Production of ethyl esters of volatile fatty acids from food waste

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Green Biobased-Chemicals

Ethyl esters of VFAs

RCOOEt

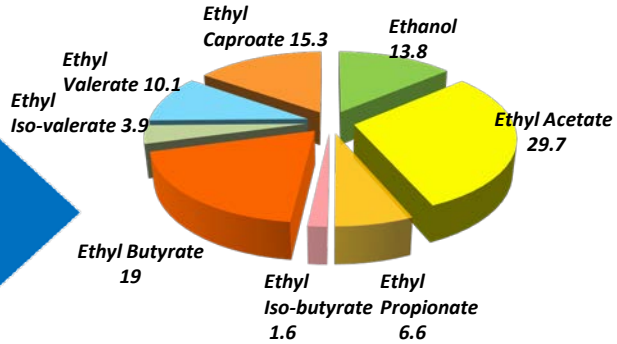
R= $-CH_3$, $-CH_2CH_3$, $-CH_2CH_2CH_3$

Over three million (MM) tons of EA have been produced worldwide, most generated by using sulfuric acid as a catalyst through a conventional process.

Green Biobased-Chemicals: Production Route

UNIROMA/UNIVE → UNIBO → IRSA

VFAs in water 25 g L^{-1} → VFAs in ethanol 20-60 g L^{-1} → Biobased solvent



Composition (%wt)

High Technology Readyness Level (TRL 5-6): Pilot-Scale investigation

- **Treviso (TV)**

A.T.S. S.r.l. WWTP

Step 1: Acidogenic fermentation

Feed characteristics

OFMSW* + SS mixture

Parameter	Unit	40-45% v/v OFMSW
TS	**gTS/kg**	**53 - 90**
TVS	**gTVS/kg**	**41 - 73**
TVS/TS	**%**	**77.5 – 81.4**
pH	-	4.5 – 4.7
COD_{VFA}	gCOD/L	3.6 - 4.9
COD_{SOL}	**gCOD/L**	**21 - 38**
TKN	gN/kgTS	31 - 34
P_{TOT}	gP/kgTS	5.2 – 7.1
COD_{SOL}:N:P	**g**	**100 : 3 : 0.9**

Step 1: Acidogenic fermentation

Fermenter conditions

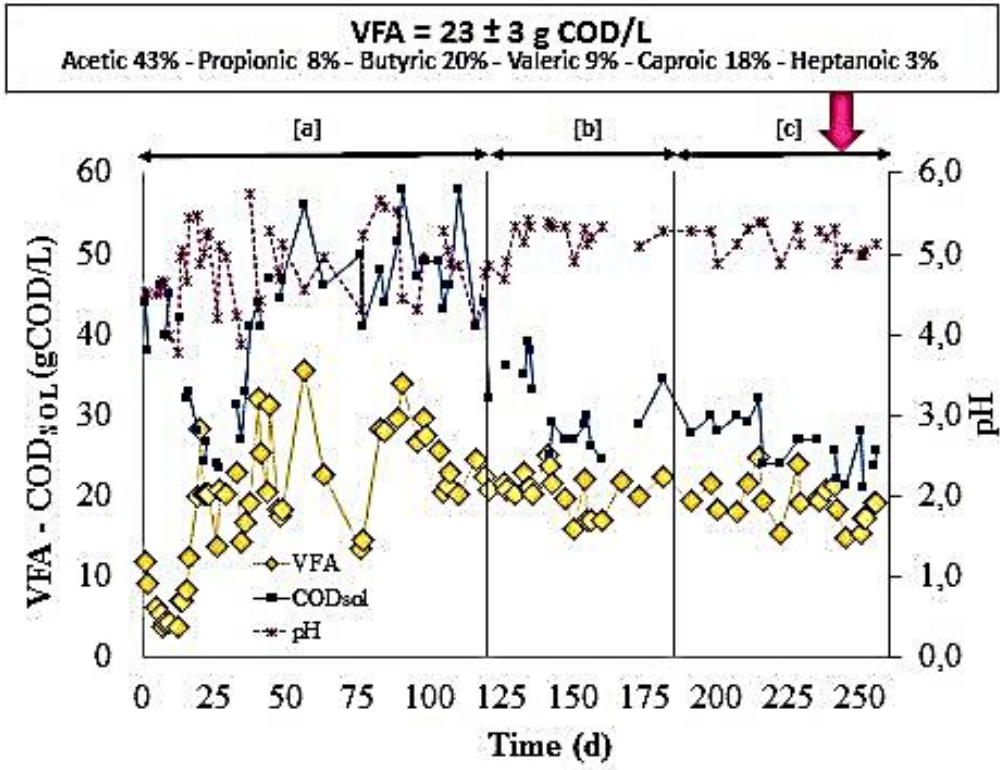
CSTR Volume = 380 L
HRT = SRT = 6 days
pH = 5.0-5.5

- Condition [**a**] - thermophilic
  T=**55°C**, OLR=**9.1** kgVS/m^3 d, **40-45%** OFMSW

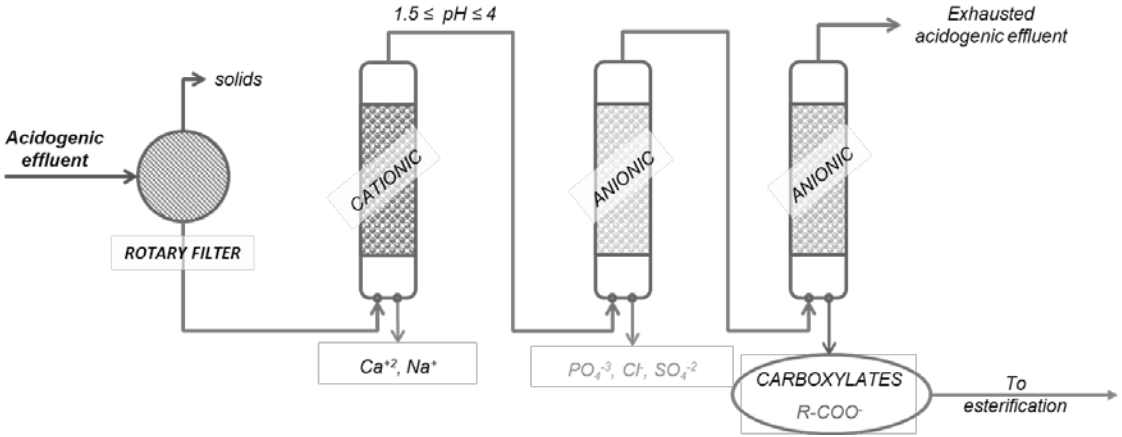
- Condition [**b**] - thermophilic
  T=**55°C**, OLR=**4.4** kgVS/m^3 d, **30-35%** OFMSW

- Condition [**c**] - mesophilic
  T=**42°C**, OLR=**4.0** kgVS/m^3 d, **30-35%** OFMSW

Acidogenic Fermentation profiles



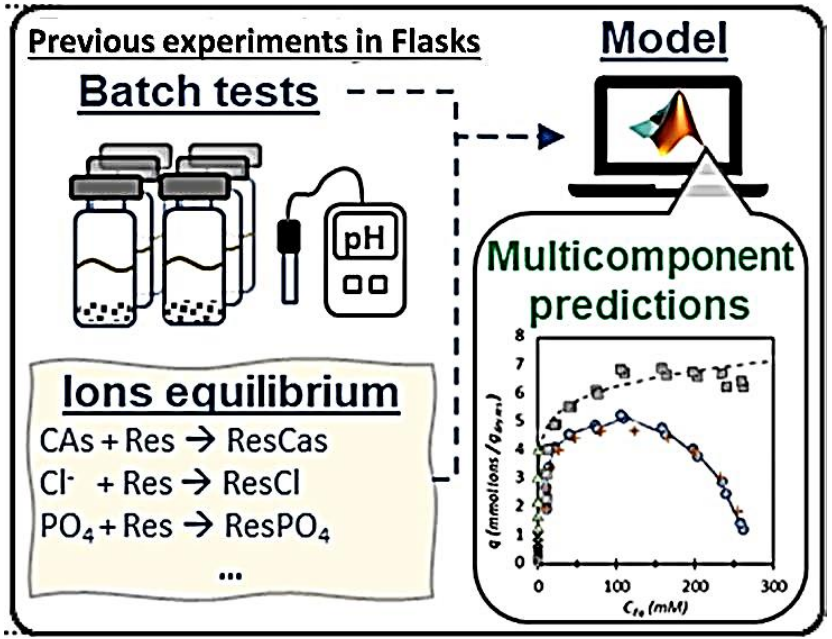
Carboxylic acids Recovery – developed strategy



- Through this configuration, the mineral components can be captured and the competition of up-taking of VFAs are significantly reduced, maximizing their recovery yield in the last column.
- A two-step study was conducted: i) a fundamental study which evaluate all the equilibrium and interaction involved during adsorption and ii) a pilot test in which the recovery of the final VFA and regeneration of the solid phase were the final target.

Experimental Set-up and main results

(1 – batch tests)



Experimental set-up:

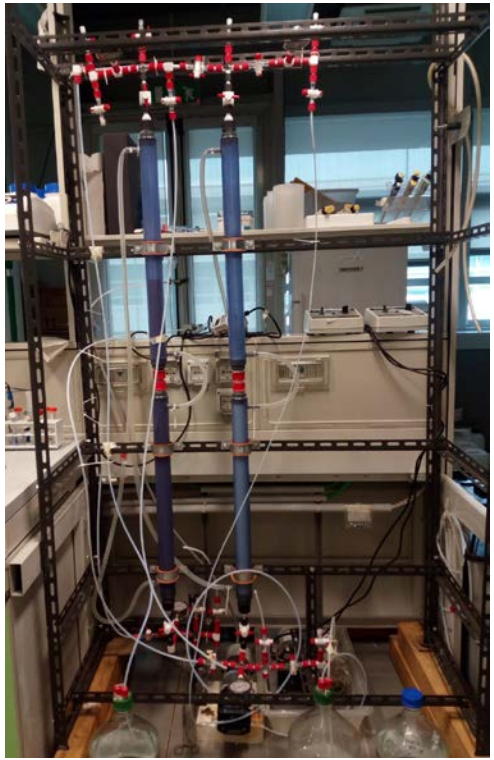
- Preliminary solid/liquid separation by conventional protocols (centrifugation / filtration)
- Na^+ separation and pH adjustment from 5.4 to about 1.5 by the exploitation of the strong cationic Lewatit-S2568H resin
- Anionic resin screening by batch adsorption tests (definition of adsorption isotherm models)

Main results:

- Besides confirming anions competition for resin exchange sites, results also evidenced that Na^+ competed with the anionic resin exchange sites for binding the carboxylates
- Other chemicals (else than VFAs) exerted a negligible competition for carboxylates adsorption.

Experimental Set-up and main results

(2 – semi pilot tests)



Experimental set up:

- The adsorbtion column was filled with resin Lewatit S365 and fed under a flow rate of 40 ml/min

Main results:

- the resin adsorption capacity was exhausted after 11 dimensionless retention times (about 80 minutes).
- The extraction was carried out by using basified or acidified ethanol to desorb VFAs
- more than 90% of VFAs were recovered in acidified alcohol
- Two different set of VFAs solutions were obtained: VFAs in alkaline (NaOH) and acid (H_2SO_4) ethanol, with VFAs content in the range of 20-60 g/L.

Characterization of the hydro-ethanolic SPE eluates

	Samples	Density (g/mL)	Ethanol (%wt)	Water (%wt)	VFAs (g/L)	
					WAX column	HP5 Column
NaOH	02/02/2019*	0.8604	69.5	25.6	34.04	33.21
	12/02/2019*	0.8685	66.5	29.0	31.56	30.33
	01/03/2019*	0.8608	68.8	25.3	41.06	38.33
	11/03/2019*	0.8686	67.1	29.3	25.70	28.01
	14/03/2019*	0.8680	67.2	29.1	24.88	33.86
	19/03/2019*	0.8504	74.8	22.1	22.42	20.46
	21/03/2019*	0.8501	74.3	21.8	26.50	20.41
H_2SO_4	26/03/2019**	0.8641	58.9	23.5	60.30	52.30
	28/03/2019**	0.8630	60.2	23.4	42.42	41.32
	02/04/2019**	0.8698	57.5	25.7	[illegible]	46.48
	04/04/2019**	0.8668	58.7	24.7	43.71	43.64
	09/04/2019**	0.8768	55.7	28.6	37.58	38.04

Total VFA content ranged among 20-60 g/L

Water content ranged among 20-30 %wt

Customized protocols were designed for the two different (alkaline and acid) eluates

Alkaline hydro-alcoholic eluates processing (use of H_2SO_4)

Hydro-alcoholic eluate

↓ Evaporation

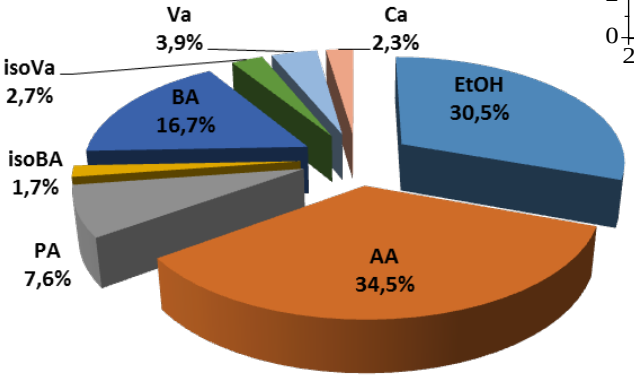
Solid Residue

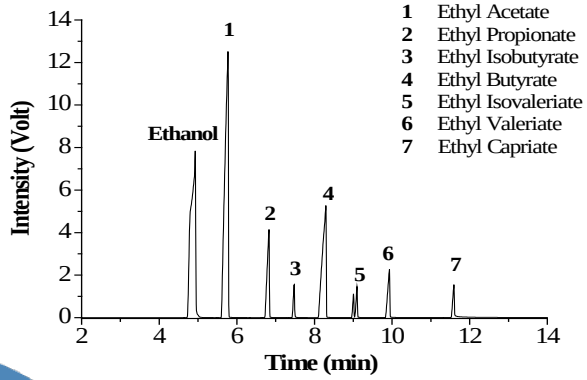
↓ EtOH, H_2SO_4

Ethanolic reacted solution

↓ Purification

Ethyl esters of VFAs





Alkaline hydro-alcoholic eluates processing (use of $AlCl_3\,6H_2O$)

Hydro-alcoholic eluate

↓ Evaporation

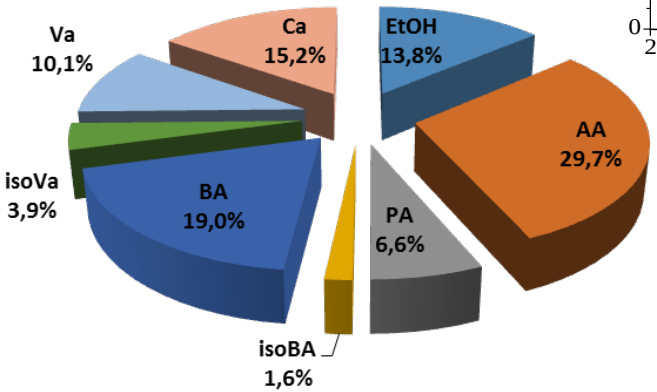
Solid Residue

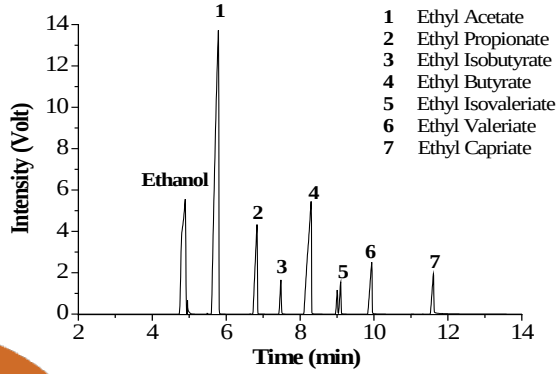
↓ EtOH, $AlCl_3\,6H_2O$

Ethanolic reacted solution

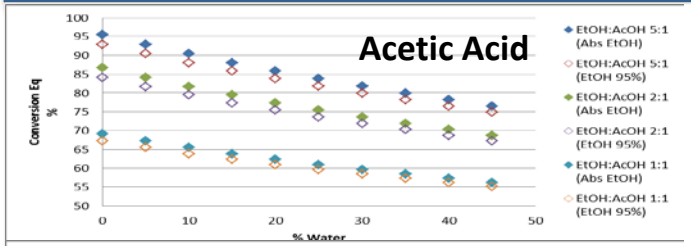
↓ Purification

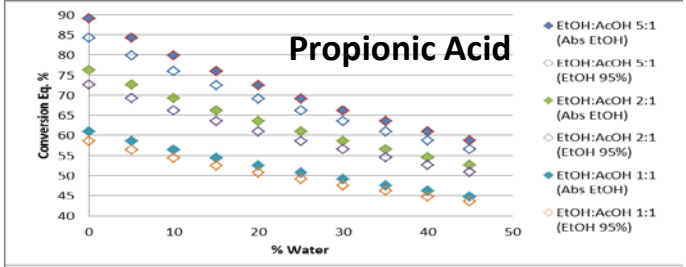
Ethyl esters of VFAs

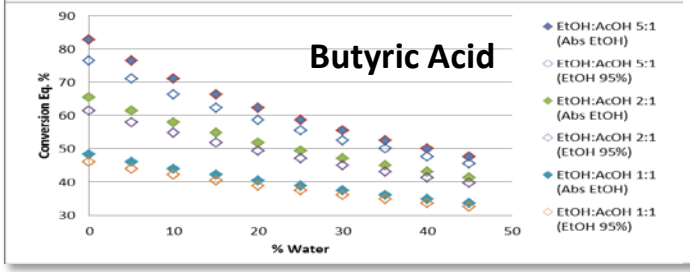




Direct use of acid SPE Eluates and evaluation of the effect of co-presence of water

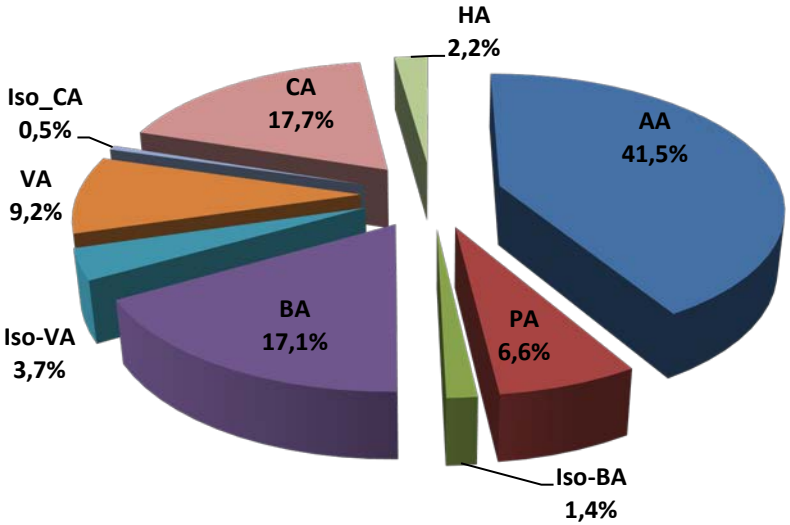


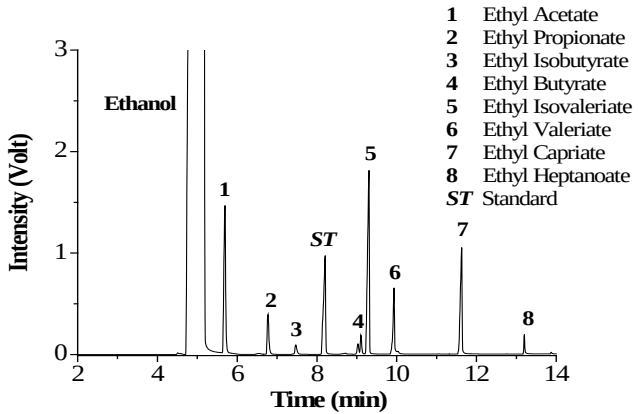




- The presence of water in the reactive system is critical, especially for long chained acids
- The use of Ethanol 95% can be considered acceptable for obtaining satisfying results

Composition of hydro-alcoholic solution





GC-FID profile of acid SPE eluate

Acid hydro-alcoholic solution processing

The presence of ethyl esters in acid samples could be reasonably explained by the capability of sulfuric acid (used as acidificant of ethanol for SPE), in promoting not only the elution of VFAs from resins, but also the immediate conversion into the relevant ethyl esters at room temperature in a single step.

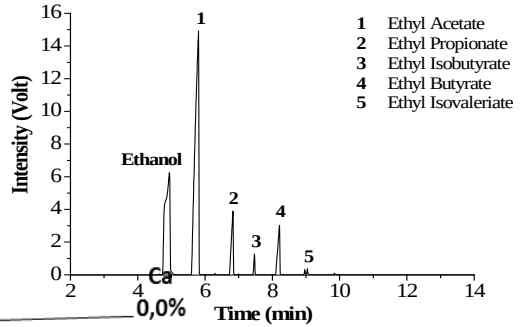
Hydro-alcoholic eluate

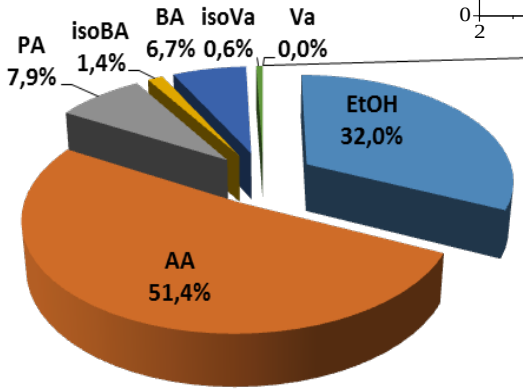
Evaporation

Distillate solutions

Purification

Ethyl esters of VFAs



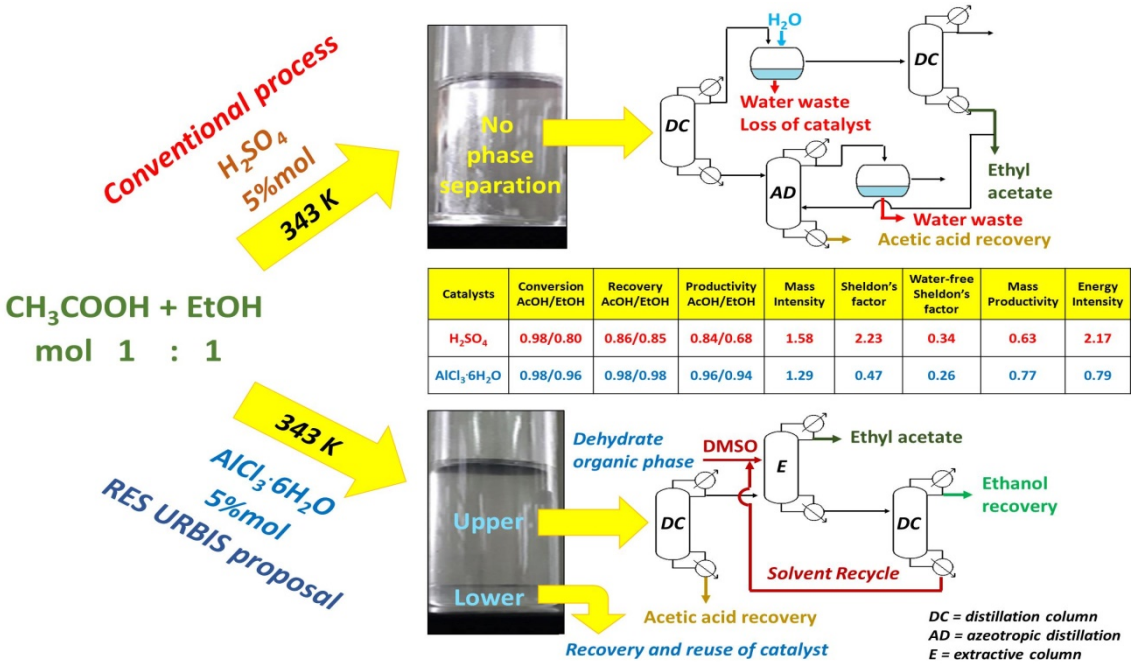


Sum up

%	Sample 1	Sample 2	Sample 3	Sample 4
	Biosolvent from Alkaline Eluate catalysed with H_2SO_4 (sample1)	Biosolvent from Alkaline Eluate catalysed with H_2SO_4 (sample2)	Biosolvent from Alkaline Eluate catalysed with $AlCl_3 \cdot 6H_2O$	Biosolvents from acid Eluates
Ethanol	30.5	20.3	13.8	32
Ethyl acetate	34.5	40.8	29.7	51.4
Ethyl propionate	7.6	8.5	6.6	7.9
Iso-Butyrate	1.7	1.8	1.6	1.4
Butyrate	16.7	17.4	19.0	6.7
Iso-Valeriate	2.7	3.0	4.0	0.6
Valeriate	3.9	4.8	10.1	-
Capriate	2.3	3.3	15.2	-

Four different samples of biosolvents were eventually achieved

Study of the direct esterification of VFAs and EtOH promoted by $AlCl_3 \cdot 6H_2O$



Catalysts	Conversion AcOH/EtOH	Recovery AcOH/EtOH	Productivity AcOH/EtOH	Mass Intensity	Sheldon's factor	Water-free Sheldon's factor	Mass Productivity	Energy Intensity
H_2SO_4	0.98/0.80	0.86/0.85	0.84/0.68	1.58	2.23	0.34	0.63	2.17
$AlCl_3 \cdot 6H_2O$	0.98/0.96	0.98/0.98	0.96/0.94	1.29	0.47	0.26	0.77	0.79

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Conclusive Remarks

- **Fermentative conditions were setted up to obtain a selective production of VFAs from OFMSW**
- **A specific configuration of adsorptive comumns was designed to maximes the recovery of VFAs**
- **$AlCl_3 \cdot 6H_2O$ is capable of promoting direct esterification between VFAs and EtOH, inducing a convenient separation of phases among products and residual reagents;**
- **It efficiently works on pure VFAs as well as on real mixture of VFAs;**
- **It is robust enough to be used on crude VFAs mixture obtained from food waste fermentation, also in presence of «contaminating» salts;**
- **A sustainable «green process» was eventually optimised;**
- **Very limited amounts of waste are co-produced at the point to be considered a «zero-waste-discharge» process.**

Acknowledgements

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