Practical Use of ARC Analysis for Thermal Stability Evaluation in Corteva

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12/6/2021, PURDUE P2SAC TUTORIALS

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  M.S. and B.S., ChE, Tianjin Univ., China
  Ph.D., ChE, Auburn Univ., Auburn, AL
- **Work Experience**
  2/2012 to 8/2017, Dow, Reactive Chemicals (RC) Subject Matter Expert
  9/2017 to present, Corteva (DowDuPont Ag division), RC Technical Leader
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  Expertise Including Calorimetry, kinetic modeling, high energy materials and flammability

  Licensed Professional Engineer in Michigan State
  ASTM E27 (Hazard Potential of Chemicals) committee member
  ACS Chemical Health and Safety Journal, Editorial Advisory Board member
  Purdue P2SAC Scientific Advisory Board member
  DiERS member

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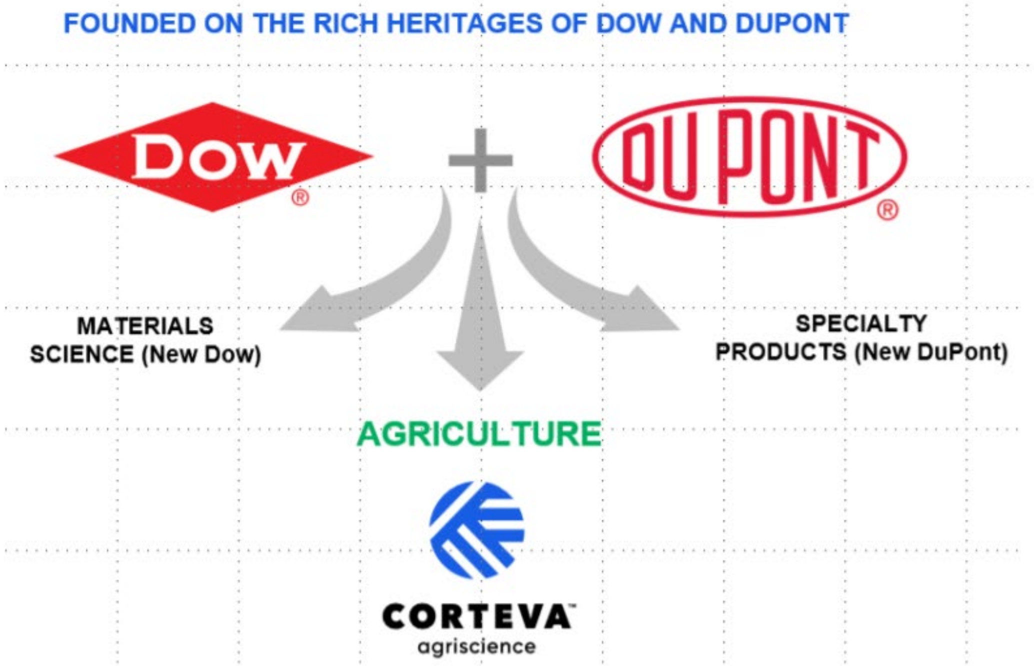

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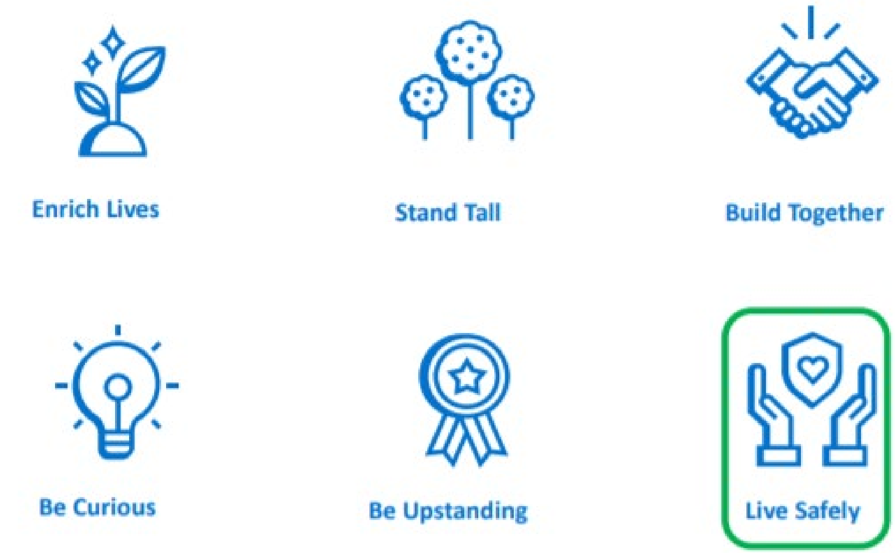
Our Purpose

To enrich the lives of those who produce and those who consume, ensuring progress for generations to come.



Agenda

- 1, General applications of ARC in Corteva Reactive Chemicals (RC)
- 2, Adiabatic limit
- 3, Pressure tubing and condensation
- 4, Sample loading size
- 5, Bomb rupture
- 6, Bomb compatibility
- 7, Low onset exotherm

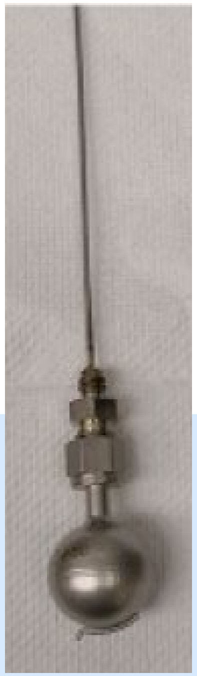
1, General Application of ARC in Corteva RC

- Default ARC testing parameter in Corteva Reactive Chemical (RC) group

Container Material:	Hastalloy-C (bottom clip)
Container Weight (Mb):	~20.8 g
Sample Weight (Ms):	4 g
Total System Volume (Vb):	9.66 ml
Head Space Atmosphere:	N2
Container Specific Heat (Cb):	0.42 J/g/ °C
Starting Temperature:	25 °C
End Temperature:	350.0 °C
Heat Step:	5 °C
Wait Time:	20 min
Calorimetric Rate Threshold:	0.02 °C/min
Stirring Rate:	No

THT esARC

NETZSCH 254



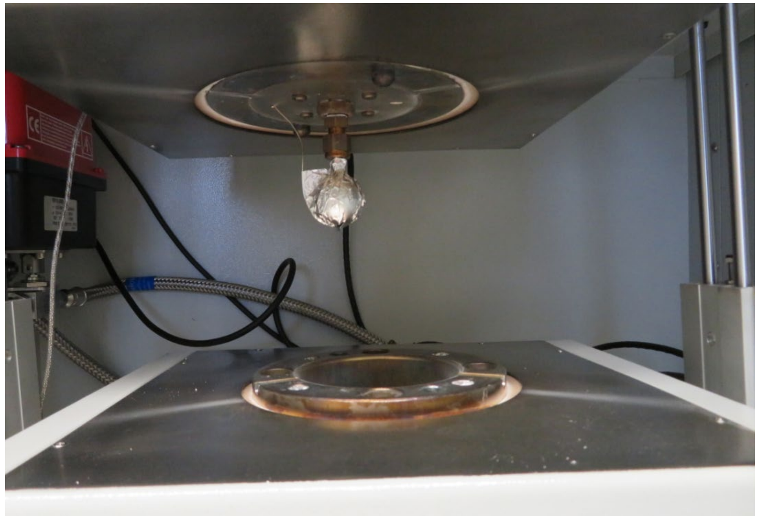
1/16" pressure through tube;

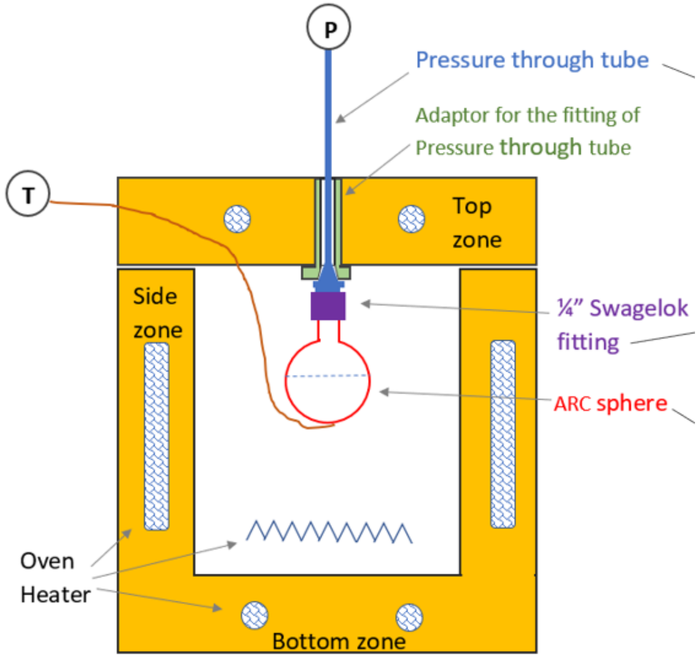
HC ARC bomb, 1" ID with ¼" OD x 1" stems, bottom clip

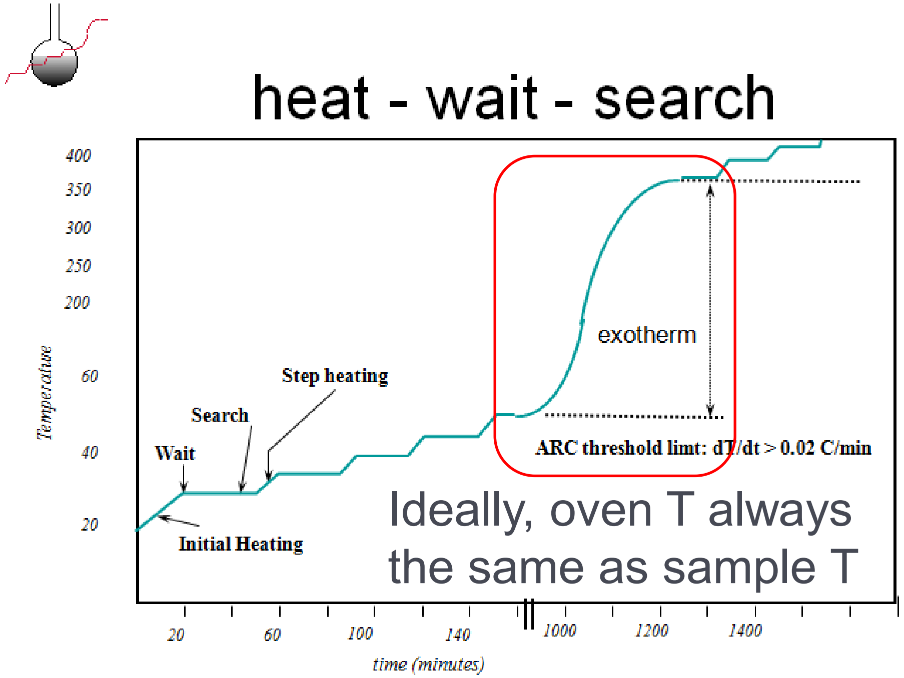
1000 psi N2 for leaking test prior to each run

1, General Application of ARC in Corteva RC

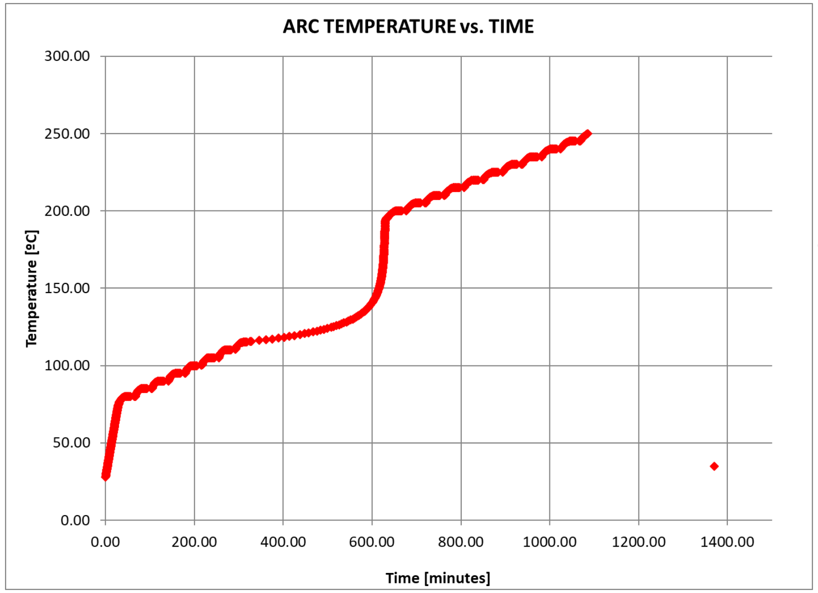
- ARC: Detect an exotherm (>0.02℃/min) and then maintain an adiabatic condition to track it.

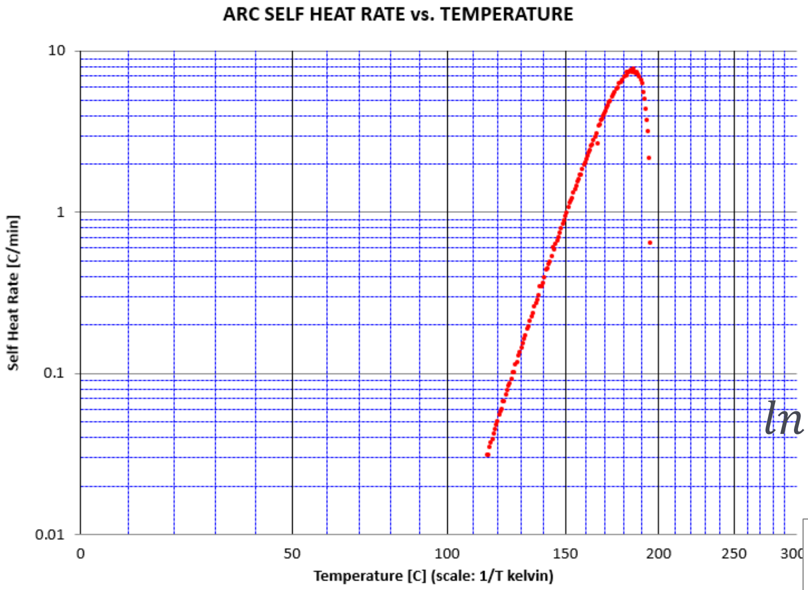






1, General Application of ARC in Corteva RC

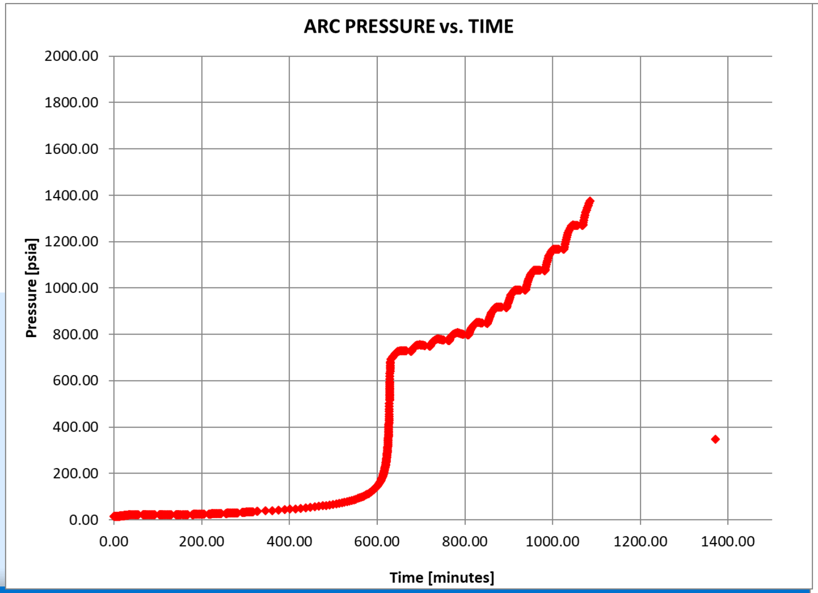


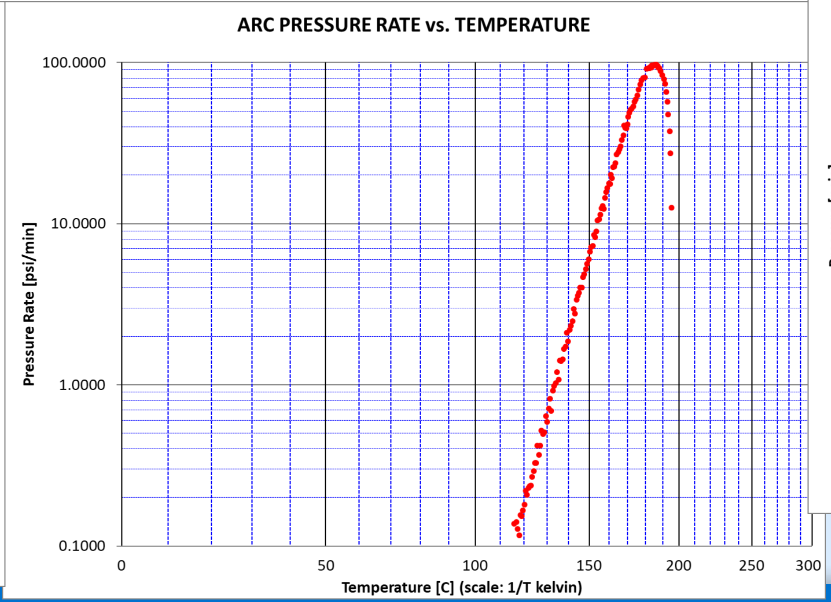


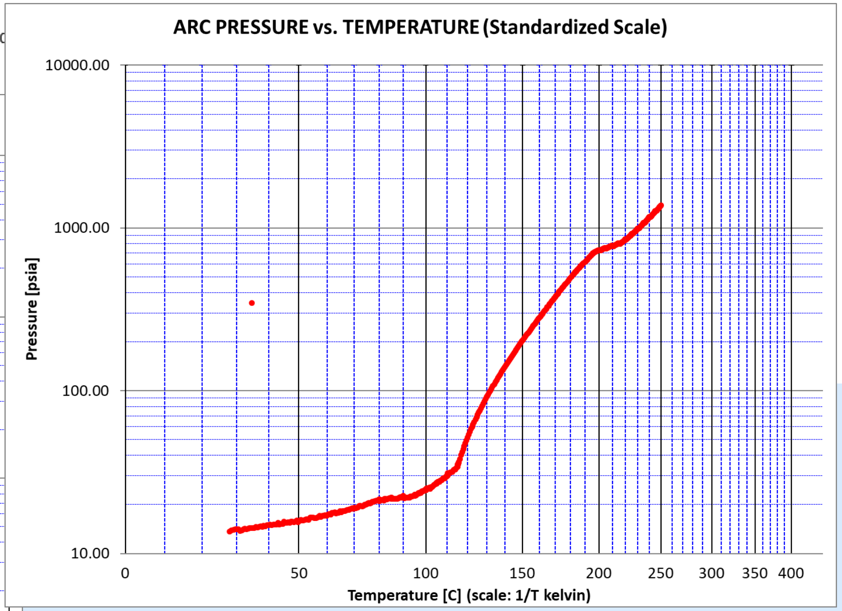
Plots for SHR/PR vs. 1/T are highly recommended

$$\frac{dT}{dt} = Ae^{-\frac{E}{RT}} \cdot \left(\frac{T_f - T}{\Delta T_{AB}}\right)^n \Delta T_{AB} \rho_0^{n-1}$$

$$ln\left(\frac{dT}{dt}\right) = \ln\left[A \cdot \left(\frac{T_f - T}{\Delta T_{AB}}\right)^n \Delta T_{AB} \rho_0^{n-1}\right] - \frac{E}{R} \cdot \frac{1}{T}$$







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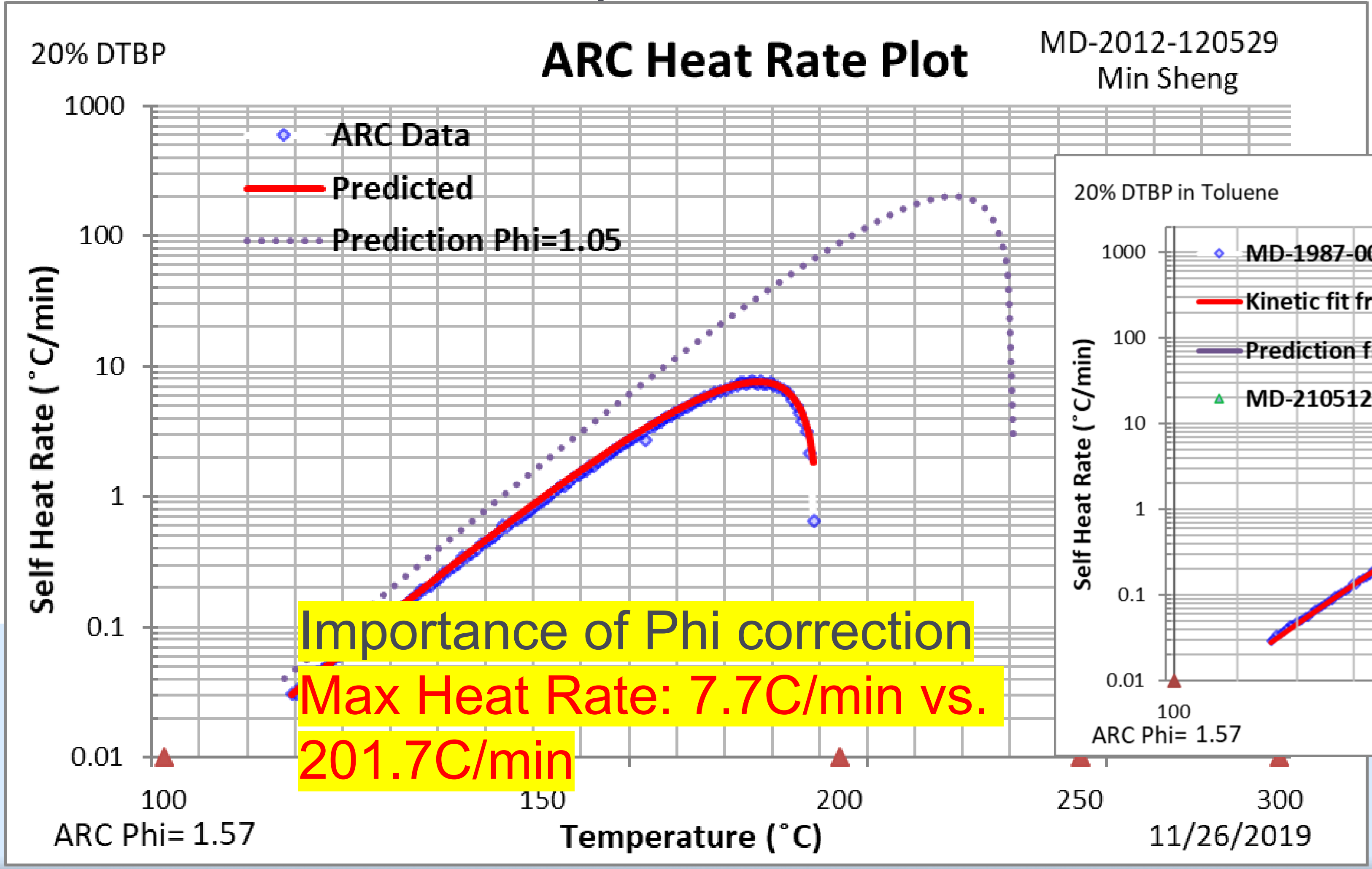
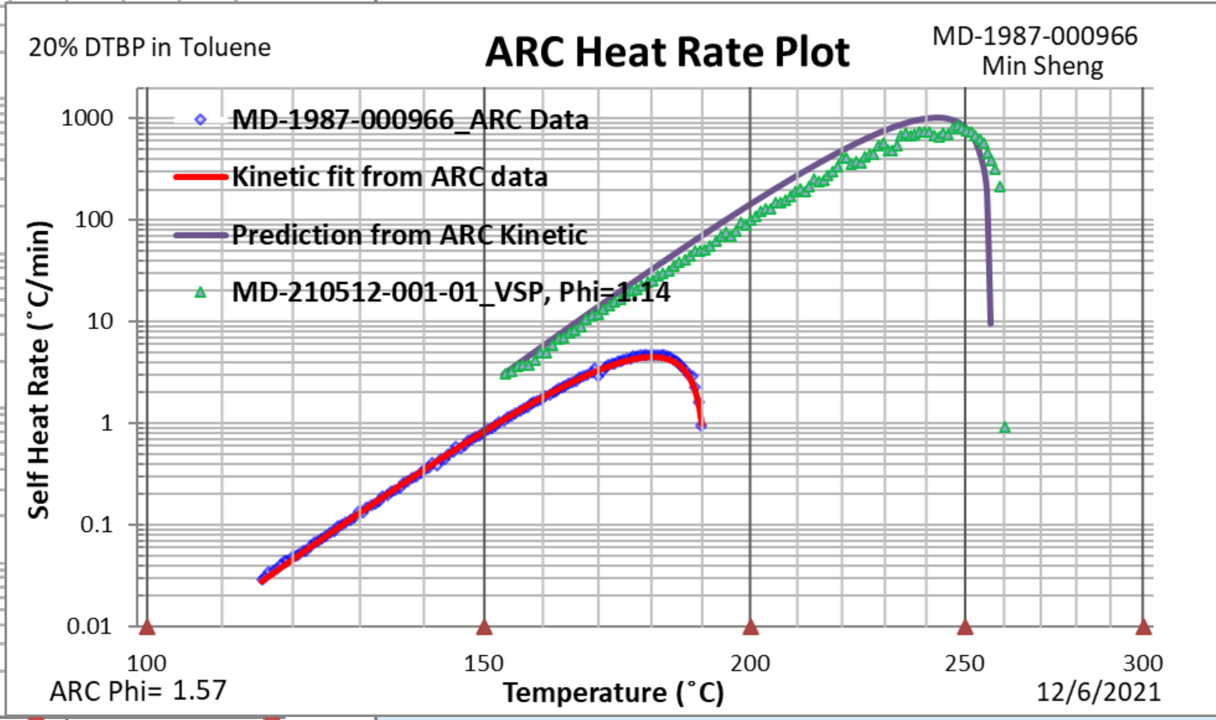
1, General Application of ARC in Corteva RC

- Phi correction is important



For adiabatic test, onset T could change max heat rate



1, General Application of ARC in Corteva RC

- Application 1: Hazard Scenario Identification and Validation (e.g., RAST/LOPA)

ARC data for reactivity evaluation

RAST outcome: TMR, TNR, uncontrolled reaction scenarios

Version 5.3.2

Equipment Loaded: R-201/B-201

< Equipment Table | Export to FSAW | Export to SRS | LOPA Worksheet > | Sort | Re | Create User Scenario | Modify User Scenario | Duplicate Scenario | Quality Check | Risk Summary >

Defines

LOPA W

SCENARIO NO	Cross Ref	Equipment Tag	Scenario Type	Initiating Event General Description	Incident Type	Outcome	Offset Factor	Layers of Protection Required	Gap in Layers of Protection
4544.01		R-201/B-201	Uncontrolled Reaction - Adiabatic	BPCS Instrument Loop Fa	Equipment Rupture at Saturatio	Chemical Exposure	2	3	3
4547.01		R-201/B-201	Uncontrolled Reaction - Adiabatic	BPCS Instrument Loop Fa	Equipment Rupture at Saturatio	Equipment Explosion	2	2	2
4545.01		R-201/B-201	Uncontrolled Reaction - Adiabatic	BPCS Instrument Loop Fa	Equipment Rupture at Saturatio	Flash Fire or Fireball	2	3	3
4541.01		R-201/B-201	Uncontrolled Reaction - Adiabatic	BPCS Instrument Loop Fa	Equipment Rupture at Saturatio	Off-Site Toxic Releas	2	4	4
4542.01		R-201/B-201	Uncontrolled Reaction - Adiabatic	BPCS Instrument Loop Fa	Equipment Rupture at Saturatio	On-Site Toxic Releas	2	3	3
4543.01		R-201/B-201	Uncontrolled Reaction - Adiabatic	BPCS Instrument Loop Fa	Equipment Rupture at Saturatio	Toxic Infiltration	2	4	4
4546.01		R-201/B-201	Uncontrolled Reaction - Adiabatic	General Utility Failure	Equipment Rupture at Saturatio	Vapor Cloud Explosi	2	5	0

< Go To Equipment Input

Equipment Tag = R-201/B-201
Key Chemical = AAAA
Physical State = Liquid

Reactivity Data Input		
Assess Reactive Scenarios Only?	No	
	Table / User	User Value
Data Reference:		
ARC TX-2005-000426-01	ARC TX-2005-000426-01	
Heat of Reaction, ΔHR (cal/g mix) =	-200	-200
Activation Energy, ΔE (Kcal/g mole) =	35	35
Detected Onset, T_0 (C) =	218.99	218.99
Detected Rate, R_0 (C/min) =	0.0216	2.16E-02
Gas Generation, k (g mole/cc mix) =	0.0009	9.00E-04
Gas Generation precedes Exotherm?	No	No
Inhibited Monomer?	No	No
Thermal Inertia (ARC or other), ϕ =	1.66	1.66
Test Method =	ARC	ARC
Limiting Reaction Rate =		cal/g mix-min
Intended reaction for this Equipment?	Yes	
Potential Catalyzed Reaction?	No	
~~Potential for "Pooling" of Reactants?~~	No	
~~Reactants in Separate Liquid Phase?~~	Yes	
~~Fraction of Reaction Heat for "Pooling"~~		Typically < 1.0
Potential Mis-Loading of Reactants?	No	
Multiple of Reaction Heat for Mis-Loading		Typically > 1.0
Potential for Mixing Incompatible Materials?	No	
Intended Exothermic Reaction (for F&EI)		
Intended Endothermic Reaction (for F&EI)		
Considered Condensed Phase Detonable?	No	

Potential for Insulation or Packing Fire			
Hofelich Index =	232	Potential =	LOW

Estimation of Frank-Kamenetskii Critical Diameter (Slab)		
Material Thermal Conductivity		watt / m C
F-K Critical Diameter at 165 deg C		cm

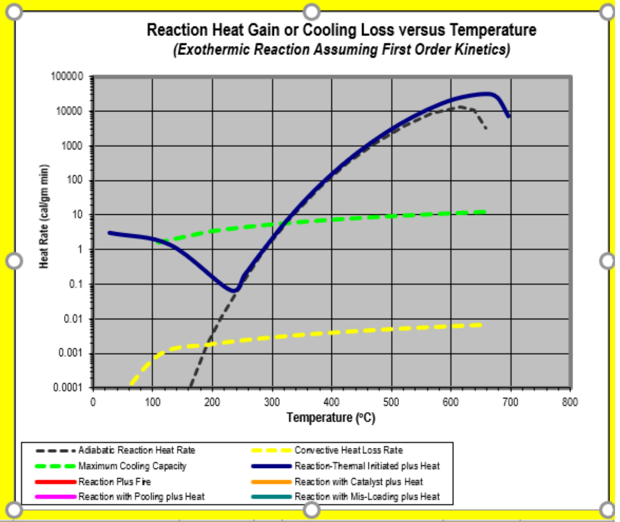
Estimation of Activation Energy from ARC Data		
Temperature, C		
Observed Rate, C/min		
Fraction Conversion		
Activation Energy =		Kcal/gm mole

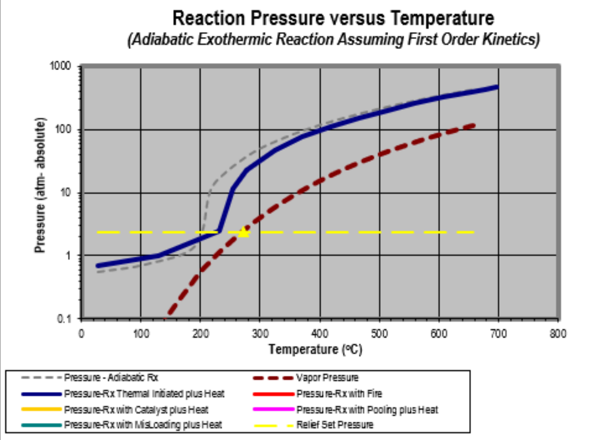
Estimation of Gas Generation		
Observed Press (atm abs) and Temp (C)		
Estimated Vapor Pressure + Inert Pad	0.92	atm
Estimated Gas Generation, k =		gm mole/cc mix

Time to Maximum Rate at Specified Starting Temperatures

Reaction Scenario Type = Reaction

Temperature (C)	TMR	Time to Relief at 272.8 deg C	
25	1292767812.3	1292767812.3	Days
50	15652885.7	15652885.7	Days
100	13958.2	13958.2	Days
165	17.4	17.4	Days





Reaction Screening Calculations					
Initial Temperature =	191.2	C	Rate at Initial Temp =	0.0018	cal/gm-min
Max Adiabatic Temp =	658.0	C	Reactivity Parameter =	12.7	
Max Adiabatic Pressure =	422.57	atm	Insulated?	Yes	
Temp of No Return, TNR =	191.2	C	Convective HT Coefficient =	0.0005	Kwatt/sq m C
TNR with Cooling =	316.8426884	C			

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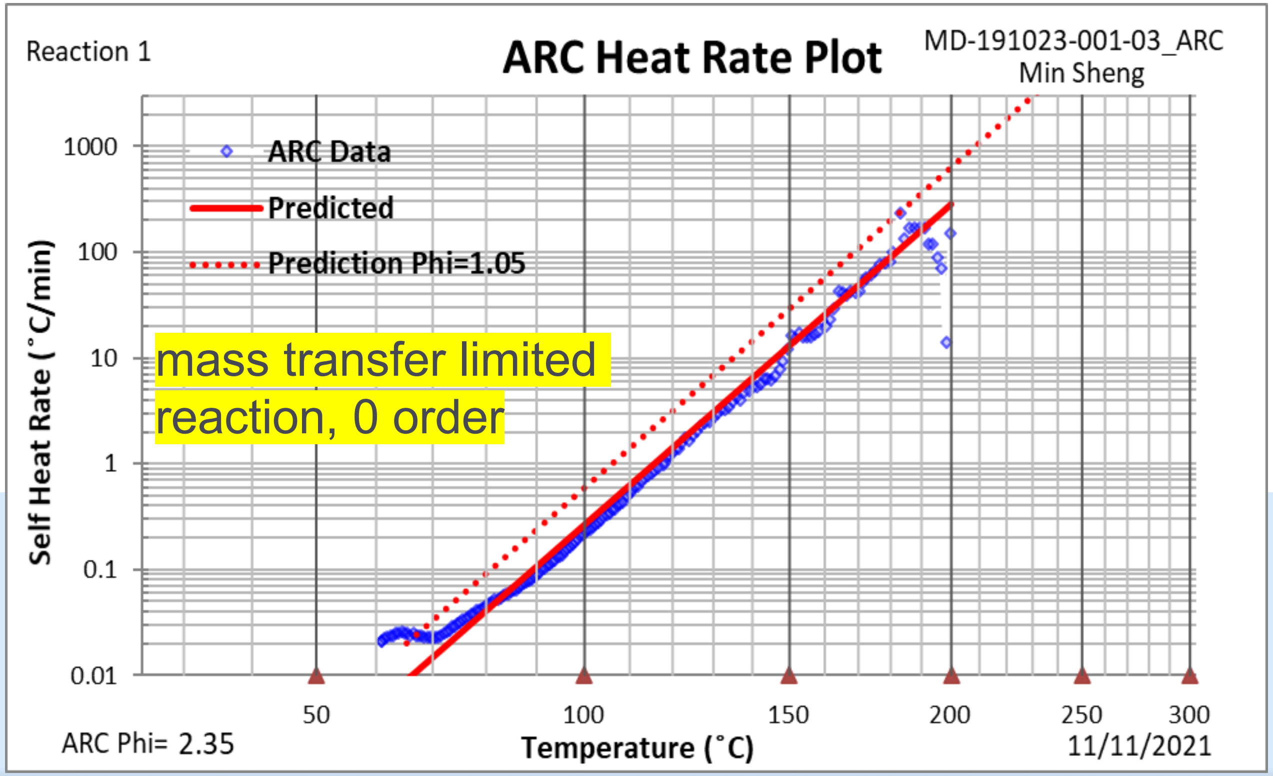
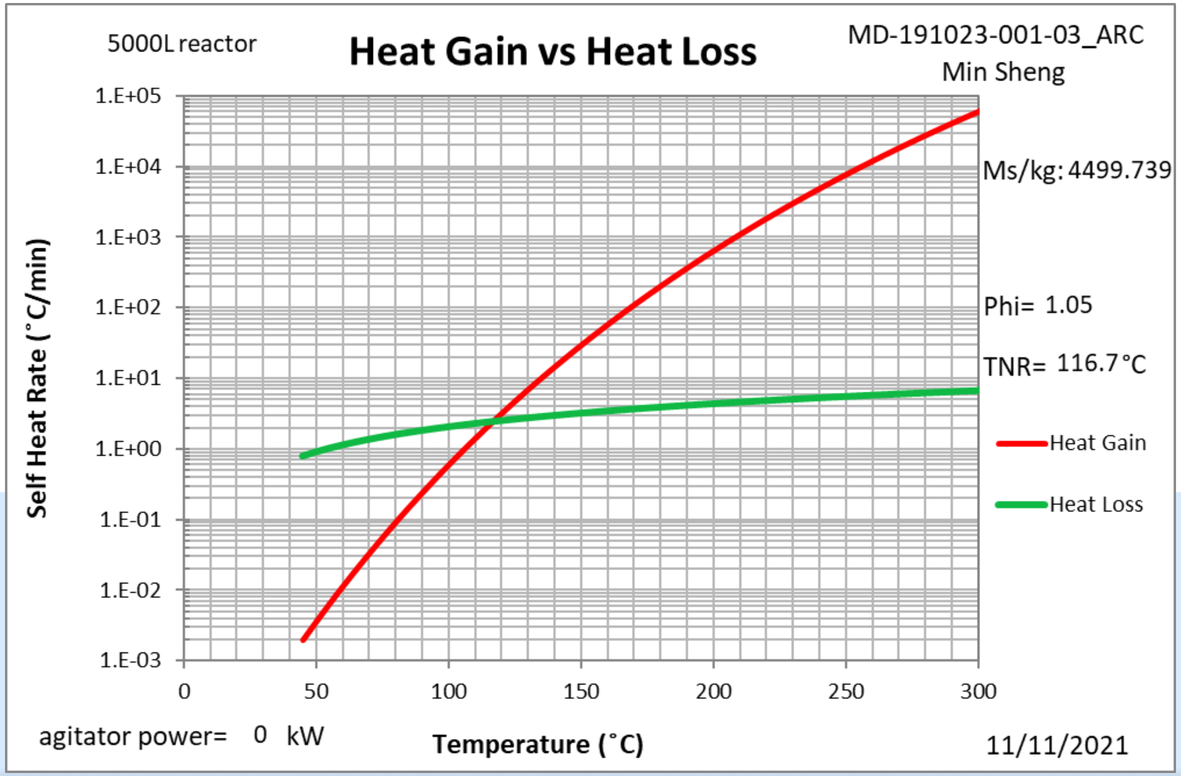
1, General Application of ARC in Corteva RC

- Application 2: Temperature of No Return (TNR) estimation

Kinetics from ARC, then build heat gain curve. Compare heat gain and heat loss to determine the TNR of a vessel.





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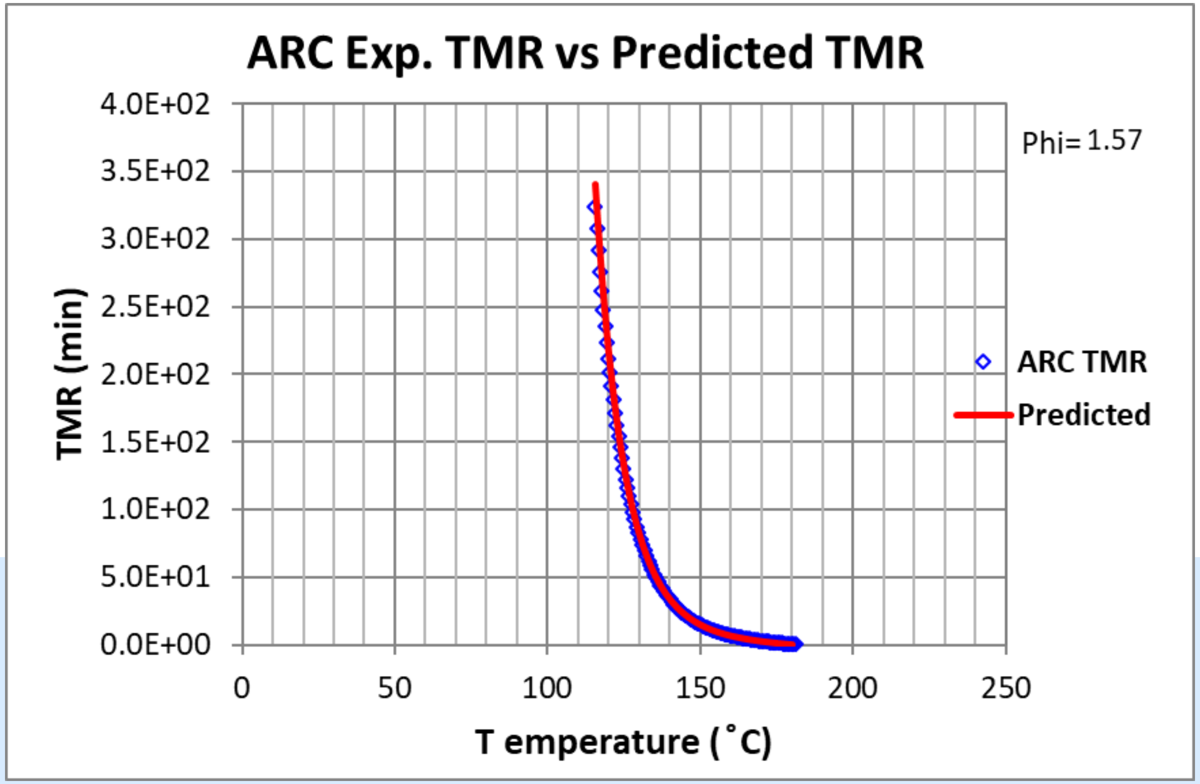
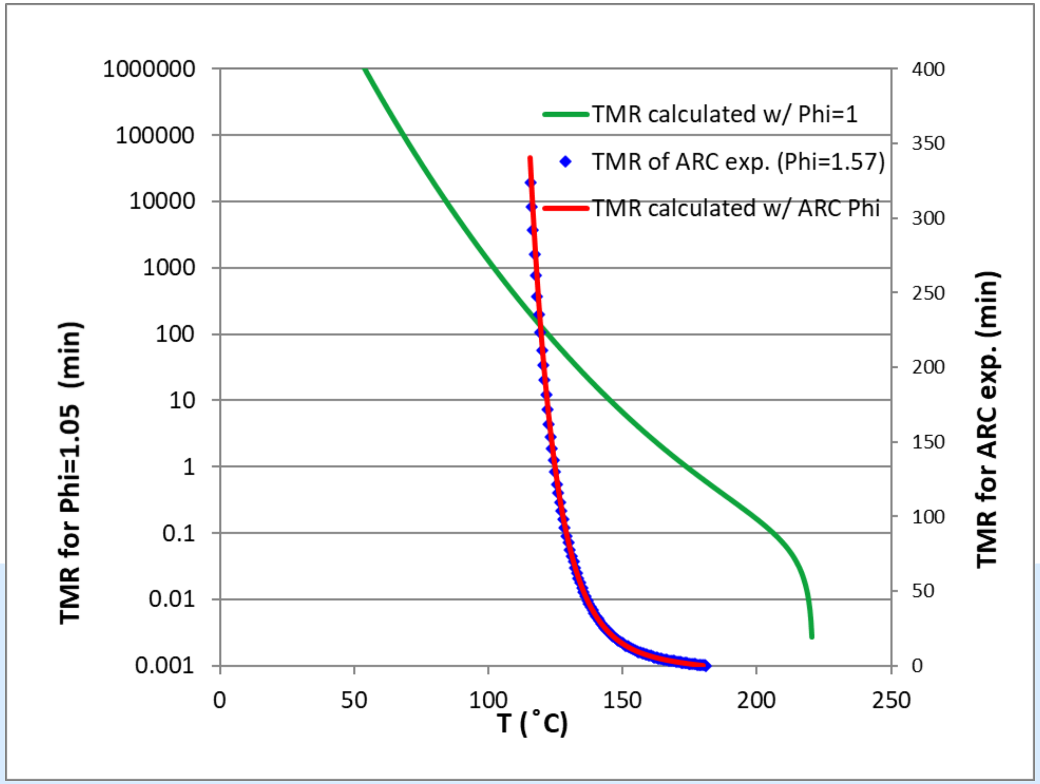
- Application 3: adiabatic Time to Max Rate (TMR) estimation (including Td24, Td8)

$$TMR = \int_{T}^{Tm} \frac{dT}{Ae^{-\frac{E}{RT}} \cdot \left(\frac{T_f - T}{\Delta T_{AB}}\right)^n \Delta T_{AB} C_0^n}$$

Numerical Method for ODE

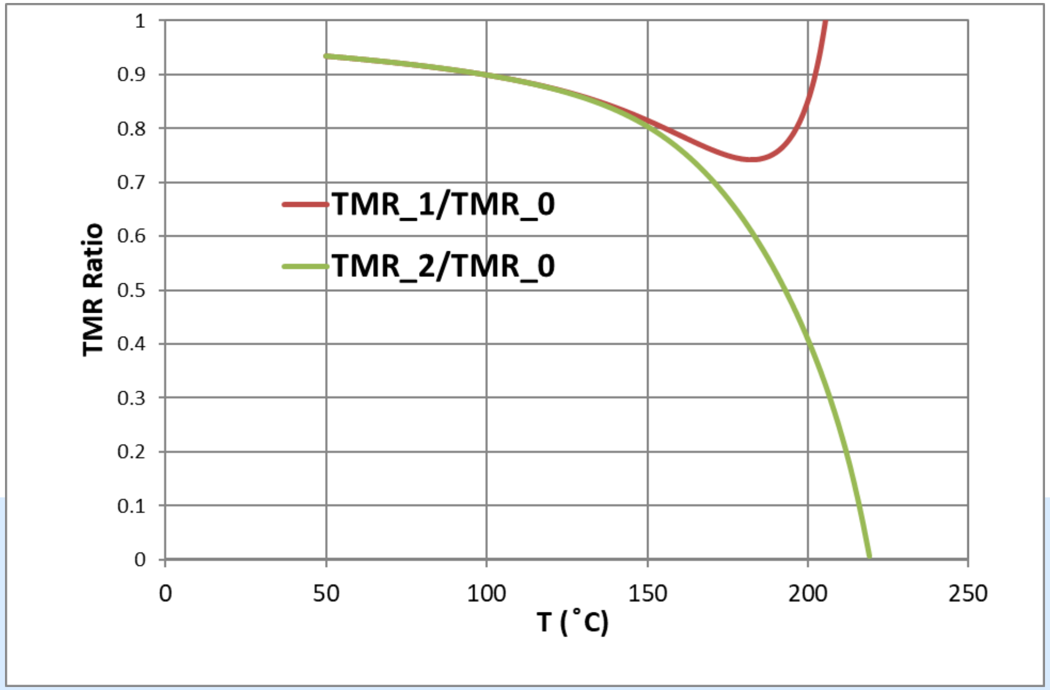


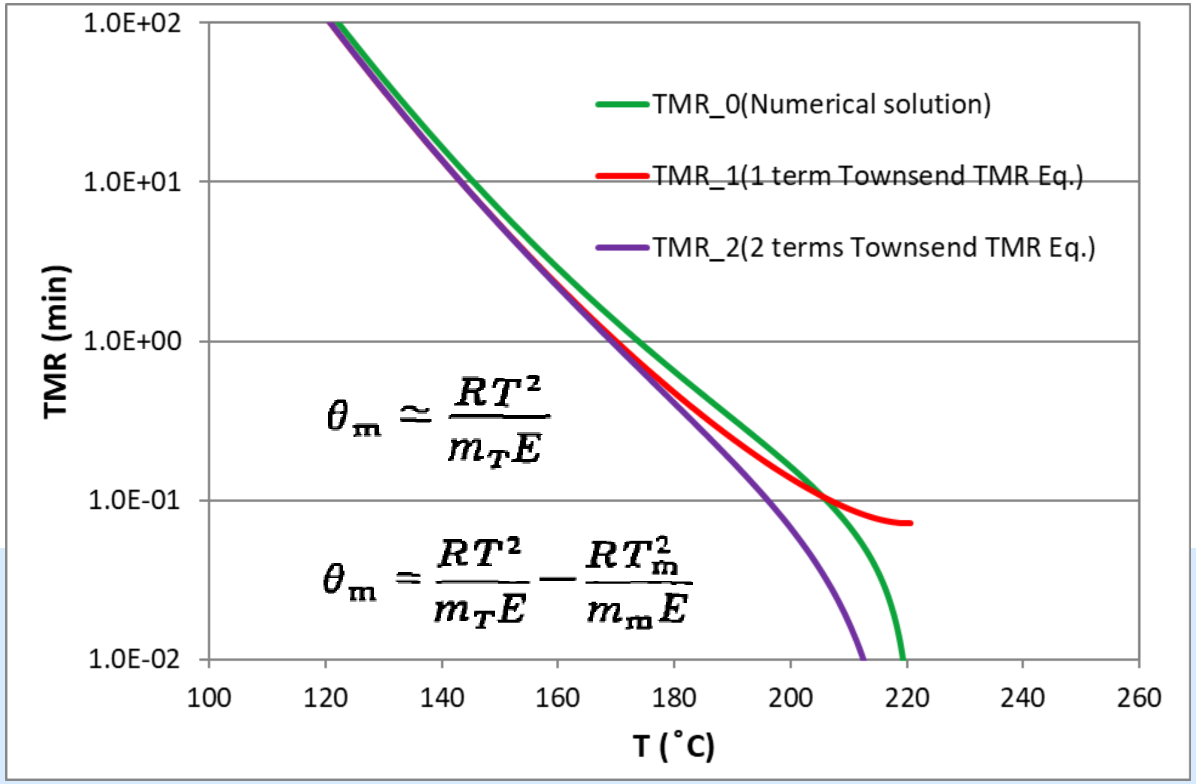


Townsend, D.I., Tou, J.C., Thermochimica Acta, 1980, 37, 1-30

1, General Application of ARC in Corteva RC

- Adiabatic Time to Max Rate (TMR) estimation (including Td24, Td8): Numerical solution vs. Townsend equations





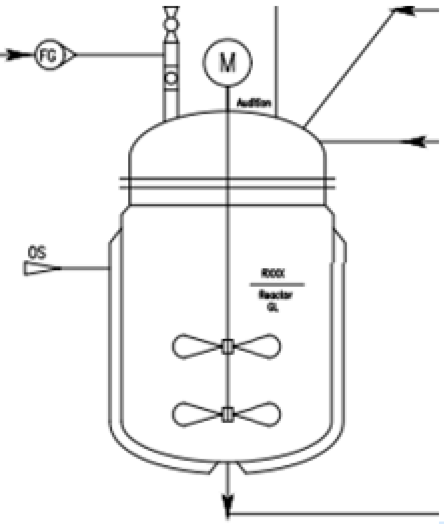
Townsend, D.I., Tou, J.C., Thermochimica Acta, 1980, 37, 1-30

1, General Application of ARC in Corteva RC

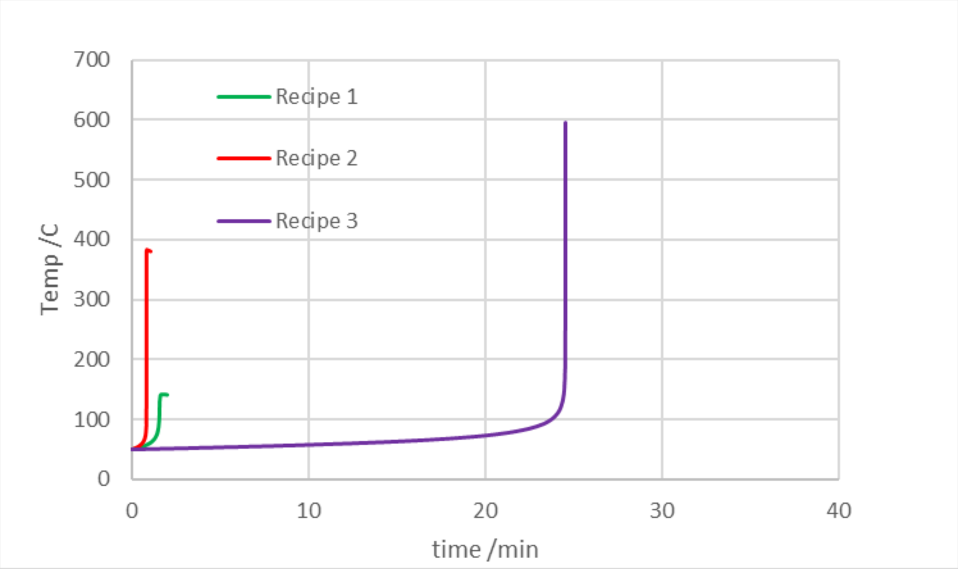
- Application 4: normal process simulation

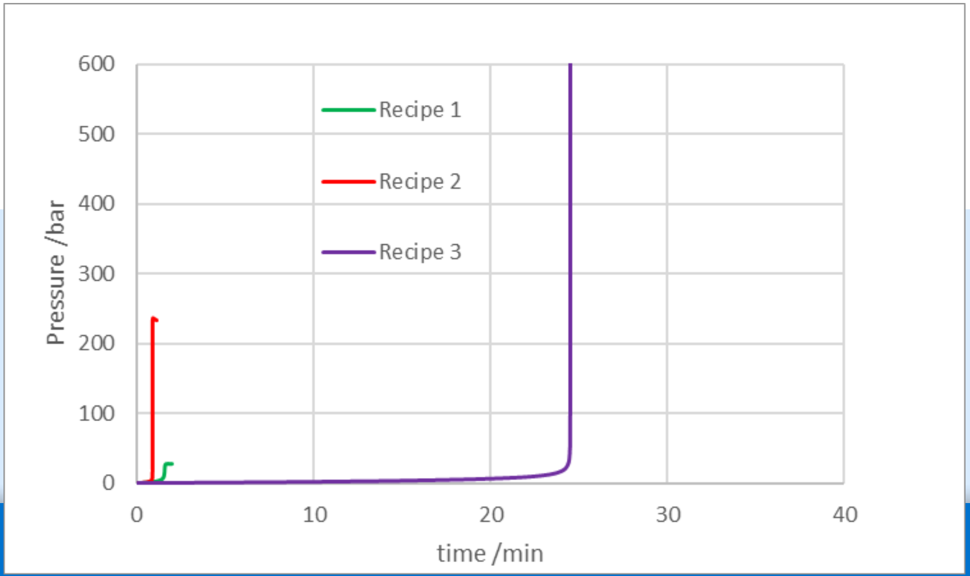
Reaction planned to run at 50C

evaluation based on following values for a pilot reactor (500L): cooling jacket 1.58 m^2 (Ø0.9m by 0.7m, 80% wet area); jacket fluid stays at 50C; overall heat transfer coefficient U=200 W/m^2-K, close system.



Data	TMR (min)	T_max (C)	P_max (bar)	Note
Recipe 1	1.74	141.2	22.6	Reactor MAWP ~10 bar
Recipe 2	0.88	384	236	
Recipe 3	24.5	637	802	



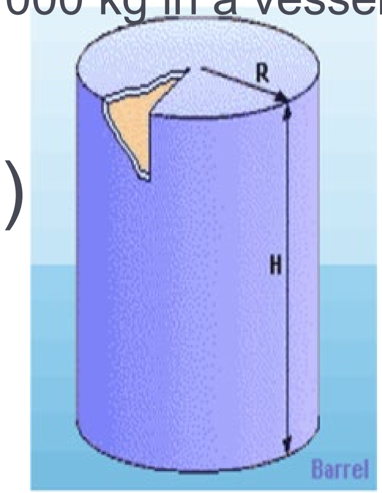


1, General Application of ARC in Corteva RC

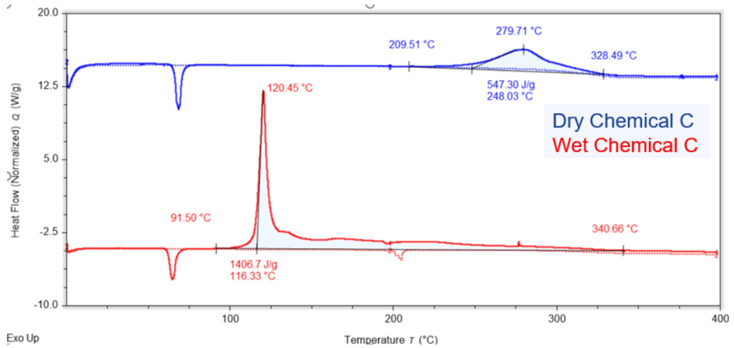
- Application 5: abnormal process simulation (e.g., SADT)

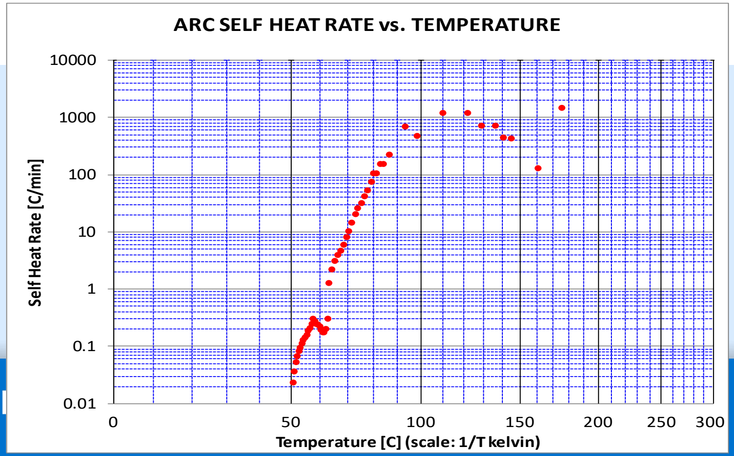
1000kg chemical C solid in a vessel, Water leaked in. At ambient condition, the reaction starts and ends as an explosion in about 12 hr.

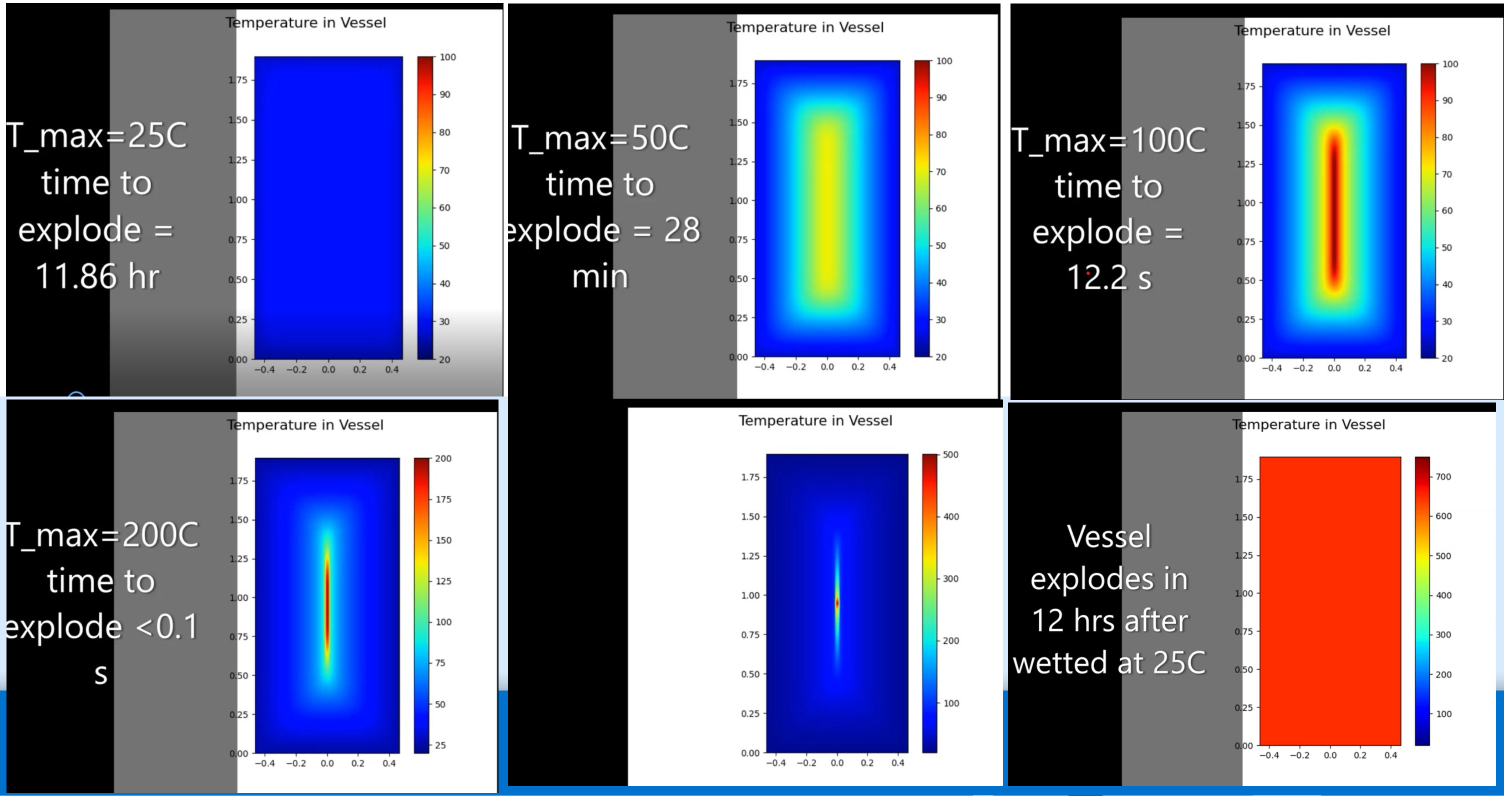
1000 kg in a vessel



D 0.93m L 1.86m







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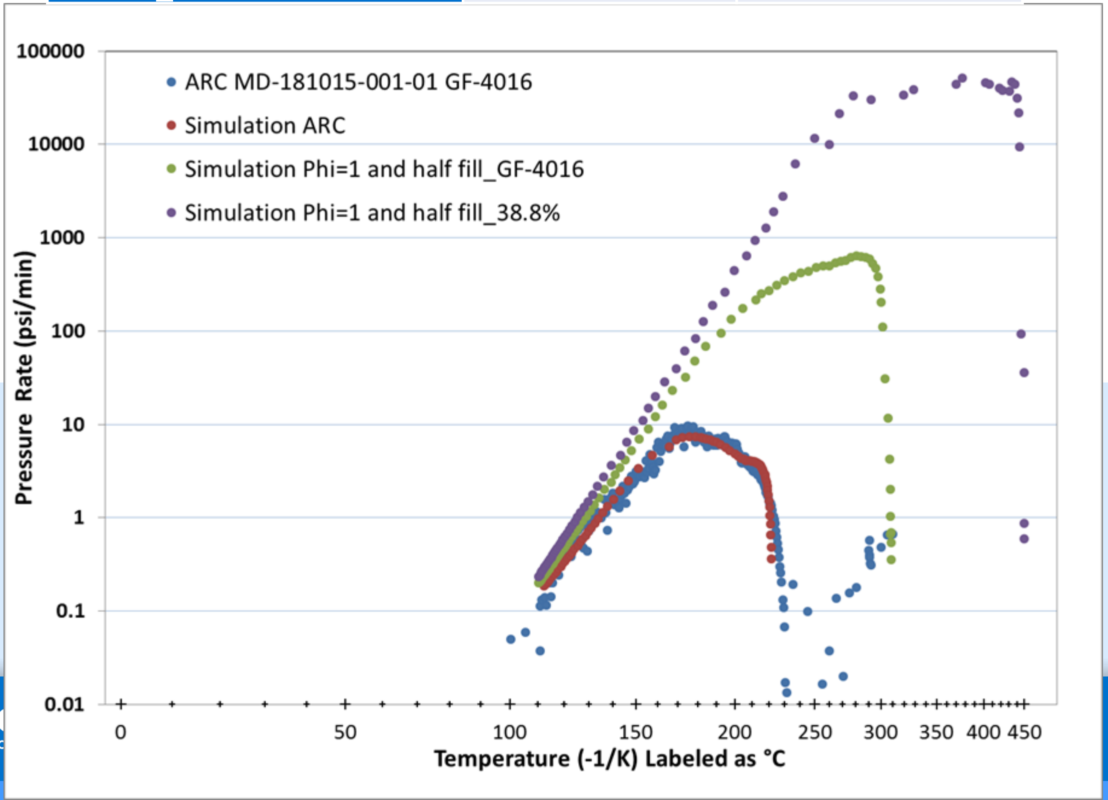
1, General Application of ARC in Corteva RC

- Application 6: reactive pressure relief sizing

Heat rate and pressure rate from ARC data, then apply various DiERS methods for vent sizing

	HR_max (C/min)	PR_max (psi/min)
TSS Simulation Phi=1 and half fill_GF-4016	44.3	637.6
TSS Simulation Phi=1 and half fill_38.8%	853	60428



Gassy system, Homogeneous venting model

		Data from the VSP Report		
8	Vc'	VSP containment vessel volume (3.95 L)	L	0.0052
9	Vn	VSP can volume (131 ml)	L	0.0052
10		VSP test type (specify open or closed)	- -	closed
11	Mm	Sample mass	g	4.495
			lb	0.010
12	Tm	Temperature at maximum pressure rise rate	°C	370
			°K	643
13	dP/dt	Maximum pressure rise rate	psi/min	60428
			psi/sec	1007.13
14	Tc	Containment temperature (open test only)	°K	- -
15	Dfo	Liquid density at set pressure	lb/ft3	62.4
16	Mo	Mass of liquid in vessel	lb	42000
17	Vc	VSP headspace volume	L	0.005

		Ideal Vent Area / Diameter		
32	Ai	Ideal area	ft2	14.5242
33	Di	Ideal diameter	in	51.60

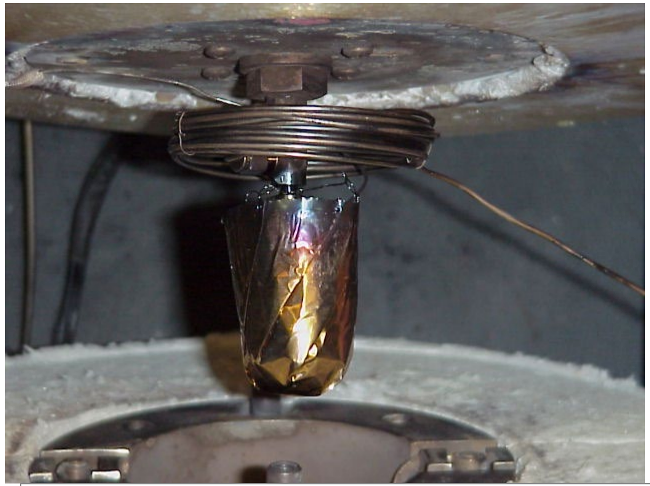
		Relief System		
34	Ft	Relief device factor	- -	0.9
35	Das	Assumed relief diameter	in	5.75
36	L	Relief system piping length	ft	100
37	L/D'	Relief system fittings equivalent length	- -	148.67
38	L/D	Total equivalent L/D	- -	357
39	N	Line losses - 4fL/D	- -	7.6
40	LF	Line factor (From figure VI-A9)	- -	0.5

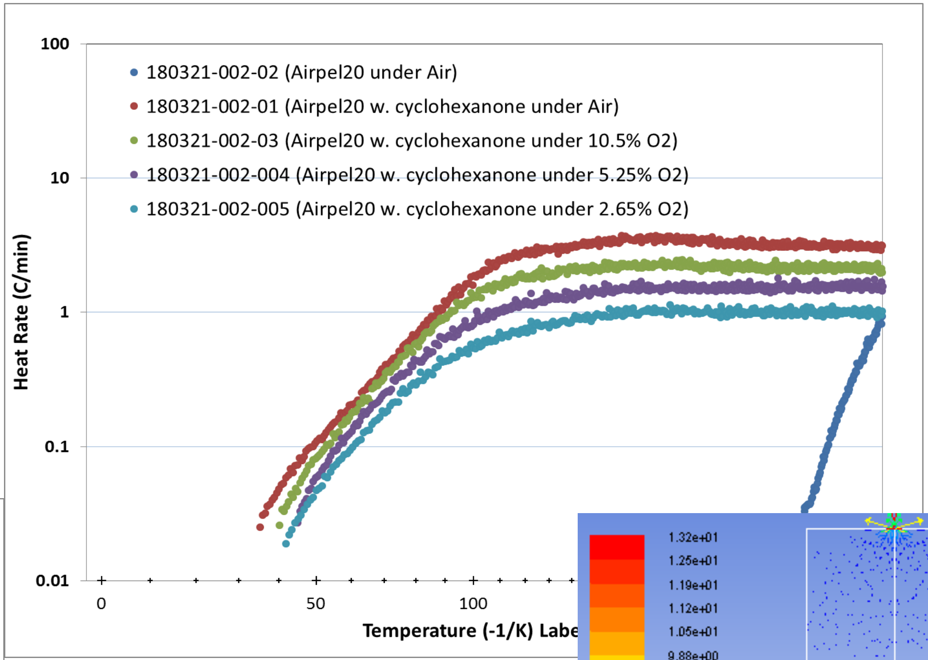
		Actual Vent Area / Diameter		
41	Aa	Actual area	ft2	32.2759
42	Da	Actual diameter	in	76.93

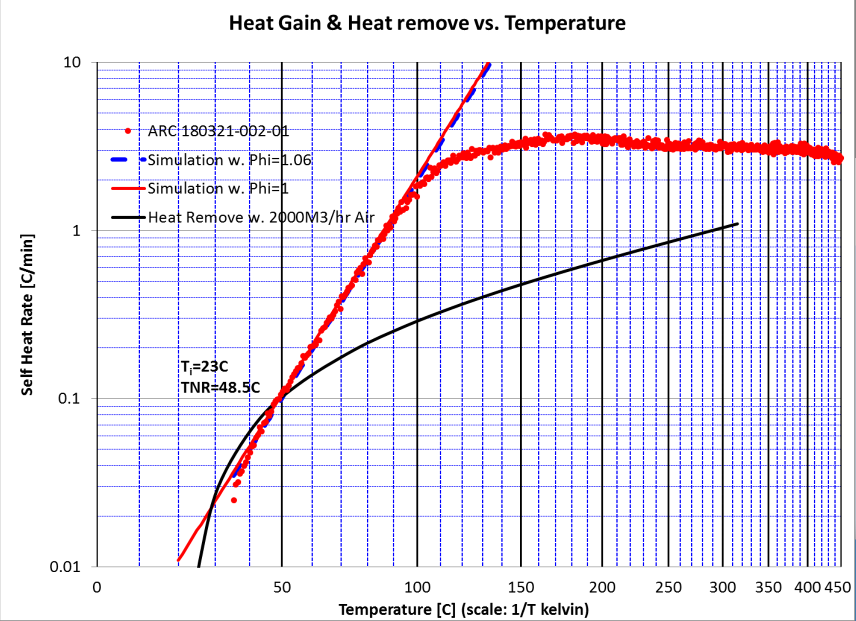
The Design Institute for Emergency Relief Systems (DIERS) Project Manual, 2010

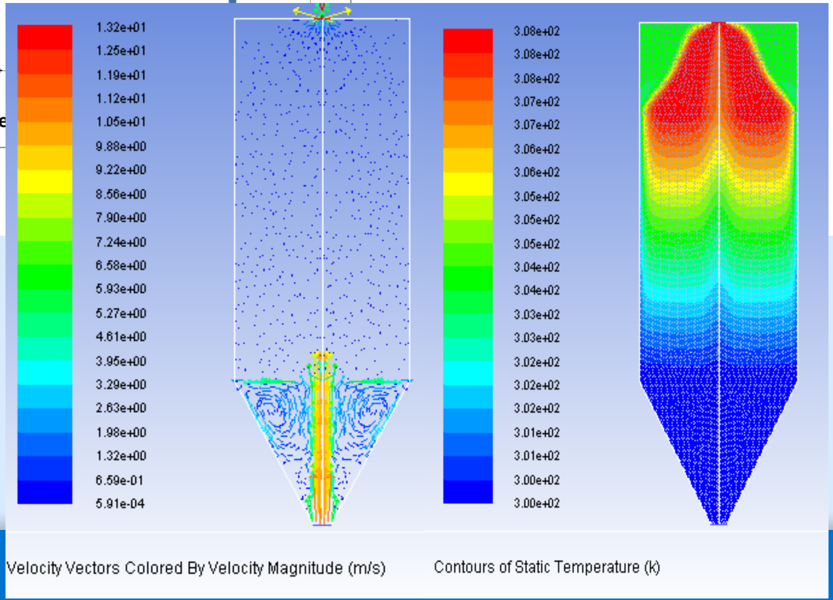
1, General Application of ARC in Corteva RC

- Application 7: Open cup ARC for oxidation reaction









1, General Application of ARC in Corteva RC

- The outcome of all applications may impact the production process and initiate process changes, which means "cost". Ensuring data accuracy is important to avoid incident, as well as reduce cost.

➔ General guidance

- Avoid to rely on a single data point to tell the reactivity hazard
- Make sure your instruments give you reliable data
- Always investigate the cause of data inconsistency
- If possible, try to get consistent data from different instruments

  e.g., ARC + DSC:

  - total heat from ARC is ~80% of that from DSC Org. Process Res. Dev. 2021, 25, 1, 108-119
  - Onset Temperature?

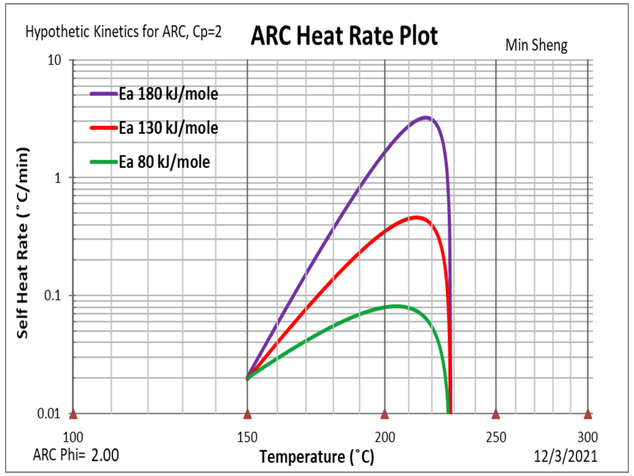
1, General Application of ARC in Corteva RC

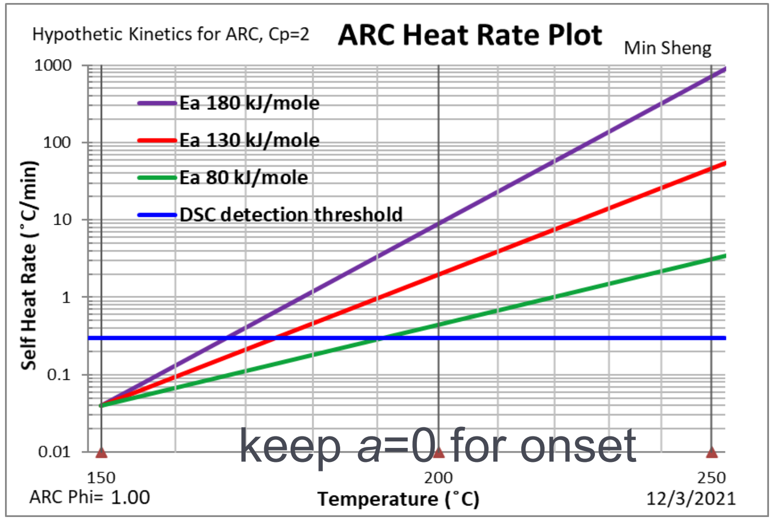
- Onset Temperature of ARC vs. that of DSC

ARC: onset T at 150C with different Ea:

ARC: Cp=2, Phi=2, onset T @ 150C & 0.02C/min			
Heat of reaction (dH) /(cal/g)	75	75	75
Activation energy (Ea) /(kJ/mole)	180	130	80
Ln(A)	38.809	24.556	10.375
Reaction order (n)	1	1	1

DSC run	Sensitivity	sample size	Detection threshold	
	10 uW	1mg	10 mW/g	0.3 C/min





ARC: Cp=2, Phi=2, onset T @ 150C & 0.02C/min; DSC: sensitivity 10 uW, sample size 1mg			
Heat of reaction (dH) /(cal/g)	75	75	75
Activation energy (Ea) /(kJ/mole)	180	130	80
Ln(A)	38.809	24.556	10.375
Reaction order (n)	1	1	1
DSC onset /C	167	174	191
Onset T difference /C	17	24	41

Higher Ea, lower onset T difference;
At onset, *a*➔0, reaction order (n) has insignificant impact

Agenda

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- 5, Bomb rupture
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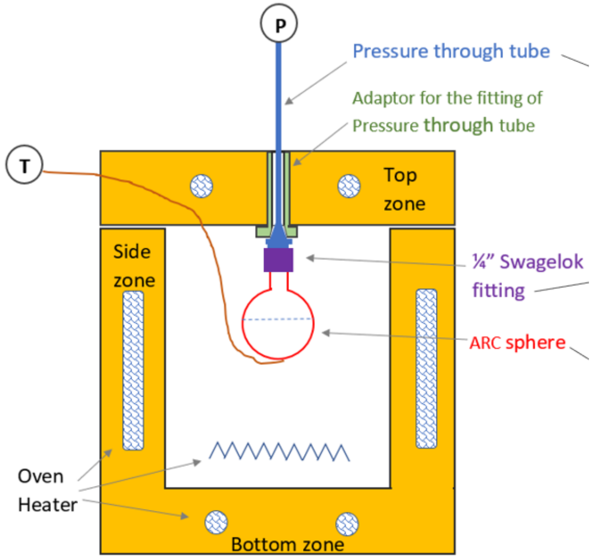
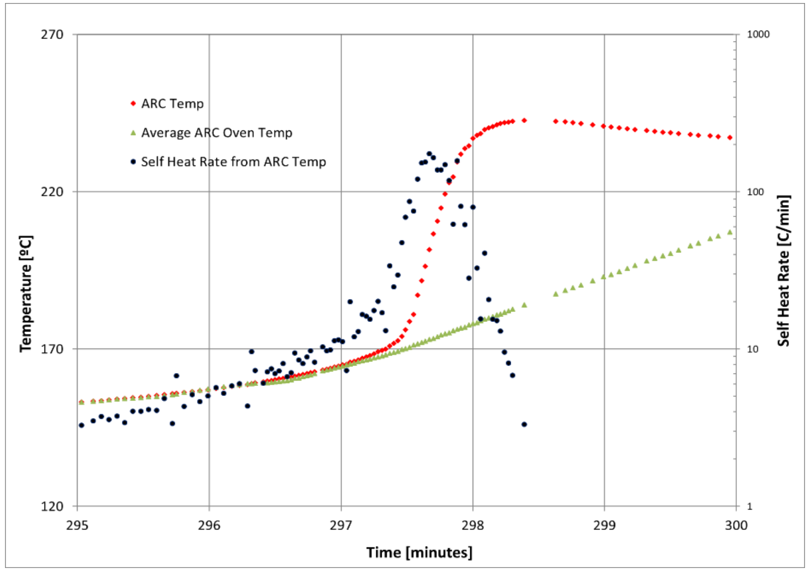
2. Adiabatic Limit of ARC

- Original Dow ARC could maintain adiabatic condition up to 20℃/min.
- Corteva THT esARC

  ARC test for 50% DTBP in toluene; 4.03g in 21.114 g Hastelloy C ARC bomb

  Slope of oven T in 297.5~300min: 15.0 ℃/min (hardware limit)



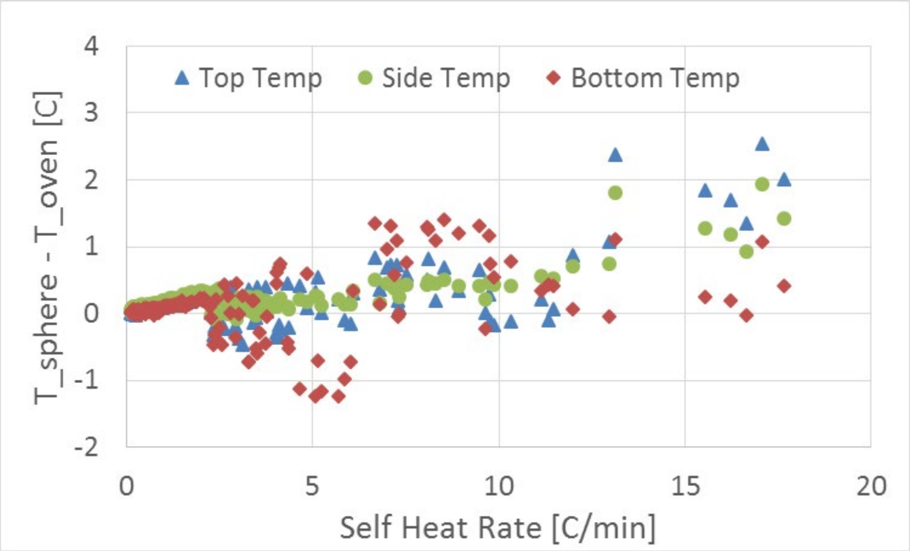


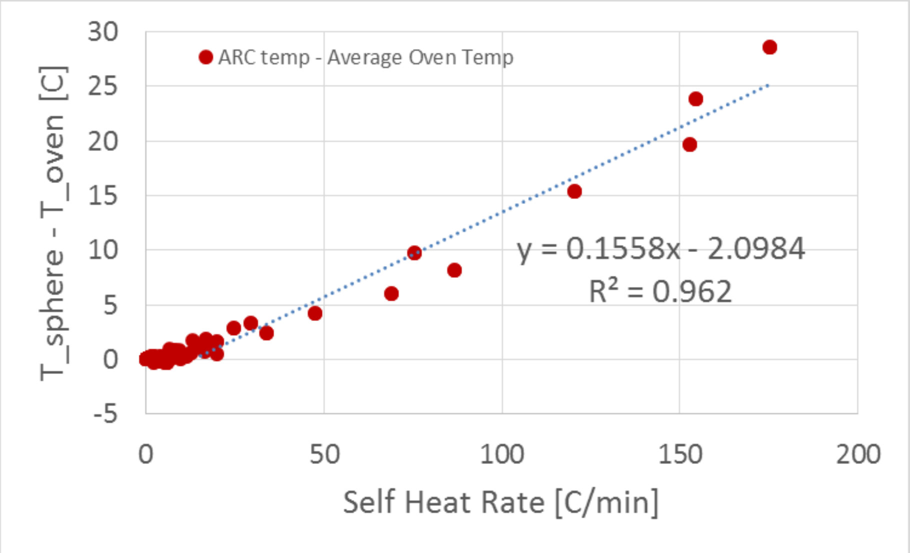
DTBP: di-tert-butyl-peroxide

2. Adiabatic Limit of ARC

- Difference between sample and oven

∆T < 1 C below ~13 ℃/min   ∆T = 0 °C at 13.5 ℃/min





We believe delay from control system lowers such limit.

Be caution if you have ARC data with high self heat rates. Thermal lag is another big issue for such data, more detail in our paper: Org. Process Res. Dev. 2021, 25, 1, 108-119

Agenda

- 1, General applications of ARC in Corteva Reactive Chemicals (RC)
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- 6, Bomb compatibility
- 7, Low onset exotherm

3, Pressure tubing and condensation

- Pressure tubing and transducer are all outside of ARC oven. The temperature of those parts will be much colder during a run.

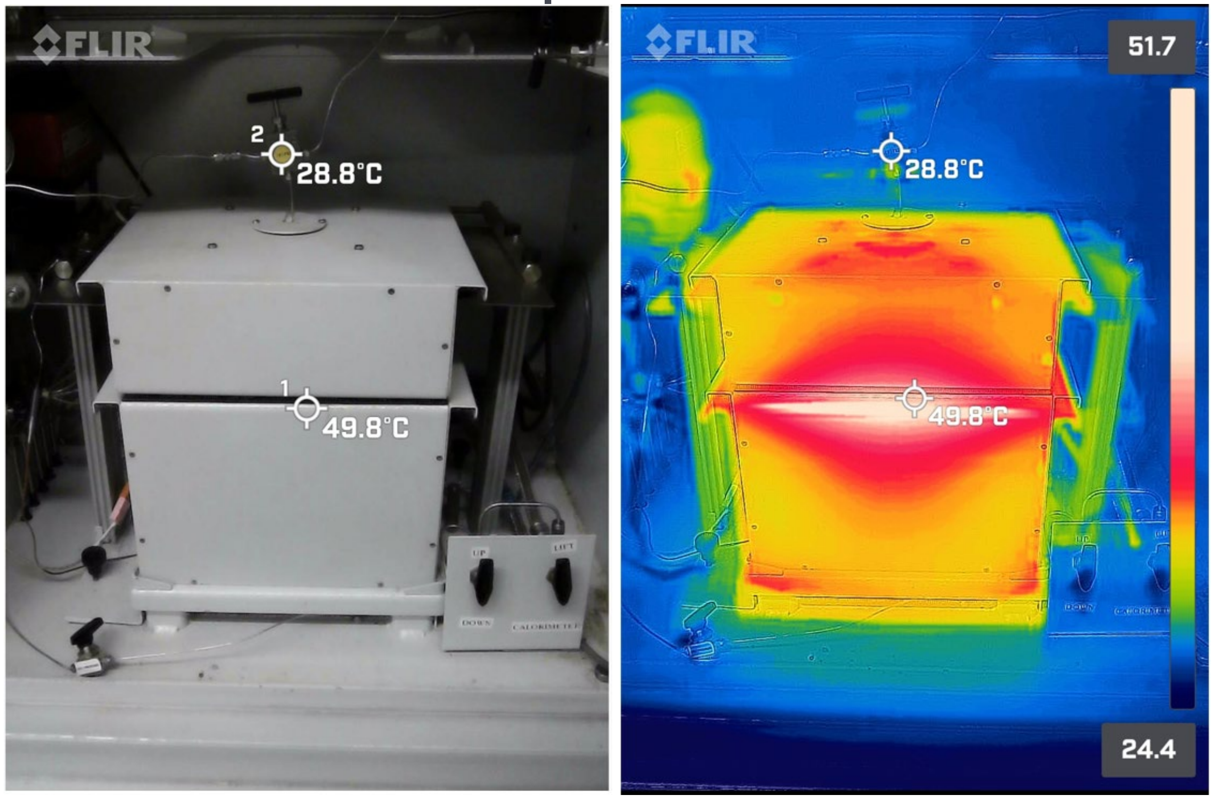
THT esARC

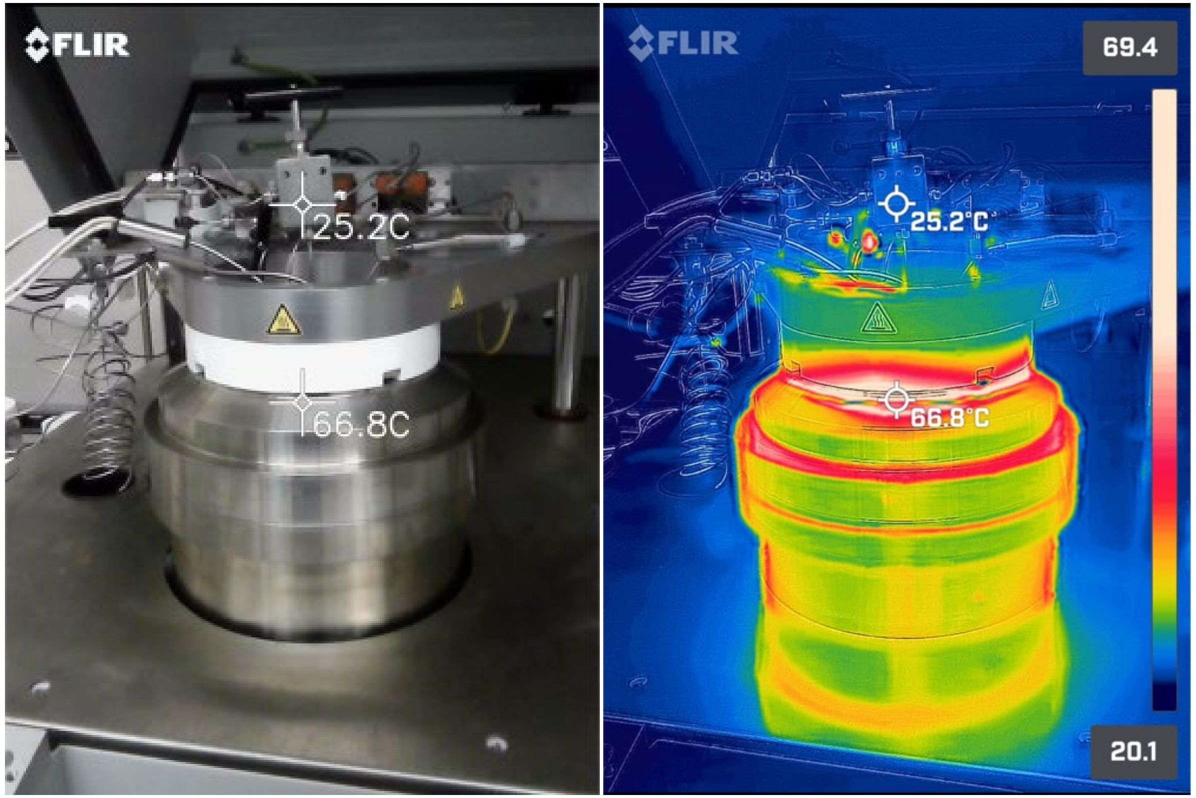
P Transducer

NETZSCH 254

3, Pressure tubing and condensation

- When ARC is isotherm at 250℃, tubing and valve are around ambient temperature

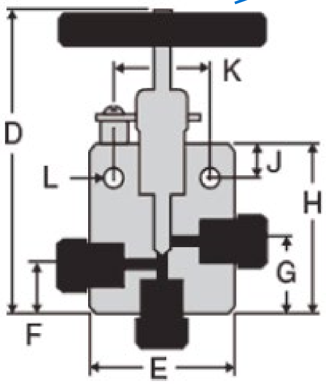




3, Pressure tubing and condensation

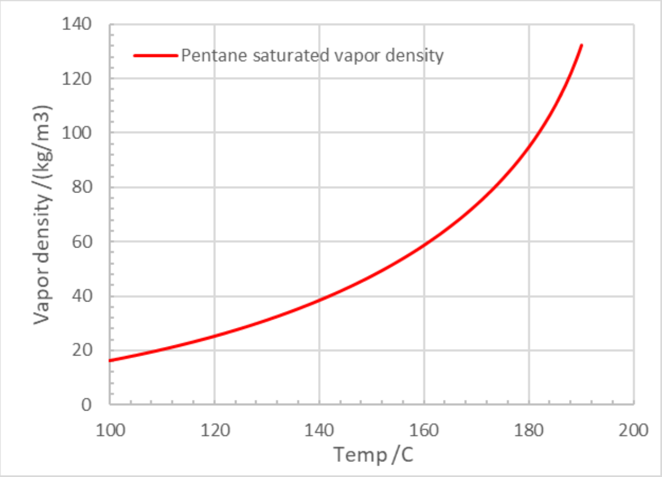
Corteva setup: to reduce sample headspace volume by using small tubing and moving P transducer closer, special valve and filling with silicone oil (Dow Corning 710).

- 1/16” tubing, 1/16” pressure through tube
- Three way taper seal needle valve (15-12AF1)
- Fill oil from transducer to valve V1 (clean & replace oil between V1 and V2 for each test)



3, Pressure tubing and condensation

Corteva setup: still a small empty space where sample can condense? N-Pentane in a HC bomb with an internal volume of 9.66cc



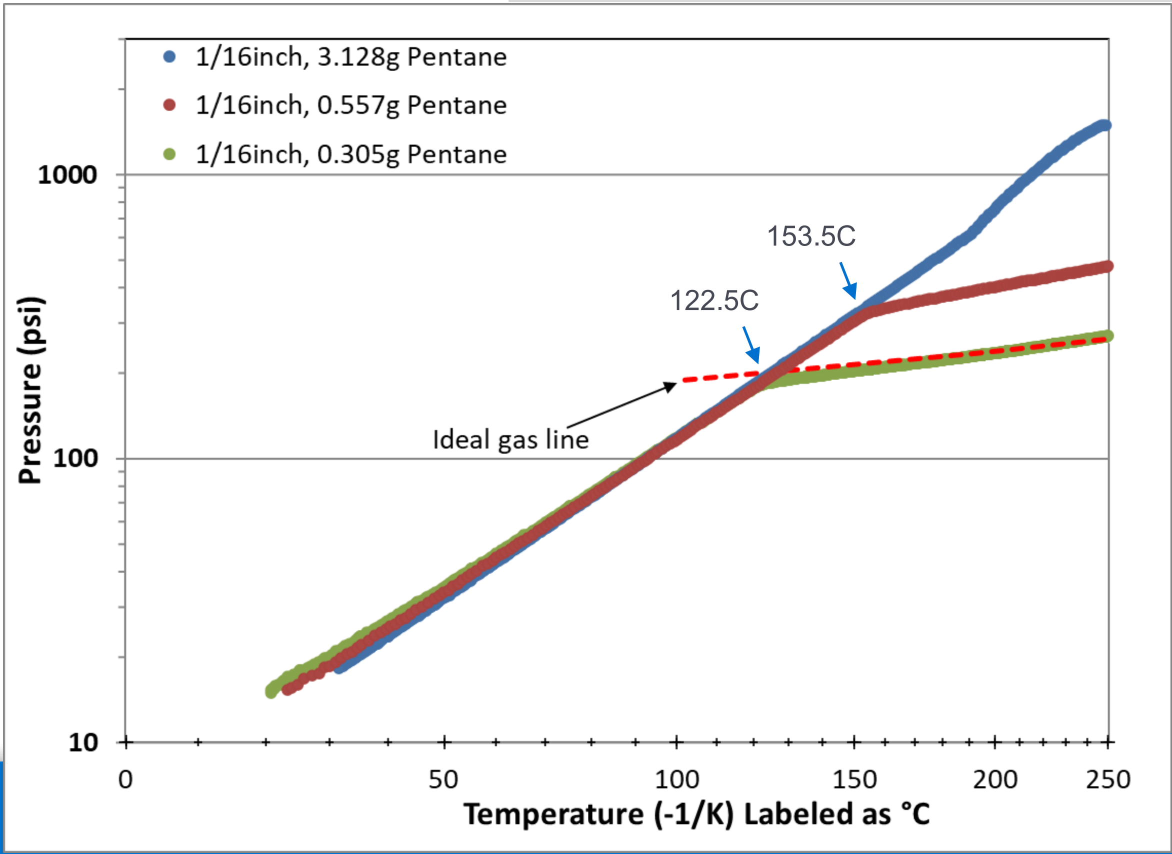
Pentane, boiling @ 36℃, Critical @ 196.5 ℃

- 3.128g: vapor pressure up to Tc
- 0.557g: vapor pressure to 153.5C, then ideal gas

➔9.66cc vapor, 0.063g condensed outside

- 0.305g: vapor pressure to 122.5C, then ideal gas

➔9.66cc vapor, 0.046g condensed outside



Corteva setup has about 0.09cc of potential empty tubing space for sample condensation during the ARC test

3, Pressure tubing and condensation

- Typical setup we saw in other labs: 1/8” Tee + ball valve, 1/8” pressure through tubing, oil from PT to Tee (1/16”tubing)

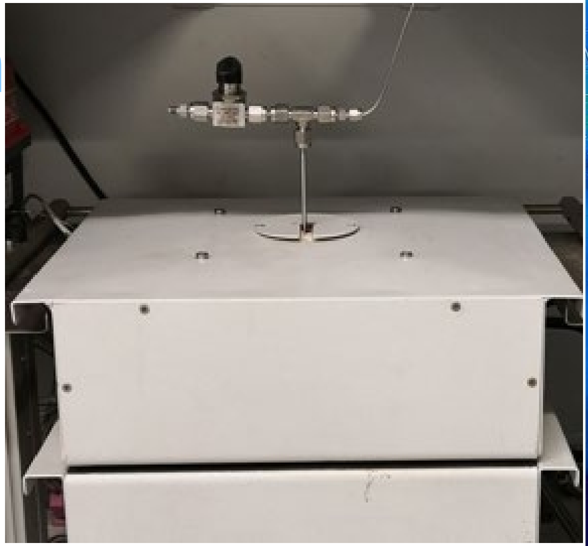
- 0.94g: vapor pressure to 150.8C, then ideal gas

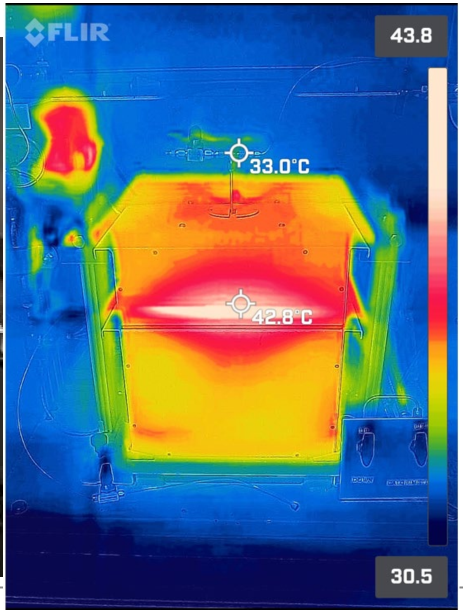
➔9.66cc vapor, 0.473g condensed outside

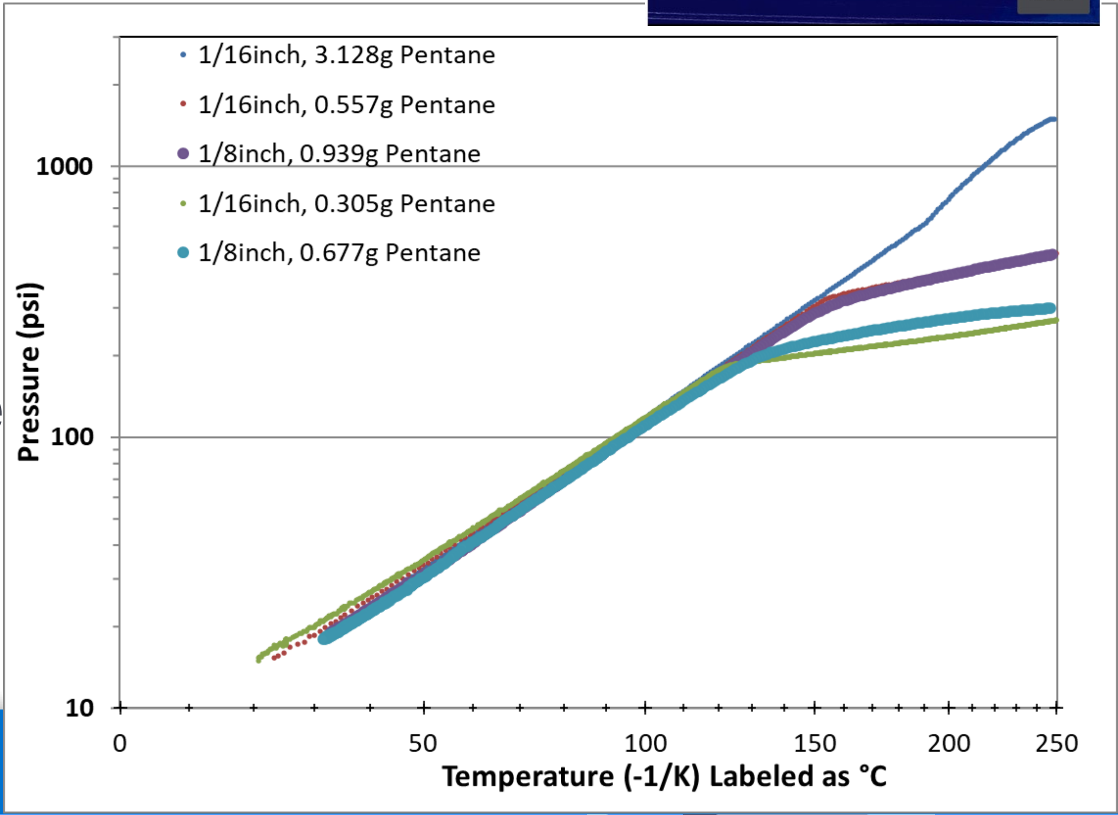
- 0.68g: vapor pressure to 130.2C, then ideal gas

➔9.66cc vapor, 0.375g condensed outside

This tubing setup has about 0.68cc of potential empty tubing space for sample condensation during the ARC test





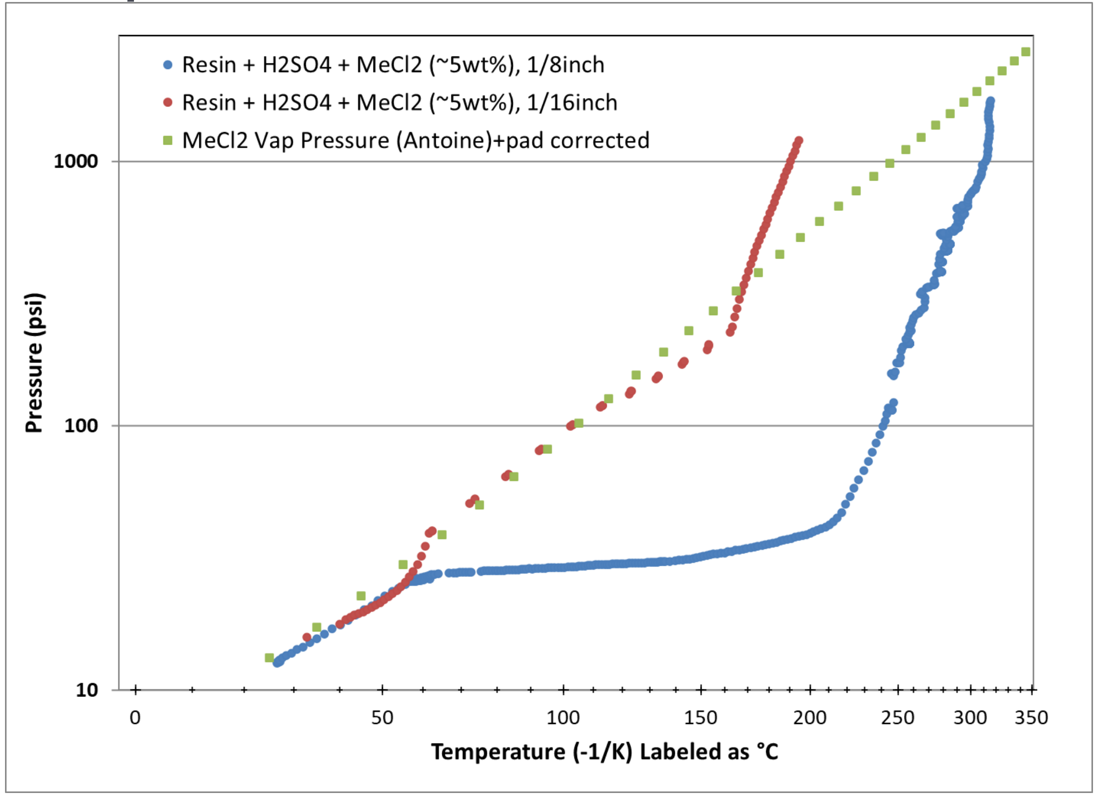


CORTEVA agriscience

3, Pressure tubing and condensation

- Why it matters?

1. Volatile components could be removed from the tested sample

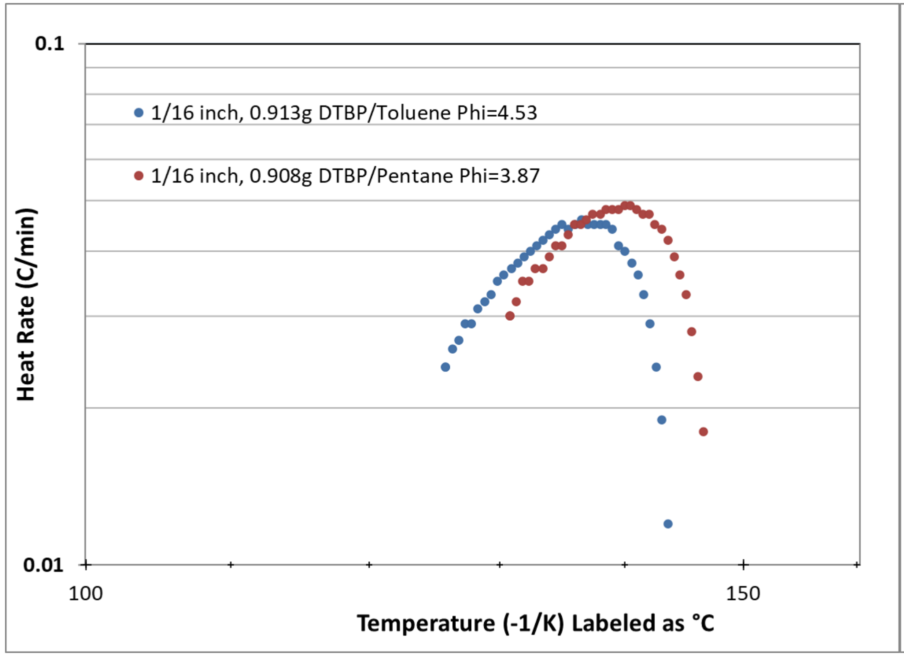


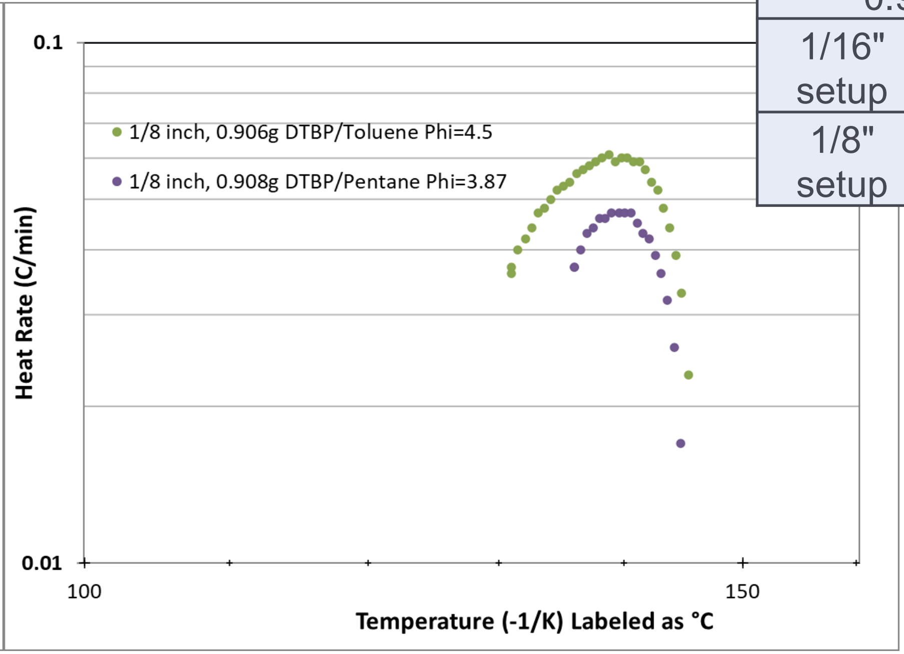
Sulfuration reaction, MeCl2 is used to swell polymer

3, Pressure tubing and condensation

- Why it matters?

2. Data consistence with volatile solvent or exotherm at high temperature (e.g., 100℃ higher than boiling point).





~0.9g sample in Ti bomb		total heat (J/g)
1/16" setup	20% DTBP in Toluene	-141
	20% DTBP in Pentane	-137
1/8" setup	20% DTBP in Toluene	-112
	20% DTBP in Pentane	-72

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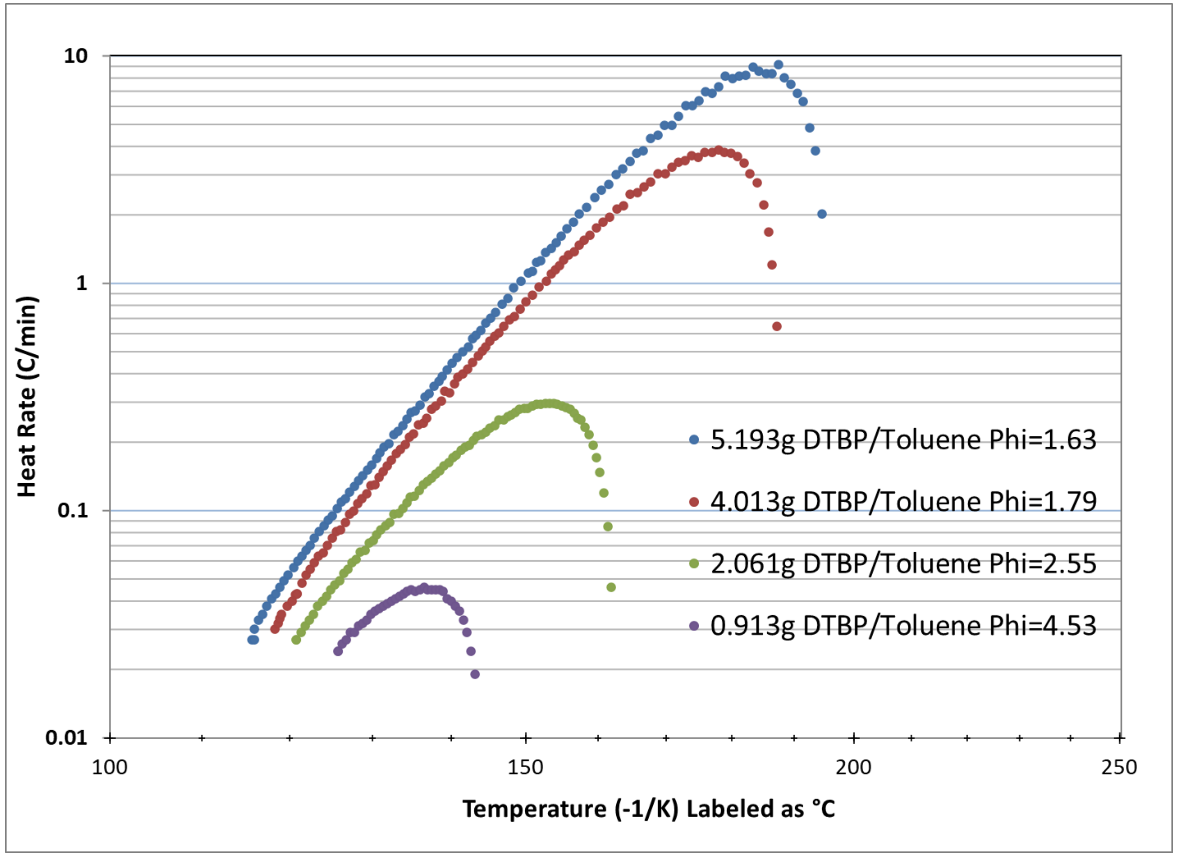
4, Sample size

- 20% DTBP in Toluene (Cp 1.746J/g/℃), Ti ARC bomb (~10.5g, Cp 0.54J/g/ ℃, 9.66cc), Corteva tubing setup

#	Sample size (g)	Onset T (℃)	Total heat (J/g)	
1	5.193	115.9	-227.7	100%
2	4.013	118.3	-214.8	94%
3	2.061	120.8	-183	80%
4	0.913	125.8	-141	62%

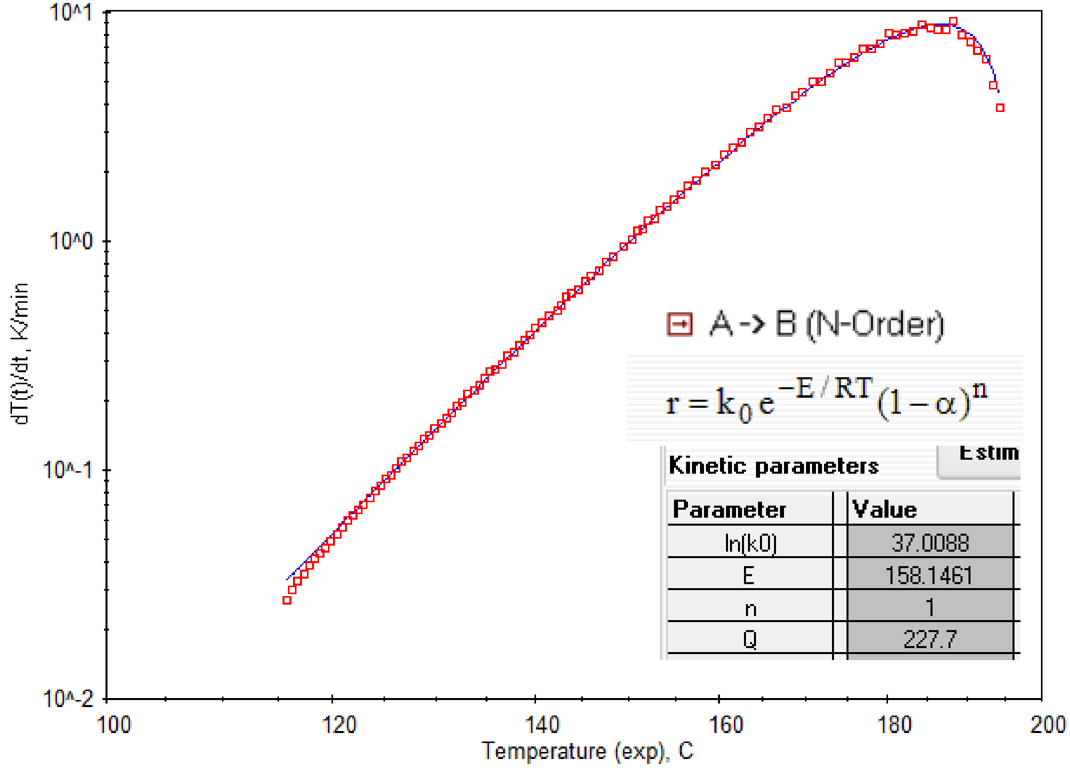
Total heat is after Phi correction. In an ideal world, it should be the same for all tests.

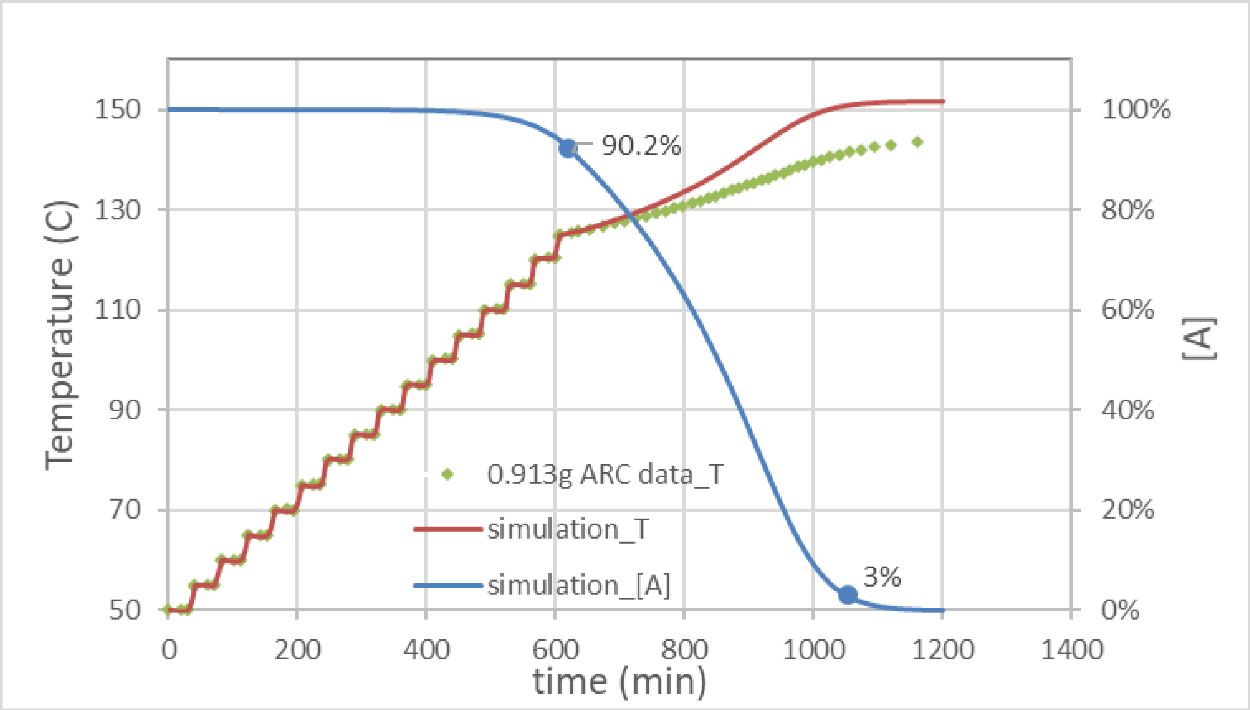
For the same sample, why #4 (0.913g) is lower by 38% than #1 (5.193g)???



4, Sample size

- Kinetic from data of 5.193g ARC, then simulate 0.913g ARC run





At onset T (125.8C) of the 0.913g ARC, [A] conversion is already 9.8% at HR≥0.02C/min, at the end of Exo, 3% left when HR<0.02C/min. ➔ 12.8% was missed by the Exo track due to instrument sensitivity (<0.02C/min)

4, Sample size

- DTBP vaporized into headspace (vapor phase)

In 0.913g ARC, exo between 125.8 ℃ and 143.6 ℃, Vapor density at 134.7 ℃: 6.06 mg/cc, From ASPEN, vapor contains 23.7wt% DTBP ➔ 0.0122g (6.7%)

- DTBP condensed into cold tubing

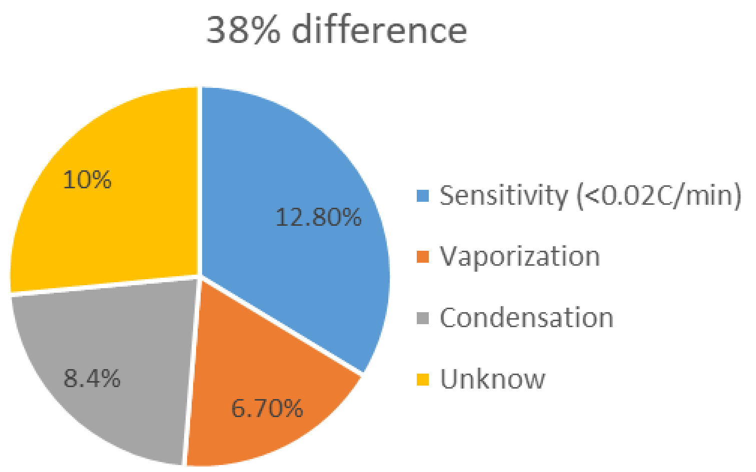
0.09cc of potential empty tubing space, density at 25C: 0.8538g/cc, assume 20wt% DTBP ➔ 0.0154g (8.4%)

➔Generally, avoid <1gm liquid sample size for ARC test

Larger sample size is better for data quality,

our default sample size is 4 gm for unknow sample,

but watch for bomb rupture.



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5, ARC Bomb Rupture

- Rupture:

1~2-week instrument down time (recertify ARC)

Put personal under chemical exposure risk

Potentially instrument damage

5, Bomb rupture

Typical ARC bomb used in Corteva RC group

ARC Bomb Type	Average Burst Pressure (psi)	Approximate Weight (gm)
FT-2 (Ti) 0.035”	7000	10.1
FS-2 316SS 0.035”	15,000	17.6
FH-2 (HC) 0.035”	14,500	20.8

From 2005 , total of 21 ruptured ARC documented in our RC database

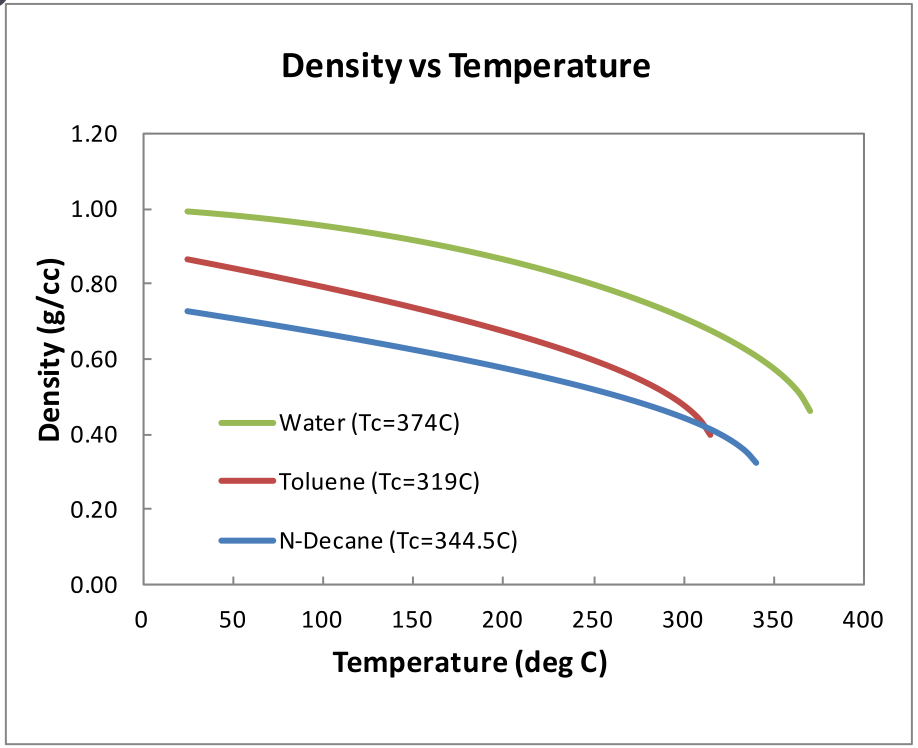
total	Cause of rupture
9	hydraulic overfill
8	high energy materials
3	Bomb compatibility

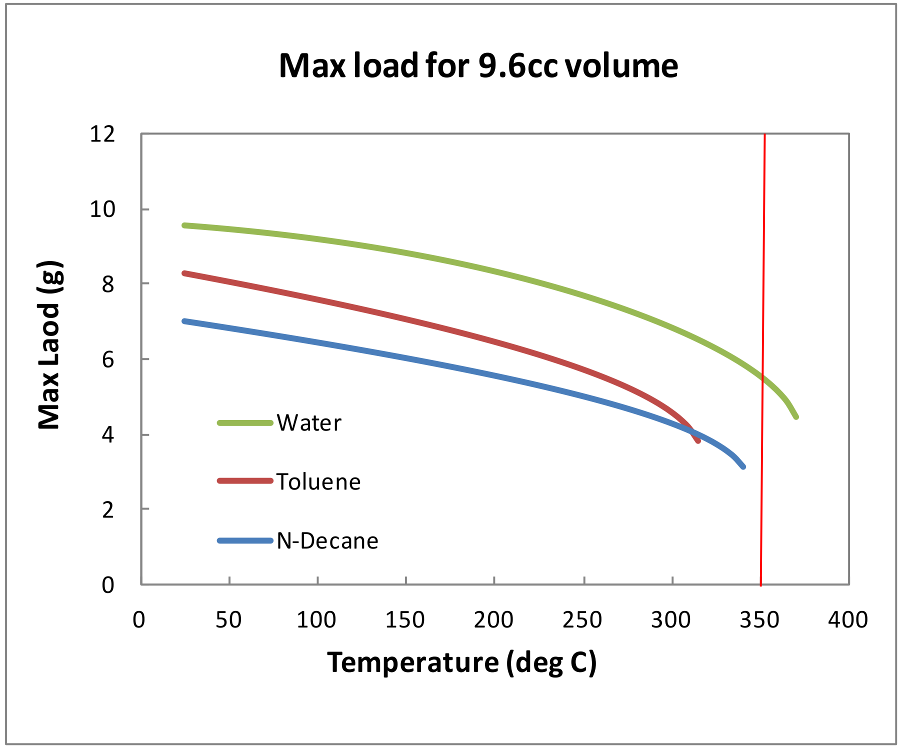
5, Bomb rupture: hydraulic overfill

- Liquid thermal expansion:

4 gm of N-Decane is 12.3cc liquid at 340^{0}C, while ARC has 9.66cc and heated up to 350C

Max load for 9.6cc ARC test (g)	
Water	5.52
Toluene	3.84
N-Decane	3.13





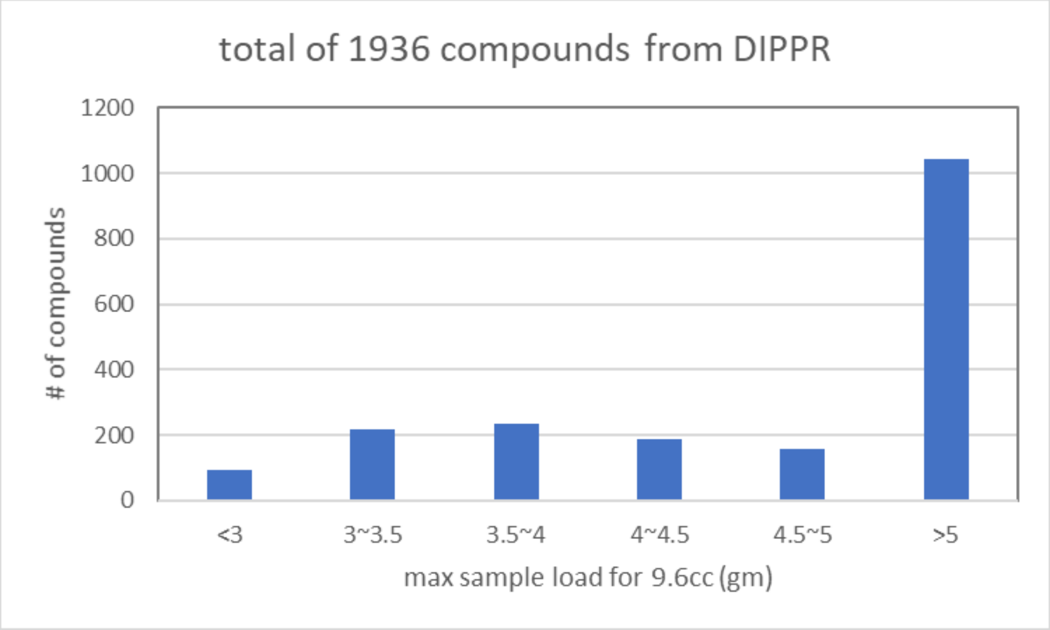
- Below the critical temperature, pressure of overfill liquid is infinitely large

5, Bomb rupture: hydraulic overfill

- How to prevent ARC rupture from hydraulic overfill? Need liquid density at the highest tested temperature

If critical T (Tc) > 350C, use density at 350C; if critical T ≤ 350C, use density at Tc-5C.

1936 compounds offer such data in DIPPR, 28% of them will have a hydraulic overfill ARC bomb with 4gm sample load.



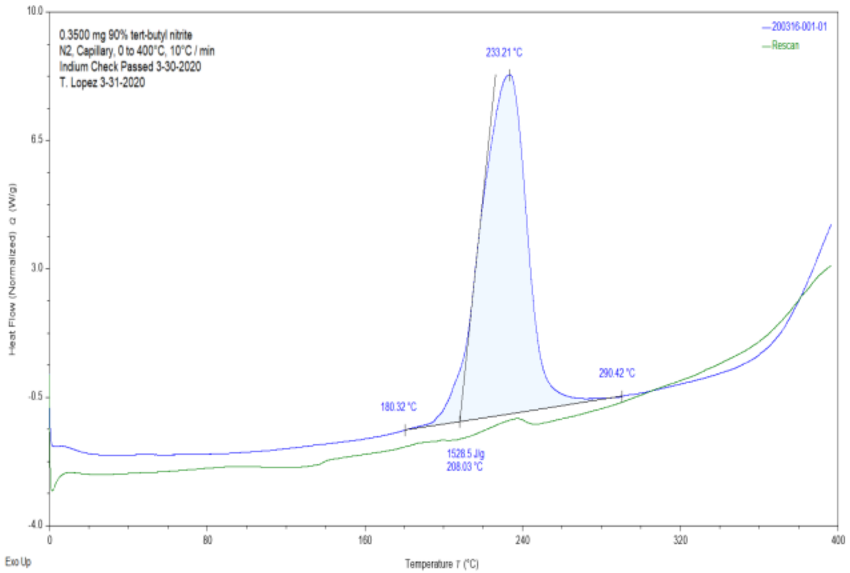
5, Bomb rupture: high energy materials

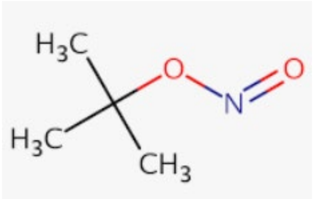
- High energy materials: contains high energy function groups or has exotherm (e.g., by DSC) over 800J/g.
- In Corteva, always perform DSC test prior to ARC. If exotherm(s) exceed 800 J/g, the sample size should not exceed 1.5-2 g for ARC test.

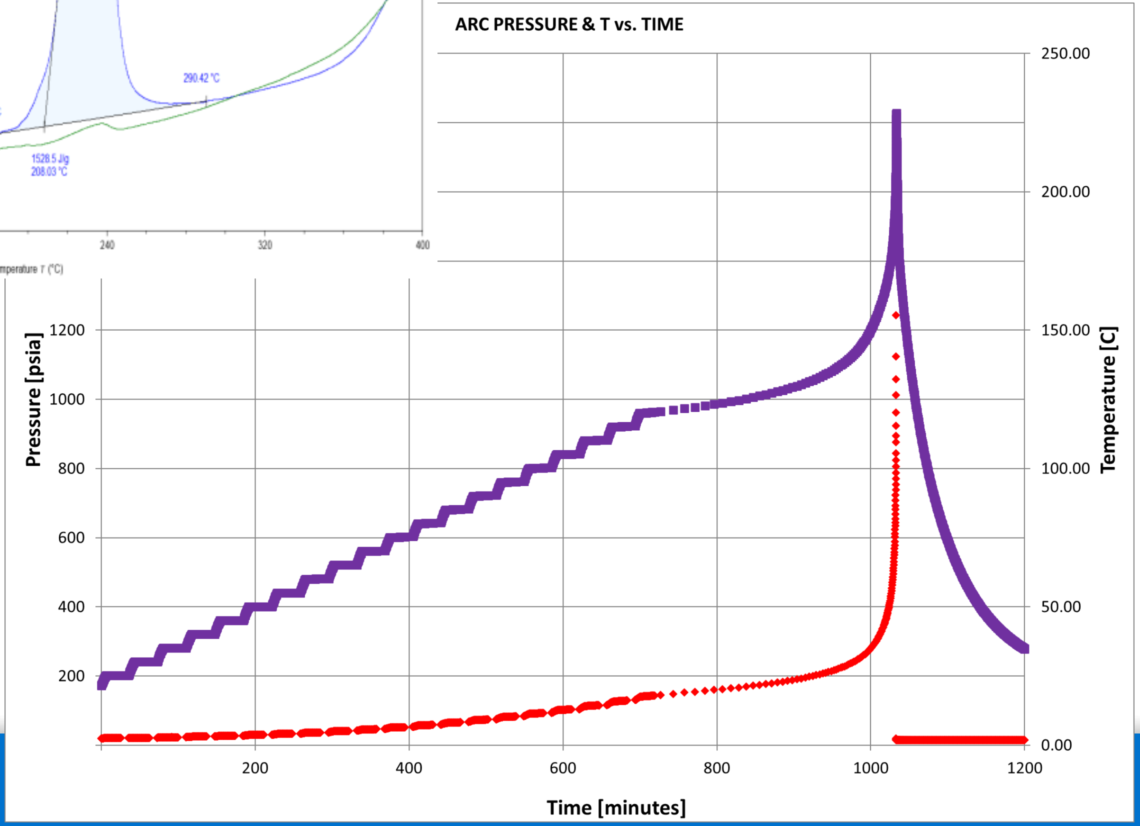
Ruptured ARC test ID	High energy materials	Heat by DSC (J/g)
TX-2007-001694.001	contains Triperoxide group	-1415
TX-110822-000016-04	contains Nitro group	-1765
MD-120605-000010-02	contains Nitro group	-2335
MD-120605-000010-03	contains Nitro group	-2335
190117-001-02	DMSO + NaH	-1230
200316-001-01	90% tert-butyl nitrite	-1529

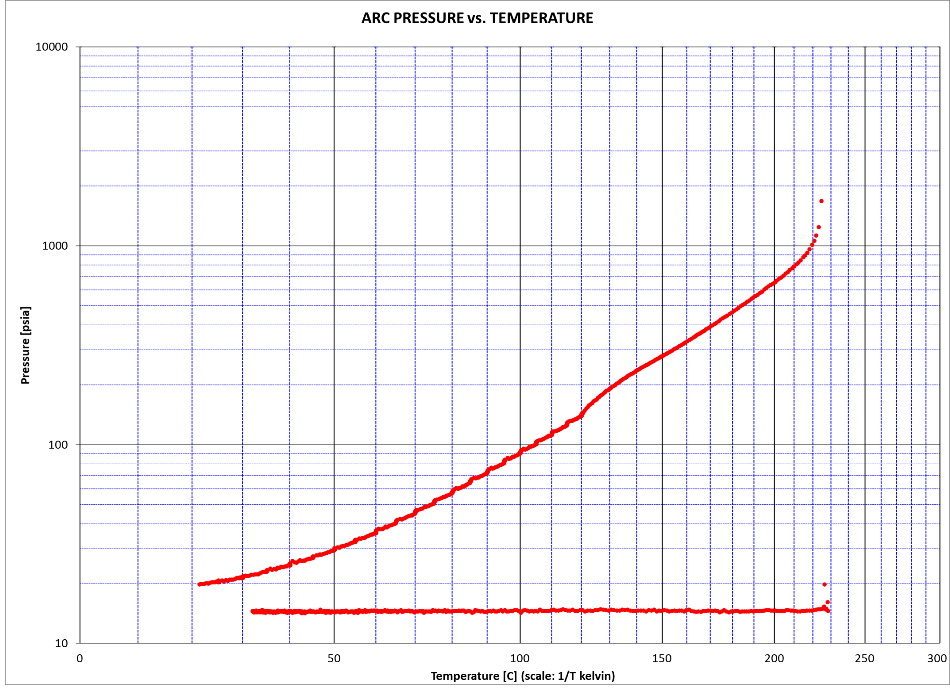
5, Bomb rupture: high energy materials

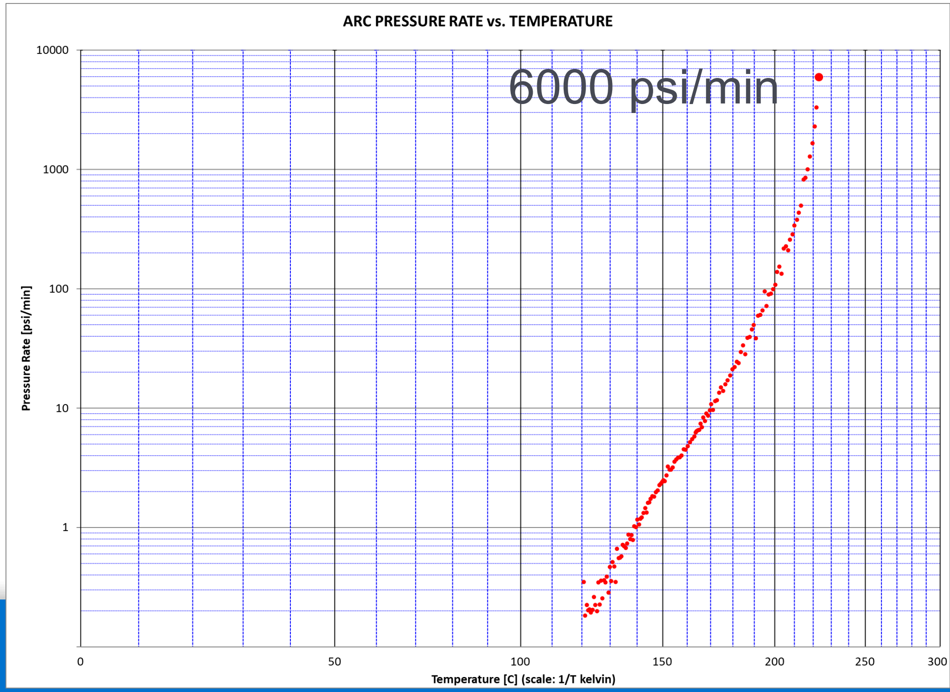
- 200316-001-01: 90% tert-butyl nitrite











5, **Bomb rupture:** high energy materials

- High energy function group

Function groups	structures	Range of decomposition energies (kJ/mol)
Alkenes, Dienes, Vinyl esters, Acrylates	-C=C-	50~90
Alkynes, Acetylenes, Metal acetylides, Haloacetylene derivatives	-C≡C-	120~170
Epoxides, Aziridine, Diazirines	Δ	70~150
Peroxides, Hydroperoxides, Peracides	-C-OO-R	230~360
Organic sulfoxides	R2-S=O	40~70
Organic sulfonyl chlorides	-SO2Cl	50~70
Hydrazines	-NHNH-	70~90
Diazo, diazonium	-N=N-, $-N{\equiv}N^+$	100~180
Azides	-N3	200~240
Oxime	-C=NOH	110~140
N-oxides	R2N:O	100~130
Nitroso	R-N=O,	150~290
Cyanates, Isocyanates, Thiocyanates	-O-C≡N, -N=C=O, -S-C≡N	50~75
Nitro, N-nitro	R-NO2, R2-N-NO2	310~430
Acyl nitrates, Acyl nitrites	-C-O-NO2, -C-O-N=O	400~480
N-halogen compounds, Hypohalites,	-N-X, -O-X	-
N-metal derivatives, Metal peroxides, Metal fulminates, Hydrides, Metal organics	-N-M, -O-O-M, MC≡N→O, MH, MR,	-

1. http://storage.dow.com.edgesuite.net/safety-dow-com/External-SOC-Form_v060612.pdf
2. Organic Process Research & Development **2002**, *6,* 877–883
3. Bretherick's Handbook of Reactive Chemical Hazards, 2017

Agenda

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6, Bomb compatibility

- Corteva DSC sample container: glass capillary or gold-plated crucible
- Typical ARC bombs are made of metals/alloys, which could react with chemicals. Sometimes it corrodes badly enough to fail.

Ruptured ARC test ID		ARC bomb material
TX-080722-000019.001	Sample contains 6%HCl and 10.5%water	Ti
TX-080804-000017.004	Sample contains 6.69 wt% HCl and 45.06 wt% H2O	Ti
210325-001-01	Sample contains HCl	S.S

Reaction of titanium with acids

Titanium does not react with most acids, under normal conditions. It will react with hot hydrochloric acid, and it reacts with HF, forming Ti(III) complexes and hydrogen gas, H_2.

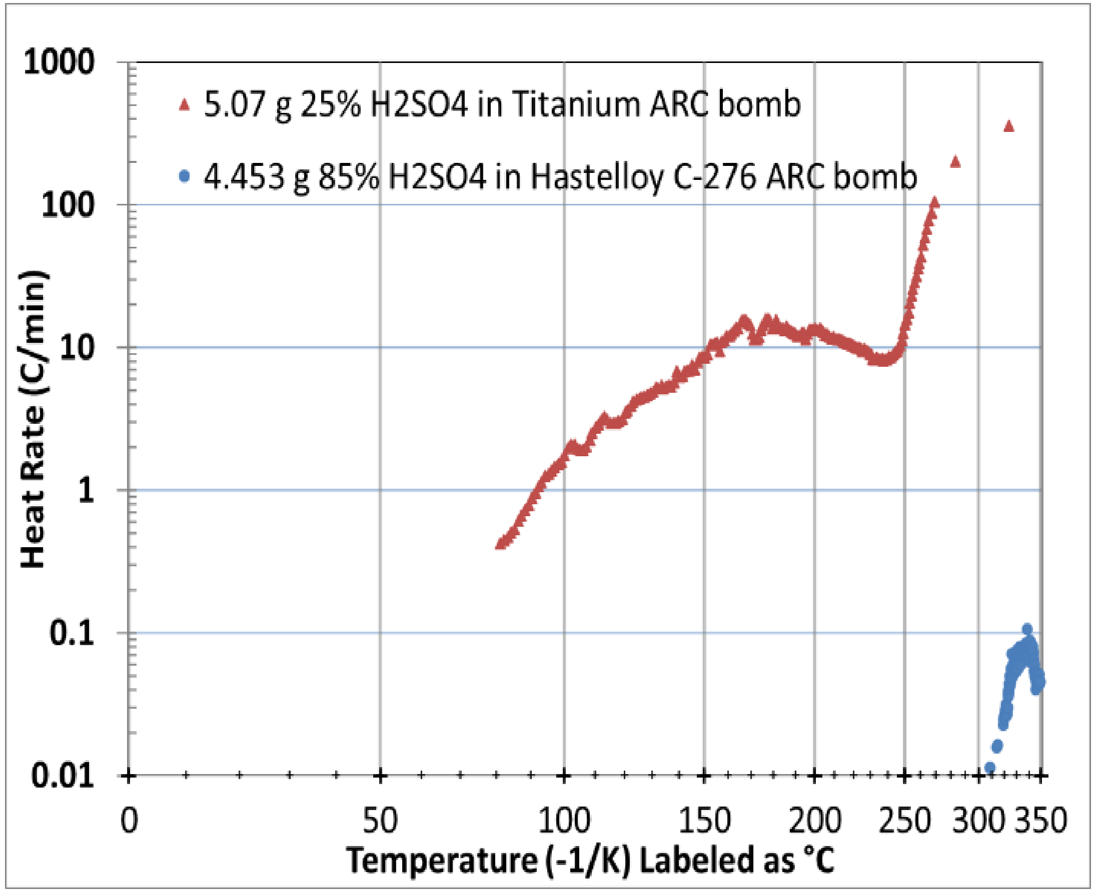
$$2\ Ti(s) + 12\ HCl(aq) \xrightarrow{\Delta} 2\ Ti[Cl_6]^{3-}(aq) + 3\ H_2(g) + 6\ H^+(aq)$$

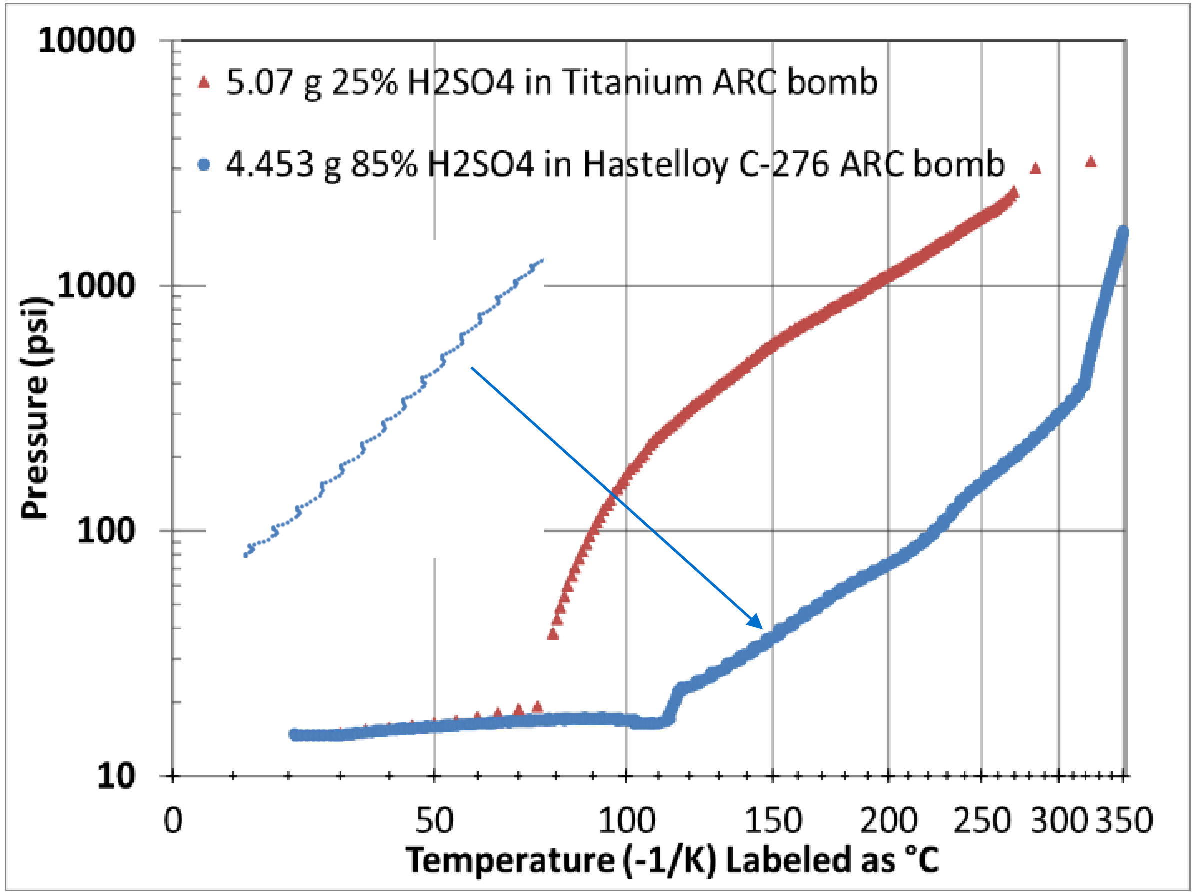
$$2\ Ti(s) + 12\ HF(aq) \longrightarrow 2\ [TiF_6]^{3-}(aq) + 3\ H_2(g) + 6\ H^+(aq)$$

https://pilgaardelements.com/Titanium/Reactions.htm

6, Bomb compatibility

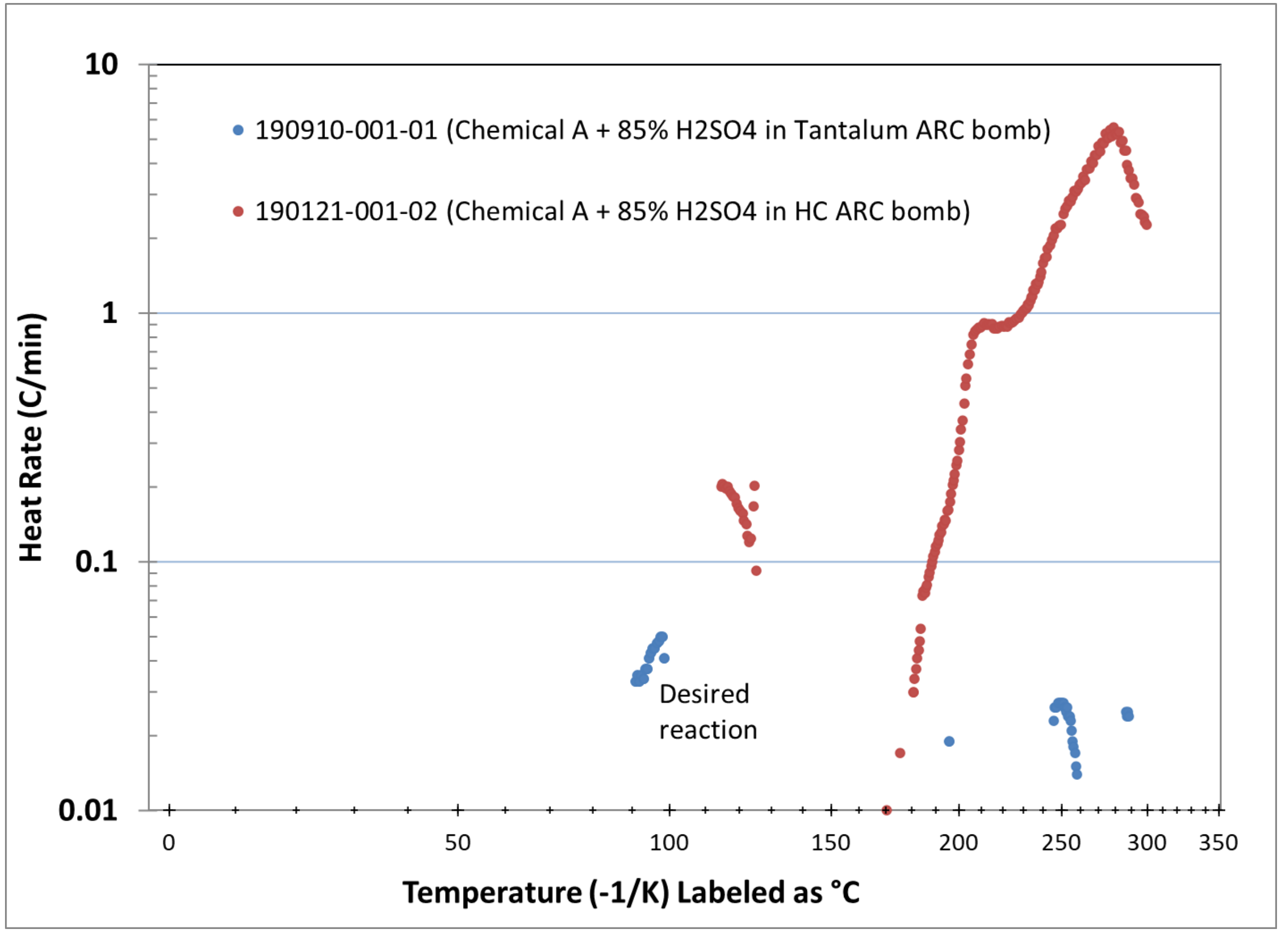
- It can also result in a FALSE Exotherm or False gas generation





6, Bomb compatibility

- Tantalum bomb can be used to reduce such false exotherm



Chemical A: a chlorinated compound, which likely accelerates the HC+H2SO4 reaction above 170C

6, Bomb compatibility

- Corteva ARC bomb compatibility chart:
  N: Incompatible (Do NOT use);
  1: highly recommmended;
  5: not recommended.

- Default ARC bomb: Hastalloy-C (1" diameter sphere, ¼" tube),

FH-2 (HC) 0.035"	14,500	20.8

Corteva ARC Bomb Chemical Compatibility Chart	304 Stainless Steel	316 Stainless Steel	Tantalum	Hastalloy-C	Titanium
Non-oxidizing Mineral Acids	N	N	2	2	5
Organic Acids	3	2	1	1	2
Caustics	3	3	N	2	2
Aliphatic Amines	2	1	3	2	5
Alkanol Amines	2	1	5	2	5
Aromatic Amines	2	1	3	2	5
Isocyanates	1	1	5	1	5
Acrylates	2	1	1	1	2
Acrylic and Methacrylic Acids	N	N	1	N	1
Epoxides (Alkylene Oxides)	2	1	3	2	4
Aldehyde, Ketones	3	1	1	1	2
Alcohols, Glycols	1	1	1	1	5
Phenols, Cresols	1	1	1	1	2
Aromatic Hydrocarbons	1	1	1	1	1
Miscellaneous Hydrocarbon Mixtures	1	1	1	1	1
Esters	2	1	1	1	2
Halogenated Hydrocarbons	5	5	1	3	1
Ethers	1	1	1	1	1
Nitro Compounds	2	1	3	2	5
Miscellaneous Water Solutions	2	2	1	1	1
Polymerizable Monomers & Olefins	1	1	2	1	2

Notes: 1 - highly recommmended; 5 - not recommended; N - Incompatible

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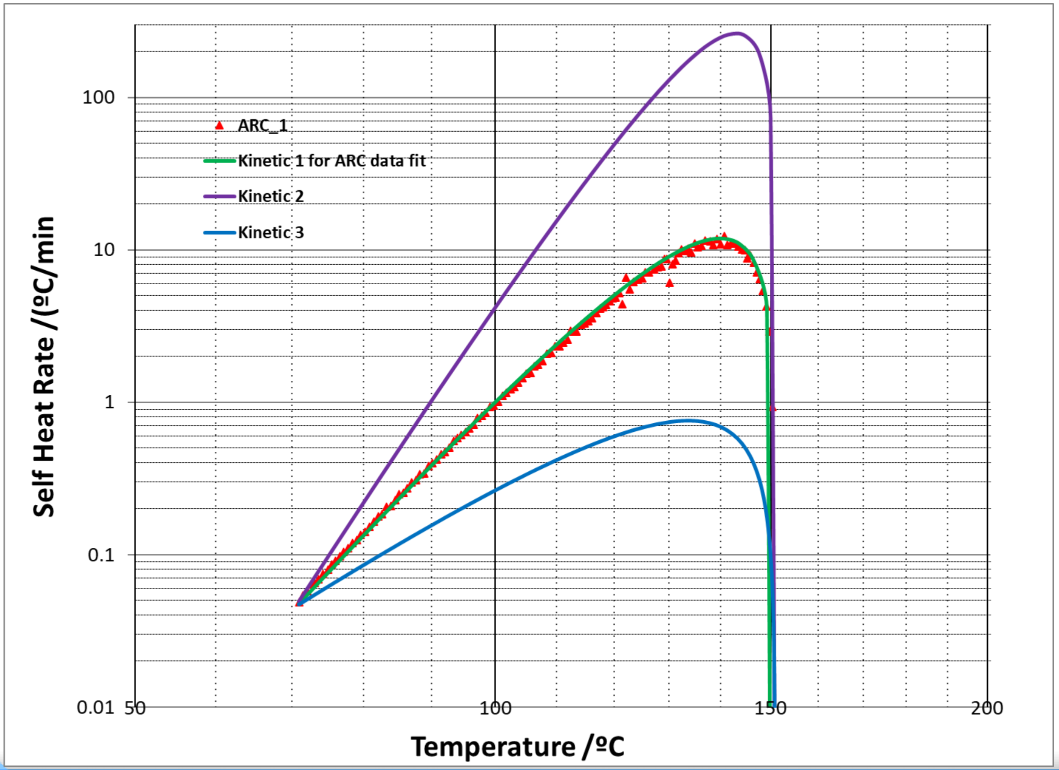
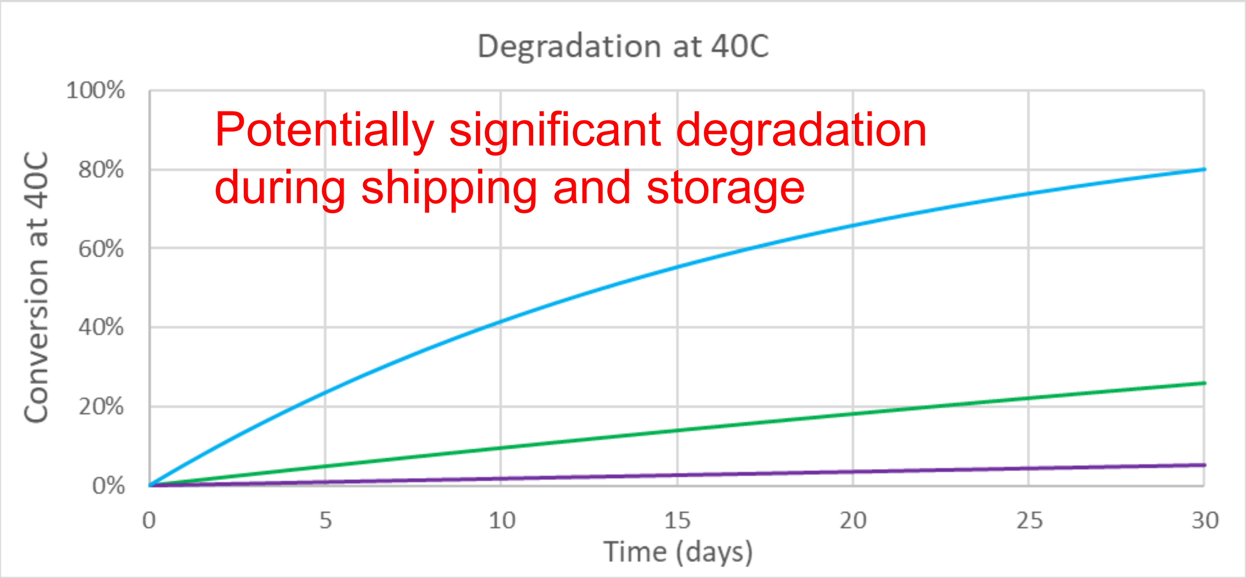
7, Low onset exotherm

A. If a sample has an exotherm detected by ARC with onset temperature below 100C (typically slow degrading sample), always watch the sample degradation during shipping and storage. Try to use a fresh prepared sample for ARC test.

	Kinetic 1	Kinetic 2	Kinetic 3
Heat of reaction (dH) /(J/g)	296.69	296.69	296.69
Activation energy (Ea) /(kJ/mole)	128.61	180	80
Ln(A)	33.434	51.434	16.434
Reaction order (n)	1	1	1



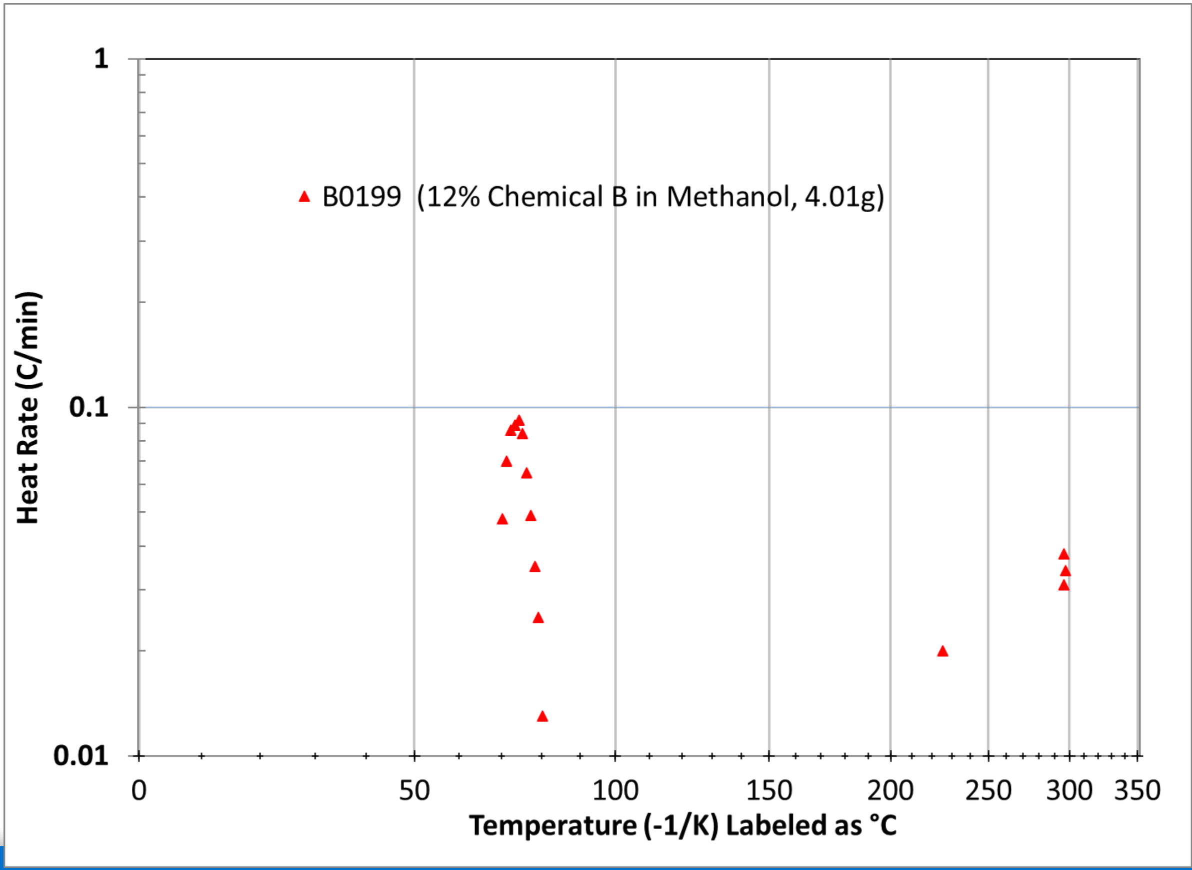


7, Low onset exotherm

- Example: an ARC data from other testing lab. Only -46 J/g energy measured by their ARC (1/8" pressure tubing setup). Based on this data, it was believed the risk of reactivity hazard is low.

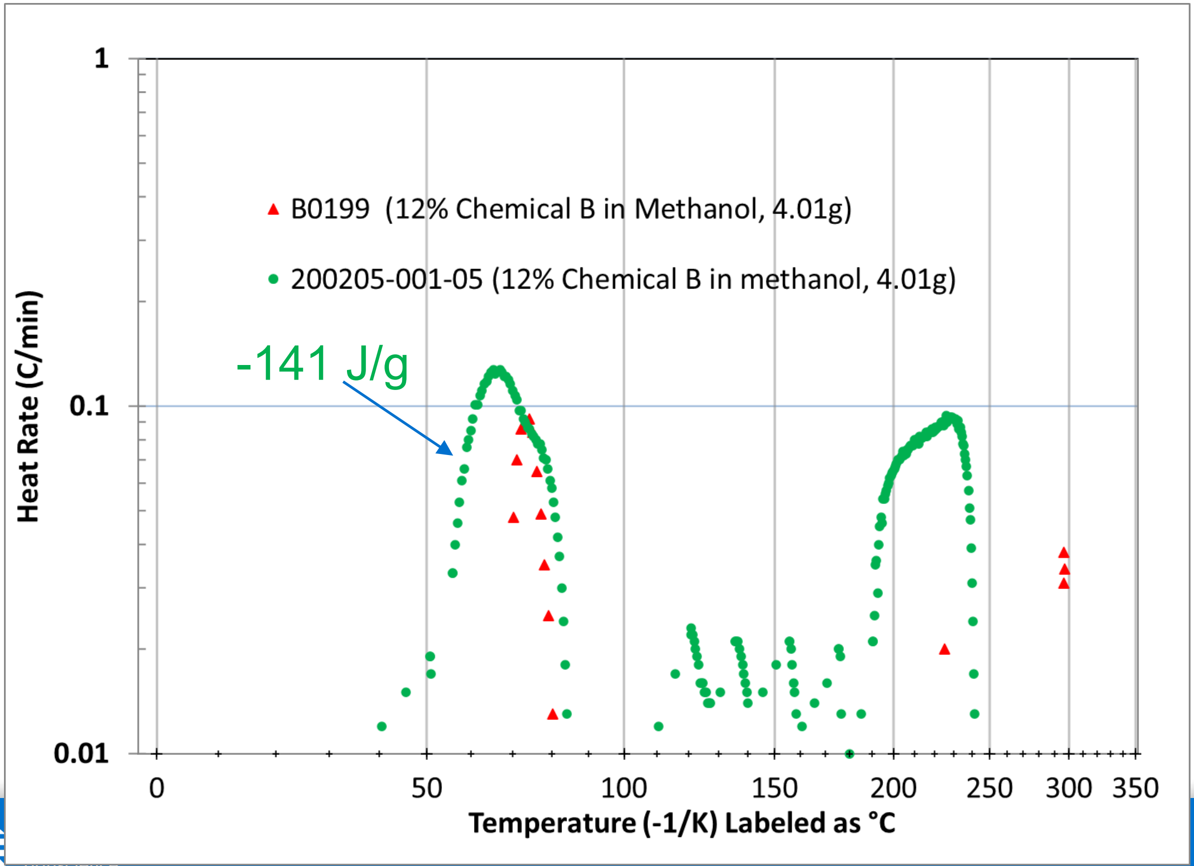
Exo	Onset T [ºC]	Peak T [ºC]	End T [ºC]	Heat [J/g]
#1	70.2	75.2	81.2	-46

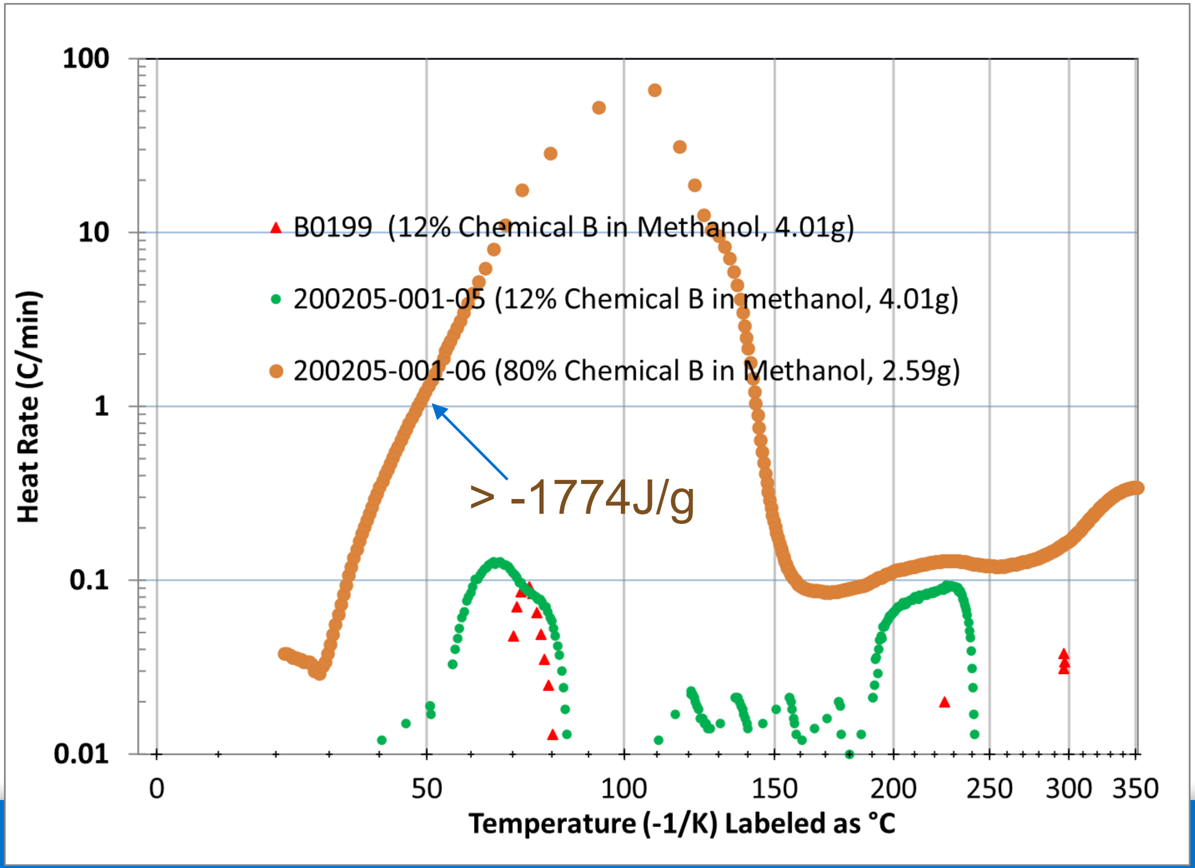
Corteva SME challenged them: onset T is so low, the sample is not freshly made, the tested sample could already degrade before the test.



7, Low onset exotherm

- Retest with a fresh prepared sample in our lab.
- New data leads to the study of worst-case scenario (20% methanol). ➔ we are glad that we didn't miss this ☺





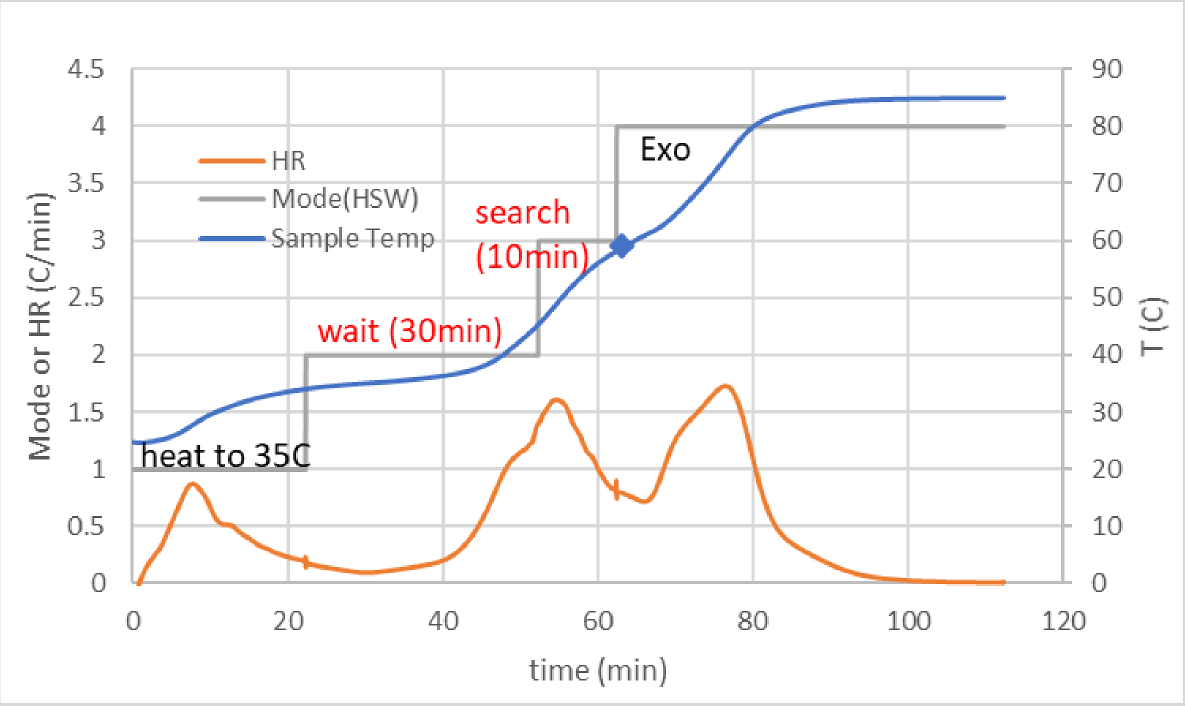
7, Low onset exotherm

B. If a sample reacts at ambient temperature (typically reacting after combine), always try to run shot-add ARC with manually started EXO mode (manually force the ARC instrument into EXO mode, and then shot in to combine chemicals).

Example: for the same sample, Corteva ARC onset at 36C, 3-party ARC onset at 58C.

3eq, shot-add ARC (no mixing) Phi=3.2?	36.2	0.24	-93 (vs. -96.3)

Fresh reagent	ARC in HC, no stirring	air, Phi=1.717	Exo	58.2	74.5	85.0	-92.0	max SHR 5.6 °C/min, max pressure rate 1.7 bar/min
			Exo	145.5	150.1	150.1	-15.8	
			Exo	160.5	218.4	244.6	-288.7	



Conclusion

- General guidance
  - Make sure your instruments give you reliable data

    Adiabatic limit;

    Pressure tubing and condensation;

    Sample loading size;

    Bomb rupture;

    Bomb compatibility;

    Low onset exotherm
  - Avoid to rely on a single data point to tell the reactivity hazard
  - Always investigate the cause of data inconsistency
  - If possible, try to get consistent data from different instruments

    e.g., ARC + DSC:

- Thank you for your time.

- Happy to answer any question!!!

- Acknowledgement: Corteva RC team, Dow RC team.