Development of extruded double base rocket propellants – alternative ballistic modifiers

Erik Tunestål*, Henrik Skifs
EURENCO Bofors AB, Björkborns Industriområde – SE-6911 86 Karlskoga - Sweden
e.tunestal@eurenco.com

Abstract
There are for the moment no regulations restricting the use of current ballistic modifiers but it could be expected due to the lead-content. Therefore Eurenco Bofors has worked on projects regarding replacing the lead-based burn rate modifiers and implementing more green alternatives. This development has also included prospects of producing these new modifiers in-house, in order to minimize the impact of ITAR and export regulations. Replacing the lead based modifiers has been demonstrated for a formulation with a burn rate of around 15 mm/s. For lower burn rate formulations the challenge is to achieve an acceptable temperature coefficient. The main performance indicator used during this study has been the pressure exponent, if no plateau effect is seen over the investigated pressure range the substance has been rejected for further evaluation. The different compositions have been mixed on a 9-kg scale and evaluated in mock-up motors with different nozzles to produce a pressure range from 5 to 25 MPa and also at different temperatures to have some information of the temperature variation.

A number of different alternatives have been evaluated some from literature such as salicylates of copper and bismuth, (United States of America Patent No. 5652409, 1996). Also other metal organic substances have been tested, some with better results than others. Copper citrate for example did not work at all in our application, there was no apparent effect in the evaluated pressure range.

The most interesting copper-compound was later synthesized at EURENCO on a 5-L scale to produce enough material for propellant sample production and ballistic testing. The synthesis method tested at EURENCO was straightforward and resulted in an 84% yield. The product was characterized using DSC, FTIR and AAS for copper content and compared with reference sample. Regarding the synthesis, treatment of the copper containing waste water needs to be considered upon further scale up.

Sourcing of materials is not straight forward, this study has re-confirmed this. The same material was sourced from two different suppliers and tested in the same composition. When evaluating the results from the mock-up motor test the results were completely different. One of the sources performs as expected with almost plateau effect over a 5 MPa pressure range and a burn rate of 20 mm/s. The other source however has a pressure exponent of 0.74 over the evaluated pressure range and overall a lower burn rate. No deviation from the specification was found for these two samples.

Background – why we are doing this – what has been done
Eurenco produces a wide range of double base rocket propellant formulations, the propellant grains are produced using solvent-less extrusion technology. The propellant is produced at the Eurenco Bofors site in Karlskoga, Sweden. Many of these propellant formulations were initially developed during the 70's and 80's or even earlier for use in the Bofors produced anti-tank and surface-to-air missile systems. With the increased regulations and new customer requirements it has called for re-development or new development of these formulations. The chemicals affected concern several parts of the formulation such as plasticizer, stabilizer, ballistic modifier and processing aids. Within

this topic stabilizers has already been discussed at IMEMTS 2015, this work is still on-going and undergoing scale-up. This paper focuses on the research and development put into identifying alternative ballistic modifiers both regarding suppliers and substances. This work has been supported by the Swedish Defence Materiel Administration, FMV.

Apart from the increasing and stricter environmental legislations a major issue for European manufacturers is the ITAR which regulates many defense-industry related raw materials which are produced in the US. This is why efforts are put into finding alternative sources and as a last resort in-house synthesis of strategic raw materials. Considering future regulations and restrictions local or in-house synthesis could be a viable option for strategic raw materials. Synthesis methods for a number of substances considered as burning rate modifiers have been developed on a laboratory scale. Each substance is made in one-pot, one-step synthesis using water as media.

Scarce raw materials

The military industry is a small community and some of the chemicals we use are more or less exclusively used in military applications. This results in a strong dependence on a specific supplier. If that supplier decides to close-down production or if regulations force them to stop, this affects the military systems directly. Recently several such cases has come up for Eurenco, where the producer either totally stopped or increase the prices more than 500%. There are several different international co-operations with the objective to identify compounds where the sourcing is or could be problematic, e.g. within NATO, EU and EDA.

As producer of energetic materials Eurenco has to keep up-to-date and informed about changes at suppliers. Looking into alternatives is also important. There are two solutions when a change in supplier is needed, either you source a new supplier or you start synthesis in-house. They both have their advantages and disadvantages which are being described in the next paragraphs.

Sourcing from new suppliers

The easiest solution seems to be sourcing the material from an alternative supplier. This could be an easy change where the new product doesn’t alter any performance. But when sourcing materials from new suppliers you can stumble upon some interesting results when evaluating products which on-paper seems to be identical. An example of this was the sourcing of a non-ITAR LC-12-10. The analysis performed at our lab showed some difference between the products but still within the specification, showed in Table 1.

Table 1 Results from two LC-12-10 sources

	US-Source	**Non-US Source**
Copper (weight-%)	10,04%	11,92
Lead (weight-%)	35,99	33,29
BET Surface (m^2/g)	11,71	15,88

But the difference in ballistic performance is extreme, there is no desired effect of the non-US source at all. In the evaluated pressure range the US source has a pressure exponent of 0.02 and the non-US source has and exponent close to 1.

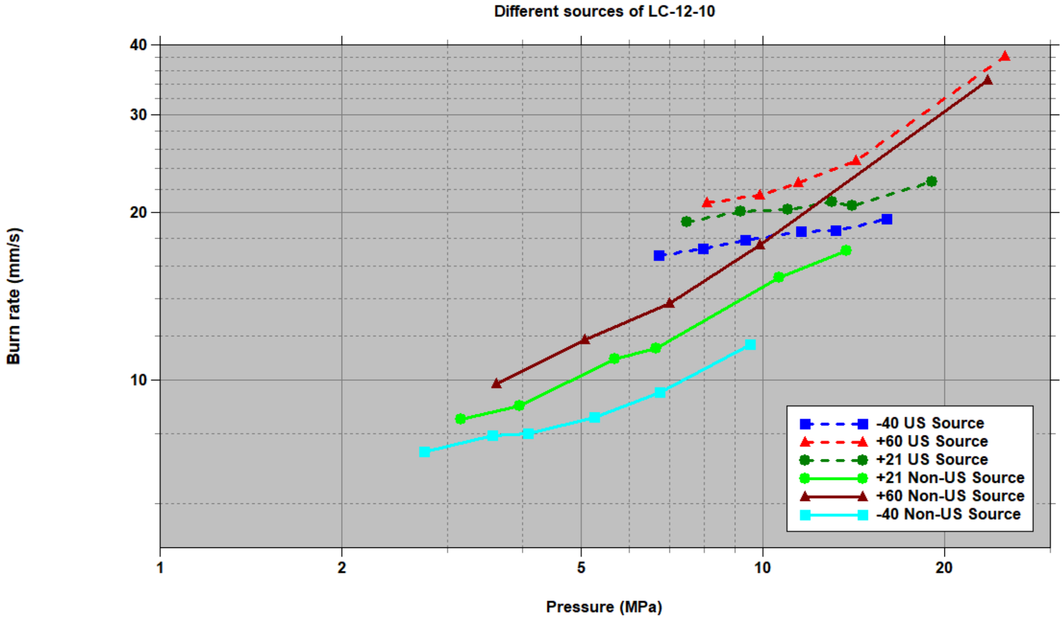

Figure 1 Burn rate results from standard rocket test.

The propellant formulations were evaluated with identical recipes were the only difference were the source of raw material. The results were confirmed in a second test. The two formulations were evaluated in mock-up motors with six different nozzles and three temperatures. The nozzle diameters were the same in the testing. The test method is described in more detail in a previous publication, (Tunestål, o.a., 2015).

The results from this tests are another confirmation of the risk of simply sourcing raw materials as if it were nuts & bolts. It also re-iterates the need for thorough testing before accepting a new supplier. Further analysis of the materials showed clear differences in differential scanning calorimetry (DSC) results, Figure 2.

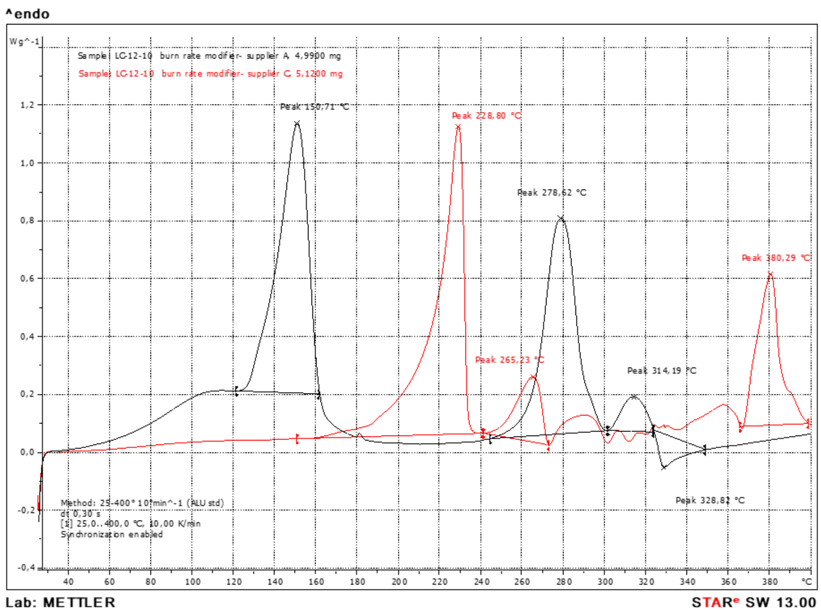

Figure 2 DSC results from two different LC-12-10 sources, US source in black.

When analyzing using Fourier Transform Infrared Spectroscopy (FTIR) they show similar pattern when looking at the wide spectrum. But more differences are apparent in the fingerprint region, a narrower part of the spectrum, Figure 3. The results from the DSC and FTIR shows that there is clear difference between the samples. This confirms that it is not enough with the metal-content and particle size, you need to have the right type of organic molecule also.

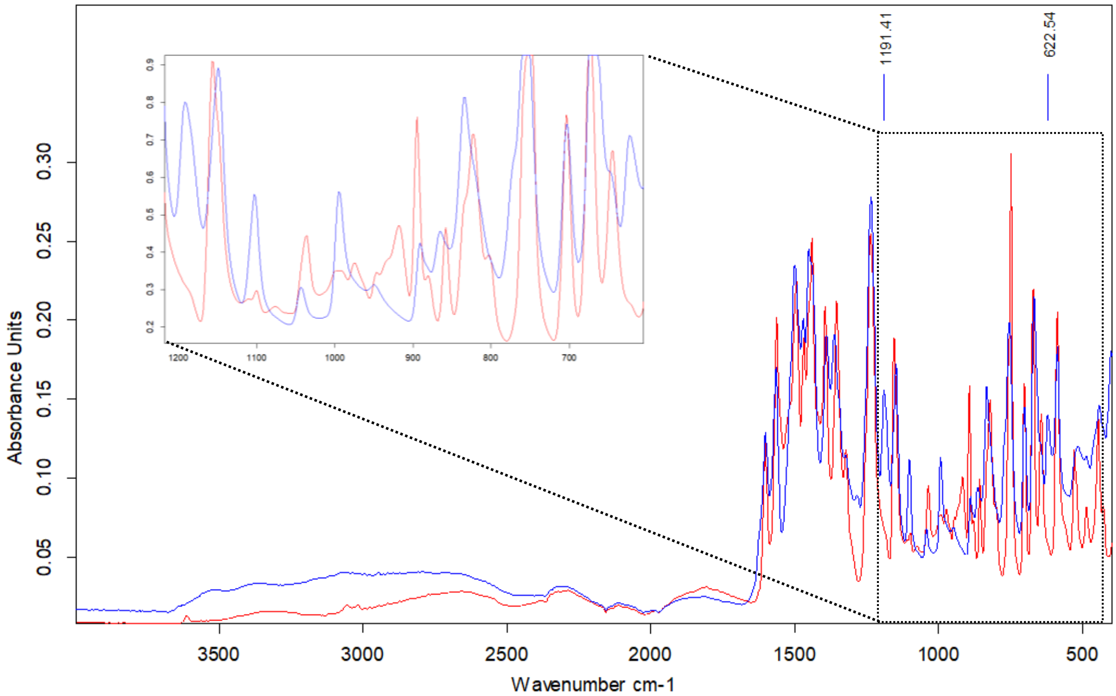

Figure 3 The FTIR spectrum for LC-12-10 from US-Source (blue) and non-US-source (red).

In-house synthesis

In some cases the only alternative is to setup an in-house material. The benefit of having an in-house synthesis is that you have total control of the production line. The drawbacks are normally the production cost and initial investment in setting up the process and identifying a good synthesis route. Eurenco Bofors already have a wide range of synthesis and processing capabilities which makes it easier and cheaper to perform tests. In the following parts our work in in-house synthesis and evaluation of copper salicylate is described.

Synthesis of copper salicylate

In extruded double base (EDB) propellants used for rocket motors one or several ballistic modifiers are used to alter the burning behavior of the formulation. The target is to reduce the pressure exponent over a defined pressure range, resulting in a so called plateau burning propellant. Aromatic lead and copper salts are known to generate this effect more details about this is found in the literature (Kubota, 2007).

Copper salicylate had been identified as a compound where the sourcing could be problematic. In this study the synthesis of copper salicylate was studied in literature and continued by small scale synthesis to identify suitable processing parameters and also to quantify the end product. The small scale synthesis trials showed that a quite straightforward synthesis route was possible with high yields, <90%. The material produced was analyzed using DSC, FTIR and AAS to compare with the reference compound and also the specification. The DSC from the synthesized sample and the sourced sample has a similar graph, but the sourced samples shows a bit earlier onset, Figure 4. At this scale the synthesized material was too little for ballistic testing.

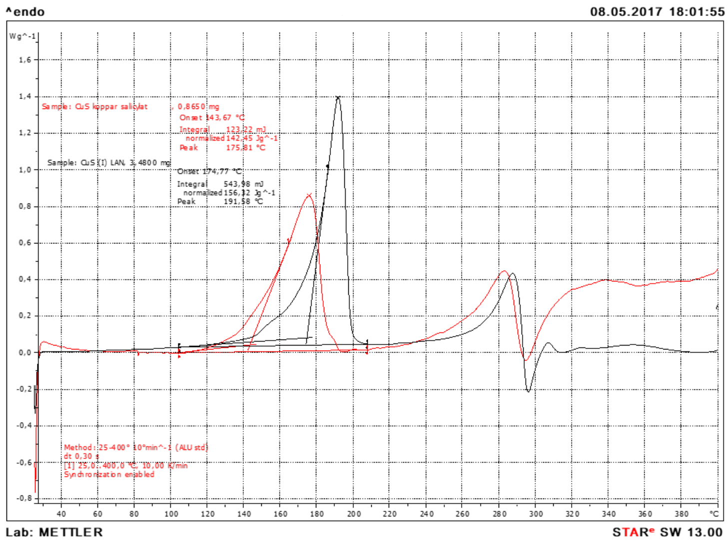

Figure 4 DSC comparing lab scale sample (black) and reference (black)

The next step was to produce enough material for a comparison of the ballistic performance. For this around 150 grams of the material is needed. The synthesis was scaled up to 5 liter scale. At this scale two different temperatures were tested to optimize yield, reaction time and possibly particle size. The material produced from the different syntheses did not look identical, there was a color difference between the two samples, Figure 5. The lower temperature sample is slightly yellowish-brownish in its tone compared to the one synthesized at higher temperature which has a more distinct green color. The yield is also higher at the higher temperature, 84% compared to 71%, this is contrary to the small scale experiments where the lower temperature had higher yield.

Figure 5 Photo of the two synthesized samples, lower (to the left) and higher (to the right) temperature.

Ballistic evaluation of synthesized copper salicylate

The synthesized material was evaluated in EDB propellant formulation. The formulation consist of nitrocellulose (50%), nitroglycerine (35%), tributylcitrate (7%), akardit II (2%) and a ballistic modifier cocktail (5% where of 1.5% is copper salicylate). This formulation is a totally lead free composition and has an energy content of approximately 910 cal/g and a, theoretical, specific impulse of 2200 Ns/kg. The evaluation is performed on mixed batches of 9 kg. These are then rolled on differential rolling mills and extruded into a tubular grain, this test method is described in previous work (TuneståI, o.a., 2015).

The tubular grains are then fired in mock-up rocket motors with different nozzles and at different temperatures. This generates a graph over burn rate at different temperatures and pressures. For this formulation the nominal graph, Figure 6, shows the graph when using the Copper Salicylate sourced from the US.

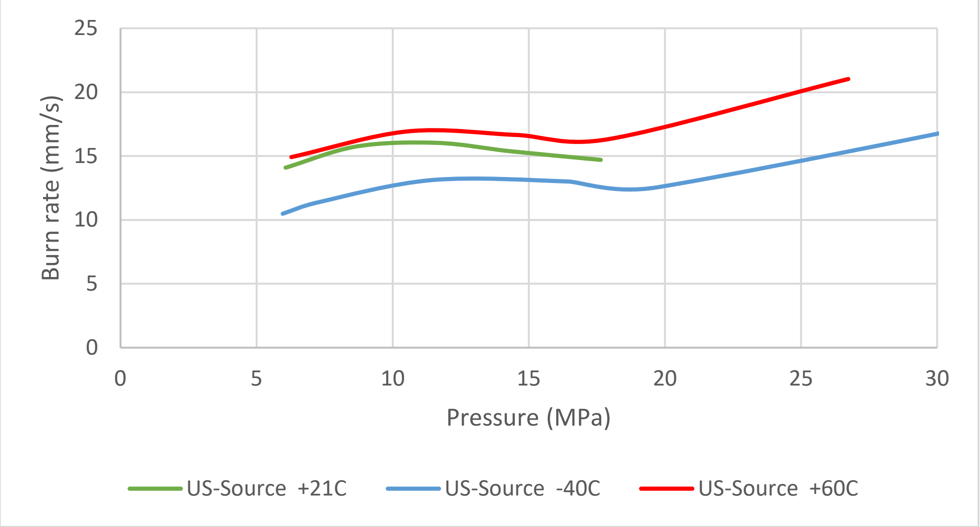

Figure 6 Burn rate vs pressure for the formulation with US-Sourced Copper Salicylate

This formulation shows a good plateau characteristics from 5 to 20 MPa. This formulation was used as a base line where the copper salicylate was exchanged and the rest of the formulation kept as constant as possible.

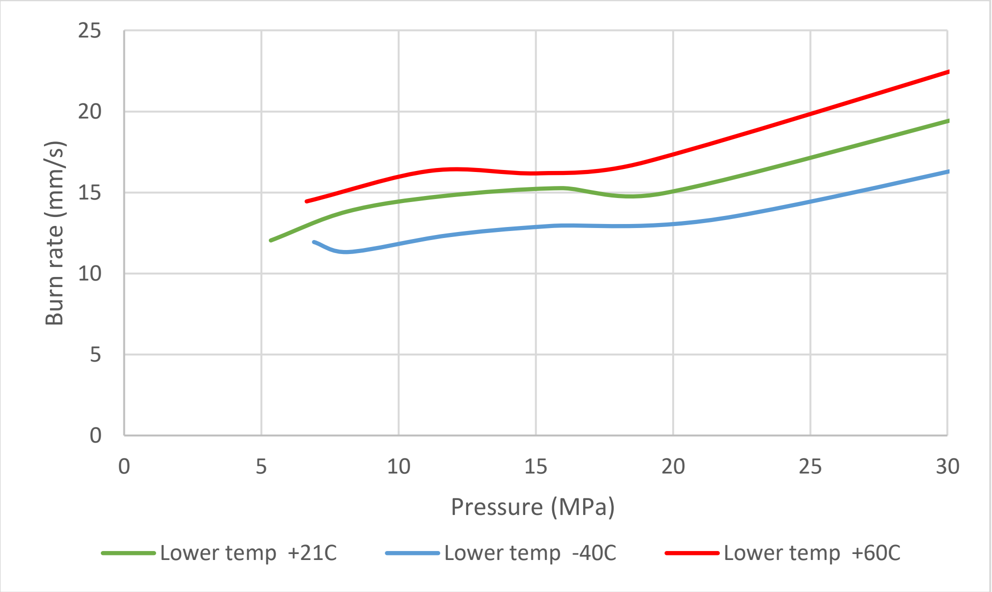

Figure 7 Burn rate vs pressure for the formulation with Copper Salicylate synthesized at lower temp

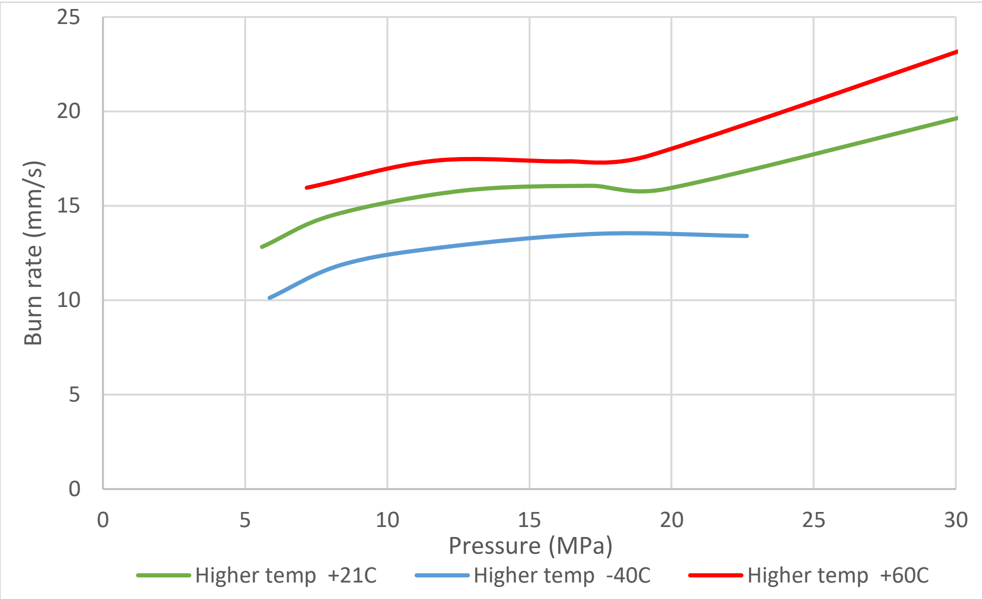

Figure 8 Burn rate vs pressure for the formulation with Copper Salicylate synthesized at higher temp

No clear difference between the three different samples can be noticed. They all have a plateau characteristic in the same pressure range. When comparing them in a joined graph, Figure 9, some small differences can be noticed. The most noticeable is that the US Source seems to have a more pronounced mesa around 17 MPa. More repetitive experiments needs to be performed to confirm if this difference is due to variations in the processing and testing or a real difference coming from the copper salicylate.

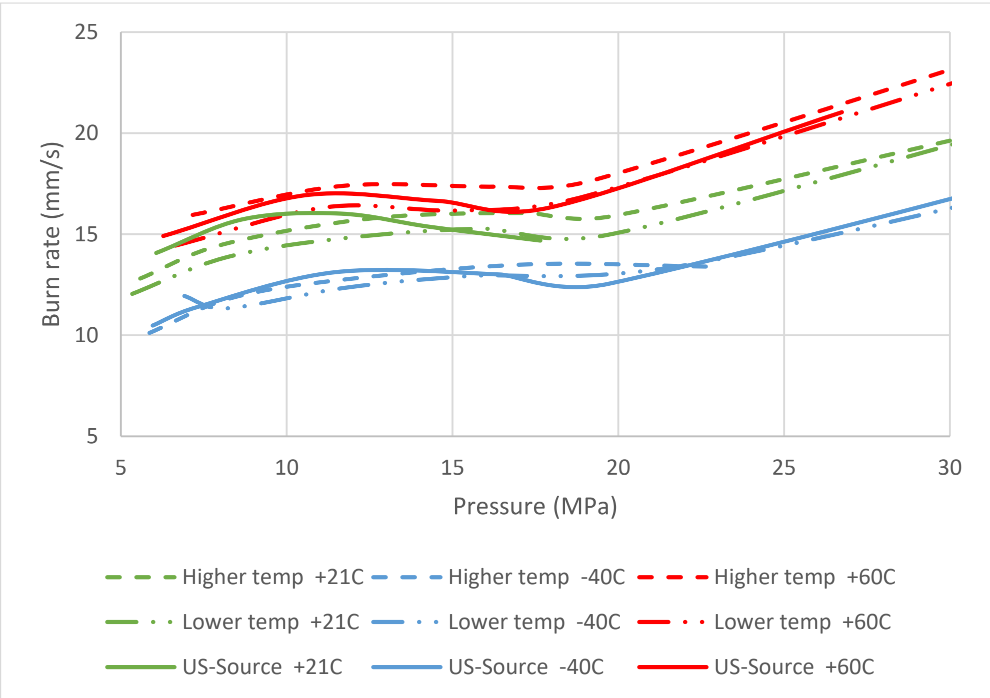

Figure 9 Comparison of the three firings

Conclusions

The results and experiences from this study shows that it is possible to produce a compound using the in-house synthesis route which has performance comparable to the sourced material. This opens up a fallback route when the supply chain is disrupted.

Regarding sourcing it has also been concluded that only following the set standards can show false positives, materials fulfilling the specification still lack the performance from a ballistic point of view. Because of this it is also important to keep an open communication with suppliers with regard to changes in processing and analysis methods.

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