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Co-pyrolysis of animal manure and plastic waste via TG-FTIR analysis

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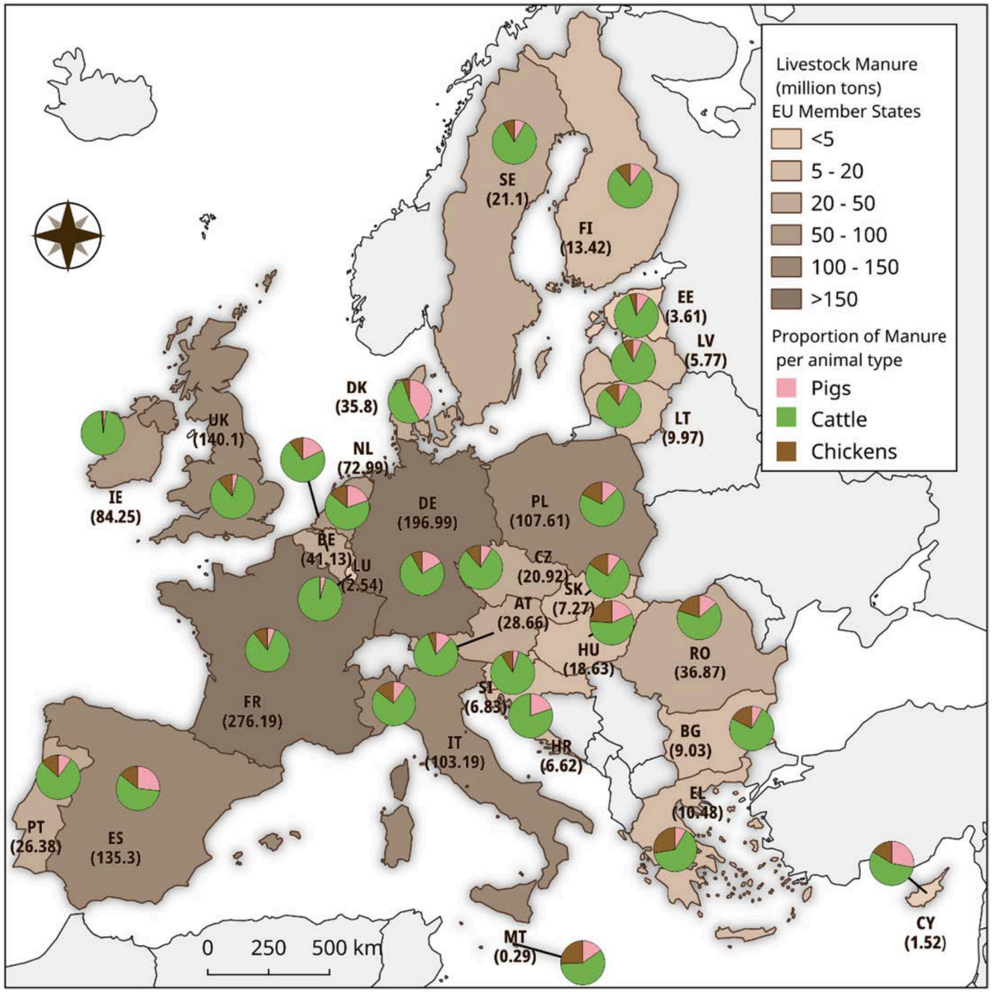
Corfu 2022

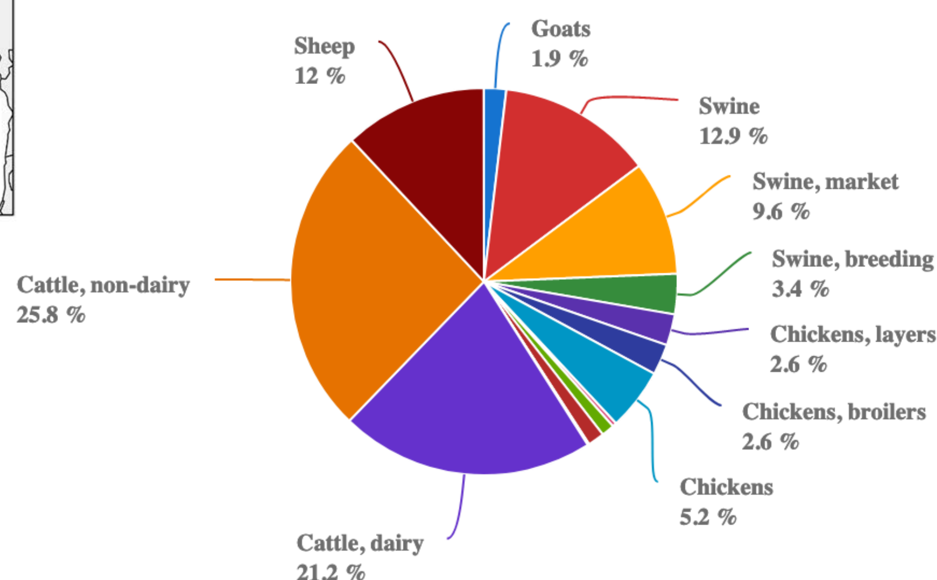
Annual manure production (million tonnes) in Europe



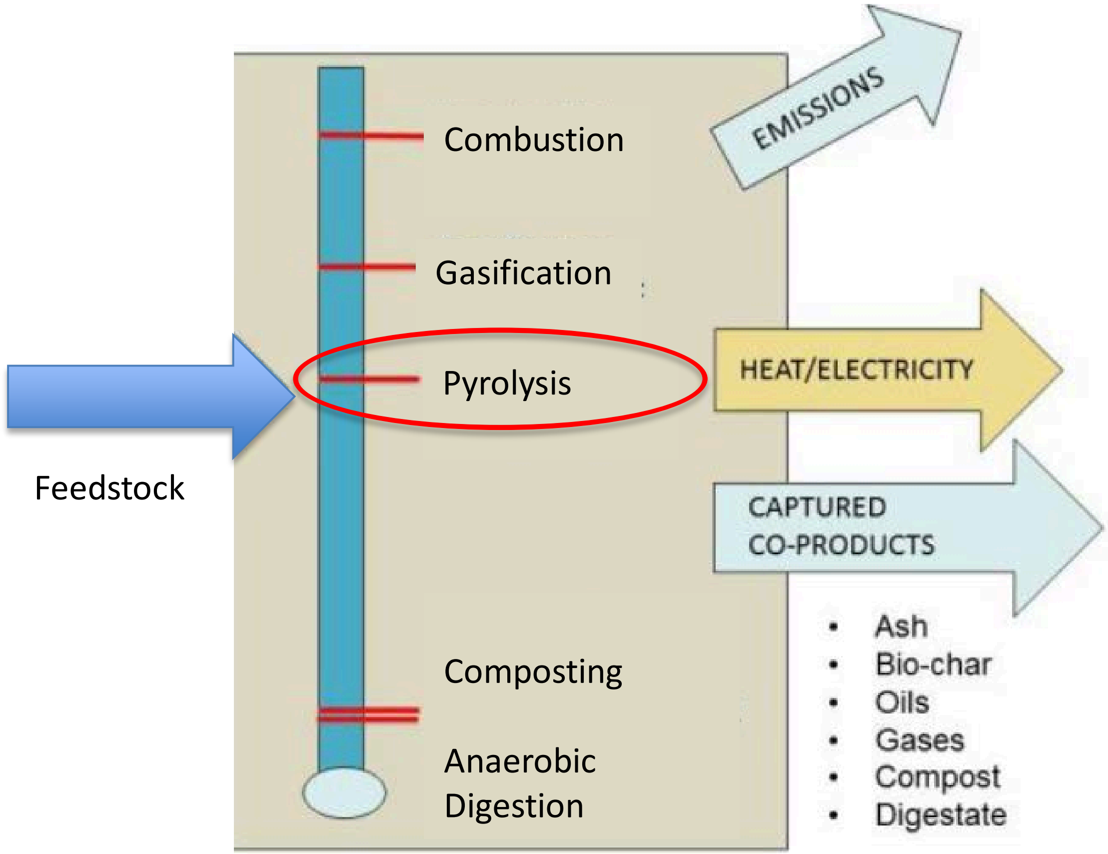
J. Koninger, E. Lugato et al. Manuere managament and soil biodiversity. Towards more sustinable food systems in the EU, Agricultural Systems, 194,2021, 103251

In the European Union (EU-27) and UK, animal farming generated annually more than **1.4 billion tonnes** of manure during the period 2016–2019.

Amount excreted in manure (N content), Cattle + (Total) by continent (2000 – 2019) (FAOSTAT)



Thermo-chemical conversion



Motivation of study

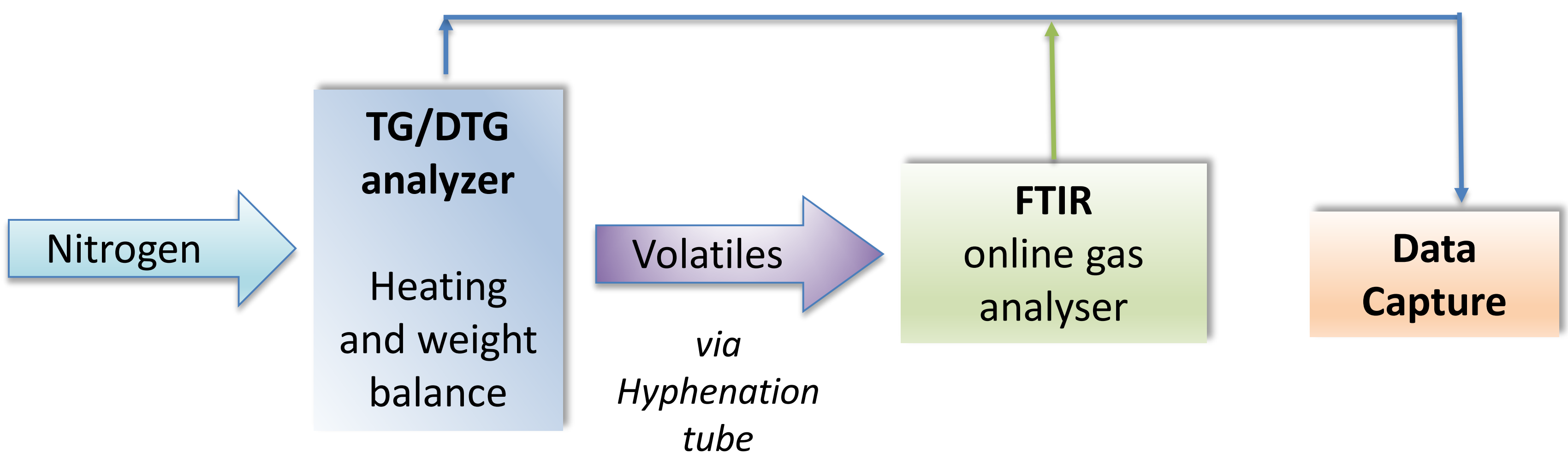
Materials

Animal manure (BULL)

Plastic waste
Polyethylene (PE)

The aim of the work is to study thermal decomposition **of blends of animal manure and plastic waste** in pyrolysis process using micro-thermal analysis techniques.

Thermogravimetry (TG-DTG) coupled with Fourier transform infrared spectroscopy (FTIR) were used to investigate the synergistic effects during the process on the thermochemical conversion of waste.



Materials

In order to identify samples individual symbols were attributed to them:

Raw materials

- animal waste (**BULL 100**)
- plastic waste (**PE 100**)

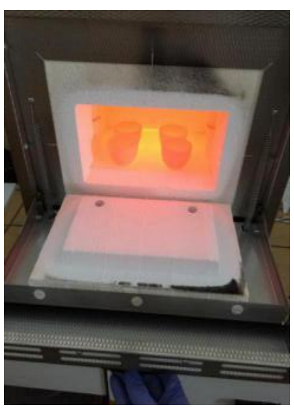
Blends

- animal waste 90% and plastic waste 10% (**PE 10**)
- animal waste 80% and plastic waste 20% (**PE 20**)

Methods

The energy parameters:

- **moisture -** PN-EN ISO 18134
- **ash -** PN-EN ISO 18122 and PN-ISO 117
- **volatile matter -** PN-EN ISO 18123
- **elementary analysis** using Vario Macro Cube analyser 2.
- **higher heating value (HHV)** with the use of the IKA Calorimeters C 200 according to PN-EN 14918:2010 and PN-ISO 1928 standard



Methods

2. The simultaneous thermal analysis TG/DTG was carried out in NETZSCH STA 449 F3 Jupiter device coupled with FTIR spectrophotometer (Tensor 27, Bruker).

- 20 mg of air-dried material
- a dry nitrogen atmosphere with the gas flow of 30 mL/min (protective) and 50 mL/min (purge).
- temperature up to 1,000°C
- heating rate: 10 K/min
- the IR spectra were recorded in the spectral region of 600–4000 cm^{-1} at a resolution of 4 cm^{-1}.
- The obtained spectra were evaluated in the spectrometer database (Opus 8.5, Brucker Optiv GmbH)) to assign individual spectra to gas components in accordance with Beer’s law.

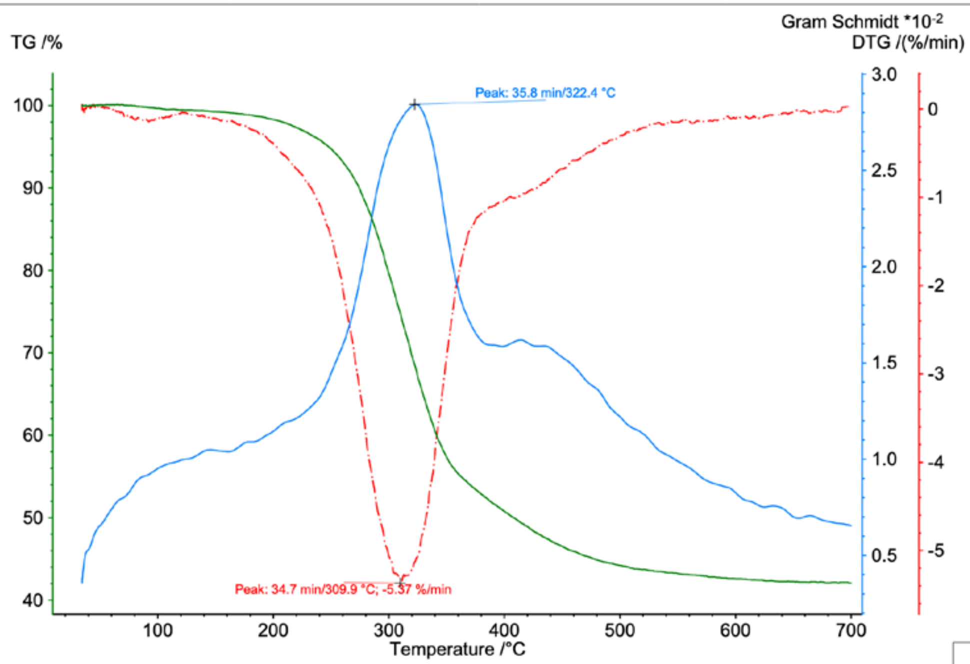
Results

The proximate and ultimate analysis

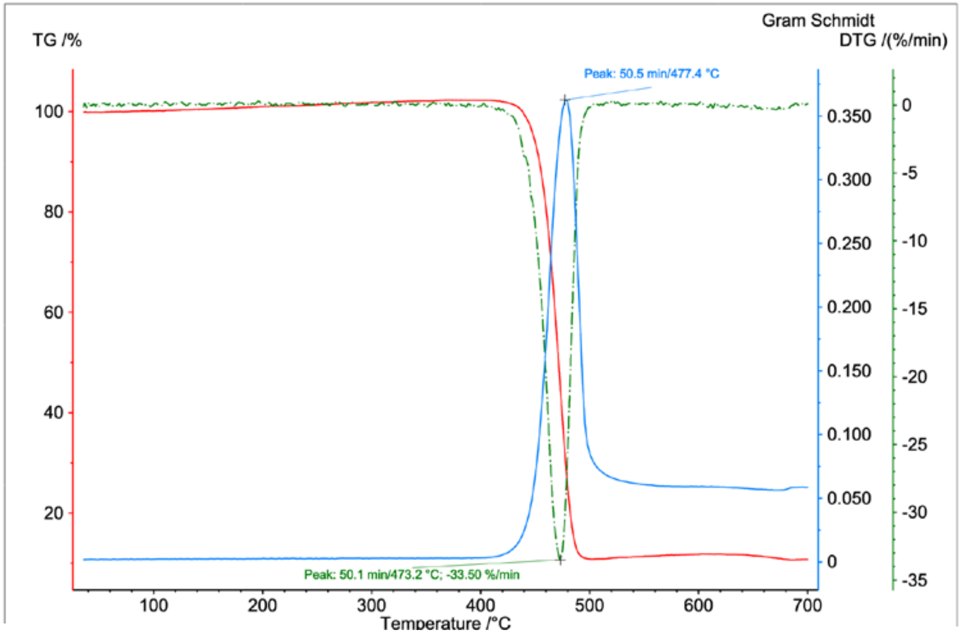
Samples	Proximate analysis wt%				Ultimate analysis wt%					O/C	H/C	HHV MJ/kg
	Moisture	Ash d.m.	VM d.m.	Fixed carbon d.m.	C d.m	H d.m	N d.m	S d.m	O d.m			
BULL 100	9.44	11,61	71.50	7.45	45.62	6.30	2.61	0.19	45.28	0.992	0.138	**17.27**
PE 100	0.18	4.40	94.51	0.91	85.88	14.29	0.00	0.85	2.98	0.046	0.174	**43.64**
PE 10	7.53	9.81	70.10	12.56	45,61	6.65	2.13	0.198	45.41	0.990	0.145	**20.07**
PE 20	6.58	10.74	71.64	11.04	49.97	7.57	1.92	0.178	40.36	0.808	0.151	**22.45**

TG/DTG curves:

Animal waste (BULL 100)

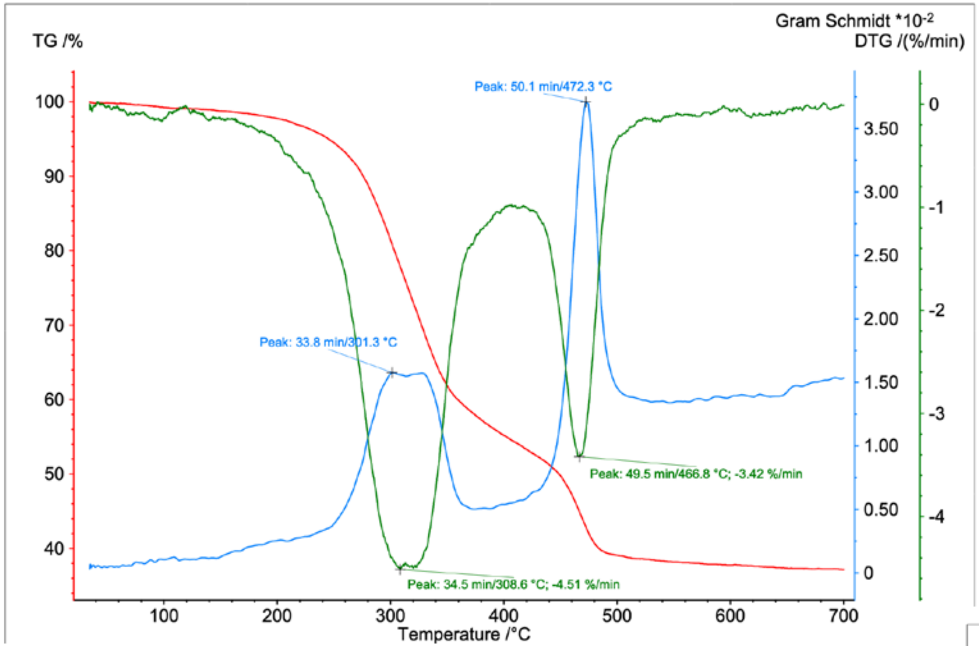


Plastic waste (PE 100)

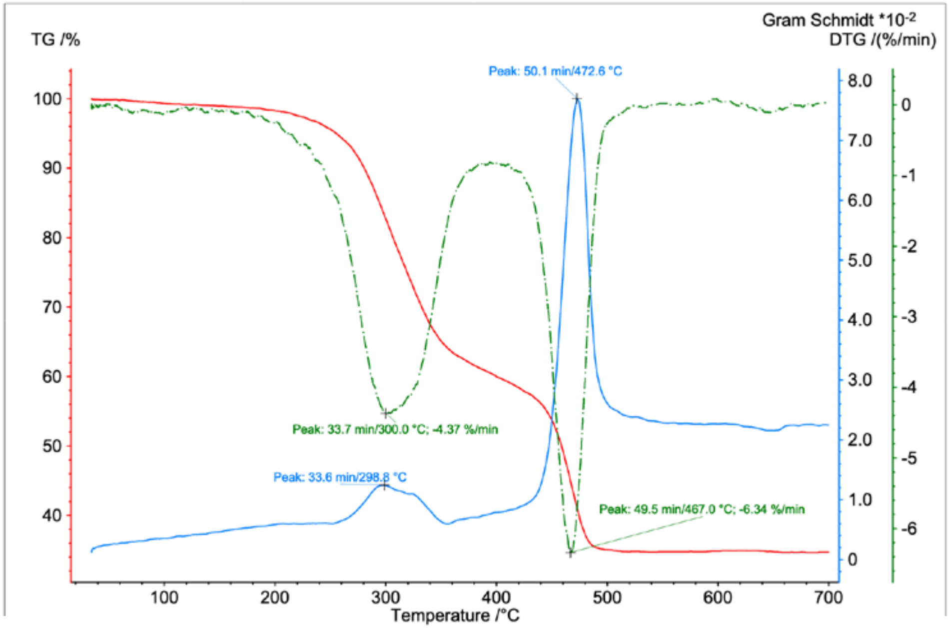


TG/DTG curves:

PE 10



PE 20



Individual stages of pyrolysis

Sample	Stage I	Stage II	Stage III
	°C	°C	°C
BULL 100	55-124	124-390	390- 600
PE	-	419-496	-
PE10	55-120	120-408	408-600
PE20	55-119	119-394	394-600

Pyrolysis parameters and synergistic effect of co-pyrolysis

Comprehensive pyrolysis index

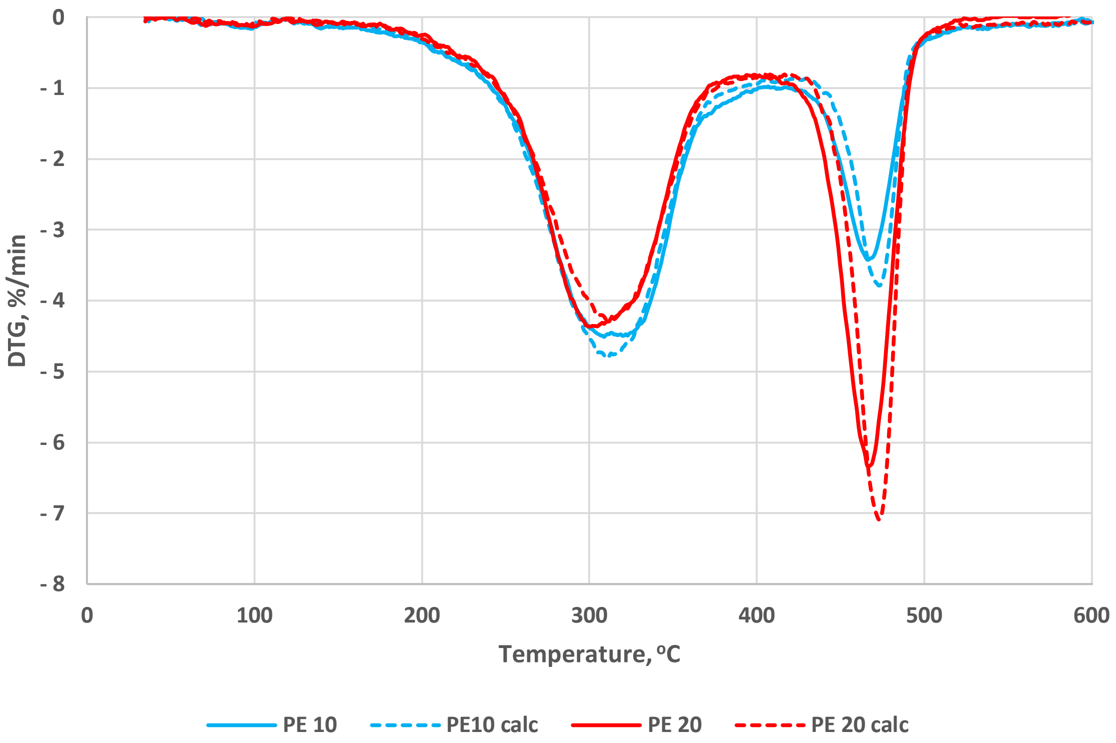
$$CPI = \frac{-(R_p \cdot R_m) \cdot m_\infty}{T_i \cdot T_p \cdot \Delta T_{1/2}}$$

where:
T_i - initial devolatilization temperature
T_p- peak temperature
m_∞ - weigh loss: m_∞ - m_f
$\Delta T_{1/2}$ - temperature interval when $R/R_p=1/2$
$-R_p$ - maximum pyrolysis rate
$-R_m$ - average weight loss rate
R_e - residual mass at the end of the reaction

Pyrolysis parameters

Symbol	Parameter	Unit	BULL100	PE100	PE10	PE20
Ti	initial devolatilization temperature	ºC	**257.7**	**451.6**	**260.7**	**258.2**
Tp	peak temperature	ºC	309.9	473.2	308.6	300
-Rp	max pyrolysis rate	%/min	5.37	33.5	4.51	4.37
1/2Rp			2.68	16.75	2.25	2.185
-Rm	average weight loss rate	%/min	-1.08	-1.63	-1.16	-1.21
Re	residual mass at the end of the reaction	%	**42.60**	**11.77**	**37.77**	**34.85**
m_∞	Mass at the end of proces	%	0.43	0.12	0.38	0.35
DT1/2		ºC	268.8	457.8	268.8	268.8
CPI 600	comprehensive pyrolysis index	**10^{-6} $\%^2/(min^2\ C^3)$**	**0.155**	**0.493**	**0.160**	**0.166**

Synergy effect of measurement and calculation

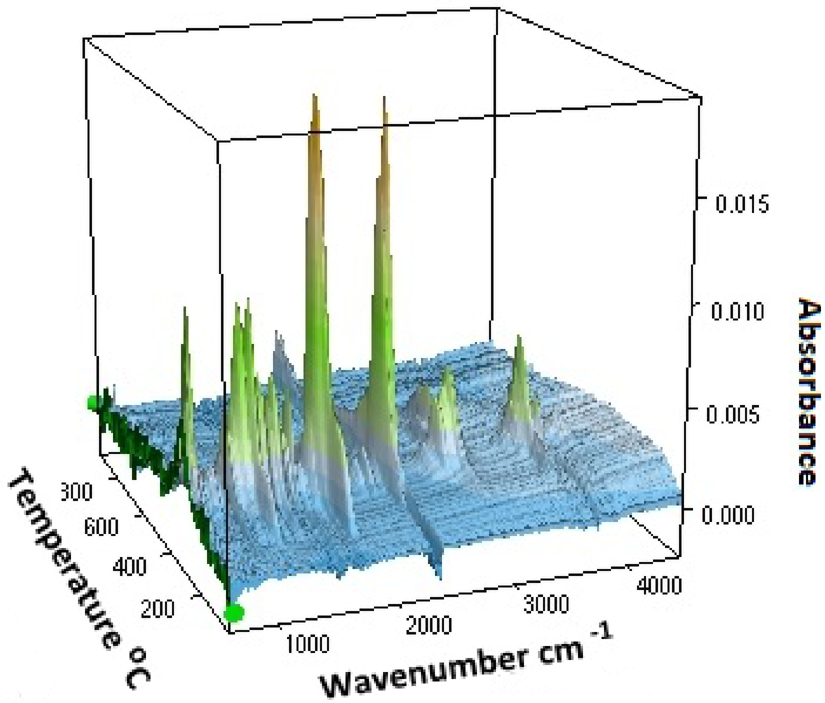


$W_{cal} = X_1W_1 + X_2W_2$

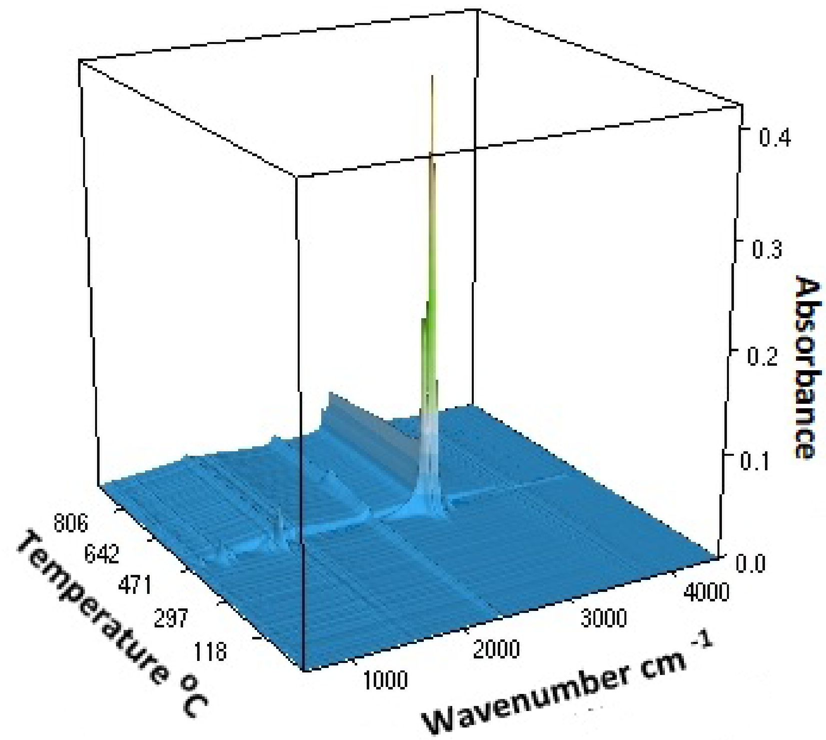
where X_1 and X_2 are the mass fraction of BULL and PE in the blend
W_1 and W_2 are the weight % from DTG of BULL and PE, respectively.

FTIR of raw materials

Animal waste (BULL)

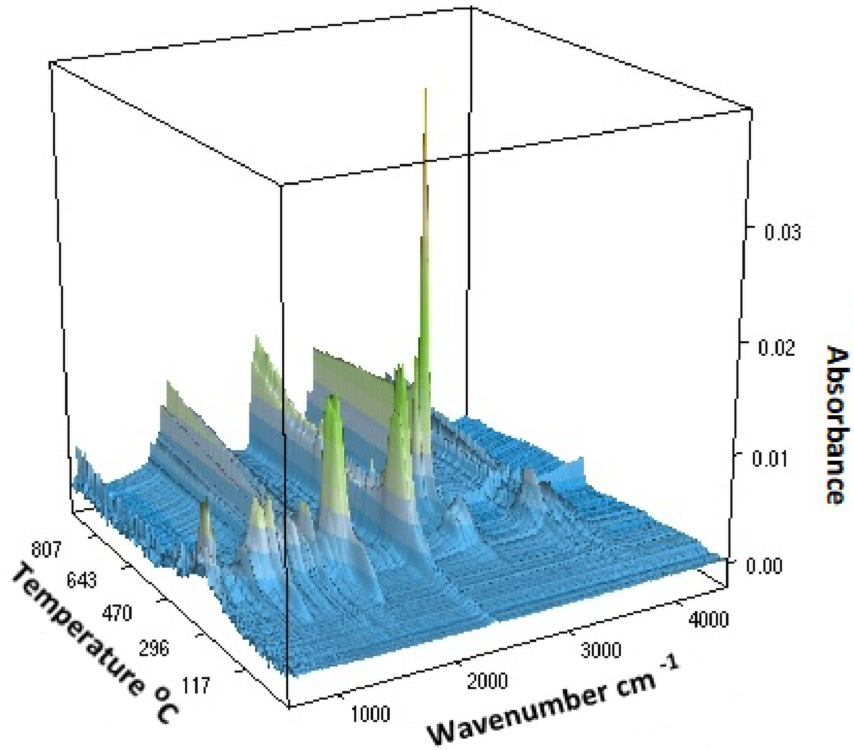


Plastic (PE)

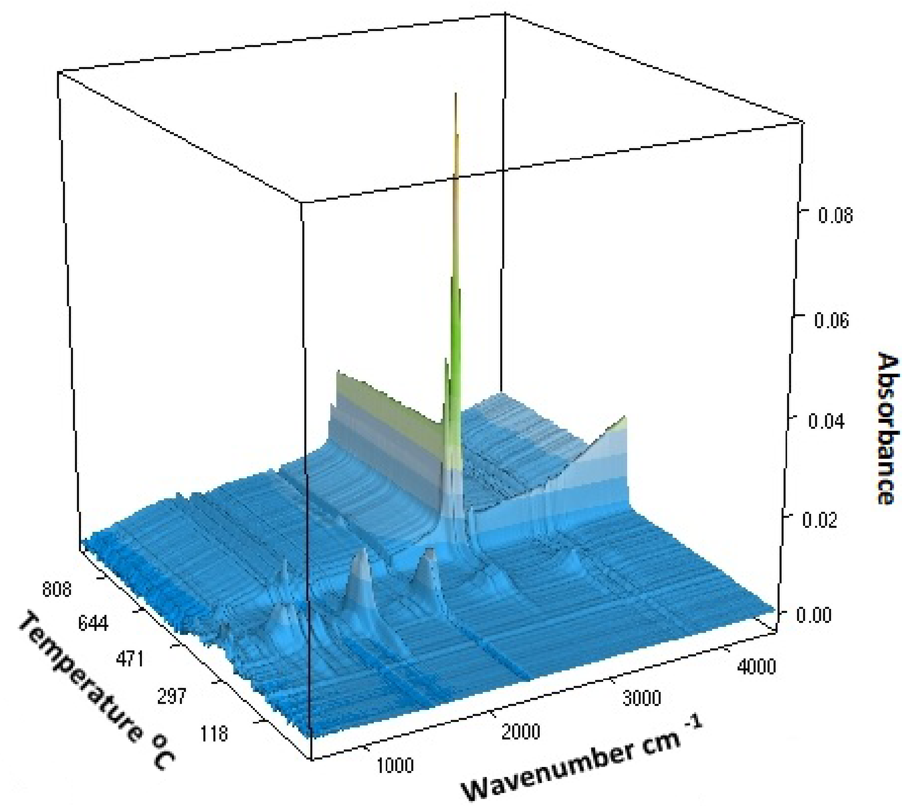


FTIR of blends

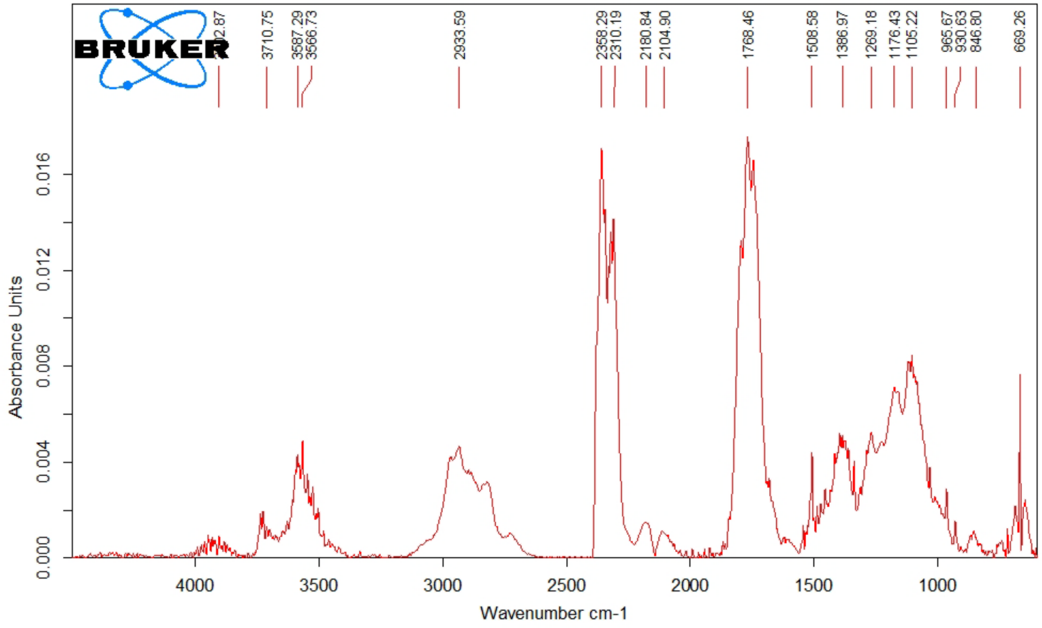
PE 10



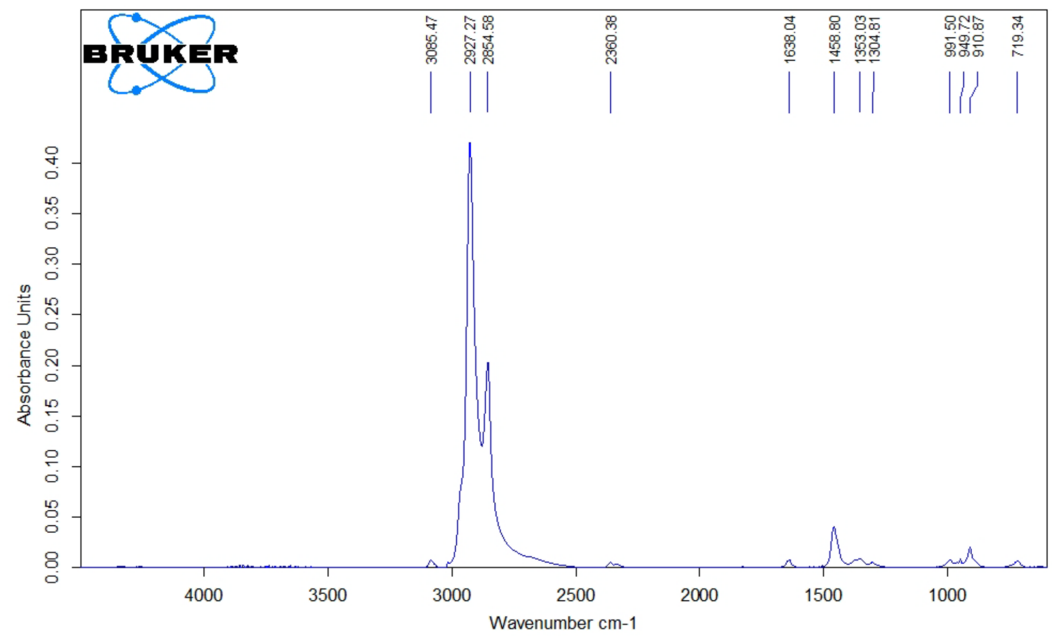
PE 20



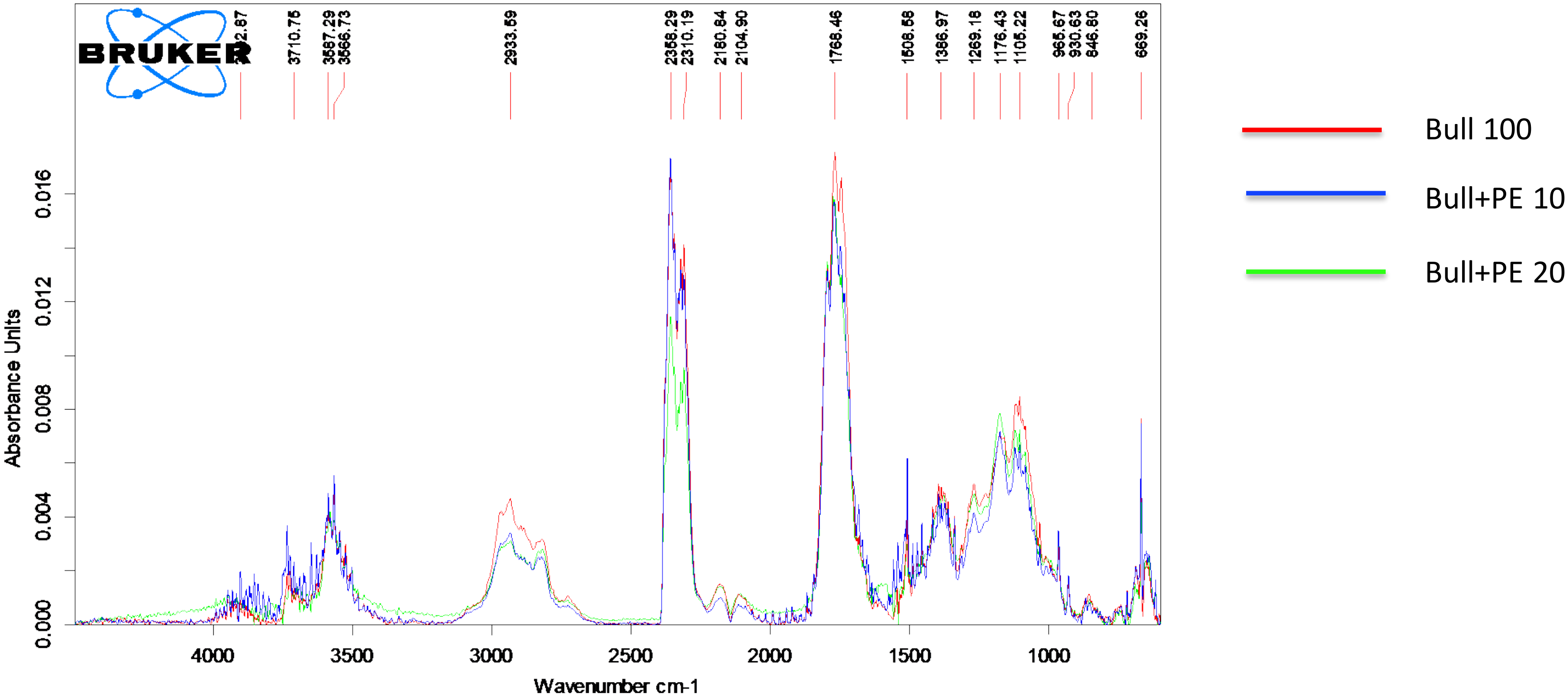
Animal waste (BULL)



Plastic waste (PE)



Compering of samples



No	Wavenumber cm^{-1}	Peak cm^{-1}	Chemical bond and possible components
1	3750-3450	3710, 3587,	H_2O
2		3566	O-H stretch
3	3620-3540	2933	Methylene C-H asymmetric stretch
4	2935-2915	2358, 2310	CO_2 (carboxylic stretch) C=O
5	2400-2260	2180, 2104	stretch Combined peak for CO and CO_2 CO
6	1800-1000	1768	Carbonyl stretch (Benzoic acid)
7	1530-1485	1508	C=C (aromatic)

No	Wavenumber cm^{-1}	Peak cm^{-1}	Chemical bond and possible components
9	1450-1330	1386	C-H (aromatic)
10	1330-880	1269,	
11	1330-980	1176,1105	C-O stretching
12	900-670	965,930	Mono-substituted aromatics, Aromatics
	900-670	846,930,846, 669	

Conclusions

- The addition of plastic waste to animal waste increased its energy parameters; 20% plastic waste in the mixture is more favourable.

- TG/DTG analysis provided a knowledge base for operating pilot scale and commercial pyrolysis units with animal manures and plastic waste as feedstocks.

- Thermal degradation of blends in pyrolysis process shows three main stages: moisture evaporation, volatilization of the light molecules, and char formation. It showed similar effects for mixtures with 10% and 20% addition of plastic waste.

- An analysis of the FTIR results led to the conclusion that carbon dioxide was the main decomposition product, with water (small quantities), carbonyl compounds, and carboxylic compounds found, among other residues.

- The co-pyrolysis of animal waste and plastic waste is an attractive process for the thermochemical conversion to green energy

Thank you for your attention

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