DESIGN OF A THERMALLY COUPLED REACTIVE DISTILLATION SEQUENCE FOR TRIETHYL CITRATE PRODUCTION.

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Recent trends in the plasticizers market have shown a shift towards the consumption of renewable and bioderived ones. Although not all bioderived plasticizers can substitute petroleum derived plasticizers in all applications, biobased are gaining acceptance because their low toxicity, biocompatibility and biodegradability. Triethyl citrate (TEC) is a well-known, Generally Recognized as Safe (GRAS), bioderived plasticizer, which has been used as a substitute for various phthalic acid esters. TEC has found its main market in application such as medical devices and children toys mainly due to the safety concerns of using phthalates. Nevertheless, its competitiveness in a broader market is limited because its high production costs. These high production costs are related to the excess of ethanol required in the process, and the energy required for its recovery and recycling, as well as the TEC separation and purification. In this sense, the economics improvement by using process intensification is desirable to increase TEC's competitiveness and its market share.

Esterification of citric acid to produce TEC involves three reversible reactions with the consecutive formation Monoethyl Citrate (MEC), Diethyl Citrate (DEC) and TEC respectively. Continual removal of produced water displaces the equilibrium towards product formation and makes this process suitable to implement in a Reactive Distillation (RD) system. Because of the presence of an azeotrope, water removal also carries away some ethanol within the distillate. In the other hand, maintaining a low temperature in the bottoms to avoid product decomposition requires to remove some ethanol from bottoms of the column. These characteristics make necessary the use of an excess of ethanol in the reaction.

Ethanol recovery and recycle is a major cost in TEC production. To enhance energy efficiency of the system further intensification of the RD system is possible via thermal coupling. This would allow separation and purification of the water-ethanol mixture inside the RD column. Then, it is the aim of this article to study TEC production using the so called reactive dividing wall column (RDWC).

Process configurations were modeled and simulated using commercial software (Aspen One 7.2). A validated NRTL-HOC thermodynamic model was used to describe phase equilibria, while kinetic models for Amberlyst 15 and methane sulfonic acid catalyzed reaction was used. Energy savings for reactive distillation are predicted between 15-80% over classical configurations of a reactor followed by separation units while RDWC predict 30-50% energy reduction over simple RD.