Development of an Efficient and Green TNT Manufacturing Process

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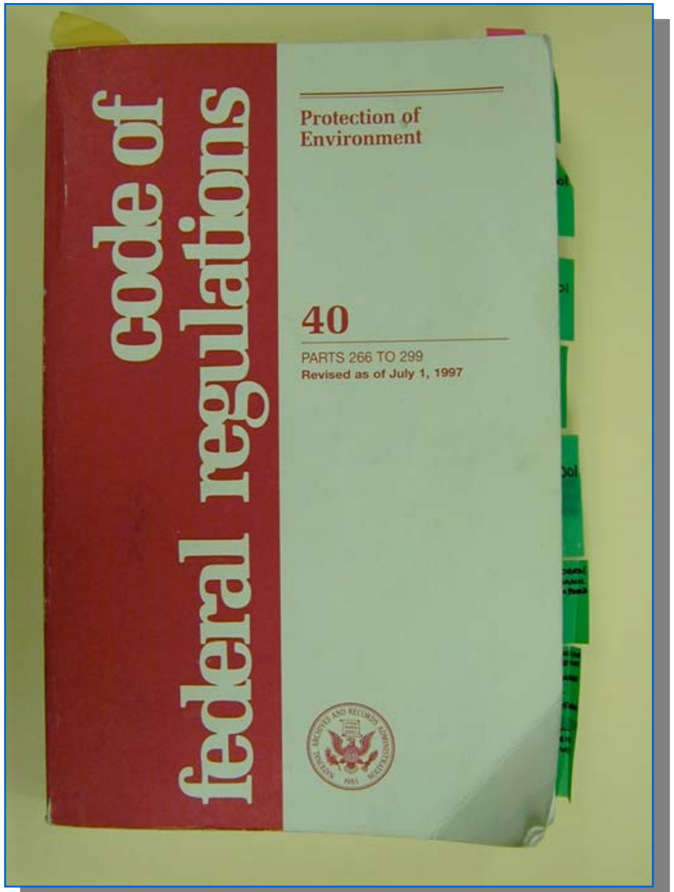
Why investigate TNT manufacturing?

- US Government issued an RFP for TNT supply and a flexible energetic materials manufacturing facility
  - 5-15 million pounds TNT
- The legacy TNT manufacturing process is environmentally unacceptable
  - Waste from traditional TNT production has severe environmental consequences
    - K047 prohibited from land disposal 40 CHR Ch. 1 §286.33
- TNT production stopped in US 15 years ago
  - It has not been restarted in a large part because of the environmental cost



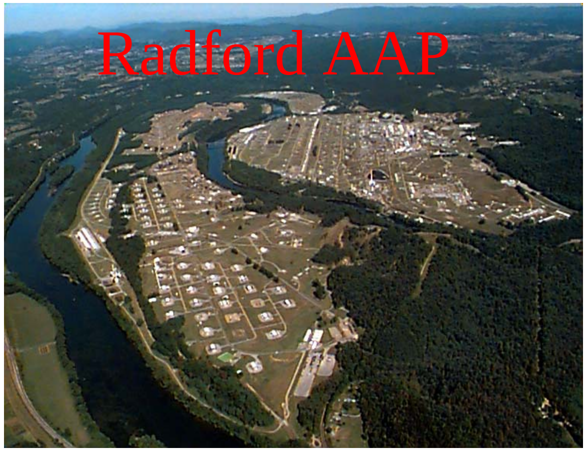
Flexible Ingredient Facility Program

Chemistry Research Program Objectives

- Design safe, efficient and “green” processes for energetic ingredient manufacture
- Design processes that fit available infrastructure
- Add minimal infrastructure to maximize flexibility
- Demonstrate practicality of new processes
- Provide data for full scale plant design
- Meet schedule and budget

Notes

- The Flexible Ingredient Facility is a concept for making a variety energetic materials available at production scale for propellants and explosives
- It is one of the most significant ingredient production facility changes in this country in over 30 years.
- The facility will be able to make both legacy energetics such as TNT and new ingredients such as NTO, Dinitroanisole, CL-20 and TEX
- It is designed to be efficient and exceed environmental requirements for hazardous emissions



TNT Chemistry – the problem

- Nitration of toluene gives TNT AND OTHER STUFF
  - 95% crude yield of organics
  - 5-10% not 246TNT (mostly 3-isomer derivatives)
  - TNT purity of ca. 99.5% is required
- Where has the 5% gone?
- How do your remove the 5-10% from the crude product?
  - What do you do with 5-10%?
    - Approximately 1M lb year!
- What do you do with nitration medium

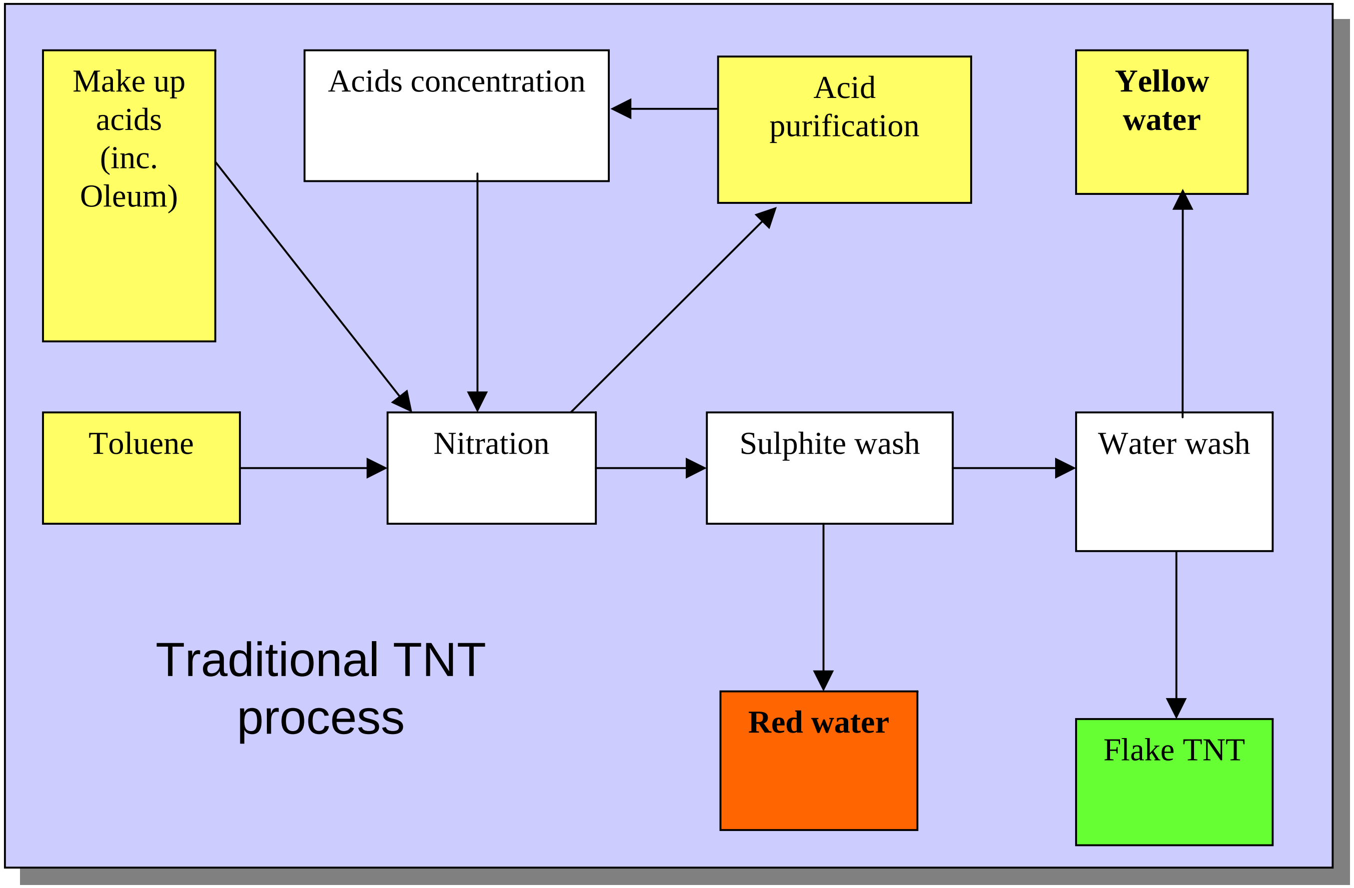
Traditional TNT Processes

Needs oleum facilities

Generates yellow water

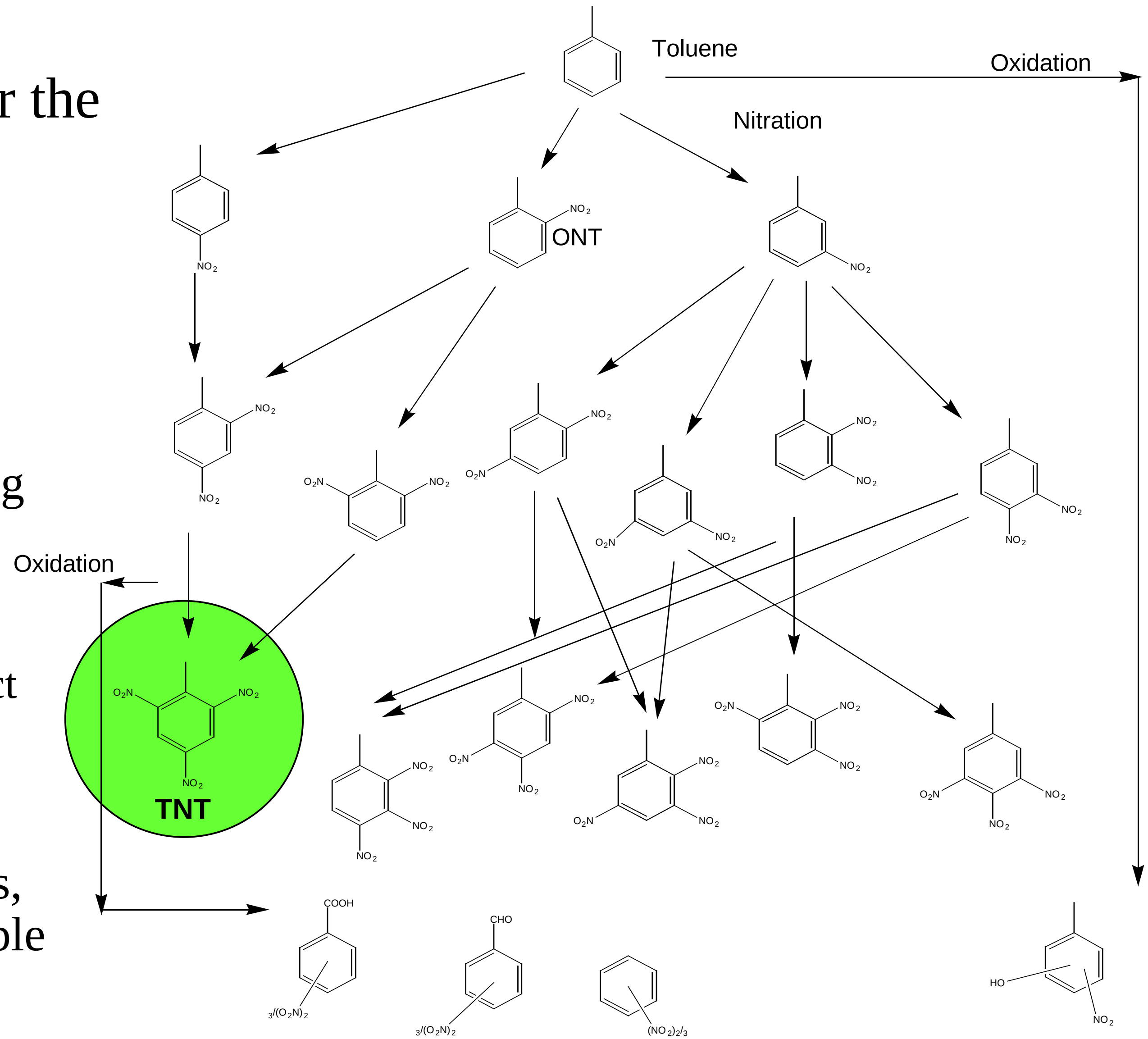
Generates red water

Requires toluene



Nitration

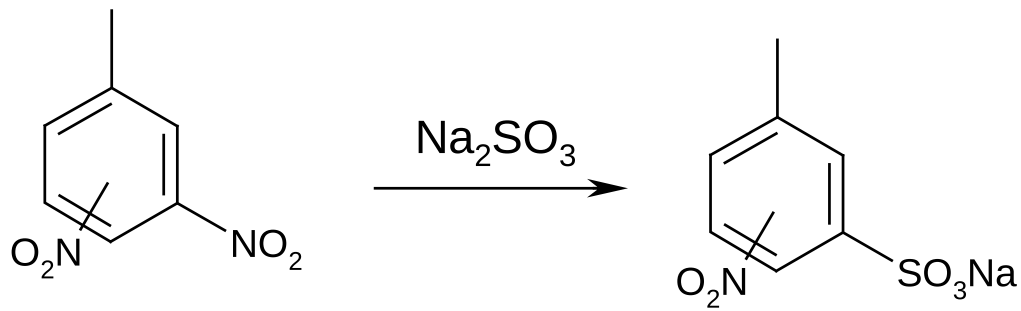
- Considerations for the synthetic route?
  - Starting material
  - By-products
  - Reagents
  - Catalysts?
  - Materials handling
    - Cost, toxicity, compatibility, environmental, facilities impact
- What engineering process?
  - Batch, continuous, single line, multiple lines



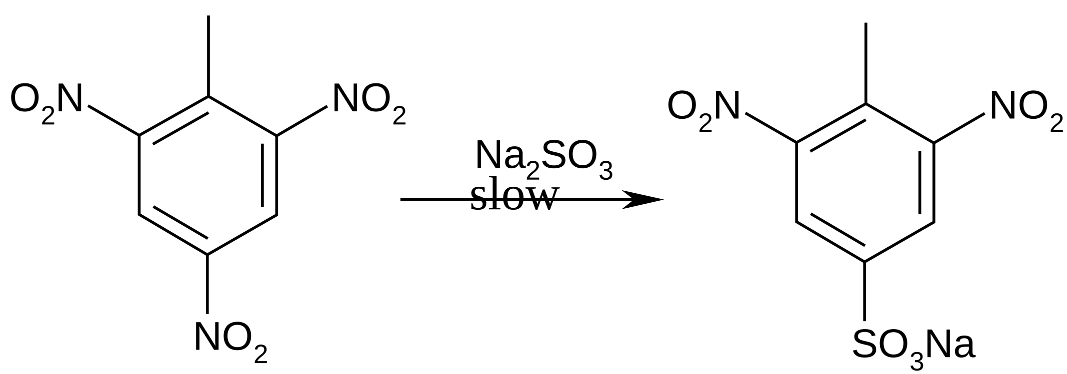
Purification

- Tradition TNT purification
  - Basic wash with sodium sulphite (sellite) removes “off isomers”, benzoic acids, alcohols and tetranitromethane
  - Product is purer TNT and basic aqueous solution of TNT and sulphonated organics
    - Only current disposal option is incineration
  - Washing doesn’t remove DNT, bibenzyl and biphenyl impurities, and it leaves the TNT contaminated ppm with “red water”
  - Poor process upset recovery possibilities
- Other option is recrystallization

“Sellite” purification

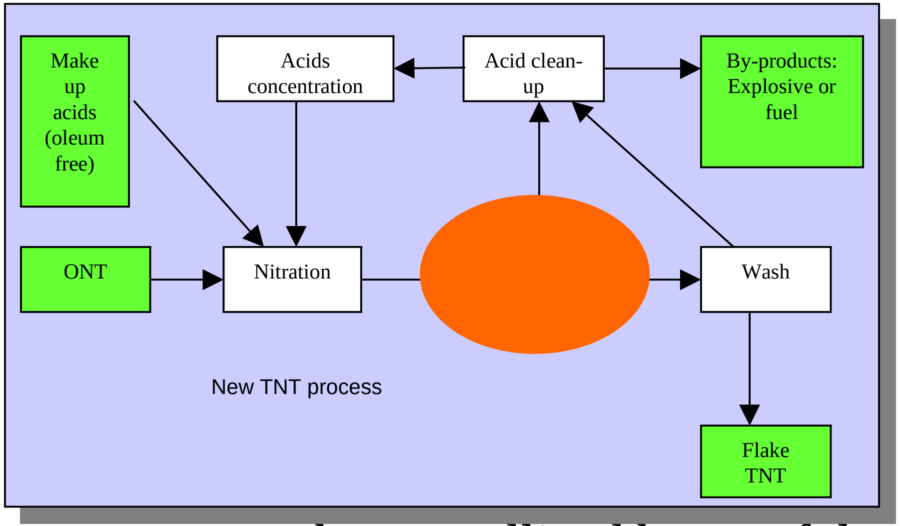


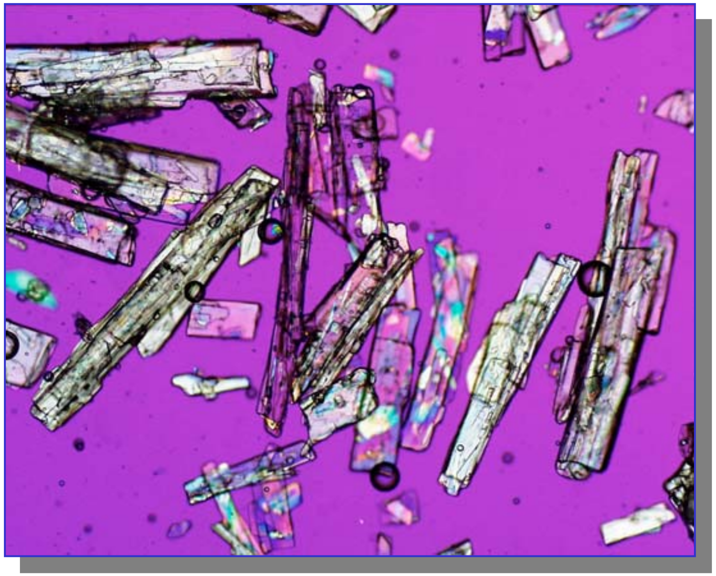
$$C(NO_2)_4 \xrightarrow{Na_2SO_3} C(NO_2)_3SO_3Na + NaNO_2 \ldots\ldots$$



New TNT Purification Technology

- Crystallization is key to avoiding Red-Water
- Traditionally, impurities reacted with sodium sulphite to give water soluble products – K047
  - 10-15% of all starting material + water





- Pure TNT can be crystallized by careful cooling and seeding of acid mixture.
- Crystallization gives two acceptable streams
  - Pure TNT, wet with acid
  - Spent acid containing the impurities
- TNT is washed with water
- Water and acid combined for purification

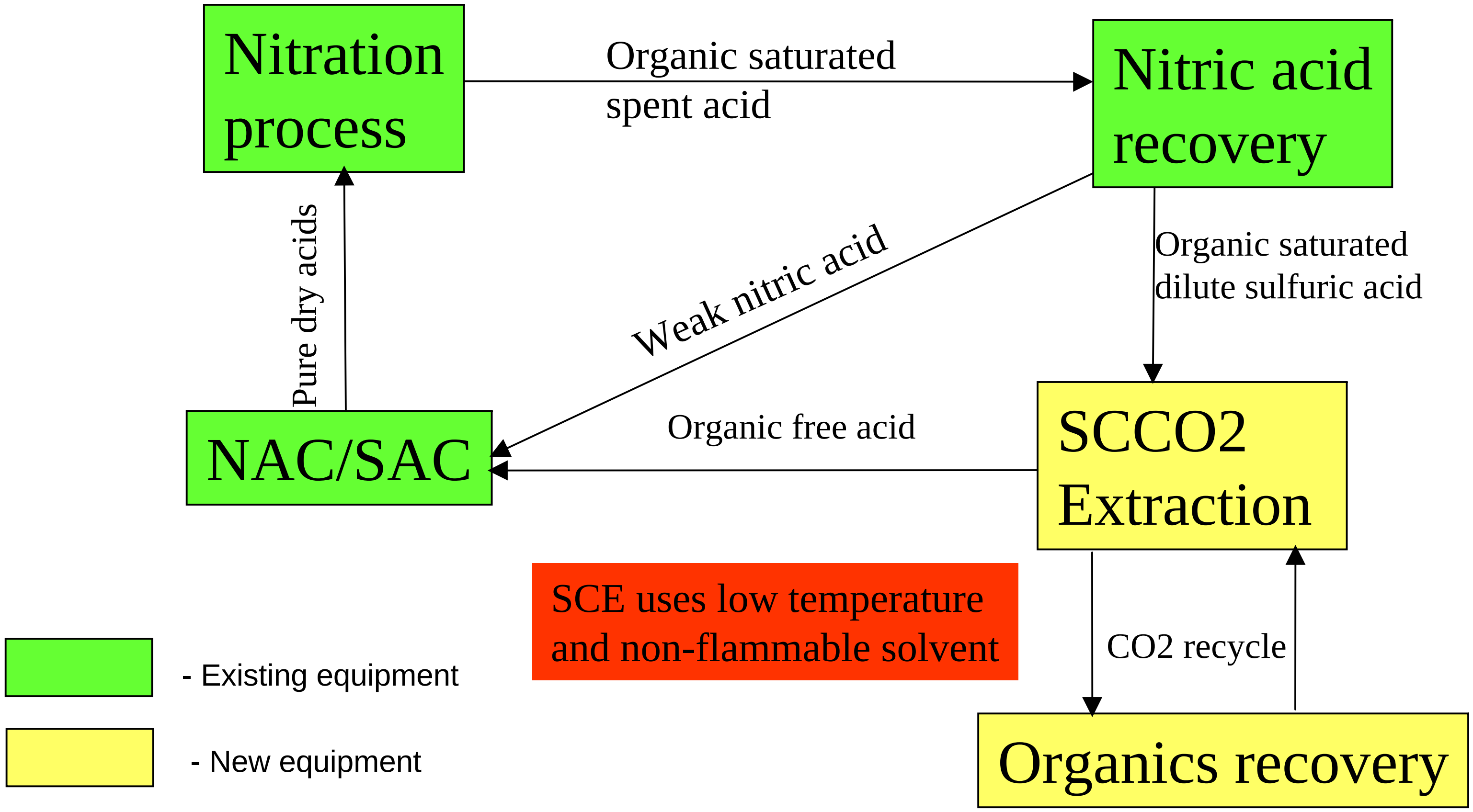
Other process streams

- Spent acid
  - The sulfuric acid left after nitration, saturated with organics and containing nitrous and nitric acid
  - Needs to be reusable (organic free) or disposable (stable) CHEAPLY
- Fumes
  - Acid vapor, NOx, SOx, VOC
- Water
  - Washing the product and cleaning vessels

Acid Purification treatment

- Before concentration and reuse, spent acid must be free from organic materials
- Options
  - Extract organics
    - Toluene/Butane
    - Super-critical carbon dioxide (SCCO2)
      - New approach for acid clean-up
      - Patented new technology
      - Very environmentally attractive
      - Developing with Chematur and INEEL
      - Treatment of extracted material
        - » Incinerate
        - » Isotrioil
  - Destroy organics
    - Pyrolysis
    - Oxidation/reduction
- New approach gives optimal solution
- Options give risk minimization

Acid Treatment

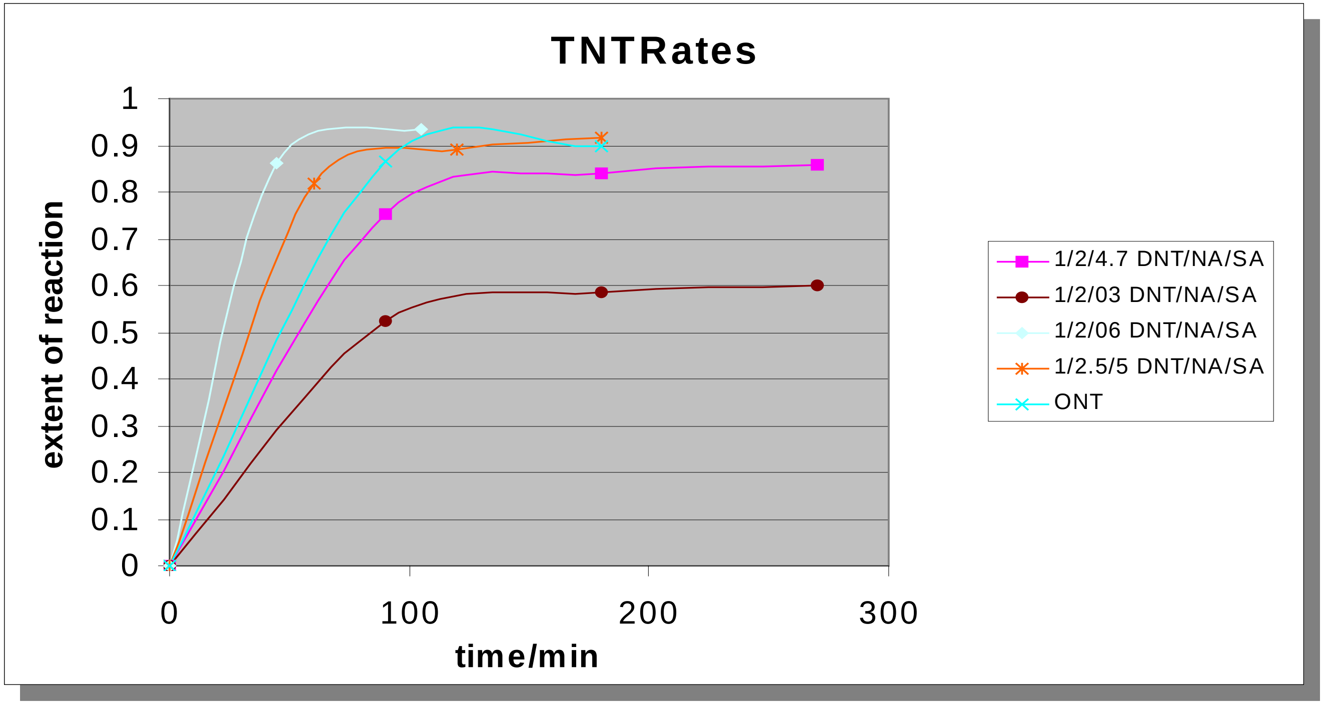


- New Acid Treatment was essential for any restart of our TNT facilities
- SCCO2 extraction fits well with existing process
- Can be used for different processes with no modification
- Demonstrated partition coefficient and obtained IP

Support for scale-up of process

- Precise nitration conditions
  - Yields, kinetics vs. conditions, process sensitivity to all variables
- Waste stream management
  - Every single process stream MUST be accounted for
- Precise crystallization conditions
  - Purity, morphology, washing
- Acid purification
  - Waste stream management
  - Demonstrate CO2 technology

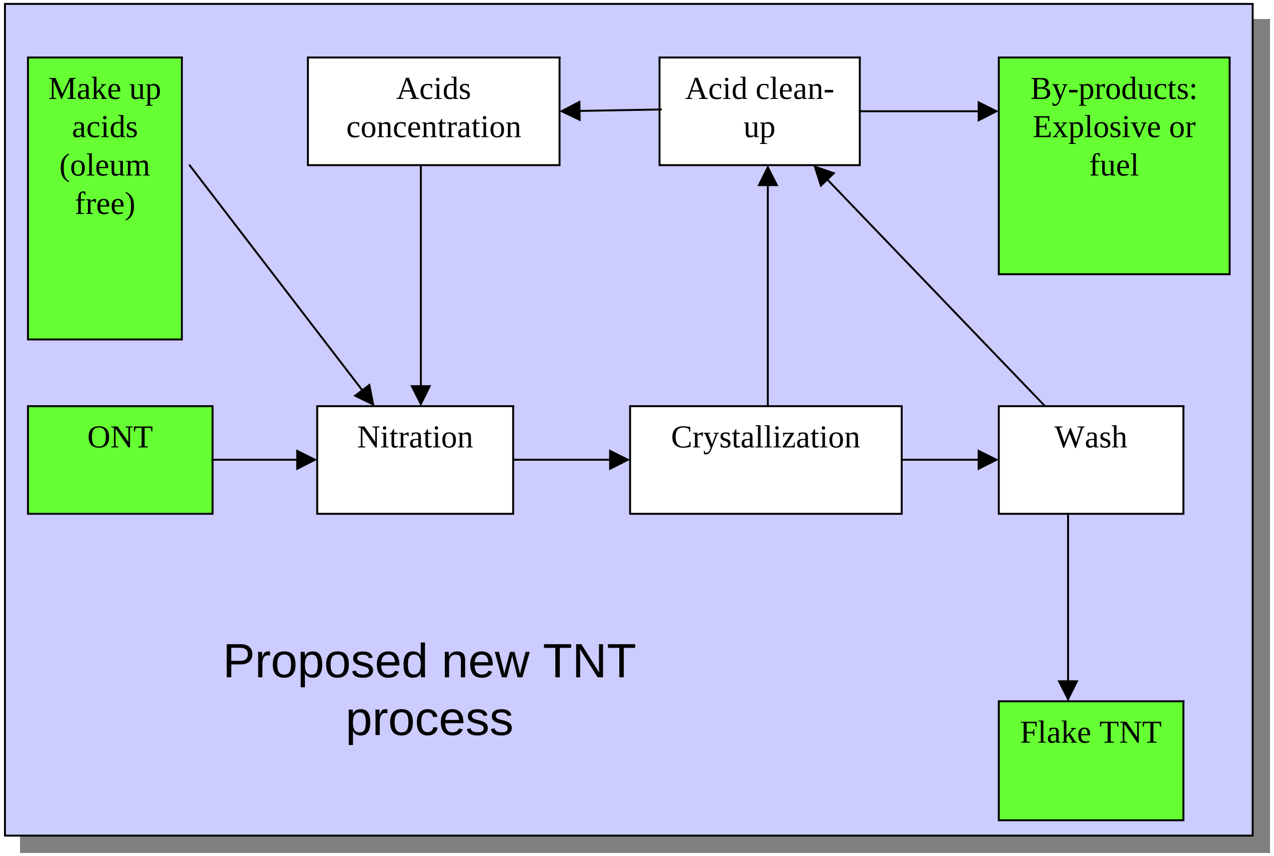
TNT Nitration Kinetics



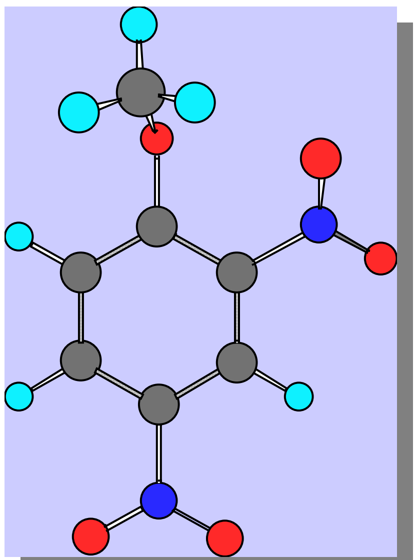
- Reaction rates are key for process control and obtaining pure TNT
- Rates are dependant on:
  - TNT partition coefficient between acid and organic phases
  - Nitrating ability of acid
- Partition coefficient is a function of acid composition, organic composition and temperature (all vary with extent of reaction)
- Nitrating ability is a function of acid composition

New TNT Process

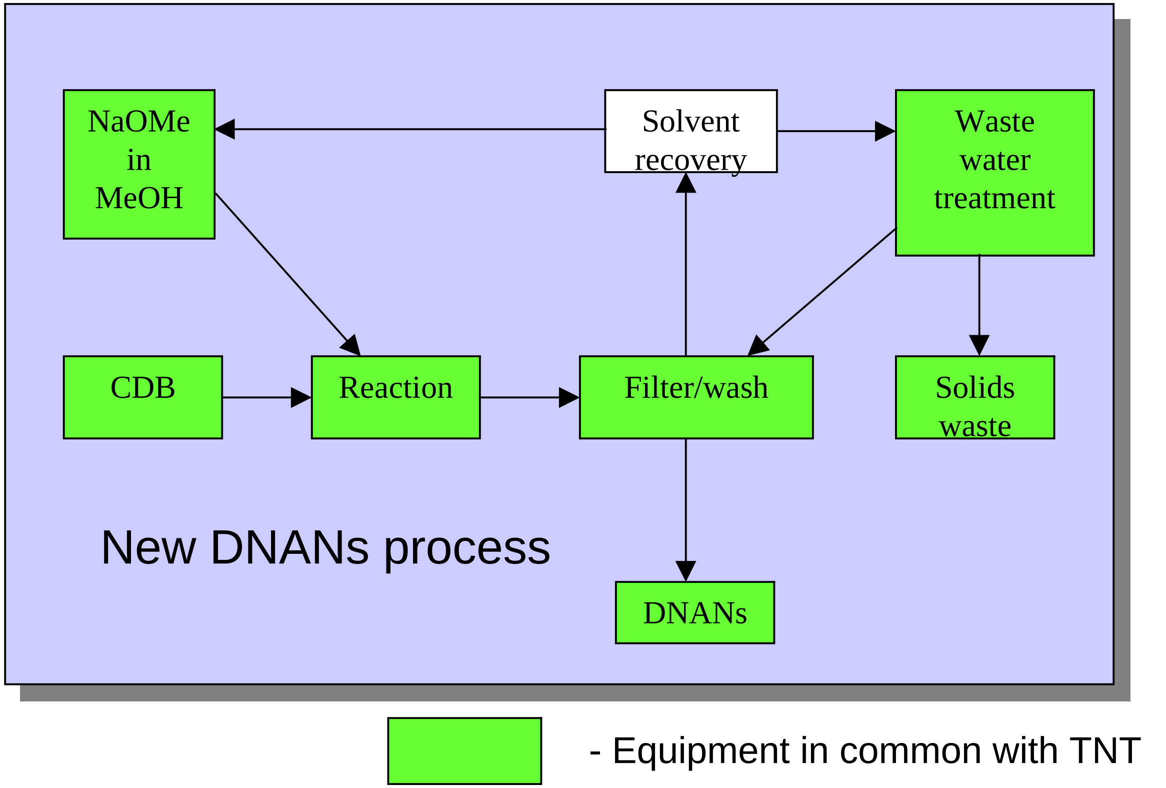
- Oleum free
- Acceptable acid clean up
- No yellow or red water
- Minimal infrastructure changes
  - Acid clean-up
  - Crystallization
- Additional process equipment readily available



New Dinitroanisole Process

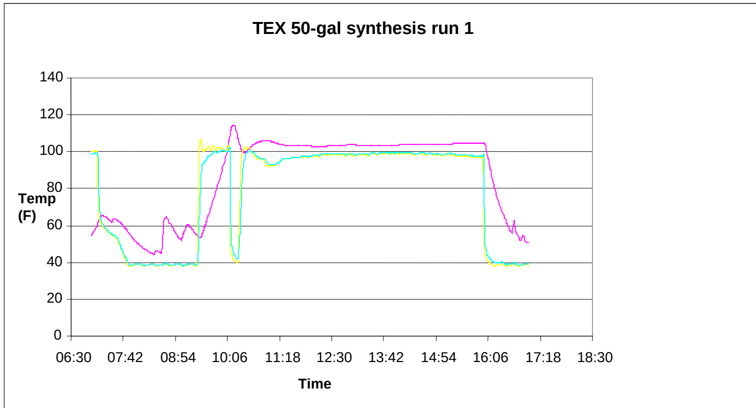


Calculated DNANs structure

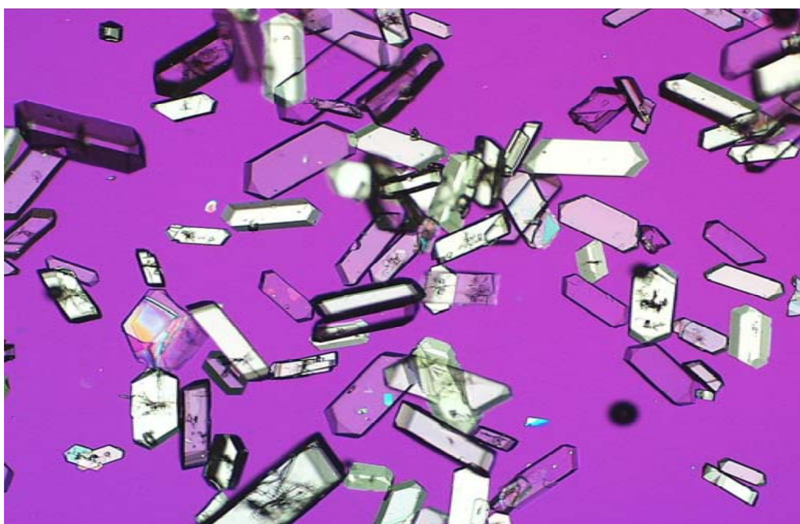


- Increased reported synthesis reaction rate 100 fold
  - Very high potential production rate
- Patented new chemistry
- MAXIMUM USE OF CURRENT INFRASTRUCTURE

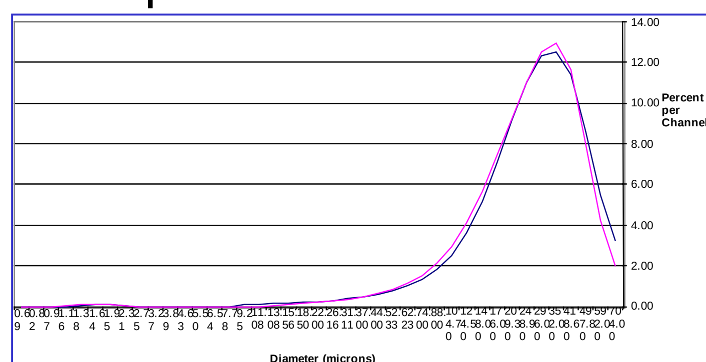
TEX/NTO/CL-20 Processes



- Processes were designed based on previous lab and pilot-plant experience
- New NTO chemistry was devised specifically for RFAAP equipment
    - Thermal and analytical data was gathered for all processes

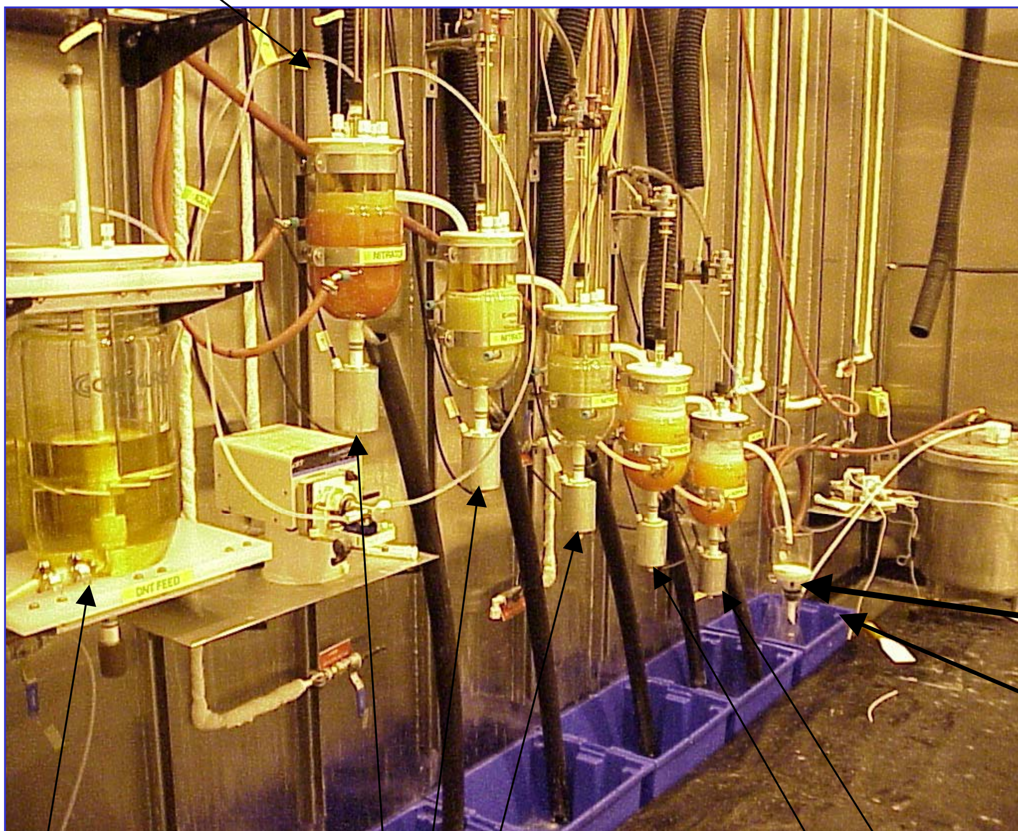


TEX Crystals



TNT Pilot plant runs

Acid feed



ONT Feed

Nitrators

Crystallizers

PURE TNT

Filter

Processes Validated

- Pure TNT from ONT (or DNT)
- Co-current nitration
- Oleum free nitration
- Continuous crystallization

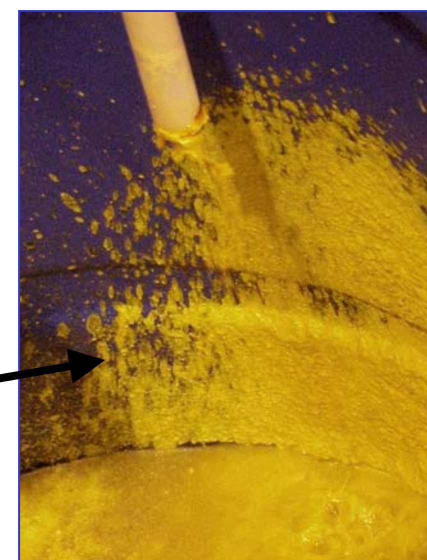
Pilot Plant Dinitroanisole

- Quality material produced on first run
- High production rate (5-10lb/hour)
- Data recorded included:
  - Hard measurements - temp.
  - Practical observations – slurry behaviour

DNANs reactors at equilibrium

Overflow to quench

Crude DNANs being quenched



Conclusions

The 1970s TNT plant at Radford AAP is being made into a modern, flexible energetics facility, able to realize practical, green production of TNT and a range of new materials.

You can teach an old dog new tricks if:

You have a great team doing the training

You can add an extra limb or two