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Kinetics Development with RSM. Part 2: Di-Tert-Butyl Peroxide Decomposition in Toluene

Process Safety and Risk Management Practices

An ioMosaic White Paper

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How Do You Develop a Kinetic Model in Process Safety Office® SuperChems™?

A kinetic model is required for upset scenarios with runaway chemical reactions that are analyzed dynamically through SuperChems™. Kinetic parameters for these chemical reactions are usually determined by trial and error, one variable at a time. The simplest case requires two parameters, the pre-exponential factor and the activation energy. Even this unpretentious condition presents obstacles. When fixing the pre-exponential factor to determine the activation energy or vice-versa, one is optimized for the fixed value of the other, which most likely is not the real optimum. Neither parameter is optimized in this manner.

It is virtually impossible to optimize kinetic parameters by trial and error when two or more factors are present, so it makes sense to consider an alternative technique. One effective method is Experimental Design, a statistical technique that simultaneously identifies the optimum of all model factors under consideration. An experimental design organizes, conducts, and interprets the results for the best outcome based on the smallest number of trials.

The word trial usually refers to experiments. When developing a kinetic model, a trial represents a SuperChems™ run with kinetic parameters that are part of the design. The typical experimental design works with squares, cubes, or hypercubes, depending on the number of input variables or predictors. A multi-dimensional cubic design is much better than trial and error. However, a superior experimental design technique can be applied to establish kinetic parameters. It is known as Response Surface Methodology (RSM) [1], carried out with a Central Composite Design (CCD) [2].

RSM is a collection of mathematical and statistical techniques for modeling and analyzing complex relationships between kinetic parameters (predictors) and kinetic rates (responses or control variables).

This white paper employs a known chemical reaction to provide the background for kinetic development with RSM. It is the exothermic reaction of di-tert-butyl peroxide decomposition in toluene. The goal is to generate kinetic parameters for SuperChems™ dynamic simulations involving runaway reactions.

“We cannot effectively develop kinetic parameters for a runaway chemical reaction by trial and error.”

The Decomposition of Di-Tert-Butyl Peroxide (DTBP) in Toluene

The overall reaction of di-tert-butyl peroxide decomposition in toluene can be summarized as follows, according to Murawski [3]:

1. $(CH_3)_3C-O-O-C(CH_3)_3 \rightarrow 2(CH_3)_3-CO\bullet$
2. $(CH_3)_3CO\bullet \rightarrow CH_3\bullet + CH_3-CO-CH_3$
3. $2\ CH_3\bullet \rightarrow C_2H_6$
4. $CH_3\bullet + C_6H_5-CH_3 \rightarrow CH_4 + C_6H_5-CH_2\bullet$
5. $CH_3\bullet + C_6H_5-CH_2\bullet \rightarrow C_6H_5-CH_2-CH_3$
6. $(CH_3)_3-CO\bullet + C_6H_5-CH_3 \rightarrow (CH_3)_3-C-OH + C_6H_5-CH_2\bullet$
7. $2\ C_6H_5-CH_2\bullet \rightarrow C_6H_5-CH_2-CH_2-C_6H_5$

Notes:

- The symbol ● represents a free radical.
- Toluene is also known as methylbenzene.
- Reaction 1 is the homolysis of the oxygen-oxygen bond that produces t-butoxy radicals. Homolysis means molecular fission where each fragment retains one of the originally bonded electrons.
- Reaction 2 is hydrogen abstraction from t-butoxy radicals to produce methane free radicals and acetone. Abstraction means the removal of an atom or group of atoms from a molecule by a free radical.
- Reaction 3 is the termination of methane radicals to yield ethane. Termination takes place when two free radicals react with each other to form a stable molecule.
- Reaction 4 is a free-radical substitution reaction in which one hydrogen free radical is transferred from methane to toluene's methyl group.
- Reaction 5 is the termination reaction in which toluene free radicals and methane free radicals react to yield ethylbenzene.
- Reaction 6 is the hydrogen abstraction of t-butoxy radicals and its reaction with toluene to produce t-butyl alcohol and toluene free radicals.

- Reaction 7 is the termination reaction in which two free radicals of toluene combine to form 1,2-diphenylethane, also known as bibenzyl.

The pressure effect will determine the best combination of products for dynamic simulations.

The Adiabatic Experiment and Thermal Inertia

The data from an adiabatic runaway reaction of 20% by mass of di-tert-butyl peroxide in toluene in an ARC test cell was obtained from an ioMosaic 2020 experiment as follows:

- 1.162 g of di-tert-butyl peroxide
- 4.641 g of toluene
- Reaction mixture mass: 1.162+4.641 = 5.803 g

On a molar basis:

> 1.162 g/(146.2300 g/g-mol) di-tert-butyl peroxide per 4.641 g/(92.1405 g/g-mol) toluene, or 0.1363 mole % di-tert-butyl peroxide per 0.8637 mole % of toluene

ARC Experiment

- Test cell:
  - Material of construction: Stainless steel
  - Mass: 17.7137 g
- Fittings:
  - Material of construction: Titanium
  - Mass 6.6172 g
- Volume available: 99.32%, less than 100% due to the presence of a stir bar

The thermal inertia of the experiment, also known as the ϕ-factor, depends on the mass of each component and the specific heat at constant volume. After all, the test volume is practically kept constant. It is common to replace the specific heat at constant volume with the more commonly available specific heat at constant pressure. SuperChems™ can calculate the specific heat of mixtures at constant volume and constant pressure at a temperature stipulated by the user. The ϕ-factor will be somewhat different, depending on the type of specific heat.

The specific heats are the following:

- Mixture: From SuperChems™, the specific heat at a constant volume for the starting mixture at the mean experimental temperature of 146.9°C is 1835 J/(kg °C).
- Test cell: Tabulated data for Stainless Steel 316 is 505 J/(kg °C) at 146.9°C
- Fittings: Titanium, specific heat 377 J/(kg °C) at the mean reaction temperature of 146.9°C. The specific heats at constant volume and pressure are the same for solids, 377 J/(kg °C). Typically, the ϕ-factor is calculated with half of the fittings mass.

The ϕ-factor or thermal inertia of the experiment is then:

$$\phi = \frac{(5.803)(1835)+(17.7137)(505)+(0.5)(6.6172)(377)}{(5.803)(1835)} = 1.96$$

Figure 1: Experimental data of DTBP decomposition in toluene. Pressure and Temperature vs. Time

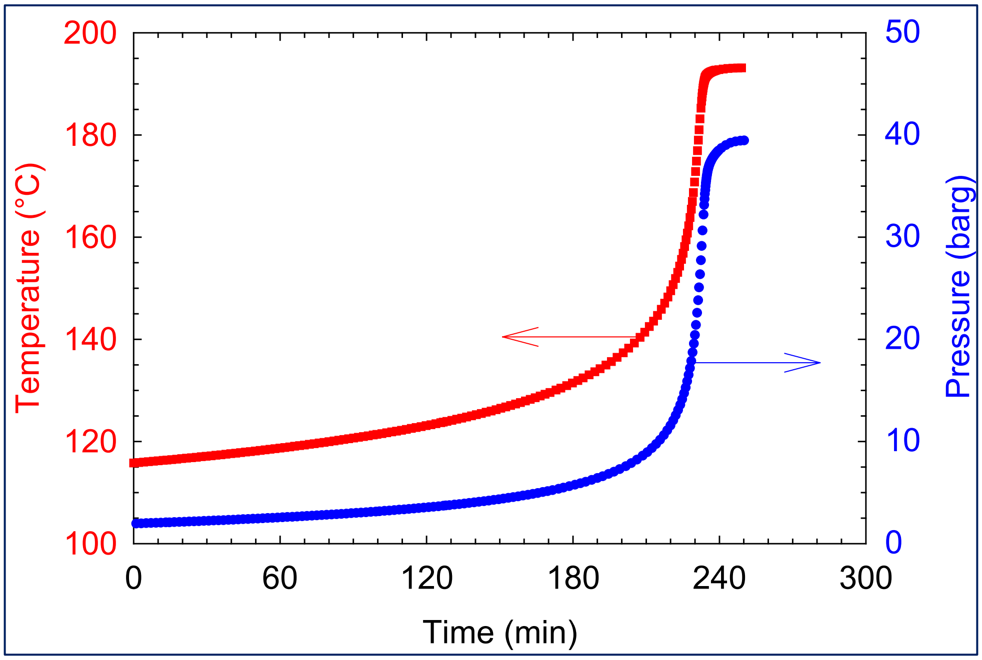


Figure 2: Experimental data of DTBP decomposition in toluene. Self-Rates vs. Temperature

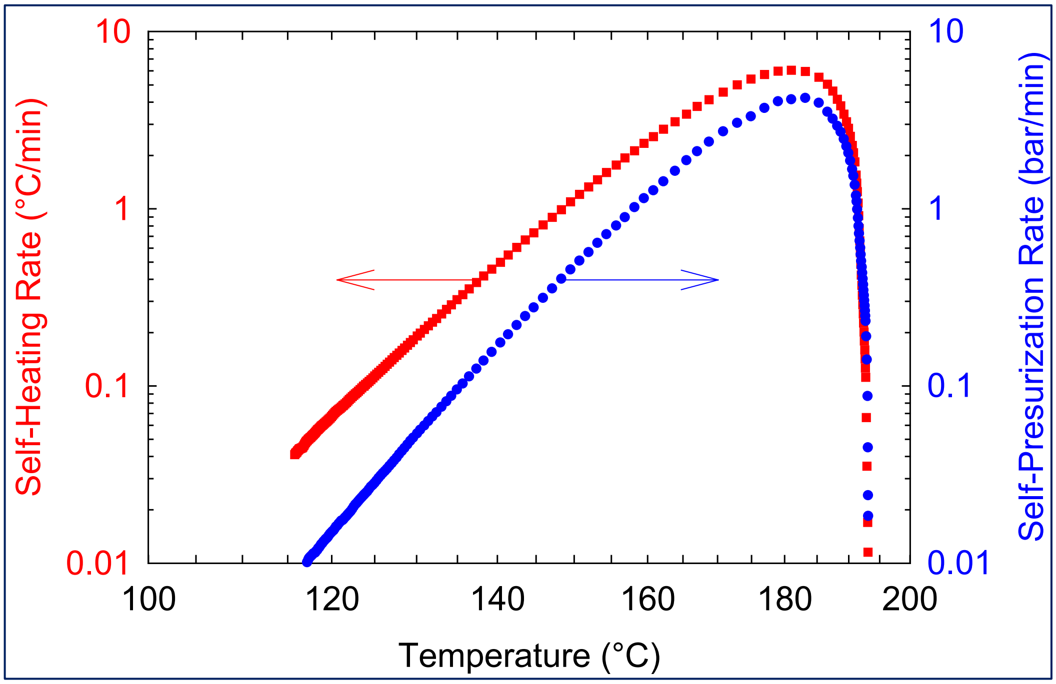
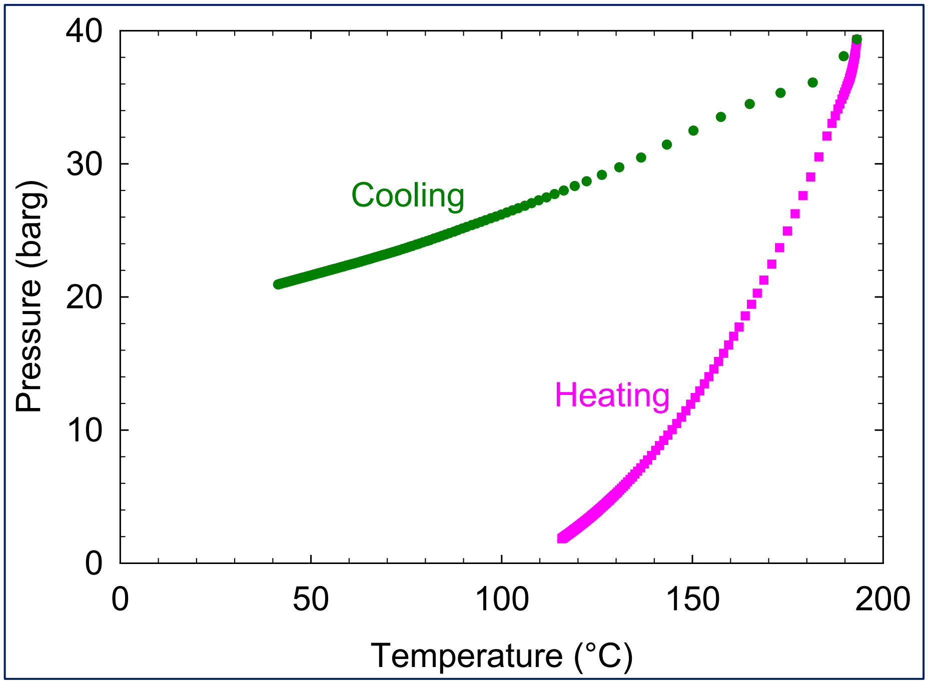


Figure 3: Experimental data of DTBP decomposition in toluene. Pressure vs. Temperature



The scope of this whitepaper is the runaway reaction, that is, the heating stage of the upset condition, to obtain kinetic and stoichiometric parameters.

Chemical Reaction Stoichiometry

The following equations can be written, given the symbols listed under Nomenclature:

Reaction 1: $$P \rightarrow 2R_1 \quad (1)$$

Reaction 2: $$R_1 \rightarrow R_2 + A \quad (2)$$

Reaction 3: $$2R_2 \rightarrow E \quad (3)$$

Reaction 4: $$R_2 + \theta \rightarrow M + R_3 \quad (4)$$

Reaction 5: $$R_2 + R_3 \rightarrow Z \quad (5)$$

Reaction 6: $$R_1 + \theta \rightarrow B + R_3 \quad (6)$$

Reaction 7: $$2R_3 \rightarrow D \quad (7)$$

The objective is to have a single equation without the R$_1$, R$_2$, and R$_3$ radicals. Algebraic manipulations can be done as follows, with stoichiometric parameters a through d:

Multiply Equation (2) by **a** and Equation (6) by **2-a**:

$$aR_1 = aR_2 + aA$$

$$(2-a)R_1 + (2-a)\theta = (2-a)B + (2-a)R_3$$

Adding the two equations:

$$2R_1 + (2-a)\theta = aR_2 + aA + (2-a)B + (2-a)R_3$$

or

$$2R_1 = aA + (2-a)B + aR_2 + (2-a)R_3 - (2-a)\theta \quad (8)$$

Now, multiply Equation (3) by **b**, Equation (4) by **c**, and Equation (5) by **d**.

$$2R_1 = aA + (2-a)B + bE + cM + \left[a-(2b+c)\right]Z + 2(1+b+c-a)R_3 - (2+c-a)\theta\, b2R_2 \rightarrow bE$$

$$cR_2 + cT = cM + cR_3$$

$$dR_2 + dR_3 = dZ$$

Adding the three equations:

$$(2b+c+d)R_2 + c\theta + dR_3 = bE + cM + cR_3 + dZ$$

or

$$(2b+c+d)R_2 = bE + cM + (c-d)R_3 + dZ - c\theta \qquad (9)$$

One among **b**, **c**, and **d** can be eliminated. Arbitrarily choose to eliminate **d**:

$$a = 2b + c + d$$

Parameter **d** can be written as a function of **a**, **b**, and **c**.

$$d = a - (2b + c)$$

In addition, from Equation (9)

$$c - d = c - \left[a - (2b + c)\right] = c - a + 2b + c = 2(b + c) - a$$

With these changes, introducing Equation (9) into Equation (8) there results:

$$2R_1 = aA + (2-a)B + bE + cM + \left[a-(2b+c)\right]Z + \left[2(b+c)-a\right]R_3 - cT + (2-a)R_3 - (2-a)\theta$$

This simplifies to:

$$2R_1 = aA + (2-a)B + bE + cM + \left[a-(2b+c)\right]Z + 2(1+b+c-a)R_3 - (2+c-a)\theta \qquad (10)$$

Introduce Equation (7) given that R_3 = D/2 into Equation (10):

$$2R_1 = aA + (2-a)B + bE + cM + \left[a - (2b+c)\right]Z + (1+b+c-a)D - (2+c-a)\theta \tag{11}$$

Introduce Equation (11) into Equation (1):

$$P + (2+c-a)\theta = aA + (2-a)B + bE + cM + \left[a - (2b+c)\right]Z + (1+b+c-a)D \tag{12}$$

The requirements are the following:

$\theta: a \le 2 + c$ – Easy to achieve because a ≤ 2 per Equation (8)

$Z : a \ge 2b + c$

$D : a \le 1 + b + c$

If the Z and D conditions are met, 2b+c ≤ 1+b+c, from which b ≤ 1

If the θ and Z conditions are met, 2+c ≥ 2b + c, or 1 ≥ b, or b ≤ 1

If the θ and D conditions are met, 2+c ≥ 1+b+c, or 1 ≥ b or b ≤ 1

Hence, b ≤ 1 for the three different combinations.

Additional requirements include:

$B : a \le 2$

$Z : \text{If } a - (2b + c) \ge 0\text{, then } 2 - (2b + c) \ge 0 \Rightarrow 2(1-b) - c \ge 0 \; or \; c \le 2(1-b)$

$D : \text{If } 1 + b + c - a \ge 0 \text{ and } -a \ge -2\text{, then } 1 + b + c - 2 \ge 0 \Rightarrow c \ge 1 - b$

The D condition is more restrictive. Since **b** varies from 0 to 1, **c** must also vary from 0 to 1.

Hence: $$\begin{cases} a \le 2 \\ 0 \le b \le 1 \\ 0 \le c \le 1 \end{cases} \tag{13}$$

Independently of the values of **a**, **b**, and **c**, Equation (12) must balance stoichiometrically for carbon, oxygen, and hydrogen

Equation (12) carbon balance:

$$P+\left(2+c-a\right)\theta=aA+\left(2-a\right)B+bE+cM+\left[a-\left(2b+c\right)\right]Z+\left(1+b+c-a\right)D$$

$$8+\left(2+c-a\right)7=a3+\left(2-a\right)4+b\ 2+c1+\left[a-\left(2b+c\right)\right]8+\left(1+b+c-a\right)14$$

$$8+14+7c-7a=3a+8-4a+2b+c+8a-16b-8c+14+14b+14c-14a$$

$$22+7c-7a=22+\left(3-4+8-14\right)a+\left(2-16+14\right)b+\left(1-8+14\right)c$$

$$22+7c-7a=22+7c-7a\Rightarrow\text{Balanced}$$

Equation (12) oxygen balance:

$$P+\left(2+c-a\right)\theta=aA+\left(2-a\right)B+bE+cM+\left[a-\left(2b+c\right)\right]Z+\left(1+b+c-a\right)D$$

$$2+0=a1+\left(2-a\right)1+0$$

$$2=a+2-a$$

$$2=2\Rightarrow\text{Balanced}$$

Equation (12) hydrogen balance:

$$P+\left(2+c-a\right)\theta=aA+\left(2-a\right)B+bE+cM+\left[a-\left(2b+c\right)\right]Z+\left(1+b+c-a\right)D$$

$$18+\left(2+c-a\right)8=a6+\left(2-a\right)10+b6+c4+\left[a-\left(2b+c\right)\right]10+\left(1+b+c-a\right)14$$

$$18+16+8c-8a=6a+20-10a+6b+4c+10a-20b-10c+14+14b+14c-14a$$

$$34+8c-8a=34+\left(6-10+10-14\right)a+\left(6-20+14\right)b+\left(4-10+14\right)c$$

$$34+8c-8a=34+8c-8a\Rightarrow\mathit{Balanced}$$

Therefore, there is a stoichiometric balance between reactants and products for this study's three types of atoms: carbon, oxygen, and hydrogen.

Experimental Design

This project aims to match as closely as possible the experimental data of di-tert-butyl peroxide decomposition in toluene as seen in Figures 1 to 3 with a SuperChems™ simulation. This will be done through Response Surface Methodology (RSM) [1], a statistics optimization technique.

RSM will be combined with Central Composite Design (CCD) [2]. Dynamic simulations must produce values close to these targets with the optimization procedure. The intent of this white paper is not to teach statistics. There are publications that the reader might consult, such as Box [4], Kiemele et al.[5], Montgomery [6], and Spiegel and Stephens [7].

Model parameters in statistics are called predictors, which are the independent variables. The goal is to match the simulation responses with the experimentation. Responses are the dependent variables. The knowledge of experimental design in statistics is a plus to read this white paper.

The approach in this study is to use a full-factorial design, augmented by central point and star points, which account for curvature, that is, quadratic terms and two-way interactions. Two-way interactions are much more common than higher-order interactions, which rarely occur. The Central Composite Design was modified with one central point instead of the standard model with multiple central points for three predictors. The reason is that the "experiments" in this evaluation are dynamic simulations with SuperChems™. Contrary to actual experiments, the results are identical with any number of runs for the same values of the predictors. Minitab is the statistical software used in this development. Other advanced statistical software could also be used.

Many predictors can be included in the design, such as pre-exponential factors, activation energies, reaction orders, binary interaction parameters, stoichiometric coefficients, and so forth. However, the design becomes increasingly complex as the number of predictors increases. For CCD with one central point, the number of SuperChems™ simulations is 2^k+2k+1, where k is the number of predictors. For two predictors, $2^2+2x2+1 = 9$ simulations are needed for the initial design. The number of simulations escalates to 15 for three predictors and 25 for four predictors. Hence, there is a practical interest in keeping the number of predictors as low as possible and splitting the design whenever possible.

The study has five predictors: the pre-exponential factor k_o', the activation energy divided by the universal gas constant (referred to as activation energy), and stoichiometric coefficients a, b, and c. If a single design is carried out, the number of SuperChems™ runs would be $2^5+2*5+1 = 43$. In this study, it was preferred to run two designs, the first to determine k_o' and B (9 basic simulations), and the second to establish the three stoichiometric coefficients (15 basic simulations). The number of simulations in each design may vary, depending on how it develops and what makes physical sense. For instance, in the second design, **a** = **b** = **c** = 0 does not make sense, so that set of predictors was not in the design.

This study has two steps to reduce the number of SuperChems simulations. However, the kinetic parameters must be corrected after running the second design, which determines the best stoichiometric coefficients. Each design will be covered individually, and then they will be combined to determine the corrected kinetic parameters.

Experimental Design 1: Kinetic Parameters

The simplest approach is to disregard the solvent reactivity. The rate of DTDP decomposition is the following:

$$-\frac{dC_p}{dt}=k'C_p^n \tag{14}$$

Based on conversion:

$$C_p=C_{po}\left(1-X\right) \tag{15}$$

$$-C_{po}\frac{d\left(1-X\right)}{dt}=k'C_{po}^n\left(1-X\right)^n \tag{16}$$

or

$$-\frac{d\left(1-X\right)}{dt}=k'C_{po}^{n-1}\left(1-X\right)^n \tag{17}$$

and

$$1-X=\frac{T_f-T}{\Delta T_a};\ T_o<T<T_f \tag{18}$$

$$\frac{-1}{\Delta T_a}\frac{d\left(T_f-T\right)}{dt}=kC_{po}^{n-1}\left(\frac{T_f-T}{\Delta T_a}\right)^n \tag{19}$$

or

$$\frac{dT}{dt} = k\left(\frac{C_{po}}{\Delta T_a}\right)^{n-1}\left(T_f - T\right)^n \tag{20}$$

or

$$\frac{dT}{dt} = k\left(T_f - T\right)^n;\ k'\left(\frac{C_{po}}{\Delta T_a}\right)^{n-1} = k = k_o e^{-\frac{B}{T}} \tag{21}$$

or

$$\frac{dT}{dt} = k_o\left(T_f - T\right)^n e^{-\frac{B}{T}} \tag{22}$$

Transform Equation (22) using logarithms to yield Equation (23).

$$\ln\left(\frac{dT}{dt}\right) = \ln\left(k_o\right) + \ln\left[\left(T_f - T\right)^n\right] - \frac{B}{T} \tag{23}$$

A convenient approach to determine the activation energy is to lump all logarithmic terms of experimental data. Equation (23) is rewritten as follows:

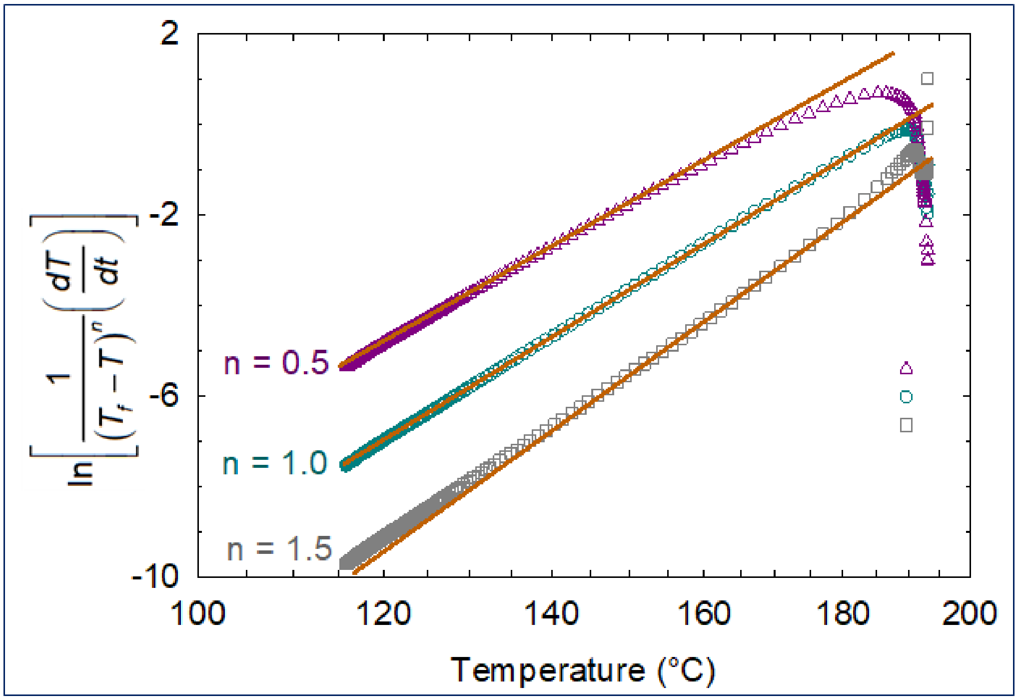
$$\ln\left[\frac{1}{\left(T_f - T\right)^n}\left(\frac{dT}{dt}\right)\right] = \ln\left(k_o\right) - \frac{B}{T} \tag{24}$$

With this method, an Excel spreadsheet can be developed from the ARC dataset to yield an intercept [ln(k_o)] and a slope (B) by straight-line regression. At this point, the main interest is to obtain the reaction order with the self-heating rate vs. temperature data presented in Figure 2.

Figure 4 plots Equation (24) in an inverse Arrhenius plot. Kinetic Lumping in the y-axis is the left-hand side of Equation (24).

Let us consider the different orders of reaction in Figure 4. The brown lines were drawn in the graph to verify linearity, i.e., they are not model-generated.

Figure 4: Regression with different reaction orders.



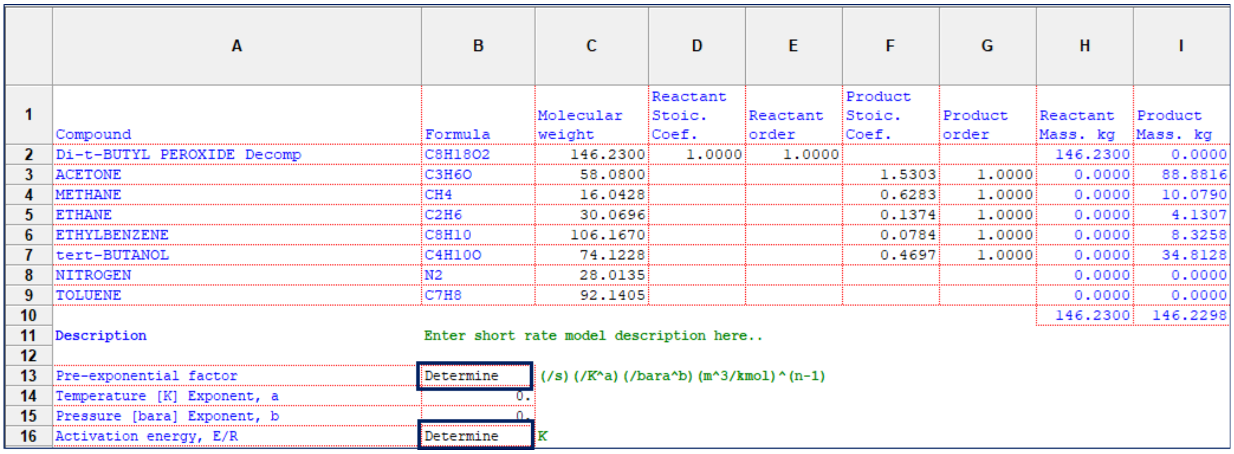
The reaction order is represented by the curve the closest to being linear in which case the overall order is 1. The lines for the overall orders 0.5 and 2.5 show significant curvatures so they can be disregarded.

RSM examines the relationship between model response variables and continuous experimental variables or factors, k_o, B, and n. The method works best when only important controllable factors are applied. This was the reason for establishing the kinetic order n = 1 in advance, so the number of controllable factors could be reduced to only two, k_o and B. In this type of study, the targets are key experimental outputs, and the “experiments” are SuperChems™ simulations with assigned values of the predictors or factors.

Figure 5 shows the SuperChems™ screen where kinetics is developed for dynamic simulations. Predictors or factors in the first design are the pre-exponential factor, k_o (s^{-1}), and the activation energy divided by the universal gas constant, B (K), as shown in Figure 5. These factors are currently unknown and will be determined in the first design.

Responses or outputs are the time to maximum self-heating rate, t_r = 5.45 min, the self-heating rate at a medium temperature of 154°C, $(dT/dt)_{mid}$ = 0.45°C/min, and the maximum self-heating rate, $(dT/dt)_{max}$ = 1.80°C/min. These self-heating rates and the time to maximum rate are based on the ARC experiment’s ϕ-factor of 1.96.

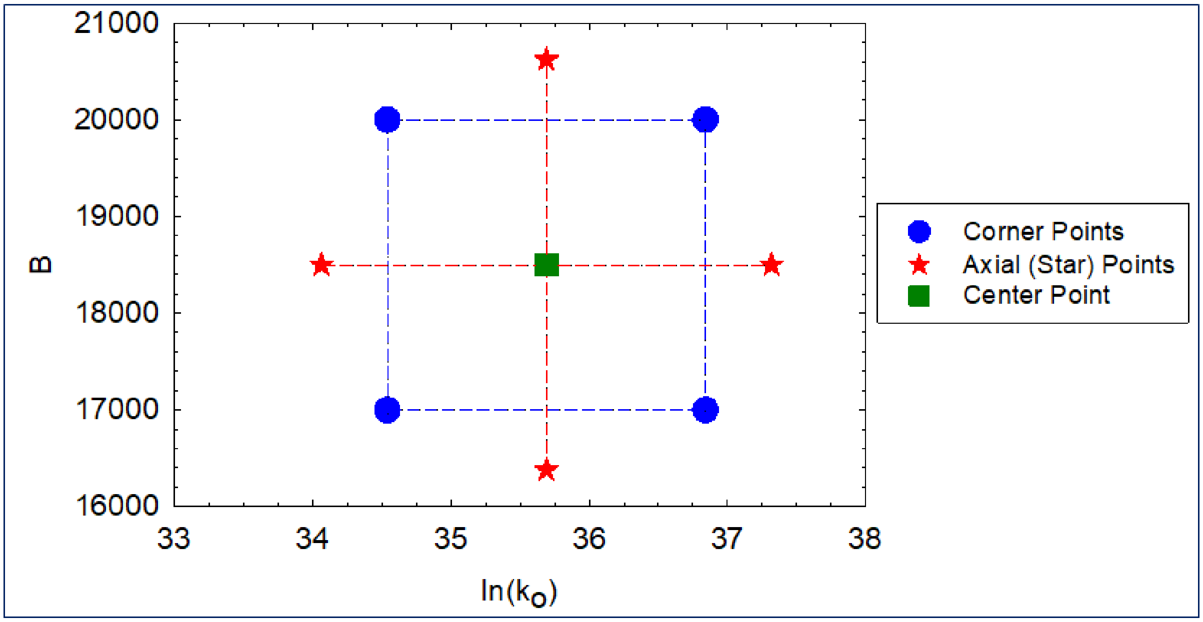
Figure 5: SuperChems™ screen showing the chemical kinetics screen



	A	B	C	D	E	F	G	H	I
1	Compound	Formula	Molecular weight	Reactant Stoic. Coef.	Reactant order	Product Stoic. Coef.	Product order	Reactant Mass. kg	Product Mass. kg
2	Di-t-BUTYL PEROXIDE Decomp	C8H18O2	146.2300	1.0000	1.0000			146.2300	0.0000
3	ACETONE	C3H6O	58.0800			1.5303	1.0000	0.0000	88.8816
4	METHANE	CH4	16.0428			0.6283	1.0000	0.0000	10.0790
5	ETHANE	C2H6	30.0696			0.1374	1.0000	0.0000	4.1307
6	ETHYLBENZENE	C8H10	106.1670			0.0784	1.0000	0.0000	8.3258
7	tert-BUTANOL	C4H10O	74.1228			0.4697	1.0000	0.0000	34.8128
8	NITROGEN	N2	28.0135					0.0000	0.0000
9	TOLUENE	C7H8	92.1405					0.0000	0.0000
10								146.2300	146.2298
11	Description	Enter short rate model description here..							
12									
13	Pre-exponential factor	Determine	(/s) (/K^a) (/bara^b) (m^3/kmol)^(n-1)						
14	Temperature [K] Exponent, a	0.							
15	Pressure [bara] Exponent, b	0.							
16	Activation energy, E/R	Determine	K						

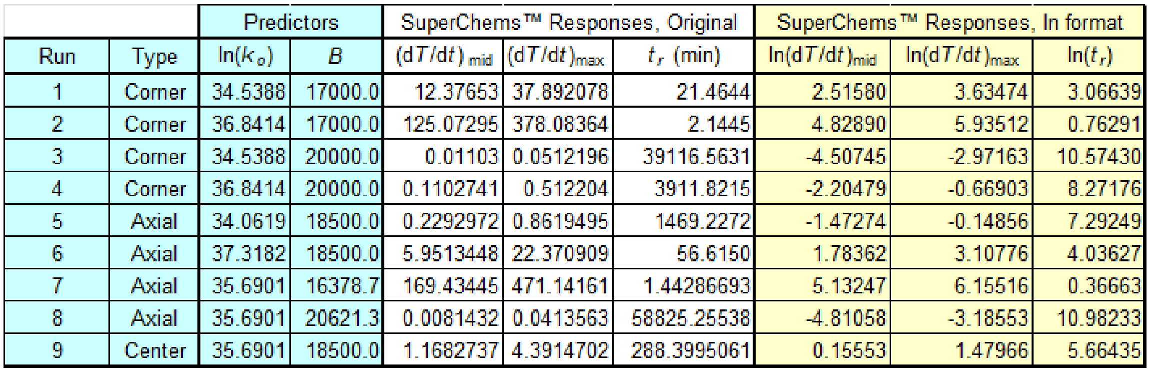
Values of k_o and B were estimated through some SuperChems™ simulations to narrow down their ranges, resulting in Figure 6. Trial-and-error may be inefficient in determining the values of the predictors, but it is a valuable approach to narrow down the RSM range for statistical analysis.

Figure 6: Central Composite Design with two variables for Experimental Design 1



$\ln(k_o)$ was chosen because k_o is in the order of 10^{15}, making the design too strongly dependent on this factor. Log transform was also used for the responses, $(dT/dt)_{mid}$, $(dT/dt)_{max}$, and t_r in Table 1. Otherwise, they would encompass several orders of magnitude, making regression more difficult to interpret.

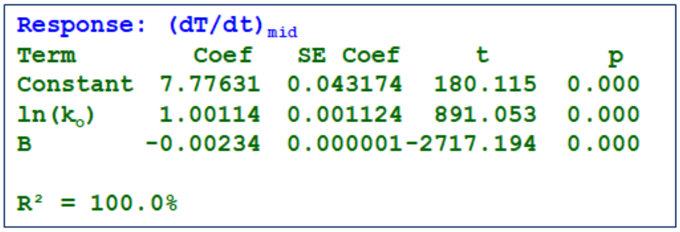
Table 1: SuperChems™ simulations of Experimental Design 1



		Predictors		SuperChems™ Responses, Original			SuperChems™ Responses, ln format		
Run	Type	$\ln(k_o)$	B	$(dT/dt)_{mid}$	$(dT/dt)_{max}$	t_r (min)	$\ln(dT/dt)_{mid}$	$\ln(dT/dt)_{max}$	$\ln(t_r)$
1	Corner	34.5388	17000.0	12.37653	37.892078	21.4644	2.51580	3.63474	3.06639
2	Corner	36.8414	17000.0	125.07295	378.08364	2.1445	4.82890	5.93512	0.76291
3	Corner	34.5388	20000.0	0.01103	0.0512196	39116.5631	-4.50745	-2.97163	10.57430
4	Corner	36.8414	20000.0	0.1102741	0.512204	3911.8215	-2.20479	-0.66903	8.27176
5	Axial	34.0619	18500.0	0.2292972	0.8619495	1469.2272	-1.47274	-0.14856	7.29249
6	Axial	37.3182	18500.0	5.9513448	22.370909	56.6150	1.78362	3.10776	4.03627
7	Axial	35.6901	16378.7	169.43445	471.14161	1.44286693	5.13247	6.15516	0.36663
8	Axial	35.6901	20621.3	0.0081432	0.0413563	58825.25538	-4.81058	-3.18553	10.98233
9	Center	35.6901	18500.0	1.1682737	4.3914702	288.3995061	0.15553	1.47966	5.66435

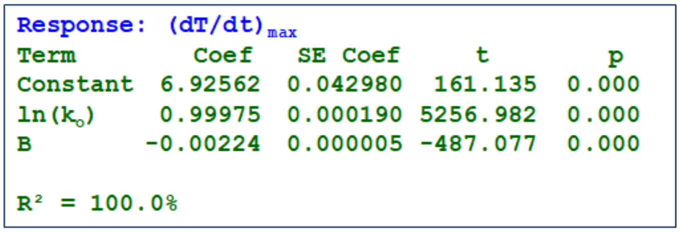
Table 2 contains the statistical output of this design. Only linear terms are statistically significant. The square terms $\ln(k_o)*\ln(k_o)$ and B*B and the interaction term $\ln(k_o)*B$ were not important for this design.

Table 2: Statistical analysis for each response of Experimental Design 1



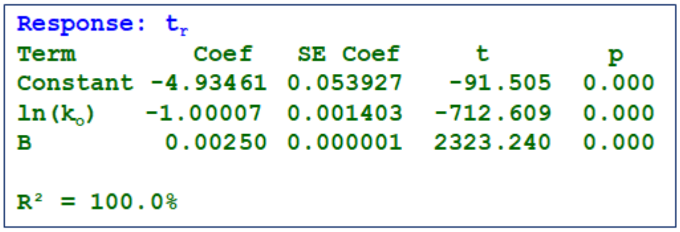
```
Response:  (dT/dt)mid
Term          Coef    SE Coef      t        p
Constant  7.77631  0.043174  180.115   0.000
ln(ko)    1.00114  0.001124  891.053   0.000
B        -0.00234  0.000001-2717.194   0.000

R² = 100.0%
```



```
Response:  (dT/dt)max
Term          Coef    SE Coef      t        p
Constant  6.92562  0.042980  161.135   0.000
ln(ko)    0.99975  0.000190 5256.982   0.000
B        -0.00224  0.000005 -487.077   0.000

R² = 100.0%
```



```
Response:  tr
Term          Coef    SE Coef      t          p
Constant -4.93461  0.053927   -91.505   0.000
ln(ko)   -1.00007  0.001403  -712.609   0.000
B         0.00250  0.000001  2323.240   0.000

R² = 100.0%
```

The statistical outputs in Table 2 can be interpreted as follows:

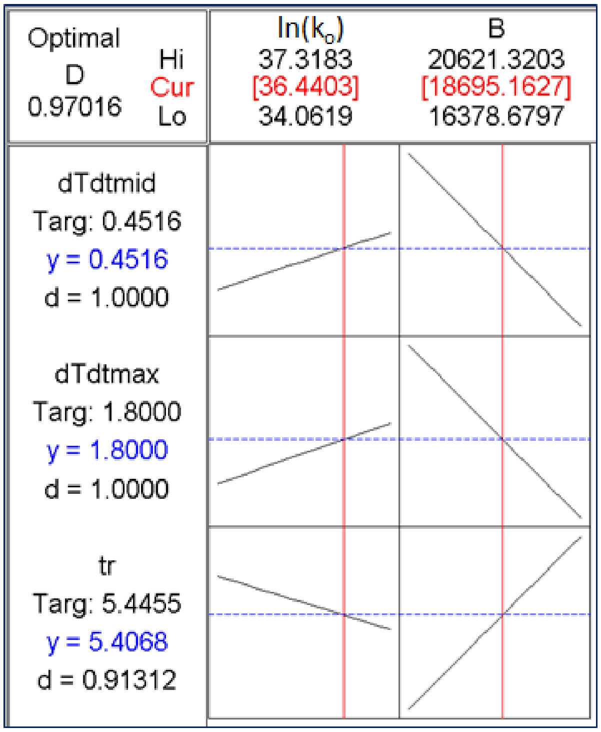
Standard Error of the Coefficients (SE Coeff): Standard deviation of the error of a given predictor to estimate the response quality. It measures the precision of the model's coefficients' estimates. The standard error of the coefficient is always positive.

t: The value of the student t-distribution to determine the p-value (probability that the null hypothesis is true)

p: Null-hypothesis test to verify whether the predictor correlates with the response. The null hypothesis (no correlation) is typically rejected at $p < 0.05$, meaning a strong correlation. A design of experiments can sometimes be more lenient, with the null hypothesis rejected for $p < 0.1$. A p-value of zero in Experimental Design 1 indicates that the constant and the linear terms $\ln(k_o)$ and B are strongly correlated with the responses $\ln(dT/dt)_{mid}$, $\ln(dT/dt)_{max}$, and t_r.

The development of a single set of parameters involves an optimization procedure. In experimental design, it is done through the desirability function 0. The higher the desirability, the better the outcome for parameter determination. The combined analysis is displayed in **Error! Reference source not found.**.

Figure 7: Desirability analysis for the predictors of Experimental Design 1



The optimal desirability D is the geometric mean of the individual desirability values d:

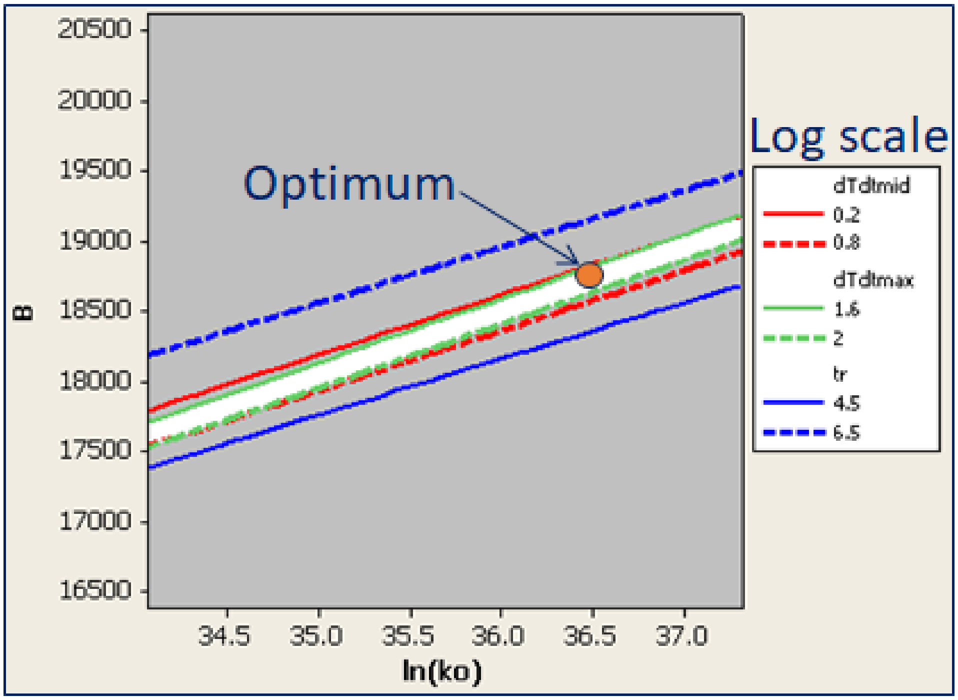
$$D = \sqrt[3]{d_1 d_2 d_3}$$
$$D = \sqrt[3]{(1.00000)(1.00000)(0.91312)}$$
$$D = 0.97016$$

Error! Reference source not found. indicates that the self-heating rates matched very well, given the maximum desirability of 1, but the time to maximum rate was not as good, with a desirability of about 0.91. The individual optima of the predictors are in red.

Table 2 shows that only the linear terms are important. This is confirmed in Figure 7, where the black lines are straight. The red lines indicate the optimum for each predictor ln(k_o) and B.

Figure 8 shows an overlaid contour plot for the two predictors, ln(k_o) and B, and a white zone, the intersection of the three response curves, $(dT/dt)_{mid}$, $(dT/dt)_{max}$, and t_r, for their assigned ranges. The design's optimum is within the white zone, as required.

Figure 8: Overlaid contour plot for Experimental Design 1



After determining the stoichiometric coefficients the kinetic parameters k_o and B might need small adjustments. This was not the case in this study. After optimizing the stoichiometric coefficients in Experimental Design 2 the kinetic parameters were still adequate: $k_o = \exp(36.4403) = 6.6961 \times 10^{15}$ and B = 18695 K.

Experimental Design 2: Stoichiometric Coefficients

Experimental Design 2 uses kinetic parameters k_o and B developed in Experimental Design 1.

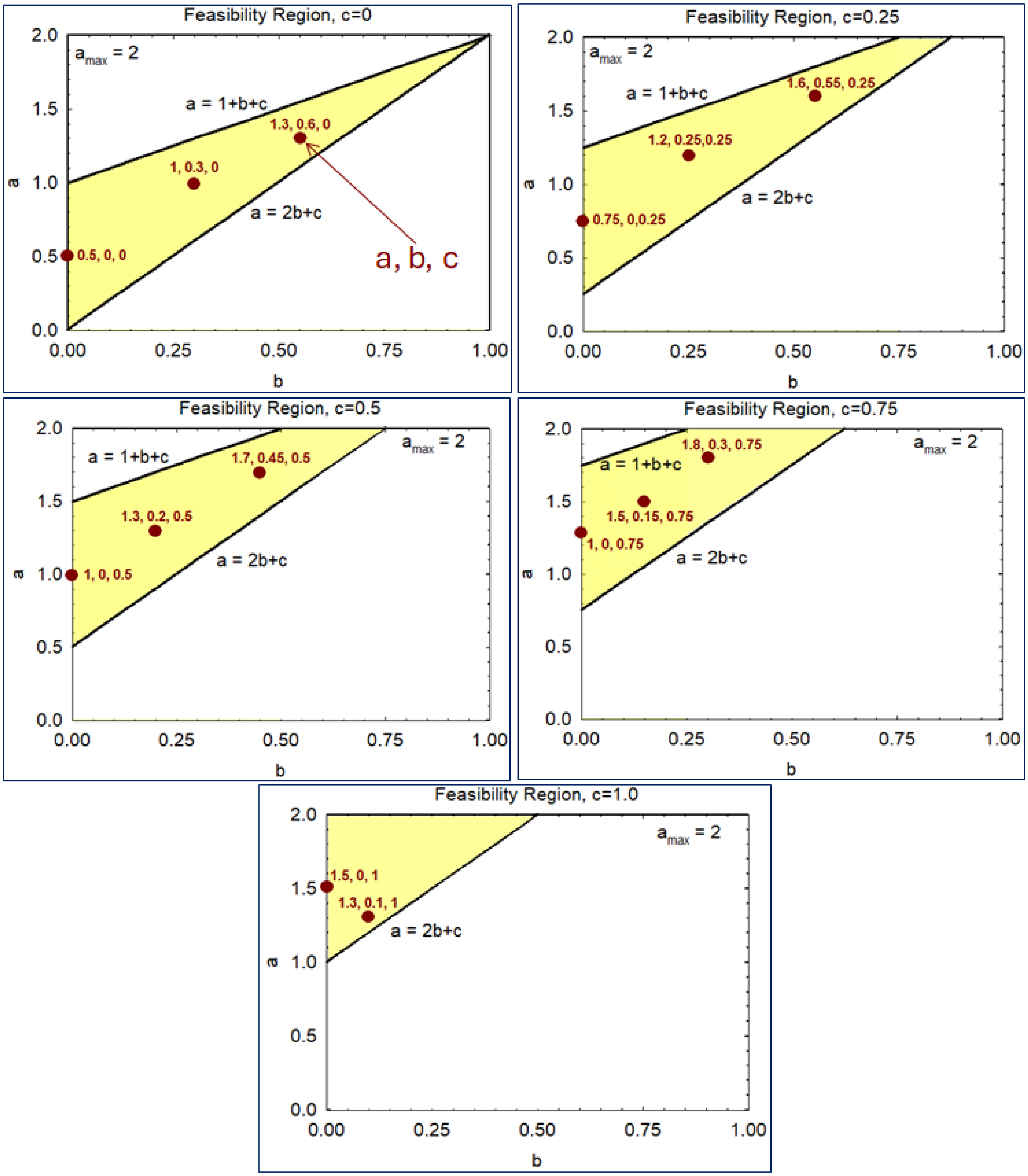
The objective of Experimental Design 2 is to establish a composition that allows simulation pressures to closely match the experimental pressures of the ARC runaway reaction of Di-Tert-Butyl Peroxide in Toluene. The predictors or factors are the stoichiometric coefficients **a**, **b**, and **c**, as observed in Equations (8) through (13).

These predictors can be determined through Response Surface Methodology (RSM), where SuperChems™ runs are the design's "experiments". Due to the limiting values of **a**, **b**, and **c**, a traditional Central Composite Design cannot be applied. Figure 9 was developed based on the limits established by Equation (13). Therefore, it is necessary to run a custom response surface design.

The 14 dots in Figure 9 represent the points of the initial design. The seven responses considered in Experimental Design 2 were the following:

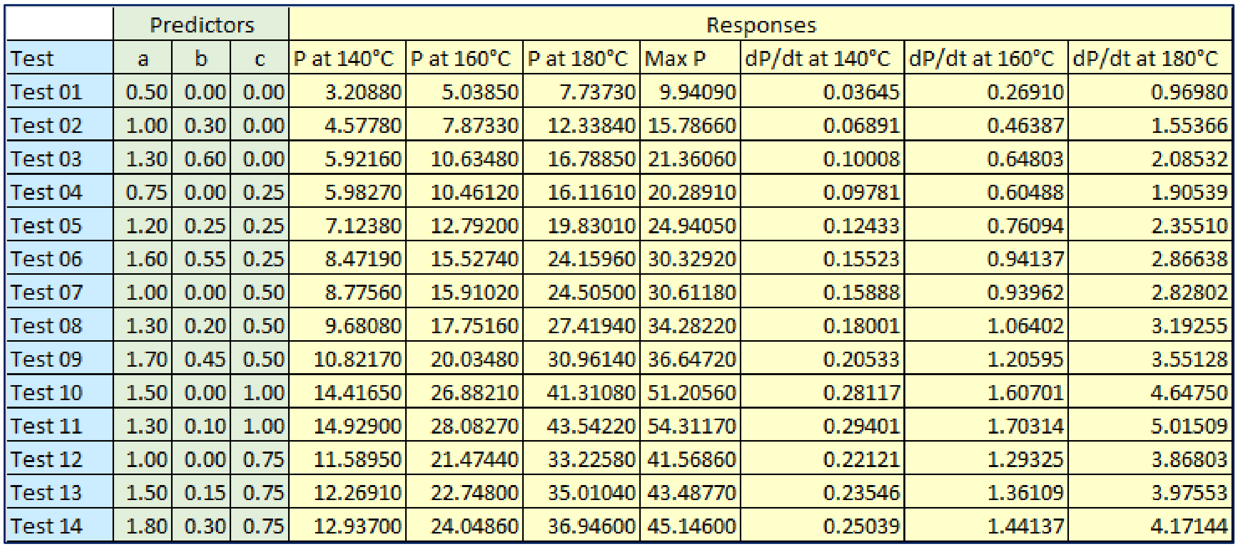
- Pressure at 140°C (8.3468 barg)
- Pressure at 160°C (16.6494 barg)
- Pressure at 180°C (28.3409 barg)
- Maximum Pressure (39.3478 barg)
- Self-pressurization rate at 140°C (0.1693 barg/min)
- Self-pressurization rate at 160°C (1.1959 barg/min)
- Self-pressurization rate at 180°C (4.0747 barg/min)

Figure 9: Predictor limits for the original Experimental Design 2



An experimental design considers linear terms (a, b, c), square terms (a^2, b^2, c^2), and interaction terms (a*b, a*c, b*c). The analysis of the first simulations of Experimental Design 2 showed that all linear terms, some square terms, and some interaction terms were statistically significant. The Minitab output is in Table 3.

Table 3: SuperChems™ simulations for the original Experimental Design 2



	Predictors			Responses						
Test	a	b	c	P at 140°C	P at 160°C	P at 180°C	Max P	dP/dt at 140°C	dP/dt at 160°C	dP/dt at 180°C
Test 01	0.50	0.00	0.00	3.20880	5.03850	7.73730	9.94090	0.03645	0.26910	0.96980
Test 02	1.00	0.30	0.00	4.57780	7.87330	12.33840	15.78660	0.06891	0.46387	1.55366
Test 03	1.30	0.60	0.00	5.92160	10.63480	16.78850	21.36060	0.10008	0.64803	2.08532
Test 04	0.75	0.00	0.25	5.98270	10.46120	16.11610	20.28910	0.09781	0.60488	1.90539
Test 05	1.20	0.25	0.25	7.12380	12.79200	19.83010	24.94050	0.12433	0.76094	2.35510
Test 06	1.60	0.55	0.25	8.47190	15.52740	24.15960	30.32920	0.15523	0.94137	2.86638
Test 07	1.00	0.00	0.50	8.77560	15.91020	24.50500	30.61180	0.15888	0.93962	2.82802
Test 08	1.30	0.20	0.50	9.68080	17.75160	27.41940	34.28220	0.18001	1.06402	3.19255
Test 09	1.70	0.45	0.50	10.82170	20.03480	30.96140	36.64720	0.20533	1.20595	3.55128
Test 10	1.50	0.00	1.00	14.41650	26.88210	41.31080	51.20560	0.28117	1.60701	4.64750
Test 11	1.30	0.10	1.00	14.92900	28.08270	43.54220	54.31170	0.29401	1.70314	5.01509
Test 12	1.00	0.00	0.75	11.58950	21.47440	33.22580	41.56860	0.22121	1.29325	3.86803
Test 13	1.50	0.15	0.75	12.26910	22.74800	35.01040	43.48770	0.23546	1.36109	3.97553
Test 14	1.80	0.30	0.75	12.93700	24.04860	36.94600	45.14600	0.25039	1.44137	4.17144

The quality of a model developed with statistics can be judged by the optimal desirability D, which depends on the individual desirability values d, as seen in Figure 10.

Figure 10: Original desirability analysis for the predictors of Experimental Design 2

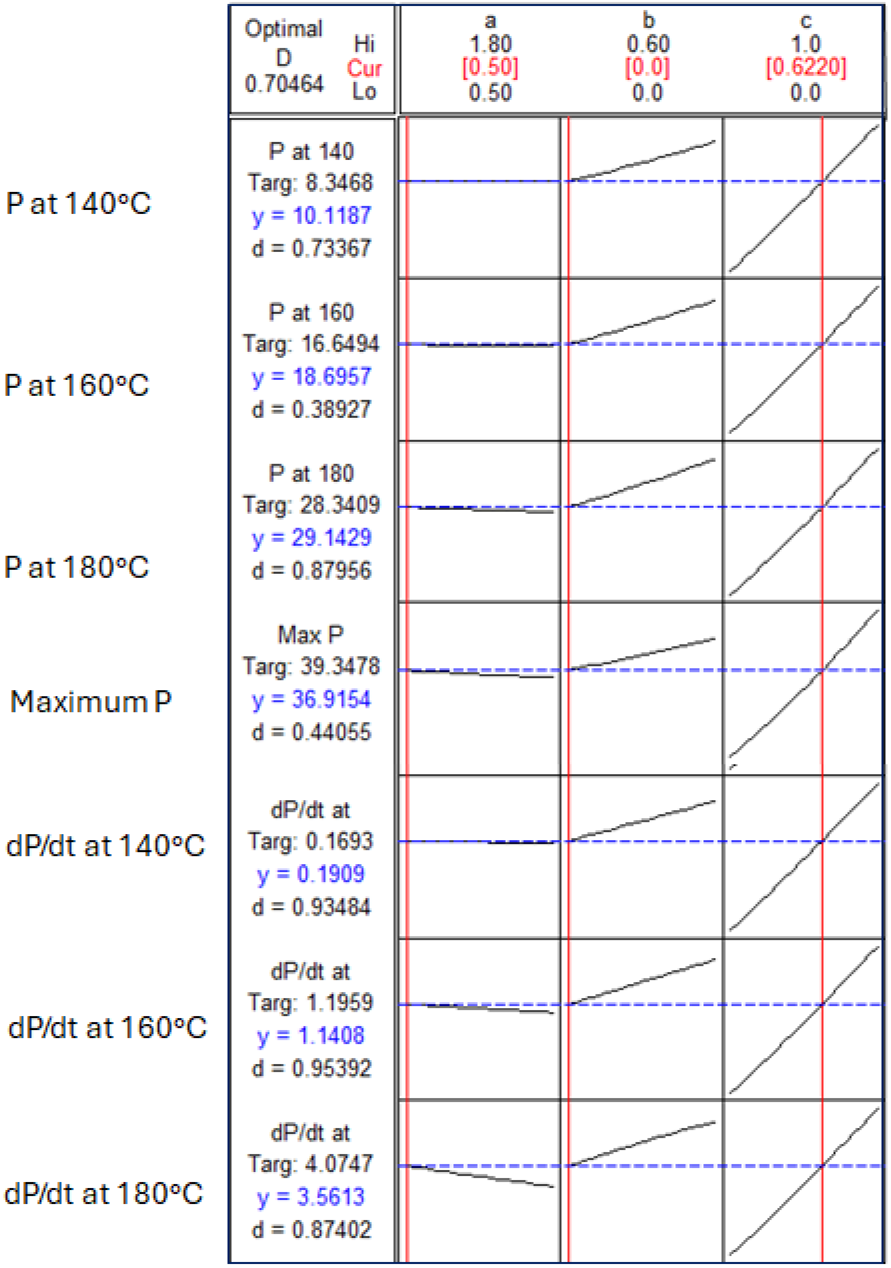
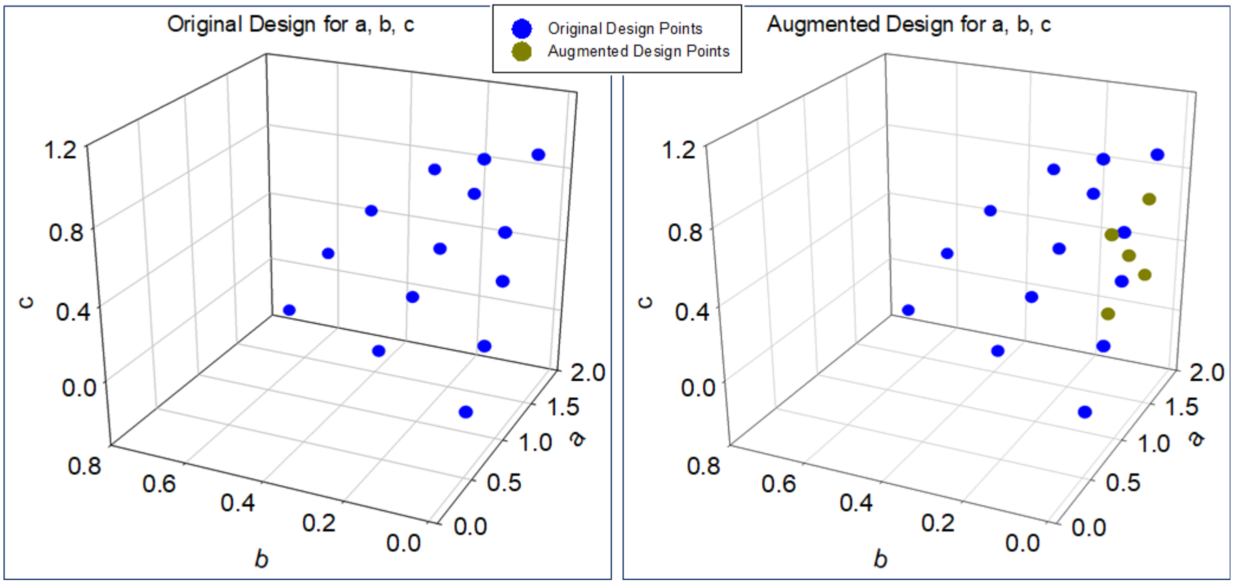


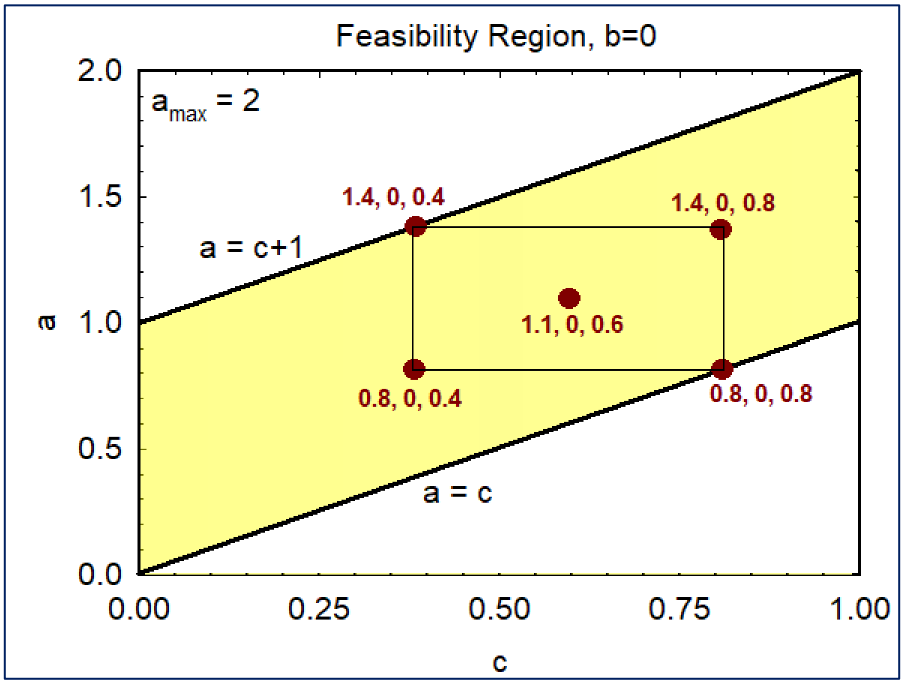
Figure 10 shows self-pressurization responses (dP/dt) with better desirability results than pressure (P). An undesirable outcome in Figure 10 is the observation that the **a** and **b** values are pegged at low values, given the positions of the red lines. This means that **a** and **b** may not have reached their optimum. The design must be improved. To achieve this goal, the original design with 14 points was augmented to 19 points, as shown in Figures 11 and 12 and the stoichiometric coefficients were adjusted according to Table 4 and Figure 13.

Figure 11: Original and augmented models for Experimental Design 2



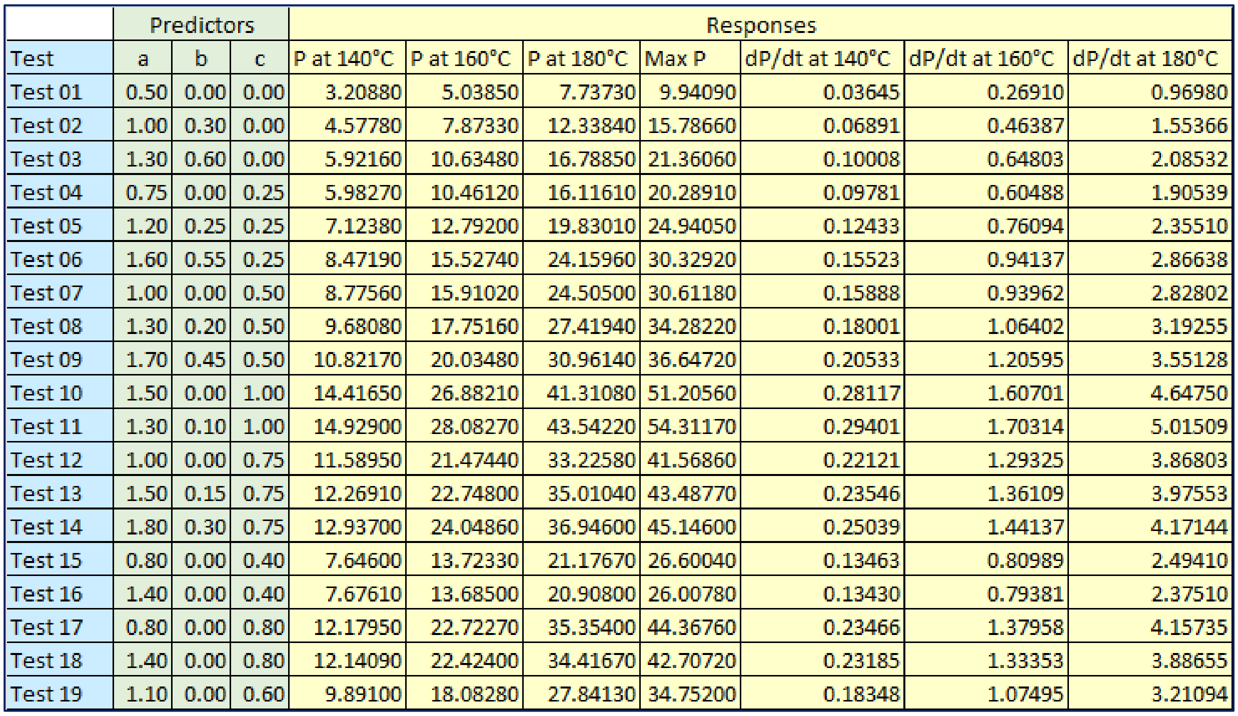
The design was augmented by five points (15 to 19) while respecting Equation (13) to attain **a** and **b** values within the limits of their ranges. All added points were at **b** = 0, as Figure 12 shows.

Figure 12: Additional points added to the original Experimental Design 2



The Minitab output with the SuperChems™ simulation for the augmented Experimental Design 2 is in Table 4.

Table 4: SuperChems™ simulations for the augmented Experimental Design 2



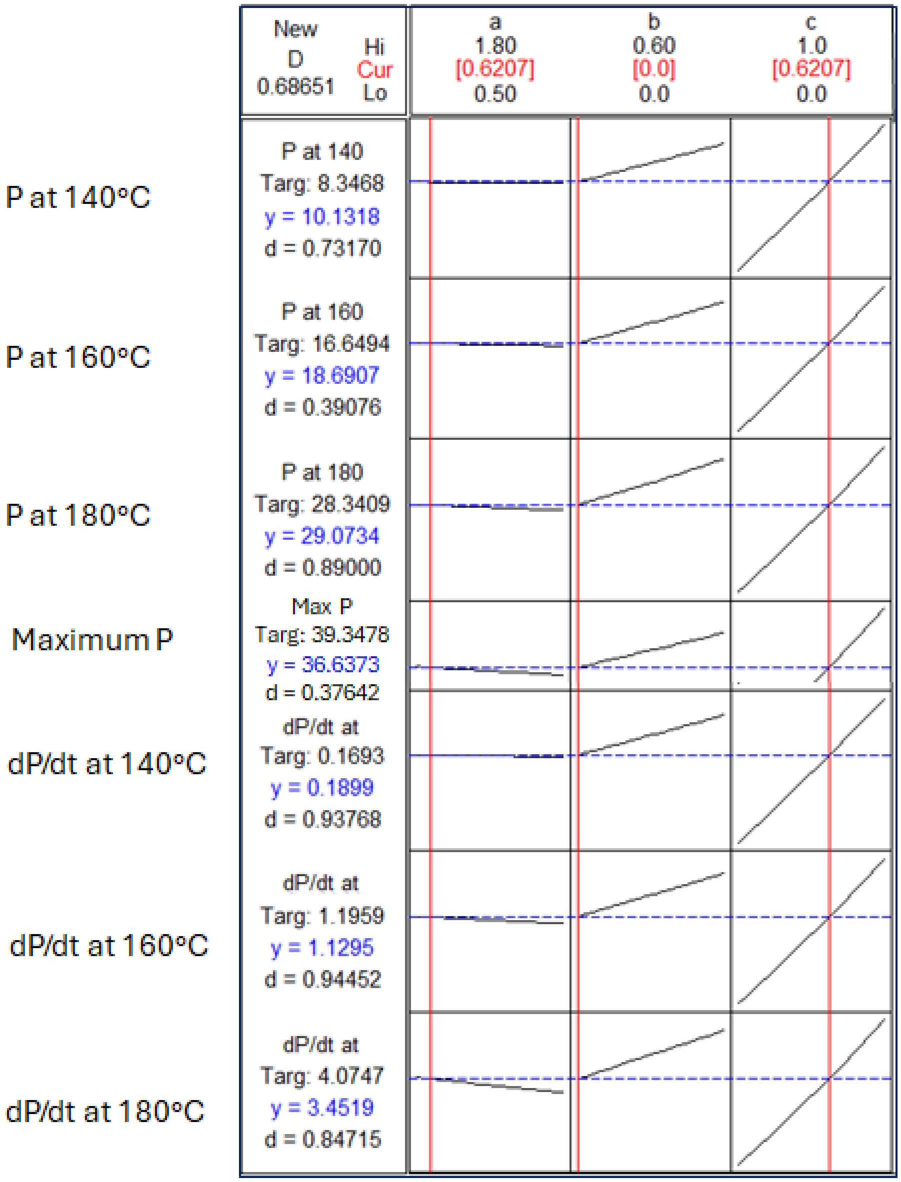
	Predictors			Responses						
Test	a	b	c	P at 140°C	P at 160°C	P at 180°C	Max P	dP/dt at 140°C	dP/dt at 160°C	dP/dt at 180°C
Test 01	0.50	0.00	0.00	3.20880	5.03850	7.73730	9.94090	0.03645	0.26910	0.96980
Test 02	1.00	0.30	0.00	4.57780	7.87330	12.33840	15.78660	0.06891	0.46387	1.55366
Test 03	1.30	0.60	0.00	5.92160	10.63480	16.78850	21.36060	0.10008	0.64803	2.08532
Test 04	0.75	0.00	0.25	5.98270	10.46120	16.11610	20.28910	0.09781	0.60488	1.90539
Test 05	1.20	0.25	0.25	7.12380	12.79200	19.83010	24.94050	0.12433	0.76094	2.35510
Test 06	1.60	0.55	0.25	8.47190	15.52740	24.15960	30.32920	0.15523	0.94137	2.86638
Test 07	1.00	0.00	0.50	8.77560	15.91020	24.50500	30.61180	0.15888	0.93962	2.82802
Test 08	1.30	0.20	0.50	9.68080	17.75160	27.41940	34.28220	0.18001	1.06402	3.19255
Test 09	1.70	0.45	0.50	10.82170	20.03480	30.96140	36.64720	0.20533	1.20595	3.55128
Test 10	1.50	0.00	1.00	14.41650	26.88210	41.31080	51.20560	0.28117	1.60701	4.64750
Test 11	1.30	0.10	1.00	14.92900	28.08270	43.54220	54.31170	0.29401	1.70314	5.01509
Test 12	1.00	0.00	0.75	11.58950	21.47440	33.22580	41.56860	0.22121	1.29325	3.86803
Test 13	1.50	0.15	0.75	12.26910	22.74800	35.01040	43.48770	0.23546	1.36109	3.97553
Test 14	1.80	0.30	0.75	12.93700	24.04860	36.94600	45.14600	0.25039	1.44137	4.17144
Test 15	0.80	0.00	0.40	7.64600	13.72330	21.17670	26.60040	0.13463	0.80989	2.49410
Test 16	1.40	0.00	0.40	7.67610	13.68500	20.90800	26.00780	0.13430	0.79381	2.37510
Test 17	0.80	0.00	0.80	12.17950	22.72270	35.35400	44.36760	0.23466	1.37958	4.15735
Test 18	1.40	0.00	0.80	12.14090	22.42400	34.41670	42.70720	0.23185	1.33353	3.88655
Test 19	1.10	0.00	0.60	9.89100	18.08280	27.84130	34.75200	0.18348	1.07495	3.21094

The quality of the augmented model can be checked through the optimal desirability D, which depends on the individual desirability values d, as seen in Figure 13. The newly optimized values are within the limits of the design. The value of b might be regarded as pegged, but it is not. Zero is the actual value of the stoichiometric coefficient b.

The optimum stoichiometric parameters are then (a, b, c) = (0.6207, 0, 0.6207), with an enthalpy of reaction of -0.802 MJ/kg. The reaction order of toluene was assumed to be zero due to its large excess compared to di-tert-butyl peroxide and its concentration was not a rate-limiting factor.

The desirability analysis for the augmented Experimental Design 2 is shown in Figure 13. No stoichiometric parameter is pegged at either end of the design.

Figure 13: Augmented desirability analysis for the predictors of Experimental Design 2



The stoichiometric parameters **a** = 0.6207, **b** = 0, and **c** = 0.6207 were converted into stoichiometric coefficients, shown in bold in Table 4. The stoichiometric coefficients were then entered under a chemical reaction SuperChems™, as Figure 15 indicates. The bottom row in columns H and I demonstrates the mass balance between reactants and products.

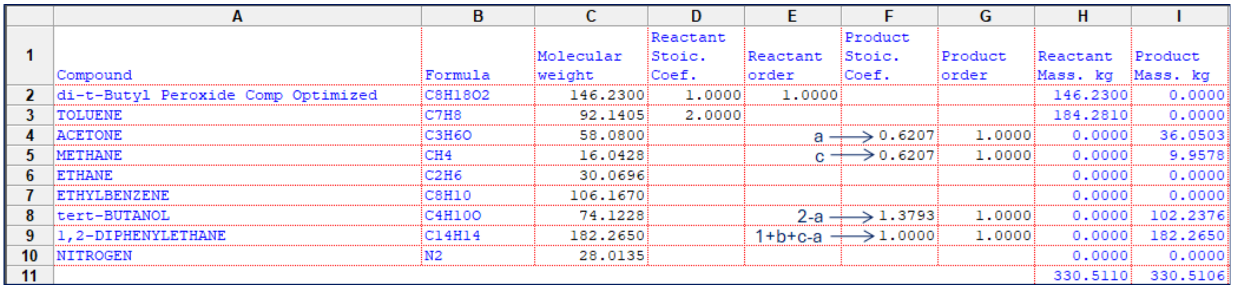
Table 4: Stoichiometric coefficients for DTBP decomposition in toluene

	Compound	Stoichiometric Coefficient
Reactants	Di-Tert-Butyl Peroxide	**1**
	Toluene	2+c-a = 2+0.6207-0.6207 = **2**
Products	Acetone	a = **0.6207**
	Methane	c = **0.6207**
	Ethane	b = **0**
	Ethyl Benzene	a-(2b+c) = 0.6207-(2*0+0.6207) = **0**
	Tert-Butanol	2-a = 2-0.6207 = **1.3793**
	Diphenyl Ethane	1+b+c-a = 1+0+0.6207-0.6207 = **1**

These stoichiometric coefficients were entered in SuperChems™ as follows:

In Figure 13 multiplying the stoichiometric coefficients from Table 4 by the respective molecular weights makes the mass of the reactants match the mass of the products, columns H and I in Figure 13.

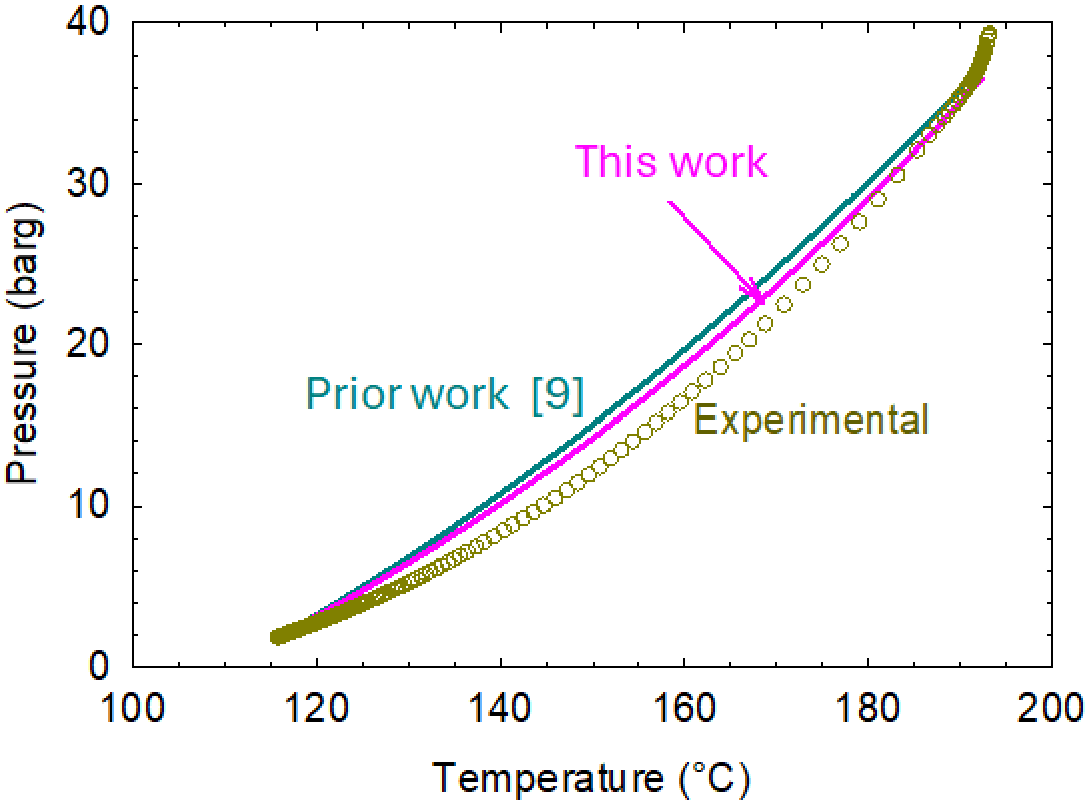
Figure 14: Composition for Experimental Design 2 in SuperChems™



	A	B	C	D	E	F	G	H	I
1	Compound	Formula	Molecular weight	Reactant Stoic. Coef.	Reactant order	Product Stoic. Coef.	Product order	Reactant Mass. kg	Product Mass. kg
2	di-t-Butyl Peroxide Comp Optimized	C8H18O2	146.2300	1.0000	1.0000			146.2300	0.0000
3	TOLUENE	C7H8	92.1405	2.0000				184.2810	0.0000
4	ACETONE	C3H6O	58.0800		a →	0.6207	1.0000	0.0000	36.0503
5	METHANE	CH4	16.0428		c →	0.6207	1.0000	0.0000	9.9578
6	ETHANE	C2H6	30.0696					0.0000	0.0000
7	ETHYLBENZENE	C8H10	106.1670					0.0000	0.0000
8	tert-BUTANOL	C4H10O	74.1228		2-a →	1.3793	1.0000	0.0000	102.2376
9	1,2-DIPHENYLETHANE	C14H14	182.2650		1+b+c-a →	1.0000	1.0000	0.0000	182.2650
10	NITROGEN	N2	28.0135					0.0000	0.0000
11								330.5110	330.5106

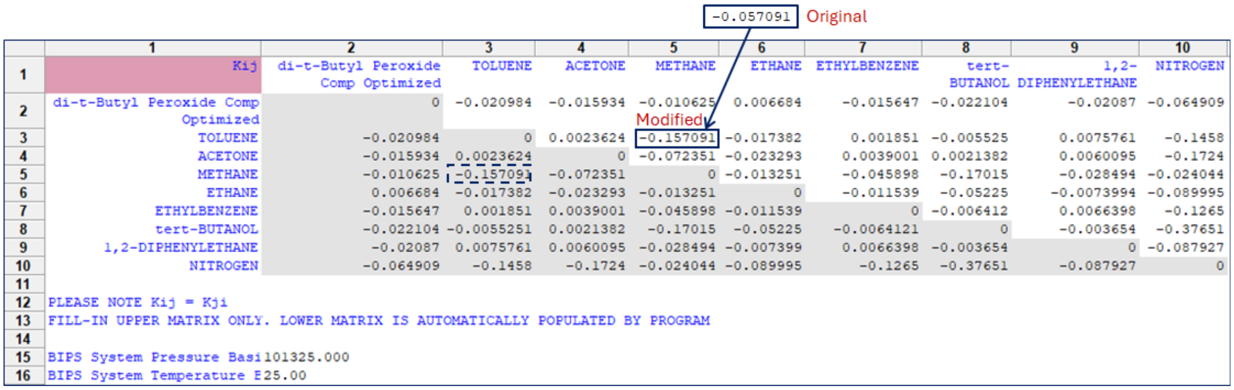
The output from a SuperChems™ simulation can be visualized in Figure 15, where the results were compared to prior work by Gonzales and Levin [9]. The current work exhibits a slight improvement compared to the preceding work, but improvements can be made to the modeling.

Figure 15: Pressure vs. temperature for the augmented Experimental Design 2



As seen in Figure 16, the toluene-methane BIP was changed from calculated -0.057091 to manually-entered -0.157091. A higher negative number for the BIP increases the attraction between the two species and favors a pressure decrease. The result of this change can be seen in Figure 17.

Figure 16: Binary Interaction Parameters (BIPs) with change for toluene-methane



-0.057091 Original

Modified

	1	2	3	4	5	6	7	8	9	10
1	Kij	di-t-Butyl Peroxide Comp Optimized	TOLUENE	ACETONE	METHANE	ETHANE	ETHYLBENZENE	tert-BUTANOL	1,2-DIPHENYLETHANE	NITROGEN
2	di-t-Butyl Peroxide Comp Optimized	0	-0.020984	-0.015934	-0.010625	0.006684	-0.015647	-0.022104	-0.02087	-0.064909
3	TOLUENE	-0.020984	0	0.0023624	-0.157091	-0.017382	0.001851	-0.005525	0.0075761	-0.1458
4	ACETONE	-0.015934	0.0023624	0	-0.072351	-0.023293	0.0039001	0.0021382	0.0060095	-0.1724
5	METHANE	-0.010625	-0.157091	-0.072351	0	-0.013251	-0.045898	-0.17015	-0.028494	-0.024044
6	ETHANE	0.006684	-0.017382	-0.023293	-0.013251	0	-0.011539	-0.05225	-0.0073994	-0.089995
7	ETHYLBENZENE	-0.015647	0.001851	0.0039001	-0.045898	-0.011539	0	-0.006412	0.0066398	-0.1265
8	tert-BUTANOL	-0.022104	-0.0055251	0.0021382	-0.17015	-0.05225	-0.0064121	0	-0.003654	-0.37651
9	1,2-DIPHENYLETHANE	-0.02087	0.0075761	0.0060095	-0.028494	-0.007399	0.0066398	-0.003654	0	-0.087927
10	NITROGEN	-0.064909	-0.1458	-0.1724	-0.024044	-0.089995	-0.1265	-0.37651	-0.087927	0
11										
12	PLEASE NOTE Kij = Kji									
13	FILL-IN UPPER MATRIX ONLY. LOWER MATRIX IS AUTOMATICALLY POPULATED BY PROGRAM									
14										
15	BIPS System Pressure Basi	101325.000								
16	BIPS System Temperature E	25.00								

Figure 17: Output comparison of pressure vs. temperature with and without toluene-methane BIP adjustment

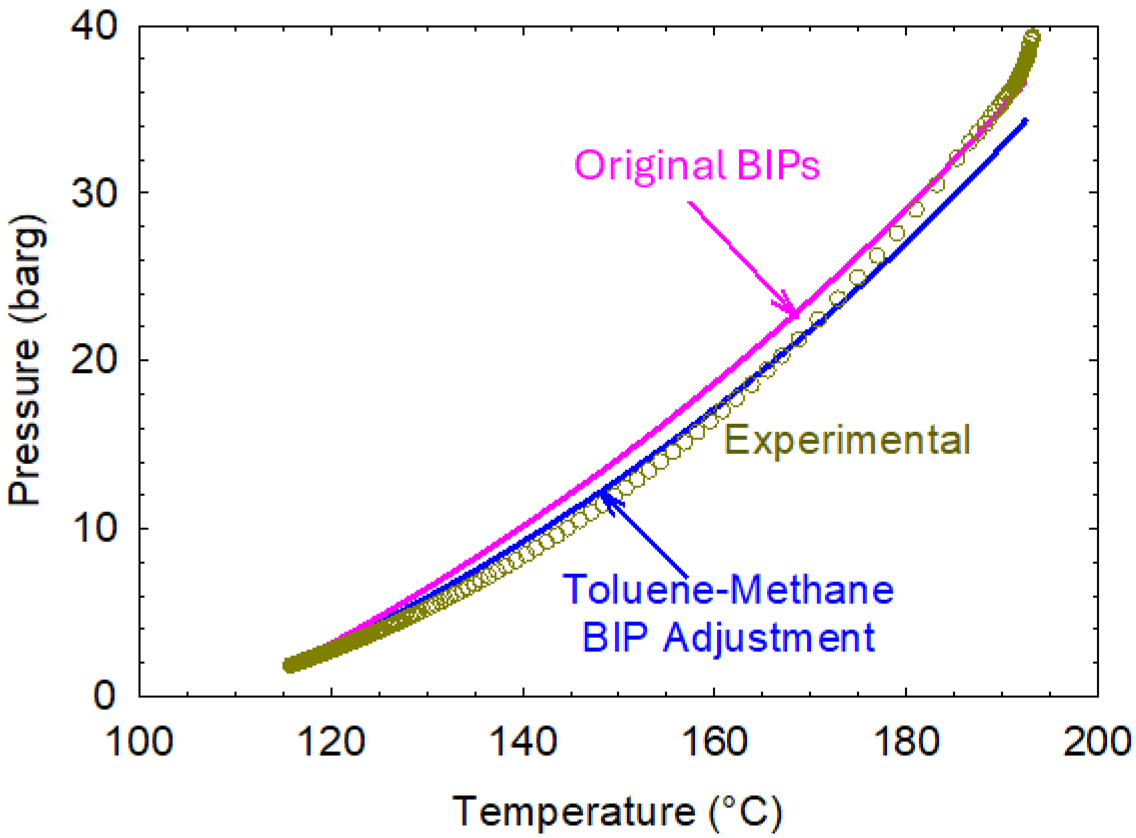


Figure 17 shows an improvement in pressure match at conditions of greater practical interest for most applications, as there is a closer match with the experimental data. The BIP modification should be considered in this case. It must be mentioned that the results with the original BIPs are better for high pressures.

The advantages of BIP modification can be visualized in Figures 18 and 19. The left-hand graphs of Figures 18 and 19 come from Figure 17 with individual simulations, Figure 18 with the original BIPs, and Figure 19 with the modified toluene-methane BIP. Each right-hand graph has a close-up of a hypothetical pressure relief at 10 barg.

Figure 18: Pressure vs. temperature, original toluene-methane BIP of -0.057091 for a scenario with hypothetical pressure relief at 10 barg

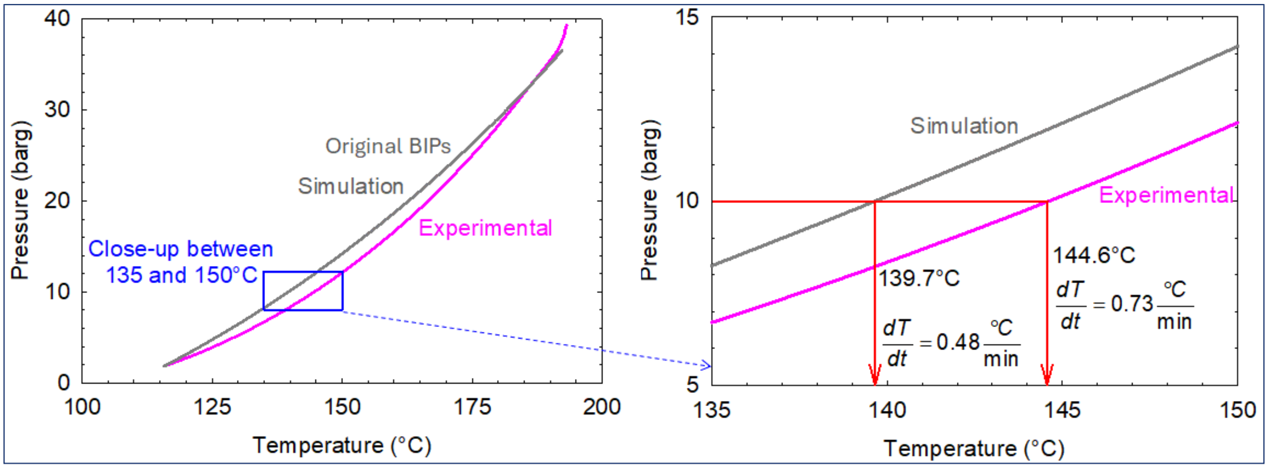
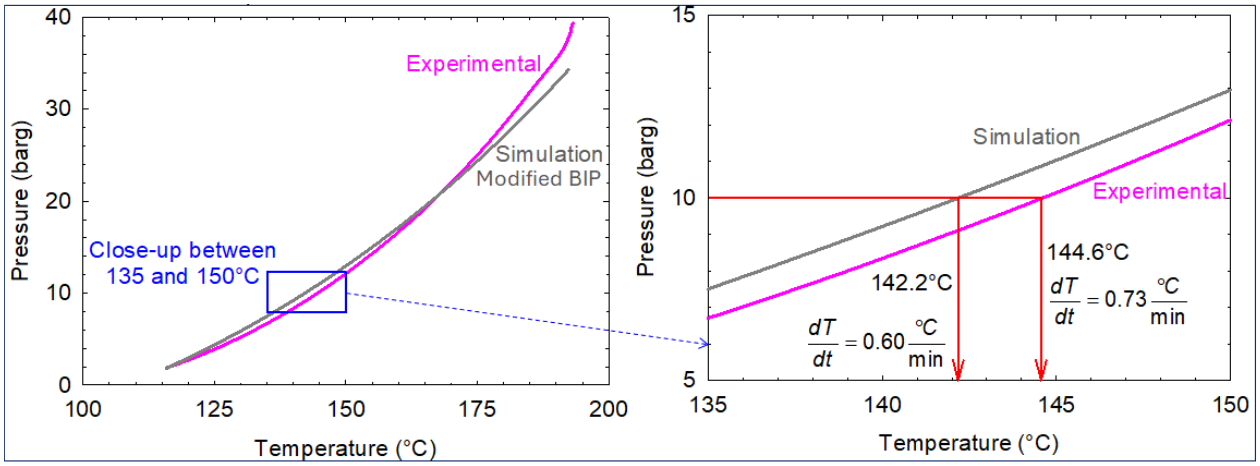


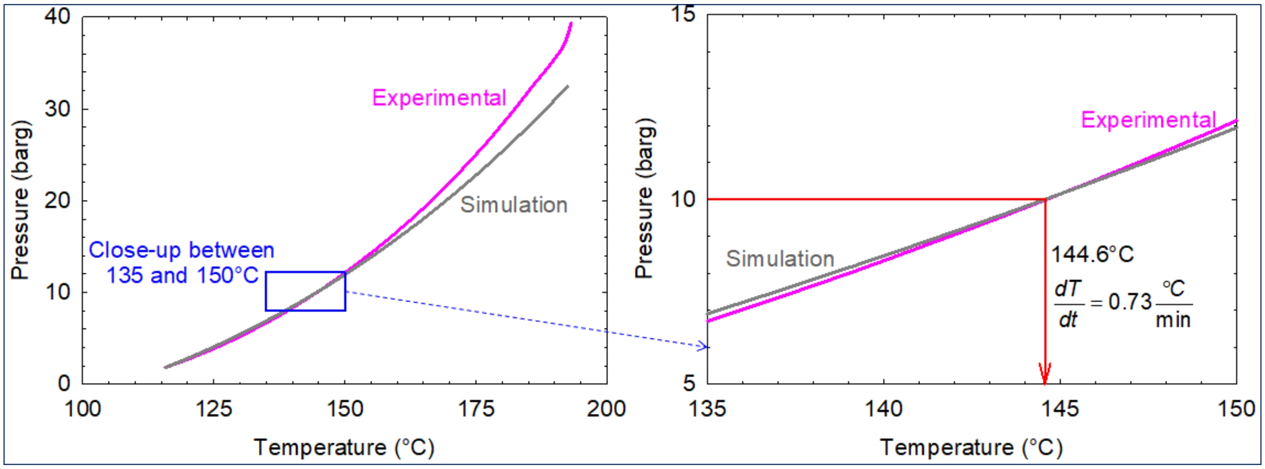
Figure 19: Pressure vs. temperature, modified toluene-methane BIP to -0.157091 for a scenario with hypothetical pressure relief at 10 barg



The experimental curves in both right-hand graphs show a self-heating rate of 0.73°C/min at 144.6°C for 10 barg. In Figure 18 without BIP adjustments, the corresponding simulated self-heating rate is 0.48°C at 137.9°C while in Figure 19 with toluene-methane BIP adjustment, the equivalent self-heating rate is 0.60°C/min at 142.2°C. The latter case exhibits a better match of simulation with experimental data.

The match of temperature and self-heating rate at 10 barg can be further improved by lowering the toluene-methane BIP to -0.248 as seen in Figure 20. There is a penalty to pay at higher pressures, but this might be acceptable for the given relief device set pressure.

Figure 20: Pressure vs. temperature, modified toluene-methane BIP to -0.248 for a scenario with hypothetical pressure relief at 10 barg



Graphs of self-rates versus temperature are important to discern model quality. They are presented in Figures 21 and 22, respectively without and with toluene-methane BIP correction. The match of self-heating rates between experimentation and simulation is excellent for both cases. For the self-pressurization rate, it can be visualized that the simulation curve is closer to experimentation at lower temperatures with toluene-methane BIP correction.

The model performance regarding pressure could be enhanced if some BIPs could be added as predictors to the design, but the RSM would become too complex. A better choice would be to perform an additional RSM with two or three BIPs as predictors and pressures at given temperatures as responses. However, Figures 19 to 22 demonstrate that the model performance is good without the additional BIP design.

Figure 21: Self-rates vs. temperature, original toluene-methane BIP of -0.057091

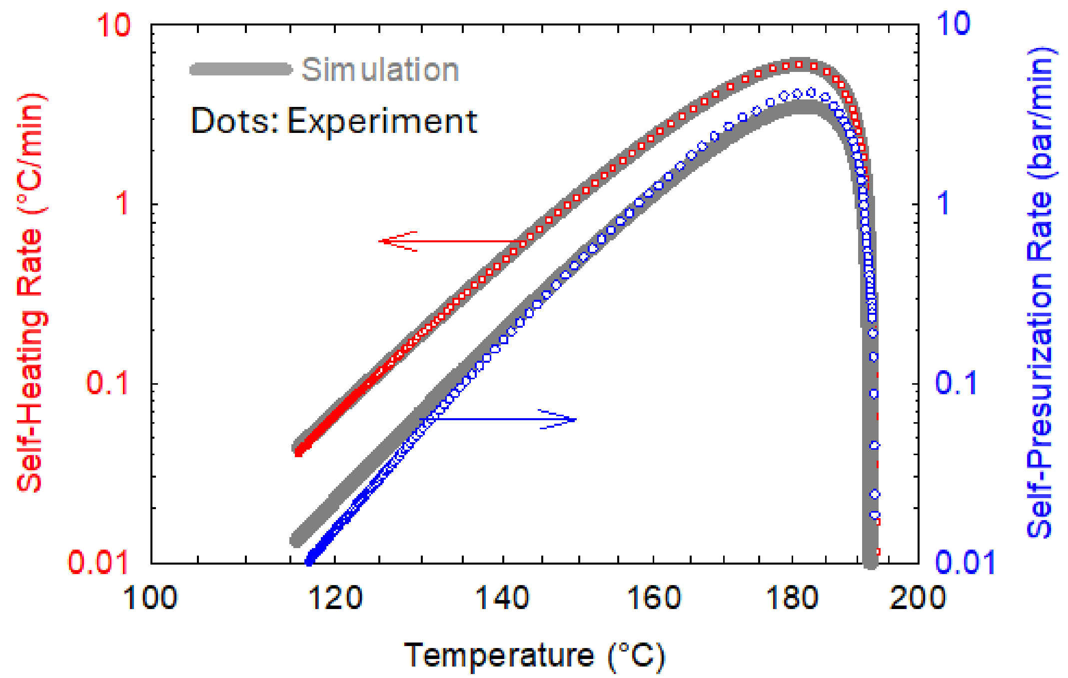
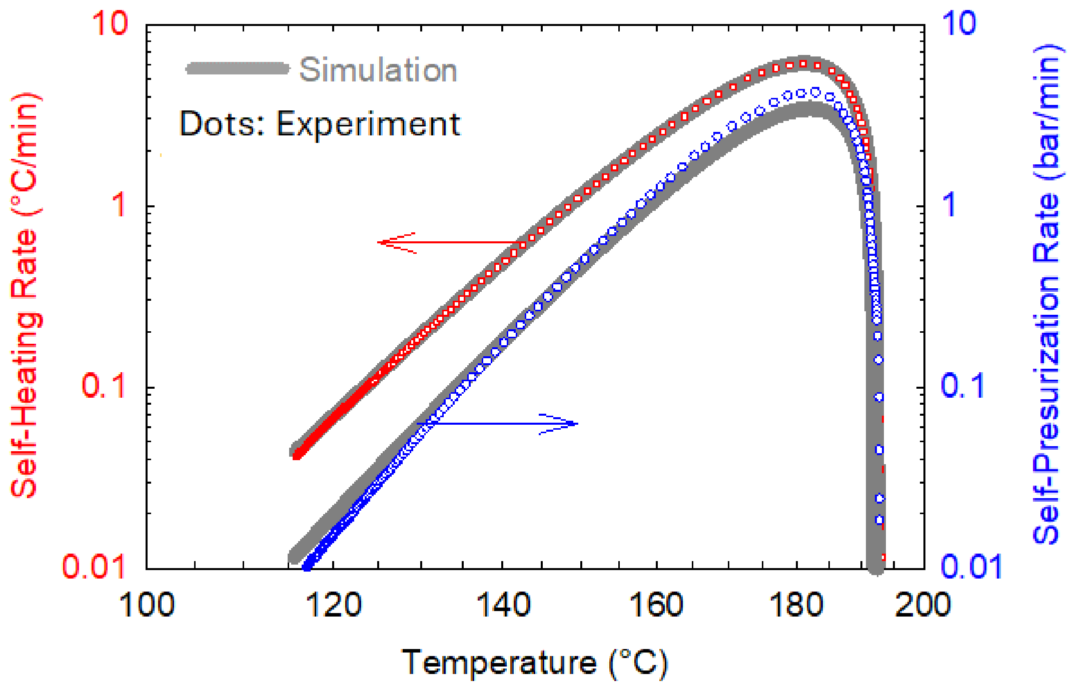


Figure 22: Self-rates vs. temperature, modified toluene-methane BIP to -0.157091



Conclusions

Two experimental designs were performed for the decomposition of di-tert-butyl peroxide in toluene:

Experimental Design 1: Kinetic modeling

Experimental Design 2: Stoichiometry modeling

Both experimental designs were based on advanced statistics for multiple predictors. The chosen method was Response Surface Methodology (RSM) with a Central Composite Design. The “experiments” of the two designs were SuperChems™ dynamic simulations based on a sealed adiabatic calorimeter. It is virtually impossible to optimize multiple predictors concurrently by trial and error. RSM is a systematic approach to simultaneously optimizing two or more predictors. This study had good agreement between experimentation and simulation with RSM-determined parameters.

After the two experimental designs, a manual adjustment was made to the binary interaction parameter (BIP) between toluene and methane. It improved the pressure-temperature agreement between experimentation and simulation in the region of practical interest, but the agreement deteriorated at very high pressures. Sometimes this compromise must be made to improve the modeling for practical operating conditions.

This white paper demonstrated the benefits of using RSM to develop kinetic and stoichiometric parameters. Any parameters can be used as predictors: activation energy, pre-exponential factor, order of each reactant, stoichiometric coefficients, BIPs, and many others. However, it is necessary to be sensitive to the fact that the number of experiments, that is, SuperChems™ runs in this case, grows substantially with the number of predictors. It becomes increasingly cumbersome to apply RSM for too many predictors. Sometimes it is possible to perform multiple experimental designs, whose combination is smaller than a single design with all predictors, as in the case of this white paper.

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Figure Sources

Figures 1-4, 6, 9, 11, 12, 15, 17-22: SigmaPlot® Scientific Graphing and Statistics Software

Figures 5, 13, 16: Process Safety Office® SuperChems™

Figures 7, 8, 10, 14: Minitab® Statistics Software

Nomenclature

a	Stoichiometric parameter
A	Acetone
B	Activation energy divided by the universal gas constant
b	Stoichiometric parameter
B	Tert-Butanol
c	Stoichiometric parameter
C_p	Concentration of di-tert-butyl peroxide
C_{po}	Initial concentration of di-tert-butyl peroxide
d	Stoichiometric parameter
D	Diphenyl Ethane
E	Ethane
k’	Kinetic rate constant adjusted for dynamic simulations
k	Kinetic rate constant, calorimetry
k_o	Pre-exponential factor (= k_o’ for a first-order reaction)
k_o’	Pre-exponential factor adjusted for dynamic simulations
M	Methane
n	Order of reaction, di-tert-butyl peroxide
P	Di-tert-butyl peroxide
R_1	Tert-butyl peroxide radical
R_2	Methane radical
R_3	Toluene radical
t	Time

T	Temperature
T_o	Onset temperature of a runaway reaction
T_f	Final temperature of a runaway reaction
X	Conversion of acetic anhydride
Z	Ethyl Benzene
ΔT_a	Adiabatic temperature rise, $T_f - T_o$
Θ	Toluene

Additional ioMosaic White Paper Resources

It is impossible to cover all aspects and facets of chemical reactivity management in one white paper. The resources provided below address in more detail several key topics and can be requested from sales@iomosaic.com or melhem@iomosaic.com:

Chemical Reactivity Management

1. Systematic Evaluation of Chemical Reaction Hazards
2. Quickly Develop Chemical Interaction Matrices with SuperChems
3. Thermal Stability Indicators
4. Calculate Phase and Chemical Equilibria Using Process Safety Office SuperChems Expert
5. An Advanced Method for the Estimation of Reaction Stoichiometry and Rates from ARC Data
6. Development of Kinetic Models - Part I. Thermal Stability
7. Development of Kinetic Models - Part II. Pressure Relief Systems
8. Forget direct scaleup vent sizing and master kinetic modeling instead
9. Polymerization Modeling for Emergency Relief Systems
10. Polymerization Reactions Inhibitor Modeling - Styrene and Butyl Acrylate Incidents Case Studies
11. Polymerization Models for butadiene, vinyl acetate, acrylates, acrylonitrile, and isoprene

Fire Modeling

2. Fire Exposure Modeling Considerations
3. RAGAGEP Considerations for Overtemperature Protection in Relief Systems

Pressure Relief and Vent Containment Design

1. Two-phase Flow Onset and Disengagement Methods
2. Vent Containment Design For Emergency Relief Systems
3. Forget the Omega Method and Master vdP Integration Instead
4. Advanced Pressure Relief Design Using Computer Simulation
5. Beware of Temperature Increase During Rapid Vessel Charging
6. Heat of vaporization considerations for relief systems applications
7. Properly Calculate Relief Systems Reaction Forces

8. Realize Better Risk Characterization of STHE Tube Failure Scenarios Through Relief Systems Dynamics Modeling
9. Relief and Flare Systems Statics vs Dynamics
10. Relief Requirements for Distillation Columns
11. Retrograde and Phase Change (RPC) Flow Considerations for Relief and Depressuring Systems
12. Retrograde and Phase Change (RPC) Flow Considerations for Relief and Flare Systems
13. Single and Multiphase Control Valve Flow
14. The Anatomy of Liquid Displacement and High-Pressure Fluid Breakthrough
15. Thermal Expansion Relief Requirements for Liquids, Vapors, and Supercritical Fluids
16. Quantify Non-Equilibrium Flow and Rapid Phase Transitions

PRV Stability

1. Analysis of PRV Stability In Relief Systems - Detailed Dynamics - Part I
2. Analysis of PRV Stability In Relief Systems - Screening - Part II
3. Analysis of PRV Stability In Relief Systems - How to Avoid the Singing PRV Problem - Part III
4. Analysis of PRV Stability In Relief Systems - On the Estimation of Speed of Sound - Part IV
5. Analysis of PRV Stability In Relief Systems - Get a Handle on PRV Stability - Part V
6. PRV stability inlet line critical length
7. PRV Stability - Bridging the 3 percent pressure loss rule gap

Fire and Explosion Modeling

1. Calculate Flammability Limits Using Process Safety Office ®SuperChems Expert
2. How Flame Arresters Work
3. Development of Reduced Analytical Models for Explosion Dynamics
4. Quantify Explosion Venting Dynamics in Vessels Enclosures and Energy Storage Systems

Process Safety Management and Automation

1. Effectively Manage Mechanical Integrity in Process Safety Enterprise®
2. Effectively Manage Changes to Processes, Chemicals, Equipment, and Personnel Using Process Safety Enterprise®
3. Properly Evaluate Building and Facility Siting Risks
4. Emergency Response and Process Hazard Analysis Charts
5. Usage of AEGL Dosage in Safety and Risk Studies
6. Driving Safety and Business Performance Through Data Mining

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[3] J. Murawski, J. S. Roberts, and M. Szwarc. Kinetics of the Thermal Decomposition of Di-t-Butyl Peroxide, J. Chem. Phys. 19, 698 (1951).

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