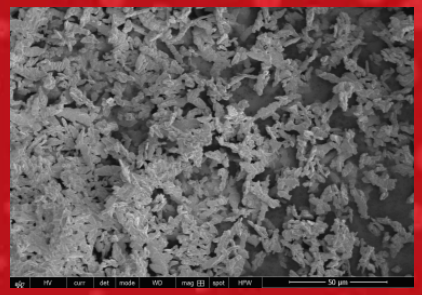
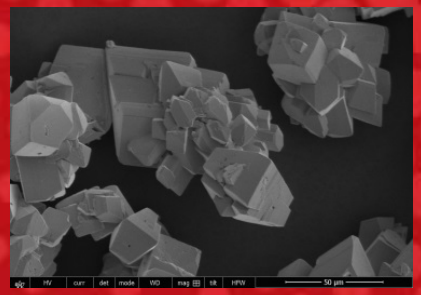




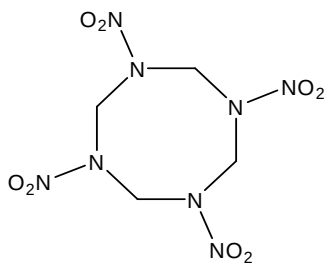
DAPO-LLM-105: improving the particle morphology and thermal stability

IMEMTS Séville (Spain) – October 21-24, 2019

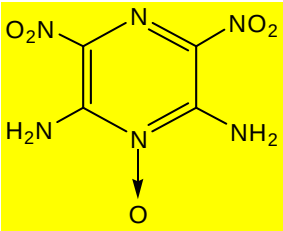
Anne Wuillaume for the CEA-Le Ripault Energetic and Organic Materials team

LLM-105: context and literature

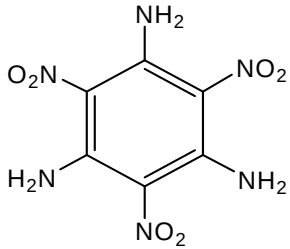
First reported in 1994 by Lawrence Livermore National Laboratory (USA) and synthesized by Dr. Philip Pagoria.



HMX



LLM-105

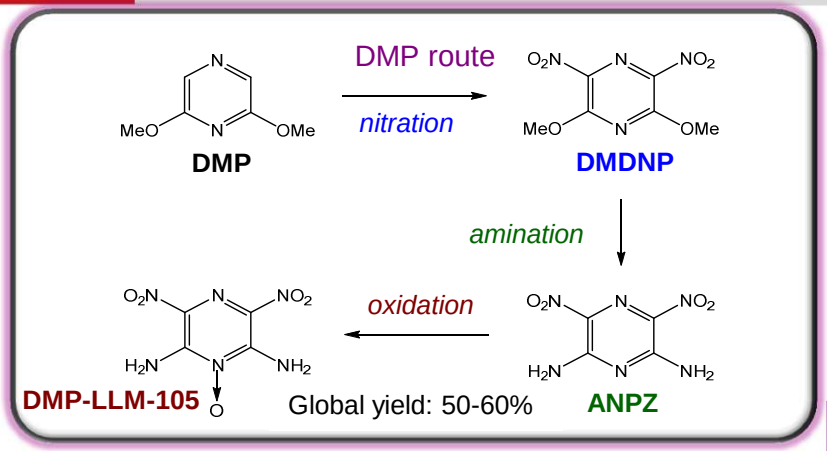


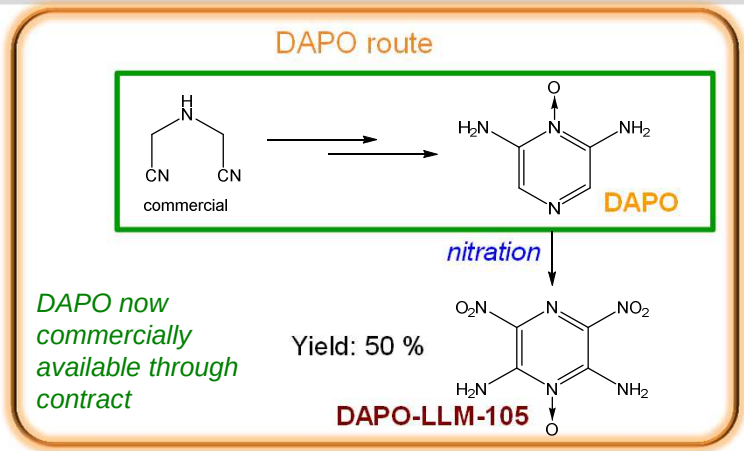
TATB

HE molecule	Drop-weight impact sensitivity (10kg hammer)	Decomposition temperature (DSC onset)	Detonation velocity
TATB	> 250 cm	370°C	7733 m/s
LLM-105	22 cm	345°C	8200 m/s
HMX	8 cm	280°C	8789 m/s

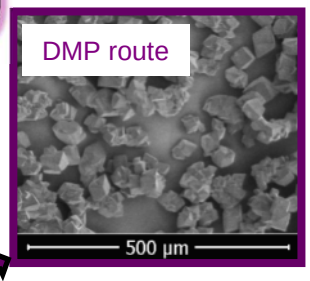
80% power of HMX
120% power of TATB

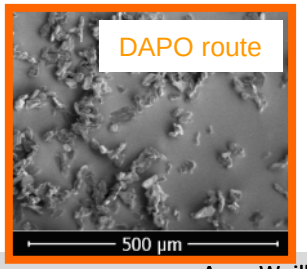
LLM-105 synthesis: state of the art





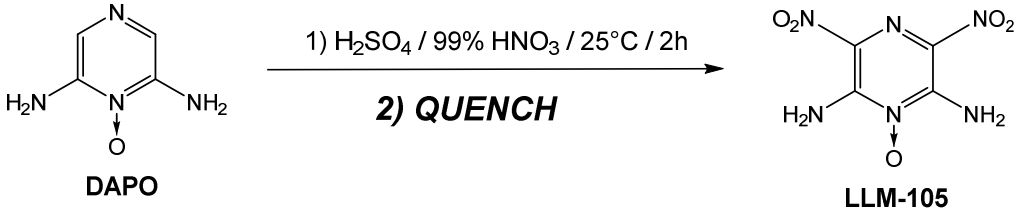
- ✓ **DMP route is very mature and well documented in the literature**
- ✓ **DMP-LLM-105 was characterized:**
  - thermal stability (VTS, DSC, ODTX) and safety tests
  - cubic, relatively coarsed particles
- ✓ **all steps involve explosive**
- ✓ **residual ANPZ (~5%) ►power slightly lower than theory**



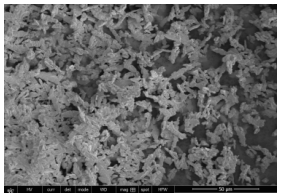


- ✓ **DAPO route has only 1 step involving explosive ► less security constrain**
- ✓ **no residual ANPZ ► power closer to theory**
- ✓ **anticipated cost reduction**
- ✓ **very small particles**
  - impact on formulation (behavior)?
  - impact on the final PBX properties?
- ✓ **recent route (US patent 2010)**
  - purity ? Thermal stability ?

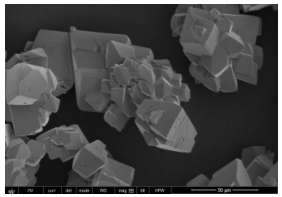
DAPO- LLM-105: quenching studies



Our efforts have been focusing on the quench
Goal: improve particle size and aspect ratio + acquire thermal stability data on DAPO-LLM-105



Water quench



Water + additive to be defined

- ✓ Nitration conditions were ignored : any improvement to the quench is believed to be useful whatever the nitrating mixture (LLM-105 is soluble in the nitration mixture)

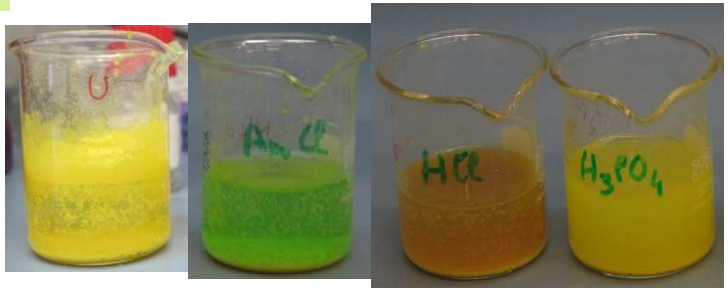
- ✓ 20 quench additives tested on 2g scale
- ✓ 10 quench additives tested on 100-500g scale

DAPO- LLM-105: quenching studies
General strategy

Screen quench additives (2g)

<u>20 quench additives tested (aqueous solution containing various additives):</u>
mineral or organic acids / ammonium salts / nitrates / water-soluble organic molecules

Select the best additives



DAPO- LLM-105: quenching studies
Selection of the best additives on 2g scale

✓ Each synthesis (~2g LLM-105) was divided into 4 portions and quenched into 4 different solutions

✓ The same procedure was used throughout the study
- stirrer shape and speed
- ice/salt cooling
- mixed acids to quench volume ratio
- quench temperature: 25-35°C
- additive concentration: 0.54 mol per 100 mL water (if soluble enough)

Selection criteria

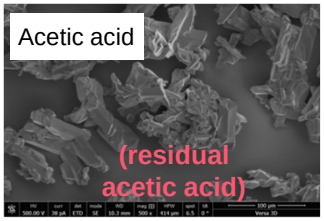
- Behavior during quench (heating, foaming…)
- DSC
- NMR (purity)
- Morphology and particle size

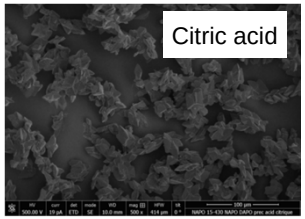
Qualitative assessment for each criterion:
- Acceptable
- Problems expected upon scale-up
- Unacceptable

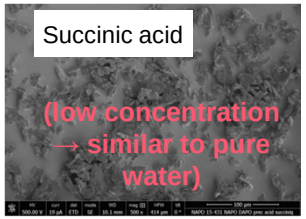
→ **Overall assessment:**

DAPO- LLM-105: quenching studies
Selection of the best additives on 2g scale

Acid additives	Acetic acid	Trichloro-acetic acid	Trifluoro-acetic acid	Formic acid	Phosphorous acid	Phosphoric acid	Citric acid	Succinic acid (low conc.)	Hydrochloric acid
Overall criteria		behavior			DSC	DSC			behavior + DSC

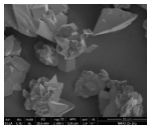




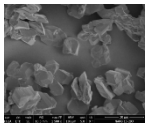


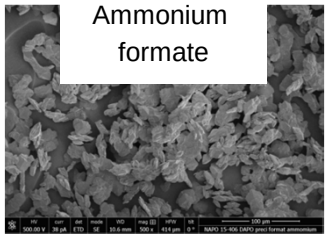
Ammonium salts	Ammonium Nitrate	Ammonium Sulphate	Ammonium Phosphate	Ammonium Formate	Ammonium chloride	Ammonium Carbamate	Ammonium Sulphamate
Overall criteria			behavior + DSC			Behavior (violent reaction)	Behavior, DSC, NMR (purity)

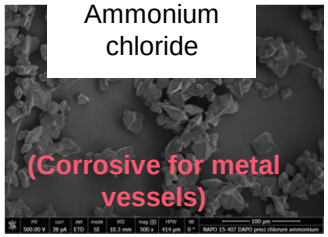
Ammonium nitrate



Ammonium sulphate

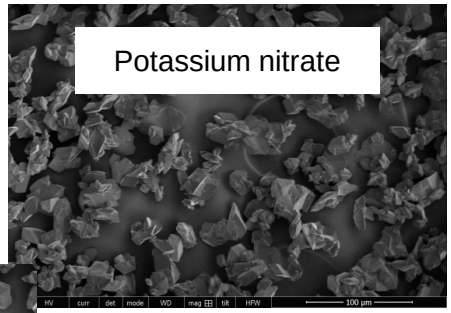


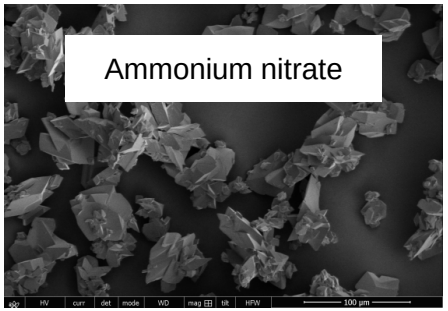


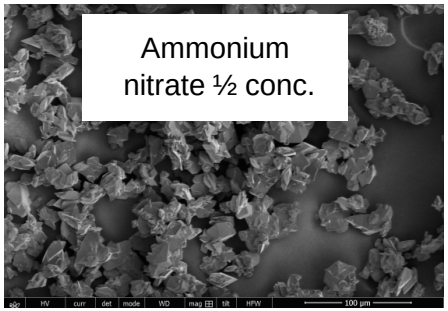


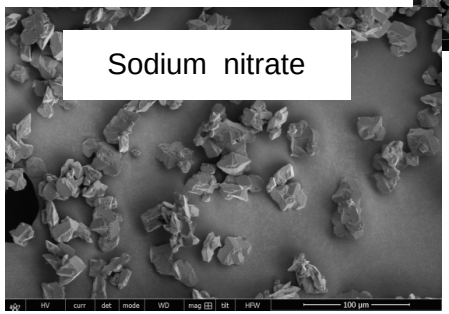
DAPO- LLM-105: quenching studies
Selection of the best additives on 2g scale

Nitrates	Ammonium nitrate	Ammonium nitrate ½ conc.	Sodium nitrate	Potassium nitrate
Overall criteria				

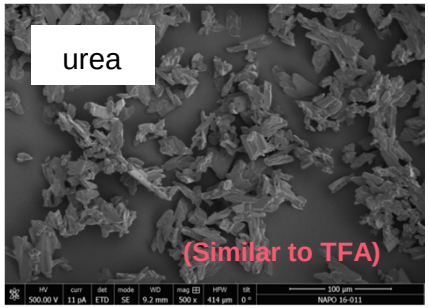








Water- soluble organic molecules	Nicotinamide	Urea
Overall criteria	DSC, RMN	



DAPO- LLM-105: quenching studies
General strategy

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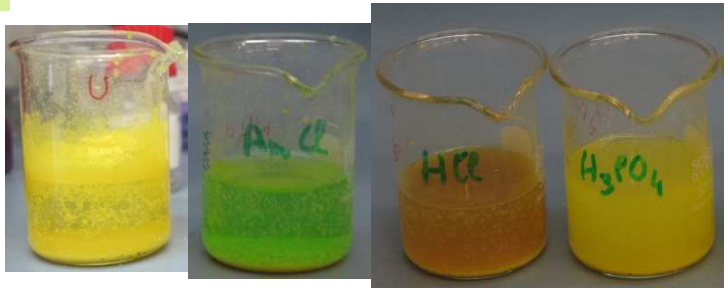
<u>20 quench additives tested (aqueous solution containing various additives):</u>
mineral or organic acids / ammonium salts / nitrates / water-soluble organic molecules



Select the best additives

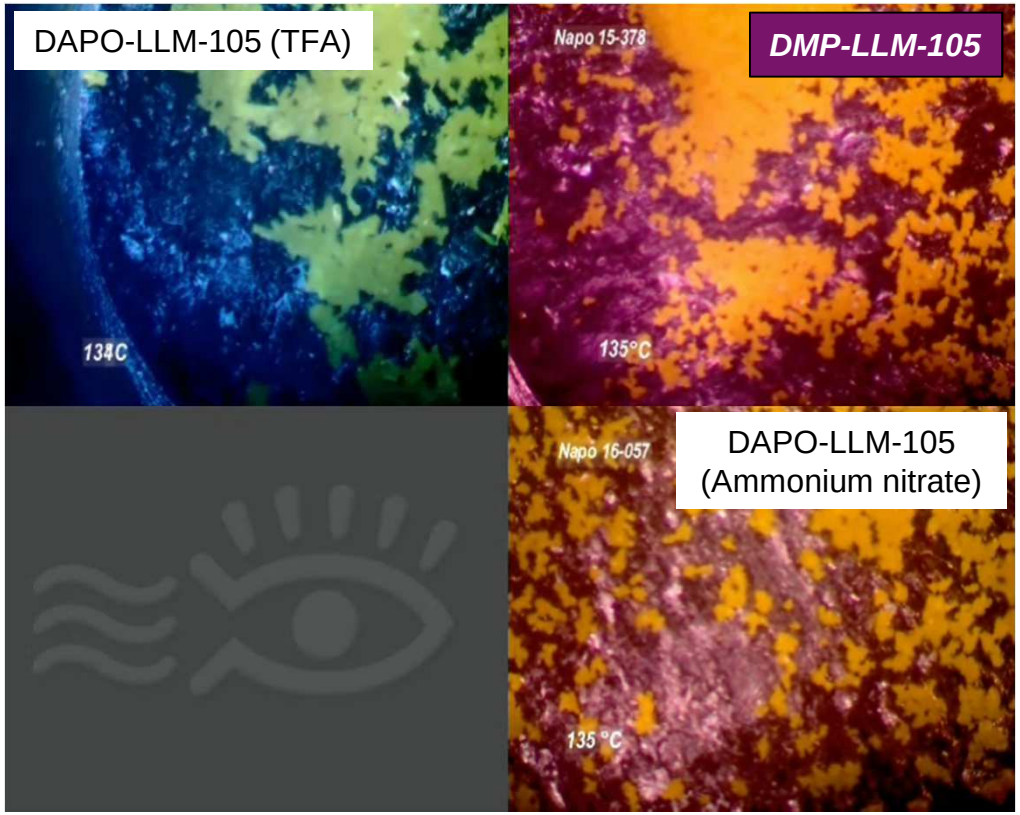
Scale-up selected additives (and pure water for comparison) to 100-500g

Select final additive

- Behavior (scalability)
- DSC/NMR
- Morphology / Particle size
- **Weight loss @120°C / VTS (140°C)**
- **Thermal stability (Thermomechanical Limit Test + Time-to-decomposition)**
- **PBXing behavior**
- **Pressing behavior of the PBX**

DAPO- LLM-105: quenching studies
Selection of the best additive on scale-up (100-500g)

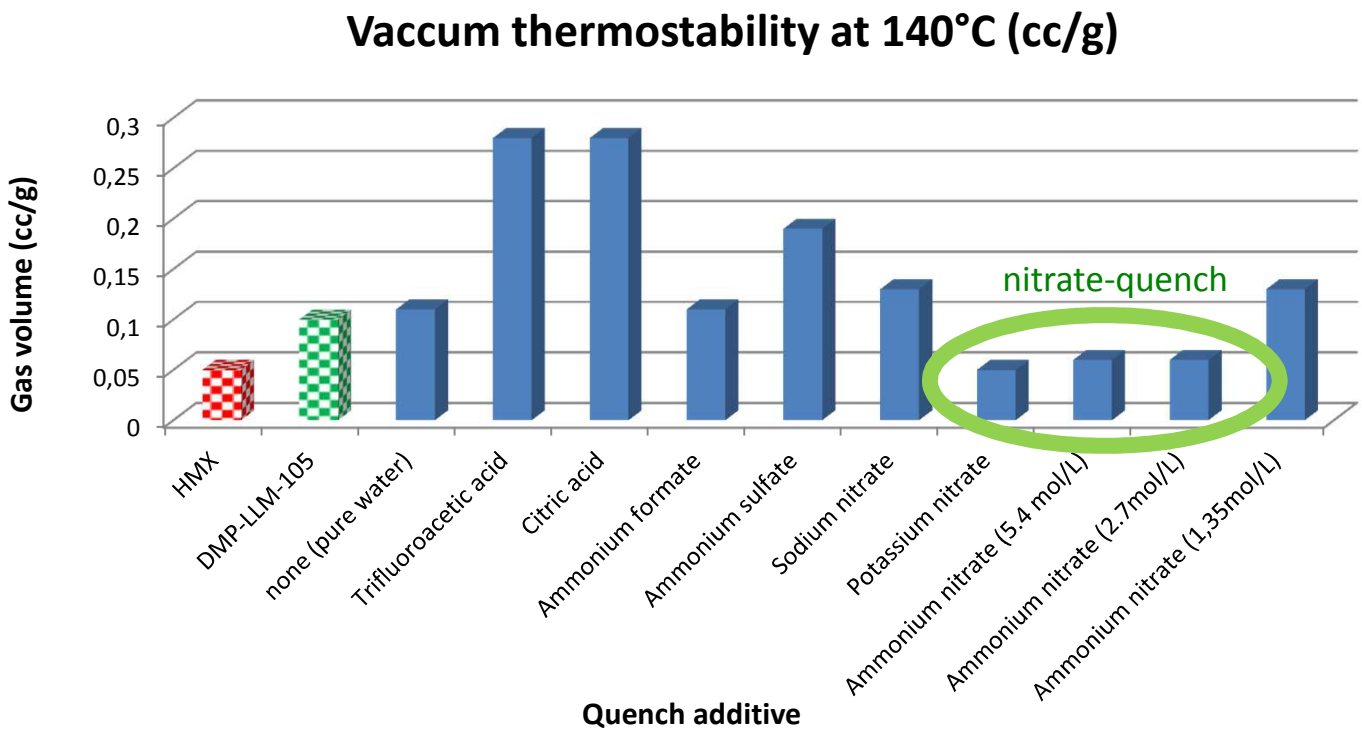
Thermal stability and behavior (DSC)



Important fragmentation of TFA quenched DAPO-LLM-105 as early as 220-230°C (phenomenon different from decomposition at 345°C)

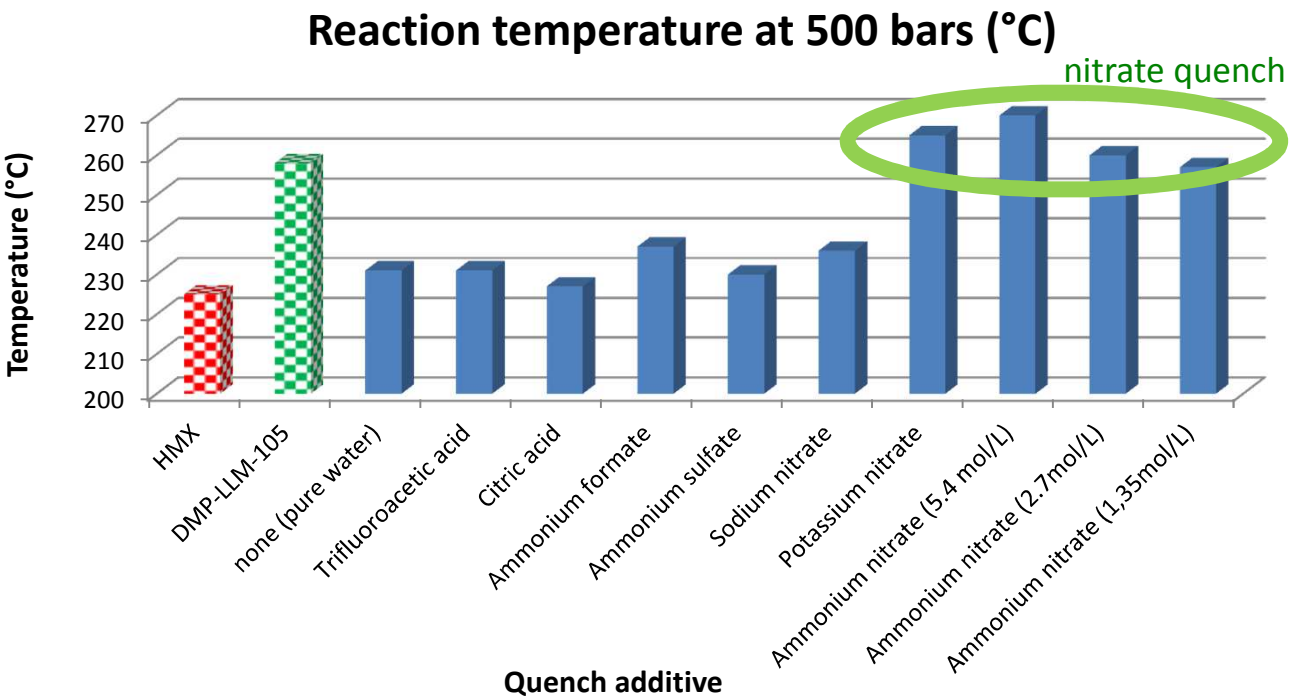
DAPO- LLM-105: quenching studies
Selection of the best additive on scale-up (100-500g)

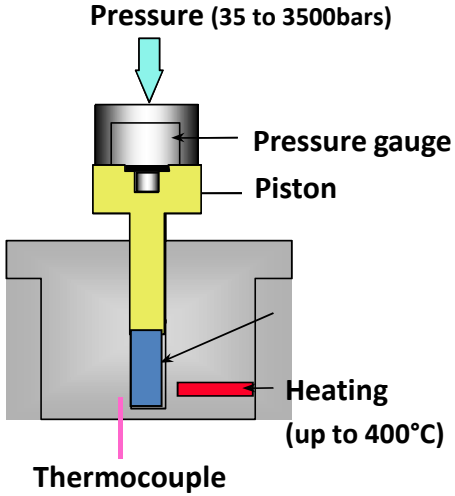
Thermal stability and behavior



DAPO- LLM-105: quenching studies
Selection of the best additive on scale-up (100-500g)

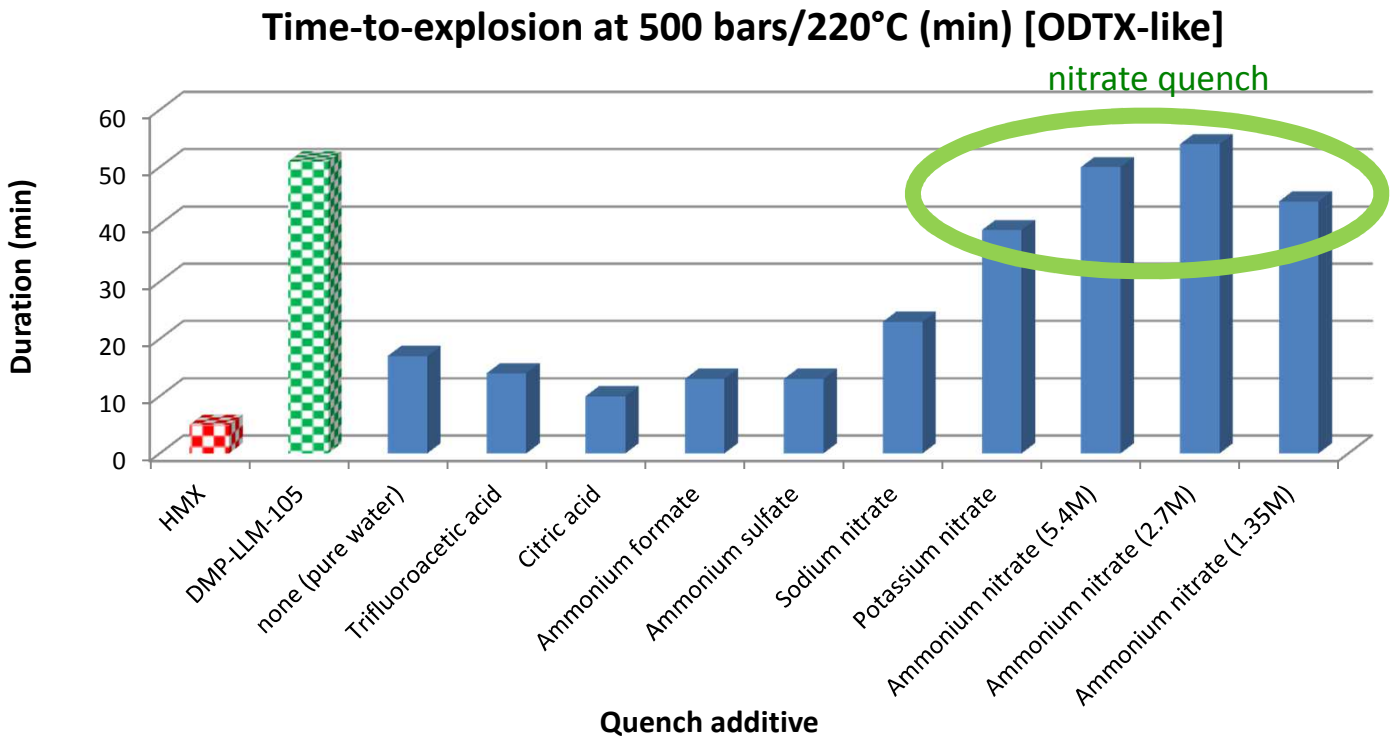
Thermomechanical behavior





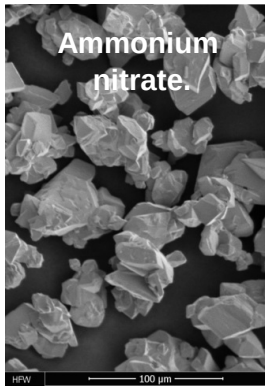
DAPO- LLM-105: quenching studies
Selection of the best additive on scale-up (100-500g)

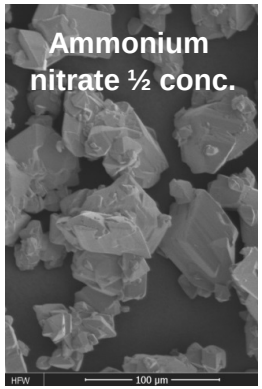
Thermomechanical behavior

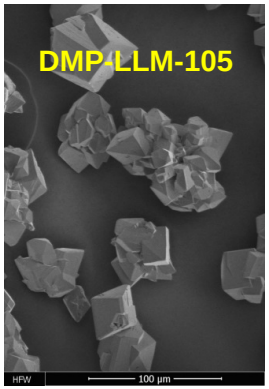


DAPO- LLM-105: quenching studies
Summary and conclusion

- ✓ Quenching DAPO-LLM-105 in aqueous nitrate solutions (ammonium or potassium nitrate) allows the synthesis of a high quality product (thermal stability and purity)
- ✓ Particles size and aspect ratio are significantly improved over the classical water quench, without requiring any recrystallization process
- ✓ These new DAPO-LLM-105 are similar to DMP-LLM-105 (morphology) with the advantage of avoiding the presence of residual ANPZ, and have slightly better insensitivity characteristics







	Drop-weight impact sensitivity	Spark sensitivity
DAPO- LLM-105 AN quenched	48.4 cm	136.4 mJ
DAPO- LLM-105 AN ½ conc. quenched	48.5 cm	113.3 mJ
DMP-LLM-105	19-24 cm	110 mJ

- ✓ The nitrate-quenched procedure has been scaled up to 500g
- ✓ This work has been published in Propellants Explos. Pyrotech., **44** (2019) and patented: PCT/EP2018/054632

Acknowledgements

- ✓ **The synthesis team :** Nicolas Pin, Eric Pasquinet, Agnès Morancey
- ✓ **The chemical and physical characterizations team :** Audrey Girault, Eric Lalière, Thierry Maillou, Gilles Sevin, Alain Bry, Nathalie Eloy, Sylvie Moulin, Pascal Palmas, Eric Bruneton, Alexandre Forzy, Alexandre Lecardeur, Marie-Lou Perdrigeat, Stéphane Quéré, Chrystel Ambard, Christelle Barthet, Maxime Biessy, Marilyne Bousquet
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Thank you for your attention