UNIVERSITEIT GENT

FACULTY OF ENGINEERING AND ARCHITECTURE

PRODUCT DISTRIBUTIONS FROM FAST PYROLYSIS OF 10 ECUADORIAN AGRICULTURAL RESIDUAL BIOMASS SAMPLES

Diana C. Vargas [a,b], SriBala Gorugantu[a], Hans-Heinrich Carstensen [a], Daniela Almeida Streitwieser [b], Guy B. Marin [a], Kevin M. Van Geem [a]*

[a] Ghent University, Laboratory for Chemical Technology, Technologiepark 914, 9052 Gent, Belgium
http://www.lct.UGent.be

[b] Laboratorio de Desarrollo de Energías Alternativas Departamento de Ingeniería Química, Universidad San Francisco de Quito, Casilla Postal: 17-12-841, Quito, Ecuador

*E-mail: Kevin.VanGeem@UGent.be

European Research Institute of Catalysis

Universidad San Francisco de Quito

Introduction

Ecuador's economy is based on the production and export of agricultural products.

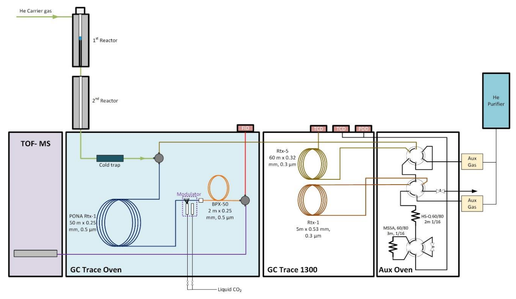
First worldwide producer and exporter of bananas

Eighth largest producer of cocoa

Main crops produced in Ecuador and residues

Crop	Acreage cultivated [ha]	Residues [ton/yr]	Types of residues
African palm	240,333	6,872,469.27	Rachis, fiber and nut shells
Cocoa	507,721	2,015,352	Hulls, pulp, leaves and wood
Coffee	113,029	104,048.31	Hulls, pulp, leaves and wood
Banana	221,775	4,926,095	Raquis, shells, fibers
Rice	411,459	2,106,695	Husk
Sugar cane	106,926	793,283.38	Bagasse, straw
Implanted Forest	148,415	319,000	Straws, roots, bark

Tandem Micro-pyrolyzer setup



Purpose:

- comprehensive analysis of product distribution of fast pyrolysis reactions of polymers including biomass
  - close mass and elementary balances
- determine intrinsic rate coefficients for solid to gas transition
  - avoid transport limitations
- study gas-phase reactions of valuable solid model substances
  - small sample sizes

Detailed features

Analytics section

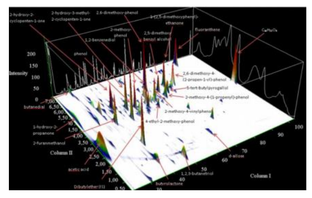
GC×GC - FID/TOF-MS
Simultaneous identification and quantification

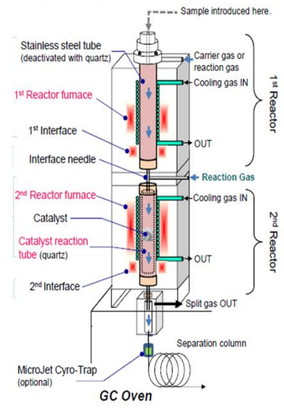
Customized Trace GC 1310 with 3 Detectors
TCD-1
Water, formaldehyde
TCD-2 and PDD
permanent gases incl. H_2
C2- components

Micro-pyrolyzer

- Two stage reactor
- Solid, liquid or gas samples
- Isothermal, linear and stepwise temperature profiles
- Large T-range: 40 - 900 ^{0}C
- Multi-shot sample introduction
- Cryo-trap for fast injection

Comprehensive 2D Gas Chromatography





Motivation of the study

- Agricultural residues are wasted and no alternative treatment other than landfill is considered.
- Residues can be used as feedstock for thermochemical processes.

Biomass

Pyrolysis

Fuels and chemicals

Various biomass are selected based on the amount of residue generated by the harvesting of the crop

Rice husk

Cocoa kernel

Palm kernel shells

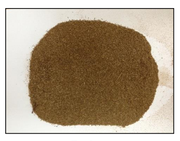
Coffee husk

Biomass characterization

- All biomass samples were characterized to determine:
- Heating value
- Elemental analysis
- Composition of cellulose, hemicellulose and lignin
- Ash content

Sample	C [%]	H [%]	N [%]	O [%]	Ash [%]	Lignin [%]	Cellulose [%]	Hemicellulose [%]
Forestry residue	38.99	3.81	0.30	29.37	24.93	61.77	14.07	4.24
Palm rachis	43.21	5.71	2.32	43.99	3.46	25.9	30.00	5.17
Palm fiber	44.82	5.27	2.52	43.55	3.46	23.7	16.41	14.73
Palm kernel shells	55.89	5.80	0.60	35.75	1.20	40.75	24.79	9.46
Fresh cocoa kernel	50.04	5.47	1.09	41.44	1.16	26.51	17.25	4.32
Rotten cocoa kernel	53.47	5.81	2.41	35.41	2.62	45.06	15.42	6.95
Coffee husks	48.09	5.80	2.36	41.78	1.20	25.09	14.05	16.12
Banana stem	45.47	5.16	1.81	45.11	1.43	16.36	21.68	15.52
Rice husk	33.68	4.81	1.27	19.41	28.24	40.12	34.45	11.80
Sugar cane bagasse	48.48	5.62	1.42	40.64	3.49	32.04	22.41	13.96

Experimental details



Dry biomass

500 µg/cup biomass

200 µg/cup glass wool

cup size

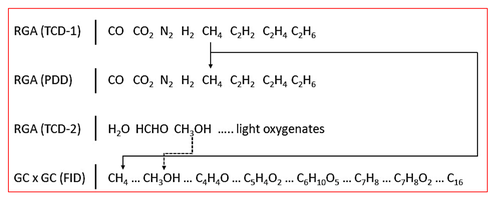
Experiments require very small amounts of substance

Fast pyrolysis conditions

- 1st reactor: 500°C, 550°C, 600°C
- No 2nd reactor
- Carrier flow rate: 210 mL/min
- Cryo-trap: 8 min @ -70^{0}C

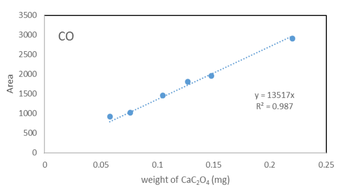
Calibration methodology

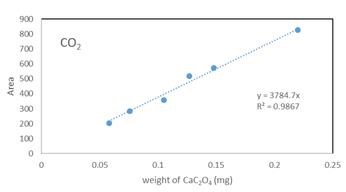
1. **RGA-TCD[1] and -PDD**: All permanent gases are calibrated absolutely,
   - by injecting a standard mixture of C_{2^-} gases.
   - CO and CO_2 are calibrated separately, through CaC_2O_4 decomposition.
2. **RGA-TCD[2]** : Methanol is used as absolute calibration component. Water and other light oxygenates (LO) are quantified relative to methanol.
3. **GCxGC-FID** :
   - CH_4 and methanol data from RGA are used to quantify light hydrocarbons and oxygenates detected on FID.
   - Furan, furfural, methyl furfural, toluene and guaiacol are chosen as absolute calibration components for furans, aromatic hydrocarbons and oxygenates.



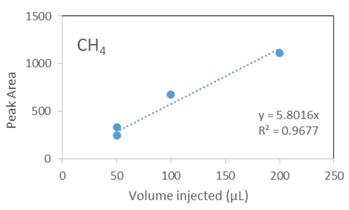
Calibration curves

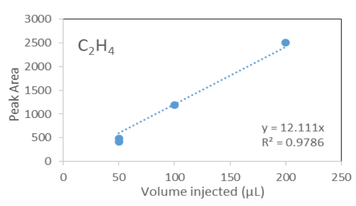
•Calcium Oxalate Calibration: $CaC_2O_4 \rightarrow CaCO_3 + CO\ ; CaCO_3 \rightarrow CaO + CO_2$



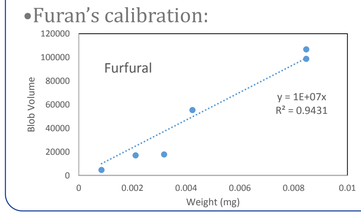


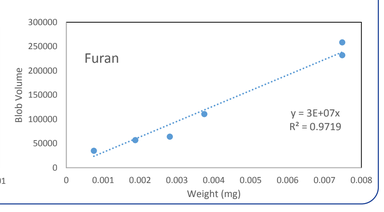
•C_{2^-} Calibration mixture:



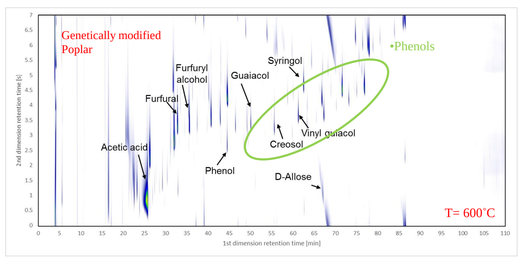


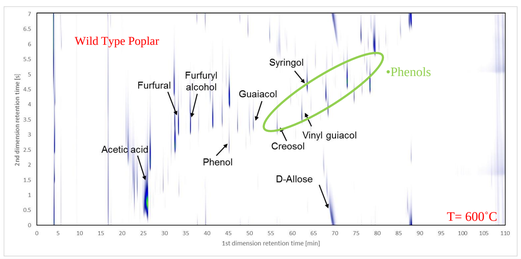
•Furan's calibration:



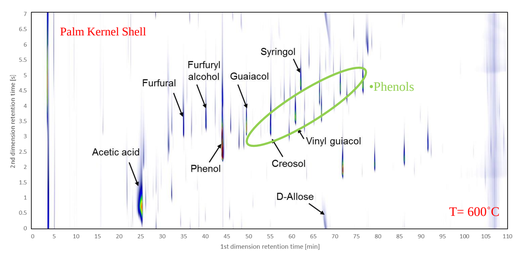


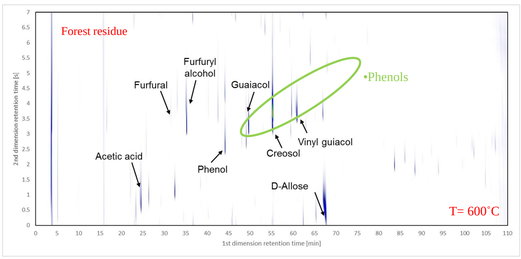
Product distribution





No visible difference in the spectra





Large difference in the amount of phenols and acetic acid produced

Conclusions

- ✓ Product distribution of biomass samples were obtained.
- ✓ Different variations in the elemental composition corresponds to different yields in the pyrolysis product distribution.

Future work

- ➢ Quantification of fast pyrolysis data obtained for 12 biomass types using the calibration factors obtained using the methodology explained
- ➢ Validation of Ranzi's model for fast pyrolysis with the experimental data

Acknowledgements

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