Calculation of ΔH, ΔS for butyric acid during a fast pyrolysis process

【Associated Sections in Selected Textbooks】

- *Introduction to Chemical Engineering Thermodynamics* [1] Sec. 6.1
- *Chemical, Biochemical, and Engineering Thermodynamics* [2]

【Module Learning Objectives】

- Calculation of enthalpy, internal energy and entropy values from PVT and heat-capacity data.

【Problem】

Agricultural residues are an emerging source of energy and technological applications. Industrial processing of biomass involves an initial pyrolysis stage in which the feedstock is converted into a carbonaceous residue, gas, and condensable volatiles, consequently. Depending on pyrolysis conditions, activated carbon, bio-fuels, value added chemicals such as PF type adhesives, phenolics, levoglucosan, octane enhancers, fertilizers and gas products such as hydrogen, methane, ethane, propane could be achieved [3].

The waste products derived from olive-oil extraction are an aqueous effluent and solid residue, mainly containing the olive skin and stone. These can be called as olive cake, olive-oil residue, olive residue or pomace. Generally, collection and disposal of the residues are becoming more difficult and expensive but if they are not used efficiently, they create environmental problems. However, vegetable oils and olive-oil residue have no sulfur content (less than 0.01 wt.%) and can be considered as clean energy source [4]. Pyrolysis could be a promising way for residue management to convert them to bio-oils which have more advantages in transport, storage, handling, retrofitting, combustion and flexibility in production and marketing.

Garcia-Ibanez et al. have studied thermal degradation of olive-oil residue in air atmosphere at three heating rates (10, 20, and 50 °C min^{-1}). They concluded that increasing the heating rate increases the thermal degradation rate [5]. Blanco Lopez et al. have studied the pyrolysis of olive stones and determined the composition of released gases. The gas released was a mixture of CO_2, CO, H_2, CH_4, C_2H_4, and C_2H_6. They found that the pyrolysis products with the highest heating value are the liquids [6]. One of the liquid product components is butyric acid or butanoic acid with chemical formula $CH_3(CH_2)_2COOH$. Butyric acid is used in the preparation of various butyrate esters.

In one biofuel plant, the butyric acid leaves a fixed bed pyrolysis reactor at 75^{o}C and 10 bar after purification. Then it enters a catalytic esterification reactor with ethanol to form ethyl butyrate in the presence of ion exchange resin (Amberlyst 15) as the catalyst. The operation condition of the esterification reactor is 25^{o}C and 1 bar.

Determine the enthalpy and entropy change of butyric acid from 75^{o}C and 10 bar to 25^{o}C and 1 bar. Note that the enthalpy change will be approximately the amount of heat that needs to be removed.

The following information is available [7].

T (^{o}C)	P (bar)	V (cm^{3}mol^{-1})	β (10^{-3}K^{-1})	κ (10^{-3}bar^{-1})
25	1	92.40	1.02	0.90
25	10	91.66	0.96	0.89
75	1	97.51	1.13	1.20
75	10	96.47	1.08	1.19

We also know that

C_p=178.6 J/(K·mol) at 25^{o}C and 1atm

C_p=186.5 J/(K·mol) at 75^{o}C and 1 atm

Bibliography

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

[2] S. Sandler, Chemical, Biochemical, and Engineering Thermodynamics, 4th Edition ed., New York: John Wiley & Sons, Inc., 2006.

[3] B. B. Uzun, A. E. Putun and E. Putun, "Composition of products obtained via fast pyrolysis of olive-oil residue: Effect of pyrolysis temperature," *Journal of Analytical and Applied Pyrolysis,* vol. 79, pp. 147 - 153, 2007.

[4] H. Topal, A. T. Atimtay and A. Durmaz, "Olive cake combustion in a circulating fluidized bed," *Fuel,* vol. 82, pp. 1049-1056, 2003.

[5] P. Garcia-Ibanez, M. Sanchez and A. Cabanillas, "Thermogravimetric analysis of olive-oil residue in air atmosphere," *Fuel Processing Technology,* vol. 87, pp. 103-107, 2006.

[6] M. C. Blanco Lopez, C. G. Blanco, A. Martinez-Alonso and J. M. Tascon, "Composition of gases released during olive stones pyrolysis," *Journal of Analytical and Applied Pyrolysis,* vol. 65, pp. 313-322, 2002.

[7] W.-T. Vong and F.-N. Tsai, "Densities, molar volumes, thermal expansion coefficients, and isothermal compressibilities of organic acids from 293.15 K to 323.15 K and at pressures up to 25 MPa," *Journal of Chemical & Engineering Data,* vol. 42, pp. 1116--1120, 1997.