# ESTIMATING THERMODYNAMIC PROPERTIES

## – THE EASY WAY


Grace is a large specialty chemicals producer based in the United States.  Grace's experts have developed an easier way to estimate thermodynamic properties using the Citrine Platform.

This will :

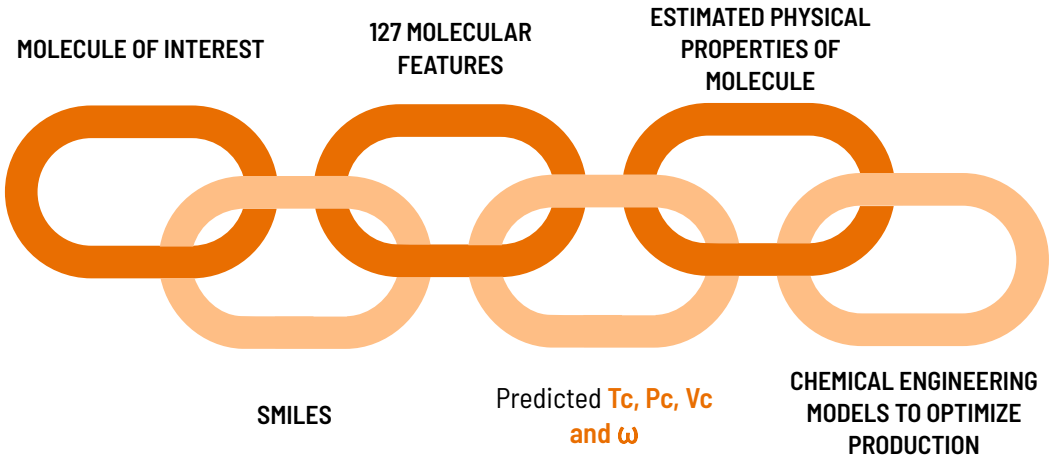
1 **SAVE TIME**

1 **ENABLE BETTER OPTIMIZATION OF CHEMICAL PROCESSES GOING FORWARD AT GRACE**

# EXECUTIVE SUMMARY

As a specialty chemicals company, Grace produces a wide variety of chemicals. To remain competitive, it needs to develop efficient manufacturing processes, with high yields, low cycle times, low impurities, and lowest energy requirements. Grace's product experts model these processes so that they can optimize them. The chemical engineering models they use require the properties of the molecules involved as inputs. Density, boiling point etc. are important. But what do you do if you can't measure these experimentally? Many molecules exist in chemical equilibria with others, constantly changing between monomer and dimer forms, making experimental measurement impossible. In this case, an alternative method of estimating these properties is needed.

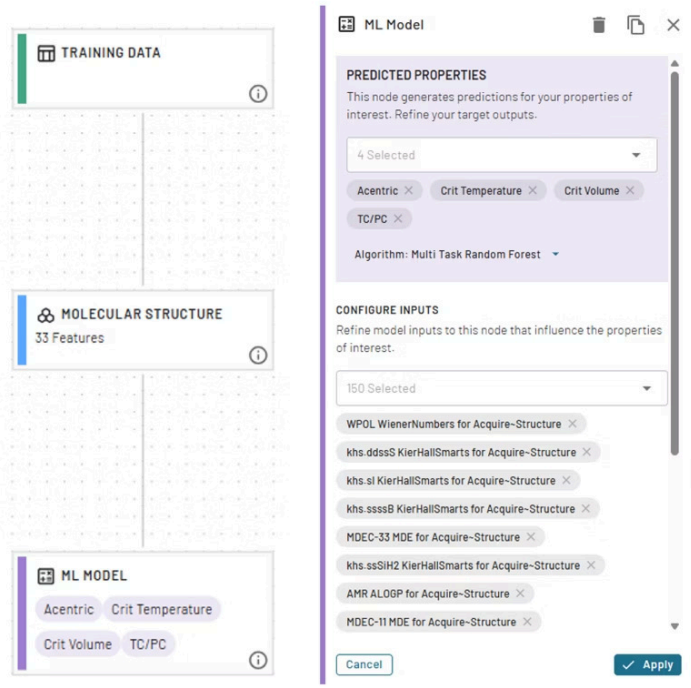
A slew of physical properties of molecules can be estimated using correlations between the actual and critical values of pressure, temperature and volume, with an acentric factor (ω) thrown in to account for not all fluids being spherical. If you have 4 values, **Tc, Pc, Vc and ω**, you can estimate the physical properties you need to know to optimize chemical processes.




Grace's experts have developed an easier way to estimate these properties using the Citrine Platform. **This will save them time and enable quicker and better optimization of chemical processes going forward at Grace.**

# PROCESS

The Citrine Platform was used to model **critical thermodynamic properties** and acentric factor for molecules based on molecular structure and chemical features of the molecules (a form of QSPR – Quantitative Structure Property Relationship). To do this, Grace needed inputs in the form of molecular features and outputs in the form of the critical thermodynamic properties.



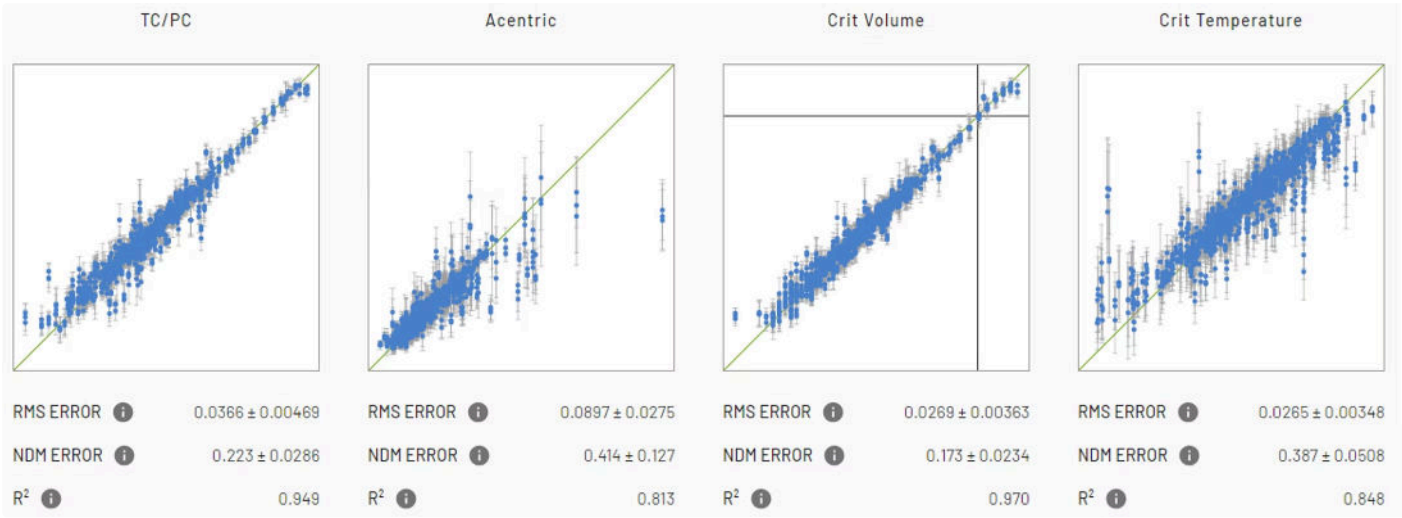

Grace used the Design Institute for Physical Properties (**DIPPR**) database from 2003 as the data source. This high-quality database contains a large number of varied chemicals with both their thermodynamic critical properties and importantly their Smiles string.

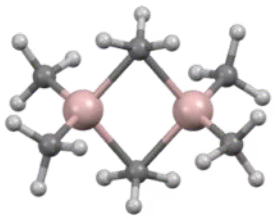
**Smiles (Simplified Molecular-Input Line-Entry System)** is a chemical notation that represents molecular structures as short lines of text that can be processed by computers.

The Citrine Platform automatically converts Smiles strings into 127 + different molecular and chemical features which can then be used as inputs to machine learning models. Machine learning models were used to predict Tc, Pc, Vc and ω based on their Smiles strings.

# OUTCOME

The resulting models had very high $R^2$ values, a measure of predicted accuracy calculated through cross validation.



But to test the accuracy further, Grace's expert tried the models out on **Trimethyl Aluminum Dimer (TMA)** one of the molecules where physical properties cannot be tested experimentally. This molecule was a particularly good challenge for the models because no aluminum species were present in the training set, but aluminum alkyls share similarities from a physical property standpoint with the hydrocarbons in the database. So, this was a very nice test of whether the model is capable of representing chemical behavior.

# TMA RESULTS

| Value | Prediction from Citrine | Grace's Internal Model Prediction |
|---|---|---|
| Critical Temperature | 575±70 K | 605K |
| Critical Pressure | 29.5±2.0 bar | 32.0 bar |
| Critical Volume | 0.43±0.09 L/gmol | 0.54 L/gmol |
| Acentric factor | 0.40±0.11 | 0.29 |

The internal model values are also consistent with what would be implied by an analysis along the lines of Beard et al.

> Beard, A. M., J. C. Mullins, C. H. Barron, and G. A. Daniels. "High-pressure phase equilibria and thermodynamic modeling for binary systems of light paraffins and aluminum alkyls." Fluid phase equilibria 158 (1999): 961 -971.

# FEEDBACK FROM THE TEAM

Garrett Dupre, Grace's Reactive Hazards Process Safety Leader, lead this project. He rapidly picked up how to use the Citrine Platform with minimal training. He usually uses software tools to perform PCAs and PLS and said that the Citrine Platform was **"a nice step up"**.

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# SUMMARY AND NEXT STEPS

The ease with which Grace can now estimate the critical thermodynamic properties of molecules is what is key here. Armed with just the Smiles string and a few minutes on the Citrine Platform, the Grace team can now estimate these values and therefore the molecular physical properties essential for all their chemical engineering models. This will accelerate process optimization, saving time and making chemical processes more efficient and profitable. The team would now like to apply this same trick to model other important parameters such as flammability limits.

### KEY BENEFITS

- Rapid property estimation
- No experimental measurement needed
- Accelerated process optimization

### TECHNICAL ACHIEVEMENT

- High $R^2$ accuracy values
- Validated on challenging molecules

### FUTURE APPLICATIONS

- Flammability limits modeling
- Expanded chemical properties
- Broader process optimization