

Implementation of Microencapsulated Fuels in Combination with Hydrogen Peroxide for Creation of New Monopropellants

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Abstract

Microencapsulated fuels offer the possibility of creating a monopropellant composed of typical bipropellant components. This approach unites the advantages of mono- and bipropellant systems, a high specific impulse combined with low technical complexity. Through the microencapsulation, the fuel becomes miscible and storable with an oxidizer. As fuel *n*-decane is used as model substance for kerosene in combination with hydrogen peroxide as oxidizer component since it is considered as green and environmentally friendly. In this work, we present further development on this entirely new concept, including investigations on the stability of the microcapsule dispersion and further optimization of the preparation process.

1. Introduction

In space propulsion, typically used liquid propulsion systems consist either of a mono- or bipropellant system.[1] Bipropellant systems have the advantage of typically high specific impulses (I_{sp}) but they are more difficult to build since they are technically complex, requiring tanks, pipes, valves for both oxidizer and fuel. In contrast, monopropellant systems are easier to build and require less structural material, which can save weight and therefore cost.[2] But on the contrary, the specific impulse of monopropellants is typically lower compared to usual bipropellant systems. From this it can be concluded, that in theory a monopropellant with a high volumetric specific impulse would be advantageous. But the formation of a monopropellant from common two-component propellants is generally difficult, since the oxidizer and fuel of common bipropellants are difficult to mix as they are usually immiscible and may also form an explosive mixture.[3]

A possible method to enable the formation of a monopropellant is the microencapsulation of the fuel component from a typical bipropellant system.[4,5] Through microencapsulation, the fuel and oxidizer are separated by the capsule wall, allowing both components to be safely stored in one tank while creating a monopropellant. This approach would combine the advantages of typical mono- and bipropellant systems (increased specific impulse and simultaneously low technical complexity). In this context, it would be convenient to use hydrogen peroxide as the oxidizer component, since it has a high density, is simple to handle and low in toxicity. It is therefore considered as a green and environmentally friendly propellant component.[6]

1.1 Implementation of microencapsulated fuels in space propulsion systems

To use encapsulated fuels in space propulsion systems with hydrogen peroxide as oxidizer, the microcapsules have to have certain properties such as:[5]

1. Chemical compatibility of the capsule material with hydrogen peroxide and vice versa
2. Capsule material should be combustible and should ideally feature a high calorific value
3. Good mechanical stability
4. Low permeability of the membrane
5. Controlled and targeted opening of the capsules possible

6. Low tendency of capsule precipitation and flocculation

Point 1 and Point 2 as well as more details about the general concept of microencapsulated fuels are described in an upcoming publication of our group.[4] The tendency of capsule precipitation (Point 6) is to be investigated in this work. The remaining points are part of future research from our group.

The capsules themselves are prepared by interfacial polymerization which has proven to be a highly versatile synthesis method for the preparation of microencapsulated fuels.[4,5] In this process, two highly reactive monomers are introduced in two immiscible phases such as water and non-polar hydrocarbons and the monomers eventually react at the interface of the phases to form a polymer.[7]

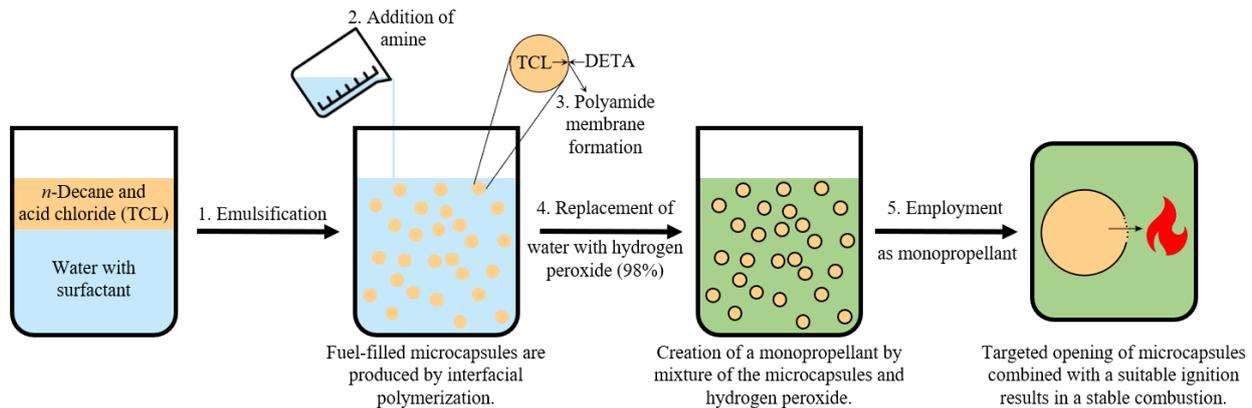


Figure 1: Schematic preparation of microencapsulated fuels and eventually the formation of microencapsulated monopropellants.[4,5]

The schematic preparation of a microencapsulated fuel is shown in Figure 1. For this, one monomer (terephthaloyl chloride; TCL) is dissolved in *n*-decane (a model substance for non-polar fuels like kerosene) and added in water. This mixture is then emulsified with the aid of a surfactant (polyvinyl alcohol; PVA). Eventually the other monomer (an organic amine; diethylene triamine; DETA) is added to the aqueous phase. As soon as the amine is added, the monomers begin to react at the *n*-decane/water interface and form a polyamide membrane which envelops the *n*-decane droplets. The size of the capsules can be influenced by the emulsification process. In addition, the wall thickness can be controlled by the amount of monomers added and the reaction time. The next step for the creation of a monopropellant from typical bipropellant components, is the replacement of the water with hydrogen peroxide. If the microcapsules are then opened in the following and the mixture is ignited by a suitable ignition method, it expectantly combusts.

Diethylenetriamine and terephthaloyl chloride were chosen as monomers because they produce a crosslinked polyamide.[8] The amounts of monomer used result in a ratio of 4.1% of the membrane mass to core mass with complete conversion, which corresponds to 30.0 mg of capsule material per 1 mL of *n*-decane. After synthesis, the capsules were then characterized by optical and electron microscopy, infrared spectroscopy (IR) and thermogravimetric analysis (TG).

1.2 Preparation of stable microcapsule dispersions

An important component is the production of a stable dispersion of the capsules. Since the capsules used here contain *n*-decane as core material, which has a lower density (0.7266 g cm^{-3}) than the continuous phase water (0.9970 g cm^{-3}),[9] the capsules settle on top over time. This process is called creaming. A stable dispersion is essential for the subsequent employment of microencapsulated fuels to ensure a homogeneous mixture of the oxidizer and fuel. To produce a stable dispersion, the system must be in a state of minimum energy. However, the state of lowest energy is achieved by coagulation. Thus, a dispersion is always in a metastable state.[10] Due to the electrochemical double layer, there is an electrostatic repulsion energy between the colloidal particles which stabilizes the dispersion to a limited extent. On the other hand, the particles are attracted to each other from a certain distance through Van der Waals (VdW) forces (Figure 2).[11]

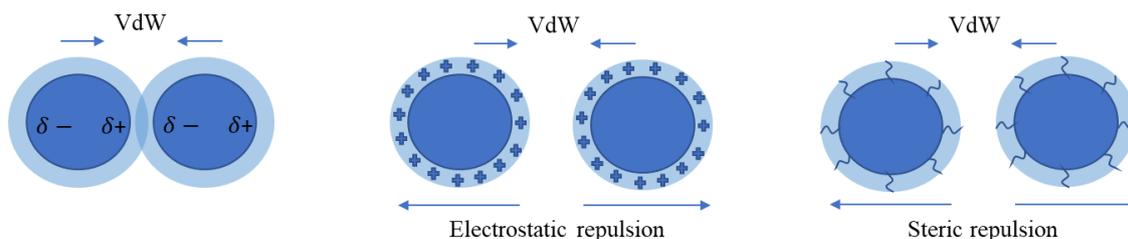


Figure 2: Exemplary attractive and repulsive forces, that can occur between particles in dispersions. [10,11]

To stabilize a dispersion, the repulsive forces must overcome the attractive forces. This can be achieved by different stabilization mechanisms. The aim is to determine the best method for capsule dispersion, for which the following methods will be tested. One possibility is to adjust the particle size, since smaller particles have a higher solubility. Additionally, dispersions are more stable the more similar the densities of the components are. [11] For this, density adjustments should be made by using a higher density propellant instead of *n*-decane. Another possibility is the use of dispersants. Dispersants can attach to the particles or disperse in the solvent. Their task is to keep the particles at a distance by steric hindrance, so that they cannot aggregate and precipitate. [12] Another option is the modification of the surface structure of the capsules for a better dispersibility in the aqueous medium. Hereby dispersant-like molecules can be covalently attached to the capsule shell and increase steric repulsion and may increase stabilizing interactions with the aqueous medium when hydrophilic substances are used. However, studies on improving the stability of microcapsules are rare. Pedaballi et al. were able to show, that organic phosphates can stabilize a dispersion of poly(-melamine formaldehyde) microcapsules in toluene. [12] In another study, also organic phosphates were used to stabilize a dispersion of poly(-urea formaldehyde) microcapsules in epoxies. [13]

In this work, the synthesis process of the microcapsules will be optimized and the preparation of stable microcapsule/water mixtures will be anticipated. This can then later be extended to the preparation of microcapsule dispersions in hydrogen peroxide. Furthermore, we will expand on these concepts and attempt to identify suitable surfactants to stabilize a dispersion of microcapsules in water.

2. Results and discussion

2.1 Synthesis of microcapsules with different sizes

Our first approach of creating stable microcapsule dispersions, was to decrease the size of the microcapsules. In comparison to earlier methods described by our group, [5] another disperser was used. The preparation is described in experimental procedure **EP1** (see section 4.3) with a range of stirring speed from 1 050 to 20 000 rpm. In Table 1, the average sizes of the microcapsules (based on the measurement of 50 capsules with optical microscopy) are shown. It can be seen that the average capsule size decreases with higher dispersion speeds. With 20 000 rpm, capsules of sizes with an average diameter as low as 4.6 μm can be produced. Optical and electronic microscopy pictures of the microcapsules can be seen in Figure 3.

Table 1: Average microcapsule size and burst temperature in dependence of the stirring speed (prepared after **EP1**).

| Stirring speed [rpm] | Average size [μm] | Standard deviation [μm] | Burst temperature [$^{\circ}\text{C}$] |
|-------------------------|-----------------------------------|---|---|
| 1 050 ^[a] | 151 | 28 | 223 |
| 5 000 ^[b] | 24.1 | 6.4 | 241 |
| 10 000 ^[b] | 11.3 | 5.1 | 245 |
| 10 000 ^[b] | 11.7 ^[c] | 2.6 | 246 |
| 15 000 ^[b] | 7.7 ^[c] | 1.2 | 257 |
| 20 000 ^[b] | 4.6 ^[d] | 0.7 | - |

^[a]Stirrer with dispersion blade; ^[b]Dispersion tool; ^[c]Washing process with centrifugation;

^[d]Average size was determined before washing.

After the synthesis, the capsules were washed repeatedly with water to remove remaining reaction products and excess DETA from the mixture. Hereby it was noticed that the creaming speed depends highly on the stirring speed. The

smaller the capsules are, the slower they settle on top of the mixture. The washing process can be accelerated by careful centrifugation. Here it has to be noted, that high centrifugation speeds seem to destroy microcapsules with an average size of under ca. 10 μm . This may be an effect of the thin walls, influenced by the overall large surface of the small capsules making them more prone to mechanical forces as they occur during centrifugation. The microcapsules which were produced with a stirring speed of over 10 000 rpm could therefore not be washed and isolated in a practical and were not further characterized.

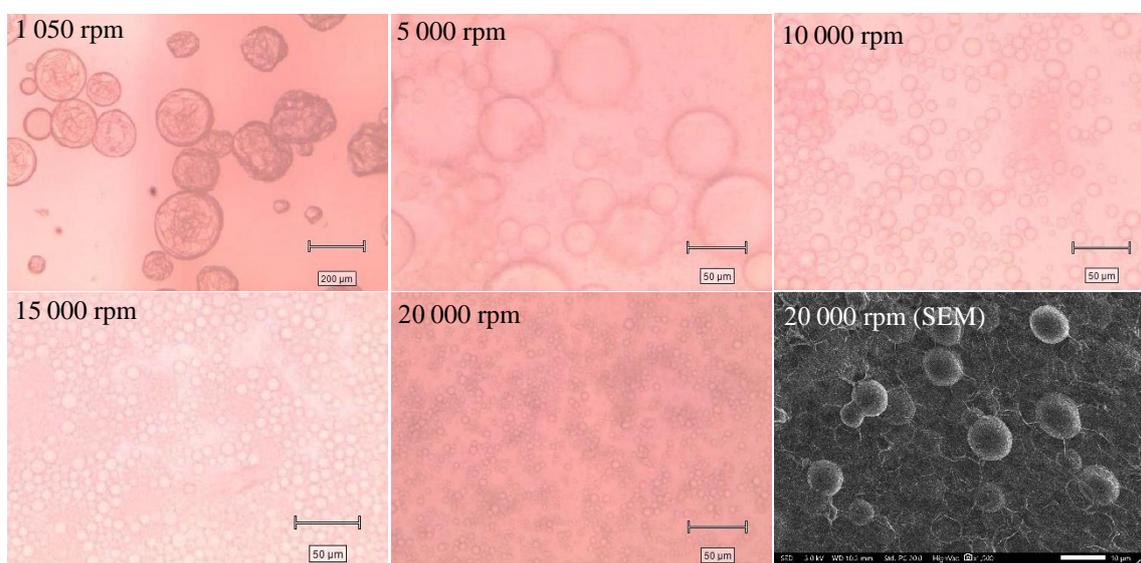


Figure 3: Optical and electronic microscopy images of microcapsules, synthesized with different stirring speeds.

A large effect of the capsule size on the dispersion stability could be observed. While the capsules at 1 050 rpm cream completely after few minutes, the capsules prepared with 10 000 rpm need more than a day of time to settle on top of the mixture directly after preparation. Capsules prepared with 15 000 or 20 000 rpm did not cream completely even after several days. It was observed, that after a few washing procedures, the creaming speed increased significantly. This could be due to a washing out of small particles responsible for the slow creaming speed or removal of reaction products or surfactant (PVA).

The capsules with a stirring speed of 1 050 to 15 000 rpm were characterized by TG (Figure 4). The first weight loss occurs at a temperature of about 100 $^{\circ}\text{C}$ and is caused by the evaporation of water that is left over from the washing process. In the next area of weight loss, the release of *n*-decane can be observed. Time-resolved infrared spectra of the emitted gases were used to identify the released substances. At the second mass loss, the capsules rupture as a result of the internal pressure of *n*-decane building up inside the capsules. Thus, this temperature can be defined as the burst temperature of the microcapsules which is determined by the onset temperature (defined by extrapolation method) of the area of mass loss. For comparison, the boiling point of pure *n*-decane is 174 $^{\circ}\text{C}$. [9] The burst temperatures of the samples are listed in Table 1. A trend can be seen that the burst temperature of the capsules increases with decreasing average capsule size. This ranges from 223 $^{\circ}\text{C}$ (1 050 rpm) up to 257 $^{\circ}\text{C}$ at 15 000 rpm. The increase of the burst temperature may be caused by a change in the volume/surface ratio of the capsules.

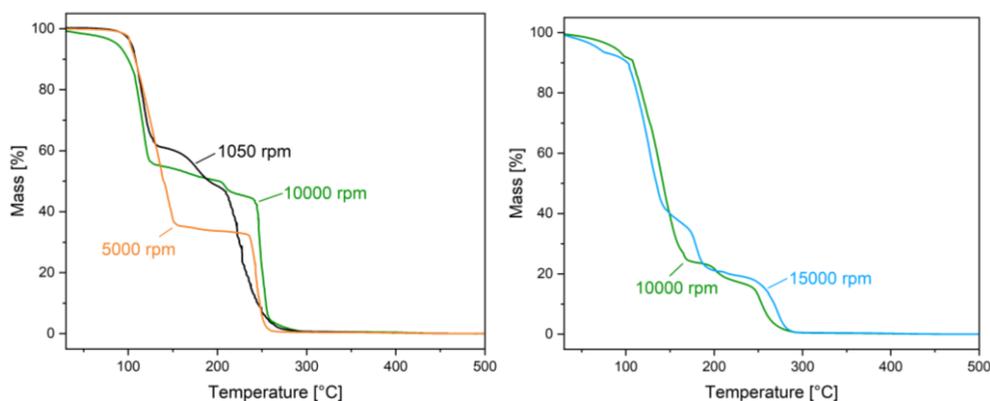


Figure 4: Thermogravimetric analysis of microcapsules, synthesized with different stirring speeds, compare to Table 1, entry 1-3 (left) and entry 4 and 5 (right).

2.2 Use of surfactants for preparation of stable microcapsule dispersions

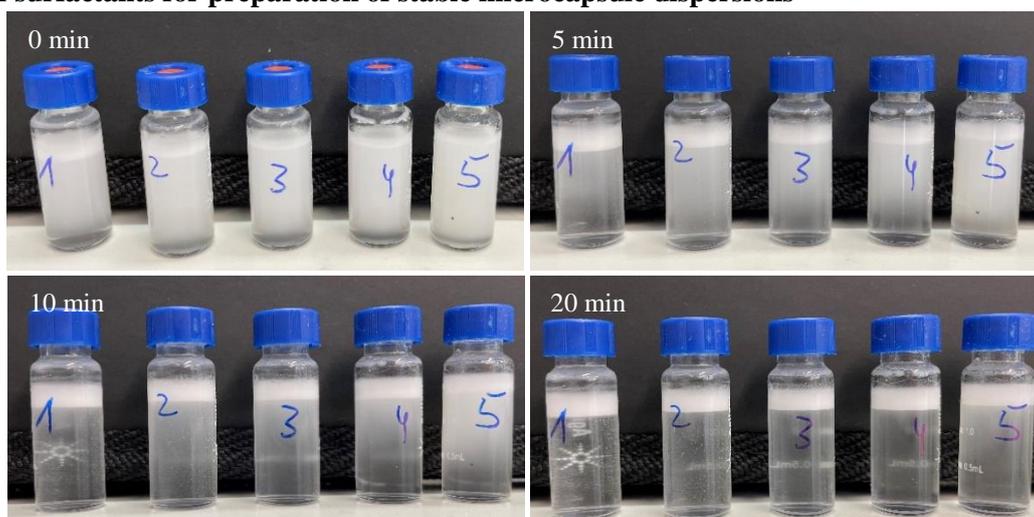


Figure 5 Photographs of microcapsule in water dispersions stabilized by PVP after different periods of time (100 mg microcapsules with 1: 0 mg, 2: 0.1 mg, 3: 1.0 mg, 4: 10 mg, 5: 100 mg PVP in 1.5 mL water; compare to Table 2, entries 12-15).

Since the use of suitable surfactants can stabilize microcapsule dispersions,[12,13] we attempted to employ hydrophilic and amphiphilic substances to stabilize the dispersions. The polyamide capsules produced after **EPI** are not prone to flocculation and through the capsule hull they can also not coalesce (compare to Figure 3). The major problem to overcome is the creaming of the capsules, since they have a lower density than the continuous phase (water). To prevent this, different surfactants (Span 80, Tween 80, Triton X-100 and polyvinylpyrrolidone (PVP)) were tested in different concentrations. In Figure 5, the use of PVP as stabilizing surfactant is shown. For this, the mixtures were shaken by hand and then allowed to stand for creaming. It can be seen that the higher the PVP concentration, the longer the dispersion remains cloudy and the capsule creaming slows down. However, after a time span of 20 minutes, even the mixture with high PVP concentrations become transparent again. An overview of all conducted experiments is given in Table 2. Here it can be noted, that the use of PVP delivered the best results so far. In addition, the influence of sonification was investigated. The mixtures were placed in an ultrasonic bath for 5 min prior to shaking. No difference in creaming speed was observed.

Table 2: Overview of conducted experiments on the stabilizing effect of different surfactants on microcapsules in water dispersions.

| Surfactant | Amount surfactant [μ L] | Amount surfactant [mg] | Amount capsules [mg] | Amount water [mL] |
|------------------|------------------------------|------------------------|----------------------|-------------------|
| Tween80 | 15.0 | 16.0 | 5 | 1 |
| Tween80 | 15.0 | 16.0 | 10 | 1 |
| Tween80 | 5.00 | 5.32 | 100 | 1 |
| Tween80 | 15.0 | 16.0 | 100 | 1 |
| Tween80 | 30.0 | 31.9 | 100 | 1 |
| Tween80 | 100 | 106 | 50 | 1 |
| Tween80 | 100 | 106 | 100 | 1 |
| Span80 | 10.0 | 10.1 | 100 | 1 |
| Span80 | 20.0 | 20.2 | 100 | 1 |
| Span80 + Tween80 | 10.0 + 10.0 | 10.1 + 10.6 | 100 | 1 |
| Span80 + Tween80 | 5.00 + 15.0 | 5.05 + 16.0 | 100 | 1 |
| PVP | - | 0.10 | 100 | 1.5 |
| PVP | - | 1.00 | 100 | 1.5 |
| PVP | - | 10.0 | 100 | 1.5 |
| PVP | - | 100 | 100 | 1.5 |

It can be concluded, that the use of surfactants has an impact on the stability of microcapsule dispersions and can suppress creaming, but only for a limited amount of time. More investigations have to be conducted concerning the dispersion stability. Hereby the preparation process of the microcapsules will be further optimized to obtain even smaller capsules reliably, which can then be mixed with even more surfactants. Also, a different core material with a density more similar to water might help to prevent capsule creaming.

3. Conclusion

In previous research, we described an entirely new propellant concept that consists of a microencapsulated fuel (*n*-decane) and hydrogen peroxide. Encapsulation makes both components miscible and safe to store. This makes it possible to create a monopropellant from typical, usually difficult to mix bipropellant components and combines the advantages of mono- and bipropellant systems: a high specific impulse and low technical complexity.[4,5]

In this work we investigated the stability of this new type of monopropellant, which can be seen as a dispersion of the microcapsules in the continuous phase. For this first experiments, we used water instead of hydrogen peroxide since it is easier to handle. Next to general considerations we studied the influence of the capsule size on the dispersion stability. Capsule size had a moderate effect; smaller capsules take longer for creaming. Furthermore, the effect of different surfactants (Span 80, Tween 80, Triton X-100 and polyvinylpyrrolidone) on the dispersion stability was investigated, but seems to have only a minor effect under the given experimental conditions. In future research, our group will further develop the synthesis process, try additional surfactants, and strive for further development with the goal of a hot gas test of this novel propellant.

4. Experimental section

4.1 General information

All solvents and reagents were purchased from Acros Organics (polyvinyl alcohol 88% hydrolyzed (MW 20 000-30 000)), Merck (*n*-decane, Span 80), Sigma Aldrich (diethylenetriamine, Tween 80 and Triton X-100) and Thermo Scientific (terephthaloyl chloride and polyvinylpyrrolidone (MW 10 000)) and were used without further purification. A Heidolph RZR 2020 with dispersion blade and an IKA T18 digital ULTRA TURRAX with a S 18 N – 19 G dispersion tool were used as dispersers. Centrifugation was conducted with a Sigma 3-18KS centrifuge.

4.2 Analytical methods

Optical microscopy Images were obtained by a Leica DM2700 M optical microscope.

Thermogravimetry (TG) Thermal analysis was conducted with a Netzsch STA 449 F3 Jupiter thermal analyzer with a Bruker Model alpha infrared spectrometer. The tests were carried out in Netzsch CrNi-crucibles under a stream of nitrogen gas with a flow rate of 50 mL/min. The starting temperature of 30 °C was increased by a heating rate of 10 °C per min. to a final temperature of 600 °C. The onset temperature was determined by extrapolation method.

Scanning electron microscopy Electron microscopy images were obtained by a Jeol JSM-IT200 InTouch Scope.

4.3 Experimental procedures

General procedure for preparation of *n*-decane filled diethylenetriamine – terephthaloyl chloride microcapsules GP1 [7]

Polyvinyl alcohol (150 mg) was diluted in water (30 mL). A solution of terephthaloyl chloride (83.7 mg, 643 μmol, 1.0 equiv.) in *n*-decane (5 mL) was added. The mixture was dispersed for 5 min. Consequently, a solution of diethylenetriamine (2.07 mL, 19.3 mmol, 30.0 equiv.) was added and the solution was gently stirred for 5 hours. Eventually the capsules were separated in a separatory funnel or by centrifugation (1 to 107 g) and washed with water (4 × 100 mL).

Acknowledgements

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