

Reduction of Acidic and Toxic Waste Streams in Explosives Manufacturing Using Electrochemical Nitration

WP20-1010

Matthew Burk
Nalas Engineering Services, Inc

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14. ABSTRACT The technical objectives of this project are listed below: <ul style="list-style-type: none"> • Task 1: Develop and Optimize Electrochemical Nitration in Batch <ul style="list-style-type: none"> -Explore C-nitration under aprotic and aqueous conditions (Toluene to DNT, Anisole to DNAN) (Nalas) -Explore O-nitration using understanding from C-nitration (alcohols to nitrate esters: nitroglycerine, BTTN) (Nalas) • Task 2: Apply Optimized Batch Conditions to Flow Reactor <ul style="list-style-type: none"> -Conduct reaction modelling for flow parameters (Nalas) -Proof of concept demonstration in flow (Nalas) -Preliminary sustainability and environmental impact assessment (Yale) 					
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Project Team

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Yale University

Background

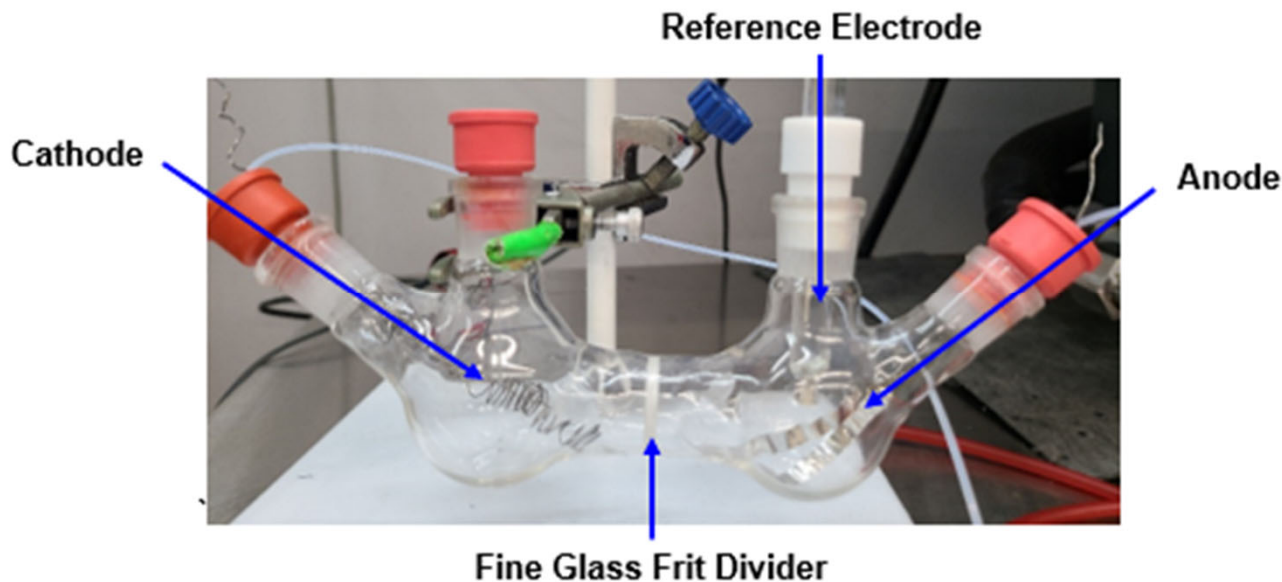
- Addressing statement of Need WPSO-20-C2 with the aim to develop innovative scalable synthetic approaches leading to the production of energetic materials that eliminate or dramatically reduce hazardous waste streams from nitration processes used in manufacturing
- Project execution October 2020

Technical Objectives, Task 1

Task 1: Develop and Optimize Electrochemical Nitration in Batch

- ◆ Explore C-nitration under aprotic and aqueous conditions (Toluene to DNT, Anisole to DNAN) (Nalas)
- ◆ Explore O-nitration using understanding from C-nitration (alcohols to nitrate esters: nitroglycerine, BTTN) (Nalas)
- ◆ Note: Yale conducted work on analogous substrates to help identify promising conditions for Nalas to try with energetic substrates for both C-nitration and O-nitrations

H-Cell:

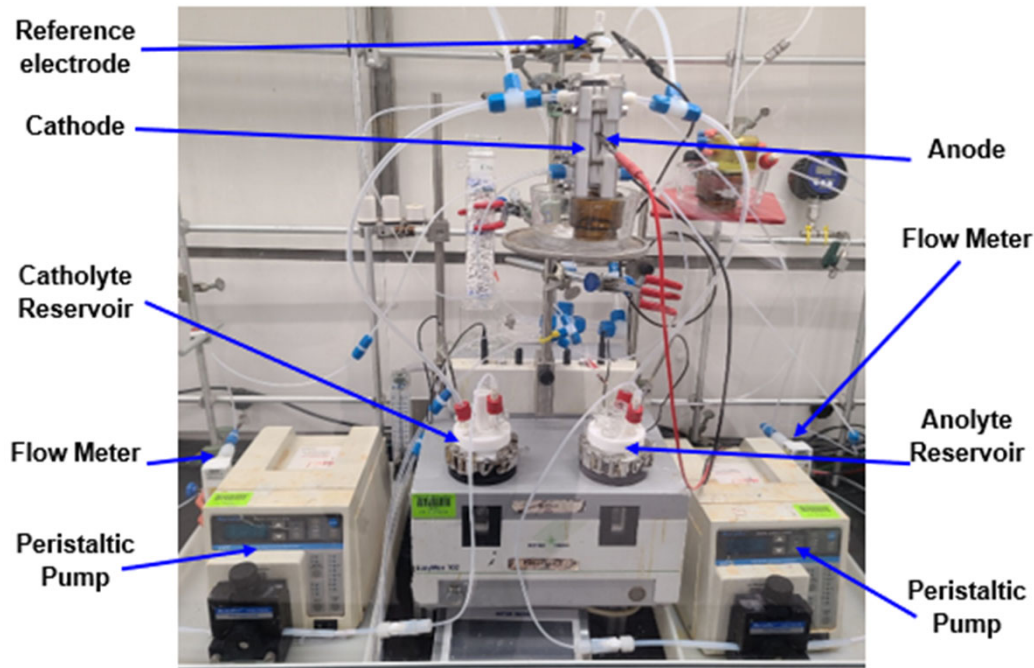


Technical Objectives, Task 2

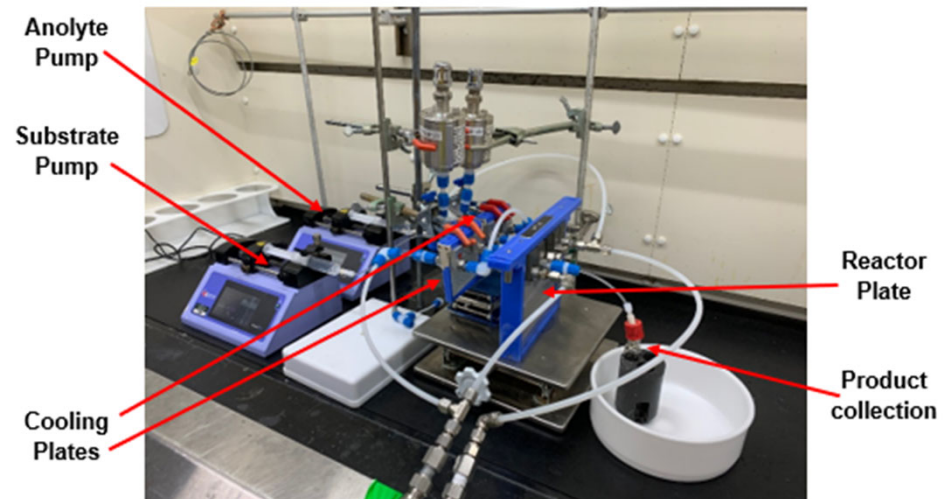
Task 2: Apply Optimized Batch Conditions to Flow Reactor

- ◆ Conduct reaction modelling for flow parameters (Nalas)
- ◆ Proof of concept demonstration in flow (Nalas)
- ◆ Preliminary sustainability and environmental impact assessment (Yale)

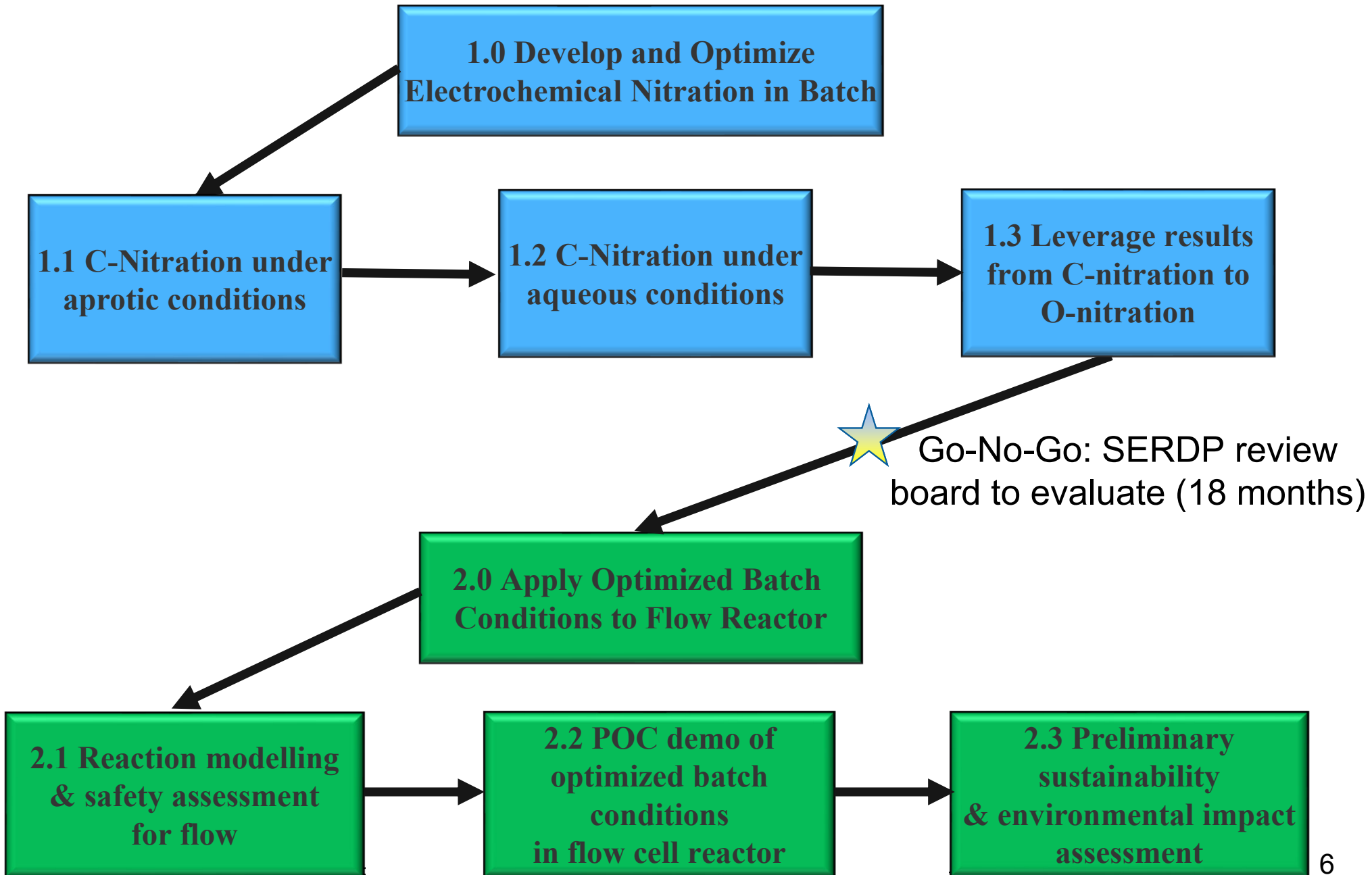
Flow Electrolysis



Flow Nitration



Technical Approach



RESULTS:
TASK 1.0 DEVELOP AND
OPTIMIZE ELECTROCHEMICAL
NITRATION IN BATCH

Task 1.0 Results

- Initial experiments were conducted in undivided cells with direct electrolysis of the substrate in the cell -> product was reduced at the cathode and overall yields were poor
- Transition to an H-cell was made where both the cathode and anode compartments were of equal size and divided by a fine glass frit.
- Direct electrolysis of substrates toluene, anisole, or glycerol with a fine frit H-cell all showed product formation,
 - ◆ Low yields, presumably due to several factors including radical recombination reactions, radical transfer or proton transfer involving the aryl methyl group (toluene) or methoxy group (anisole)
 - ◆ Difficult further oxidation of the electron deficient mono nitro products at the anode to the reactive radical cation species
- Cyclic voltammograms suggested that productive product formation was occurring due to formation, in the anode compartment, of nitronium ions
- Developed 2 step method

2 Step Method

- Step 1: Oxidize NO_2 in the anode to produce solutions of nitronium ion or N_2O_5
- Step 2: Harvest nitronium or N_2O_5 solutions for nitrations of anisole, toluene, and glycerol, 1,2,4- butanetriol

Result:

- Clean high yielding C-nitration of anisole to DNAN with N_2O_5 , and DNT with low meta content with nitronium
- Clean high yielding O-nitration with N_2O_5 giving NG and BTTN

H-Cell after electrolysis



Cathode

Anode

1. Harvest
anode
nitronium or
 N_2O_5

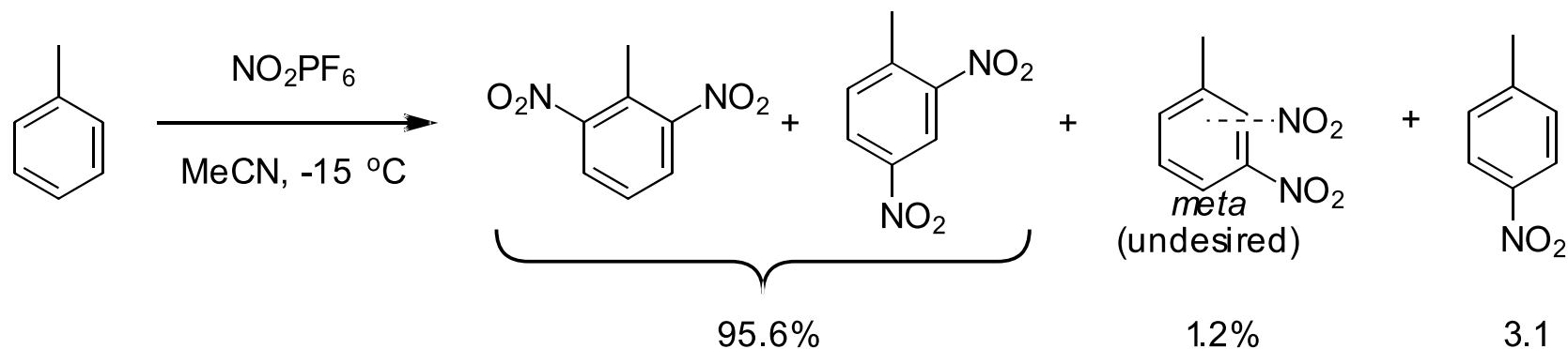
2. Add to
nitration
substrate



Isolated DNT

Two-step Conversion of Toluene to DNT Using Nitronium Solutions

Summary of toluene nitration with nitronium hexafluorophosphate in acetonitrile, gives low meta isomer DNT



- Average meta isomer content across 7 runs from 23 to $-15\text{ }^\circ\text{C}$ is **1.5 area%** by GC versus 4-5 % in mixed acid nitration
- Comparable to literature results with non-electrogenerated NO_2PF_6

TNT Specification Versus meta-Isomers

- Meta isomers lower the melting point of TNT
- DOD mil spec (MIL-DTL-248D) calls out a minimum melting point of 80.20° C (Type I) or 80.40° C (Type II)
- A meta content must be less than 0.85% or 1.3% to maintain acceptable melting point of 80.40 or 80.20 (respectively)
- If TNT can be synthesized with a meta content of ~1%, sellite treatment and/or recrystallization may be avoided
- Huge environmental and cost advantages!

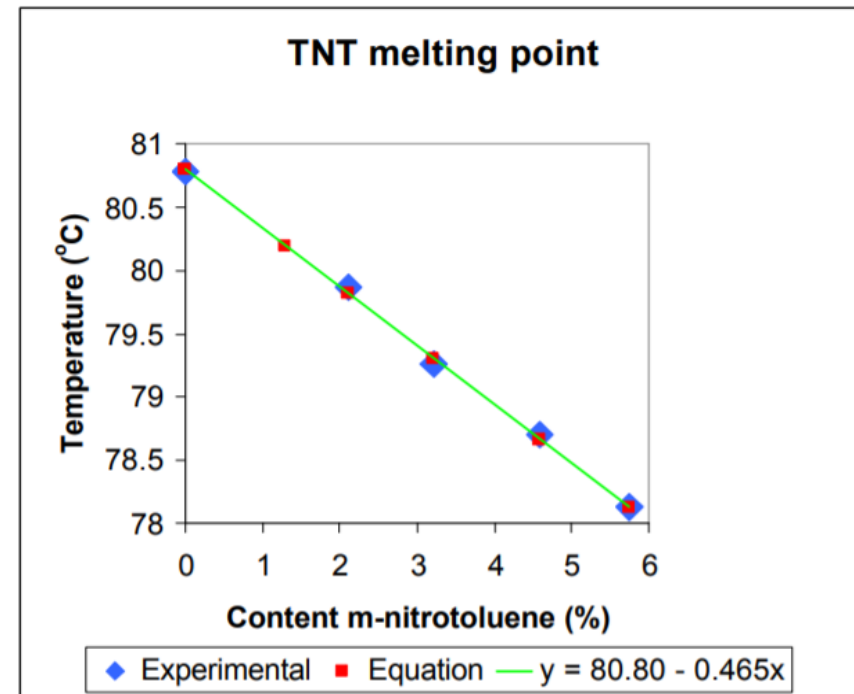


Figure obtained from SERDP project final report WP1408, Ross Millar, QinetiQ Ltd

Salt Survey

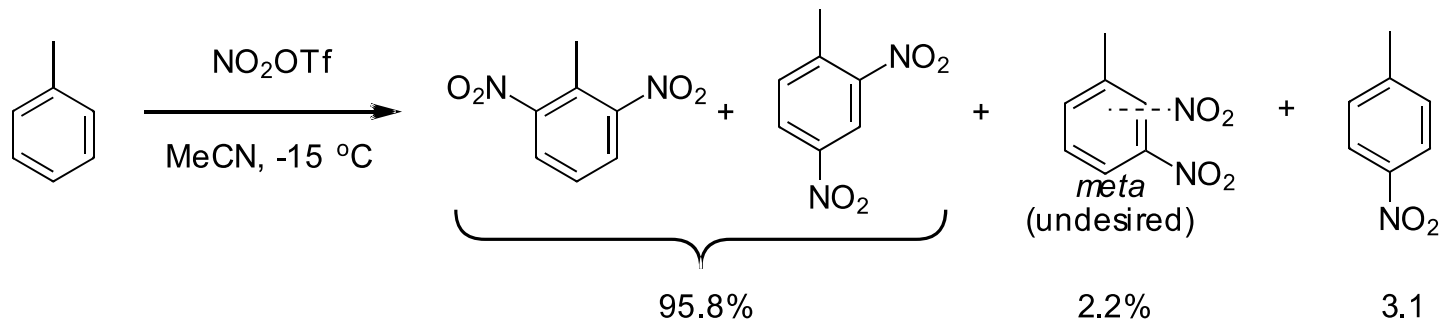
Hexafluorophosphate was found to have poor (~75%) recovery from the nitration reaction which is not sustainable, prompting exploration of other charge carrying salts

Charge Carrier Salt	C-nitration (toluene to DNT)	C-nitration (anisole to DNAN)	O-nitration (1,2,4-butanetriol to BTTN)	O-nitration (glycerol to nitro-glycerin)	Salt Recovery	Issues
TBAHFP	Green	Green	Not attempted	Not attempted	Red	High organic solubility = difficult isolation
Lithium tetrafluoroborate	Green	Not attempted	Not attempted	Not attempted	Red	Instability during salt recovery and recycling
Lithium triflimide	Green	Not attempted	Not attempted	Not attempted	Red	High organic solubility = difficult isolation
Lithium triflate	Green	Not attempted	Not attempted	Not attempted	Green	Costly salt
Lithium nitrate	Yellow	Green	Green	Green	Green	Low solubility

Salts surveyed for use in the electrochemical generation of nitronium species and their use in nitration reactions. Green = success with method or product, Yellow = partial success with further optimization possible, Red = not practical, not optimizable for scale

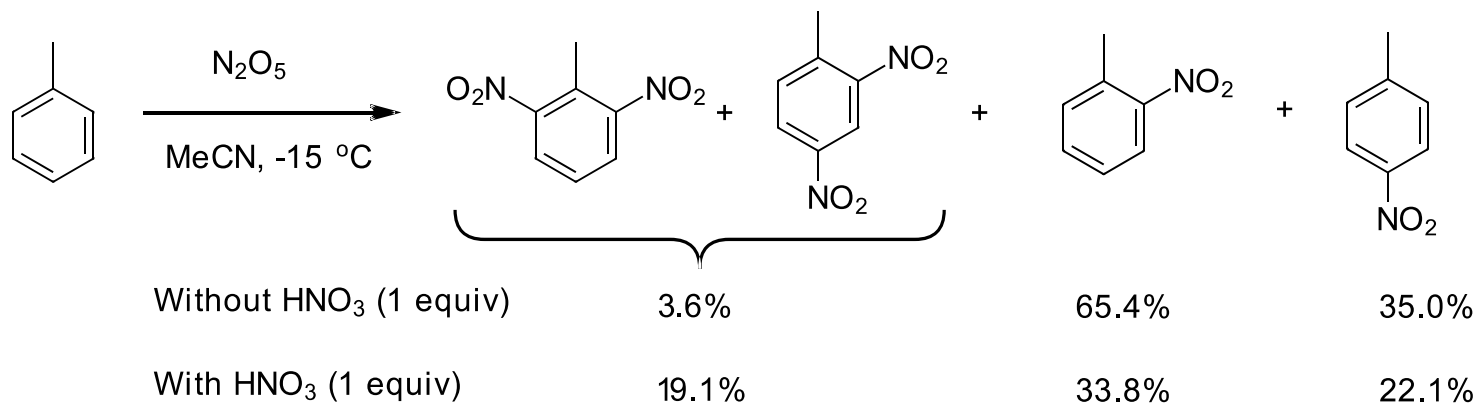
Two-step Conversion of Toluene to DNT Nitronium Solutions, Other Salts

Toluene nitration using lithium triflate as charge carrying salt producing nitronium triflate



Meta isomer content was found to be **2.2 area%** by GC

Toluene nitration using lithium nitrate as charge carrying salt (N_2O_5)



- Toluene nitration Using N_2O_5 in acetonitrile results in mostly MNT
- qNMR analysis is likely too insensitive to determine small amounts of meta isomer formed

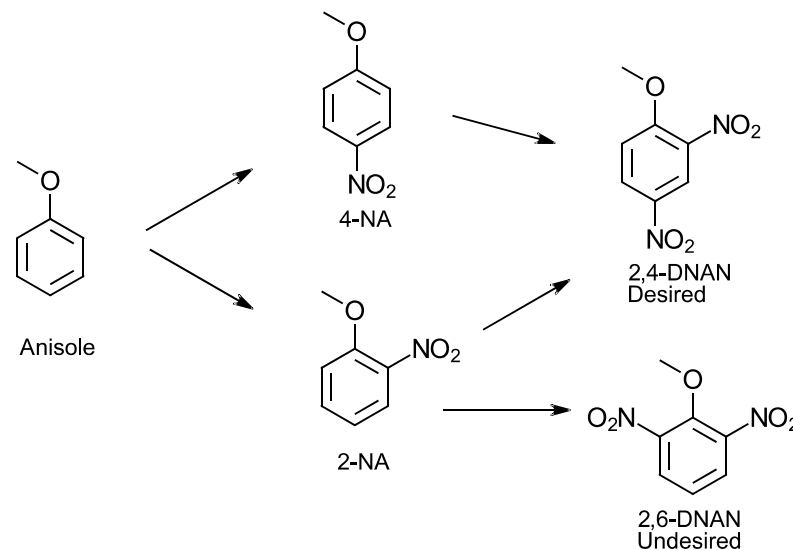
Conductive Salt Decision Making

- The reactivity, useability and recovery of various salts to make nitronium species is understood
- Many salts are costly and have poor recovery or
- Many nitronium species that are too highly reactive for active substrates like anisole
- Lithium nitrate as a soluble conductive salt which when electrolyzed with NO_2 provides N_2O_5 was favored.

N_2O_5 is useful for C-nitration of anisole and O-nitration of glycerin and 1,2,4-butanetriol– Focused on these substrates and not toluene --per SERDP direction

Example of C-Nitration of Anisole to DNAN Using N_2O_5

- Nitration of anisole was initially studied using electrochemically generated nitronium hexafluorophosphate which was found to be too reactive resulting in decomposition (data not shown).
- Using lithium nitrate to give N_2O_5 after electrolysis provided the correct reactivity

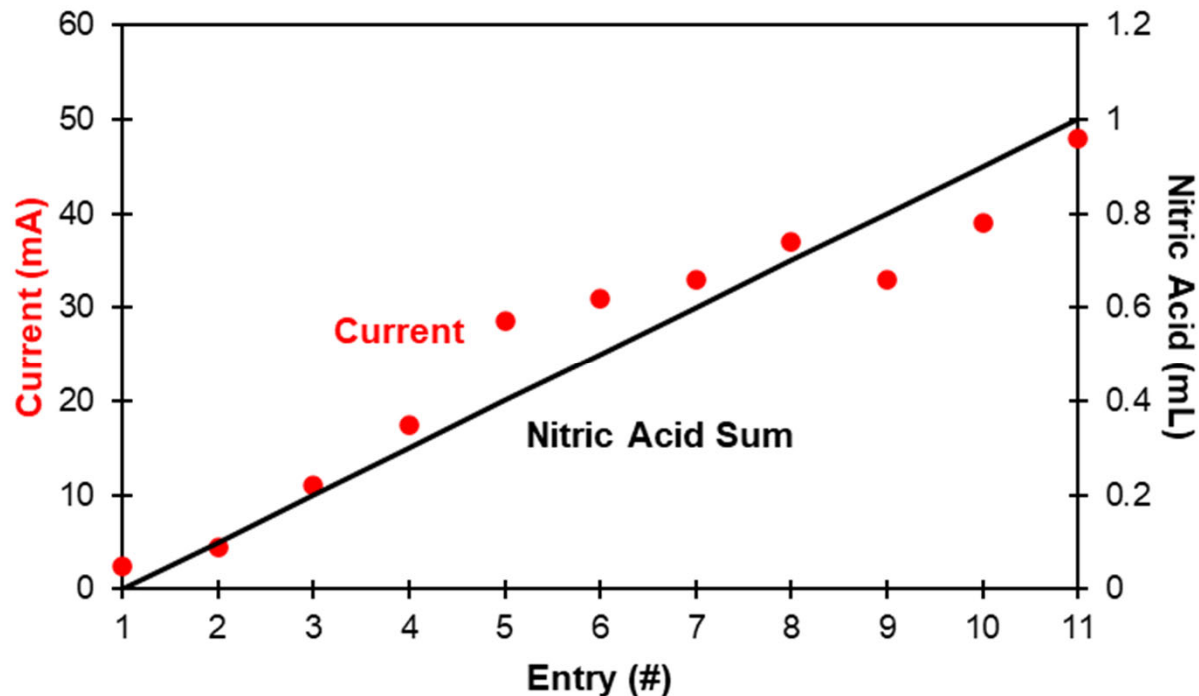


H-cell electrolysis to give N_2O_5 , followed by nitration

Reaction	Temp. (°C)	Starting Material	Product(s) <i>in situ</i> Yield (%) qNMR				
			2-NA	4-NA	2,4-DNAN	2,6-DNAN	Total <i>In-Situ</i> Yield
NAL-093-11005-S3	-15 to 20	Anisole	14.1	14.1	60.1	8.6	96.9

- The 2,4 to 2,6 ratio of DNAN isomers is a respectable 7.0

Conductivity Study In H-cell with <1 equiv. Nitric Acid



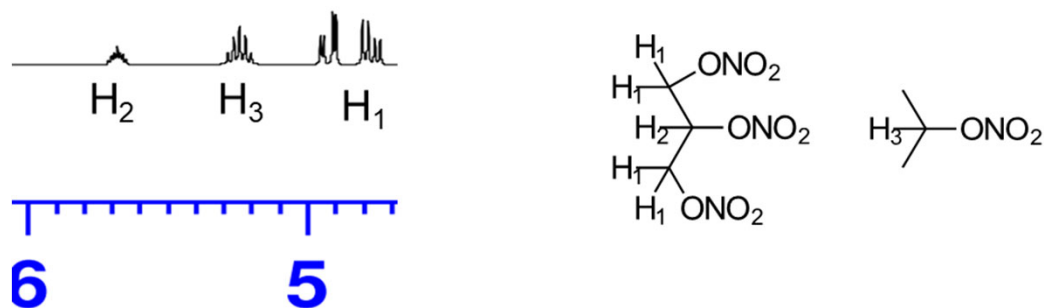
Addition of 1 equivalent of nitric acid increased the conductivity by ~10X

Method: Total nitric acid volume versus maximum current in an H-cell charged with only ACN and lithium nitrate. Each entry represents adding 0.1 eq (0.1 mL) of nitric acid relative to lithium nitrate sequentially starting with the cathode (entry 2) and then the anode (entry 3). Entry 1 is lithium nitrate in ACN with no nitric acid. The current (48 mA) from entry 11 is equivalent to the current passed by TBAHFP in ACN.

O-Nitration under Aprotic Conditions: Glycerin to Nitroglycerin

- Experimental results from NAL-093-10965 where lithium nitrate was used in conjunction with NO_2 to make N_2O_5 in ACN that was used to nitrate glycerin in a second reaction. Notable is the good *in situ* yield. Yields were determined by qNMR.

Reaction	Temp. (°C)	Starting Material	Yield of 1,2,3-Trinitroglycerin <i>in situ</i> (%)
NAL-093-10965-S2	-15 to 20	Glycerin	100.0



- The relevant NMR resonances of the nitroglycerin spectrum showing a clean baseline with no evidence of either glycerin or nitrite ester. As part of a control in the reaction 2-propanol was successfully nitrated concurrently.

Testing Membrane Separators for Conductivity

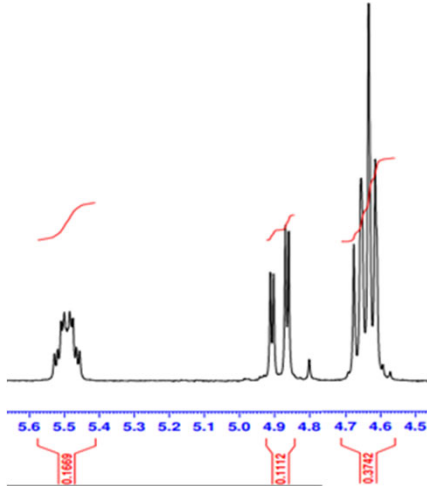
- **Goal:** of transitioning to a flow system, glass frits, which often crack in flow cells, were replaced with a membrane that allows charged species to pass but effectively separates cathode from anode.
- **Method:** A two-piece H-cell fitted with one of 5 different membranes was tested and their conductivity compared with that of the fine frit H-cell. In these studies, saturated solutions of lithium nitrate in ACN were used to test conductivity

Divider	Pore Size (μm)	Thickness (μm)	Voltage (V)	Current (mA)
Fine glass frit	5	3000	1.8	4.0
WP-020-80	2	80	1.9	4.4
FP-100-300	10	300	1.7	4.5
WP-100-100	1	100	1.7	4.3
LWP-300-75-HOP	30	75	1.9	3.7
HP-010-50	0.1	50	0.91	0.08

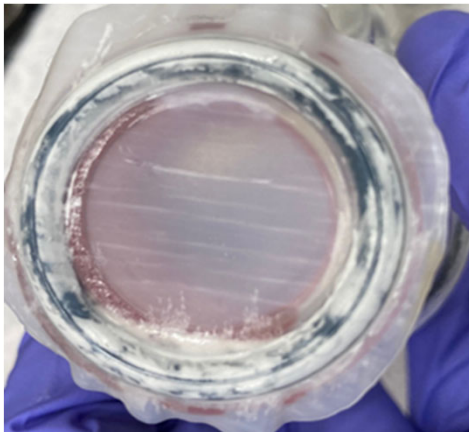
Three membranes had conductivity comparable to the fine glass frit divided H-cell used in previous experiments (shown with green highlight).

O-Nitration Under Aprotic Conditions using N₂O₅: 1,2,4-Butanetriol to BTTN

Method: 2.2 volts and 50 mA of current were attained accelerating the formation of N₂O₅ due to addition of a small amount of nitric acid. The anolyte solution was then harvested and added to 1,2,4-butanetriol in ACN at - 15 °C to make BTTN in quantitative yield assessed by qNMR



NMR spectrum showing relevant down field signals of BTTN formed from N₂O₅ produced at the anode of a membrane two-piece membrane divided H-cell.



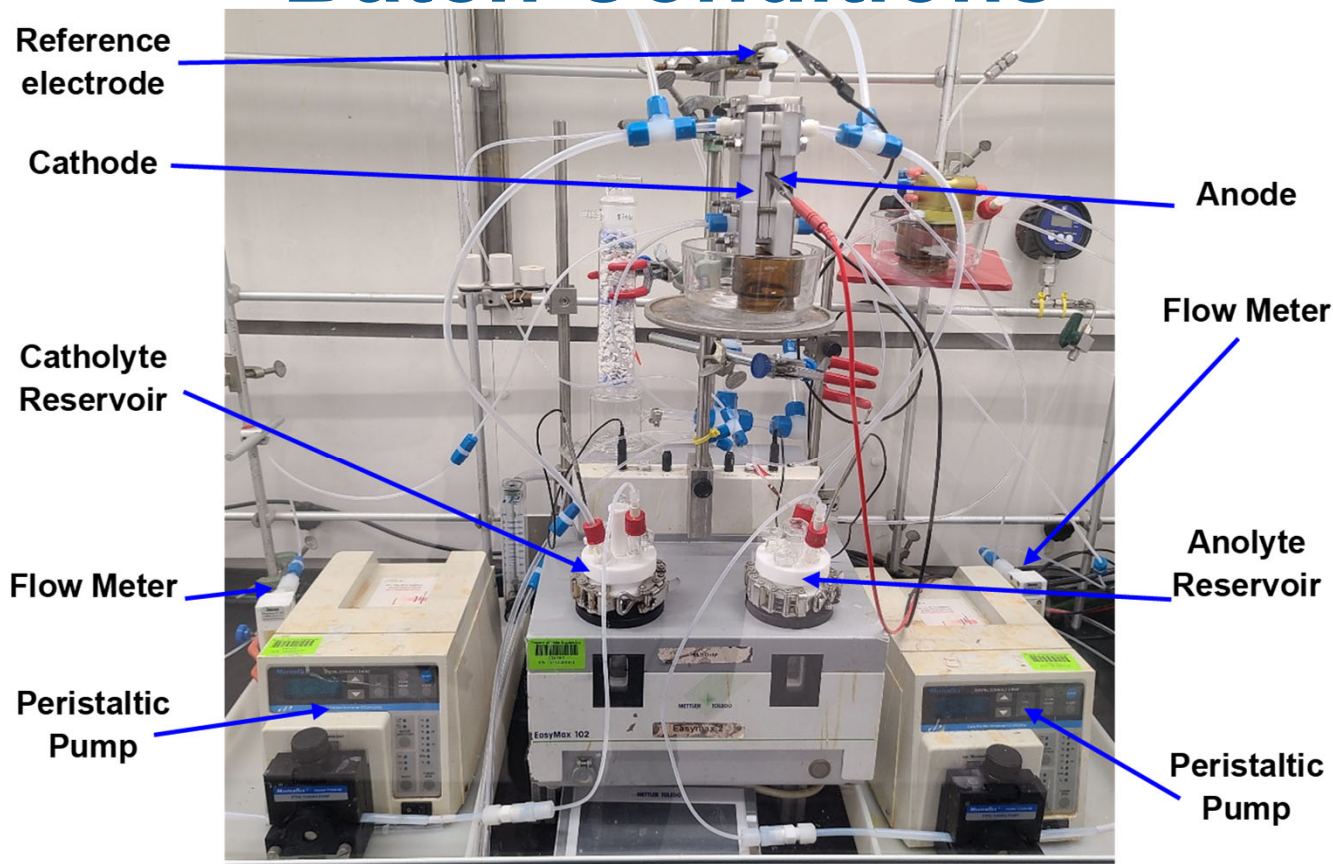
The FP-100-300 membrane shown on one half of the two-piece H-cell. This photograph was taken just after producing N₂O₅ electrolytically in the anode compartment.

Summary Task 1

- Direct nitration of substrates in the anode compartment is low yielding
- A two-step process was developed making nitronium or N_2O_5 , in a divided electrolysis cell, which is then used to nitrate substrates
- DNT with low meta isomer content $\sim 1.5\%$ was realized but salt recovery was impractical
- N_2O_5 derived from NO_2 and lithium nitrate under electrolysis conditions was found to make DNAN and Nitrate esters BTTN and NG in high yield
- Addition of <1 equivalent of nitric acid greatly increases current
- The use of a membrane separator during electrolysis demonstrates a path forward for flow electrolysis

RESULTS:
**TASK 2.0 APPLY OPTIMIZED
BATCH CONDITIONS TO FLOW
REACTOR**

Task 2: Flow Electrolysis using Optimized Batch Conditions



Anolyte and catholyte in two 100 mL EasyMax reactors with 1 M lithium nitrate, 1 M NO_2 , 0.7 M of nitric acid in a mixture of 60 wt% ethylene carbonate 40 wt% acetonitrile at 0 °C. Electrolytic flow cell equipped with platinum clad niobium electrodes, 100 nm wide pore, 30 μm thick hydrophilic PTFE membrane. Solutions stirred to dissolve maximum amount of salt and pumped to the flow cell. Constant current electrolysis until the over potential limit is reached or all the NO_2 is consumed.

Flow Electrolysis using Optimized Batch Conditions for Nitration in a Second Step

- Unlike in the H-cell, in flow, hydrophilic membranes were used
- Hydrophilic membranes, upon contact with the system's solvent, spontaneously self-displace air in the pores allowing conductivity.

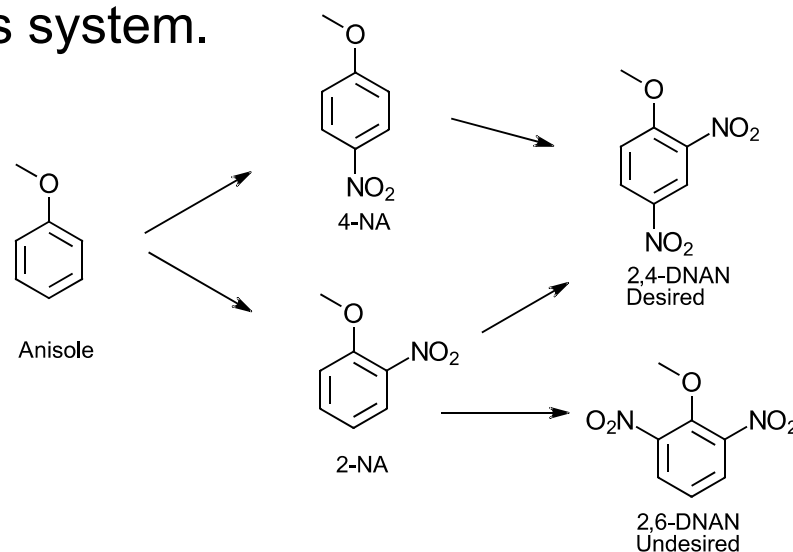
Membrane	Pore Size (nm)	Thickness (μm)	Current (mA)
HPW-010-30	100	30	345
HHPW-003-30	30	30	117
HPW-005-15	50	15	285

Pore sizes and thicknesses with resulting currents from applied voltage of 9.97 V for different hydrophilic membranes.

- Electrolysis currents increased by 20-fold from batch conditions, 42-fold with 1 equivalent of nitric acid present

Need for a Solvent with Improved Lithium Nitrate Solubility

- Flow electrolysis to make N_2O_5 with second step nitration using optimized batch nitration conditions stalled during the electrolysis nevertheless N_2O_5 produced in flow successfully mononitrated anisole and gave DNAN from 4-NA
- Due to highly increased current, flow electrolysis synthesized N_2O_5 fast and consumed all $LiNO_3$ dissolved in the acetonitrile solvent.
- $LiNO_3$ kinetics of dissolution were not as fast as the electrolysis.
- This prompted a search for solvents that could hold larger quantities of lithium nitrate and in turn allow for the efficient production rates of N_2O_5 in the flow electrolysis system.



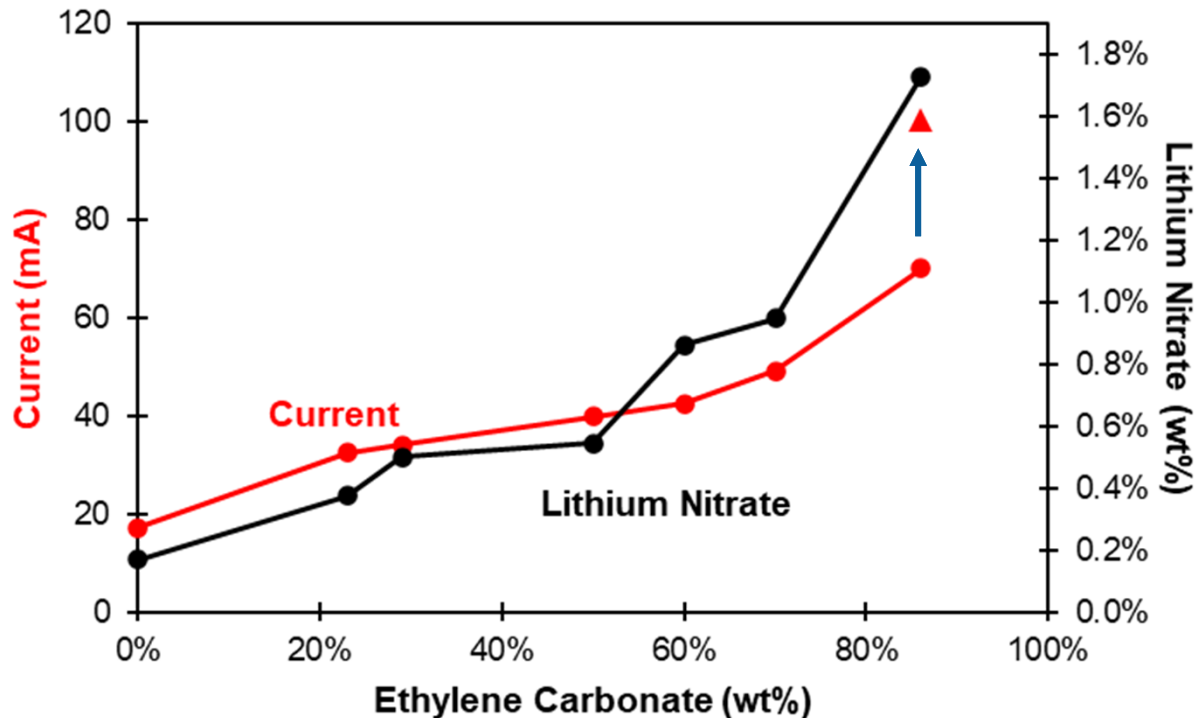
Search for a Solvent with Improved Lithium Nitrate Solubility

Solvent combinations and their resulting lithium nitrate concentrations at saturation at RT showed that ethylene carbonate was promising

Solvent	Concentration (wt%)	Current at 10 V (mA)
Acetonitrile	0.17	17.1
90% ACN/10% Ethylene Carbonate	0.34	N/A ¹
90% ACN/10% Sulfolane	0.33	N/A ¹
77% ACN/23% Ethylene Carbonate	0.37	32.5
71% ACN/29% Ethylene Carbonate	0.50	35.1
72% Sulfolane/28% ACN	3.30	6.5

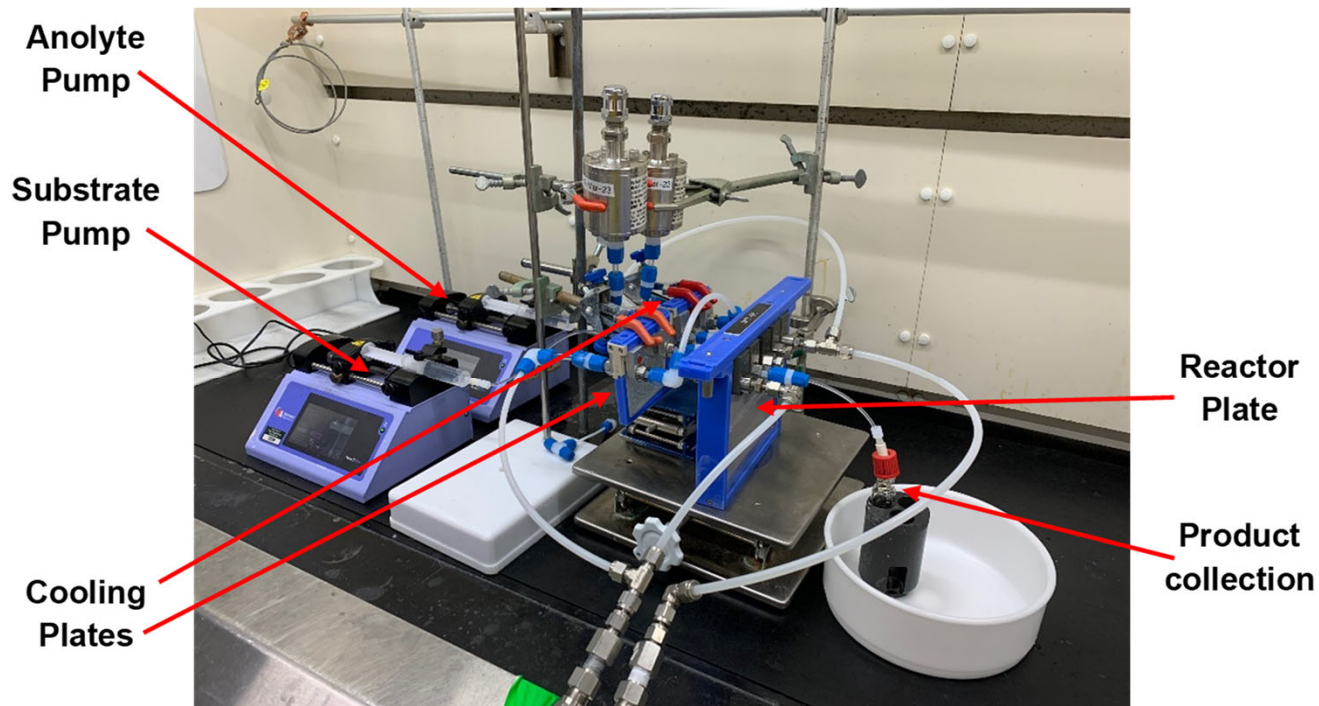
¹Currents seen had high amounts of noise due to low conductivity. Accurate recordings could not be made.

Search for a Solvent with Improved Lithium Nitrate Solubility



- The red circle trend depicts current as a function of weight percent ethylene carbonate in acetonitrile
- The triangle shows the increase in current achieved when 1 molar equivalent of nitric acid was added to an 86 wt% ethylene carbonate solution
- The black trend depicts the lithium nitrate concentration at varying concentrations of ethylene carbonate in acetonitrile as measured by ion chromatography.

Flow Nitration Setup in the Corning Advanced-Flow™ Reactor (AFR)



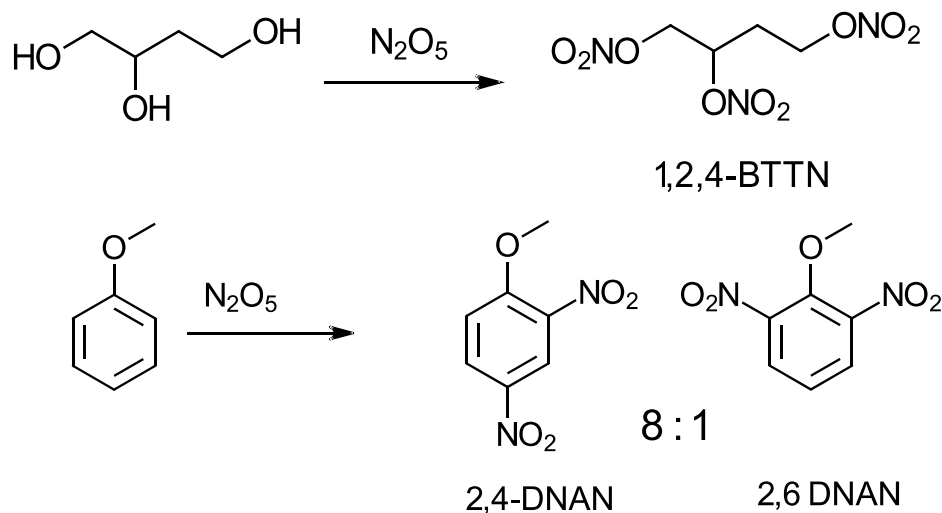
Standard method for flow nitration: anolyte from electrolysis flowed through a cooled low flow Corning Glass AFR plate kept at 0 °C using Harvard syringe pump at 1.35 mL/min, separately and simultaneously the chosen substrate in acetonitrile flowed in a Harvard syringe pump at 1.35 mL/min. The streams then combined in a Corning AFR G1 lab reactor plate kept at 0 °C. Samples were collected each minute once material began exiting the mixing plate for the duration of the experiment. These samples are then analyzed with qNMR.

C and O Nitration in the Corning Advanced-Flow™ Reactor (AFR)

- All reactions used the ethylene carbonate/acetonitrile solvent system

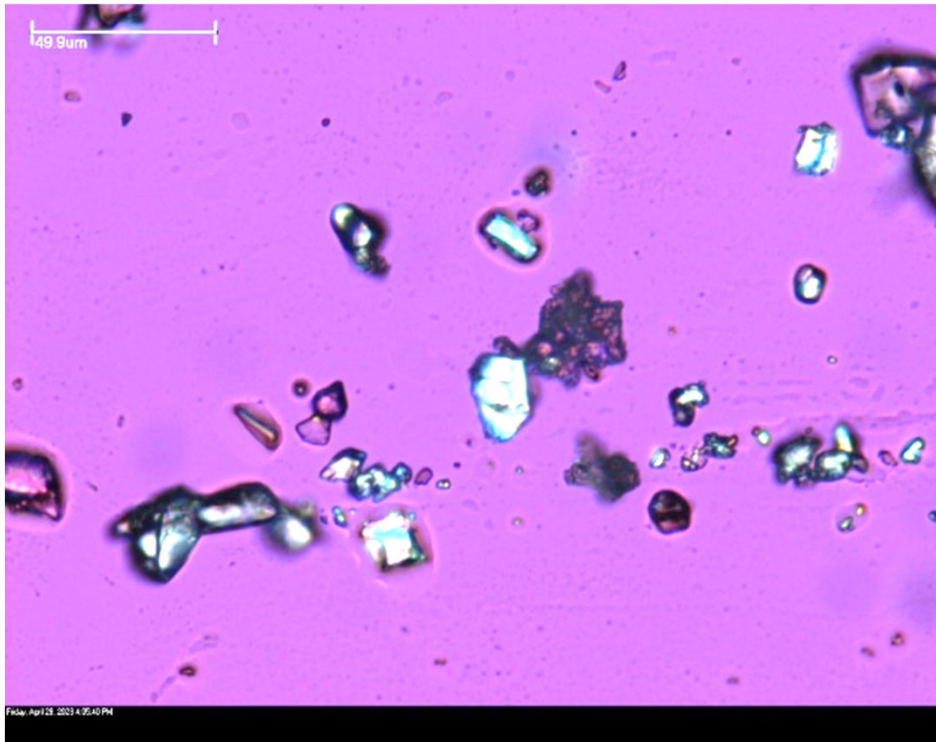
Reaction	Temp. (°C)	Starting material	Substrate to N ₂ O ₅ ratio	Products	Yield <i>in situ</i> qNMR (%)
NAL-113-11973	0	Toluene	1:3	2-MNT, 4-MNT	86
NAL-113-12046	0	1,2,4-Butanetriol	1:10	1,2,4-BTTN	100
NAL-113-12059	0	Anisole	1:2	2,4-DNAN 2,6-DNAN	88 9
NAL-113-12144 ^a	-5	Anisole	1:9	2,4-DNAN 2,6-DNAN	89 11

^aElectrolysis and nitration both completed in flow



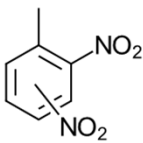
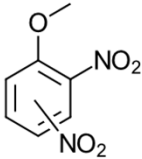
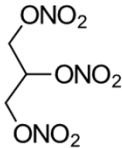
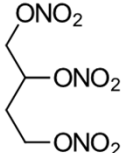
Product and Reagent Recovery Towards Sustainability

- **Unoptimized Method:** Recover the acetonitrile from the nitration mixture via rotary evaporation, add water to induce biphasic formation, add a seed crystal of DNAN, hold at 0 °C for 24 hr. Once crystallization was complete, vacuum filtered washed with 2-propanol, dried under a vacuum.
- Isolate crystalline 2,4-DNAN with isomer ratio of 20:1 2,4-DNAN to 2,6-DNAN in a 70% yield.



Polarized light microscope image of DNAN isolated by acetonitrile evaporation and water addition showing blocky crystalline DNAN.

Accomplishments

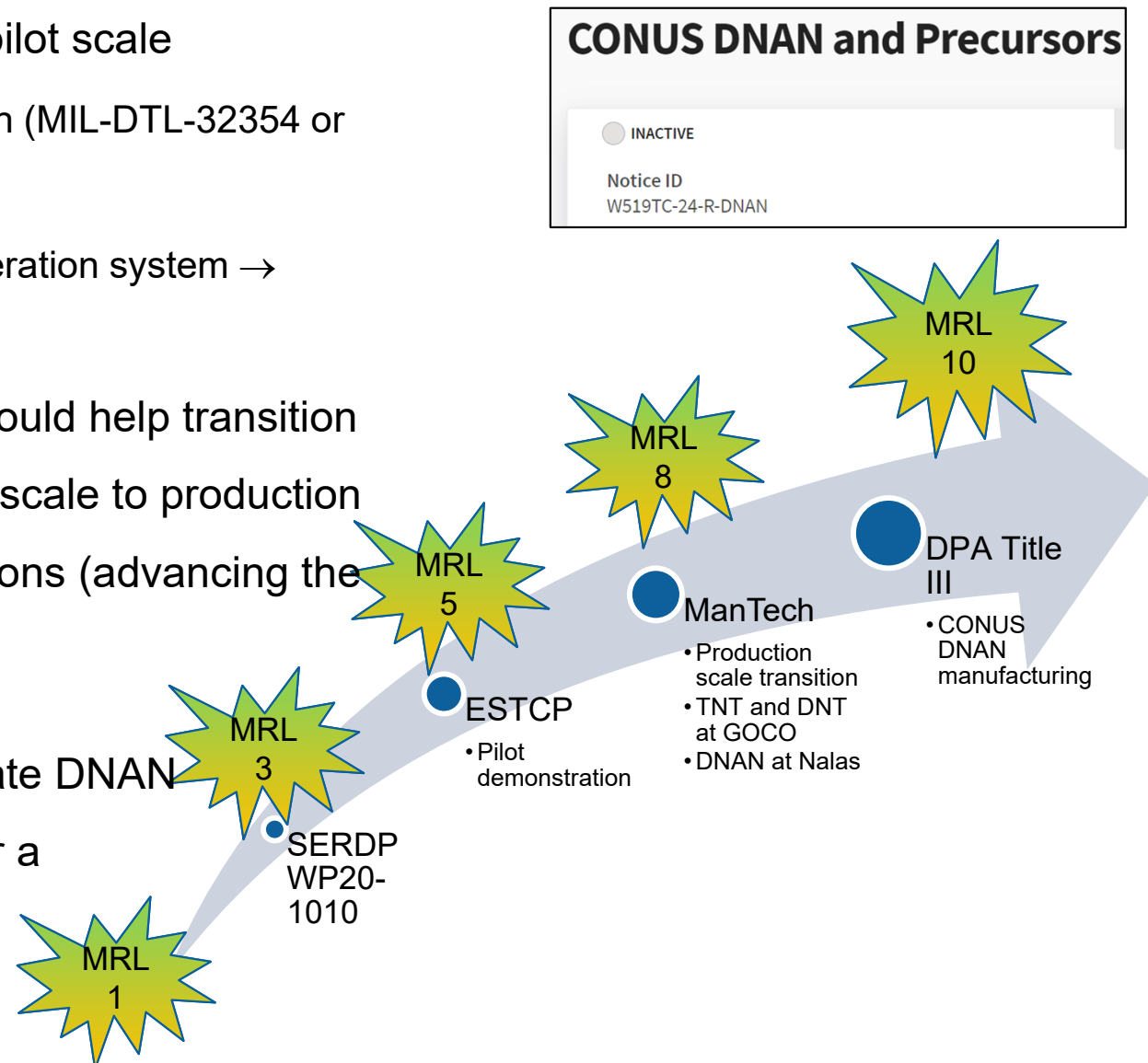
Successful 2-Step Electrochemical Nitrations			
 DNT (87%) ¹	 DNAN (98%) ²	 NG (quant) ²	 BTTN (quant) ²

¹Isolated Yield, ²In situ yield

- **Robust:** The nitrating species (N_2O_5 or nitronium triflate) are electrochemically generated using either lithium nitrate or lithium triflate, respectively, as carrier salts with NO_2 in either acetonitrile or ethylene carbonate/acetonitrile mixtures.
- **Adaptable:** The electrolysis and N_2O_5 generation works well both in batch and flow systems.
- **Scalable:** Both the flow electrolysis and flow nitration systems can be fed any volume of material and produce a proportionally scaled product throughput.
- **Reproducible:** The two-step electrolysis and nitration has been performed successfully many times using a variety of substrates.
- **Economical:** Reagents including salts as well as solvent can be recovered from the product mixture.
- **Green:** No sulfuric acid and up to only 1 eq of nitric acid is used with the only expended reagents being electrons and NO_2 . Acetonitrile, ethylene carbonate, and lithium nitrate can all be recycled back into the process.

DNAN Transition Plan

- Potential ESTCP program to refine and demonstrate electrochemical nitrations at larger pilot scale
 - ◆ DNAN will need to meet specification (MIL-DTL-32354 or STANAG 4776)
 - ◆ Can leverage Nalas' pilot N_2O_5 generation system → operational in 2024
- ManTech program (OSD or Army) could help transition electrochemical nitrations from pilot scale to production scale demos and qualify in formulations (advancing the MRL)
- DPA Title III program could help create DNAN manufacturing capability at Nalas for a CONUS, environmentally-friendly, low-cost source



TNT Transition Plan

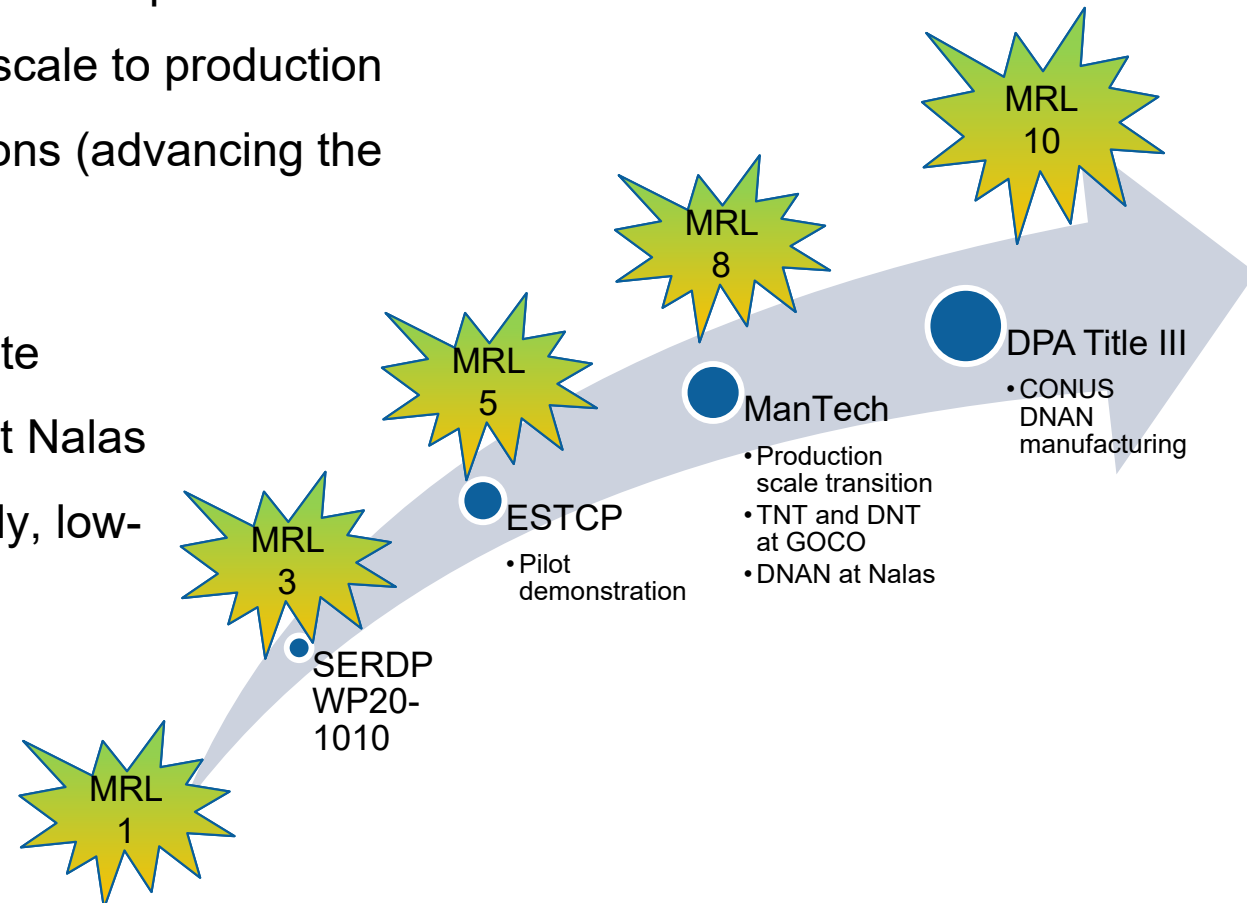
- Potential ESTCP program to refine and demonstrate electrochemical nitrations at larger pilot scale
 - ◆ TNT will need to meet specification (MIL-DTL-248D) using low-meta isomer DNT from electrochemical process
- ManTech program (OSD or Army) could help transition electrochemical nitrations from pilot scale to production scale demos and qualify in formulations (advancing the MRL)
- DPA Title III program could help create MNT/DNT manufacturing capability at Nalas for a CONUS, environmentally-friendly, low-cost source for TNT precursor

Sources Sought: Construction and Operation of TNT Facility

● ACTIVE

Contract Opportunity

Notice ID
W519TC-23-R-0122



SUMMARY OF YALE'S CONTRIBUTIONS- A VALUED PARTNER

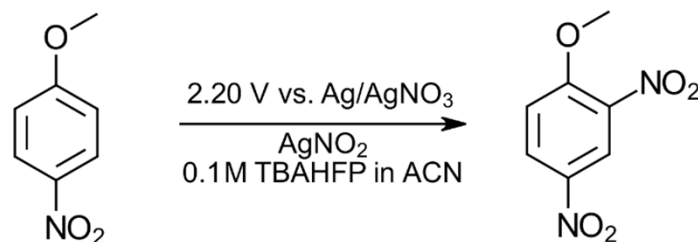
Yale: Comparative Life Cycle Assessment of Conventional and Novel DNAN Synthesis

- Cradle-to-gate life cycle assessment of producing 2,4 DNAN from the novel electrochemical route versus a highly optimized conventional route
- Evaluated 18 discrete categories of environmental impacts
- Sensitivity of bench scale electrochemical route to solvent recovery and lithium recovery evaluated

- Findings indicate that the novel bench scale electrolysis 2-step process has higher environmental impact than the conventional DNAN synthesis
- Notably, the comparison is not fair as the novel bench scale synthesis is being compared with a long established highly optimized conventional synthesis, nevertheless within 3-fold within most impact categories
- Further optimization of the novel synthesis is within reach as the process is scaled

Yale: Explored Alternative Nitrating Reagents Without NO₂ for Anisole Nitration

- Evaluation of various reaction conditions for anisole nitration in the aqueous phase were explored but ultimately, none were found to produce DNAN. Low yields of 2-NA or 4-NA were observed.
- Nitration of 4-NA to DNAN was possible with AgNO₂
- Electrolytes examined in ACN solvent: LiNO₃, TBANO₃, TBANO₂, NaNO₂, AgNO₃, AgNO₂,
- Electrolytes examined in ACN/H₂O solvent: NaClO₄, TBANO₃, TBANO₂, LiNO₃, KNO₃, KNO₂, AgNO₂, NaNO₂



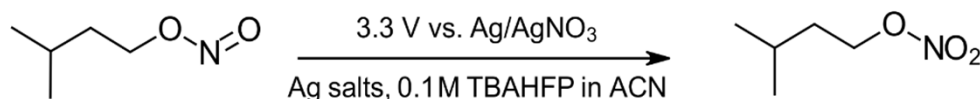
Entry	Electrode	Temp. (°C)	2,4-DNAN yield (%) ^a
1	Pt	RT	48.8
2	Glassy Carbon	RT	37.3
3	Carbon Paper	RT	49.5
4	Carbon Paper	40	trace
5	Carbon Paper	0	50.3

^a Based on GC analysis with biphenyl as an internal standard

Nitration of anisole under a variety of conditions without NO₂ produces only moderate yield of desired products

Yale: Explored Alcohol Nitration Using AgNO_2 to Produce nonenergetic Nitrate Esters

- Isoamyl nitrite to isoamyl nitrate conversion using electrolysis with **silver slats**. Reactions were completed using a divided cell, glassy carbon counter electrode, Ag/AgNO_3 (10 mM AgNO_3) reference electrode, 25 mM substrate, 50 mM Ag salts unless it specifies, 0.1 M TBAHFP in ACN.

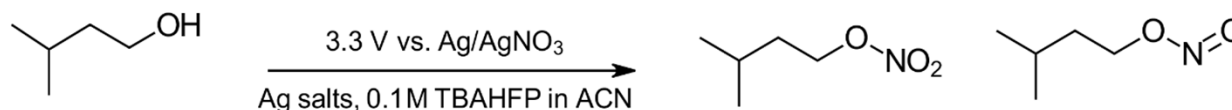


Entry	Electrode	Ag Salt	Yield of isoamyl nitrate ester in situ (%) ^a
1	Pt	AgNO_2	72
2	Carbon Paper	AgNO_2	78
3	Glassy Carbon	AgNO_2	97
4	Glassy Carbon	AgNO_3	98
5	Glassy Carbon	AgOAc	52
6	Glassy Carbon	CuCl_2	0
7	N/A	AgNO_2	0
8*	Glassy Carbon	0.2 equiv. (5 mM AgNO_2)	89

*Catalytic in silver salt

Yale: Alcohol Nitration Using AgNO_2

- Nitration of isoamyl alcohol using AgNO_2 . Reactions were completed using a divided cell, glassy carbon counter electrode, Ag/AgNO_3 reference electrode, 25 mM substrate, 50 mM AgNO_2 , 0.1 M TBAHFP in ACN, and held for 3 hr unless noted.

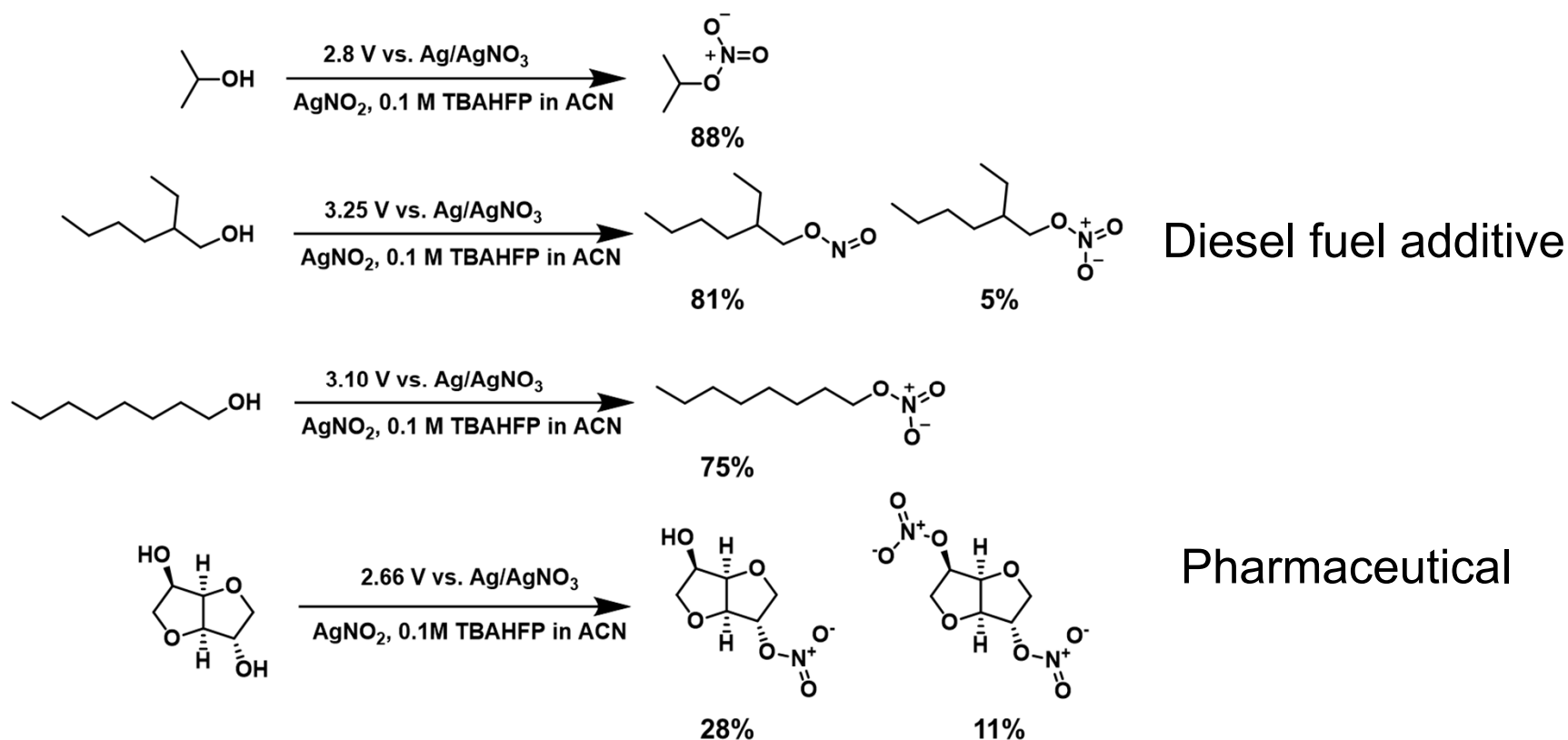


Entry	Electrode	Anode Chamber	Cathode Chamber	Conversion (%)	Isoamyl nitrite Yield (%) ^a	Isoamyl nitrate Yield (%) ^a
1	Glassy Carbon	50 mM AgNO_2	50 mM AgNO_2	100	0	52
2	Pt	50 mM AgNO_2	50 mM AgNO_2	100	0	51
3	Carbon Paper	50 mM AgNO_2	50 mM AgNO_2	84	59	25
4 ^b	Carbon Paper	50 mM AgNO_2	50 mM AgNO_2	100	0	68
5	Glassy Carbon	10 mM AgNO_2 , 40 mM TBANO_2	50 mM AgNO_2	100	0	35
6	Glassy Carbon	10 mM AgNO_2 , 40 mM TBANO_2	50 mM $\text{Ni}(\text{NO}_3)_2$	100	42	40
7 ^c	Glassy Carbon	20 mM AgNO_2	20 mM AgNO_2	100	0	92

^aBased on qNMR using 1,2,4,5-tetrachlorobenzene as internal standard; ^b reaction time: 4h, ^c 10 mM substrate, under continuous argon bubbling.

Yale: Alcohol Substrate Diversity Nitration Using AgNO_2

- Nitration of isopropanol, 2-ethylhexanol, 1-octanol, and isosorbide (from top to bottom) (reaction conditions: glassy carbon working electrode, glassy carbon counter electrode, Ag/AgNO_3 reference electrode, 10 mM substrate, 20 mM AgNO_2 , constant potential electrolysis at specific oxidation potential, total charge passed: $\sim 1.2 \text{ F/mol}$).



Yale, a Project Partner

- Performed an expert comparative analysis of sustainability for the synthesis of DNAN by our novel electrolysis/flow method versus the classic DNAN synthesis
- Complimented Nalas experiments which used electrolysis of NO_2 to make nitrating agents by performing electrolysis experiments replacing NO_2 with electrochemically active salts
- Yale found several electrochemically active salts result in anisole nitration and the formation of nitrate esters is possible electrochemically
- These nitration reactions were not able to be optimized for scale up
- These nitration reactions are novel, and the formation of nitrate esters could be useful for lab scale synthesis— the subject of a draft publication

Back UP



Two-step Conversion of Toluene to DNT Nitronium Solutions, Other Salts

Toluene nitration using lithium triflate as charge carrying salt producing nitronium triflate

Reaction	Temp. (°C)	Toluene Nitrated Products Area% (GC)								
		Toluene	2-NT	3-NT	4-NT	2,6-DNT	2,4-DNT	3,4-DNT	2,3-DNT	2,5-DNT
NAL-093-10899	-15	-	-	-	3.1	35.8	62.0	0.6	1.3	0.3
NAL-093-10914	-15	-	68.4	2.1	29.2	0.1	0.2	-	-	-

Meta isomer content was found to be **2.2 area%** by GC

Toluene nitration using lithium nitrate as charge carrying salt (N₂O₅)

Temp. (°C)	Toluene Nitrated Product(s) in situ Yield (%) qNMR ¹								
	Nitric Acid	2-NT	3-NT	4-NT	2,6-DNT	2,4-DNT	3,4-DNT	2,3-DNT	2,5-DNT
-15 to 0	None	66.5	-	34.6	-	-	-	-	-
-15 to 25	None	65.4	-	35.0	-	3.6	-	-	-
-15 to 0	None	55.5	-	28.0	-	-	-	-	-
-15 to 25	1 eq	33.8	-	22.1	11.3	7.8	-	-	-
-15 to 25	1 eq	44.5	-	25.1	8.2	5.1	-	-	-

- Toluene nitration Using N₂O₅ in acetonitrile results in mostly MNT
- qNMR analysis is likely too insensitive to determine small amounts of meta isomer formed

Two-step Conversion of Toluene to DNT Using Nitronium Solutions

Summary of toluene nitration with nitronium hexafluorophosphate in acetonitrile, gives low meta isomer DNT

Sample from	Area% (GC)						
	Toluene	2-NT	3-NT	4-NT	2,6 DNT	2,4 DNT	3,4 DNT
NAL-069-09996							
1 (S1-T)	5.2	-	-	-	24.6	68.8	1.4
2 (S2-T)	0.8	-	-	-	27.5	70.7	1.0

Temperature study

Sample from	Temp (°C)	qNMR Material Balance	Area% (GC)							
			Toluene	2-NT	3-NT	4-NT	2,6-DNT	2,4-DNT	3,4-DNT	2,3-DNT
NAL-069-10194										
1	23	quant ¹	4.4	-	-	-	27.2	66.5	0.7	1.3
2	0	quant ¹	3.0	-	-	-	30.9	64.9	0.4	0.9
3	-15	quant ¹	7.1	1.3	1.0	-	31.5	57.6	0.5	1.1

¹The measured values were within the error of the qNMR method of 100% yield.

- 15 °C Temperature study

Sample from	Temp. (°C)	Area% (GC)								
		Toluene	2-NT	3-NT	4-NT	2,6-DNT	2,4-DNT	3,4-DNT	2,3-DNT	2,5-DNT
NAL-093-10814										
1 (<i>in situ</i>)	-15	-	-	-	3.1	34.2	61.4	-	1.2	-
6 (isolated)	-15	-	-	-	2.3	33.2	64.3	-	0.9	0.2

Average meta isomer content across 7 runs from 23 to -15 °C is **1.5 area%** by GC versus 4-5 % in mixed acid nitration

Comparative Life Cycle Assessment of Conventional and Novel DNAN Synthesis

Impact assessment results for novel chemistry synthesis for 1 gram of DNAN.

Lithium recovery (electrolysis)		69-78%	69-78%	69-78%	69-78%	99%	99%	99%	99%
Solvent recovery (electrolysis)		90%	99%	90%	99%	90%	99%	90%	99%
Solvent recovery (nitration)		90%	90%	99%	99%	90%	90%	99%	99%
Ref. unit	Impact category								
m ³	Water consumption	3.80E-04	2.90E-04	3.10E-04	2.20E-04	3.60E-04	2.70E-04	2.90E-04	2.00E-04
kg SO ₂ -eq	Terrestrial acidification	2.00E-04	1.70E-04	1.70E-04	1.50E-04	1.90E-04	1.60E-04	1.60E-04	1.40E-04
m ² a crop-eq	Land use	3.10E-04	2.40E-04	2.70E-04	2.00E-04	2.60E-04	1.90E-04	2.20E-04	1.50E-04
kg NO _x -eq	Ozone formation, Terrestrial ecosystems	6.52E-05	5.41E-05	5.65E-05	4.53E-05	5.93E-05	4.82E-05	5.06E-05	3.94E-05
kg 1,4-DCB	Human non-carcinogenic toxicity	1.84E-02	1.49E-02	1.61E-02	1.26E-02	1.69E-02	1.34E-02	1.46E-02	1.12E-02
kg P-eq	Freshwater eutrophication	6.91E-06	5.70E-06	6.11E-06	4.89E-06	6.20E-06	4.98E-06	5.39E-06	4.18E-06
kg N-eq	Marine eutrophication	1.06E-05	6.25E-06	6.21E-06	1.87E-06	1.01E-05	5.78E-06	5.73E-06	1.39E-06
kg 1,4-DCB-eq	Marine ecotoxicity	1.89E-03	1.53E-03	1.66E-03	1.30E-03	1.74E-03	1.38E-03	1.51E-03	1.14E-03
kg CFC11-eq	Stratospheric ozone depletion	3.11E-07	3.10E-07	3.10E-07	3.09E-07	2.65E-07	2.64E-07	2.64E-07	2.63E-07
kg 1,4-DCB_eq	Freshwater ecotoxicity	1.46E-03	1.18E-03	1.28E-03	1.00E-03	1.34E-03	1.07E-03	1.16E-03	8.90E-04
kg PM _{2.5} -eq	Fine particulate matter formation	5.08E-05	4.35E-05	4.47E-05	3.74E-05	4.78E-05	4.05E-05	4.17E-05	3.44E-05
kg oil-eq	Fossil resource scarcity	1.12E-02	7.75E-03	8.38E-03	4.90E-03	1.09E-02	7.44E-03	8.07E-03	4.59E-03
kBq Co-60-eq	Ionizing radiation	1.26E-03	9.60E-04	1.11E-03	8.10E-04	1.21E-03	9.10E-04	1.06E-03	7.60E-04
kg NO _x -eq	Ozone formation, Human health	6.31E-05	5.25E-05	5.48E-05	4.42E-05	5.72E-05	4.67E-05	4.89E-05	3.84E-05
kg Cu-eq	Mineral resource scarcity	5.30E-04	5.10E-04	5.10E-04	4.90E-04	1.20E-04	1.00E-04	1.10E-04	8.85E-05
kg CO ₂ -eq	Global warming	3.29E-02	2.63E-02	2.76E-02	2.11E-02	3.06E-02	2.41E-02	2.54E-02	1.88E-02
kg 1,4-DCB	Human carcinogenic toxicity	7.80E-04	6.20E-04	6.70E-04	5.20E-04	6.70E-04	5.20E-04	5.60E-04	4.10E-04
kg 1,4-DCB	Terrestrial ecotoxicity	9.78E-02	7.63E-02	8.31E-02	6.16E-02	9.06E-02	6.91E-02	7.59E-02	5.43E-02



Comparative Life Cycle Assessment of Conventional and Novel DNAN Synthesis

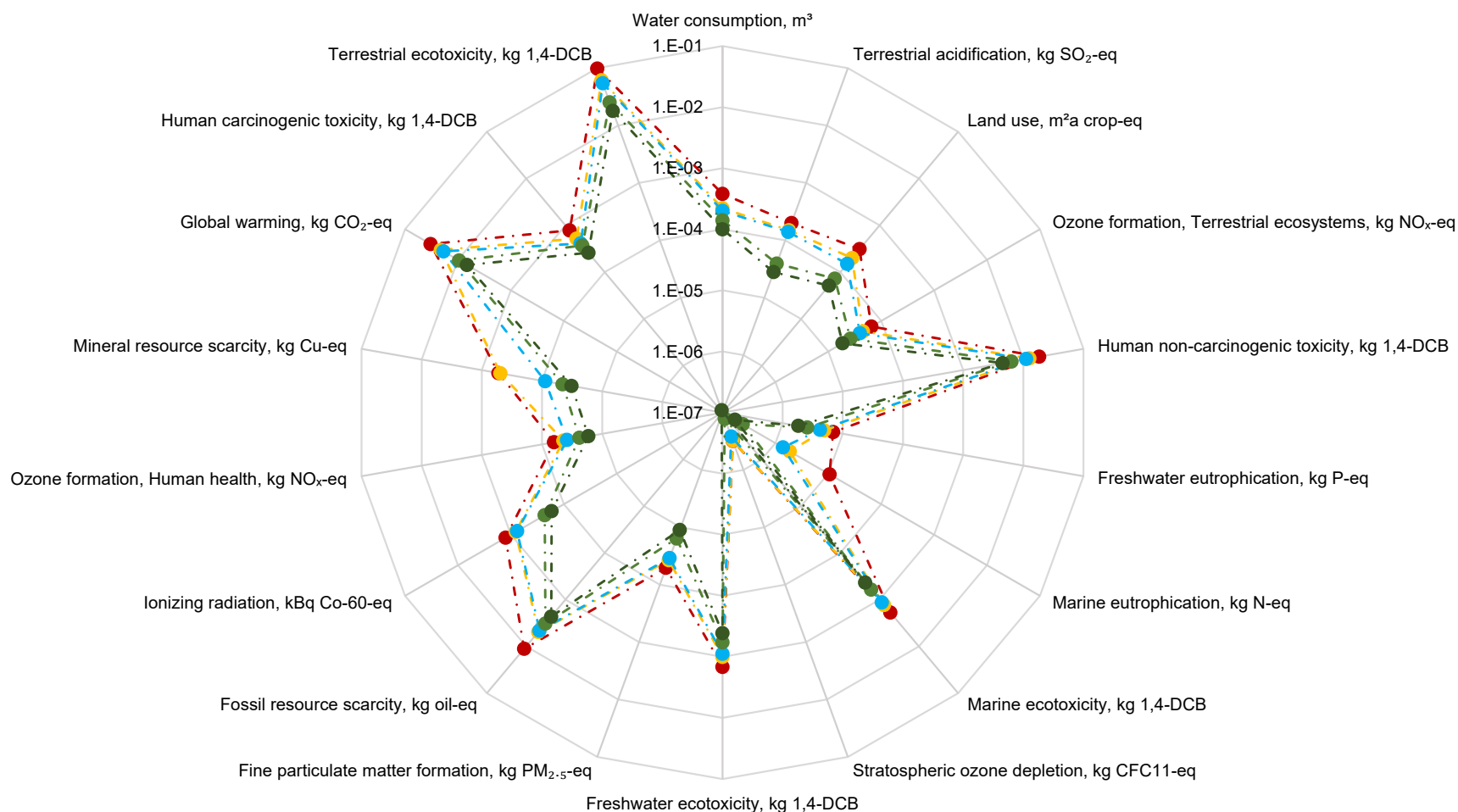
Impact assessment results for conventional synthesis of 1 gram of DNAN.

Reference Unit	Impact Category	Conventional, 70% yield	Conventional, 85% yield	Conventional, 98.7% yield
m ³	Water consumption	1.40E-04	1.20E-04	1.00E-04
kg SO ₂ -eq	Terrestrial acidification	3.94E-05	3.24E-05	2.79E-05
m ² a crop-eq	Land use	7.25E-05	5.97E-05	5.15E-05
kg NO _x -eq	Ozone formation, Terrestrial ecosystems	2.60E-05	2.14E-05	1.85E-05
kg 1,4-DCB	Human non-carcinogenic toxicity	6.37E-03	5.24E-03	4.52E-03
kg P-eq	Freshwater eutrophication	2.57E-06	2.11E-06	1.82E-06
kg N-eq	Marine eutrophication	2.42E-07	2.00E-07	1.72E-07
kg 1,4-DCB-eq	Marine ecotoxicity	6.10E-04	5.00E-04	4.30E-04
kg CFC11-eq	Stratospheric ozone depletion	1.28E-07	1.06E-07	9.10E-08
kg 1,4-DCB-eq	Freshwater ecotoxicity	5.80E-04	4.80E-04	4.10E-04
kg PM _{2.5} -eq	Fine particulate matter formation	1.57E-05	1.29E-05	1.11E-05
kg oil-eq	Fossil resource scarcity	3.24E-03	2.67E-03	2.30E-03
kBq Co-60-eq	Ionizing radiation	2.30E-04	1.90E-04	1.70E-04
kg NO _x -eq	Ozone formation, Human health	2.39E-05	1.97E-05	1.70E-05
kg Cu-eq	Mineral resource scarcity	4.55E-05	3.74E-05	3.23E-05
kg CO ₂ -eq	Global warming	9.53E-03	7.84E-03	6.76E-03
kg 1,4-DCB	Human carcinogenic toxicity	3.70E-04	3.00E-04	2.60E-04
kg 1,4-DCB	Terrestrial ecotoxicity	2.53E-02	2.08E-02	1.80E-02



Comparative Life Cycle Assessment of Conventional and Novel DNAN Synthesis

-●- Novel, 69-78%^a, 90%^b, 90%^c
 -●- Novel, 69-78%^a, 99%^b, 99%^c
 -●- Novel, 99%^a, 99%^b, 99%^c
 -●- Conventional, 70% yield
 -●- Conventional, 98.7% yield



^a lithium recovery at electrolysis, ^b solvent recovery at electrolysis, ^c solvent recovery at nitration

Target plot demonstrating impact results of green chemistry and conventional syntheses of 1 g DNAN, log scale.

Publications

- Journal article on the O-nitration work is being drafted by the Yale coworkers
- Yale/Nalas Filed a patent on this work in November 2023



Page 1 of 2
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ELECTRONIC ACKNOWLEDGEMENT RECEIPT

APPLICATION #
PCT/US23/81103

RECEIPT DATE / TIME
11/27/2023 02:32:33 PM Z ET

ATTORNEY DOCKET #
98199.00120

ELECTROCHEMICAL ALCOHOL NITRATION SYSTEMS AND METHODS

BACKGROUND

1. Government Support

- 5 This invention was made with government support under SERDP SEMS WP20-C2-1010 awarded by the Strategic Environmental Research and Development Program within the U.S. Department of Defense. The government has certain rights in the invention.

WP-1010: Reduction of Acidic and Toxic Waste Streams in Explosives Manufacturing Using Electrochemical Nitration

Performers:

- *Nalas Engineering Services, Inc., Yale University*

Technology Focus

- *Electrochemical nitration to energetic materials eliminating the use of large excesses of nitric and sulfuric acid*

Research Objectives

- *Develop innovative scalable synthetic approaches to the production of energetic materials that eliminate/reduce hazardous waste streams from nitration processes used in manufacturing*

Project Progress and Results

- Success for the nitration of anisole to DNAN with high selectivity of 2,4-DNAN (20:1 2,4-DNAN to 2,6-DNAN), toluene to DNT, MNT (meta less than 2%), glycerin to nitroglycerin (NG) quantitatively, and 1,2,4-butanetriol to butanetriol trinitrate (BTTN) quantitatively

Technology Transition

- *ESTCP to demonstrate electrochemical nitrations at larger pilot scale*

