

3RD YEAR VACATION PROJECT REPORT

**The development of simplified model for the Orion
Carbons Pty (Ltd) thermal black furnace and
preheater**

For

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Introduction and background

Orion Carbons in Port Elizabeth manufactures carbon black, an additive used in many industries, the foremost being local tyre manufacturing. Thermal Black, the type of carbon black the Orion PE plant manufactures, consists of amorphous carbon sheets tangled together, a few micrometres in size. The process used to synthesise these particles is well explained in the project proposal and in Orion's provided literature and therefore will not be repeated.

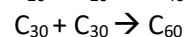
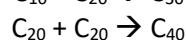
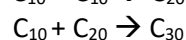
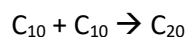
The purpose of this project is to build a process model to allow for a better understanding of what factors affect the type of carbon black created in the furnaces and the amount that is created. Unfortunately, the thermodynamic data for the compounds involved in the process is limited and much of the allocated time for the project was spent compiling a thermodynamic database for the compounds. There also exists little in literature on the reaction kinetics of the formation of carbon black from a feed of naphthalene, one of the two feeds used at the Port Elizabeth plant.

Aim of project

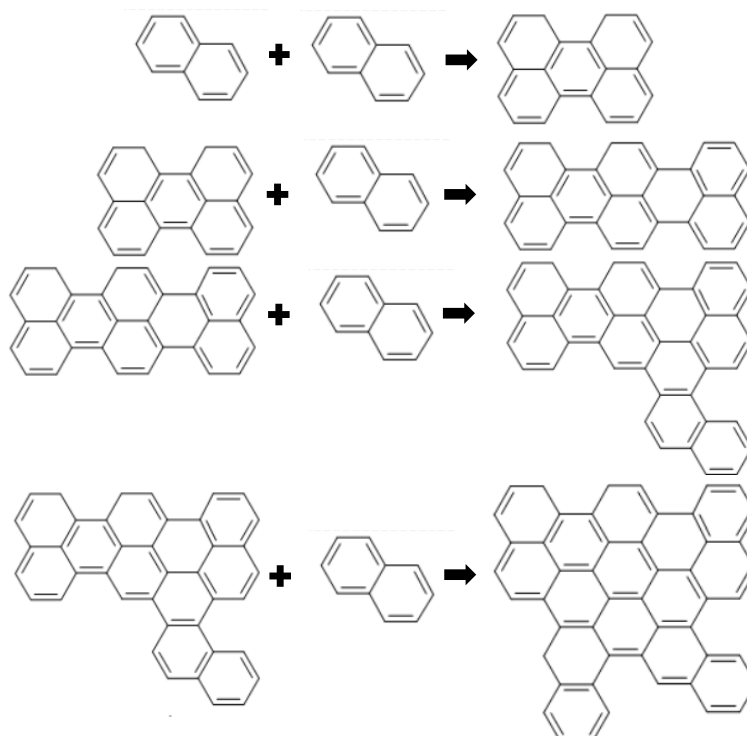
The aim of the project was to deliver a Gibbs reactor model of the reactor-heater-exchanger process.

Results and discussion

It was proposed that the carbon black molecules are formed from a synthesis of smaller carbon black intermediate molecules, such as the feed component, naphthalene, a C_{10} molecule. This would follow a pattern similar to the following:



The feed, naphthalene, is a C_{10} structure ($C_{10}H_8$) and it is proposed it polymerises without breaking aromatic bonds in a pattern similar to Figure 1 to form the intermediate components that agglomerate together to form carbon black molecules (see Figure 2).



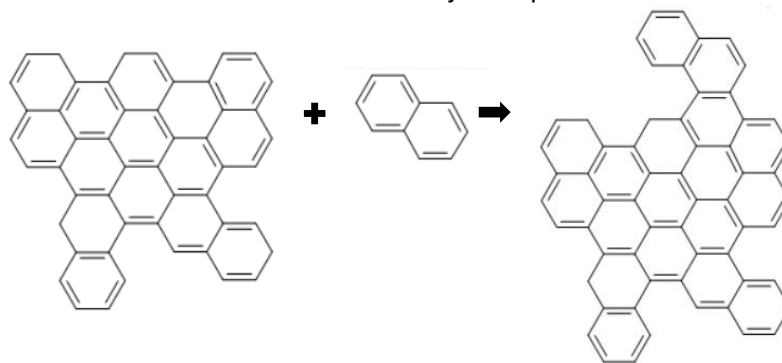


Figure 1: Formation of carbon black component structures by polymerisation

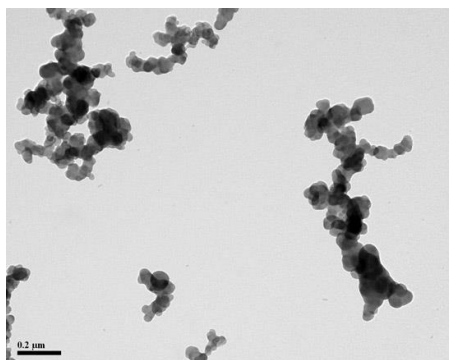


Figure 2: Carbon black molecule showing agglomeration of different intermediate structures, taken from Karl (2015)

As mentioned, there was very little thermodynamic data (for up to 3000K temperatures) for the components involved in the reaction, namely naphthalene, carbon dioxide, carbon monoxide, water, nitrogen, oxygen, hydrogen, carbon black intermediate products and carbon black. This information is needed as the process takes place at these high temperatures. Most of the allocated time for the project was spent building the thermodynamics database for these components to these high temperatures. This was also done so that a Gibb's reactor (the reaction going to assumed thermodynamic equilibrium in a few seconds) could be modelled. The intermediates assessed were C_{20} , C_{30} , C_{40} , C_{50} , C_{60} , C_{70} , C_{80} , C_{90} , C_{100} and C_{110} molecules (see appendix for full formulas).

For the components other than the carbon black intermediate products and carbon black, the NIST heat capacity values were found (using Thergas) and fitted to a $C_p = a + \frac{b}{T} + c + dT + eT^2$ equation (see appendix for a, b, c, d, e values and C_p vs T graphs). For the carbon black intermediate products, the NIST heat capacity values data for 9 aromatic compounds were assessed (using Thergas) and the group contributions of the ACH and AC carbon groups were re-calculated, similar to the Constantinou & Gani (1994) method (see Equation 1 for C&G method and appendix for a1, a2, b1, b2, c1, c2 contributions of each component, 1 representing the ACH contribution and 2 the AC contribution). Only 9 compounds were assessed as the 127-character limit for linear formula in Thergas restricted the size of the compounds that could be analysed (see appendix for list of 9 compounds and group contribution data). Using these group contributions, the heat capacities of the carbon black intermediate products were fitted to a $C_p = a + \frac{b}{T} + \frac{c}{T^2}$ equation, equation 124 in the thermodynamic database PCD manager (omitting d and e). (See appendix for a, b, c values and C_p vs T graphs for intermediate compounds.)

$$C_p^\circ = \left[\sum_k N_k(C_{pA1k}) + W \sum_j M_j(C_{pA2j}) - 19.7779 \right] \\ + \left[\sum_k N_k(C_{pB1k}) + W \sum_j M_j(C_{pB2j}) + 22.5981 \right] \theta \\ + \left[\sum_k N_k(C_{pC1k}) + W \sum_j M_j(C_{pC2j}) - 10.7983 \right] \theta^2 \quad (\text{J mol}^{-1} \text{ K}^{-1}) \\ \theta = (T - 298)/700$$

Equation 1: Constantinou & Gani (1994) method for estimating heat capacity of compounds

In the above equation, N_k represents the number of first-order groups of type k in the molecule, F_{1k} is the contribution for the first order group labelled $1k$, and N_j is the number of second order groups of type j in the molecule, F_{2j} is the contribution for the second-order group labelled $2j$ to the specified property F , and T is the temperature in Kelvin. For all 9 compounds analysed and the intermediate compounds built, only first-order groups were used. W is set to zero for the first-order calculations and 1 for the second order calculations (Poling, et al., 2001).

A new thermodynamic database in PCD Manager was created, the component “pyrene” was copied and the ACH and AC groups changed to correspond to the carbon black intermediate species. Pyrene was chosen as it had a high ratio of carbon to hydrogen atoms (16:10), a property of carbon black and its intermediates. The a , b and c values of equation 124 of the heat capacity estimation were changed and the number of AC and ACH carbons were changed. After these were changed, the critical and molecular values for the component were re-estimated using the Constantinou and Gani (1994) method. This database was loaded into COCO and a Gibb’s reactor simulation of the process was run, but there appeared to be some issues in the solutions obtained as the reference point (and phase) of the ideal gas Gibb’s free energy of the compounds differed. It was decided that Professor Möller would consult Dr Van Baten (the creator of COCO) to find out how the Gibb’s reactor chose the 4 equations that determined the products.

After the lack of progress in simply loading the thermodynamics database from PCD manager into COCO, it was decided that the longer route of loading the database into Scilab, creating a Gibb’s reactor in Scilab and then loading this reactor back into COCO would work smoother. Prof Möller created the Gibb’s reactor using an IPOPT solver and the thermodynamics database that was built was loaded into this. The process ran, but unfortunately the time allocated to this work ended here.

It should also be noted that the Solids thermodynamics database could not run in COCO alongside the ChemSep thermodynamics database. In the beginning of the project, it was attempted to create graphite, a solid, from an appropriate naphthalene and air feed using a Gibb’s reactor in COCO. However, creating a solid from liquids using the COCO Gibb’s reactor did not work. During the trip to Port Elizabeth to meet Mr Madlokazi (the chemical engineer on the Orion plant and the future Master’s student tackling this problem) it was decided that working to create solid graphite sheets may not be what is happening in the process, but that amorphous carbon may be forming and agglomerating to form carbon black. There was also some uncertainty as to when in the process the polymerisation of the intermediates ended and the agglomeration of these to form carbon black began. It was decided that this would be chosen using Mr Madlokazi’s prior knowledge during his work on this problem.

ΔH and ΔG were found using the following equations:

$$\Delta H = H_{f298} + \int C_p dT$$

$$\Delta G = \Delta H - T\Delta S$$

Equation 2 and 3: Thermodynamic equations relating Gibb's free energy, entropy and enthalpy

The above equations were used to carry out a thermodynamic equilibrium calculation for the Scilab Gibb's reactor. Unfortunately, it was not possible to create a kinetics model of the reaction due to the time constraints.

Conclusions and recommendations

It is recommended that a kinetics approach to the problem still be carried out and the kinetics equations developed. It is also recommended that Mr Madlokazi make use of the chemical engineering electron microscope to assess the samples he brings from the Orion plant. This may give a better idea of when agglomeration begins and polymerisation ends.

It is also recommended that a phase check be built into the Gibb's reactor in Scilab and that the reference state for the ideal gas of each component be investigated. Prof Möller's consultation with Dr Van Baten should yield how the 4 equations in the COCO Gibb's reactor are chosen.

Appendix

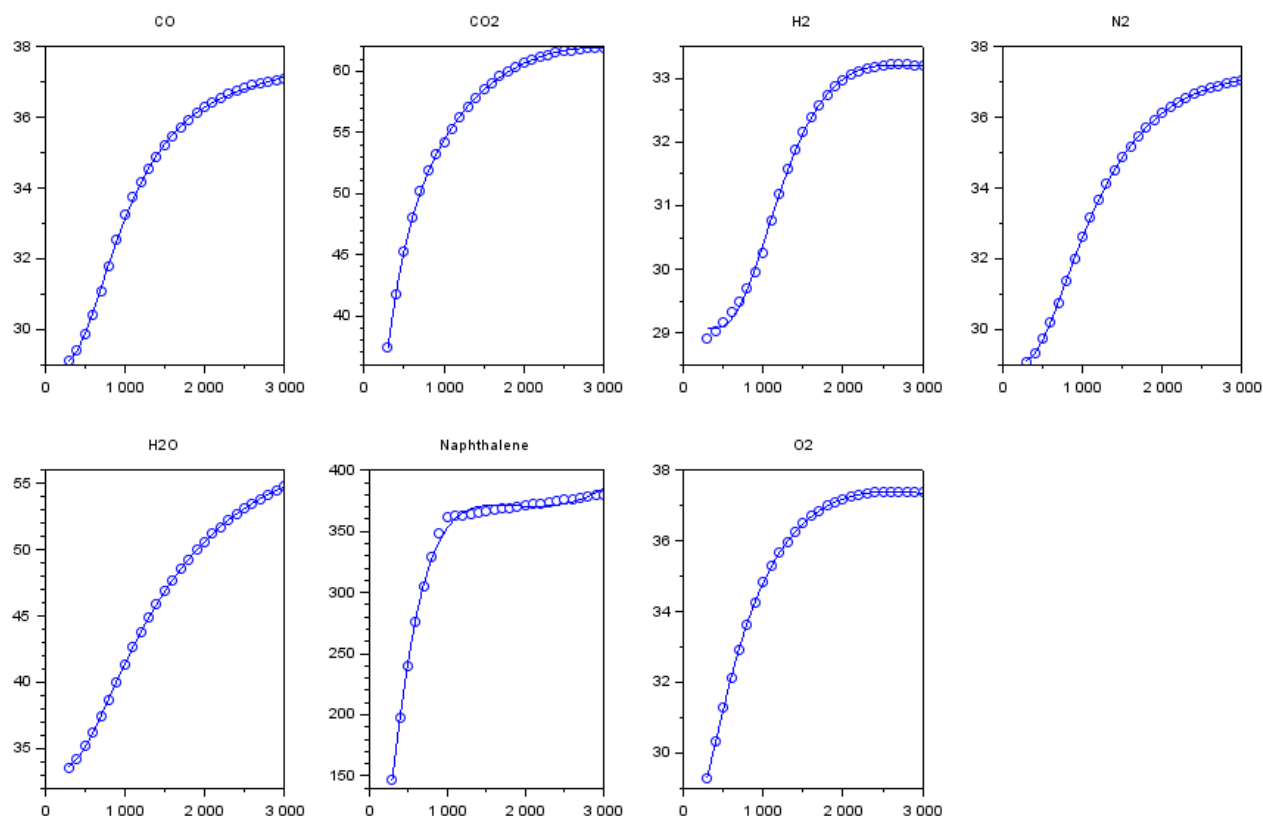


Figure 3: Heat capacity [kJ/mol.K] vs temperature [K] for 7 components involved in the reaction (excluding carbon black and its intermediate products). Dots indicate the NIST heat capacities given and the solid lines indicate the predicted heat capacities using the $C_p = a + \frac{b}{T} + c + dT + eT^2$ equation fitted.

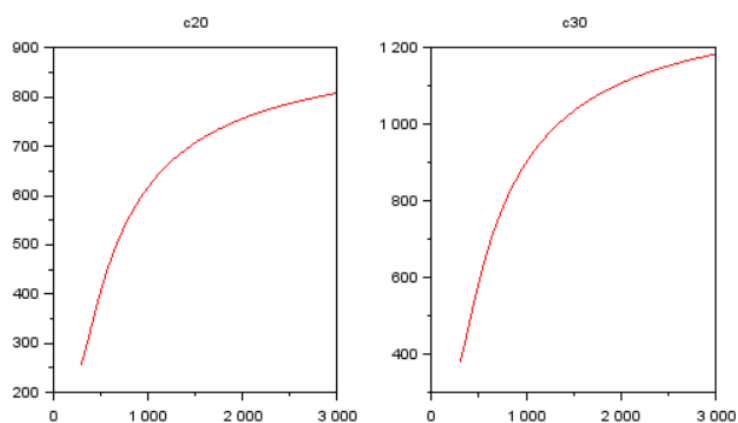


Figure 4: Heat capacity of carbon black intermediates C₂₀H₁₂ and C₃₀H₁₆ [kJ/mol.K] vs temperature [K] predicted using ACH and AC group contribution data

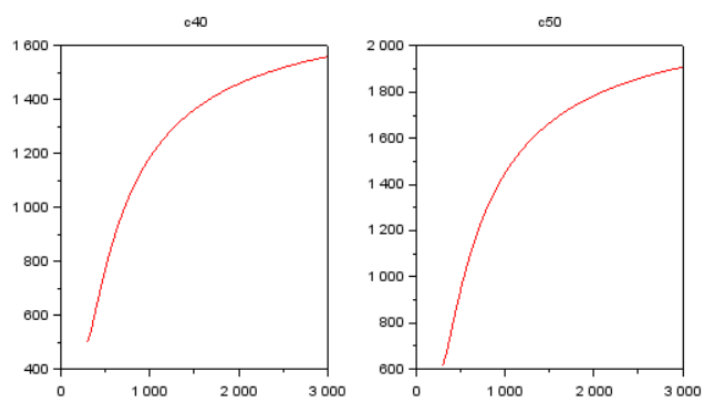


Figure 5: Heat capacity of carbon black intermediates $C_{40}H_{20}$ and $C_{50}H_{22}$ [kJ/mol.K] vs temperature [K] predicted using ACH and AC group contribution data

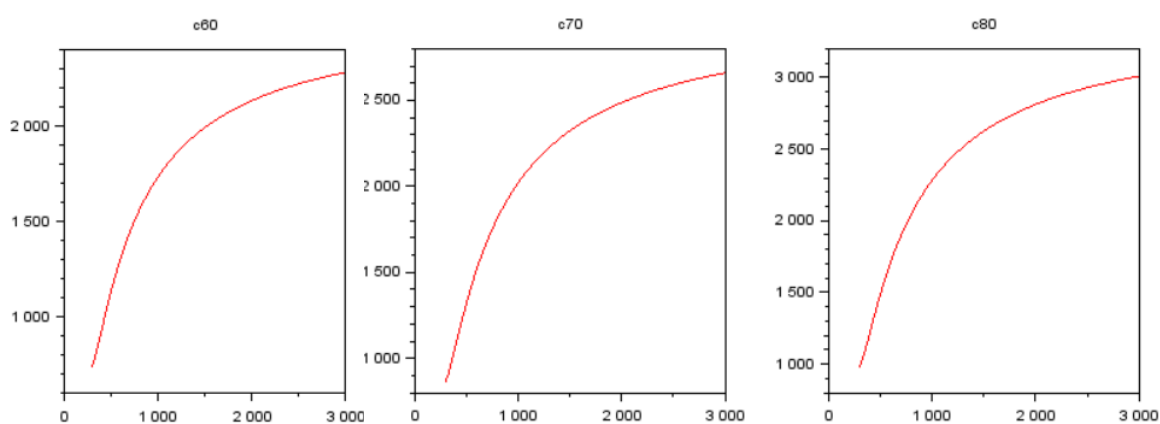


Figure 6: Heat capacity of carbon black intermediates $C_{60}H_{26}$, $C_{70}H_{30}$ and $C_{80}H_{32}$ [kJ/mol.K] vs temperature [K] predicted using ACH and AC group contribution data

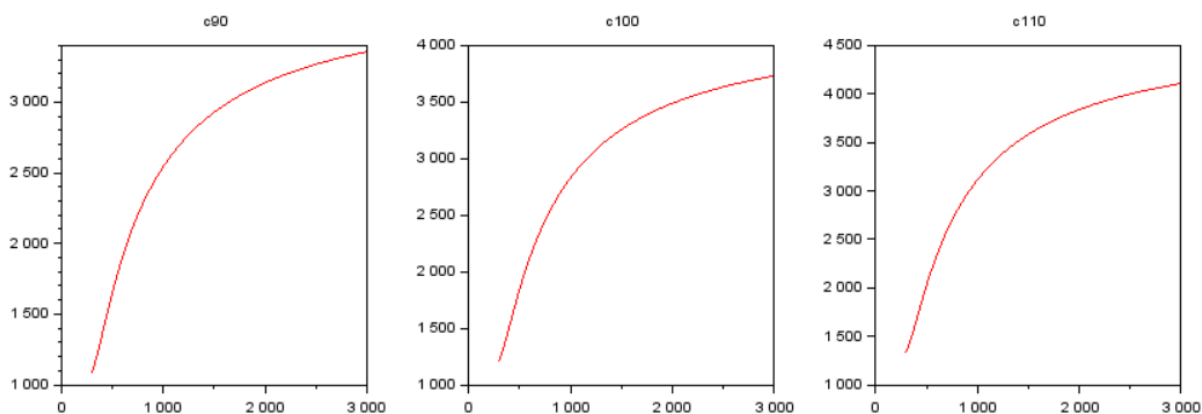


Figure 7: Heat capacity of carbon black intermediates $C_{90}H_{34}$, $C_{100}H_{38}$ and $C_{110}H_{42}$ [kJ/mol.K] vs temperature [K] predicted using ACH and AC group contribution data

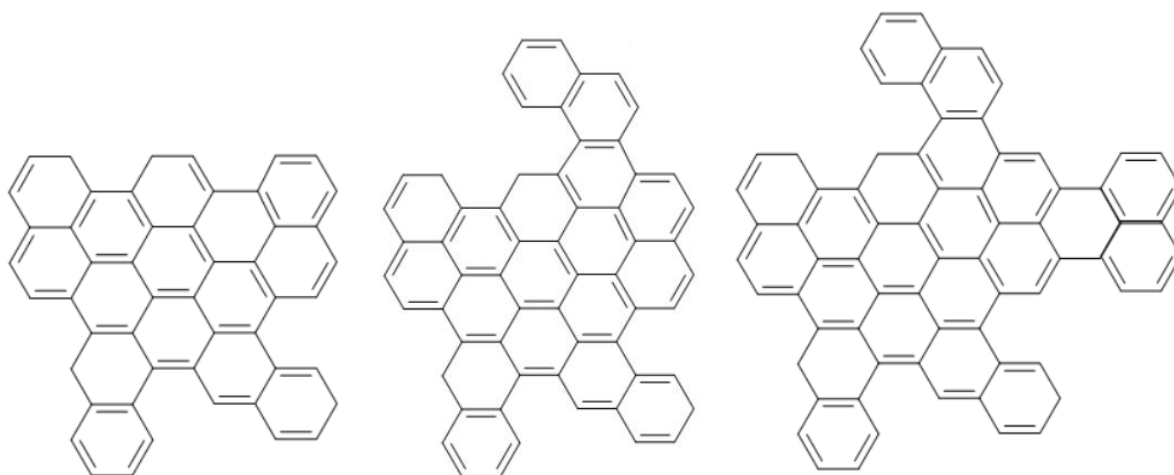
Figure 8: $C_{10}H_8$, $C_{20}H_{12}$, $C_{30}H_{16}$ and $C_{40}H_{20}$ Figure 9: $C_{50}H_{22}$, $C_{60}H_{26}$ and $C_{70}H_{30}$

Table 1: a, b and c values for heat capacity correlation equation (equation 124 in PCD manager) and number of ACH and AC carbons for carbon black intermediate compounds.

| Carbon black intermediate value | Number of ACH carbons | Number of AC carbons | Equation 124 a value | Equation 124 b value [$\times 10^{-3}$] | Equation 124 c value [$\times 10^{-6}$] |
|---------------------------------|-----------------------|----------------------|----------------------|---|---|
| $C_{20}H_{12}$ | 12 | 8 | 919.30341 | -348.29647 | 44.936442 |
| $C_{30}H_{16}$ | 16 | 14 | 1348.1883 | -514.06913 | 67.074212 |
| $C_{40}H_{20}$ | 20 | 20 | 1777.0731 | -679.84178 | 89.211981 |
| $C_{50}H_{22}$ | 22 | 28 | 2175.1911 | -837.23885 | 111.0193 |
| $C_{60}H_{26}$ | 26 | 34 | 2604.0759 | -1003.0115 | 133.15707 |
| $C_{70}H_{30}$ | 30 | 40 | 3032.9608 | -1168.7842 | 155.29484 |
| $C_{80}H_{32}$ | 32 | 48 | 3431.0787 | -1326.1812 | 177.10216 |
| $C_{90}H_{34}$ | 34 | 56 | 3829.1967 | -1483.5783 | 198.90948 |
| $C_{100}H_{38}$ | 38 | 62 | 4258.0816 | -1649.351 | 221.04725 |
| $C_{110}H_{42}$ | 42 | 68 | 4686.9664 | -1815.1236 | 243.18502 |

Table 2: First, second and third group contributions for ACH and AC

| Group contribution | Value |
|----------------------|------------|
| A ₁ (ACH) | 52.118543 |
| A ₂ (ACH) | 36.735112 |
| A ₃ (ACH) | -19.08994 |
| B ₁ (AC) | -14.902149 |
| B ₂ (AC) | 2.3129123 |
| B ₃ (AC) | 2.1476867 |

Table 3: Aromatic compounds used in re-calculating the ACH and AC group contribution values and corresponding number of ACH and AC carbons

| Aromatic compound | Number of ACH carbons | Number of AC carbons |
|---|-----------------------|----------------------|
| C ₁₈ H ₁₂ (Naphthacene) | 12 | 6 |
| C ₁₃ H ₉ | 9 | 4 |
| C ₁₄ H ₁₀ (Anthracene) | 10 | 4 |
| C ₁₇ H ₁₁ | 11 | 6 |
| C ₁₆ H ₁₀ (Pyrene) | 10 | 6 |
| C ₂₀ H ₁₂ (Perylene) | 12 | 8 |
| C ₆ H ₆ (Benzene) | 6 | 0 |
| C ₁₀ H ₈ (Naphthalene) | 8 | 2 |
| C ₁₉ H ₁₁ | 11 | 9 |

Table 4: a, b, c, d and e coefficient values for heat capacity estimation equation created ($C_p = a + \frac{b}{T} + c + dT + eT^2$) [kJ/mol.K]

| Component | A value | B value | C value | D value | E value |
|------------------|-----------|------------|-----------|------------|--------------------------|
| CO | 29.004787 | -1787.3823 | 3.65026 | -0.0005176 | 6.613x10 ⁻⁸ |
| H ₂ | 29.060367 | -3993.514 | 5.5063942 | -0.0013746 | 0.0000002 |
| N ₂ | 29.048787 | -1881.3936 | 3.4599935 | -0.0003422 | 3.042x10 ⁻⁸ |
| Naphthalene | 83.378875 | -778.93719 | 6.9454048 | -0.0006927 | 0.0000001 |
| O ₂ | 28.467434 | -898.74851 | 2.8792121 | -0.0001317 | -8.405x10 ⁻¹¹ |
| H ₂ O | 33.476982 | -1641.7101 | 3.7395256 | -0.0000261 | -6.294x10 ⁻⁹ |
| CO ₂ | 22.158971 | -300.19292 | 3.699867 | 0.0000955 | -2.264x10 ⁻⁸ |

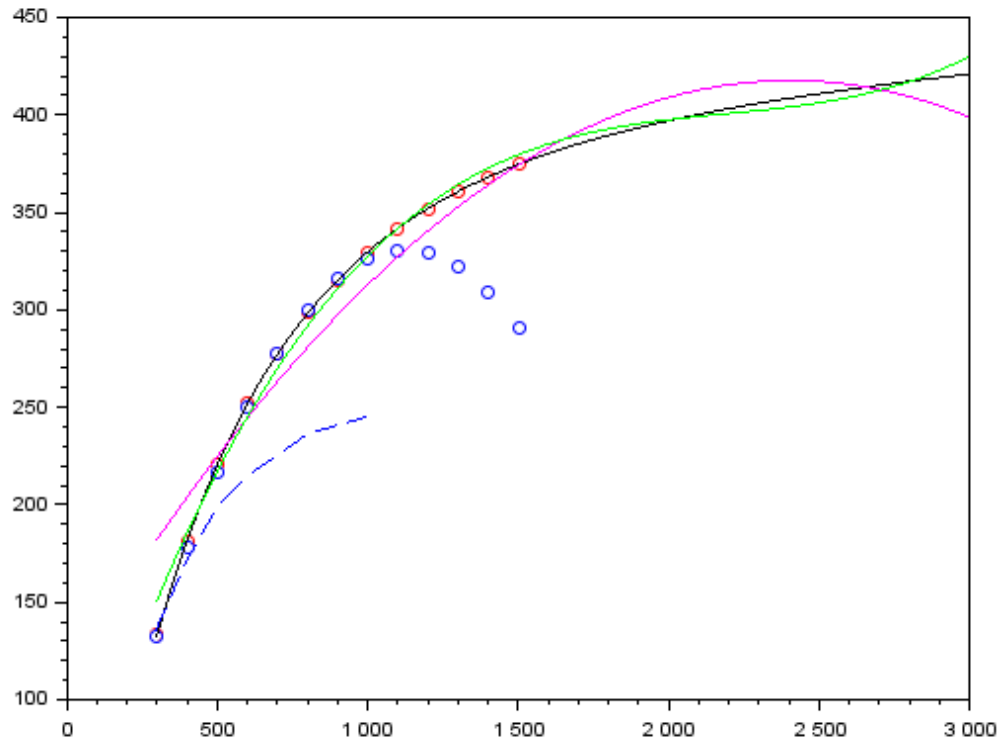


Figure 10: Heat capacity of naphthalene [kJ/mol.K] vs temperature [K] using different approximation techniques. Red dotted line shows the NIST database values for 298K – 1500K, blue dotted line shows the values obtained using the Constantinou & Gani (1994) approach, the solid black line shows an estimation using NIST data, extrapolated to 3000K ($C_p = a + b\theta + e^{-\theta} + e^{-2\theta}$ with $\theta = \frac{T-298}{700}$). The magenta line shows an approximation using NIST data, extrapolated to 3000K ($C_p = a + b\theta + c\theta^2$, same θ). The green line shows an approximation using NIST data, extrapolated to 3000K ($C_p = a + b\theta + c\theta^2 + d\theta^3$, same θ). The dotted blue line shows the approximation using the Benson method. The exponential method (using NIST data) extrapolated seemed the most promising.

References

Constantinou, L. & Gani, R., 1994. New group contribution method for estimating properties of pure compounds. *AIChE Journal*, 40(10), pp. 1697-1710.

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