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AGH UNIVERSITY OF SCIENCE AND TECHNOLOGY

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2022 CPOTE

Hydrothermal carbonization as part of the biorefining of cheese whey

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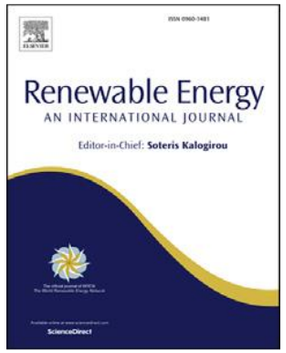
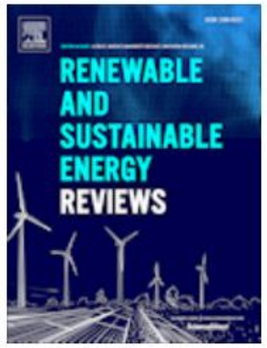
OUTLINE

- Introduction
- Materials:
  - Fermentate from dark fermentation
  - Cheese whey
  - Active sludge
- Methods:
  - Hydrothermal carbonization HTC
  - Solid and liquid HTC products characteristics
- Results
- Conclusions





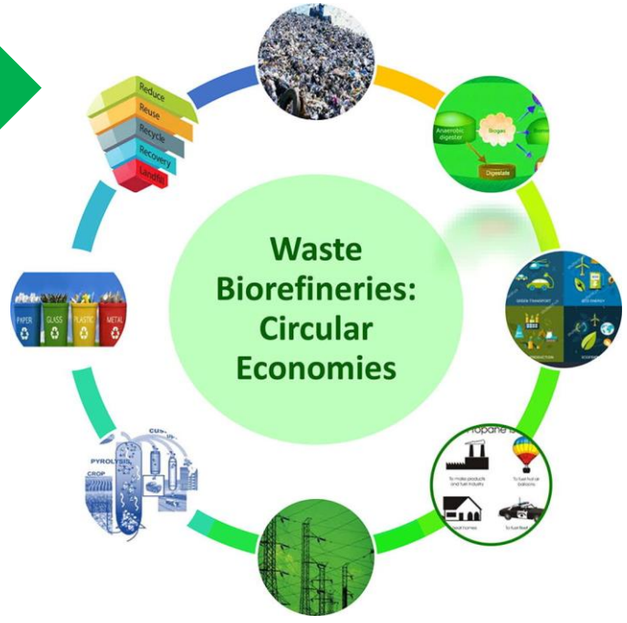
energies

MOTIVATION

https://ec.europa.eu/eurostat/en/web/products-eurostat-news/-/ddn-20220502-2
https://ec.europa.eu/info/strategy/priorities-2019-2024/european-green-deal_en

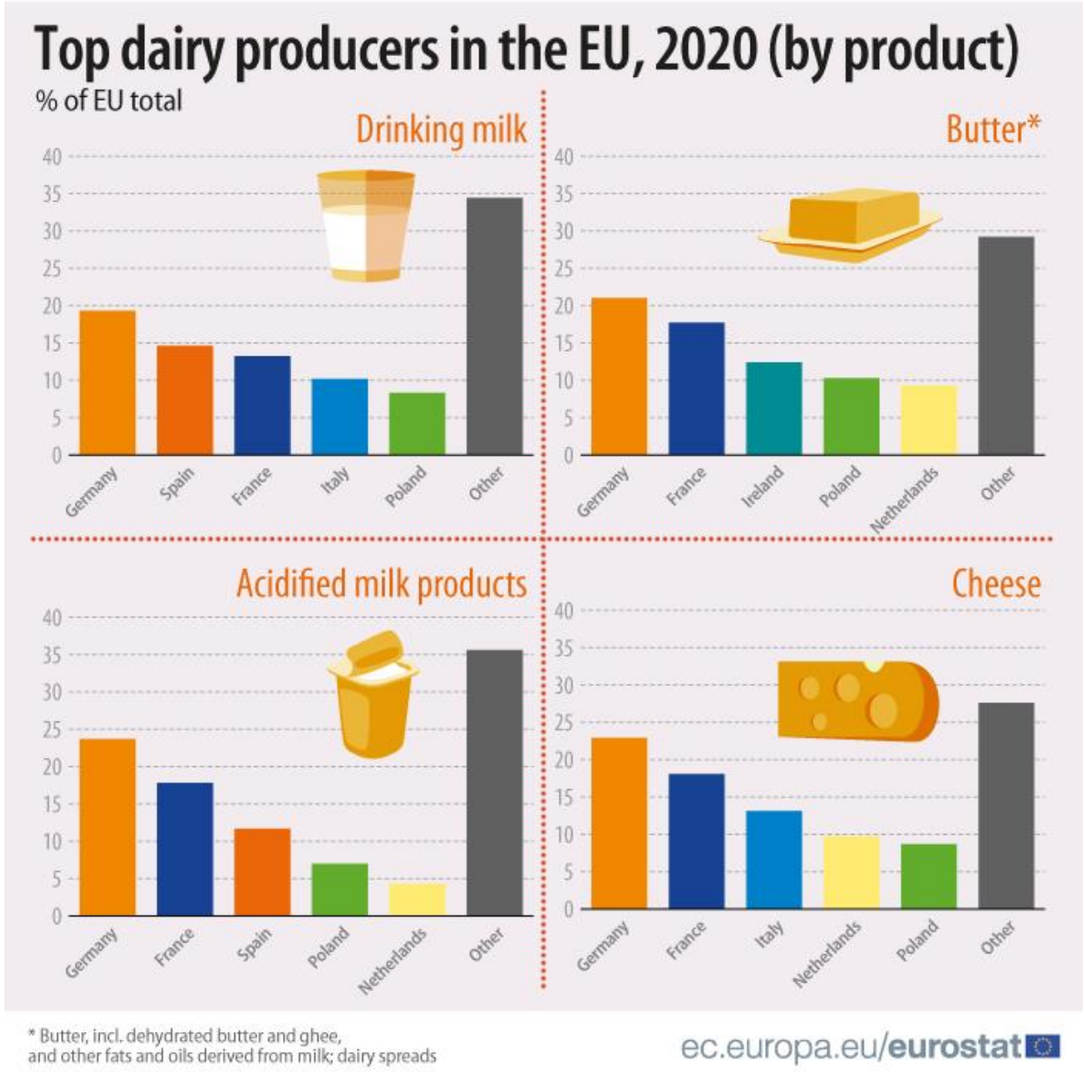
ORGANIC WASTE STREAMS

https://biconsortium.eu/news/vision-circular-bio-society-2050



Bioresource Technology 241 (2017) 1101-1117

CHEESE WHEY



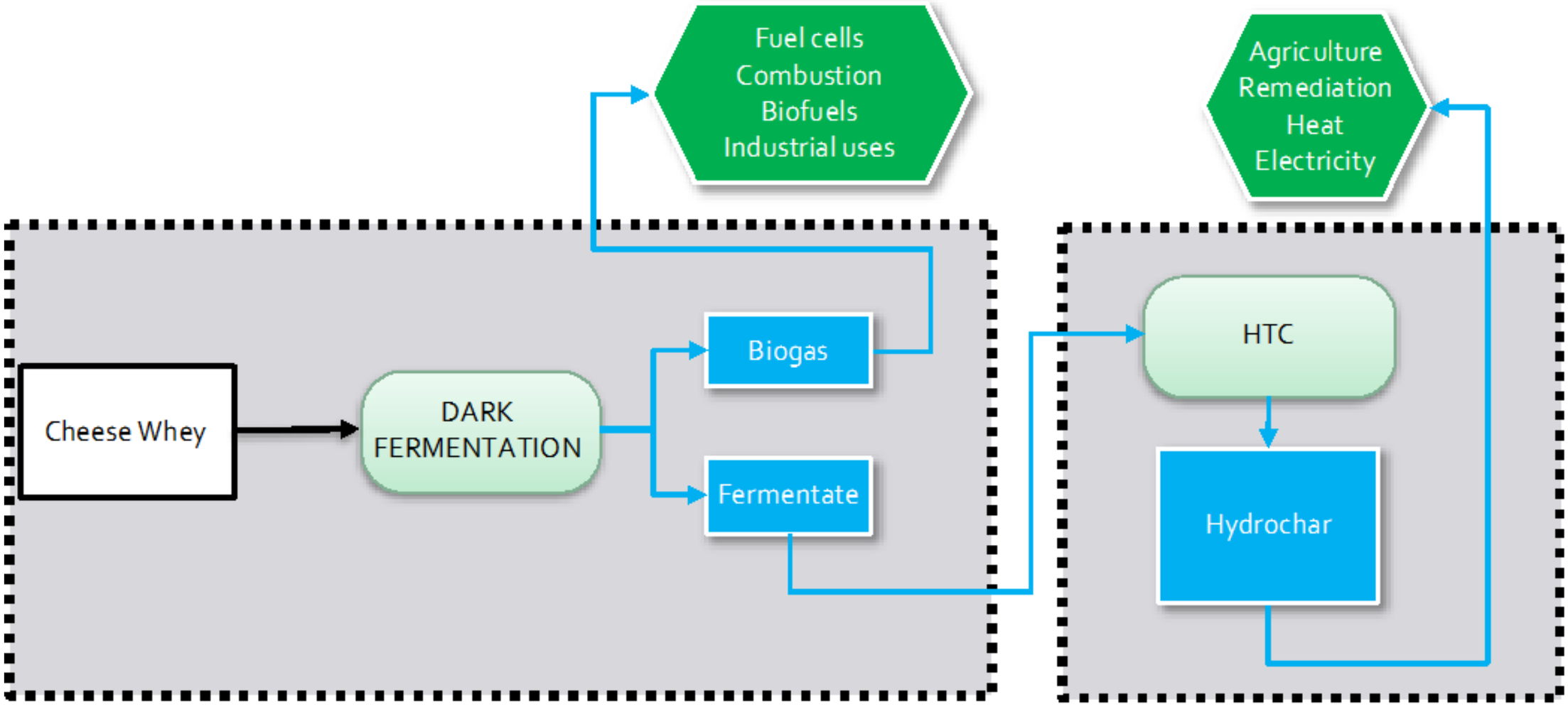
cheese-making process

precipitation and removal of the milk casein

cheese whey

Highly Organic !

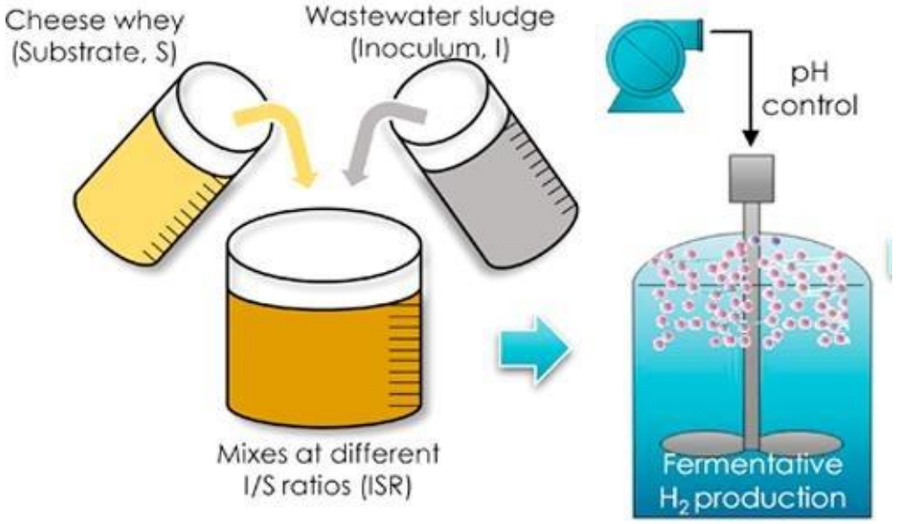
RESEARCH CONCEPT



DARK FERMENTATION CONDITIONS

	CW	AS
Total Solids (TS), g/l	74.0 ± 3.5	21.9 ± 0.24
Volatile Solids (VS), g/l	63.9 ± 3.5	15.7±0.3
Total Organic Carbon (TOC), g/l	38.1 ± 1.3	---

Test	ID	CW/AS, $gTOC_{CW}/gVS_{AS}$	$TS_{mixture}$, g/l	pH
1	**F/M=1**	1	37	6
2	**F/M=2**	2	45	6
3	**CW=100%**	---	74	6



M. Akhlaghi, M. Rosaria Boni, G. De Gioannis, A. Muntonic, A. Polettini, R. Pomi, A. Rossi, D. Spig. A parametric response surface study of fermentative hydrogen production from cheese whey. Bioresource Technology 244 (2017) 473–483

HTC PROCEDURE

BIO-BASED ORGANIC WASTE

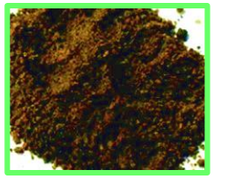
HTC REACTOR

EVACUATION PROCESS

VACUUM SEPARATION

FILTRATE

Liquid properties:
- ✓ pH
- ✓ COD
- ✓ TOC
- ✓ conductivity
- ✓ phenol index
- ✓ N and NH_4-N
- ✓ PO_4-P
- ✓ Mg content
- ✓ Ca content

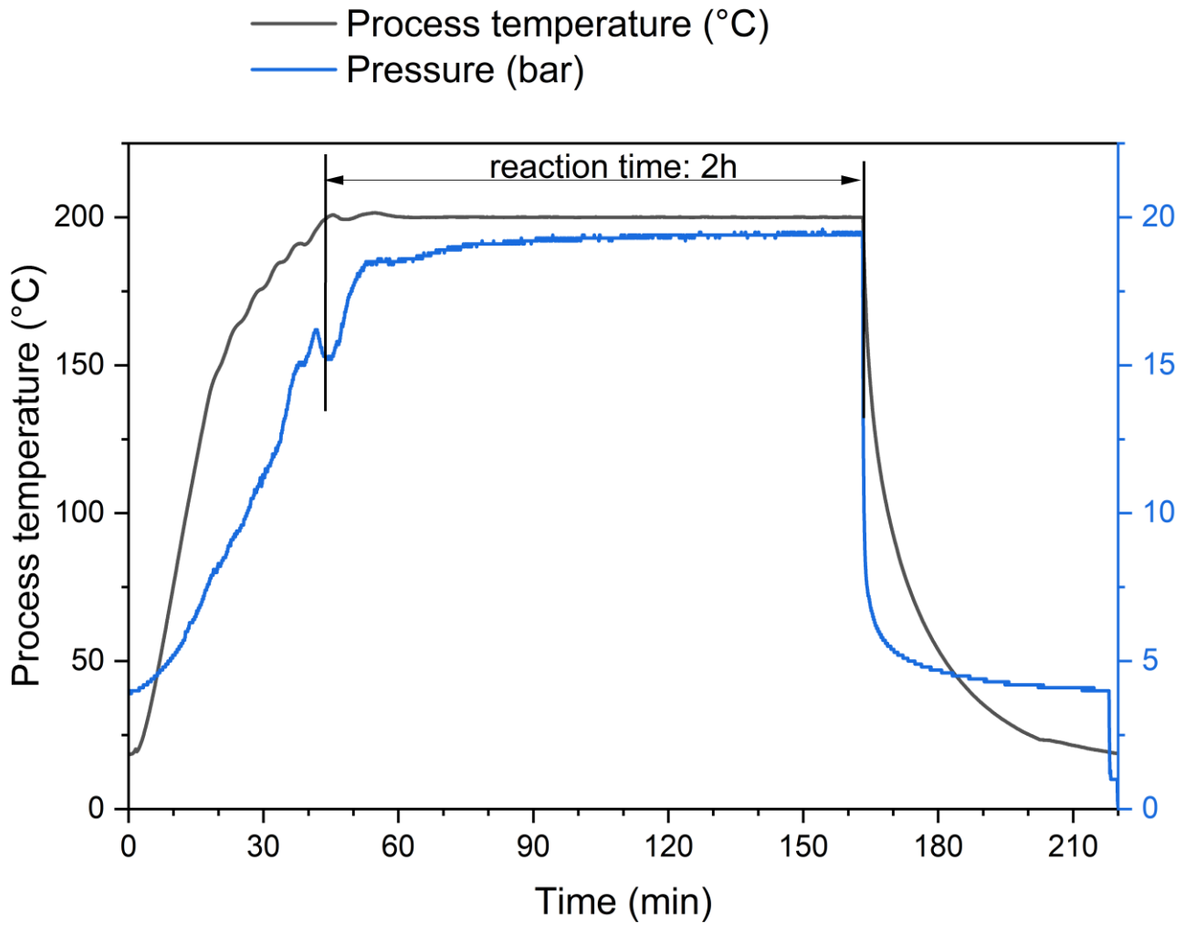


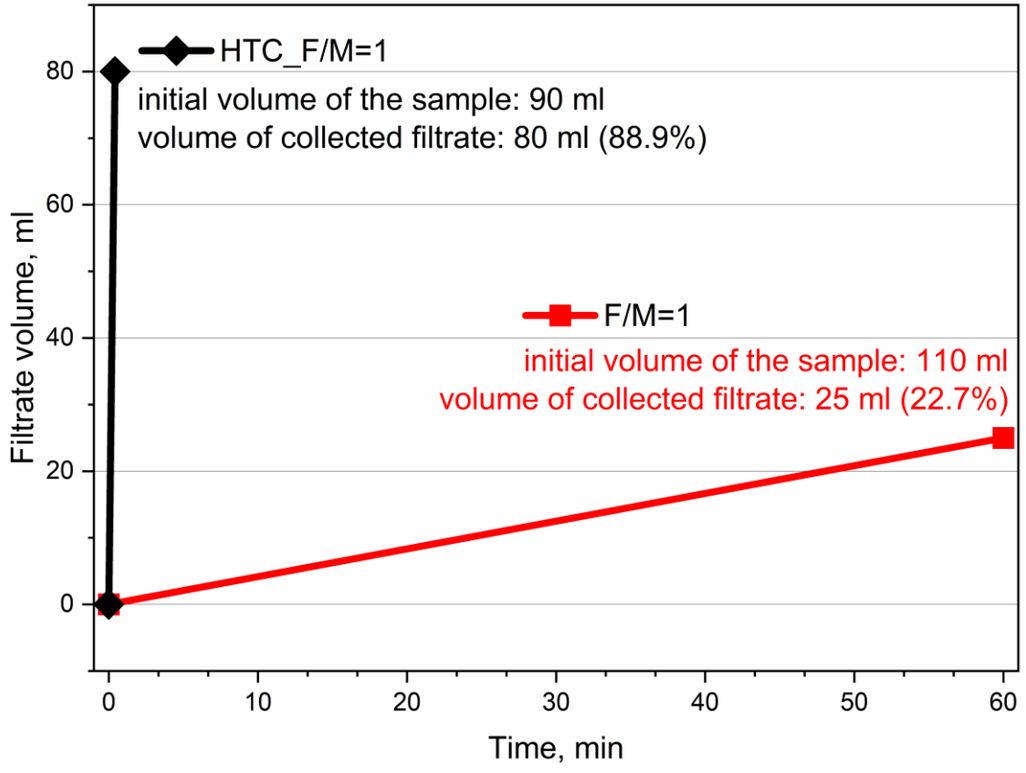
HYDROCHAR

Fuel characteristics:
- ✓ chemical analysis
- ✓ physical analysis
- ✓ mass and energy yields
- ✓ HHV
- ✓ TGA

Conditions of the process	
Residence time	2 and 4 h
Temperature	200 and 220 °C

HTC PARAMETERS: p, t and filtration





F/M=1; HTC 200°C; 2h

HTC PRODUCT DISTRIBUTION

Sample	solid fraction, %	liquid fraction, %	gas and losses, %
F/M=1; HTC 200 C, 2h	1.06	95.64	3.30
F/M=1; HTC 200 C, 4h	1.03	95.92	3.05
F/M=1; HTC 220 C, 2h	-	-	-
F/M=2; HTC 200 C, 2h	0.49	98.78	0.72
CW=1; HTC 200 C, 2h	0.18	96.99	2.83

METHODS for SOLID SAMPLES

Type of analysis	Norm/method	Instrument
Ultimate analysis	PKN-ISO/TS 12902:2007	Elemental Analyser Truespec CHNS 628 Leco, USA 
Higher heating value	Friedl equation	$HHV = 3{,}55 \cdot C^2 - 232 \cdot C - 2230 \cdot H + 51{,}2 \cdot C \cdot H + 131 \cdot N + 20600$
Thermal analysis (TGA)	10 K/min of heating rate 800 °C of temperature in an air atmosphere	Mettler Toledo 

METHODS for LIQUID SAMPLES

Type of analysis	Norm/method	Instrument
Ultimate analysis	PKN-ISO/TS 12902:2007	Elemental Analyser Truespec CHNS 628 Leco, USA
pH value **conductivity**	-	Multifunctional analyzer CX-461 Elmetron, Zabrze, Poland 
chemical oxygen demand (COD) **total organic carbon (TOC)** **phenol (C_6H_5O)** **phosphate (PO_4-P)** **ammonium (NH_4-N)** **calcium (Ca)** **magnesium (Mg)** **nitrogen (N)**	manufacturer's instructions	Spectrophotometer Merck Spectroquant Prove 100 Thermoreactor Merck Spectroquant® Series TR 420  

PHYSICAL and CHEMICAL PROPERTIES of HYDROCHARS

Sample	C, %	H, %	N, %	HHV, MJ/kg	EDR	mass yield,%	loss weight,%	energy yield, %
F/M=1	40.30	5.57	5.91	16.86	-	-	-	-
F/M=2	36.80	5.31	4.39	15.61	-	-	-	-
CW=1	-	-	-	-	-	-	-	-
F/M=1; HTC 200°C; 2h	31.70	4.26	2.11	14.50	0.86	84.33	15.67	72.53
F/M=1; HTC 200°C; 4h	31.10	4.21	2.00	14.40	0.85	81.73	18.27	69.78
F/M=1; HTC 220°C; 2h	30.00	3.98	1.98	14.33	0.85	-	-	-
F/M=2; HTC 200°C; 2h	31.50	4.42	1.92	14.34	0.92	31.30	68.70	28.76
CW=1; HTC 200°C; 2h	32.10	4.48	1.99	14.44	-	-	-	-

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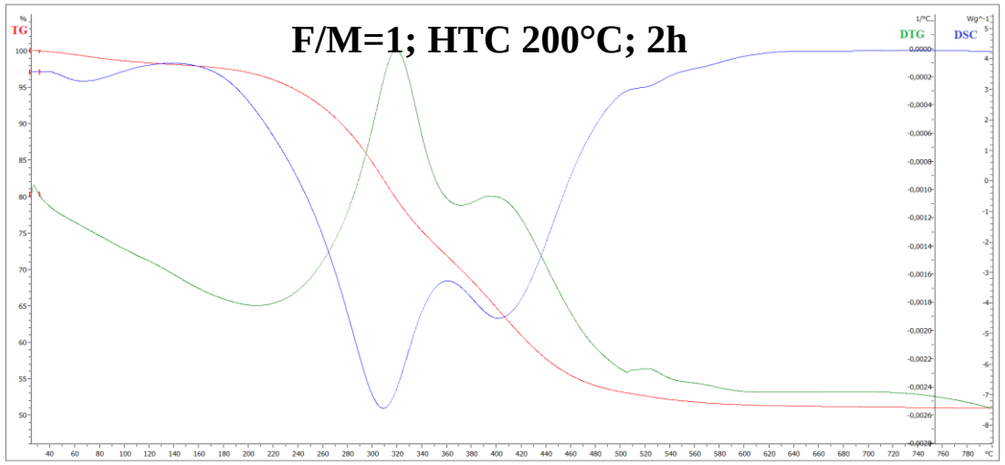

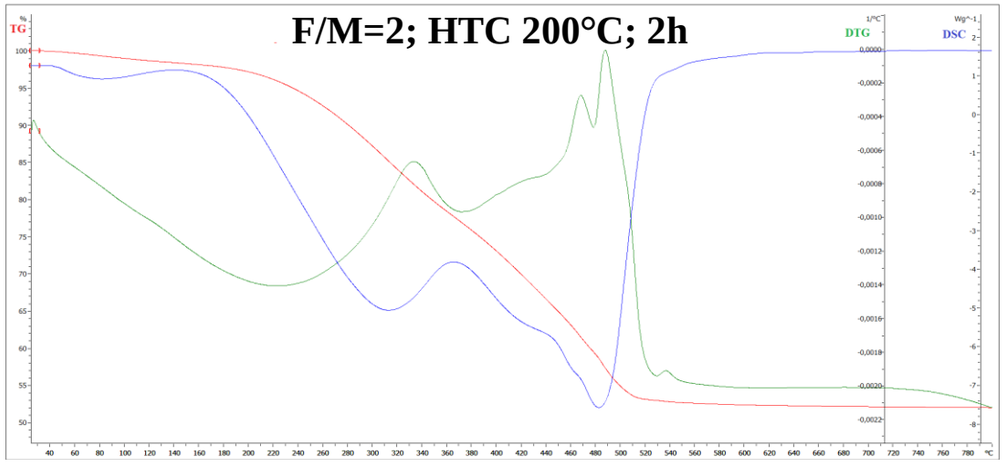

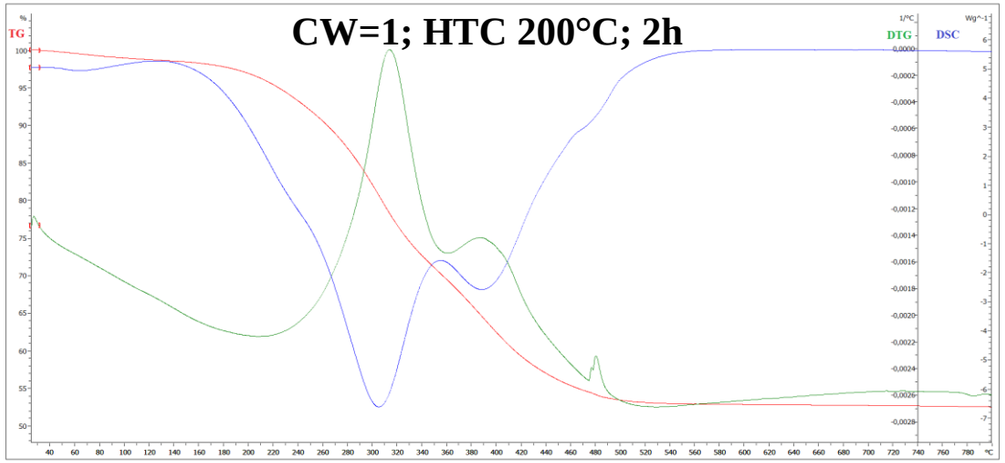

TG/DTG and DSC of HYDROCHARS

LIQUID PHASE ANALYTICAL RESULTS

Liquid sample	C, %	H, %	N, %	pH	Conductivity, mS/cm	TOC, mg/l	COD, mg/l
F/M=1	2.60	11.71	0.10	6.11	8.71	12 400	21 990
F/M=2	1.92	10.00	0.12	6.69	10.44	17 700	27 340
CW=1	2.91	10.20	0.11	6.44	20.70	22 700	62 670
F/M=1; HTC 200°C; 2h	2.50	11.08	0.15	5.41	8.94	16 500	27 390
F/M=1; HTC 200°C; 4h	2.50	11.12	0.15	5.45	8.90	14 900	27 630
F/M=1; HTC 220°C; 2h	2.02	10.10	0.15	5.56	9.05	15 700	27 170
F/M=2; HTC 200°C; 2h	2.03	9.60	0.12	5.84	11.10	17 700	34 940
CW=1; HTC 200°C; 2h	2.74	9.90	0.10	5.82	20.60	23 500	55 930

LIQUID PHASE ANALYTICAL RESULTS

Phenol, phosphate, ammonium, calcium, magnesium and nitrogen contents

Liquid sample	C_6H_5OH, mg/l	PO_4-P, mg/l	NH_4-N , mg/l	Ca, mg/l	Mg, mg/l	N, mg/l
F/M=1	24.25	310.0	160.0	162.5	173.0	425
F/M=2	18.75	297.5	147.5	302.5	163.0	375
CW=1	61.50	590.0	95.0	137.5	242.0	700
F/M=1; HTC 200°C; 2h	28.50	140.0	360.0	32.5	94.5	950
F/M=1; HTC 200°C; 4h	26.75	112.5	395.0	30.0	55.5	1 025
F/M=1; HTC 220°C; 2h	34.25	125.0	462.5	37.5	70.5	1 100
F/M=2; HTC 200°C; 2h	30.00	150.0	302.5	42.5	74.5	875
CW=1; HTC 200°C; 2h	42.25	257.5	187.5	27.5	109.5	600

CONCLUSIONS

- ✓ Hydrothermally carbonized bio-based organic waste was easily filtrated.
- ✓ The main product of hydrothermal carbonization process was highly organic liquid phase with high COD and Phenol index values.
- ✓ The elemental and thermal analyses of hydrochar confirmed its fuel properties.
- ✓ Hydrothermal carbonization caused an increase of nitrogen and ammonium in the post-processing liquid indicating that it could potentially be employed for agricultural uses.

ACKNOWLEDGEMENTS

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http://www.dicea.uniroma1.it/node/1220

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