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

Antonio José de Almeida MEIRELLES
School of Food Engineering / State University of Campinas (FEA/UNICAMP)

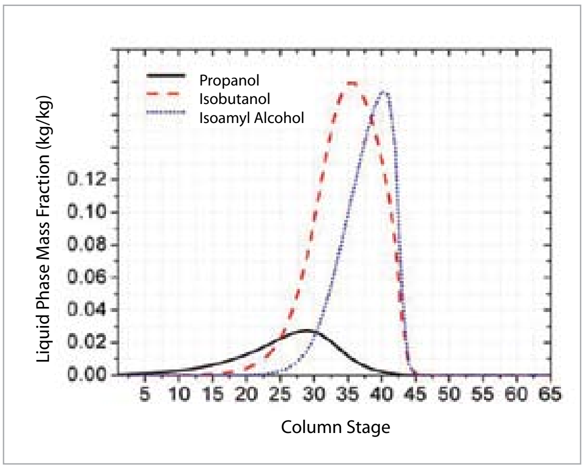

Figure 1. Concentration profiles of high alcohols in bioethanol distillation columns BB1 (Batista and Meirelles, 2009)

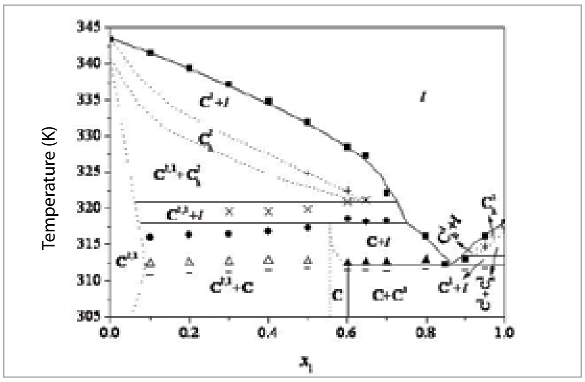

Figure 2. Phase diagram for the system lauric acid (1) + stearic acid (2). (■) fusion temperature; (●) peritectic temperature; (▲) eutectic temperature; (×) metatectic temperature; (+), (△), (–) transitions temperatures on the solid phase; (❍) transition on the solid phase of the pure component (Costa et al., 2009)

This project aims to optimize the purification processes used in the production of biofuels and to enhance the added value of byproducts generated during such processes. In the case of bioethanol, the distillation process will be investigated taking into account minor components relevant for product quality, according to standards fixed by the legislation for biofuels and the requirements of the raw materials for the chemical, pharmaceutical, cosmetics and food industries. The configurations of distillation columns currently in use in sugar mills will be investigated by experimental means in the industrial units and by process simulation. A comprehensive investigation of the phase equilibrium of wine will be carried out, taking into account a complete set of minor components. New and innovative configurations for distillation columns will be proposed, aiming at better product quality, equipment flexibility, higher ethanol recovery, lower energy consumption and better byproduct quality. Such configurations will be further tested for concentrating the bioethanol obtained from wine with a high alcohol content and from cellulosic residues. In the case of ethylic biodiesel, a comprehensive investigation of the different types of phase equilibrium occurring throughout the whole production process will be carried out. The use of ethylic alcohol as a solvent for extracting vegetable oils from seeds and grains, and for deacidifying crude oils by liquid-liquid extraction, as well as its use as a reactant in biodiesel production will be studied, with the purpose of integrating biodiesel and bioethanol productions. The optimization of the whole production process, including the oil extraction and deacidification, biodiesel reaction and purification, will be performed by simulation. In the case of biocompounds, strategies for enhancing the value of byproducts generated during the production of biofuels will be investigated. For instance, the fractionation of higher alcohols generated as a sidestream during the distillation of bioethanol, the use of glycerol in the production of surfactants and emulsifiers, the recovery of nutraceuticals from edible oils, and the formulation and fractionation of fatty mixtures based on solid-liquid equilibrium data.

SUMMARY OF RESULTS TO DATE AND PERSPECTIVES

The binary distillation of bioethanol is a frequent research topic found in the literature. However its distillation taking into account the real complexities of wine composition and the industrial column configurations is a subject largely unexplored. The simulation tools available nowadays make it possible to reproduce the industrial process with a high degree of reliability, providing a firm basis for optimizing it and suggesting new configurations that can improve the efficiency of the bioethanol distillation. The distillation 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 (*Figure 1*), affecting the whole concentration process in a significant way. Strategies for controlling bioethanol contamination with light components were also developed.

Due to several drawbacks, ethylic biodiesel is almost not produced on an industrial scale. If these drawbacks were solved, an approach based on the use of bioethanol in several steps of biodiesel production, from seed to tank, would become technically feasible. Traditional and innovative techniques for deacidifying crude vegetable oils were investigated by experimental trials and simulation. The innovative techniques used bioethanol as a solvent or extractant. The 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 process and product formulation. The physical-chemical properties and equilibrium data were correlated and measured for fatty mixtures containing fatty acids, fatty esters, fatty alcohols, triacylglycerols and nutraceutical compounds (*Figure 2*).

MAIN PUBLICATIONS

Boros L, Batista MLS, Vaz RV, Figueiredo BR, Fernandes VFS, Costa MC, Krähenbühl MA, Meirelles AJA, Coutinho JAP. 2009. Crystalization behaviour of mixtures of fatty acid ethyl esters with ethyl stearate. *Energy & Fuels*. **23**:4625-4629.

Batista FRM, Meirelles AJA. 2009. A strategy for controlling acetaldehyde content in an industrial plant of bioethanol. *International Symposium on Advanced Control of Chemical Processes* (ADCHEM), Istanbul, Turkey.

Ceriani R, Gani R, Meirelles AJA. 2009. Prediction of heat capacities and heats of vaporization of organic liquids by group contribution methods. *Fluid Phase Equilibria*. **283**:49-55.

Costa MC, Rolemberg MP, Meirelles AJA, Coutinho JAP, Krähenbühl MA. 2009. The solid-liquid phase diagrams of binary mixtures of even saturated fatty acids differing by six carbon atoms. *Thermochimica Acta*. **496**:30-37.

Cren EC, Cardozo L, Silva EA, Meirelles AJA. 2009. Breakthrough curves for oleic acid removal from ethanolic solutions using a strong anion exchange resin. *Separation and Purification Technology*. **69**:1-6.

Silva CAS, Sanaiotti G, Lanza M, Follegatti-Romero LA, Meirelles AJA, Batista EAC. 2010. Mutual solubility for systems composed of vegetable oil plus ethanol plus water at different temperatures. *Journal of Chemical and Engineering Data*. **55**:440-447.

Falleiro RMM, Meirelles AJA, Krähenbühl MA. 2010. Experimental determination of the (vapor plus liquid) equilibrium data of binary mixtures of fatty acids by differential scanning calorimetry. *Journal of Chemical Thermodynamics*. **42**:70-77.

Scanavini HFA, Ceriani R, Cassini CEB, Souza ELR, Maugeri F, Meirelles AJA. 2010. Cachaça production in lab-scale alembic: modeling and computational simulation. *Journal of Food Process Engineering*. **33**:226-252.

Antonio José de Almeida Meirelles

Faculdade de Engenharia de Alimentos
Universidade Estadual de Campinas (UNICAMP)
Rua Giuseppe Maximo Scolfaro, 501 – Casa 8
Cidade Universitária
CEP 13083-100 – Campinas, SP – Brasil

+55-19-3788-4037
tomze@fea.unicamp.br