

Developing a Predictive Correlation for the Heat Capacity of Ill-defined Liquid Hydrocarbons

Nafiseh Dadgostar and John M. Shaw

Department of Chemical and Materials Engineering, University of Alberta

Introduction

- ❖ No reliable methods for predicting liquid heat capacities of ill-defined hydrocarbons (bitumen, heavy crude oils, boiling fractions). Estimation errors using existing techniques for heat capacity can exceed 40 %
- ❖ Critical properties, and/or molecular structure are required for all current estimation techniques
- ❖ These inputs are purely speculative for heavy hydrocarbons
- ❖ Statistical mechanics provides sound bases for correlation development [1- 4]

Objective

- Development of a “universal” correlation to predict liquid heat capacity, which requires **elemental analysis** rather than molecular structure, density, critical properties as inputs. The **Similarity Variable (α)**, rooted in quantum mechanics, is obtained directly from the elemental analysis:

$$\alpha = \frac{N}{M} = \frac{\sum_{i=1}^n v_i}{\sum_{i=1}^n v_i M_i} = \frac{\sum_{i=1}^n x_i}{\sum_{i=1}^n x_i M_i} = \frac{\sum_{i=1}^n w_i}{\sum_{i=1}^n w_i M_i}$$

Motivation: Successful results for direct calculation for heat capacities of organic solids [1], and ideal gases have been realized on this basis.

Procedure:

- Choose a current successful correlation
- Re-define coefficients as functions of α

Methodology – direct substitution approach

Lee and Kesler [5] developed a well accepted approach for calculating the isobaric heat capacity of petroleum fraction liquids remote from the critical region:

For $T_r \leq 0.85$,

$$C_p = A_1 + A_2 T + A_3 T^2$$

$$A_1 = -1.17126 + (0.023722 + 0.024907 \text{ sp gr})K \\ + (1.14982 - 0.046535K) / \text{sp gr} \\ A_2 = (10^{-4})(1.0 + 0.82463K)(1.12172 - 0.27634 / \text{sp gr}) \\ A_3 = (-10^{-8})(1.0 + 0.82463K)(2.9027 - 0.70958 / \text{sp gr})$$

C_p = Isobaric heat capacity for liquid petroleum fraction in BTU/(R.lb)
 T_r = reduced temperature, T/T_{pc}
 T = temperature in degree Rankine
 T_{pc} = pseudocritical temperature in degrees Rankine
 K = Watson characterization factor = $(T_b)^{1/3}/\text{sp gr}$
 sp gr = specific gravity 60 F/60 F
 T_b = boiling point in degree Rankine

Drawbacks of Lee-Kesler correlation:

- ✓ specific gravity and T_b are not always available or known
- ✓ 25 % errors for unsaturated compounds such as aromatics are encountered.

- Drawbacks of the L-K correlation are not resolved by re-defining parameters (A_1, A_2, A_3) as functions of α .

Compound	Lee-Kesler Correlation (100. σ)	Direct Substitution (100. σ)	General Approach (100. σ)
C_9H_{20} (2,2,3,3-Tetramethylpentane)	1.54	23.88	1.17
$C_{15}H_{30}$ (Decylcyclopentane)	2.35	24.10	2.00
$C_{18}H_{14}$ (o-Terphenyl)	15.56	22.18	0.15
$C_{13}H_9N$ (Benzo[h]quinoline)	25.24	25.20	3.83
$C_{18}H_{34}O_2$ (Oleic acid)	10.78	25.26	6.41

Methodology – general approach

- Retain the cubic form and redefine the parameters in terms of α only:

$$C_{p,liq} = a_0 + (a_{11}\alpha + a_{12}\alpha^2)T + (a_{21}\alpha + a_{22}\alpha^2)T^2 + (a_{31}\alpha + a_{32}\alpha^2)T^3$$

- Set “a.” = to the Einstein heat capacity term:

$$a_0 = (A_1\alpha + A_2\alpha^2) * 3R \left(\frac{\theta}{T}\right)^2 \frac{\exp\left(\frac{\theta}{T}\right)}{\left[\exp\left(\frac{\theta}{T}\right) - 1\right]^2} \rightarrow \text{At 200K and above} \sim 24.5$$

$$a_0 = (A_1\alpha + A_2\alpha^2) * 24.5$$

Training Data Set:

- 15 compounds (paraffins, naphthenes, aromatics, and sulfur/oxygen/nitrogen derivatives)
- 103 data point in the range of 200-450 K

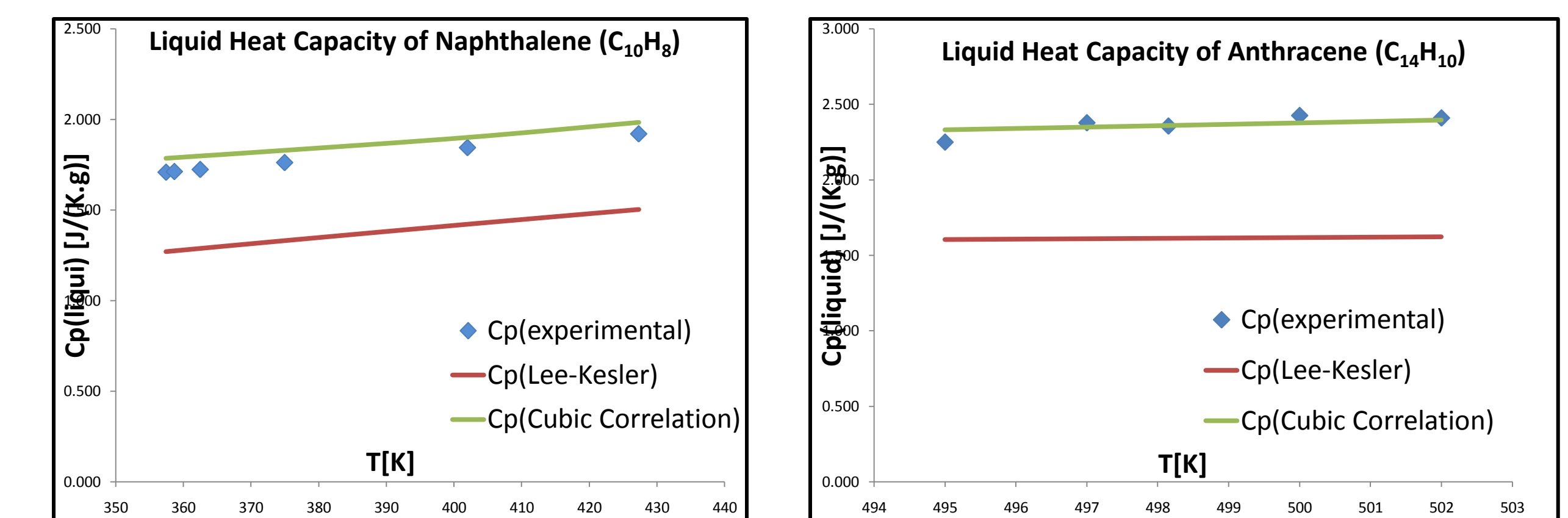
One theoretical term, and only six universal coefficients!

Results and Discussion

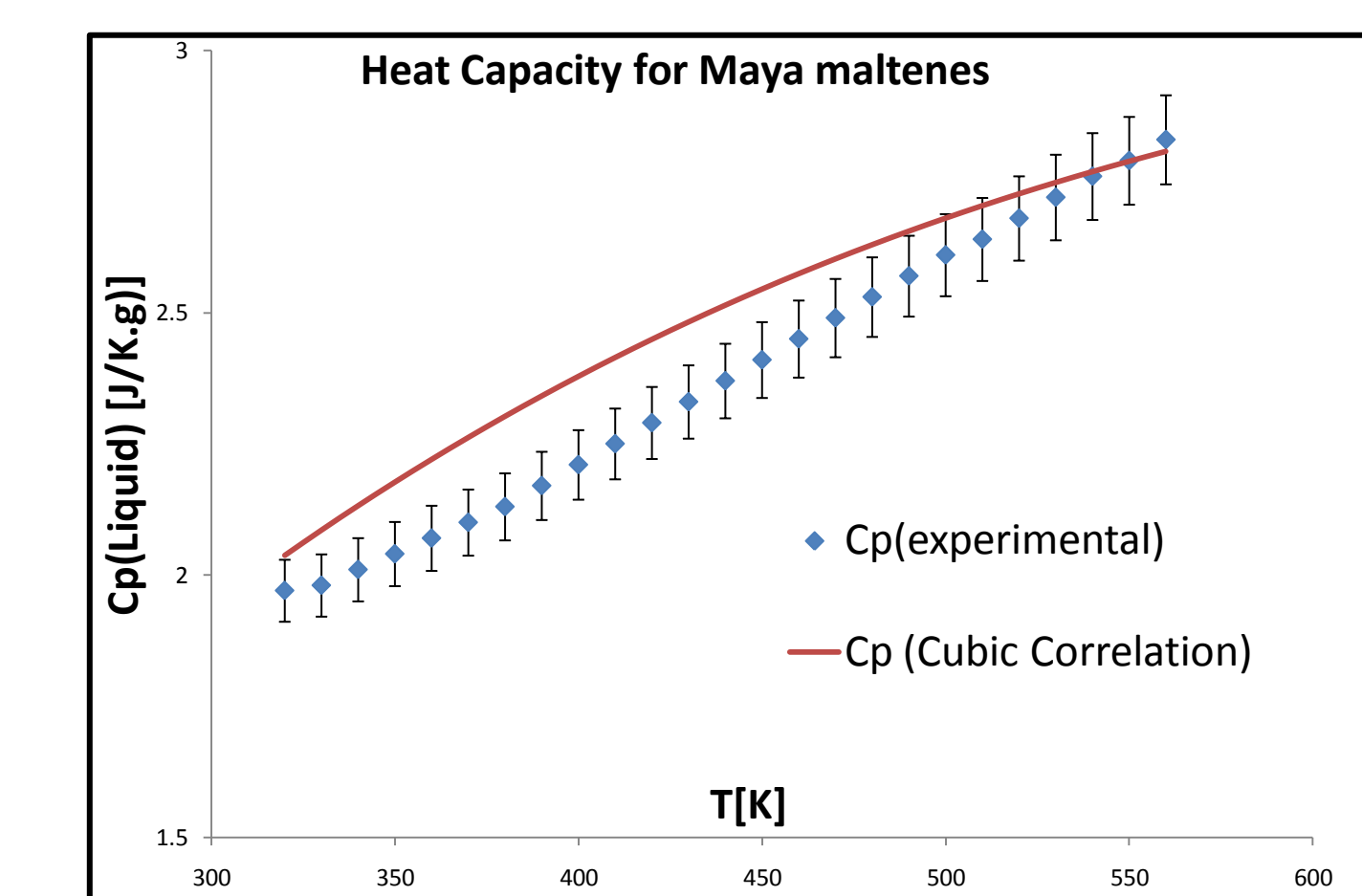
Quality of Training Set Correlation

Standard Deviation of the Fit (σ_F)	0.020 [J/(K.g)]
Average Absolute Deviation (ϵ)	0.104 [J/(K.g)]
Average Relative Deviation (δ)*100	4.94

Comparison of the cubic correlation with Lee-Kesler



- ✓ Significant improvement for unsaturated cyclic hydrocarbons
- ❖ **Predictive Character of the Correlation for Heavy Hydrocarbons** Maya Maltenes ($\alpha = 0.188$ mol/g) [6]



- ✓ No other method can predict $C_{p,liq}$ for ill-defined hydrocarbons, as their critical & structure properties are unknown.

Summary

- As noted previously for solids and ideal gases, current heat capacity models for liquids appear to be unnecessarily complicated, restrictive, and inaccurate.
- Universal heat capacity correlations rooted in quantum mechanics have apparent potential for predicting liquid heat capacities for both pure and ill-defined hydrocarbons.
- The cubic correlation proposed here provides superior performance and is more broadly applicable than the LK method, an industrial benchmark method and requires only the elemental composition of the fluid as an input.
- Future work includes additional training and testing of the coefficients appearing in the correlation and treatment of the asymptotic behavior of heat capacity in the critical region.

Acknowledgements

This research was supported by Natural Science and Engineering Research Council of Canada (NSERC), Alberta Innovates, KBR Energy and Chemical, Halliburton Energy Services, Imperial Oil Resources, ConocoPhillips Canada Resource Corp., Shell Canada Ltd., Nexen Inc., Virtual Materials Group (VMG), and Total E&P Canada Ltd.

[1] V. Lastovka, M. Fulem, M. Becerra and J. M. Shaw, Fluid Phase Equilibria 268 (2008), 134–141

[2] M. Zábbranský, V. Růžička, Jr., V. Majer and E.S.Domalski, J.Phys.Chem.Ref.Data Monograph No. 6, American Chemical Society, Washington, D.C., (1996).

[3] M. Zábbranský, V. Růžička, Jr. and E.S.Domalski, J. Phys. Chem. Ref. Data, Vol. 30, No. 5, (2002).

[4] M. Zábbranský, Z. Kolská, V. Růžička, Jr. and E.S.Domalski, J. Phys. Chem. Ref. Data, Vol. 39, No. 1, (2010).

[5] Private Communication, B. I. Lee and M. G. Kesler, Mobil Oil Corp., Princeton, N.J. (1975).

[6] M. Fulem, M. Becerra, A. Hasan, B. Zhao and J. M. Shaw, Fluid Phase Equilibria 272 (2008) 32-41.