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Design of Safe Energetic Processes Using the Advanced Flow Reactor

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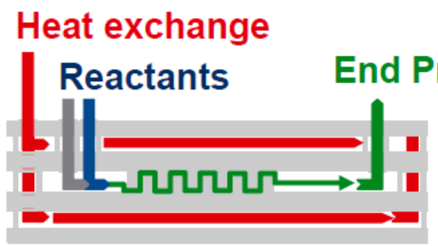
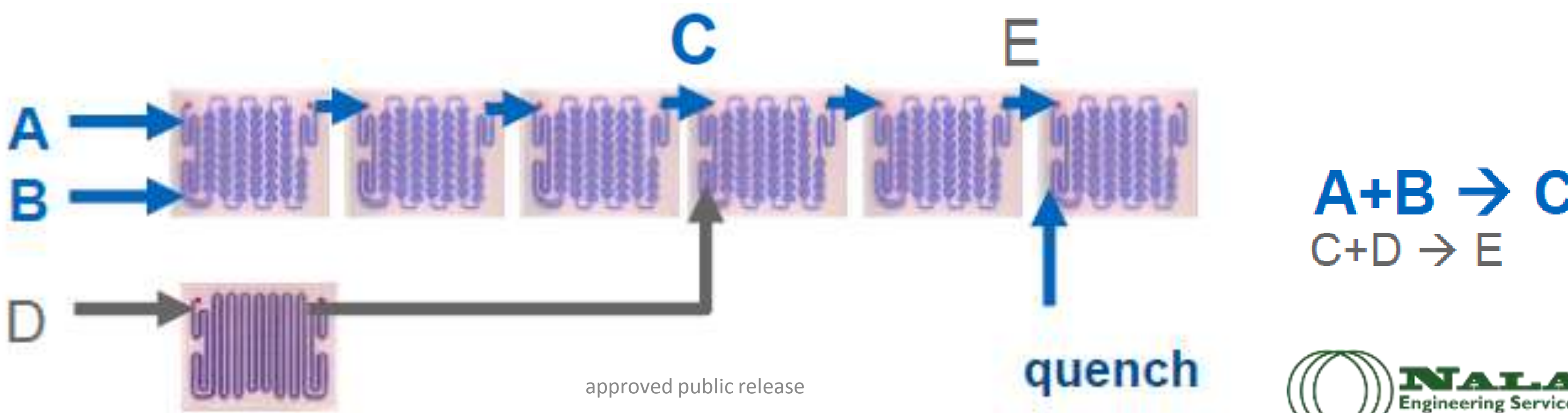
SOLUTIONS THAT SCALE

Corning Advanced-Flow™ Reactor Design
What is it?

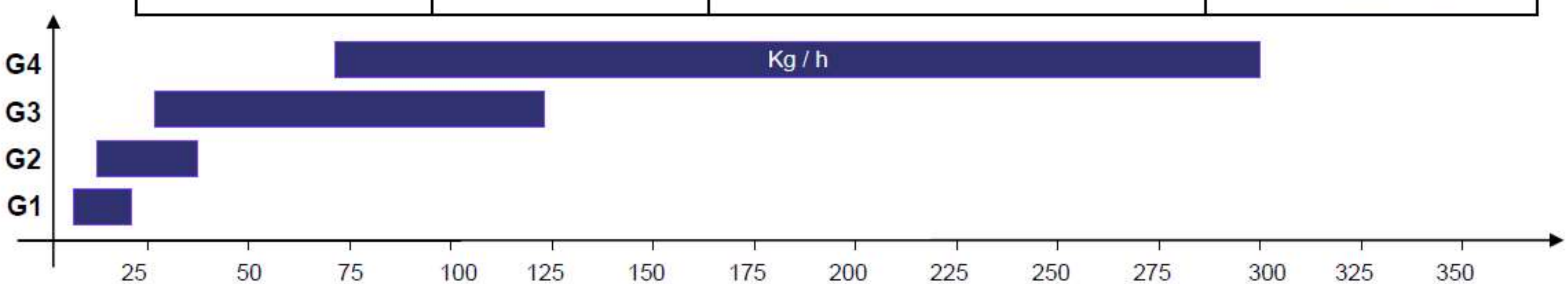


- Glass plate sandwich!
- Modular and flexible
- Similar mixing through each system (LF – G4)
- Similar heat exchange through each system (LF-G4)
  - ***Greater than 100 times heat transfer compared to batch***!!
- Limitations—at the mercy of reaction kinetics



Scalability

	Low Flow	G1	G2	G3	G4
Single Plate volume (ml)	0.45	8 – 11	21 – 25	55 – 65	200 – 260
T° -60 to 200°C P° up to 18 bar	High flexibility, metal-free reaction path From laboratory to production: a seamless scale-up				
	• Low internal volume • Use minimal number of reactants	• Small volume • Scalability from test to production • Process dev.and optimization tool	• Continuous production of large amount of chemicals • Several tons annually	• Realize potential of full scale economy	• Large volume • small footprint • Processing > 300 kg/hr • Superior corrosion resistance of SiC



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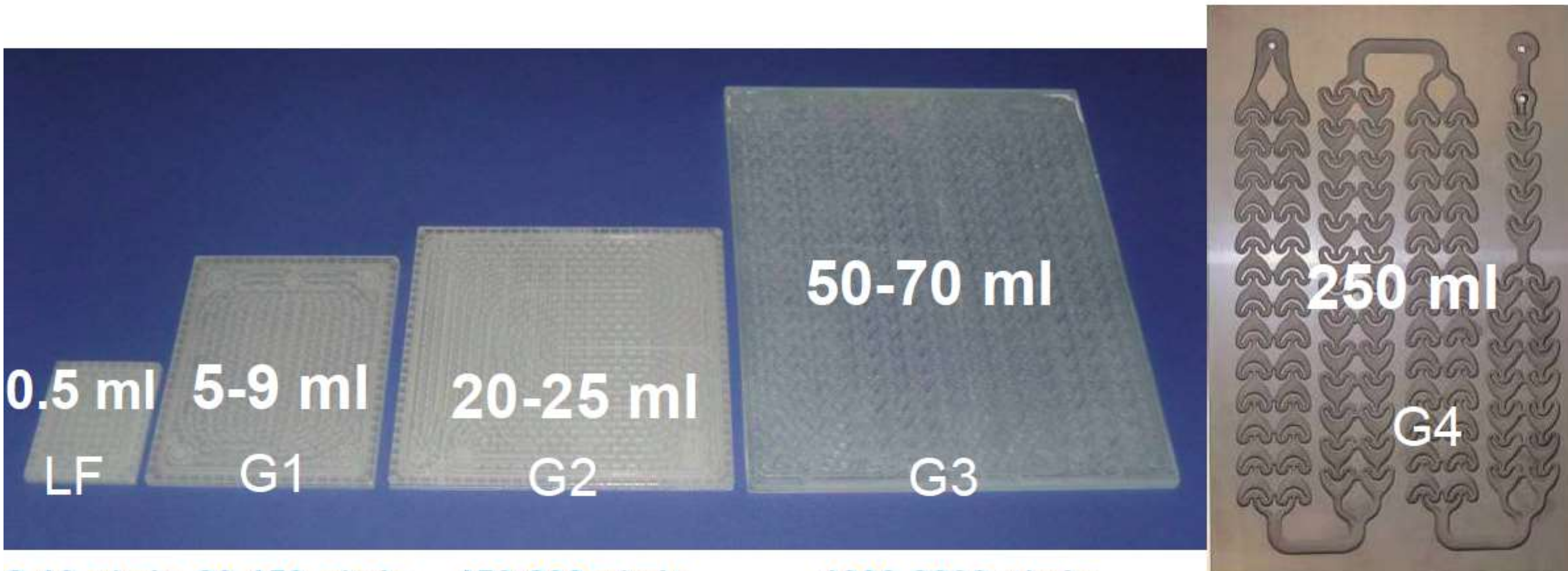
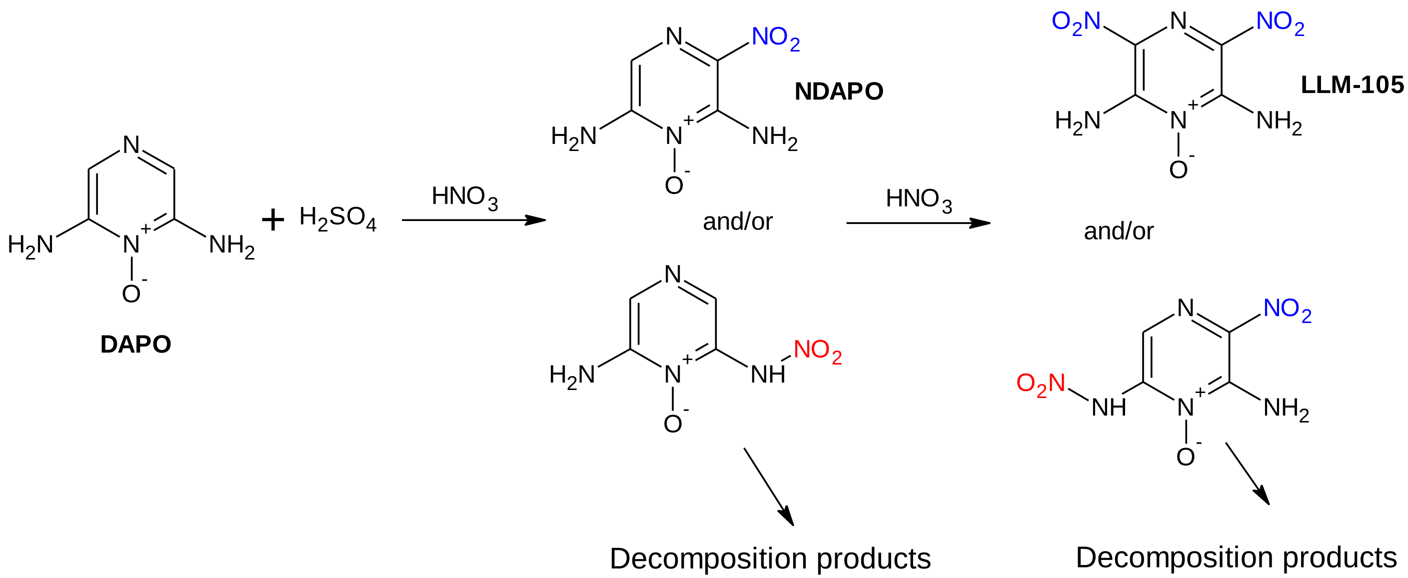
Fluidic Module Volumes and Feed Rates



2-10 g/min 30-150 g/min 150-600 g/min 1000-3000 g/min 1000-4500 g/min

LLM-105 from DAPO

- Proposed reaction scheme for LLM-105 from DAPO



- Yield loss believed to be due to competitive N-nitration vs. C-nitration

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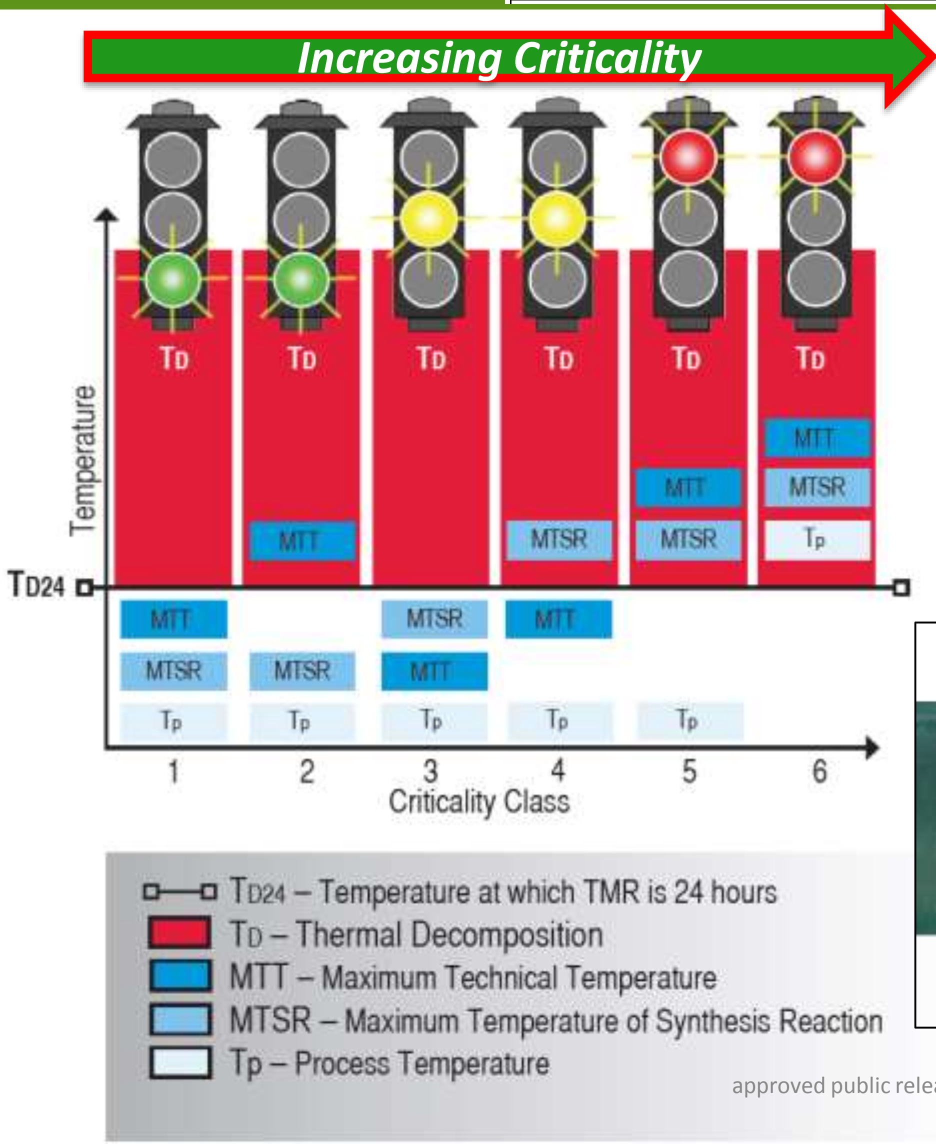
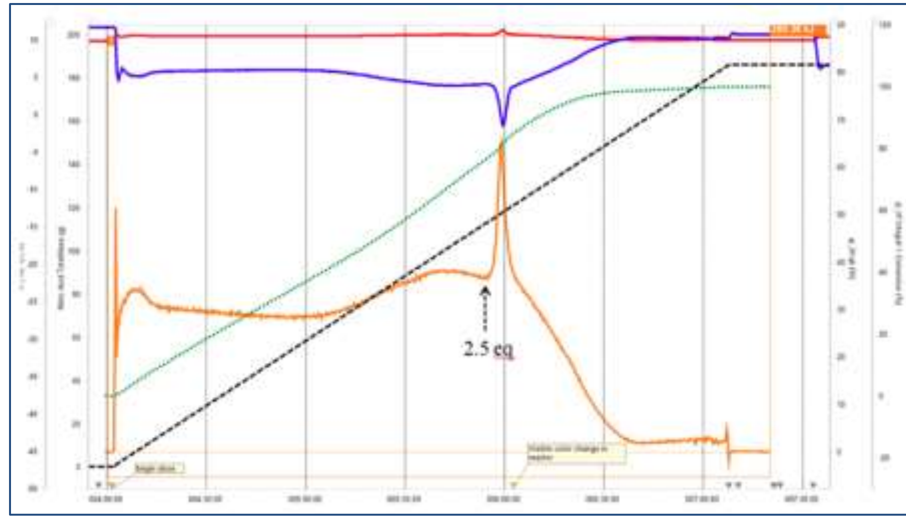
Safety

Summary of Criticality Class Data		
Key Parameters	**Value**	**Comments**
Formation of LLM-105 from DAPO		
Heat of Reaction (100 g of DAPO)	280.4 kJ	Exothermal, medium (-189.0 kJ/kg)
$\Delta T_{adiabatic}$	126 K	Medium
MTSR (Tp +ΔTadiabatic)	49°C (133 °C)	Assumed 25% accumulation (conservative), Tp=7°C
T_{D24}	96°C	Based on ARSST
MTT	138°C	Boiling point of 20% Oleum





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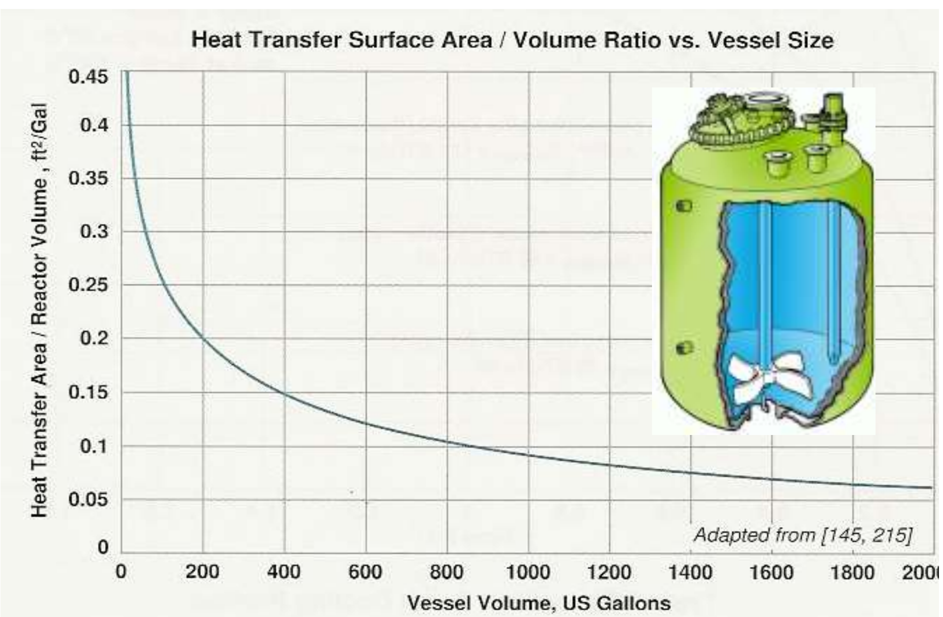
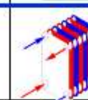
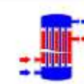
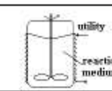
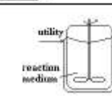
Benefits of Heat Transfer

- Batch reactors have increasingly less heat transfer rate as they increase in scale (reduced surface area, increased volume)
- Long dose times/slow throughput, large volumes of unstable materials



Method		Volumetric heat transfer coefficient (MW/m^3K)
Ceramic SiC fluidic modules		1.5
*Corning glass fluidic modules (water/water, ~ 0.7 m/s)		1.6
*Plate (*metallic*, 4 mm spaced; water/water, 1 m/s)		1.25
*Shell and tubes (*metallic*; water/water; 1 m/s)		0.2
*Batch with external heat exchanger		10^{-2}
*Jacketed batch		10^{-3}

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KINETIC MODEL

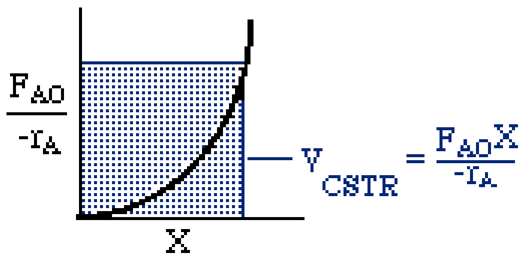
Reaction Monitoring

EasyMax system

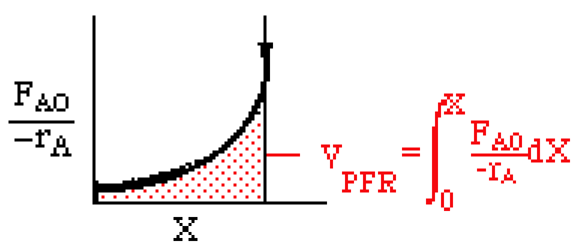
- Temperature logging
- Easy sampling/ reaction quenching
- Low volume
- Efficient

Fogler, Scott, ***Elements of Chemical Reaction Engineering***, Prentice Hall, 3rd, edition

CSTR



PFR



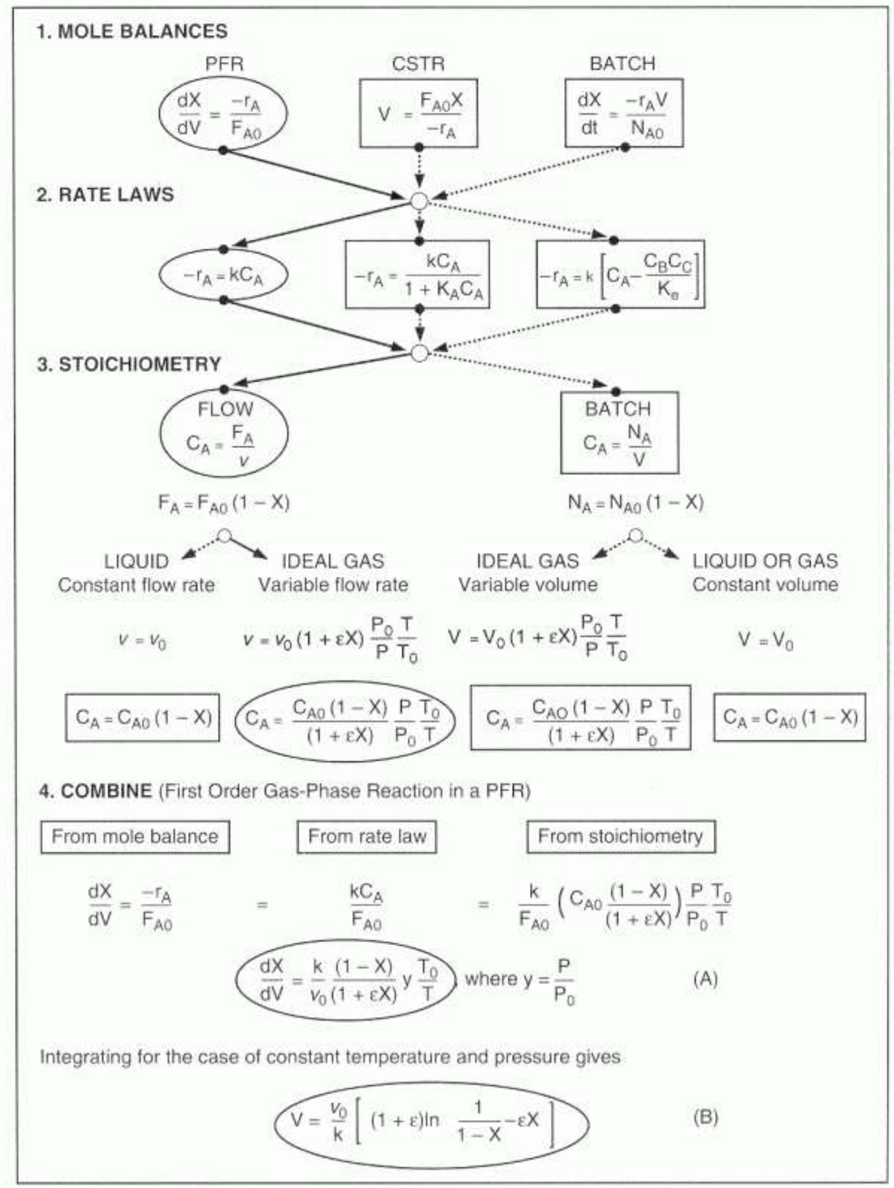
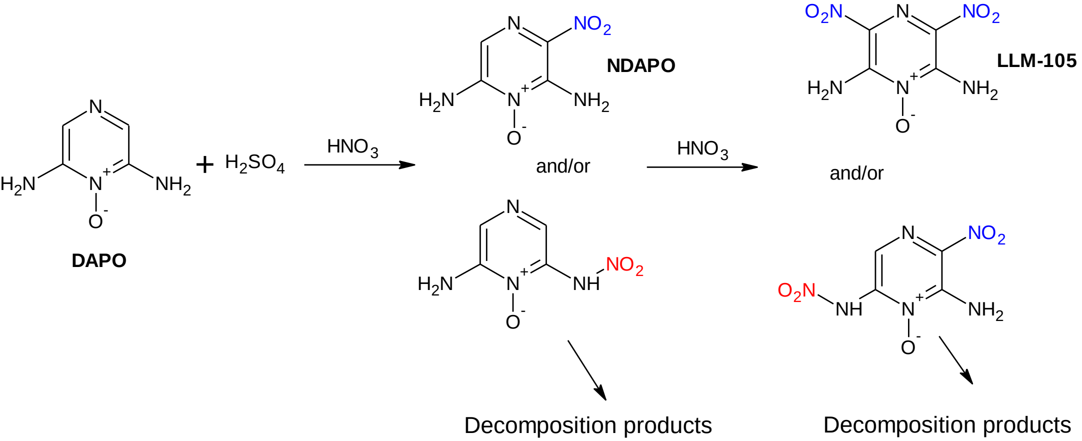
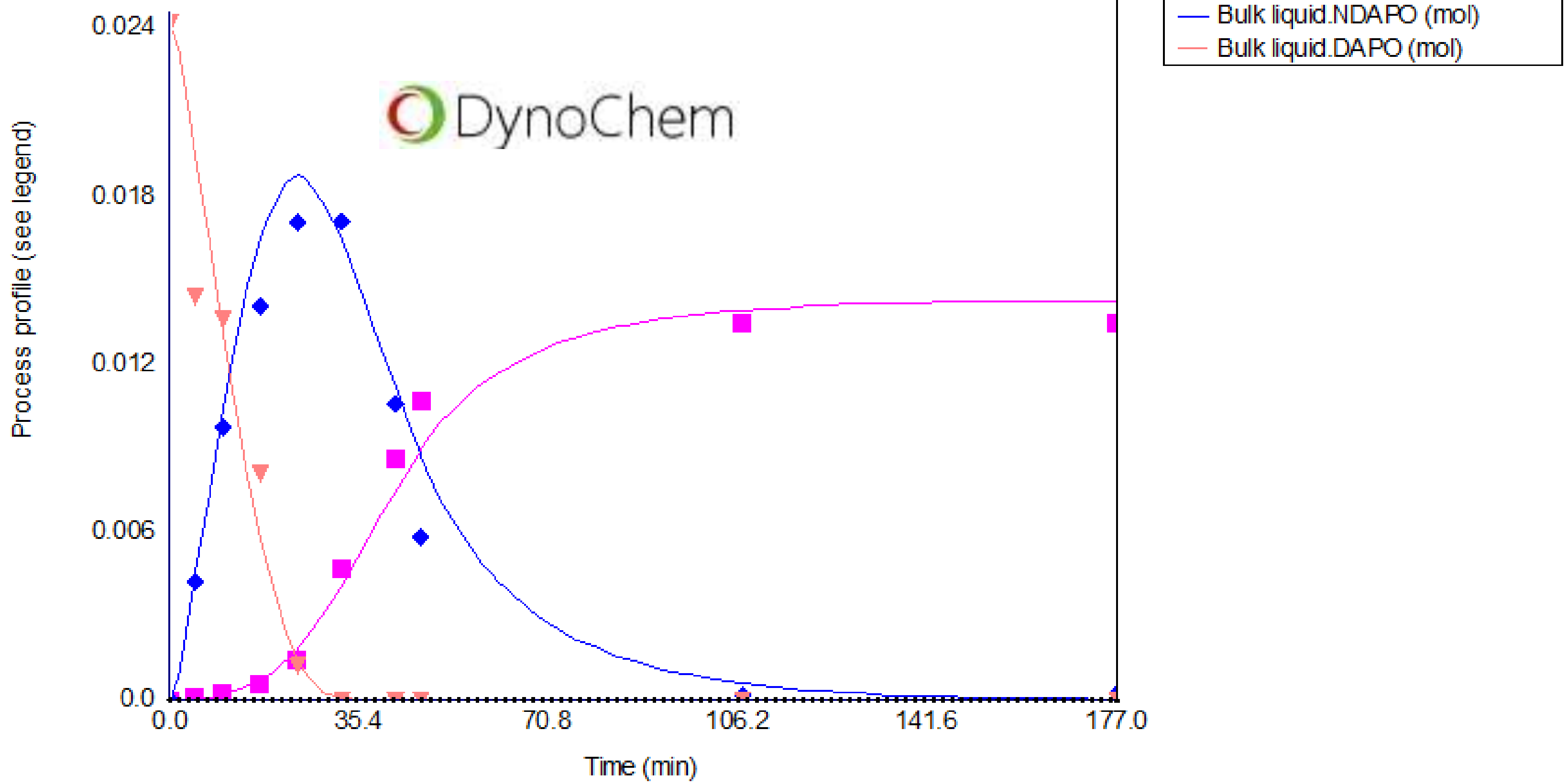


Figure 4-2 Algorithm for isothermal reactors.





Solid points are the HPLC samples, Lines are the model

Data and Model

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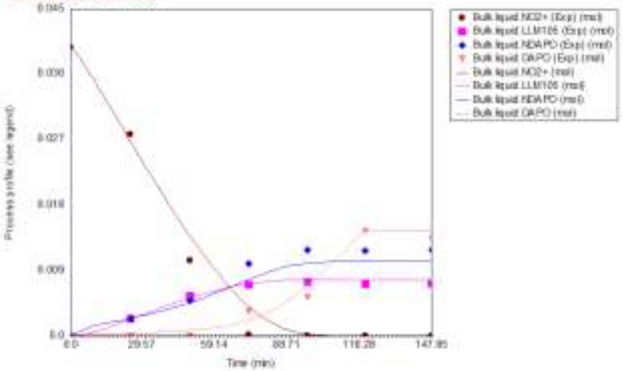
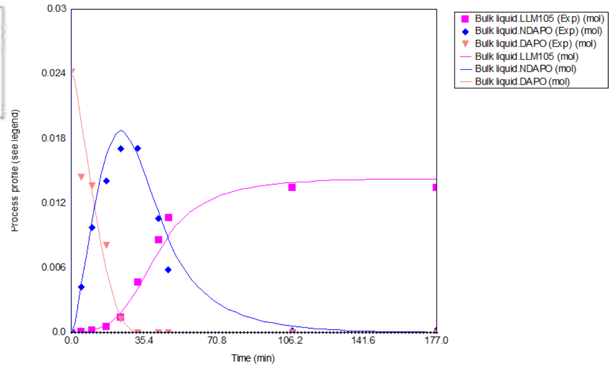
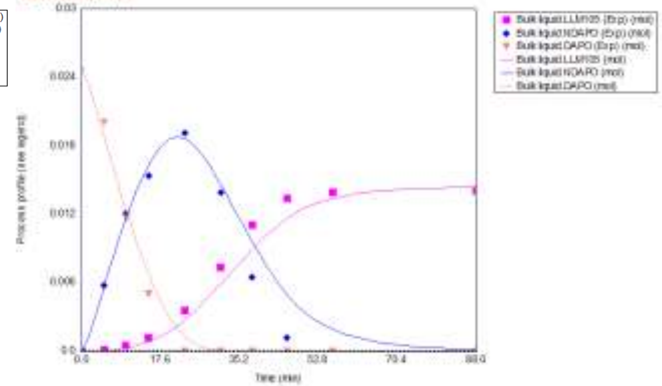
EASYMAX reverse



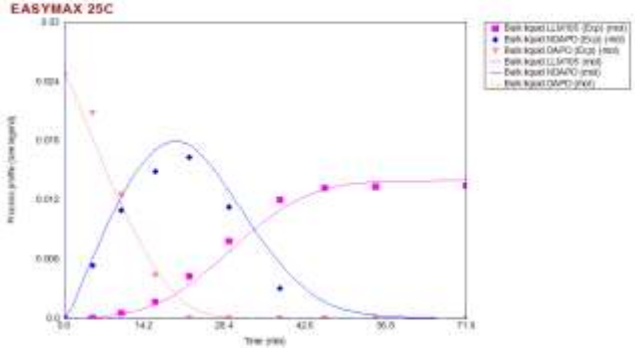
EASYMAX 5C



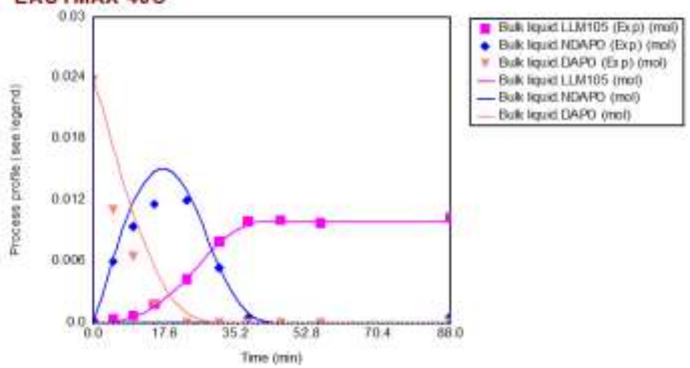
EASYMAX 15C



EASYMAX 25C



EASYMAX 40C



Reaction Kinetics for DAPO

- Kinetics regressed from five reactions.
  - Four reaction where nitric dosed to DAPO in sulfuric acid
    - Each done at a separate temperature (5 ^oC, 15 ^oC, 25 ^oC and 40 ^oC)
  - One done where DAPO dosed to nitric at 15 ^oC
- Model Fit to the follow reaction mechanism

$$k = k_{ref} * e^{-\frac{Ea}{R} * \left(\frac{1}{T} - \frac{1}{T_{ref}}\right)}$$

$T_{ref} = 15\ ^oC$

Reaction 1	DAPO	+	NO2+	>	NDAPO			
Reaction 2	NDAPO	+	NO2+	>	LLM105			
Reaction 3	NDAPO	+	NO2+	+	H2O	>	Decomp1	
Reaction 4	DAPO	+	2NO2+	+	H2O	>	Decomp2	

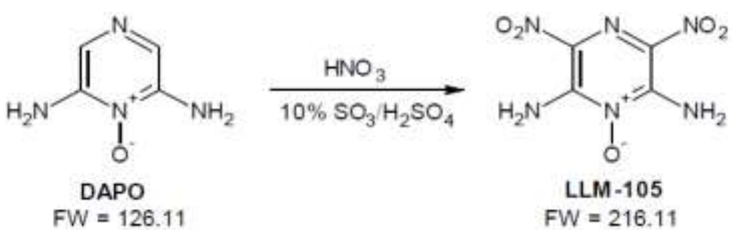
Decomposition of DAPO is second order in nitric

- Regressed rate constants, activation energies and heats of reaction

Reaction	k_{ref}	Units	Ea	Units
1	1.81E-02	L/mol.s	34.01	kJ/mol
2	1.15E-03	L/mol.s	49.99	kJ/mol
3	2.17E-04	L2/mol2.s	76.69	kJ/mol
4	1.63E-03	L3/mol3.s	50.00	kJ/mol

Reaction #									ΔHrxn kJ/mol
1	DAPO	+	NO2+	>	NDAPO				-29.049
2	NDAPO	+	NO2+	>	LLM105				-141.035
3	NDAPO	+	NO2+	+	H2O	>	Decomp1		-148.419
4	DAPO	+	2NO2+	+	H2O	>	Decomp2		-25

Temperature drives decomposition of NDAPO



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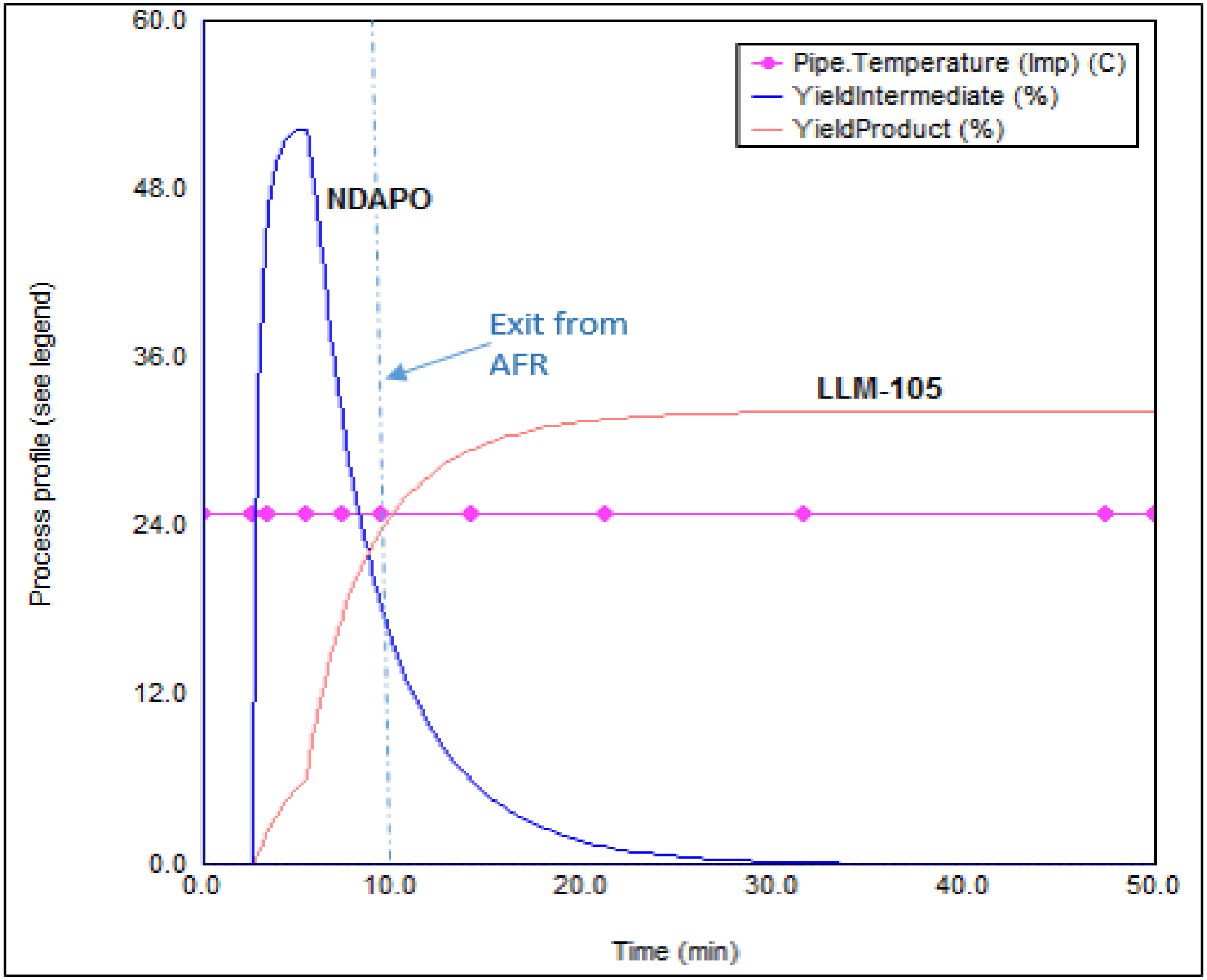
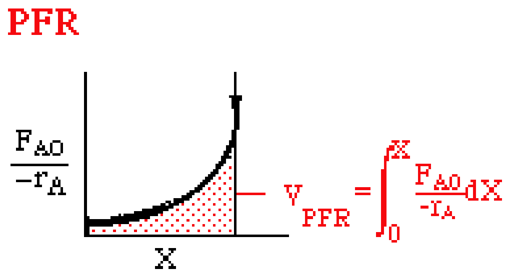
DynoChem process model simulation of LLM-105 reaction in a PFR





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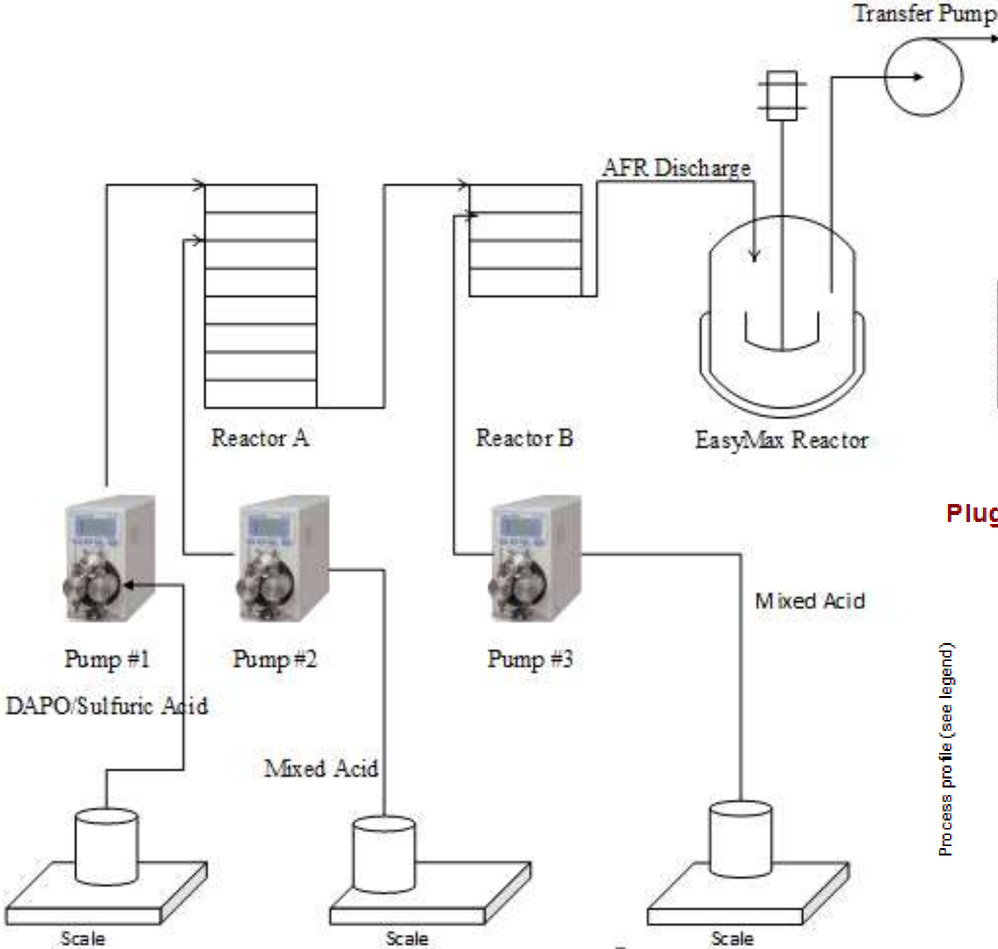
PFR and CSTR Models

	PFR configuration with one feed	PFR configuration with two feeds	PFR configuration with three feeds	3 CSTR
DAPO Feed rate (kg/hr)	1.24	1.24	1.24	1.24
Nitric acid equivalence	5.4	1.35 per feed x 2, 2.7 total	0.9 per feed X 3, 2.7 total	2.7
Nitric feed points	At entrance	At entrance, and 0.77m from entrance	At entrance, 0.77, and 1.89m from entrance	40% reactor 1, 40% reactor 2, 20% reactor 3
Feed temperatures (^oC)	15	5	5	5
Jacket temperature (^oC)	5	-5 entire length	-5 entire length	-13.7 reactor 1, -8.5 reactor 2, -3.8 reactor 3
Max reactor temperature (^oC)	55	32.3	20.3	5.1
Yield to LLM-105 %	5.3	43.6	52.6	52.8
Reactor length (m)	1.0	2.0	4.0	N/A
Reactor volume (L)	4.0	8.1	16.2	2x5 +1x10 =20L
Production rate (kg/hr)	0.122	0.926	1.117	1.062

High nitric eq. and feeding all at once leads to elevated temperatures and low yields

Proposed Configuration



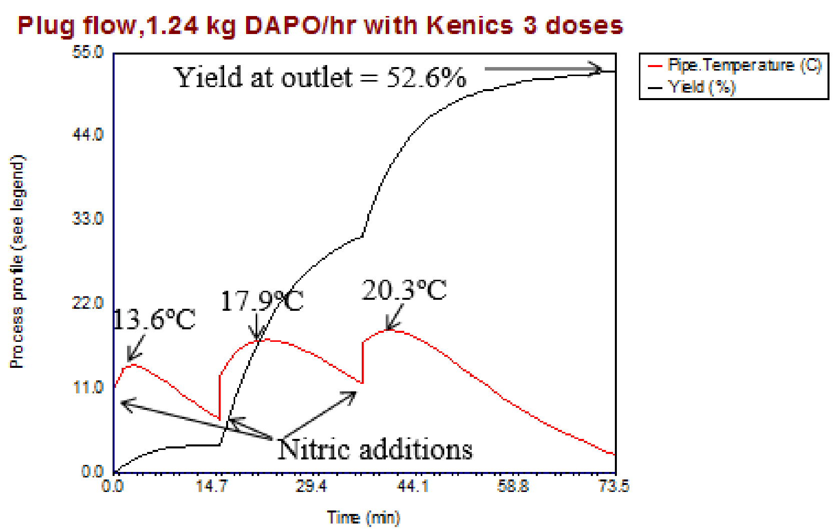
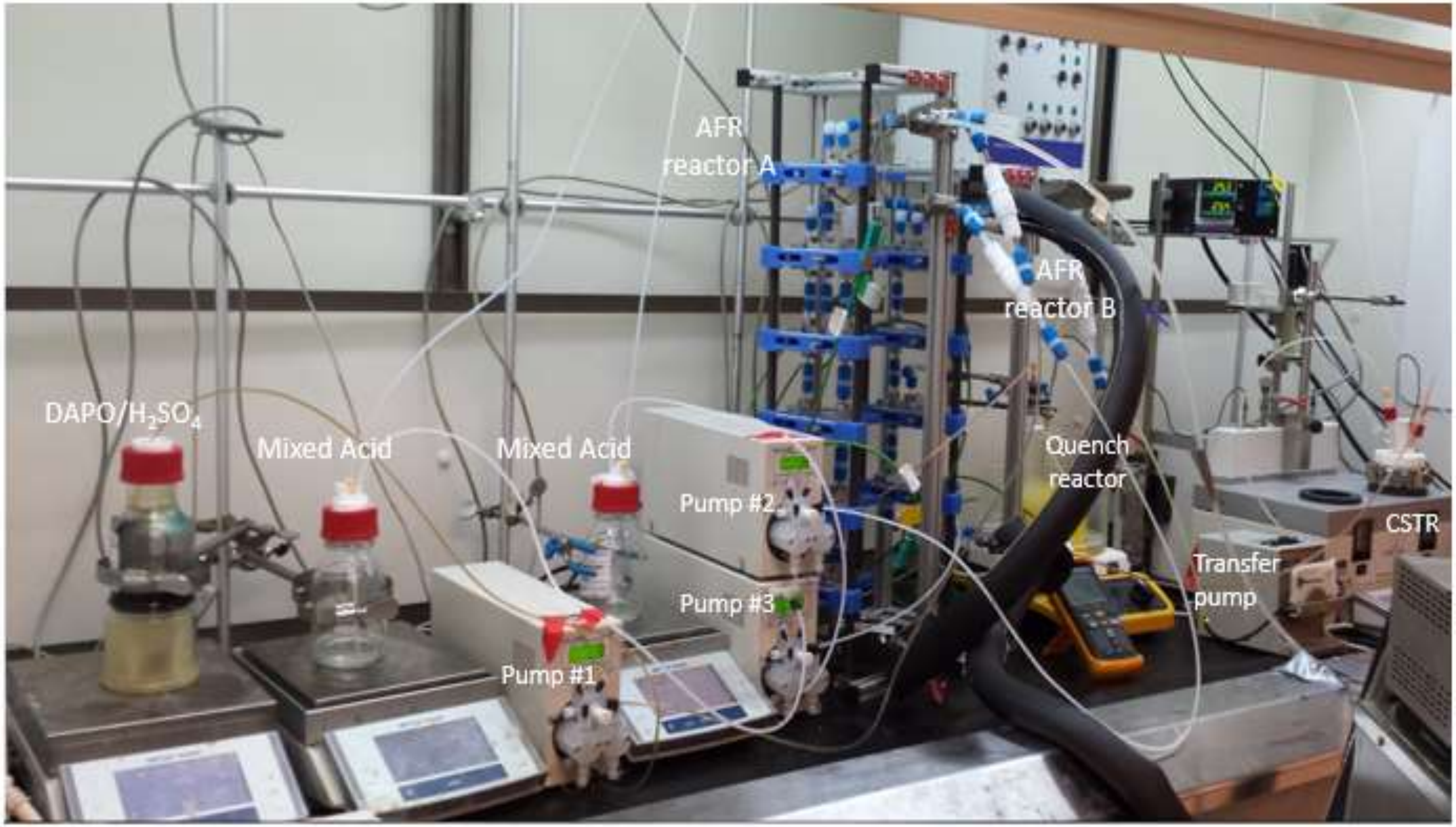
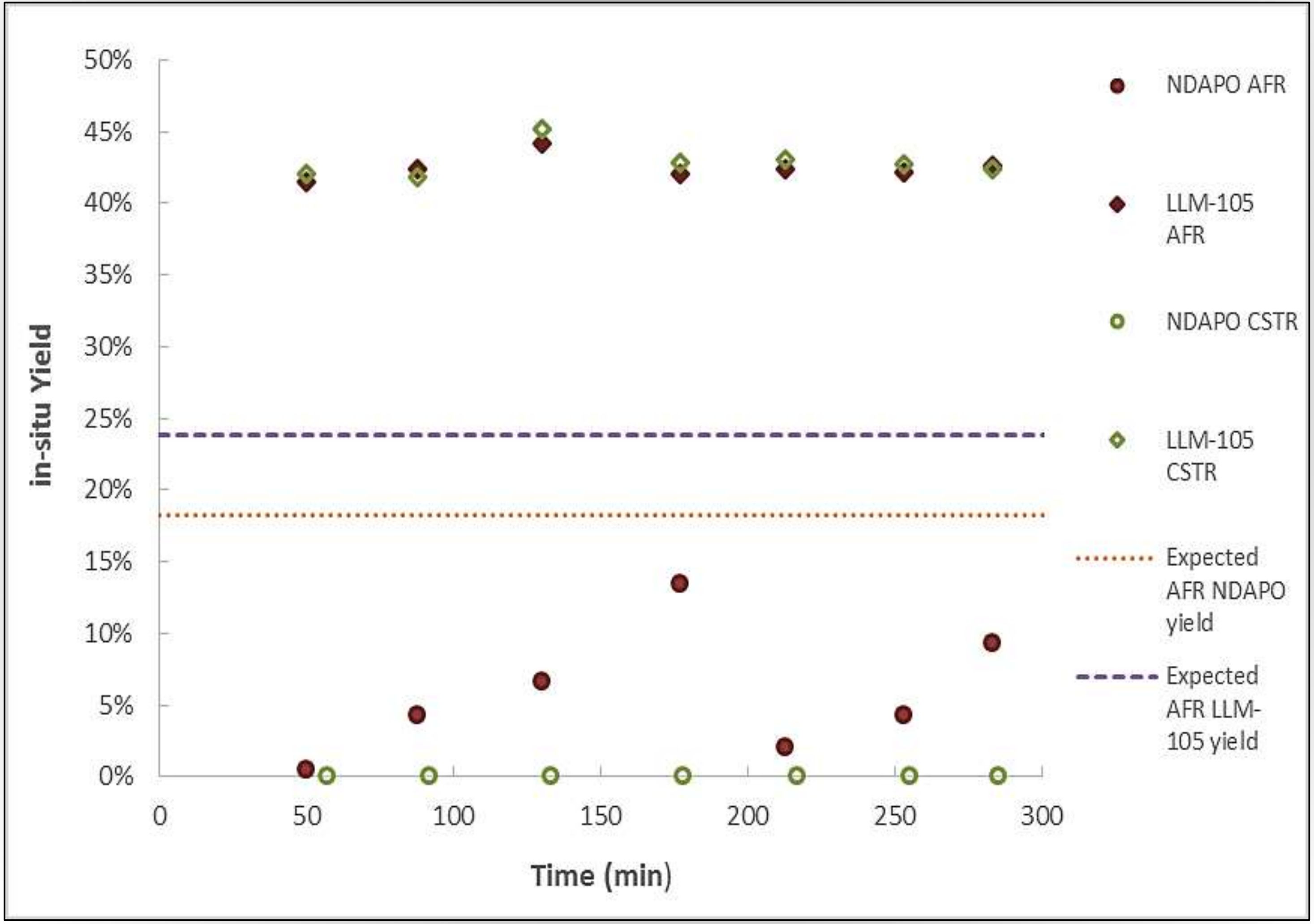


Photo of Setup



Review of Results



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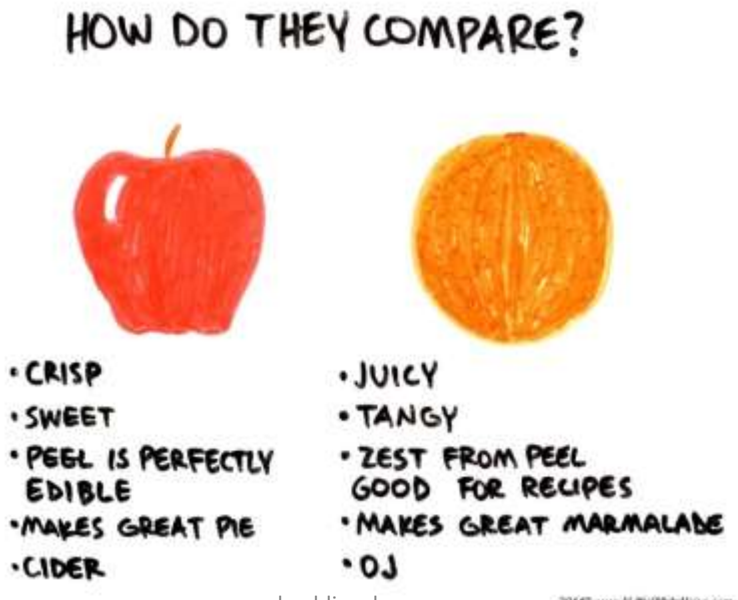
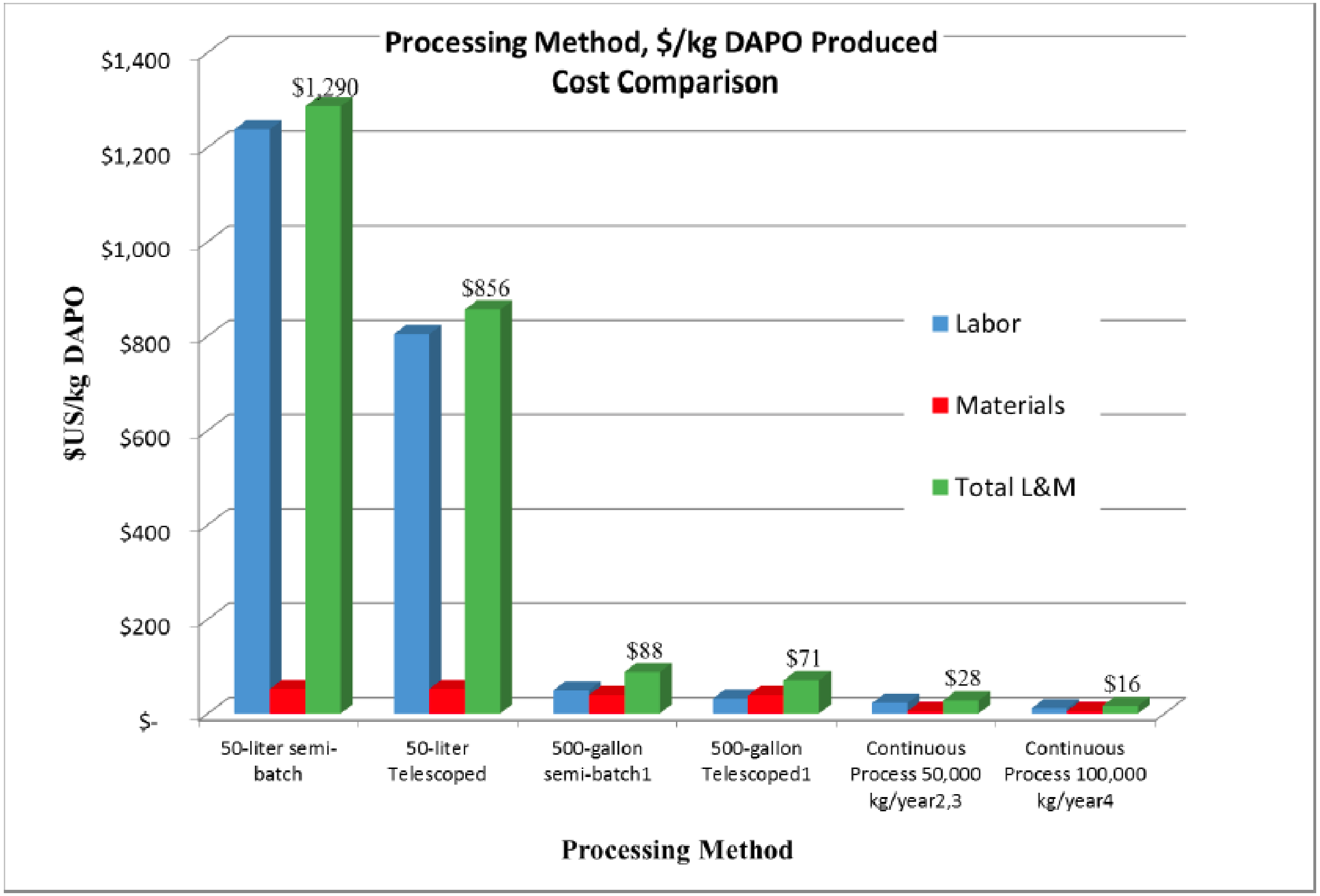
Batch vs AFR
What if there was something better?

- How do we know if our reaction is mass transfer limited?
- How do we know if our reaction is mixing sensitive? Selectivity?
- If batch reactors are utilized to determine mass transfer and mixing sensitivities we limited to **batch reactor** limitations.
- When we start using **better tools** we expect better results.



Cost

Applying Continuous to DAPO



Summary

- LLM-105 can be made continuously, but the feed of nitric needs to be split across the reactor to prevent high nitric acid concentrations
- Mixing in the reactors needs to be able to dissipate nitric concentration gradients.
- Fast exothermic reactions may lead to local temperature spikes
  - Not an issue with AFR due to high heat transfer coefficients across scale
- Minimize amount of nitric acid to limit DAPO and NDAPO decomposition