Hexanoic and levulinic acids esterification for ethyl and hexyl esters production by using AlCl3.6H2O as a catalyst

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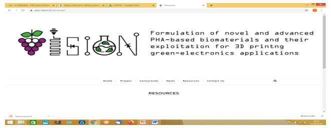
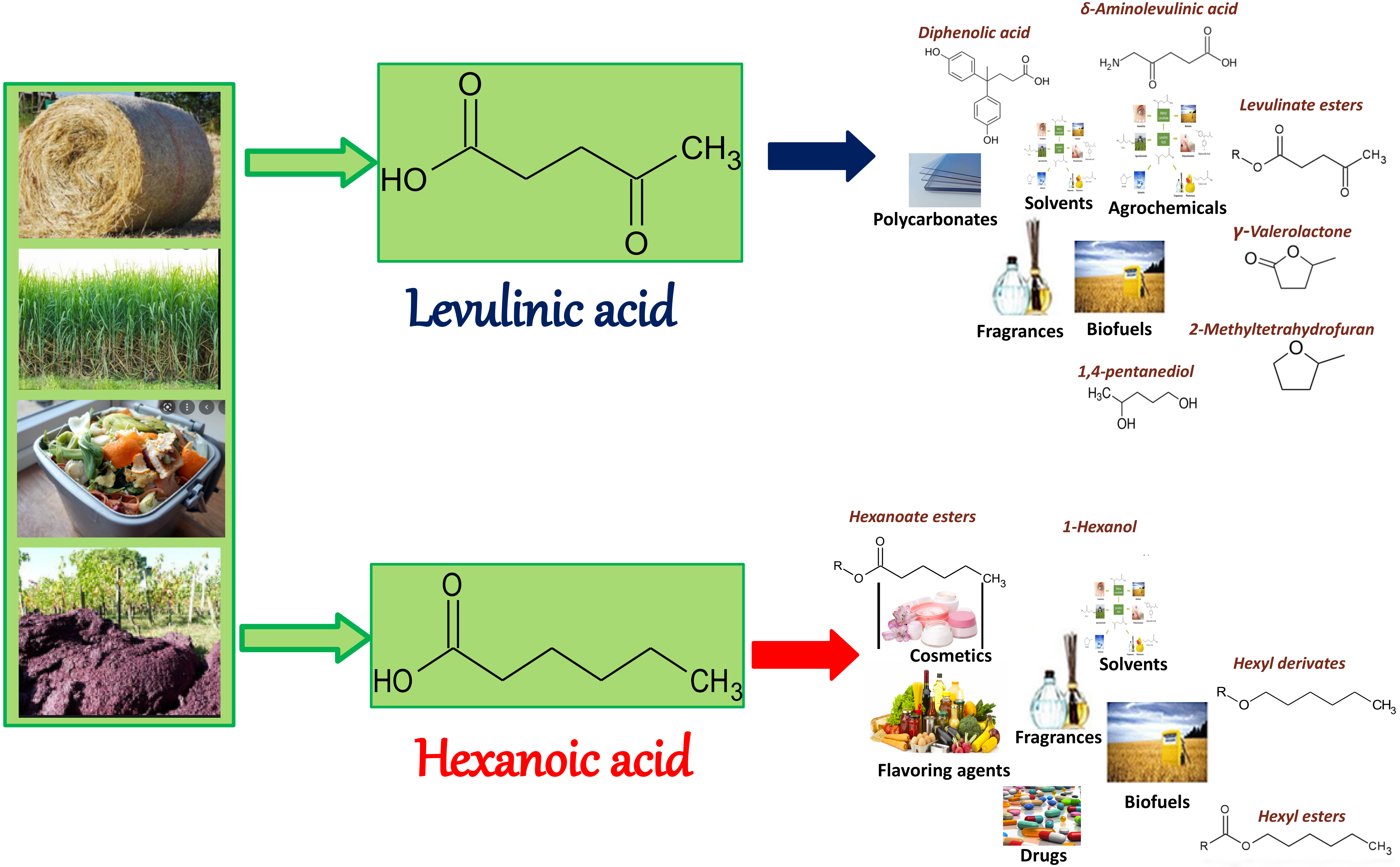


Introduction



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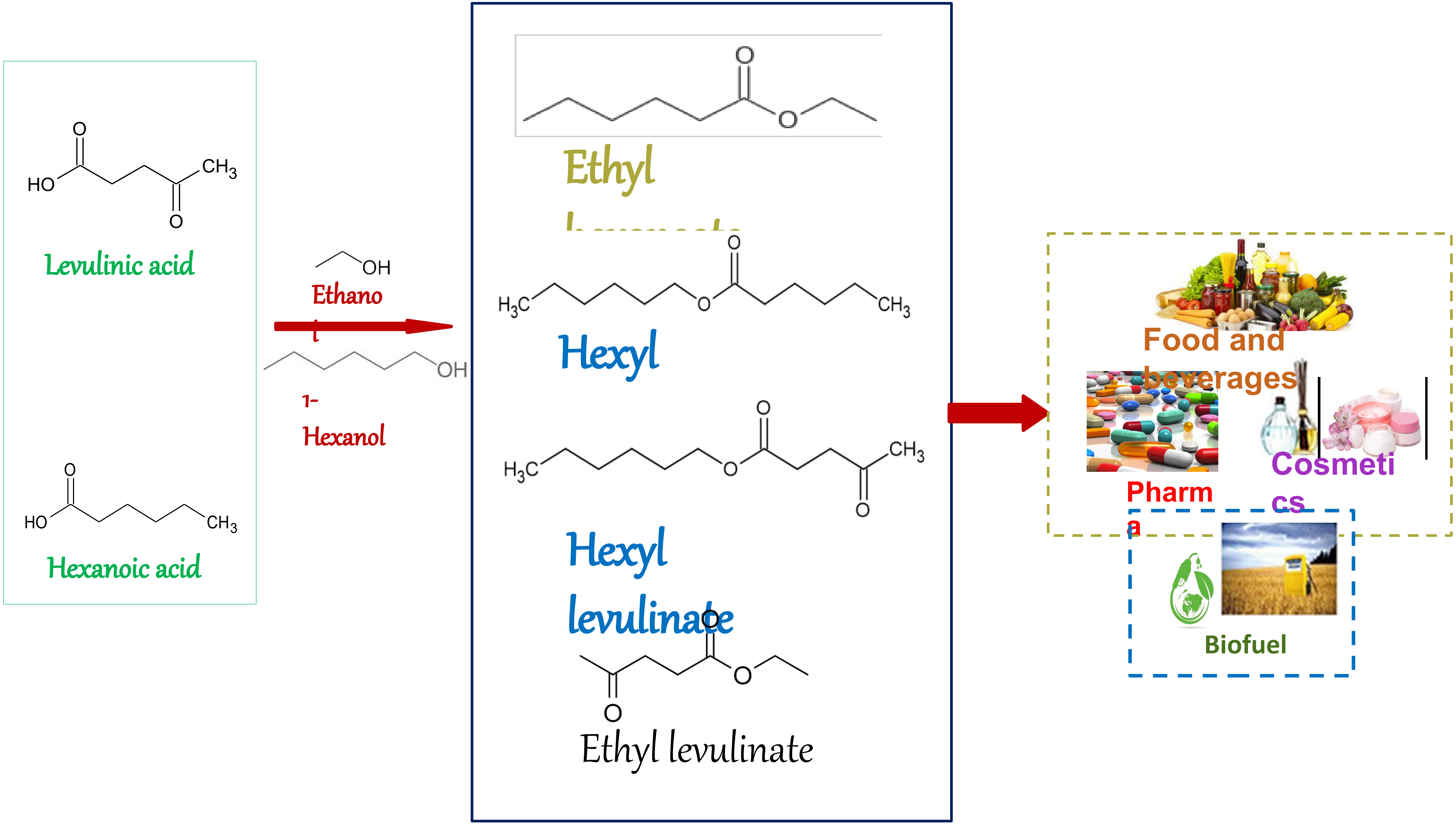
Introduction



Outlook

1. Esterification reactions of hexanoic acid with ethanol and 1-hexanol and levulinic acid with 1-hexanol by using $AlCl_3 \cdot 6H_2O$ as catalyst
   - Kinetic and thermodynamic study
   - Reaction tests with different amounts of catalyst and alcohol
     - Process intensification by using $AlCl_3 \cdot 6H_2O$: high reaction yields and phase separation
   - Relationship between catalyst and Keq
   - Catalyst Recoverability and Reusability
2. Focus on the esterification reaction of hexanoic acid with ethanol:
     - Reaction tests on real samples of hexanoic acid produced through the fermentation of grape pomace

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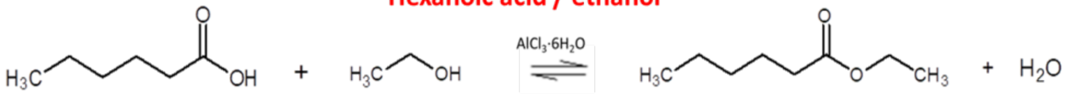
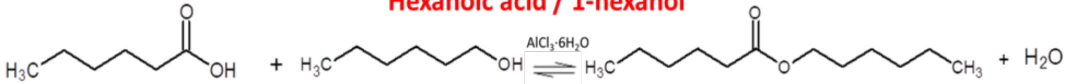
Kinetic and thermodynamic study

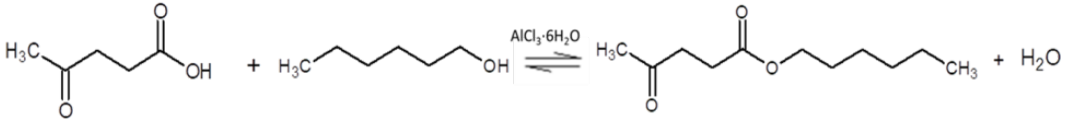
Hexanoic acid / ethanol



Hexanoic acid / 1-hexanol



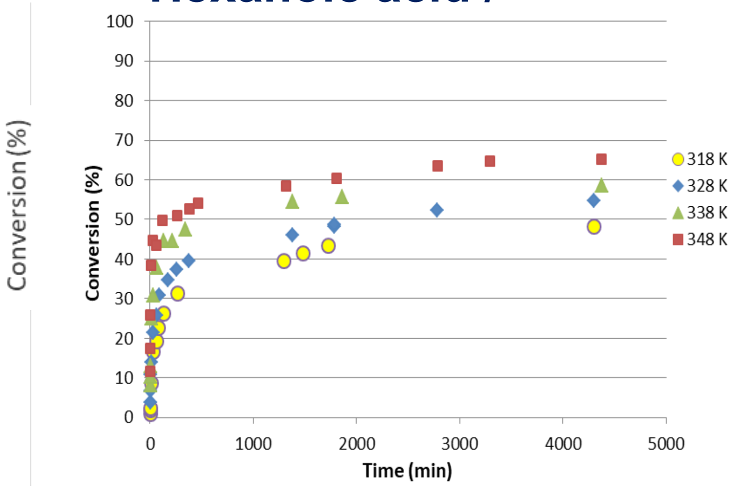
Levulinic acid / 1-hexanol



Reactive conditions

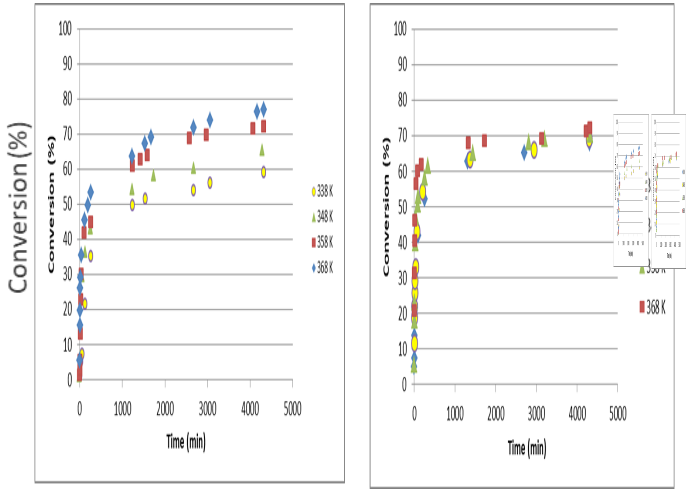
- Alcohol : Acid : AlCl3·6H2O=1: 1: 0.01 mol
- Temperatures:
  - -from 318 to 348 K (ethanol)
  - -from 338 to 368 K (1-hexanol)
- Time = 72 h

Hexanoic acid /



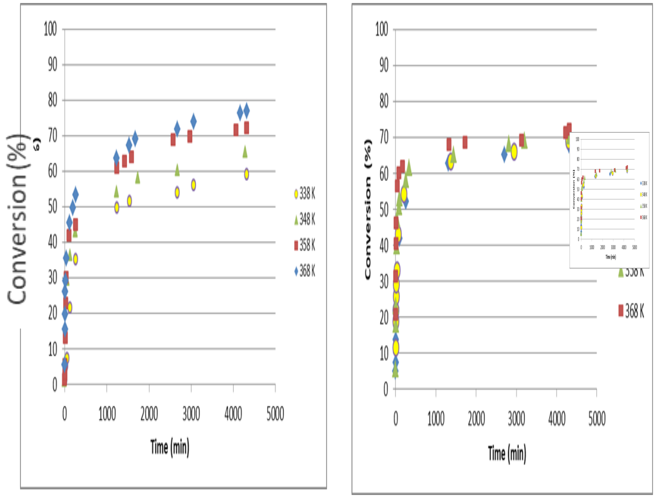
66 ± 0.4%

Hexanoic acid / 1-



76 ± 0.6%

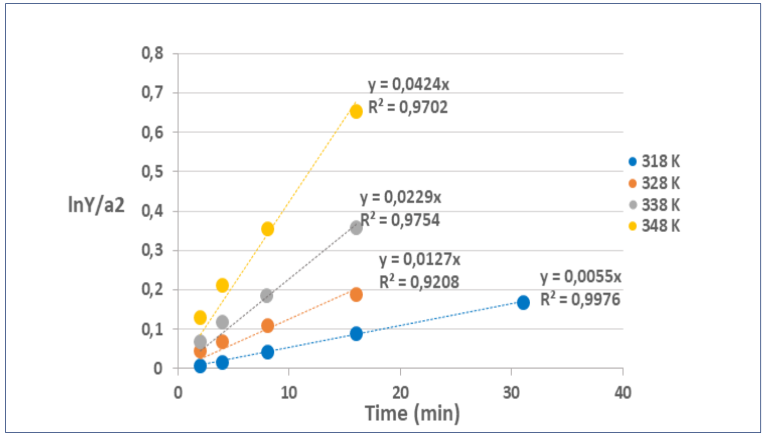
Levulinic acid / 1-



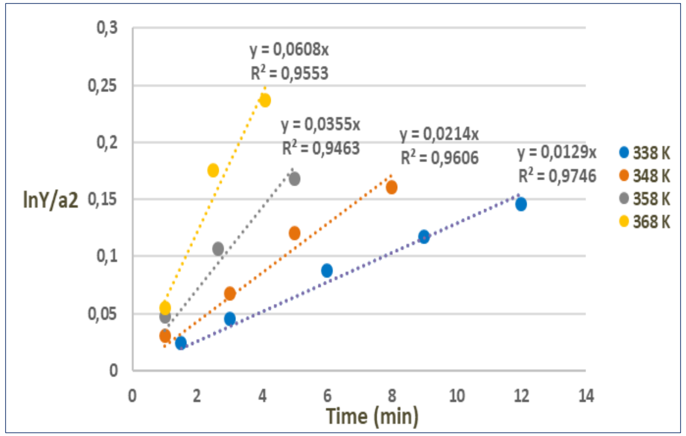
72.2 ± 0.4%

Kinetic and thermodynamic study

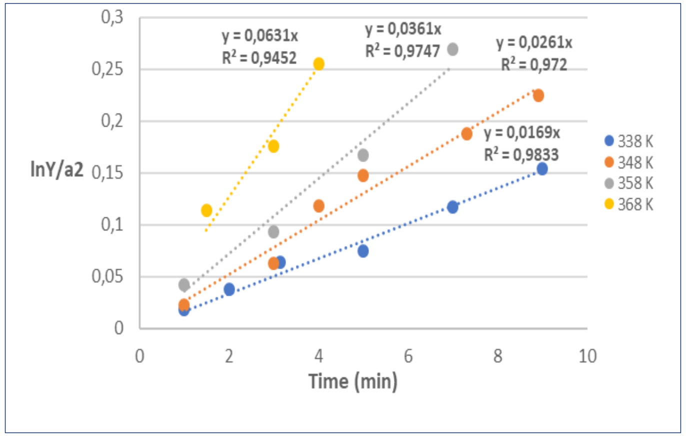
Hexanoic acid / Ethanol



Hexanoic acid / 1-Hexanol

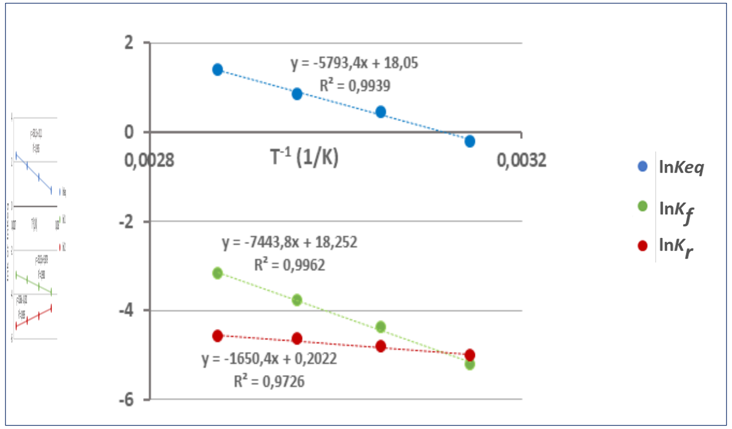


Levulinic acid / 1-Hexanol



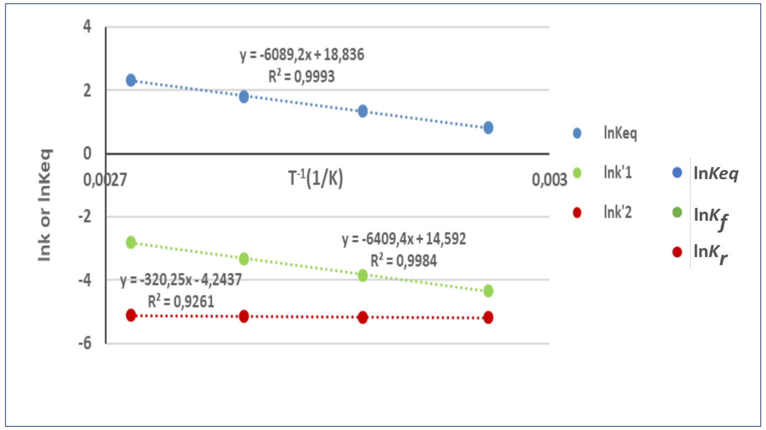
Kinetic and thermodynamic study

Hexanoic acid / Ethanol



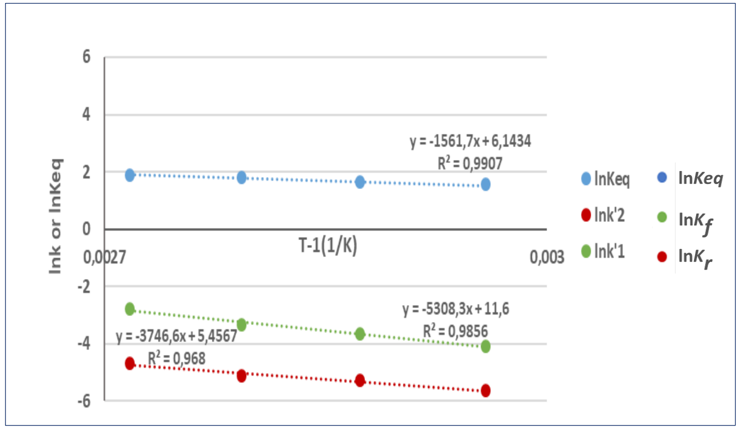
Ea (KJ/mol)	Ea-1 (KJ/mol)	ΔH0 (KJ/(mol)	ΔS0 (J/(mol*K))
61.9	13.7	48.2	150.1

Hexanoic acid / 1-



Ea (KJ/mol)	Ea-1 (KJ/mol)	ΔH0 (KJ/(mol)	ΔS0 (J/(mol*K))
53.3	2.7	50.6	156.6

Levulinic acid / 1-Hexanol



Ea (KJ/mol)	Ea-1 (KJ/mol)	ΔH0 (KJ/(mol)	ΔS0 (J/(mol*K))
44.1	31.2	13.0	51.1

Outlook

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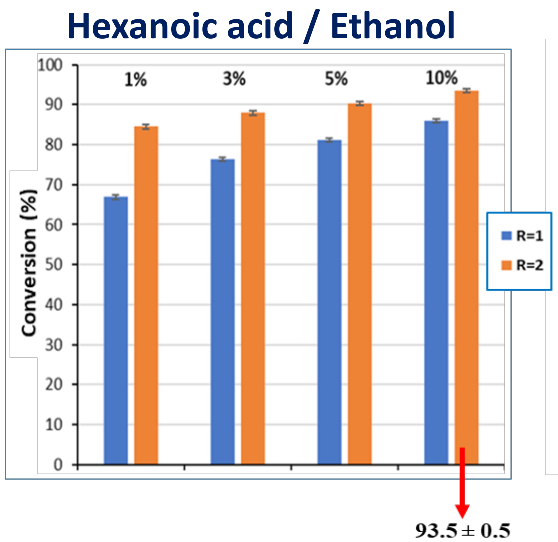
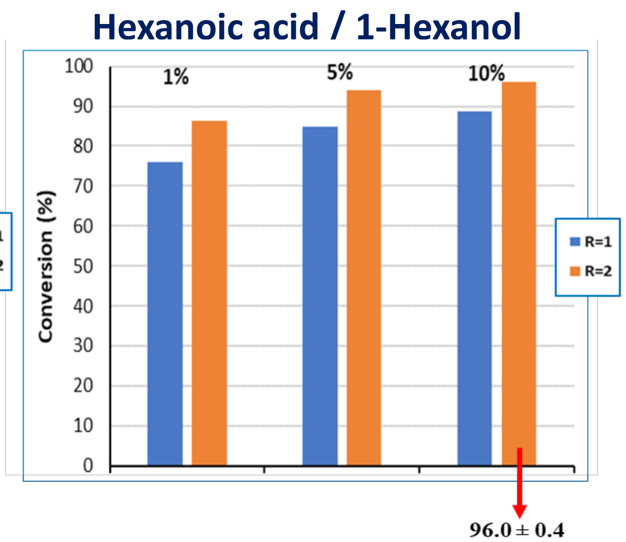
   - Kinetic and thermodynamic study
   - **Reaction tests with different amounts of catalyst and alcohol**
     - Process intensification by using $AlCl_3 \cdot 6H_2O$: high reaction yields and phase separation
   - Relationship between catalyst and K_{eq}
   - Catalyst Recoverability and Reusability
2. Focus on the esterification reaction of hexanoic acid with ethanol:
   - Reaction tests on real samples of hexanoic acid produced through the fermentation of grape pomace

Reaction tests with different amounts of catalyst and alcohol

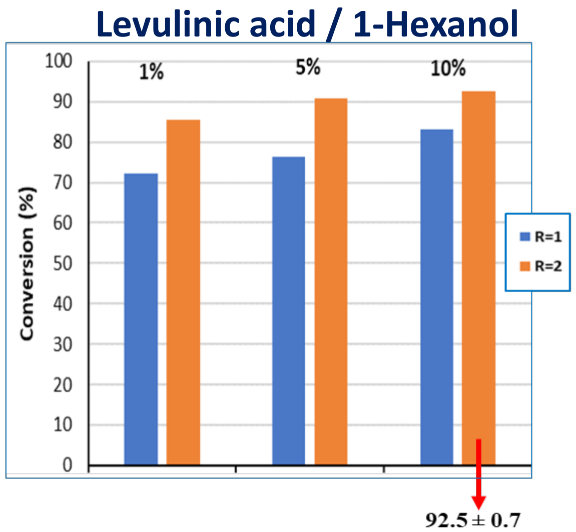
- Alcohol: Acid molar ratio (R): 1, 2
- AlCl3.6H2O: Acid molar ratio : 1, 3, 5, 10%
- Temperatures: 348 K (Ethanol)
  368 K (1-Hexanol)



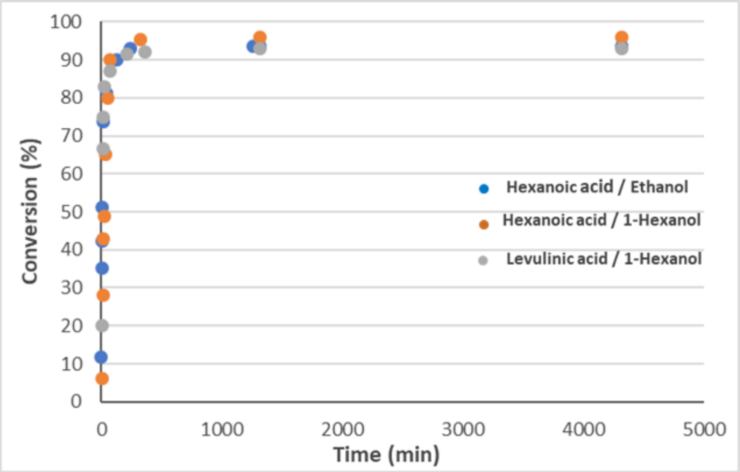
93.5±0.5%



96.0±0.5%



92.5±0.7%



Maximum conversions reached after 5 hours

Outlook

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   - Relationship between catalyst and Keq
   - Catalyst Recoverability and Reusability
2. Focus on the esterification reaction of hexanoic acid with ethanol:
     - Reaction tests on real samples of hexanoic acid produced through the fermentation of grape pomace

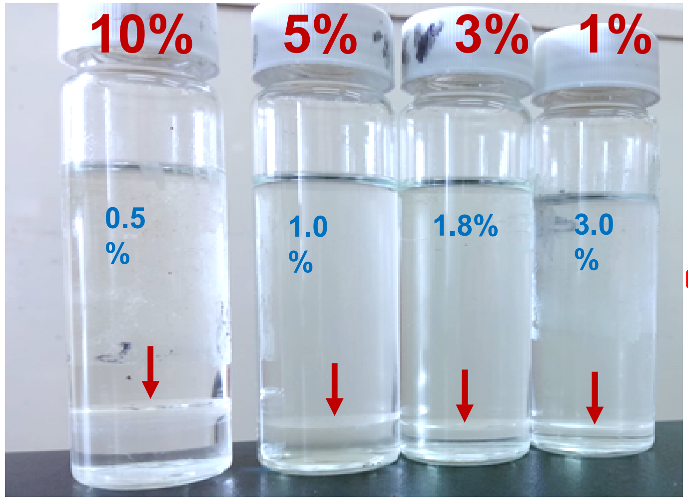
Process intensification by using AlCl3.6H2O: high reaction yields and phase separation

△ AlCl3.6H2O

- Unreacted acid
- Unreacted alcohol
- **Ester**
- Water

- Water
- AlCl3.6H2O
- (Ethanol)
- (Ethyl hexanoate)

Ethanol: Hexanoic acid: AlCl3.6H2O = 2:1:0.1 molar ratio



Increase in the amount of the lower phases with the increase of AlCl3.6H2O amount:

- **The increase of AlCl3.6H2O allows to obtain higher conversions (more water produced);**
- **AlCl3.6H2O, entirely distributed in the lower phase, draws out water from the upper phase.**

Outlook

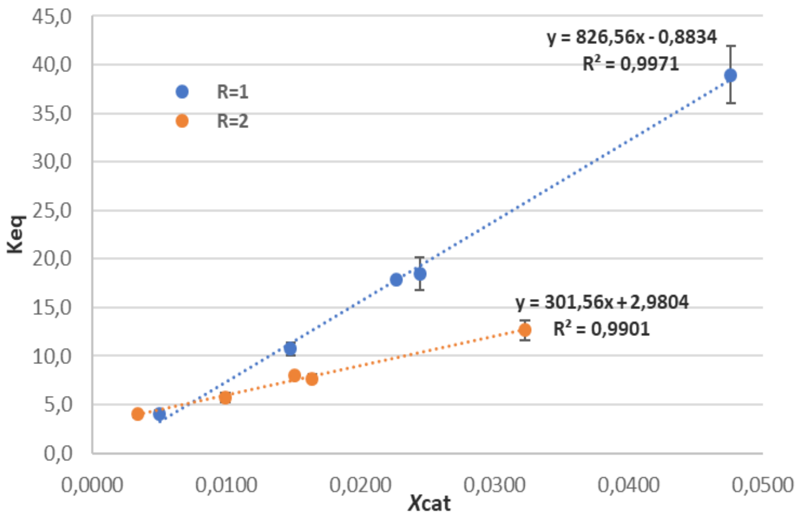
1. Esterification reactions of hexanoic acid with ethanol and 1-hexanol and levulinic acid with 1-hexanol by using $AlCl_3.6H_2O$ as catalyst
   - Kinetic and thermodynamic study
   - Reaction tests with different amounts of catalyst and alcohol
   - Process intensification by using $AlCl_3.6H_2O$: high reaction yields and phase separation
   - **Relationship between catalyst and Keq**
   - Catalyst Recoverability and Reusability
2. Focus on the esterification reaction of hexanoic acid with ethanol:
   - Reaction tests on real samples of hexanoic acid produced through the fermentation of grape pomace

Relationship between catalyst and Keq

Hexanoic acid / Ethanol

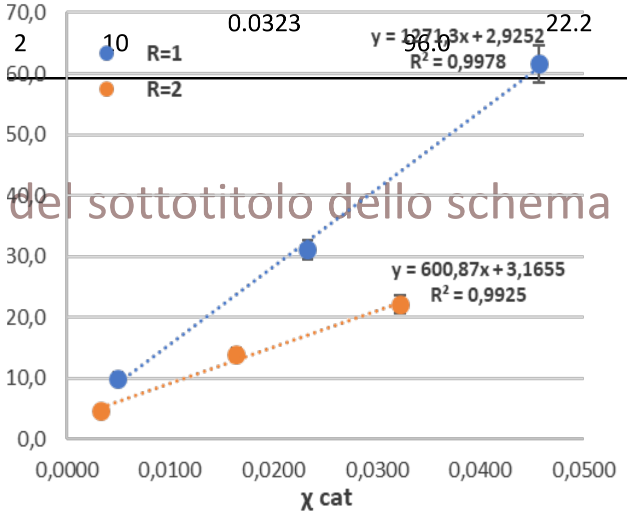
R	Catalyst (% mol)	Xcat (mol/mol)	Conversion (%)	Keq
1	1	0.0050	66.0	4.1
1	3	0.0148	76.3	10.4
1	5	0.0244	81.1	18.5
1	10	0.0476	86.2	39.0
2	1	0.0033	84.5	4.0
2	3	0.0099	87.9	5.7
2	5	0.0164	90.3	7.7
2	10	0.0323	93.5	12.7

**Homogeneus systems*



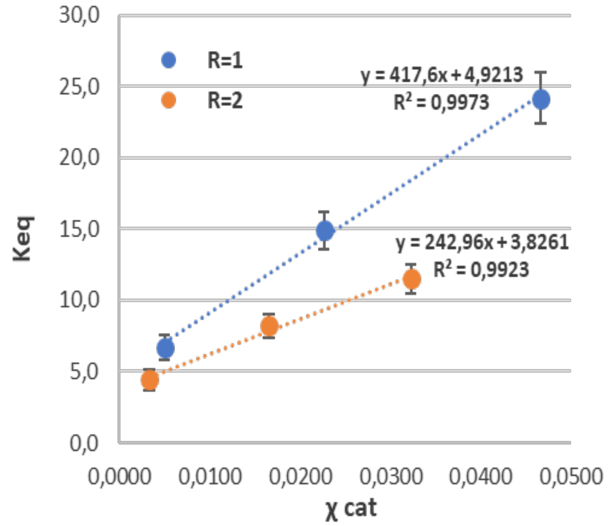
Hexanoic acid / 1-Hexanol

R	Catalyst (% mol)	χ cat (mol/mol)	Conversion (%)	Keq
1	1	0.0050	76.0	10.0
1	5	0.0164	84.8	31.1
1	10	0.0323	88.6	61.6
2	1	0.0050	86.2	4.7
2	5	0.0164	94.0	13.9
2	10	0.0323	96.0	22.2



Levulinic acid / 1-Hexanol

R	Catalyst (% mol)	χ cat (mol/mol)	Conversion (%)	Keq
1	1	0.0050	72.2	6.7
1	5	0.0164	76.5	14.9
1	10	0.0323	83.1	24.2
2	1	0.0050	85.5	4.4
2	5	0.0164	90.8	8.2
2	10	0.0323	92.5	11.5



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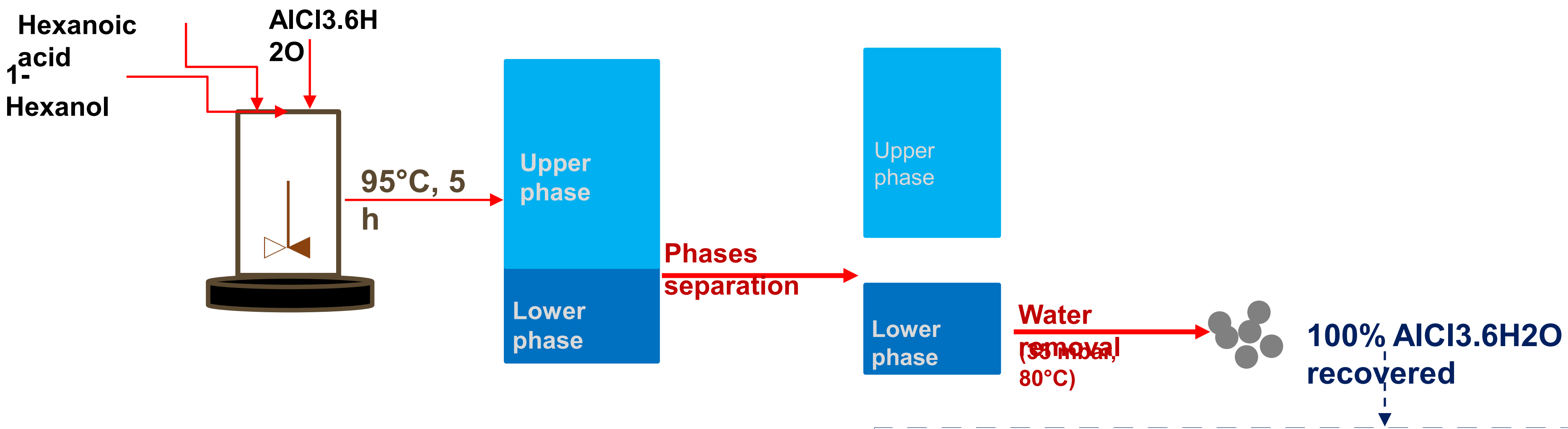
   - Process intensification by using $AlCl_3.6H_2O$: high reaction yields and phase separation
   - Relationship between catalyst and Keq
   - **Catalyst Recoverability and Reusability**
2. Focus on the esterification reaction of hexanoic acid with ethanol:
   - Reaction tests on real samples of hexanoic acid produced through the fermentation of grape pomace

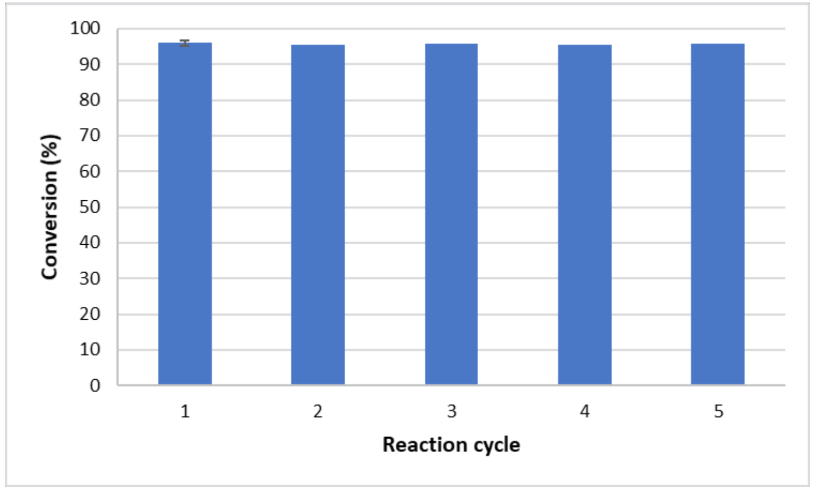
Catalyst Recoverability and Reusability



Confirmed by:

- *Gravimetrical determination*
- Cl- *and* Al3+ *determination by titration:* (Cl- = 45 ± 2% vs 44.09%*)
  (Al3+ = 10.4 ± 0.8% vs 11.18%*)

*theoretical values

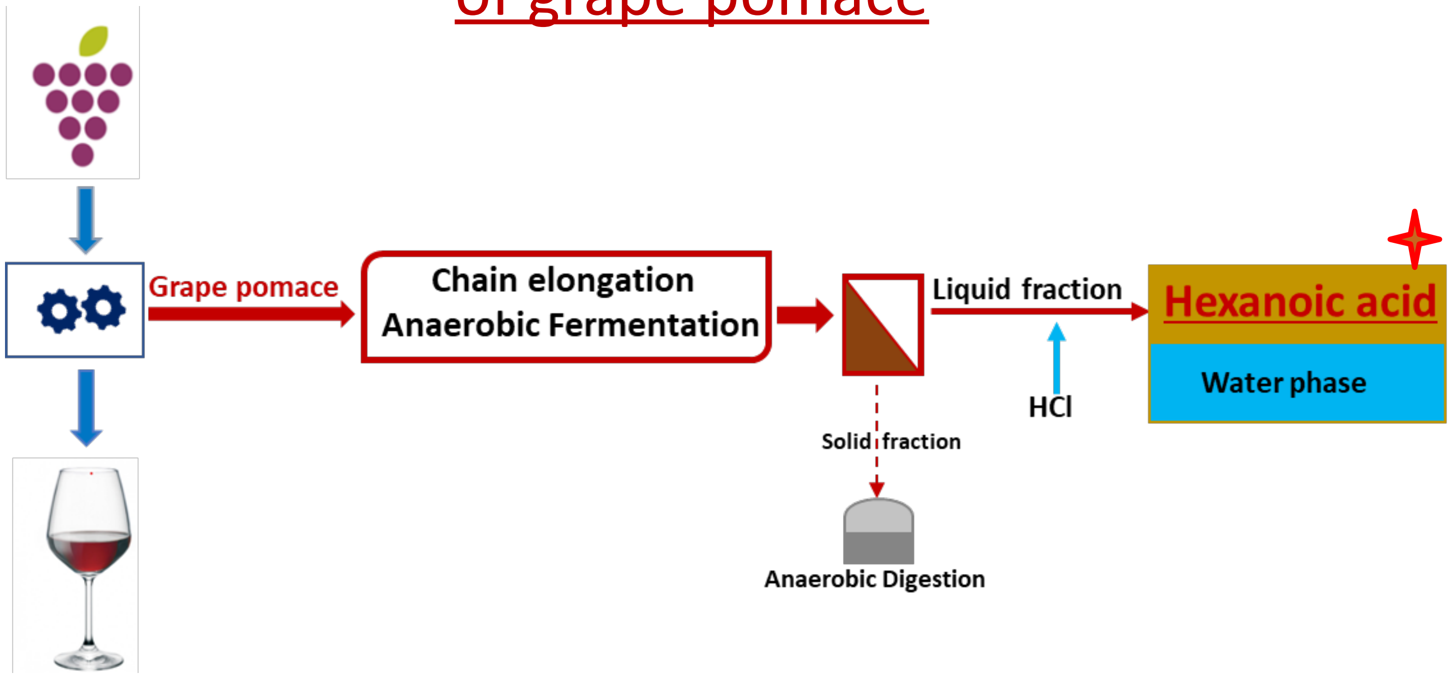


AlCl3.6H2O maintains its effectiveness even after several reaction cycles

Outlook

1. Esterification reactions of hexanoic acid with ethanol and 1-hexanol and levulinic acid with 1-hexanol by using AlCl3.6H2O as catalyst
   - Kinetic and thermodynamic study
   - Reaction tests with different amounts of catalyst and alcohol
   - Systems composition at the end of the reactions
   - Relationship between catalyst and Keq
   - Catalyst Recoverability and Reusability
2. **Focus on the esterification reaction of hexanoic acid with ethanol:**
   - **Reaction tests on real samples of hexanoic acid produced through the fermentation of grape pomace**

Reaction tests on real samples of hexanoic acid produced through the fermentation of grape pomace



Reaction tests on real samples of hexanoic acid produced through the fermentation of grape pomace

Red grape pomace (RGP)

Hexanoic acid: 87%
Butyric acid: 8.0%
Valeric acid: 0.9%
Water: 4.8%
Polyphenols: 0.08%

White grape pomace (WGP)

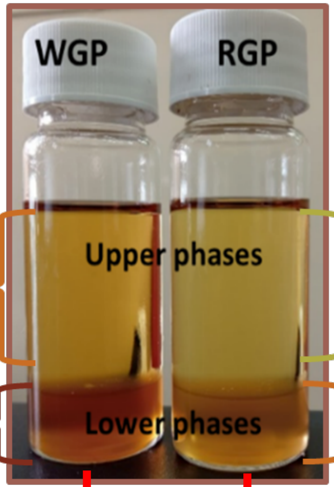
Hexanoic acid: 87%
Butyric acid: 4.9%
Valeric acid: 1.2%
Water: 5.1%
Polyphenols: 0.09%

Ethanol, AlCl3.6H2O
75°C, 5 h

Acids: Ethanol: AlCl3.6H2O= 1: 2: 0.1 mol

Ethyl hexanoate: 68.9%
Ethanol: 18.7%
Hexanoic acid: 3.9%
Ethyl butyrate: 3.1%
Water: 2.0%
Ethyl valerate: 0.9%
Valeric and Butyric acids: <0.3%

$AlCl_3 \cdot 6H_2O$: 36.6%
Water: 27.9%
Ethanol: 32.3%
Ethyl hexanoate: 4.1%

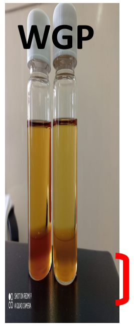


Ethyl hexanoate: 68.7%
Ethanol: 18.4%
Hexanoic acid: 4.0%
Ethyl butyrate: 5.3%
Water: 1.9%
Ethyl valerate: 0.9%
Valeric and Butyric acids: <0.3%

$AlCl_3 \cdot 6H_2O$: 36.7%
Water: 28.1%
Ethanol: 32.5%
Ethyl hexanoate: 4.0%

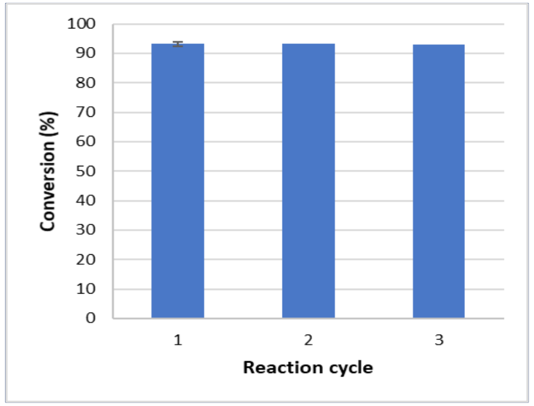
93.2 ± 0.6% **93.3 ± 0.5 %** **93.5 ± 0.3%**

Catalyst Recoverability and Reusability



(35 mbar, 80°C)

100% AlCl3.6H2O recovered



Conclusions

AlCl3.6H2O was tested as catalyst for the esterification reactions of levulinic and hexanoic acids with ethanol and 1-hexanol for obtaining **ethyl hexanoate, hexyl hexanoate** and **hexyl levulinate**

- **AlCl3.6H2O promoted process intensification:**

  -Very high reaction yields (92,5%, 93.5% and 96%) were obtained for the three esterification reactions;

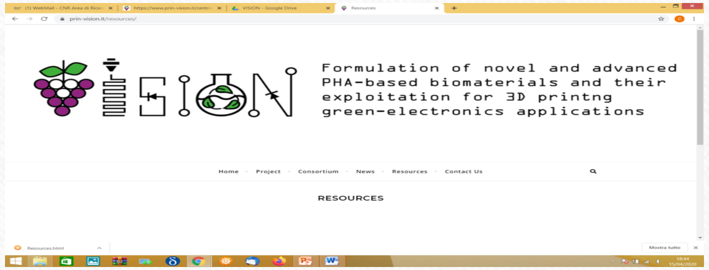
  -Phase separation was favoured by the presence of the catalyst, thus simplifying the purification process of the ester, already separated from most of the water produced from the reaction.

- **AlCl3.6H2O can be very easily and completely recovered and reused many times, without loss in its catalytic effectiveness.**

- **The catalytic effectiveness of AlCl3.6H2O and its recoverability and reusability were fully mantained even when the reaction was performed on real samples of hexanoic acid produced from grape pomace.**

The use of AlCl3.6H2O could lead to an effective and greener synthesis of these esters, minimizing the consumption of resources and reducing the waste produced, if compared to the more common mineral acids.

Acknowledgments



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Formulation of novel and advanced PHA-based biomaterials and their exploitation of 3D printing green-electronics applications

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