Work Programme 2016 - 2017
Call CIRC-05-2016

A sustainable pathway to convert volatile fatty acids coming from fermented food waste into bio-based solvents

L. di Bitonto, C. Pastore

7TH INTERNATIONAL CONFERENCE ON SUSTAINABLE SOLID WASTE MANAGEMENT

26-29 June 2019, Heraklion, Crete Island, Greece

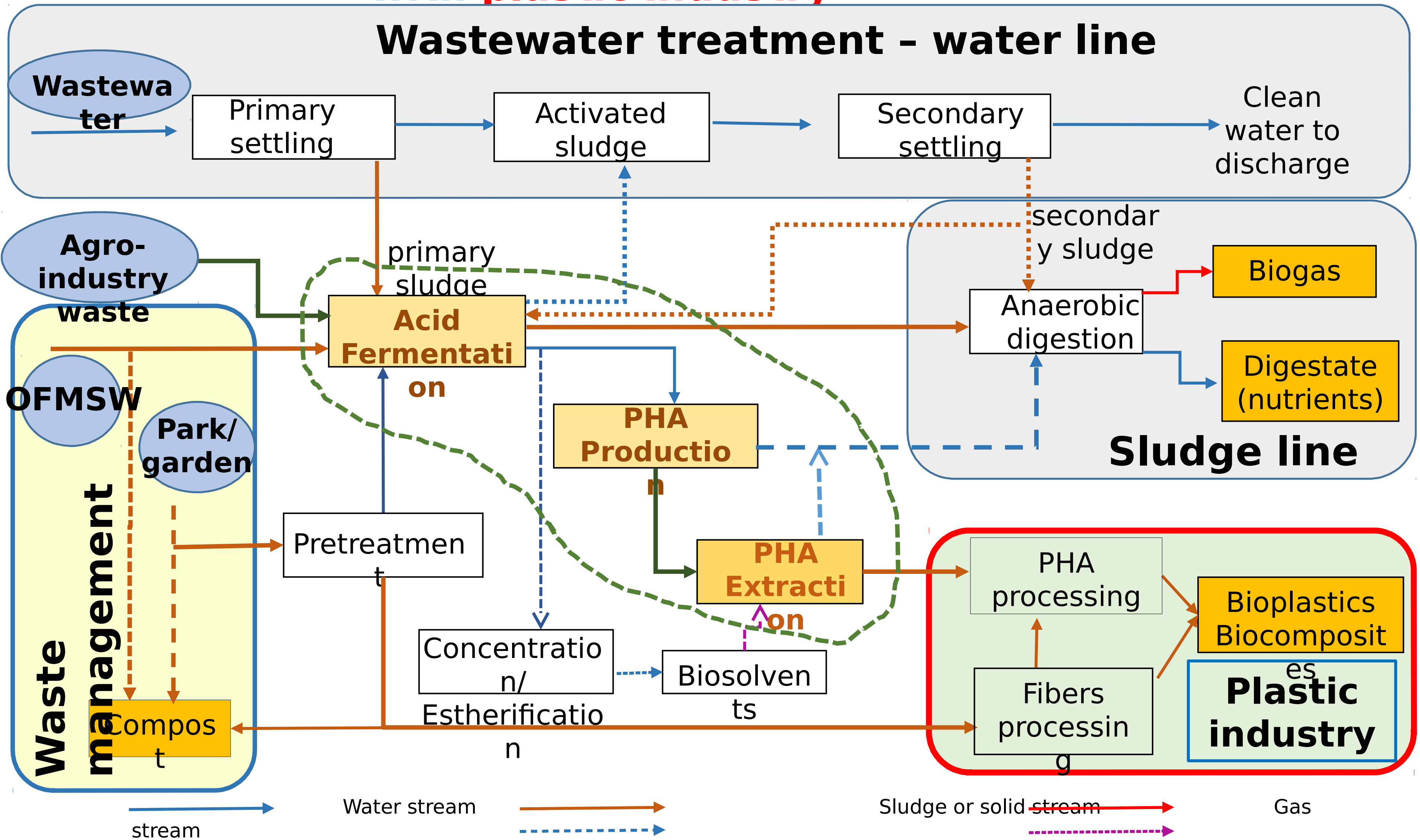
Green Biobased-Chemicals

Ethyl esters of VFAs

RCOOEt

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

Linking the urban biowaste biorefinery with existing waste/wastewater treatment facilities and with plastic industry

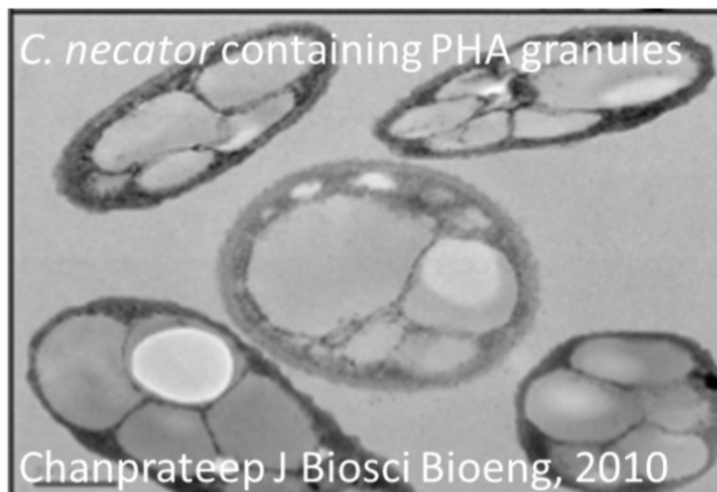


FROM URBAN BIO-WASTE

- **the organic fraction from separate collection of municipal solid waste** (**55 g TS/d from OFMSW**)
- **excess sludge from treatment of urban wastewater** (**39 g TS /d from WWS**), with possible further integration with wastewater treatment (water line)
- garden and parks waste
- possibly, some waste from food-processing facilities (to be selected, based on similar composition)

TO BIO-BASED PRODUCTS

- **polyhydroxyalkanoate (PHA), a biodegradable natural biopolymer**
- related PHA-based bioplastics (e.g through blends)
- fibers (to be also used for PHA-based biocomposites).
- bio-based solvents (to be also used in PHA extraction)



Green Biobased-Solvents

1

Acetic Acid
Propionic Acid
Butyric Acid
Lactic Acid
VFAs

Ethanol
Alcohols

Fermented FW

2

Ethyl-Esters of VFAs

To be used in Extraction of P
(Task 2.4)

CONCEPTUAL SCHEME

State of the art of production of Ethyl Esters of VFAs

$$RCOOH + EtOH \overset{cat}{\rightleftharpoons} RCOOEt + H_2O$$

R = CH_3; CH_3CH_2; $CH_3CH_2CH_2$

Nature of Catalysts

1. Mineral Acids (homogeneous and heterogenised)
2. Cationic Resins
3. Zeolites
4. Metal Oxides
5. Metal phosphates and or sulphate
6. Enzymes (free and supported)
7. Ionic Liquids

In the case of Acetic Acid
Molar ratio RCOOH:EtOH of 1:1,
T in the range (310-350 K),
NO co-solvents
Final equilibrium yields does not exceed 70%mol in Ethyl Acetate

Technical solutions adopted to improve EE yields:
- Use of molar excess of reactants (EtOH)
- Physical removal of Water (Special reactors, Distillative column, reactive column, etc.)
- Chemical Removal of water (chemical traps, zeolites, etc.)

Production of Ethyl-Esters of VFAs: Drawbacks

$$RCOOH + EtOH \overset{cat}{\rightleftharpoons} RCOOEt + H_2O$$

$R = CH_3; CH_3CH_2; CH_3CH_2CH_2$

- Unfavourable Thermodynamics (low final yields and Acids Conversion)

The use of classic homogeneous mineral acids as catalysts (H_2SO_4, HCl, p-toluen sulphonic acid, etc.) has the following relevant drawbacks:

- Highly Corrosive;
- Not-easily recoverable from final mixture
- Production of a final waste (salt)

- High-Energy demanding procedure (azeotropic distillation) for the Recovery of Ethyl-Esters from the resulting mixture

Res Urbis approach:

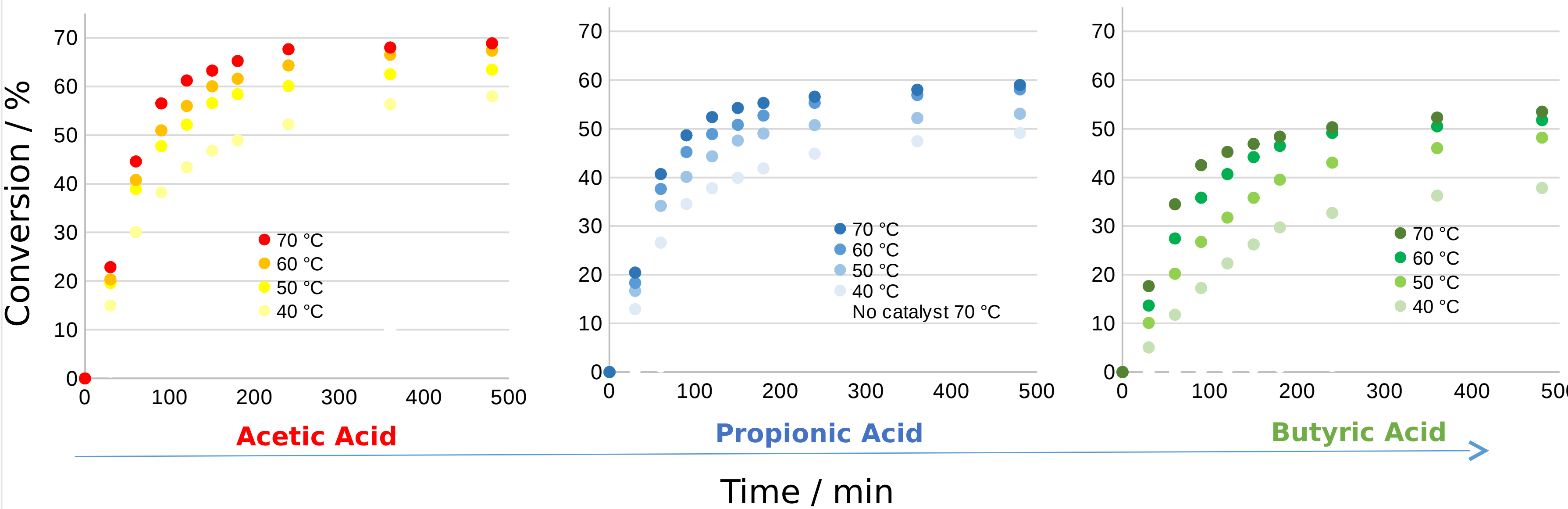
$AlCl_3{\cdot}6H_2O$ was tested as a catalyst

di Bitonto, L., Pastore, C. (2019) Renewable Energy, 143, pp. 1193-1200
di Bitonto et al. (2016) Renewable Energy, 90, pp. 55-61
Pastore et al. (2015) Applied Catalysis A: General, 501, pp. 48-55
Pastore et al. (2014) Biores Technol, 155, pp. 91-98

Production of Ethyl-Esters of VFA: preliminary investigation on pure organic acids (1)

$$RCOOH + EtOH \rightleftharpoons RCOOEt + H_2O$$

R = CH_3; CH_3CH_2; $CH_3CH_2CH_2$



2-5 **0,9-2** **0,**

Effect of T and R on kinetics and final equilibrium composition

Production of Ethyl-Esters of VFA: preliminary investigation on pure organic acids (2)

$$RCOOH + EtOH \rightleftharpoons RCOOEt + H_2O$$

R = CH_3; CH_3CH_2; $CH_3CH_2CH_2$

Homogeneous second order model is applicable

$$v = \frac{d[RCOOH]}{dt} = k_1([RCOOH][EtOH] - \frac{[RCOOEt][H_2O]}{K_{eq}}$$

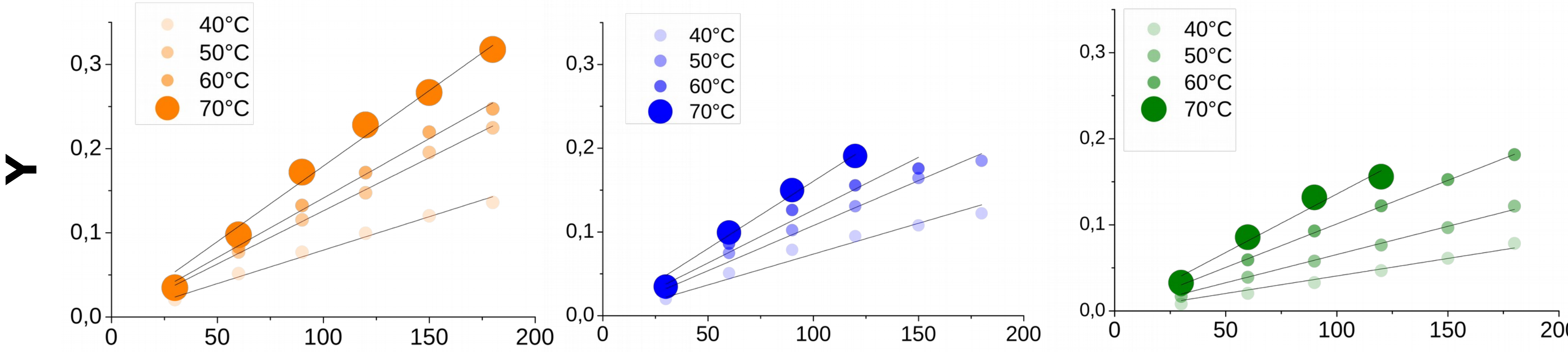
In the case of a molar ratio RCOOH:ROH=1:1*

$$Y = \frac{1}{2\left(\frac{1}{X_{eq}} - 1\right)[RCOOH]_{t0}} \ln\left[\frac{X_{eq} - (2X_{eq} - 1)X_t}{X_{eq} - X_t}\right] = k_1 t$$

In which X_{eq}, X_t, $[RCOOH]_{t0}$ and k_1 represent respectively the Acid conversion at the *equilibrium*, at the *t* time, starting molar concentration of the organic acid and the kinetic constant for the forward reaction.

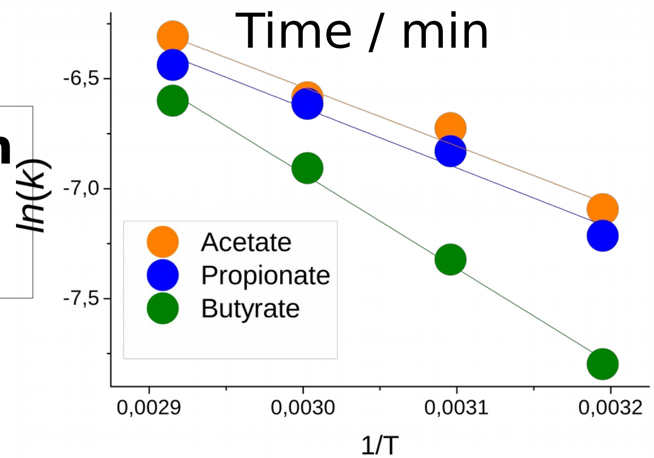
*Altıokka & Çıtak, Applied Catalysis A: General 239 (2003) 141–14

Production of Ethyl Esters of VFA: preliminary investigation on pure organic acids (3)



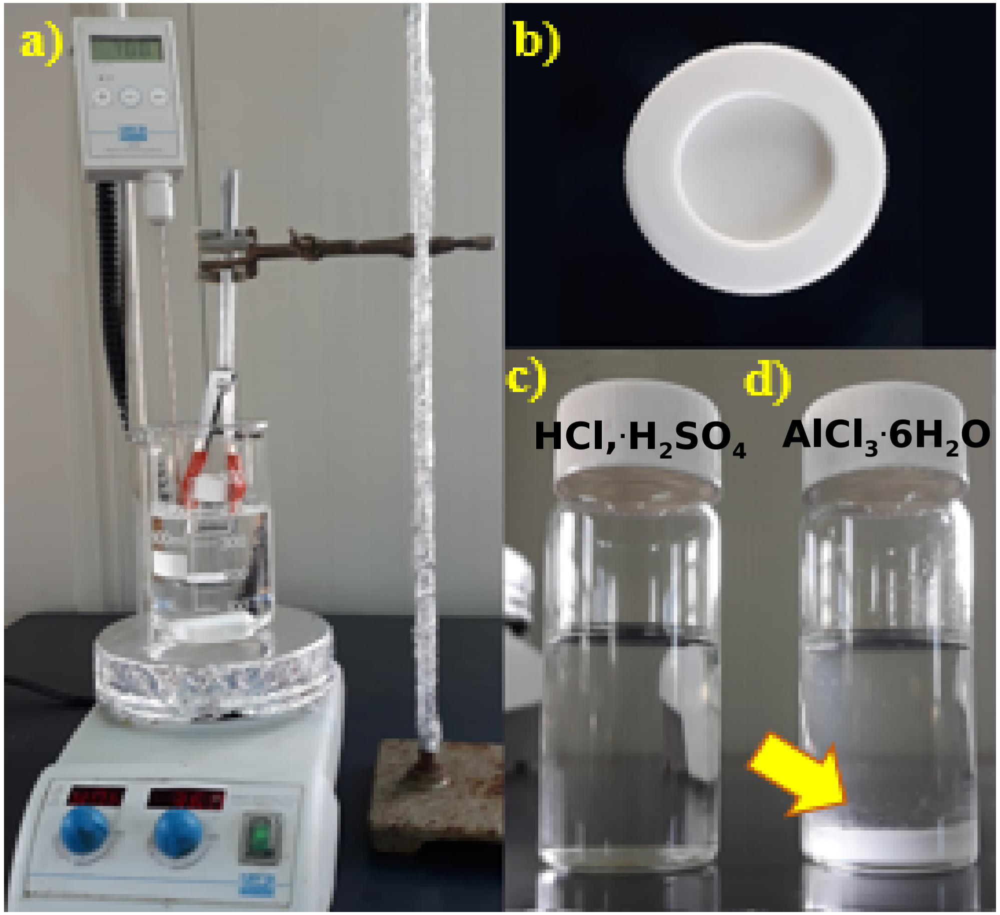
Arrhenius Equation

$$\ln(k_1) = \ln(A) - \frac{E_a}{R}\frac{1}{T}$$



Acid	E_a
	KJ mol $^{-1}$
Acetic	22.3
Propionic	22.8
Butyric	35.8

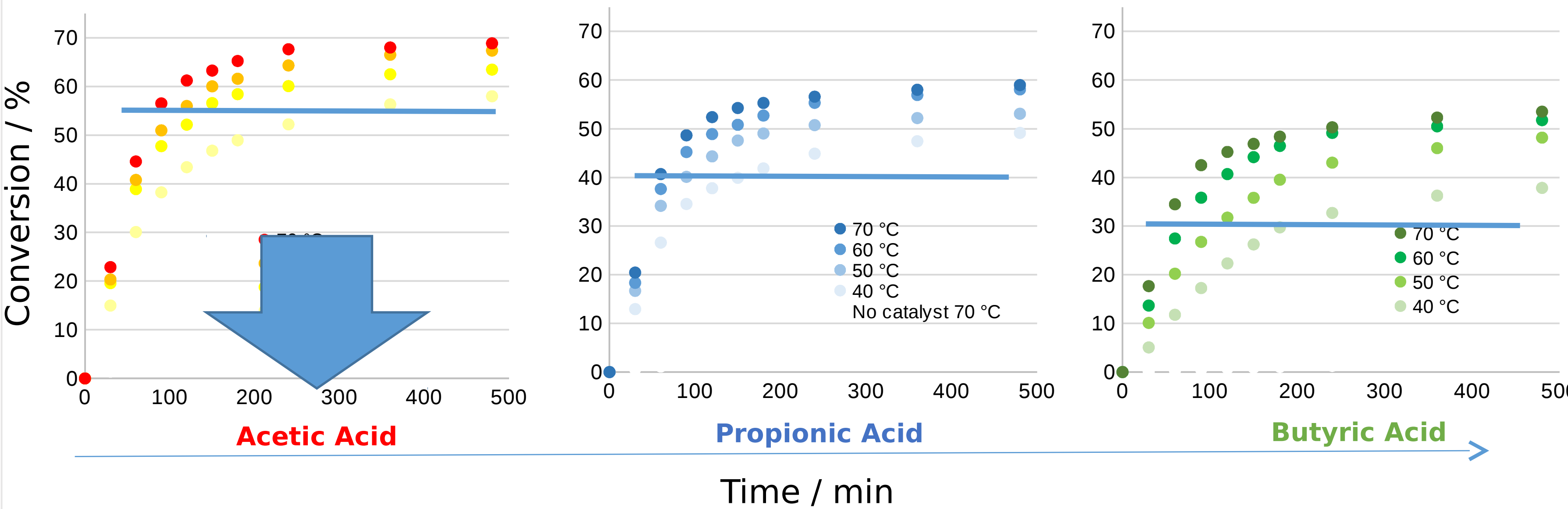
Intensification of the process: optimization of operative conditions in order to improve the production and the simultaneous separation of products



Production of Ethyl-Esters of VFA: preliminary investigation on pure organic acids (5)

$$RCOOH + EtOH \rightleftharpoons RCOOEt + H_2O$$

R = CH_3; CH_3CH_2; $CH_3CH_2CH_2$



2-5 **0,9-2** **0,**

Effect of T and R on kinetics and final equilibrium composition

Intensification of the process: Effect of the amount of catalyst on the phase behaviour (1)

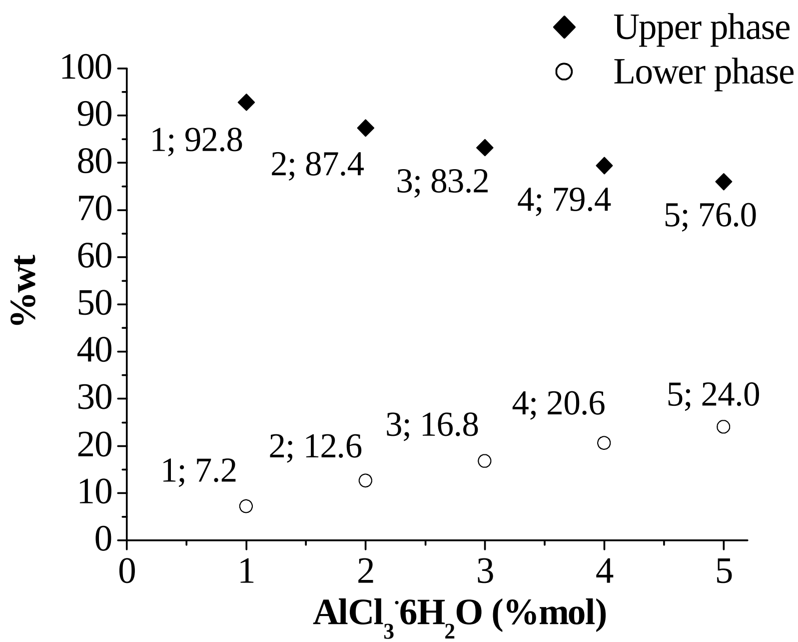
1. Synthetic solution with EtOH, AcOH, AcOEt and H_2O in their equilibrium composition is perfectly homogeneous

2. Addition to this solution of conventional mineral Acids did not produce any change

Intensification of the process: Effect of the amount of catalyst on the phase behaviour (2)

0 1% 2% 3% 4%

Intensification of the process: Effect of the amount of catalyst on the phase behaviour (3)



With the increase of the catalyst, the reaction became fast and the bottom aqueous phase increased.

Distribution of components between the two phases

Catalyst load	1%mol	2%mol	3%mol	4%mol	5%mol
Upper phase					
Acetic acid (%wt)	98.8	96.7	95.6	95.0	92.3
Ethanol (%wt)	95.4	92.8	88.8	87.4	86.7
Ethyl acetate (%wt)	99.7	99.5	99.3	99.1	98.9
Water (%wt)	62.0	39.9	25.9	11.5	1.4
$AlCl_3 \cdot 6H_2O$ (%wt)	16.5	5.6	3.3	2.2	1.2
Lower phase					
Acetic acid (%wt)	1.2	3.3	4.4	5.0	7.7
Ethanol (%wt)	4.6	7.2	11.2	12.6	13.3
Ethyl acetate (%wt)	0.3	0.5	0.7	0.9	1.1
Water (%wt)	38.0	60.1	74.1	88.5	98.6
$AlCl_3 \cdot 6H_2O$ (%wt)	83.5	94.4	96.7	97.8	98.8

1. More than 99% of Ethyl Acetate were always dissolved and recovered into the organic layer

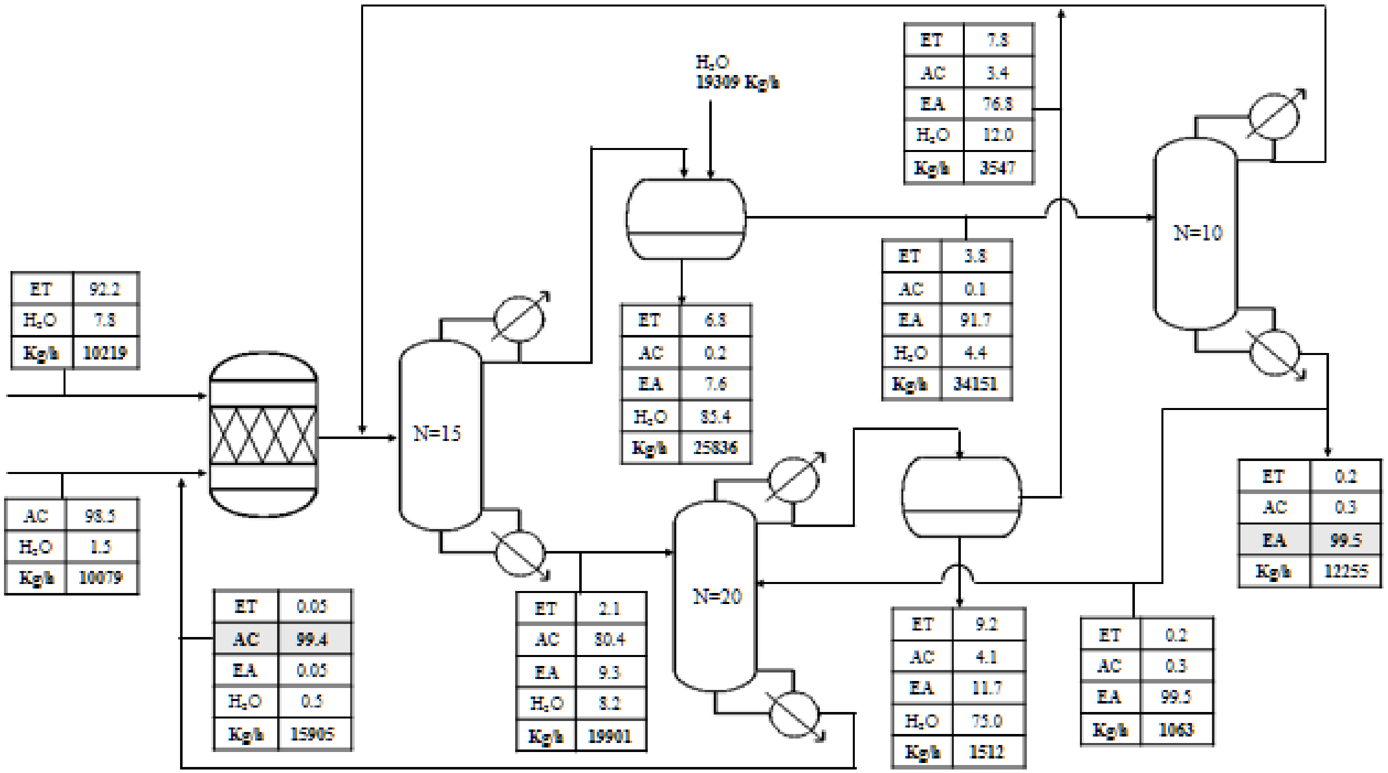
2. 95-97% of $AlCl_3 \cdot 6H_2O$ was dissolved in the aqueous phase

3. Higher was the amount of of the catalyst, less was the amount of water into the organic layer

Advantages

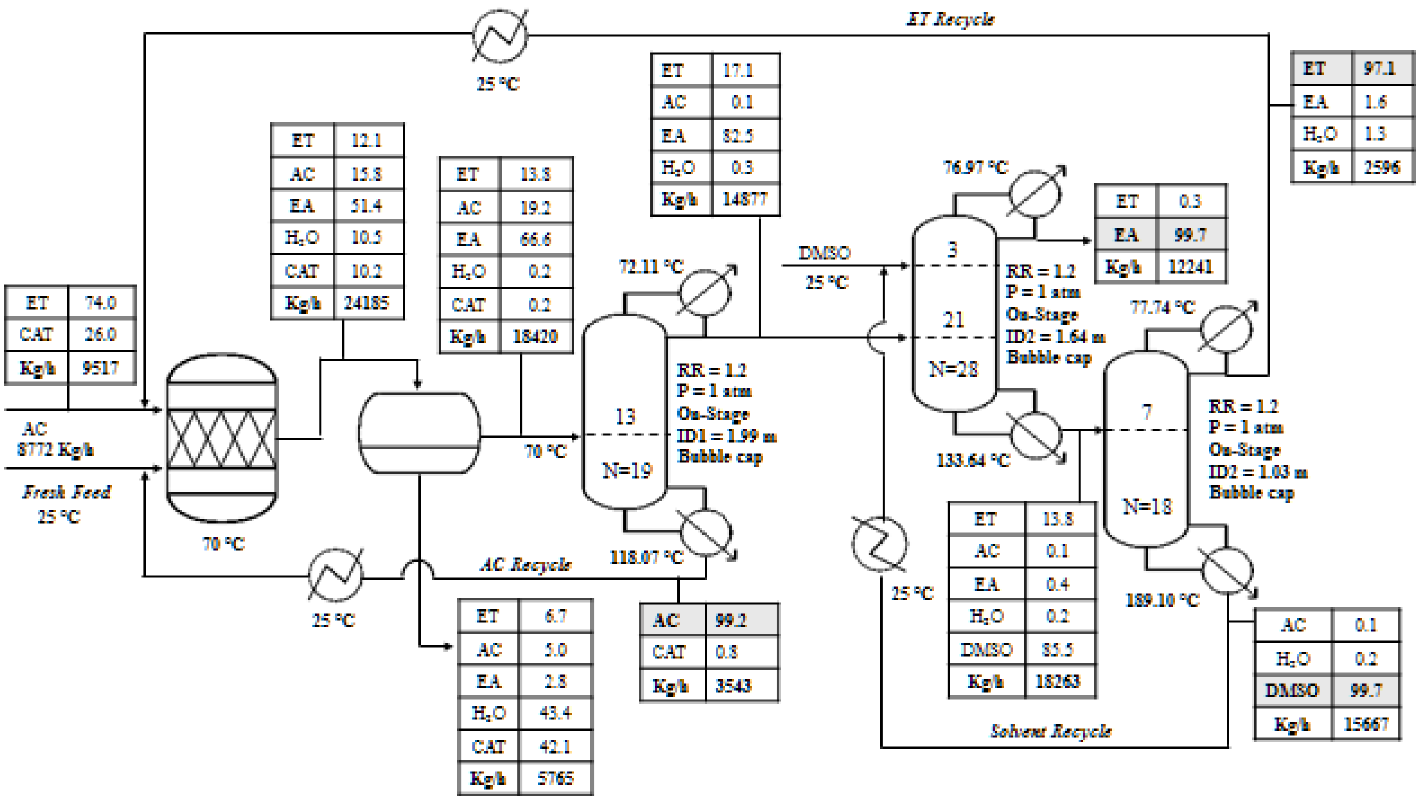
Simulation of an industrial production of Ethyl Acetate through $AlCl_3 \cdot 6H_2O$ catalysis and comparison with the present industrial process based on H_2SO_4 catalysis: evaluation of productivity, recovery, profitability, Sheldon Factor and Energy Intensity.

Simulation of an industrial production of Ethyl Acetate through H_2SO_4 catalysis



M.A. Santaella et al. / Chemical Engineering and Processing 96 (2015) 1–13

Simulation of an industrial production of Ethyl Acetate under $AlCl_3\ 6H_2O$ catalysis



Comparison of processes: evaluation of productivity, recovery, profitability, Sheldon Factor and Energy Intensity

$$\text{Conversion}(X) = \frac{\text{moles of HAC Converted}}{\text{moles of HAC Fed}}$$

$$\text{mass Intesity}(MI) = \frac{\text{Total mass fed (kg)} - \text{Water (kg)}}{\text{mass of product (kg)}}$$

$$\text{Recovery}(Rc) = \frac{\text{moles of EtAc in product Stream}}{\text{moles of HAC Converted}}$$

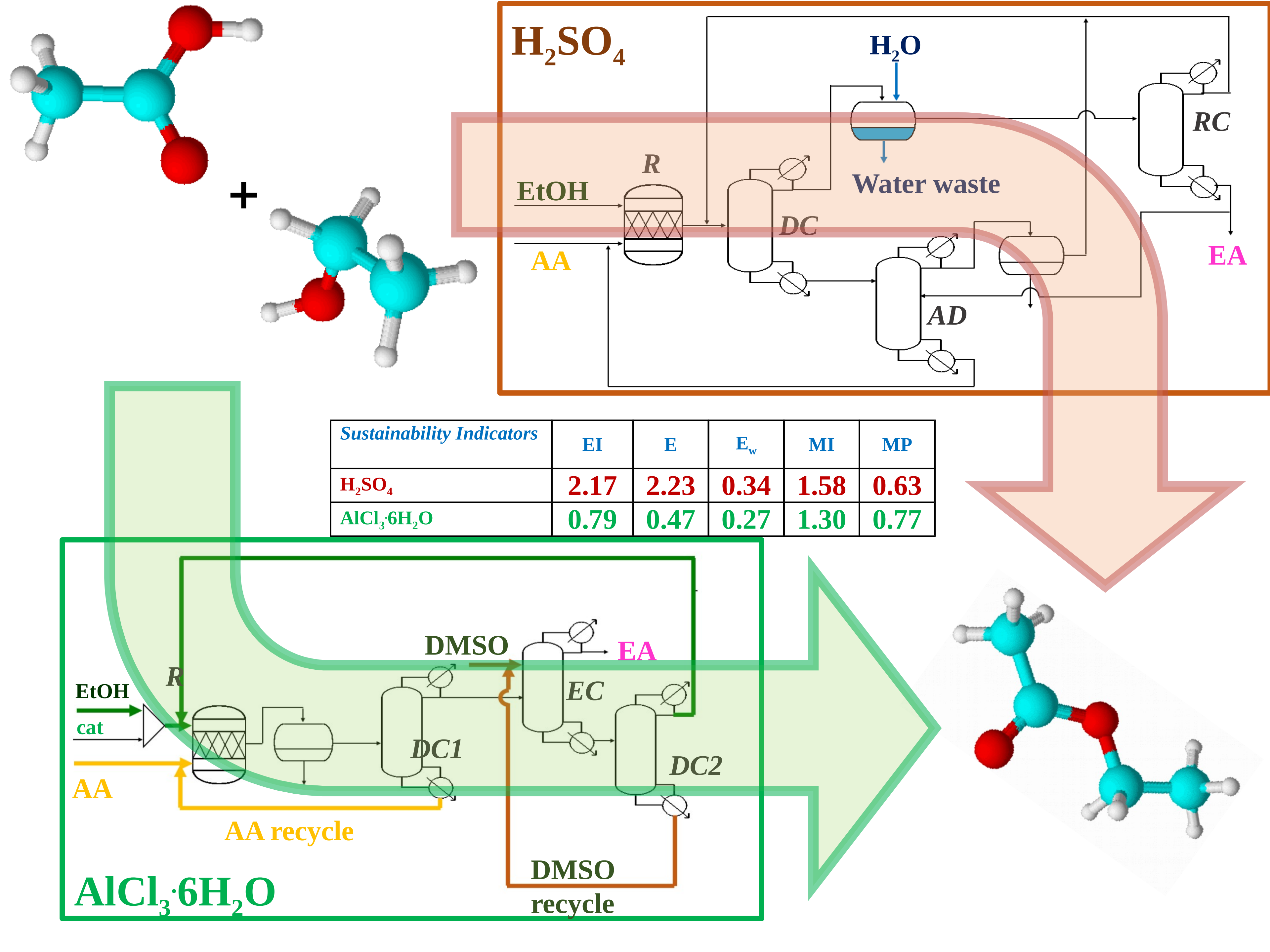
$$\text{Mass productivity}(MP) = \frac{1}{MI} \times 100$$

$$\text{Productivity}(P) = X \times Rc = \frac{\text{moles of EtAc in product Stream}}{\text{moles of HAC Fed}}$$

$$\text{Energy intensity}(EI) = \frac{\text{Energy used}(W)}{\text{mass of product (kg)}}$$

$$E = \frac{\text{Total waste streams (kg)}}{\text{mass of product (kg)}}$$

$$E_W = \frac{\text{Total waste streams (kg)} - \text{Water in waste streams(kg)}}{\text{mass of product (kg)}}$$



Sustainability Indicators	EI	E	E_w	MI	MP
H_2SO_4	2.17	2.23	0.34	1.58	0.63
$AlCl_3 \cdot 6H_2O$	0.79	0.47	0.27	1.30	0.77

Conclusions

1. Thermodynamic (K_{eq}) and kinetic parameters (k_1 and E_a) for direct esterification of VFAs and Ethanol mediated by aluminum hydrated salts (study on pure reagents)
2. Intensification of the process: operative conditions in order to promote the production and the simultaneous separation of products
3. The effect of different concentration of catalyst ($AlCl_3 \cdot 6H_2O$) was evaluated on kinetics and on final separability of phases
4. Different EtOH:VFAs molar ratio was studied for acetic, propionic and butyric acids
5. The effect of the use of azeotropic-ethanol was evaluated on the equilibrium
6. Simulation of an industrial production of Ethyl Acetate through $AlCl_3 \cdot 6H_2O$ catalysis and comparison with the present industrial process based on H_2SO_4 catalysis: evaluation of productivity, recovery, profitability, Sheldon Factor and Energy Intensity.

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nk you for your kind attent

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