VLE Calculation Based on K-Value Correlations and Raoult's Law for Fast Pyrolysis of Mallee Woody Biomass [1]

[Module Learning Objectives]

• VLE calculation based on K-value correlations and Raoult's law

[Associated Sections in Selected Textbooks]

• Introduction to Chemical Engineering Thermodynamics [2] Sec. 10.4, 10.6

[Process Background and Problem]

In the past 30 years, significant progress has been made in developing pyrolysis technologies for converting lignocellulosic materials into fuel and chemicals.

In Western Australia (WA), mallee eucalypts are being developed as woody crops for managing dry-land salinity in the low-to-medium rainfall (300-600 mm mean annual rainfall) "wheat-belt" agricultural area. Mallee is a dedicated crop of multibranched shrubs or short trees able to be harvested on a short cycle and able to rapidly regenerate as coppice for every 3-4 years, which make it an ideal candidate for biomass pyrolysis.

In a study conducted by Garcia-Perez etc., the effect of pyrolysis temperature on the yields of liquid, char, gas, and the water content of bio-oil were studied [1]. Figure 1 shows variations of the yields of gases with pyrolysis temperature. The pyrolytic gases were rich in CO_2 , CO, methane, ethane, and propane. The yield of hydrogen was generally very low but increased with temperature. These results are in agreement with those reported by others for fast and slow pyrolysis reactors.



One gas product from a particular fast pyrolysis plant contains methane (1), ethane (2) and propane (3). Assuming the validity of the Raoult's law, with the following Antoine equation and parameters [3]:

$$\log_{10} P(\text{bar}) = A - \frac{B}{T(\text{K}) + C}$$

P = vapor pressure (bar)

T = temperature (K)

Table 1	Antoine	equation	parameters	[2]	1
I able I	mome	equation	parameters	L	

	A		
Species\Parameters	А	В	С
Methane (1)	3.9895	443.028	-0.49
Ethane (2)	3.93835	659.739	-16.719
Propane (3)	4.01158	834.26	-22.763

Make the following VLE calculations for the system.

- (a) BUBL P, given $x_1=0.10$, $x_2=0.40$, and t = 175K
- (b) DEW P, given $y_1=0.7, y_2=0.2$, and t = 175K
- (c) BUBL T, given $x_1=0.15$, $x_2=0.35$, and P = 2.5bar
- (d) DEW T, given $y_1=0.8$, $y_2=0.15$, and P = 2.5bar

Bibliography

- M. Garcia-Perez, X. S. Wang, J. Shen, M. J. Rhodes, F. Tian, W.-J. Lee, H. Wu and C.-Z. Li, "Fast pyrolysis of oil mallee woody biomass: effect of temperature on the yield and quality of pyrolysis products," *Industrial & engineering chemistry research*, vol. 47, pp. 1846--1854, 2008.
- [2] J. Smith, H. Van Ness and M. Abbott, Introduction to Chemical Engineering Thermodynamics, 7th Ed. ed., New York: McGraw Hill, 2005.
- [3] NIST, [Online]. Available: http://webbook.nist.gov/cgi/cbook.cgi?ID=C74986&Mask=4&Type=ANTOINE&Plot=on#ref-3.