SOLID-LIQUID EQUILIBRIUM OF FATTY COMPOUNDS AND BIODIESEL FLASH POINT

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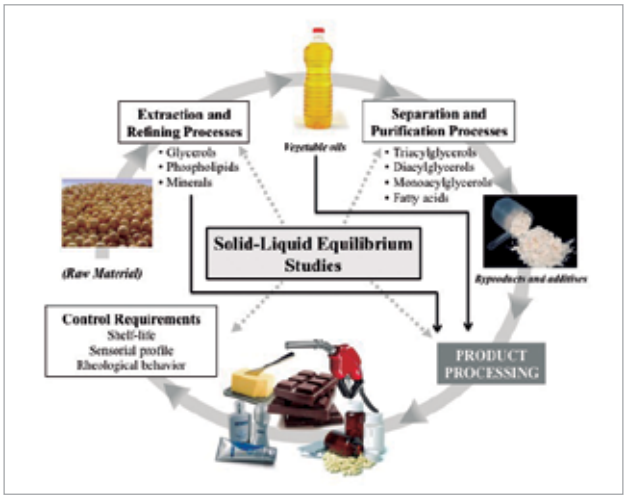

Figure 1. Action fields of solid–liquid equilibrium studies in the vegetable oil processing industry (Maximo et al., 2014)

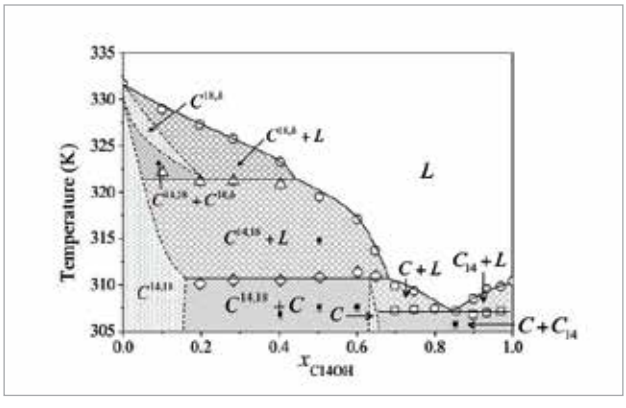

Figure 2. Solid–liquid phase diagram of the C14OH + C18OH system based on step- scan DSC. (○) Melting temperature; (□) eutectic reaction; (◊) peritectic reaction; (Δ) metatectic reaction; (■) solid-solid transition. (- - -) and (—) are guides to the eyes. L: liquid phase; C_{14}: C14OH on solid state, $C^{14,18}$: solid solution rich in C18OH; C: peritectic compound; and $C^{18,h}$: metatectic compound (Carareto et al., 2014)

The growing worldwide demand for new renewable energy sources puts the Brazil in a privileged position in the world due to our large experience in the ethanol production from sugar cane and also due to the large portion of farmland in our territory. In this way Brazil is one of the most capable country in the world to development the biorefineries. To realize this favorable situation it is necessary the development of new technologies related to the biocompounds, especially fatty compounds. It is important to study and understand all equilibrium conditions that can be observed during the processing of vegetable oils, since its extraction, processing refine until biodiesel production. The purpose of this research project is to construct solid-liquid equilibrium (SLE) phase diagrams of fatty compounds and investigate the different solid-solid (SSE) and solid-liquid (SLE) equilibrium regions. Besides the phase diagram, the flash point of ethylic and methylic biodiesel is going to be determined. SLE experimental data could be used to improve the separation processes and to propose new separation methods. Flash point data is an important property that must be observed in storage, transportation and production of biodiesel. Furthermore, in the near future, there is an intention of use these data to formulate products that should attend market requirements and physicochemical properties necessary for their distribution and use.

SUMMARY OF RESULTS TO DATE AND PERSPECTIVES

It has been determined over than 30 solid-liquid equilibrium (SLE) phase diagrams of fatty compounds. The results have been found for binary mixtures formed by two fatty alcohols and mixtures of one fatty alcohol plus one fatty acid and such results are showed mostly very complex due to the occurrence of eutectic, peritectic and metatectic reactions and also by the solid solution formation. The systems formed by one triacylglycerol plus a fatty alcohol or fatty acids are simple ones in which they have been presenting just only the eutectic reaction and/or solid solution formation.

The SLE phase diagrams of fatty acid ethyl esters (FAEEs) of three binary mixtures were measured using high pressure microscopy in the range of 0.1–80 MPa. It was showed a linear dependence of pure FAEE from the pressure and that the binary phase diagrams are only slightly affected by the pressure, even at 80 MPa.

In terms of thermodynamic models, it was successfully purposed a new procedure, namely "Crystal-T algorithm" to describe some binary mixtures of triacylglycerols plus fatty alcohols that have been presenting a solid solution formation considering the non idealities of the solid and liquid phases. Moreover, the traditional Margules 3-suffix and NRTL equations may also be used to describe the liquidus line of such a systems. The FAEE high pressure data was also modeled employing a model previously applied to alkanes using the Soave-Redlich-Kwong equation to liquid phase fugacity coefficient with the LCVM mixing rule.

The Flash point (FP) is one of the most important physicochemical properties for establishing the potential for fire and explosion of a hazardous material such as a fuel and also for ensuring safe storage and transportation. FP data has been determined for binary and ternary mixtures formed by ethylic esters and for some ethylic biodiesel.

The path forward is related to the ongoing determination of the binary SLE phase diagrams consisted by triacylglycerols plus fatty alcohols or fatty acids and the determination of ternary SLE phase diagrams of such a substances along with the challenge of describing the determined systems through thermodynamic equations. Furthermore, the FP studies will be continued using methyl esters associated with the thermodynamic modeling of the experimental data. In order to have a complement of experimental work, it will be determined the heat capacity of some triacylglycerol compounds which are very important and critical for modeling as well as for computational simulation of such systems during processing and even for the new products formulation.

MAIN PUBLICATIONS

Carareto NDD, Castagnaro T, Costa MC, Meirelles, AJA. 2014. The binary (solid + liquid) phase diagrams of (caprylic or capric acid) + (1-octanol or 1-decanol). *J. Chem. Thermodyn*. **78**: 99-108.

Carareto NDD, Santos AOS, Rolemberg MP, Cardoso LP, Costa MC, Meirelles, AJA. 2014. On the solid–liquid phase diagrams of binary mixtures of even saturated fatty alcohols: systems exhibiting peritectic reaction. *Thermochim. Acta*. **589**: 137-147.

Carareto NDD, Costa MC, Meirelles, AJA. Pauly J. 2014. High pressure solid–liquid equilibrium of fatty acid ethyl esters binary systems. *Fluid Phase Equilibria*. **382**: 158-163.

Maximo GJ, Costa MC, Meirelles AJA. 2014. Solid-liquid equilibrium of triolein with fatty alcohols. *Brazilian J. Chem Eng*. **30**: 33-43.

Maximo GJ, Carareto NDD, Costa MC, Santos AOS, Cardoso LP, Krähenbühl MA, Meirelles AJA. 2014. On the solid–liquid equilibrium of binary mixtures of fatty alcohols and fatty acids. *Fluid Phase Equilibr*. **366**: 88-98, 2014.

Maximo GJ, Costa MC, Coutinho JAP, Meirelles AJA. 2014.Trends and demands in the solid-liquid equilibrium of lipidic mixtures. *RSC Adv*. **4**: 31840-31850.

Maximo GJ, Costa MC, Meirelles AJA. 2014. The Crystal-T algorithm: a new approach to calculate the SLE of lipidic mixtures presenting solid solutions. *Phys. Chem. Chem. Phys*. **16**: 16740-16754.

Matos FC, Costa MC, Meirelles AJA, Batista EAC. 2015. Binary solid–liquid equilibrium systems containing fatty acids, fatty alcohols and triolein by differential scanning calorimetry. *Fluid Phase Equilibr.* **404**: 1-8.

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