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Production of ADN particles for WP7 using new method

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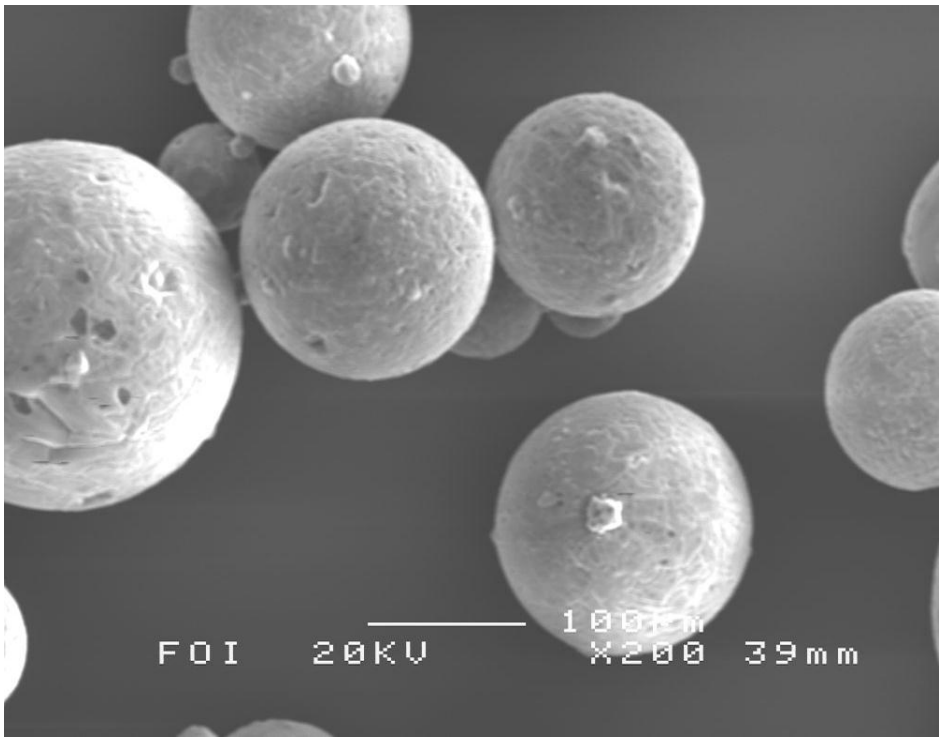

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Front page picture; SEM photo of spray prilled ADN.

Summary

The ADN received from EUB has high purity but the particles are needle shaped and not suitable for propellant formulation. Spherical particles, prills, are preferred. The most suitable method to produce ADN prills is by spray prilling.

In HISP deliverable D3.3 the up-scaled spray prilling method is described. In this report the capacity of the up –scaled spray prilling method has been verified. During four days a total amount of 45 kg prilled ADN was produced and the maximum amount of prills produced during one day was 16 kg. This is well above the requested amount of 10 kg per day.

Contents

1 Introduction

In order to obtain high specific impulse a high solid loading is required. However, high solid loading increases the viscosity of the uncured propellant. Thus, the maximum solid loading and impulse is limited by processing constraints. To obtain a castable propellant formulation with reasonable viscosity and high solid loading, particles with minimum spatial extension are required. For this reason the particles should have a low aspect ratio or more preferably a spherical shape.

Today ADN is produced by EUB in Sweden and available in larger amounts for evaluation and research. The purity of the material produced is above 99% and it has a high thermal stability. However, the particle shape of the ADN received from EUB is needle shaped and thus not suitable for formulation.

Two different methods to produce spherical ADN particles, prills, have been developed; i.e. spray prilling (FOI) and emulsion prilling (ICT). The production of prilled ADN using these methods, and the delivery of the required amount of prilled ADN to respective project partner, are described in HISP deliverable D3.1.

In the HISP project the following methods to produce ADN particles with suitable morphology have also been studied;

- Recrystallization (TNO)
- Grinding/milling (FOI)

The different methods studied have been compared and evaluated in HISP deliverable D3.2. Among the methods evaluated, spray prilling was the most promising method and was selected to be up-scaled. The scaling up of the spray prilling method is described in HISP deliverable D3.3.

The objective of this work was to demonstrate that the up-scaled spray prilling method can produce at least 10 kg prilled ADN per day as requested in the HISP project Description of Work.

2 Description of the spray prilling process

In the spray prilling process crude ADN is melted in a vessel equipped with a bottom valve. To improve the heat transfer and hence shorten the melting time, the vessel is equipped with a stirrer. The molten ADN is then pumped and sprayed through a nozzle into a container containing a liquid medium. The melted ADN droplets solidify into particles (prills) in the liquid medium. The prills are produced using up to 2000 g ADN per batch. After spraying, the prills are dried in two steps; first by vacuum filtration in the collection vessel, and then, to fully dry the prills, using a fluidized bed. 0.5 weight-% fumed silica (Cab-O-Sil) is added to the dried prills to prevent caking. The amount of ADN per batch is selected so that the melting- and spraying time is consistent with the drying time of the prills. Time for the different steps of the prilling process is displayed in Table 1. The prilling equipment is further described in HISP delivery D3.3.

Table 1. Run time of the different steps during the prilling procedure (2000 g ADN).

Step	**Time (minutes)**[a]
Melting	10
Spraying	2.5
Drying	13
Sieving and packing	20

a) Melting and spraying is done simultaneously as the previous prill-round is being dried.

2.1 Production of ADN prills

The scaled up process of prilling ADN was made to increase the production rate to at least 10 kg ADN-prills per day. Crude ADN batches 20129009 and 20129034 manufactured by EURENCO Bofors were used. Two large batches of prilled ADN, FP12011 and FP12061 (prilled in the scaled up spray prilling equipment described in HISP delivery D3.3) was mixed together and homogenized to form a 45 kg batch. Each spraying of ADN was made using 1500-2000 g crude-ADN. After the spraying the ADN-prills was dried, 0.5% Cab-o-Sil was added as an anti-caking agent and sieved using a 750 µm sieve. The 45 kg batch was then homogenized, weighed and put into polyethylene cans with air-tight lids. The cans were put in black ESD bags together with silica gel as a drying agent. Prilling and packing took place in a controlled environment with a RH of 14-22% and a temperature of 23-25°C.

To control the size of the prills and to narrow the size distribution, the spray pressure and pump speed were adjusted. Production parameters for the whole process are displayed in Table 2 to Table 4. The total time to produce 45 kg prilled ADN was four days and as a maximum 16 kg ADN was prilled during one day.

Table 2. Batch information.

Crude ADN batch	20129009 and 20129034
Prilled ADN batch	FP12011/FP12061
Amount prilled ADN	45 kg
Additive	Cab-o-Sil M5 (0.5%)

Table 3. Spray prilling process parameters.

Melt time	10 minutes
Each spray	1500-2000 g
Losses	~7% (including particles >710 µm)
Temperature of recirculating heating	105ºC
Spraying pressure	1.5 & 3 bar
Spray nozzle	SU5
Room temperature and humidity during production	23-25ºC 14-22% RH
Medium for solidification	dried n-heptane
Temperature of medium	22-23ºC
Drying agent for medium	Molecular sieves, 4Å

Table 4. Sieving and packing.

Sieving	< 710 µm
Can	1500 - 2000 ml
Drying agent	Silica gel with moisture indicator

3 Analysis of prilled ADN

The homogenized ADN batch number FP12011/FP12061 was subjected to the following analysis:

- Particle density measurements at 25°C
- Particle size and distribution
- DSC (25 to 120°C at a heating rate of 10 K/minute)

The apparatuses and the experimental procedures used are further described in section 3.1.

The results from the analysis are presented in Table 5 to Table 7 and in Figure 1 and Figure 2.

Table 5. Result from He-pycnometer measurements.

Batch	**Measurement #**	**Density (g/cm^3)**	**Average (g/cm^3)**[a]
FP12011/FP12061	#6418:1	1.7742	1.776 (0.001)
	#6418:2	1.7868	
	#6418:3	1.7856	

a) Standard deviation within parenthesis.

The particle size and distribution in Table 6 are presented as three volume fractions; low 10%, 50% and high 10% (shown as $d_{0.1}$, $d_{0.5}$ and $d_{0.9}$) and size distribution span, *S*.

Table 6. Result from particle size distribution analysis.

Batch	**Measurement #**	$d_{0.1}$ **(µm)**	$d_{0.5}$ **(µm)**	$d_{0.9}$ **(µm)]**	***S***
FP12011/FP12061	1	69	230	410	1.48

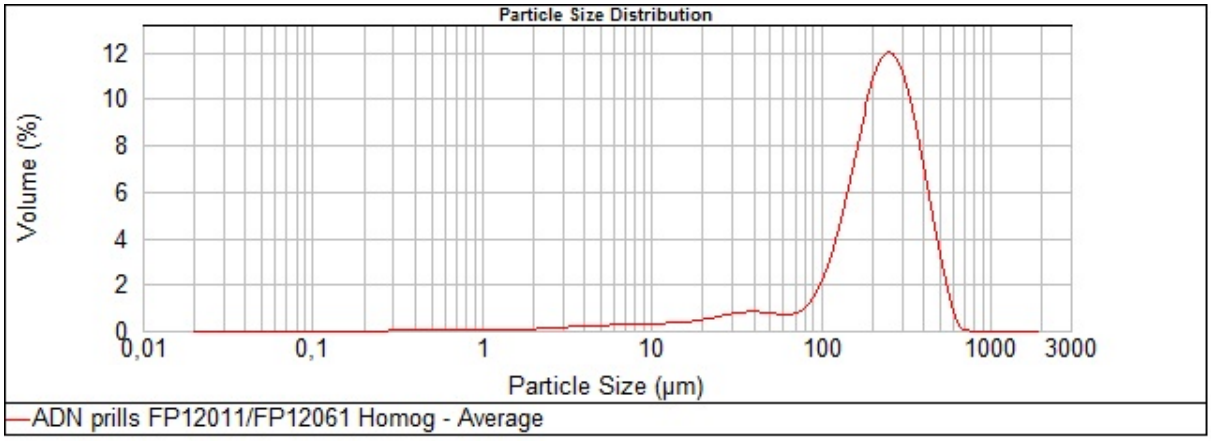

Figure 1. Result from particle size distribution measurement.

Thermal properties of prilled ADN measured by DSC are shown in Table 7 and Figure 2. T_m = melt temperature (°C) and ΔH_m = melt enthalpy (J/g).

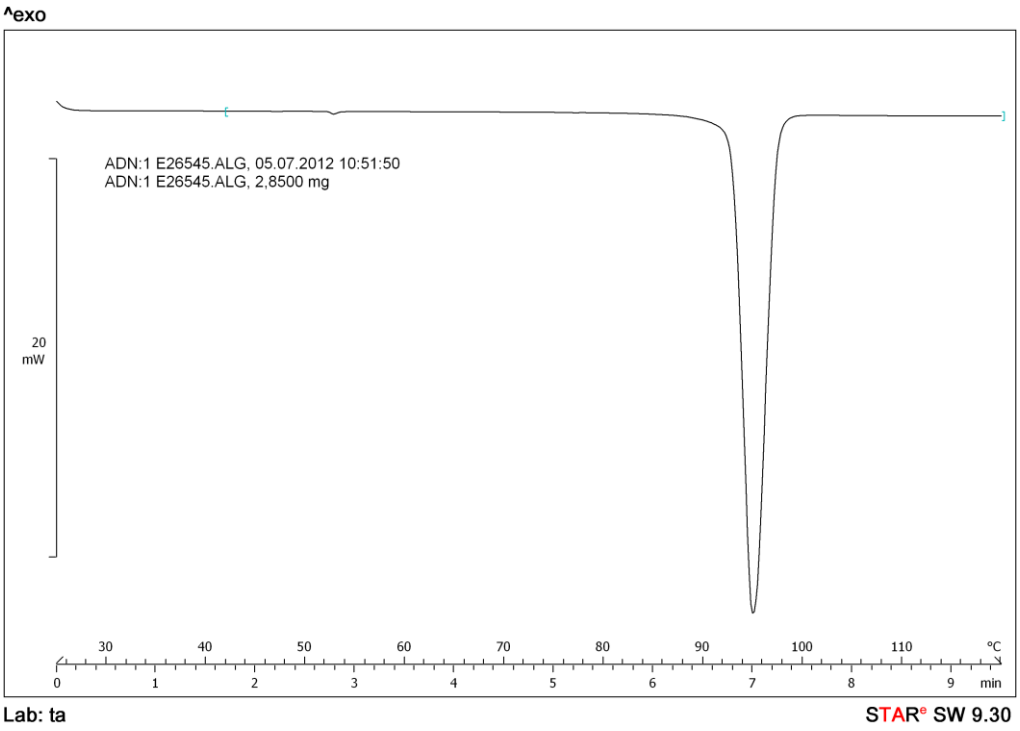

Figure 2. DSC thermogram for prilled ADN, batch FP12011/FP12061, at a heating rate of 10 K/min.

Table 7. Results from DSC measurements.

Batch	Measurement #	T_m (°C)	ΔH_m (J/g)	Purity (mol %)
FP12011/FP12061	#6418:4	92.9	143.7	99.9
	#6418:5	92.3	143.2	99.7

The particle density of the material was 1.776 g/cm^3, which is in line with previous studies [1]. The purity of ADN was estimated using the Mettler Toledo STARe software v 8.10. The method is based on analysis of the DSC melting peak by using the van't Hoff equation, as described in the literature [2]. The melting point (92.6°C), heat of melting (143 J/g) and the estimated purity (99.8 mol %), all indicating the material to be very pure and in accordance with previous studies [1].

3.1 Analytical methods

3.1.1 Particle density

Density measurements were performed at room temperature using a Micromeritics AccuPyc 1330 gas pycnometer, operating in a helium atmosphere (99.996%, AGA Gas). The volume of the measuring cell was approximately 10 cm^3 and it was filled to approximately 80% volume. Before each analysis, the system will be purged for a total of 10 times and after each analysis, the density will be calculated. The deviation between each run must be less than 0.0007 g/cm^3 or the result will be excluded. The density of each sample will then be determined after 5 successful consecutive runs. To verify the calibration, Micromeritics AccuPyc 1330 calibration standard (6.37203) was used.

3.1.2 Particle size analysis

The particle size distribution was measured using a Malvern Mastersizer 2000. *n*-heptane with lecithin (4 drops/l) was used as dispersant. Ultrasound treatment (40% efficiency, 240 seconds) was used to breakup possible agglomerates. The sample was subjected to 3 consecutive runs at a pump speed of 2200 rpm. The particle size diameter is presented as three volume fractions; low 10%, 50% and high 10% (shown as d_{10}, d_{50} and d_{90}). Particle size span, *S*, was calculated according to Equation 1.

$$S = (d_{90} - d_{10}) / d_{50} \quad (1)$$

3.1.3 Differential scanning calorimetry, DSC

A Mettler Toledo DSC 822 differential scanning calorimeter was used to determine melting point and ΔH_m of ADN particles. The apparatus was purged with nitrogen (80 ml/min). The sample, approximately 2 mg, was put in a 40 µl aluminium cup with pierced lid and was heated from 25°C to 120°C at a rate of 10 K/minute. The temperature and heat flow was calibrated using indium (ME-29749 Mettler-Toledo, Sweden).

4 Conclusions

The capacity of the up –scaled spray prilling method has been verified. During four days a total amount of 45 kg prilled ADN was produced and the maximum amount of prills produced during one day was 16 kg. This is well above the requested amount of 10 kg per day.

The prills produced were analysed and the results show that they are very pure and in accordance with previous studies.

5 References

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2. Standard Test Method for Mol Percent Impurity by Differential Scanning Calorimetry; E 928-85; ASTM: 1985.