Hexanoic and levulinic acids esterification for ethyl and hexyl esters production by using $AlCl_3 \cdot 6H_2O$ as a catalyst

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The growing awareness of environmental issues directs research and industry towards new green synthetic paths for obtaining chemicals and biofuels. Hexanoic acid and levulinic acid are platform molecules obtainable from biomasses that can be used as precursors for the synthesis of interesting compounds for industrial purposes (Cheon et al., 2014) (Hayes and Becer, 2020). Among them, ethyl hexanoate, an apple-pineapple flavour compound, and hexyl hexanoate have several applications in food and beverage, cosmetic and pharmaceutical fields (de Barros et al., 2012; Gawas et al., 2018), the latter also with a potential application as a fuel additive (Fioroni et al., 2019) as well as ethyl and hexyl levulinate (Joshi et al., 2011; Mortazavi Tabrizi et al., 2019).

The esterification of hexanoic and levulinic acids with alcohols such as ethanol and 1-hexanol, both derivable from biomasses (Dekishima et al., 2011; Manochio et al., 2017), could represent a completely green synthetic route for obtaining esters if a green catalyst is used.

This work reports kinetic and thermodynamic studies of the esterification reactions of hexanoic and levulinic acids with ethanol and 1-hexanol for the production of ethyl and hexyl esters by using $AlCl_3 \cdot 6H_2O$ as a catalyst, which was chosen for its effectiveness in the catalysis of the esterification reaction, in addition to its reusability (Pastore et al., 2015).

Reactions were carried out at four different temperatures (318-348 K for reactions with ethanol;338-368 K for reactions with 1-hexanol), with an acid: ethanol: catalyst 1:1:0,01 molar ratio. Reactions were monitored over time and rate constants of the backward and forward reactions (k'1, k'2) and thermodynamic parameters (Keq, Ea, ΔH^0, ΔS^0) were determined, the latter by using Arrhenius and Van't Hoff equations.

Table 1. Thermodynamic parameters (Keq, Ea, Ea^{-1}, ΔH^0, ΔS^0) evaluated for the esterification reactions of levulinic and hexanoic acids with ethanol and 1-hexanol.

Ethanol-Hexanoic acid

Keq				**Ea (KJ/mol)**	**Ea^{-1} (KJ/mol)**	**ΔH (KJ/(mol)**	**ΔS (J/(mol*K))**
318 K	**328 K**	**338 K**	**348 K**	61,9	15,01	40,8	127,6
0,8786	1,6403	2,4464	4,1975				

Ethanol-Levulinic acid

Keq				**Ea (KJ/mol)**	**Ea^{-1} (KJ/mol)**	**ΔH (KJ/(mol)**	**ΔS (J/(mol*K))**
318 K	**328 K**	**338 K**	**348 K**	56,4	14,2	10,5	40,2
2,3459	2,5517	2,7778	2,8992				

Hexanol-Hexanoic acid

Keq				**Ea (KJ/mol)**	**Ea^{-1} (KJ/mol)**	**ΔH (KJ/(mol)**	**ΔS (J/(mol*K))**
338 K	**348 K**	**358 K**	**368 K**	27,7	27,0	54,7	168,1
2,0416	3,7723	6,2858	10,0278				

Hexanol-Levulinic acid

Keq				**Ea (KJ/mol)**	**Ea^{-1} (KJ/mol)**	**ΔH (KJ/(mol)**	**ΔS (J/(mol*K))**
338 K	**348 K**	**358 K**	**368 K**	43,3	29,6	13,7	53,3
4,6947	5,1194	5,9853	6,9504				

All the reactions investigated are slightly endothermic (Table 1); higher conversions were then obtained at the highest temperature used: conversions of 67% and 76% were determined for hexanoic acid with ethanol and 1-hexanol, respectively; 63% and 73% for levulinic acid with ethanol and 1-hexanol, respectively.

At the end of each reaction, two phases were observed: the upper phase was constituted mostly by the ester, followed by the unreacted acid and alcohol and a very small amount of water; the lower phase was constituted by water and the catalyst, with the latter thus carrying out a process intensification, facilitating the subsequent purification of the product. To further increase the yields, the use of an alcohol: acid 2:1 molar ratio and the increase of the amount of the catalyst (up to 10% molar with respect to acid) was investigated.

By using the aforementioned molar ratio between the reactants and an amount of catalyst equal to 10% molar with respect to the acid, a conversion of the hexanoic acid equal to 95% and 96% was obtained for the reactions with ethanol and hexanol, respectively. For levulinic acid lower conversions, equal to 85% and 93%, were obtained for reactions with ethanol and 1-hexanol, respectively. The use of such an amount of catalyst was beneficial for improving the yield and for reducing the water content in the upper phase, simplifying so the subsequent purification of the ester. Specifically, regarding the first aspect, a direct proportionality between Keq and the molar fraction of the catalyst was observed for all the four reactions studied (Figure 1), and it could be associated with the ability of the catalyst in hindering the backward reaction.

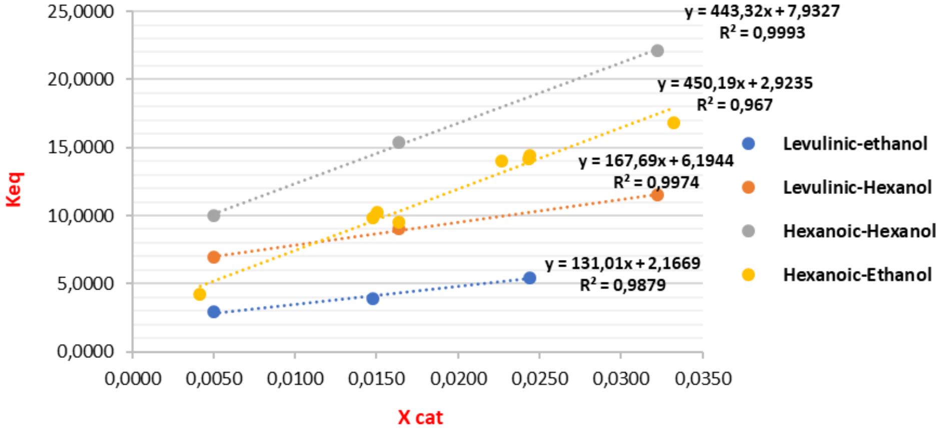

Figure 1. Relationship between the equilibrium constant (Keq) and the molar fraction of the catalyst (X cat).

Then $AlCl_3\cdot 6H_2O$ has proven to be extremely effective in process intensification. This aspect, together with the fact that the catalyst could be totally recovered by gravimetric separation of the lower phase and evaporation of the residual water, could lead to obtaining a practically zero-waste process.

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References

Cheon, Y., Kim, J.S., Park, Jun Bum, Heo, P., Lim, J.H., Jung, G.Y., Seo, J.H., Park, J.H., Koo, H.M., Cho, K.M., Park, Jin Byung, Ha, S.J., Kweon, D.H., 2014. A biosynthetic pathway for hexanoic acid production in Kluyveromyces marxianus. Journal of Biotechnology 30(6), 182–183.

de Barros, D.P.C., Azevedo, A.M., Cabral, J.M.S., Fonseca, L.P., 2012. Optimization Of Flavor Esters Synthesis By Fusarium Solani Pisi Cutinase. Journal of Food Biochemistry 36.

Dekishima, Y., Lan, E.I., Shen, C.R., Cho, K.M., Liao, J.C., 2011. Extending carbon chain length of 1-butanol pathway for 1-hexanol synthesis from glucose by engineered Escherichia coli. Journal of the American Chemical Society 133(30), 11399-401.

Fioroni, G., Fouts, L., Luecke, J., Vardon, D., Huq, N., Christensen, E., Huo, X., Alleman, T., McCormick, R., Kass, M., Polikarpov, E., Kukkadapu, G., Whitesides, R.A., 2019. Screening of potential biomass-derived streams as fuel blendstocks for mixing controlled compression ignition combustion, in: SAE Technical Papers.

Gawas, S.D., Lokanath, N., Rathod, V.K., 2018. Optimization of enzymatic synthesis of ethyl hexanoate in a solvent free system using response surface methodology (RSM). Biocatalysis 4(1), 14-26.

Hayes, G.C., Becer, C.R., 2020. Levulinic acid: A sustainable platform chemical for novel polymer architectures. Polymer Chemistry 11(25), 4068-4077.

Joshi, H., Moser, B.R., Toler, J., Smith, W.F., Walker, T., 2011. Ethyl levulinate: A potential bio-based diluent for biodiesel that improves cold flow properties. Biomass and Bioenergy 35, 3262–3266.

Manochio, C., Andrade, B.R., Rodriguez, R.P., Moraes, B.S., 2017. Ethanol from biomass: A comparative overview. Renewable and Sustainable Energy Reviews 80, 743-755.

Mortazavi Tabrizi, M., Najafi Chermahini, A., Mohammadbagheri, Z., 2019. Synthesis of hexyl levulinate as a potential fuel additive from levulinic acid over a solid acid catalyst. Journal of Environmental Chemical Engineering 7, 103420.

Pastore, C., Barca, E., del Moro, G., Lopez, A., Mininni, G., Mascolo, G., 2015. Recoverable and reusable aluminium solvated species used as a homogeneous catalyst for biodiesel production from brown grease. Applied Catalysis A: General 501, 48–55.