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A novel solution for utilizing liquid fractions from slow pyrolysis and hydrothermal carbonization - Acidification of animal slurry

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A NOVEL SOLUTION FOR UTILIZING LIQUID FRACTIONS FROM SLOW PYROLYSIS AND HYDROTHERMAL CARBONIZATION – ACIDIFICATION OF ANIMAL SLURRY

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SPIRE
Sustainable Process Industry through Resource and Energy Efficiency

VTT

European Commission

MOBILE FLIP

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Mobile and Flexible Industrial Processing of Biomass – MOBILE FLIP

- MOBILE FLIP aims at developing and demonstrating mobile processes for the treatment of underexploited agro- and forest based biomass resources into products and intermediates.
- Applications for solid and liquid fractions derived from torrefaction, pyrolysis and hydrothermal carbonizations (HTC)

Pilot version of mobile pyrolysis unit (RAUSSI OY)

HOW TO USE THE LIQUID FRACTION

?

Liquid fraction from pyrolysis

Willow (*Salix*), Scots pine bark, Scots pine forest residue, wheat straw

Gas for energy

Bench scale pyrolysis unit at VTT

Liquid

Temperature 280 → 375 / 475 ˚C
Liquid fraction for energy(?)

Temperature < 280 ˚C
“Tar free” acidic liquid fraction

Biochar

Environ Sci Pollut Res
DOI 10.1007/s11356-017-8823-x

ENVIRONMENTAL FUNCTIONS OF BIOCHAR

Quantitative characterization of pore structure of several biochars with 3D imaging

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Liquid fraction from HTC

10-l Hastelloy C276 stirred autoclave reactor at VTT

- HTC liquid derived from four sequential runs
  - 260 ˚C, 60 min, 6 h
- The same liquid was recycled in each run
  → Concentration of liquid
- Raw material
  - Willow (*Salix*)

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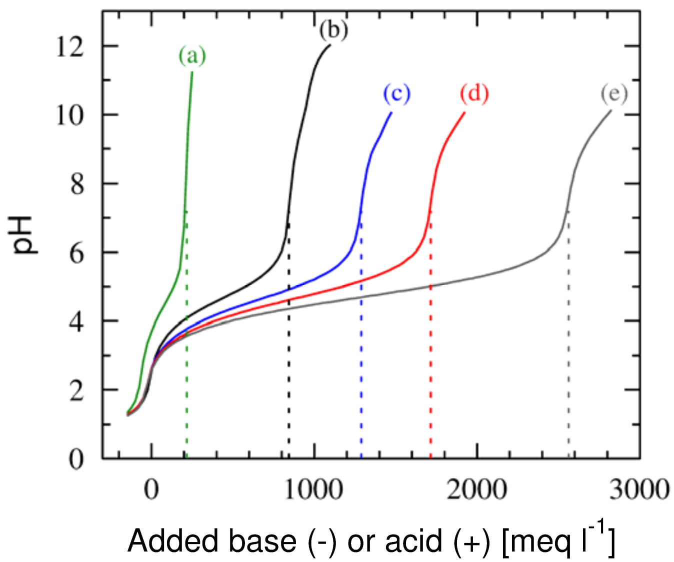
Liquid characterization

- Titration curves over pH range 1.3 to >10
  - Total acidity
- Short chain acids were measured
  - P/ACE MDQ capillary electrophoresis (CE)

Total acidity of HTC and slow pyrolysis liquids



Titration curves: HTC willow (a) Scots pine bark (b), Scots pine forest residues (c), wheat straw (d), and willow (e). Dotted lines indicate the equivalent point for each liquid

- Willow → highest total acidity
  - 2560 meq l^{-1}
- Straw > Scots pine park > forest residue
- HTC liquid had lowest total acidity
  - 220 meq l^{-1}

The acid composition of HTC and slow pyrolysis liquids

Liquid	Concentration (g l^{-1})							
	Acetic acid	Lactic acid	Glycolic acid	Levulinic acid	Succinic acid	Butyric acid	Propionic acid	Formic acid
HTC willow	12 (71)	3.3 (13)	2.2 (10)	0.5 (1.5)	0.3 (1.8)	0.3 (1.2)	0.2 (1.0)	0.1 (0.8)
Pyrolysis								
Willow	150 (93)	0.7 (0.3)	1.6 (0.8)	0.2 (0.1)	0.2 (0.1)	0.3 (0.1)	2.3 (1.2)	5.3 (4.3)
Scots pine bark	48 (85)	0.6 (0.7)	1.4 (2.0)	0.2 (0.2)	0.1 (0.2)	0.4 (0.5)	1.3 (1.9)	4.3 (9.9)
Scots pine forest residue	70 (83)	0.9 (0.7)	1.8 (1.7)	0.1 (0.1)	0.1 (0.1)	0.4 (0.3)	2.9 (2.8)	7.0 (11)
Wheat straw	92 (86)	1.4 (0.9)	1.8 (1.3)	0.9 (0.4)	0.1 (0.1)	0.3 (0.2)	6.8 (5.2)	4.6 (5.6)

Contribution of each acid to the total acidity (%) is given in parenthesis

- Pyrolysis: Acetic acid > Formic acid
- HTC: Acetic Acid > lactic and glycolic acid
  - Low concentrations!

Acidification of animal slurry

- WHY: to reduce nitrogen losses from livestock production
- HOW: Addition of acids to manure lowers ammonia emissions
- BENEFITS:
  - Farmer → better nitrogen use efficiency
  - Reduced ammonia emissions
    - threat for humans and environment
- **Can liquids derived from pyrolysis and HTC replace strong sulfuric acid used currently?**

Photos: Paula Biveson and Henning Foged, Baltic Slurry Acidification

Simple experimental setup

- How much pyrolysis and HTC liquid is required to lower slurry pH to 5.5?
- Pig and cattle slurry
  - Initial pH 8.2 and 7.6
  - Addition of acidic liquid to slurry until pH 5.5 was reached
- 1 HTC liquid and 4 liquids derived from pyrolysis

- Concentrated sulfuric acid as a control (H_2SO_4 >95 %)
  - “business as usual”

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Results

- The amounts of pyrolysis liquids needed was roughly 20- to 60-fold compared to sulfuric acid
- Performance of liquid derived from Willow was the most promising
- Liquid from HTC process was too dilute

	Added volume (l t^{-1})					
	Sulfuric acid	Scots pine bark	Scots pine forest residue	Wheat straw	Willow	HTC
Pig slurry						
pH 6.0	1.1	69	44	30	21	258
pH 5.5	1.3	85	58	42	29	376
Cattle slurry						
pH 6.0	3.1	142	98	77	51	532
pH 5.5	4.1	221	148	110	76	868

Possibilities of Using Liquids from Slow Pyrolysis and Hydrothermal Carbonization in Acidification of Animal Slurry

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Conclusions

- Use of pyrolysis liquids in acidification of manure is possible
- Whether it is economically and environmentally feasible is worth of further studies
  - Search for financing and interested companies in progress
- Process optimization → more concentrated acid fraction?
- Concept does not aim to produce “ a high value added product”
  - Aim is to get rid of pyrolysis liquid with low cost
  - Solution for remote areas where?
- Higher value applications for liquids are needed!

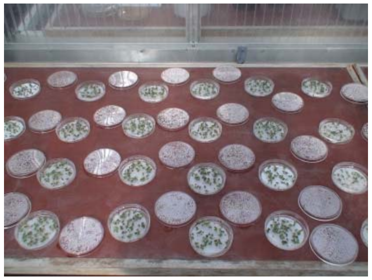
Next step: Pyrolysis liquids in plant protection

Laboratory and greenhouse experiments

repell
ent

insect
icide

Herbi
cide



Manuscript: "*Plant based pyrolysis liquids as herbicide, insecticide and mollusk repellent*"

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