# Solid-liquid phase diagrams of fatty binary mixtures

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## Introduction

The increasing population and economic growth of a number of developing countries, conjugated with dwindling petroleum reserves, has amplified the world demand for alternative energies. Moreover, to a large extent climate changes have been linked to the burning of fossil fuels which leads to the emission of large quantities of greenhouse gases. In this scenario it is important to develop new renewable energy sources that can meet the global energy demands without harming the environment. Biodiesel and bioethanol are among the most promising new alternative fuel sources generating a new industry segment called biorefinery. It is possible that, in a no so distant future, biorefineries will produce a large variety of bioproducts that will be applied in many sectors of the chemical industry.

In the case of the oleochemical industry, based in the vegetable oil and biodiesel production some compounds such as fatty acids, triacylglycerols, fatty alcohols and nutraceutical compounds can be present in practically all process stages. These substances, in some stages considered as byproducts, can be separated and sold as added value products used in the formulation of cosmetic, pharmaceutical or food products, for example.

In turn, fatty acid ethyl or methyl esters, components of biodiesel, should attend several specifications that stipulate the limit values for the low-temperature properties of the fuel, such as the Cloud Point, CP (EN 23015, ASTM D-2500), the Pour Point, PP (ASTM D-97, ASTM D-5949), the Cold Filter Plugging Point, CFPP (EN 116, IP-309, ASTM D-6371) and the Low Temperature Filterability Test, LTFT (ASTM D-4539)5. The Cloud Point (CP), for example, is the temperature at which a hazy appearance develops on a fuel upon cooling due to the crystallization of the heavier fatty acid esters. With further temperature decrease the crystal particles grow and agglomerate, reducing the capacity of the liquid to flow through porous media plugging the fuel filters. The importance of the knowledge of the solid-liquid equilibrium of fatty esters remains in the purification of biofuel too as well as in the formulation of the biofuel whereas a biodiesel produced from oils or fats with considerable amounts of saturated triglicerides will display high cloud points, for example.

The aim of this study was determine and analyze a set of phase diagrams of binary fatty mixtures due to the importance of such components in the vegetable oil and biodiesel production, its added value when pure and the possibility of products formulation. It was determined by differential scanning calorimetry technique (DSC) 85 phase diagrams: 13 mixtures formed by two saturated fatty acids, 12 mixtures of saturated fatty alcohols, 27 mixtures of ethyl esters, 3 mixtures of methyl esters, 16 mixtures of one saturated fatty alcohol plus one saturated fatty acid and more 14 binary mixtures of saturated or unsaturated fatty acids with triacylglycerols. The solid phase of some phase diagrams were studied using X-ray diffraction, FT-Raman spectroscopy and optical microscopy.

**Results and discussion**

The phase diagrams of fatty substances can exhibit or not the eutectic and peritectic reactions. Both reactions, generally, are responsible to the shape of the *liquidus* line of each system. If the eutectic reaction occurs in one system its *liquidus* line will present an inflexion point that is approximately the eutectic composition. When both reactions occur, eutectic and peritectic ones, two inflexion points can be observed in the *liquidus* line of the system. The occurrence of these reactions implies in difficulties to develop separation processes and in the equilibrium regions.

In the studied systems, independently of the mixture, all of the phase diagrams exhibit the eutectic point. The eutectic composition is not the same for the systems varying with the mixtures components. For example, in the system formed by myristic acid + lauric acid the eutectic composition is around 0.75 molar fraction of the lighter component, in the system 1-decanol + 1-tetradecanol the eutectic point 0.85 whereas in the system 1-hexadecanol + myristic acid is located around 0.6 molar fraction of the lighter component.

In some systems the eutectic point was observed in a composition very close to the pure component with smaller melting temperature of the mixture. In these systems the eutectic temperature it is very close to the melting temperature of the pure component too interfering on the data interpretation. This is the case of ethyl oleate + ethyl palmitate system and more than ten of the ethylic systems studied. This closeness observed principally in ethyl systems suggests that the larger differences in the melting temperatures of the pure components of the mixtures, that is the case of unsaturated ethyl esters and saturated ones, are the responsible by this effect.

The peritectic reaction was also observed in the phase diagrams constructed. This reaction is more common in saturated fatty acids systems than in the others. This reaction was observed in all of the systems formed by saturated fatty acids and was observed in just  in four systems formed by saturated fatty alcohols, in three systems formed by fatty alcohol + fatty acid, in five ethylic systems and in two methylic systems. The occurrence of peritectic reaction seems to be related to the difference between the carbon chain of each mixture component and the carbon chain itself, for example, the end group and the molecule conformation.

In some of the studied systems was also observed the occurrence of solid solution in one or in both extremes of the phase diagram. Just for systems formed by fatty alcohols occurs a large region of miscibility in the phase diagrams that seems forbidden the occurrence of both, peritectic and eutectic reactions.

In summa, the phase diagrams of binary fatty mixtures exhibit quite complex behavior, still not fully understood that holds many challenges and discoveries.

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**Author Publications**

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