Application of modified Raoult's law in a fat/oil to biodiesel process

【Associated Sections in Selected Textbooks】

- Introduction to Chemical Engineering Thermodynamics [1] Sec. 10.5

【Module Learning Objectives】

- VLE calculation using modified Raoult's law.

【Problem】

Recent rises in petroleum prices and other energy concerns make it increasingly necessary to develop renewable energy sources with smaller environmental impacts. In recent years, there have been increased demands for biodiesel, which is a mixture of fatty acid methyl esters (FAMEs) derived from a variety of oils and fats. Biodiesel combustion decreases emissions of CO_2 and unburned hydrocarbons. The renewable and environmentally friendly aspects of biodiesel give it potential to ensure the sustainability of energy sources in the future [2].

Conventional biodiesel production involves a transesterification reaction of triglycerides from bio-oils with an alcohol that results in the production of FAMEs and also glycerol. Glycerol is a product that is in higher supply than its current demand. So, instead of producing glycerol as a by-product, Saka et al. [3] proposed a two-step process for converting oils and fats to fatty acids and triacetin. This process uses subcritical acetic acid followed by the conversion of fatty acids to FAMEs using supercritical methanol. From an economic point of view, the simultaneous production of FAMEs and triacetin in a one-step reaction is a promising prospect in which methyl acetate can be produced from methanol and acetic acid. Methyl acetate was proven to enhance biodiesel properties such as viscosity, flash point, and oxidation stability. Triacetin was also shown to be a valuable antiknock additive.

In short, this ideal scenario improves the quality of biodiesel and minimizes the cost of processing biodiesel additives. This reaction is made possible by the transesterification of triglycerides and methyl acetate to produce FAMEs with triacetin as the byproduct instead of glycerol [2].

In the two-step process, one reaction involved is methanol and acetic acid forming methyl acetate and water. For a system contains methanol(1)/methyl acetate(2), the following equations provide a reasonable correlation for the activity coefficients:

$\ln \gamma_1 = A x_2^2$ $\ln \gamma_2 = A x_1^2$ where $A = 2.771 - 0.00523T$

In addition, the following Antoine equations provide vapor pressures:

$\ln P_1^{sat} = 16.59158 - \frac{3{,}643.31}{T - 33.424}$ $\ln P_2^{sat} = 14.25326 - \frac{2{,}665.54}{T - 53.424}$

Where T is in kelvins and the vapor pressures are in kPa. Assuming the validity of Modified Raoult's Law, calculate:

(a) P and $\{y_i\}$, for T = 313.15 K and $x_1 = 0.30$.
(b) P and $\{x_i\}$, for T = 313.15 K and $y_1 = 0.70$.
(c) T and $\{y_i\}$, for P = 101.33 kPa and $x_1 = 0.80$.
(d) T and $\{x_i\}$, for P = 101.33 kPa and $y_1 = 0.20$.
(e) The azeotropic pressure, and the azeotropic composition, for T = 313.15 K.

Bibliography

[1] J. Smith, H. Van Ness and M. Abbott, Introduction to Chemical Engineering Thermodynamics, 7th Ed. ed., New York: McGraw Hill, 2005.

[2] C.-Y. Wei, T.-C. Huang and H.-H. Chen, "Biodiesel Production Using Supercritical Methanol with Carbon Dioxide and Acetic Acid," *Journal of Chemistry,* vol. 2013, 2013.

[3] S. Saka, Y. Isayama, Z. Ilham and X. Jiayu, "New process for catalyst-free biodiesel production using subcritical acetic acid and supercritical methanol," *Fuel,* vol. 89, pp. 1442--1446, 2010.