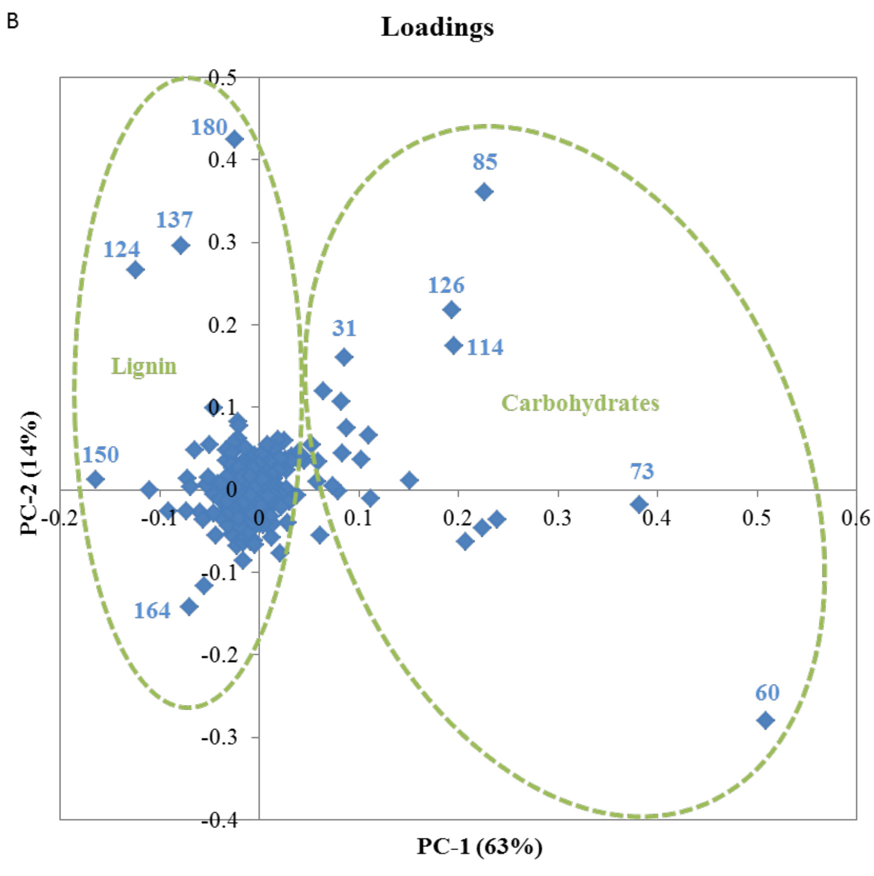
Vapor yield

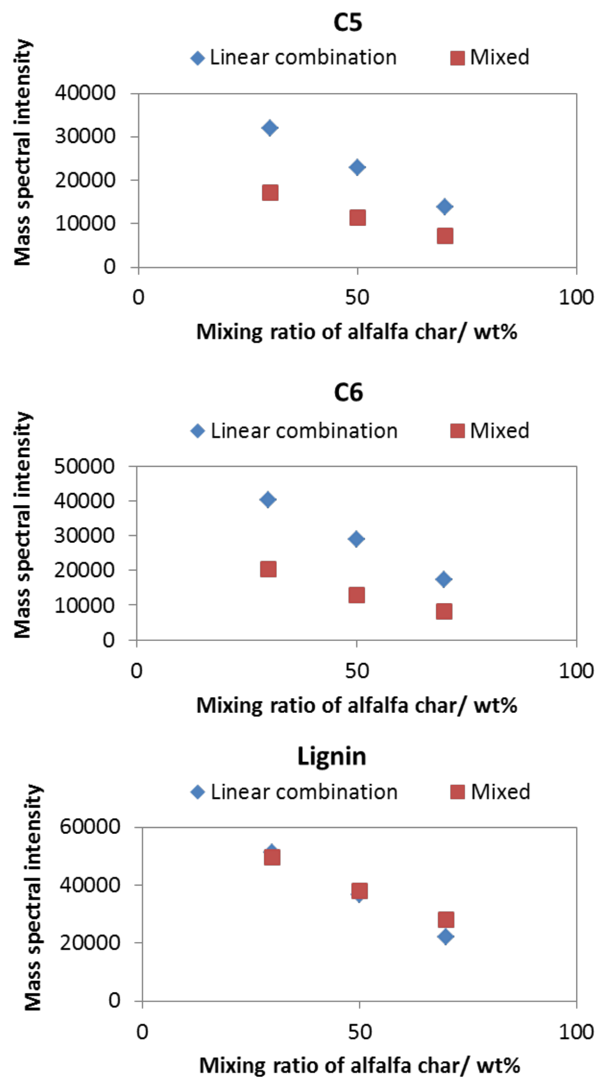


Vapor composition



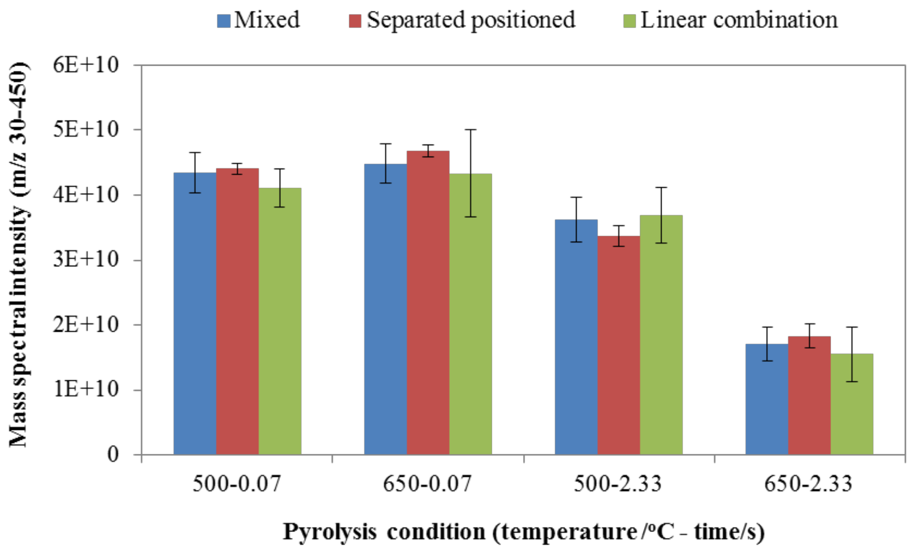
Interaction due to inorganics and char



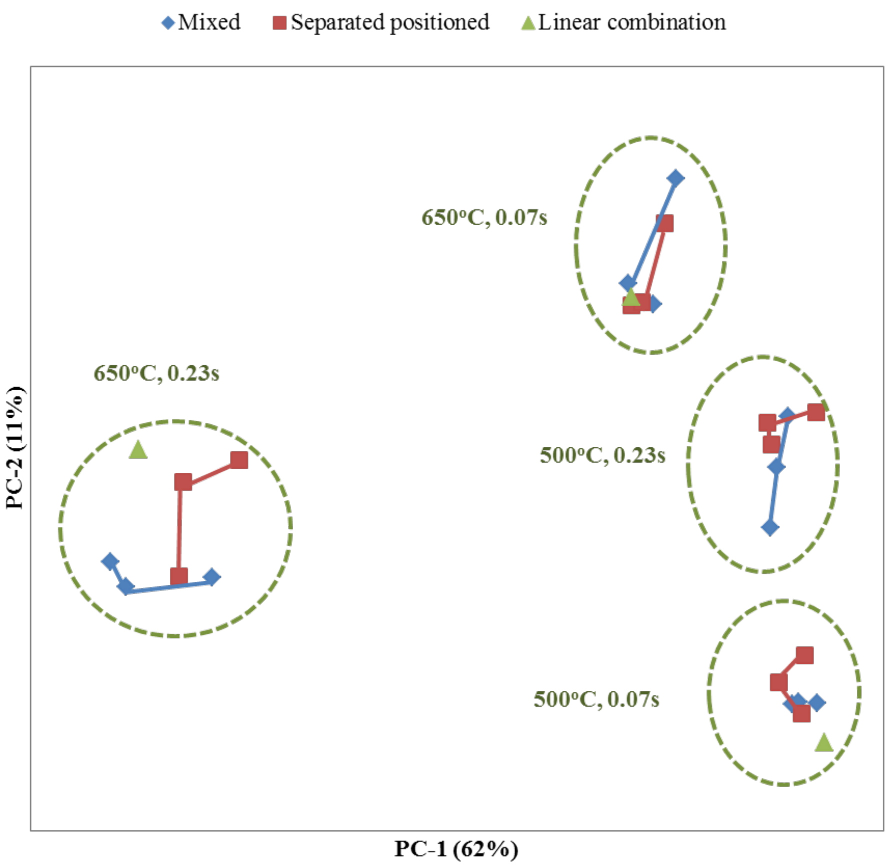


Impact of pyrolysis condition

Vapor yield



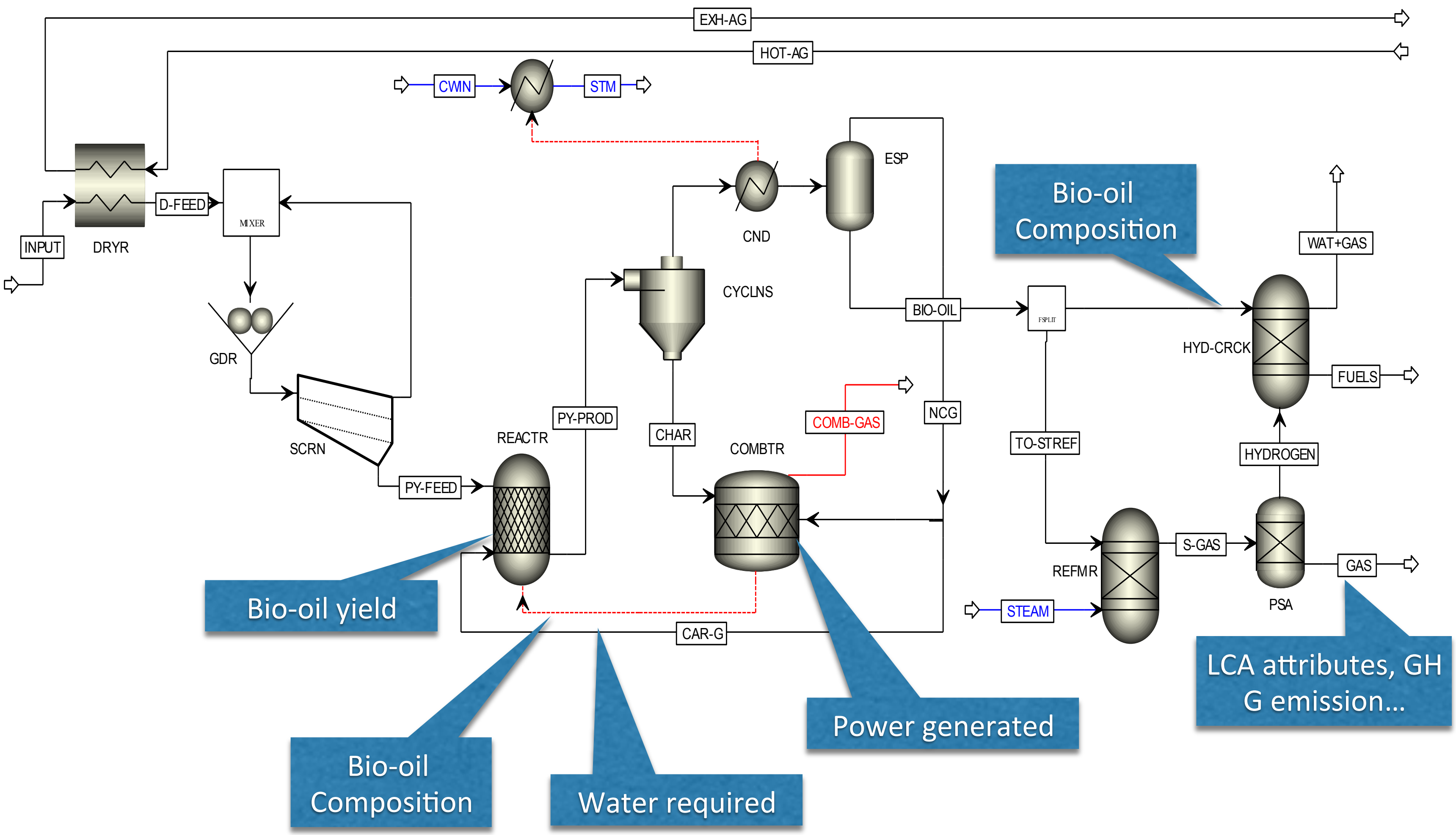
Vapor composition



Effects of Isolated Bio-oil on Composition and Economics/LCA

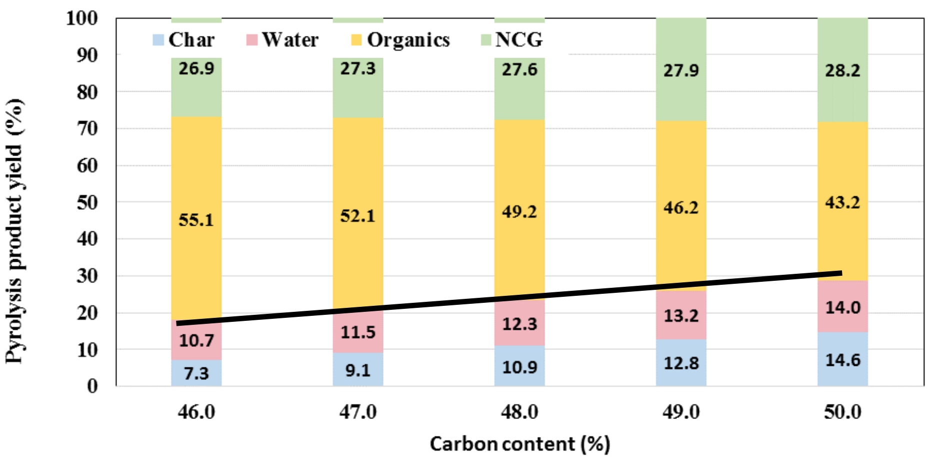
- Collected experimental data from 12 biomass sources – fluid bed, 550^{o}C, bio-oil was a combination of ESP/chilled condenser
- Chemical characterization of fractions, e.g., bio-oil, water, char, gases
- Chemical composition of bio-oil shows complex differences in carbohydrate and lignin derived fragments
- Experimental data used on ASPEN process models

Process Simulation-Schematic

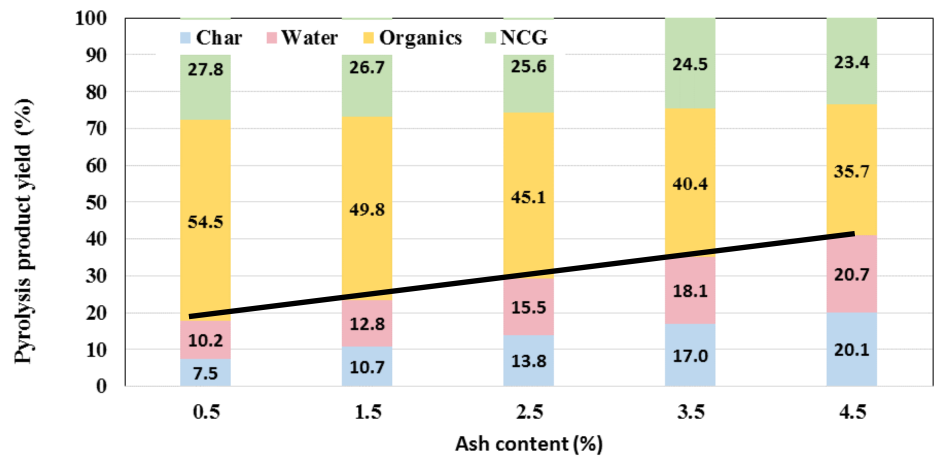


Experimental Data-driven Approach

Ash 1%



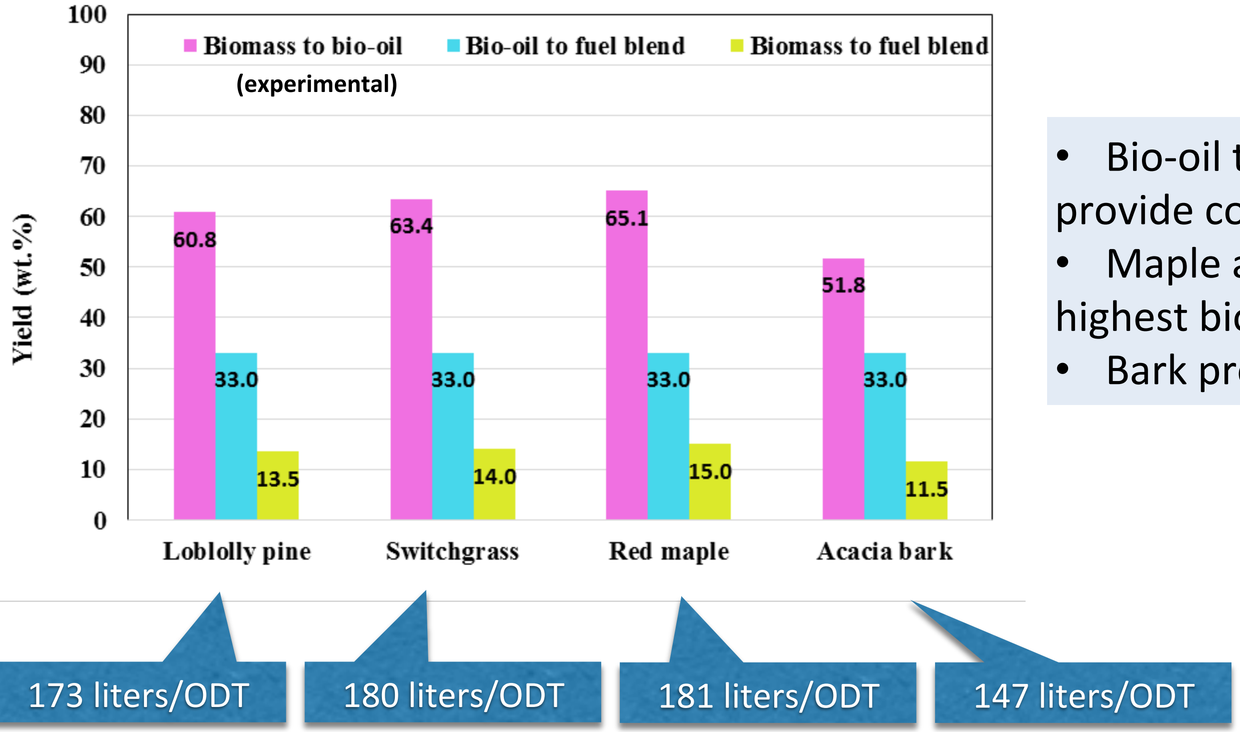
Carbon 47%



- Linear correlation between biomass carbon and ash content, and pyrolysis products.
- Higher yields of the organic liquid fraction is obtained for lower carbon content.
- Ash significantly decreases organic liquid yield, increasing water and polyols.

- **The empirical model shows good correlation to prior work.**

From the process simulation



- Bio-oil to fuel conversion fixed to provide constant plant production volume.
- Maple and switchgrass provided the highest bio-oil yields (organics + water).
- Bark produced lowest yields (52%)

These results highlight the importance of the process simulation and the subsequent techno-economic evaluations!

From the process simulation

Key data…

Biomass	Moisture content (%)	Power deficit kWh	ChW (l/l fuel)	CW (l/l fuel)	M-upW (l/l fuel)	H_2 (MMscfd)
Pine	30	1630	40.9	291	1.4	3.5
SWG	10-20	1470	38.7	265	1.4	3.6
Maple	45	1680	40.1	265	1.4	3.6
Bark	45	1100	42.6	320	1.4	3.1

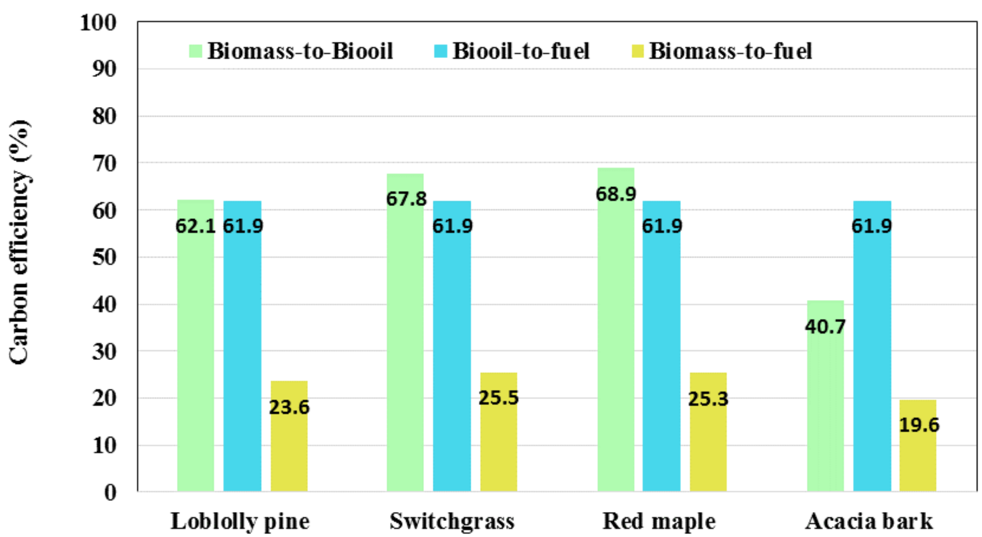
Highest char production

Lowest yields

Less bio-oil to upgrade

Initial MC	Final MC	Air consumed Kg/ODT	ΔH Gcal/h	Gcal/Kg of Evap. H_2O
25 %	7 %	5200	-26	0.005
35 %	7 %	7600	-41	0.005
45 %	7 %	11500	-65	0.005
50 %	7 %	13900	-81	0.005

From the process simulation

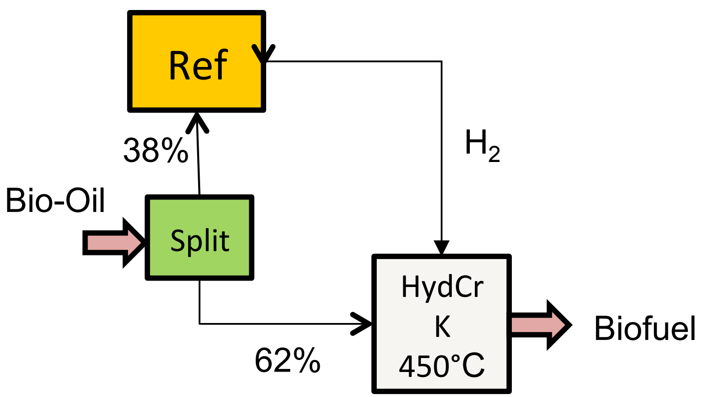


- Biomass-derived intermediates contain far more oxygen than petroleum, resulting in high H_2 demand.
- Oxygen must be removed limiting overall efficiency.

- ~23% carbon efficiency.
- PNNL model - 50% higher yield if using natural gas instead of bio-oil to make H_2.

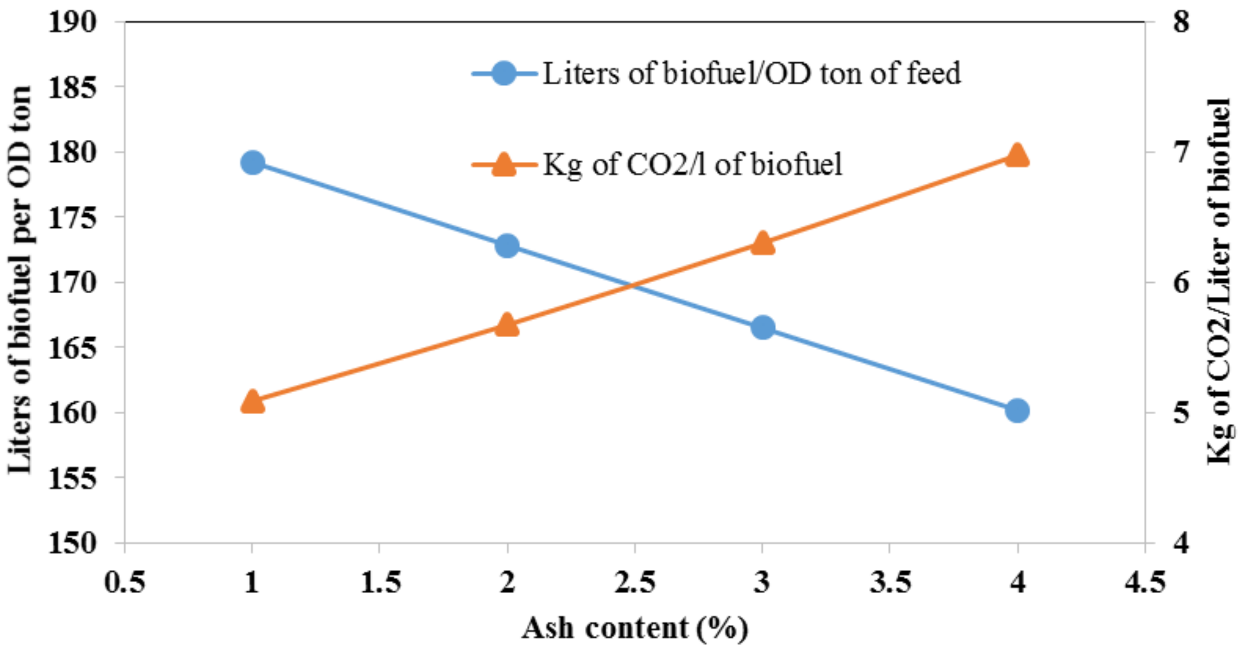
The process configuration plays an important role in final results.

Modeling allows evaluation of many options



Simplified schematic

Impact on GHG emissions



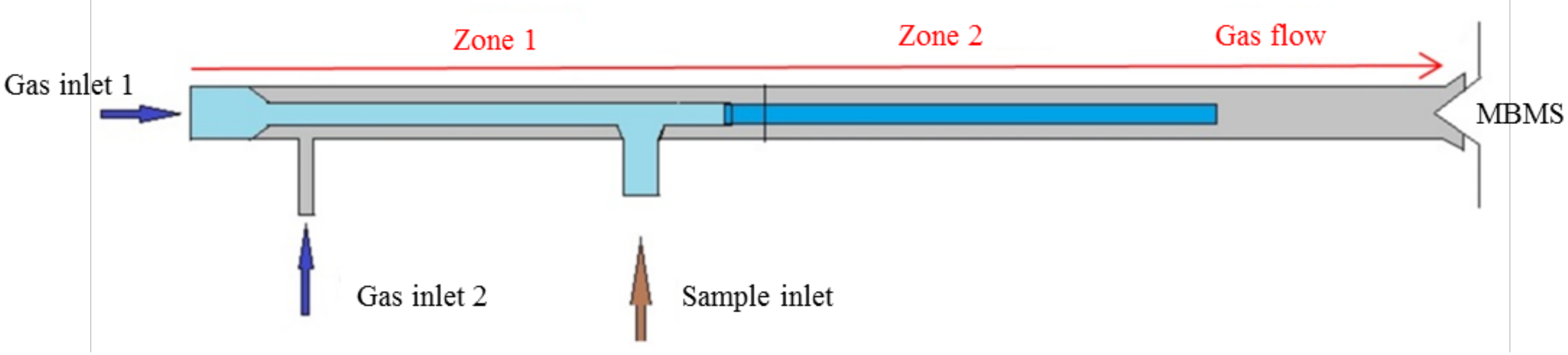
- Two streams in the process dominate GHG emissions; (1) the off-gasses after drying/combustion, and (2) the gasses produced during steam reforming and hydrocracking.
- High ash content contributes to higher GHG emissions. More char combustion required.
- **This engineering process model used as basis for LCA predicting GHG emissions**

Effects of Biomass Source also Impacts Product Composition in Gasification

- Used py-MBMS to study
  - the initial ‘vapors’,
  - the ‘gasification’ of the ‘vapors’, and
  - the ‘gasification’ of the pyrolysis ‘char’
- The effects of biomass source follow even for gasification

Py-MBMS reaction of chars - Experimental

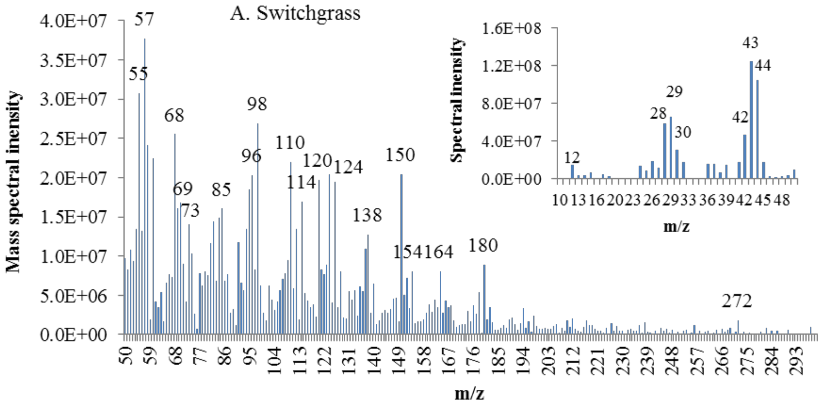
Raw biomass feedstock: switchgrass, alfalfa, pine, oak
Pyrolysis condition: T = 500°C, 700°C
Gasification condition: T = 950°C; Steam = 60 Vol%



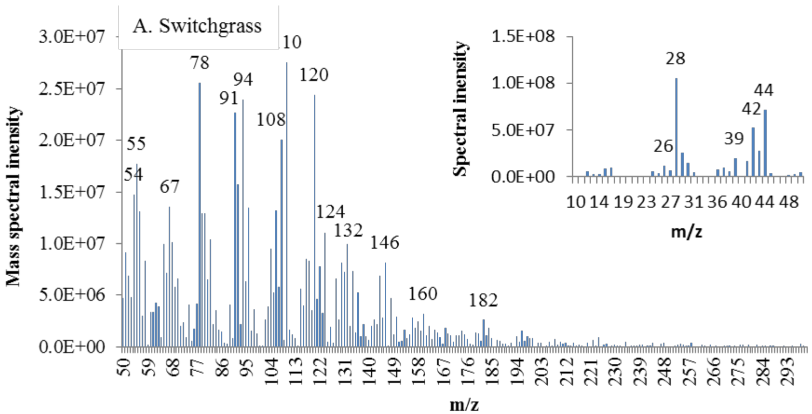
- **Tar A is from gasification of pyrolysis vapor**
  - ✓ Sample inlet: Raw biomass
  - ✓ Zone 1 condition: Pyrolysis condition
  - ✓ Zone 2 condition: Gasification condition
- **Tar B is from gasification of pyrolysis char**
  - ✓ Sample inlet: Biomass char
  - ✓ Zone 1 condition: Gasification condition
  - ✓ Zone 2 condition: Gasification condition

- **Total tar = Tar A + Tar B**

Pyrolysis vapor spectra



Pyrolysis temperature = 500°C



Pyrolysis temperature = 700°C

- **Very Complicated**
- **Very Different**

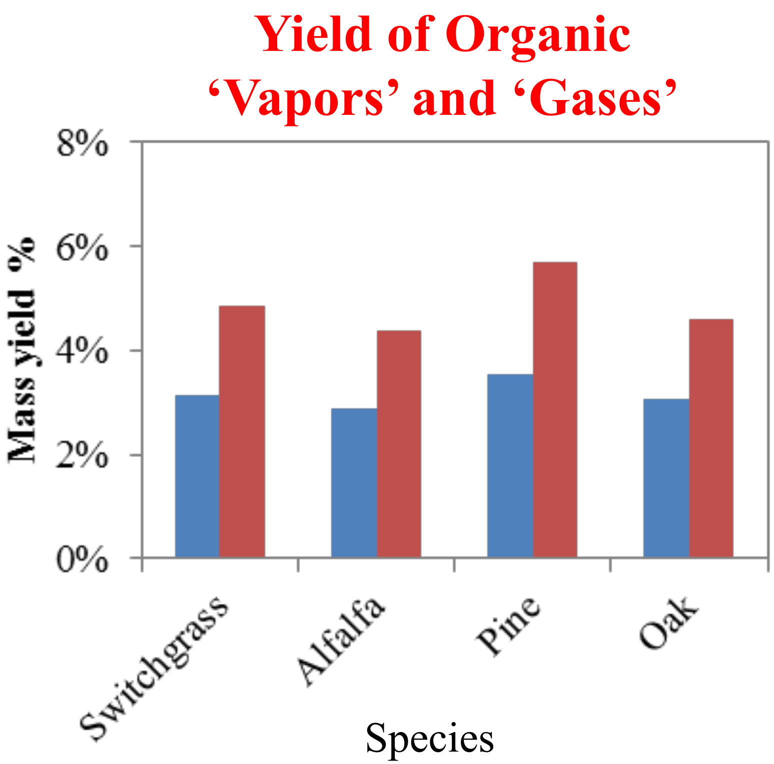
Pyrolysis char fuel properties

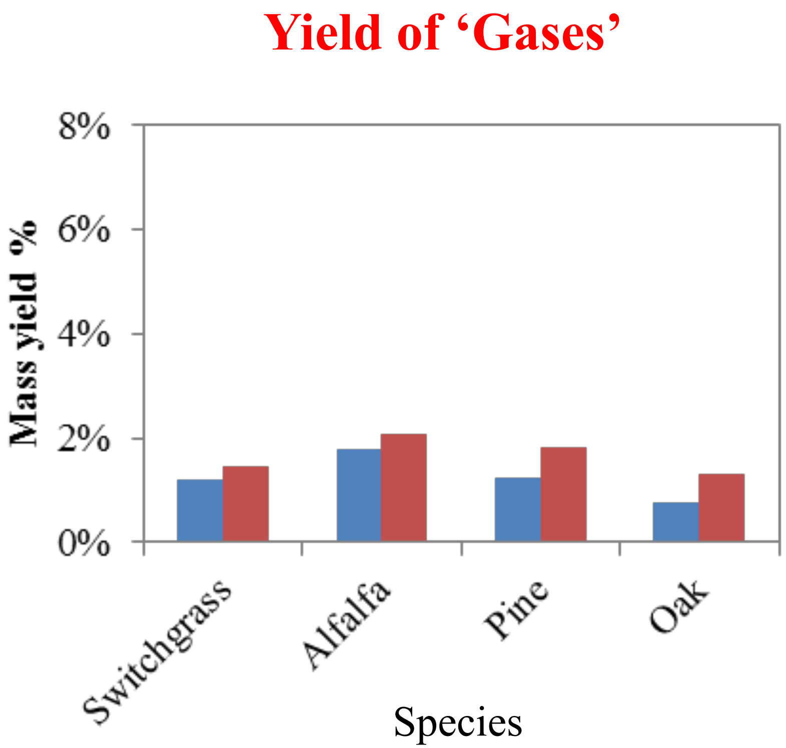
Table 5.2 Ultimate analysis results and ash content of 500°C pyrolysis char

Species	Carbon %	Hydrogen %	Nitrogen %	Oxygen%	Ash %	[a]Nitrogen yield%	[b]Ash yield %
Switchgrass	60.4	4.9	1.2	11.4	22.1	33.8	85.0
Alfalfa	56.0	4.9	3.2	17.4	18.5	36.6	50.0
Pine	77.5	5.5	0.5	14.6	1.9	22.6	63.2
Oak	79.8	4.9	0.2	13.7	1.4	21.7	54.3

[a]Nitrogen yield = Nitrogen content of char x char yield/ Nitrogen content of raw biomass x 100%
[b]Ash yield = Ash content of char x char yield/ Ash content of raw biomass x 100%

Tar yields (Based on raw mass)





Pyrolysis temperature = 500°C; Gasification temperature = 950°C

Pyrolysis temperature = 700°C; Gasification temperature = 950°C

Conclusions

- The source of the biomass does impact the products from TC process
- Bio-oil yield and composition vary with biomass source, particularly sensitive to ash and char
- Bio-oil yield and composition impacts the downstream processes, economics and LCA
- Gasification of vapors and char continue to show the effects of biomass source, e.g., initial composition, ash, and char

Gracias – Thank You!