

PHASE EQUILIBRIUM AND PURIFICATION PROCESSES IN THE PRODUCTION OF BIOFUELS AND BIOCOMPOUNDS

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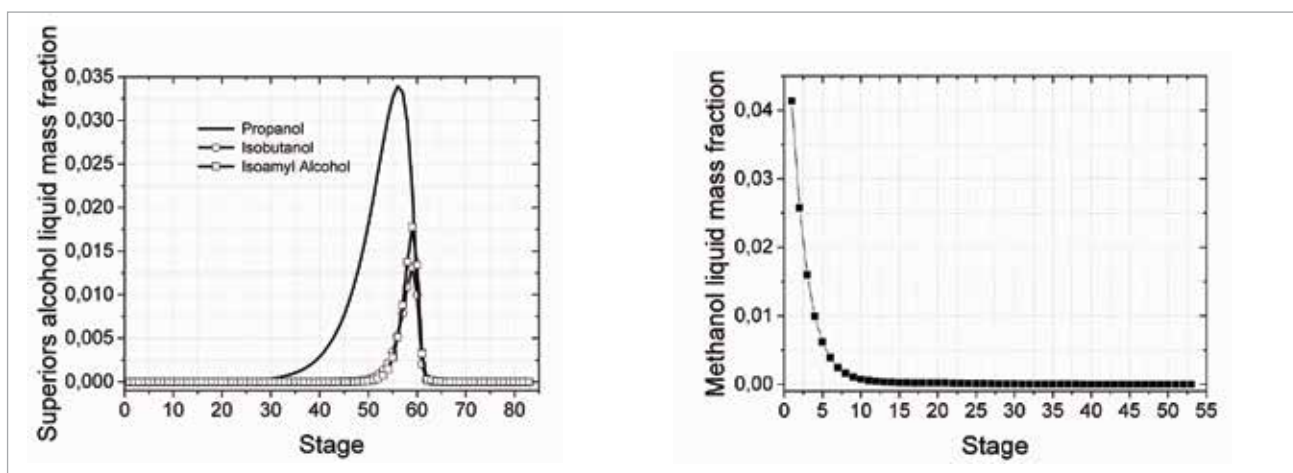


Figure 1. Superior alcohols profile in rectifier column (a) and methanol profile in demethylizer column (b) (Batista, Follegatti-Romero and Meirelles, 2013)

This project aims to optimize purification processes used during biofuels production and to enhance the added value of byproducts generated in those processes. In the case of bioethanol, the distillation process was investigated taking into account minor components relevant for product quality, according to legislation standards for biofuels and for the requirements of a raw material for chemical, pharmaceutical, cosmetics and food industries. Configurations of distillation columns actually used in sugar mills were investigated by experimental measurements in those industrial unities and by process simulation. A comprehensive investigation of the wine phase equilibrium was carried out, taking into account a complete set of minor components. New and innovative configurations of distillation columns were proposed, aiming at better product quality, equipment flexibility, higher ethanol recovery, lower energy consumption, and better byproducts quality. Such

configurations were further tested for concentrating bioethanol obtained from wine with high alcohol content and from cellulosic residues. In case of ethylic biodiesel, a comprehensive investigation of the different types of phase equilibrium occurring along the whole production process was carried out. The use of bioethanol, as a solvent for extracting vegetable oils from seeds and grains and for deacidifying crude oils by liquid-liquid extraction, as well as a reactant in biodiesel production can integrate biodiesel and bioethanol productions. In the case of biocompounds, strategies for enhancing the value of byproducts generated during biofuels production were investigated. For instance, the fractionation of high alcohols generated as a sidestream during bioethanol distillation, the use of glycerol in the production of surfactants and emulsifiers, the recovery of nutraceuticals from edible oils, the formulation, fractionation and transformation of fatty mixtures based on solid-liquid equilibrium data.

SUMMARY OF RESULTS TO DATE AND PERSPECTIVES

Bioethanol binary distillation is a frequent research topic found in the literature. However, its distillation taking into account the real complexities of wine composition and industrial column configurations is a subject largely unexplored. The simulation tools available nowadays make possible to reproduce the industrial process with a high degree of confidence, providing a firm basis for optimizing it and suggesting new configurations that can improve the efficiency of bioethanol distillation. The distilling behavior of several minor components, classified into light, middle volatility and heavy compounds, were investigated in the production of spirits, hydrated ethanol and neutral alcohol. Middle volatility components, despite their very low content in the original wine, achieve high concentrations in specific parts of the distillation column, affecting in a significant way the whole process. Strategies for controlling bioethanol contamination with those components, such as superior alcohols and methanol in neutral alcohol production, were also developed (Figure 1).

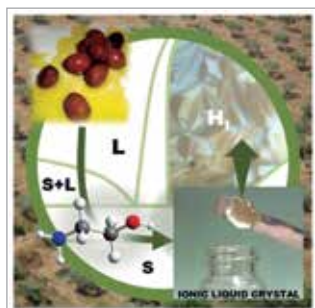


Figure 2. Ionic liquids synthesized from fatty acids (extracted from vegetable oils). These compounds presented interesting liquid-crystalline behavior above melting temperature which is quite important for pharmaceutical applications (Maximo et al., 2013)

Due to several drawbacks, ethylic biodiesel is almost not produced in an industrial scale. If these drawbacks are solved, an approach based on the bioethanol use in several steps of biodiesel production, from the seed to the tank, becomes technically feasible. Traditional and innovative techniques for deacidifying crude vegetable oils were investigated by experimental runs and simulation. The innovative techniques used bioethanol as solvent or extractant. Biodiesel reaction

occurs in a two-phase environment, requiring information on the corresponding equilibrium data. Such data were measured and correlated in situations suitable for homogeneous catalysis and biocatalysis.

The production of biofuels generates byproducts whose added value can be increased by fractionation or transformation. Phase equilibrium data provide the basis for optimizing the purification processes; product formulations and biocompound synthesis (Figure 2). Physical-chemical properties and equilibrium data were measured and correlated for fatty mixtures containing fatty acids, fatty esters, fatty alcohols, triacylglycerols, nutraceutical and lipidic protic ionic liquid crystal compounds.

MAIN PUBLICATIONS

Rodrigues CEC, Gonçalves CB, Marcon EC, Batista EAC, Meirelles AJA. 2014. Deacidification of rice bran oil by liquid-liquid extraction using a renewable solvent. *Separation and Purification Technology*. v. 132, p. 84-92, 2014.

Robustillo MD, Barbosa DF, Meirelles AJA, Pessôa Filho PA. 2014. Solid-liquid equilibrium of binary and ternary mixtures containing ethyl oleate, ethyl myristate and ethyl stearate. *Fluid Phase Equilibria*. **370**: 85-94.

Maximo GJ, Costa MC, Meirelles AJA. 2014. The Crystal-T algorithm: a new approach to calculate the SLE of lipidic mixtures presenting solid solutions. *PCCP. Physical Chemistry Chemical Physics*. **16**: 16740.

Ferreira MC, Meirelles AJA, Batista EAC. 2013. Study of the fusel oil distillation process. *Industrial & Engineering Chemistry Research*. **52**: 2336-2351.

Basso RC, Silva CAS, Sousa COL, Meirelles AJA, Batista EAC. 2013. LLE Experimental data, thermodynamic modeling and sensitivity analysis in the ethyl biodiesel from macauba pulp oil settling step. *Bioresource Technology*. **131**: 468-475.

Batista FRM, Meirelles AJA. 2013. Computational simulation applied to improve fuel bioethanol distillation. *Zuckerindustrie (Berlin) / Sugar Industry (Berlin)*. **138**: 645-650.

Batista FRM, Follegatti-Romero LA, Meirelles AJA. 2013. A new distillation plant for neutral alcohol production. *Separation and Purification Technology*. **118**: 784-793.

Maximo GJ, Santos RJBN, Lopes SJA, Costa MC, Meirelles AJA, Coutinho JAP. 2013. Lipidic protic ionic liquid crystals. *ACS Sustainable Chemistry & Engineering*. **2**: 682.

Bessa LCBA, Ferreira MC, Batista EAC, Meirelles AJA. 2013. Performance and cost evaluation of a new double effect integration of multicomponent bioethanol distillation. *Energy (Oxford)*. **63**: 1-9.

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