Developing a predictive correlation for the heat capacity of ill-defined liquid hydrocarbons

John M. Shaw*, Nafiseh Dadgostar

Department of Chemical and Materials Engineering, University of Alberta, Edmonton, Alberta T6G 2G6, Canada
(corresponding author: jmshaw@ualberta.ca.)*

There are currently no reliable methods for predicting liquid heat capacities of ill-defined hydrocarbons, such as bitumen and heavy crude oils and their partly processed fractions. Estimation errors using existing techniques for heat capacity can exceed 40 %. Far from critical points, ideal gas heat capacities comprise 75% of the heat capacity of liquids [1]. The uncertainty of the current methods for calculating ideal gas heat capacities is less than 5%. If ideal gas heat capacity is taken as a basis for calculation, the source for the large deviations is inaccurate values predicted from Equations of State for the difference between the heat capacity of a liquid and an ideal gas. This difference is frequently referred to as a departure function. There are different formats for departure functions in the literature. As equations of state are employed to calculate the departure function, the main challenge in improving the accuracy of calculated liquid heat capacities using this approach is examining which format works best for the broadest spectrum of hydrocarbons.

Preliminary results suggest that typical formulations employed in process calculations are incomplete and can underestimate departure function values. We recognize that the resulting liquid phase heat capacity values may not be accurate enough for design work. Thus, development of a "universal" correlation based on the direct use of liquid phase heat capacity data and a similarity variable (α), defined as the number of atoms in a molecule divided by molecular mass and rooted in quantum mechanics, to predict liquid heat capacity are explored. This approach has already led to successful methods for direct calculation for heat capacities of ill-defined organic solids [2, 3], and ideal gases [5]. This approach is also expected to yield significantly improved heat capacity estimates vis-à-vis current practice, as only the elemental analysis of a material needs to be available to provide accurate heat capacities on a unit mass basis.

In this work, coefficients appearing in a widely used and well regarded correlation by Lee and Kesler [4], for calculating isobaric heat capacities of liquid petroleum fractions, are generalized as functions of the similarity variable, α. The variables in their correlation, equation 1, are specific gravity (sp gr) and Watson characterization factor (K). Preliminary results are reported.

For $T_r \leq 0.85$,

$$C_p = A_1 + A_2 T + A_3 T^2 \qquad (1)$$

Where:

C_p = Isobaric heat capacity for liquid petroleum fraction in BTU per (lb.R)

A_1 = -1.17126 + (0.023722+0.024907sp gr)K +(1.14982-0.0465/ sp gr)

A_2 = (10^{-4})(1.0+0.82463K)(1.12172 – 0.27634/sp gr)

A_3 = (-10^{-8})(1.0+0.82463K)(2.9027-0.70958/sp gr)

T_r = reduced temperature, T/T_{pc}
T = temperature in degree Rankine
T_{pc} = pseudocritical temperature in degrees Rankine
K = Watson characterization factor
sp gr = specific gravity 60 F/60 F

References

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