Review Article

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Powering Green Chemistry with Microspheres and Microcapsules

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Introduction

The world of today needs and uses huge amount of energy. As second and third world countries rise and first world countries improve their level of life, a slowing of energy consumption cannot be seen, despite the efforts for energy conservation. Fossil energies as gas and oil have an even increasing importance, despite their environmental drawbacks. Nuclear energy - even though that some countries as Germany try to replace it with renewable energies- plays still an important factor, not only because of the low costs and a carbon dioxide free operation, but also for new applications as the destruction of nuclear waste. Renewable energies are used and developed strongly and will play a very important role in the future. Even solar technology, were recent price falls and loss of subsidiaries forced many companies out of business, is not dead and is still used in an increasing number of installations. Rising applications for biofuel and new processes are on their way replacing fossil fuels by using electricity during low use times from renewable sources such as off shore wind turbines and simultaneously harvest carbon dioxide.

Besides energy related applications, also in other fields such as agricultural and farming new technologies are desperately sought for. For example the replacement of chemical fertilizers with natural ones, that are produced from sustainable materials, is a major research focus of the EU. In husbandry it is more and more important and desired to remove pharmacological treatment of animals with e.g. antibiotics and replace it by the use of natural materials such as plant extracts and probiotics. Last but not least, the replacement of harvested feed with vegetable sourced feed, such as the replacement of fish in a salmon diet with plant derived products, are major challenges at this time to increase the total food production for the always hungry world.

The multitude of those applications have one thing in common: In many of them Microspheres or Microcapsules are used. They are used in many different forms, ranging from feed capsules, pharmacological active capsules, encapsulated cells and microbes, catalysts and catalyst carriers, filter materials, encapsulated chemicals in self healing coatings over ceramics for high temperature insulating material or proppants in shale oil and gas recovery, right to being the energy source itself in the form of nuclear fuel or solar cells.

An increasing amount of those Microspheres and Microcapsules are nowadays produced with the BRACE Processes, also known as laminar flow drip casting or vibrating nozzle processes. As a pioneer in the industrial application of the processes using Rayleigh's Theorem, BRACE is implementing these processes for more than 30 years, holding many patents in the field and experience going back to the first large applications for producing nuclear fuel by these processes.

Since then the world changed, or at last broadened its view. BRACE is developing, manufacturing and engineering its technology in many fields, ranging from food and feed, over cosmetic and pharma, to medical and chemical fields. Last but not least, BRACE is highly active in the area of green chemistry related products as solution provider for developing, contract manufacturing and production line engineering for products as feed and food additives and ingredients, pharmaceutics, cosmetics, catalysts and catalyst carriers, filter materials, absorbents, nuclear fuel, electronic solder balls, additives, polymers, proppants, solar cells, and many more.

In many of those fields, granules are used for a considerable amount of time with purposes as dosing, transport, handling and of course release control. However, granules produced with conventional processes as spray drying/cooling, spheronisation, extrusion or dripping have a number of drawbacks. Those are for example broad size distribution, difficult control over produced sizes, deformed shape, low density, onion shell type of structure, difficult scale up or cost of processing. All these problems can be overcome with a versatile, scalable and cost efficient process producing monomodal particles of highly spherical shape out of almost any thinkable material.

Such a process ideally is able to produce many different sizes, materials and in addition matrix encapsulated Microspheres as well as core-shell encapsulated Microcapsules (picture).

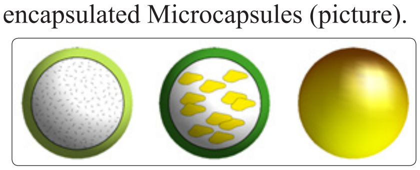

Figure 1: Schematic drawing of Microcapsules and Microspheres. From left to right: Microcapsule with solution as core, Microcapsule with cell suspension as core, Microsphere with matrix encapsulated active agent

The main difference between these two types of microgranules is in the release profile. While Microspheres usually have diffusion controlled release profiles with a permanent release rate which is kinetically controlled by the particle size, Microcapsules expel their content by a single high burst as the shell breaks (picture 2).

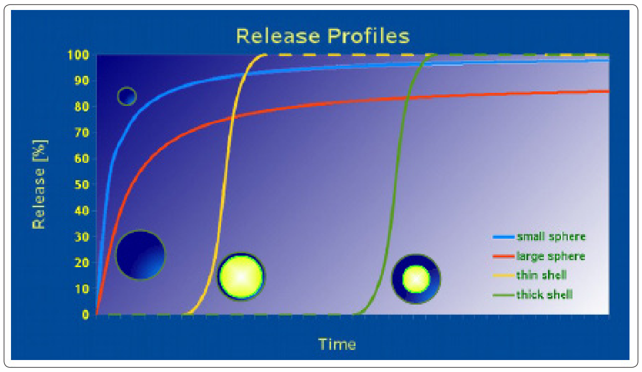

Figure 2: Release profiles of different types of Microspheres and Microcapsules. While small Microspheres have a fast release profile, larger Microspheres have slower release rates. The burst time of Microcapsules depend on the thickness of their shell.

BRACE Microsphere and Microcapsule processes

The BRACE-Processes for producing Microspheres and Microcapsules are basically laminar flow breakup processes with vibrating nozzles. As opposed to other such processes as rotating disc or rotating cylinder laminar flow breakup processes, the setup is comparatively simple, robust, easy to maintain as well as space and energy saving. In addition, the vibration offers a much better control over the grain size as uncontrolled laminar flow breakup processes. These processes produce particles with monomodal grain size distributions with a single sharp maximum. Dmin/dmax-values lower than 1.10, 1.05 or even 1.01 are common for spherical granules produced with those processes (see figure). It is possible to obtain Microspheres or Microcapsules in a diameter range of 50-6000µm, with special nozzles larger and smaller particles are possible. A wide range of shell materials are usable with this highly scalable process. The processes combine low space and energy consumption with high throughput and very high flexibility concerning the materials to be used. All installations can be customer tailored to meet all necessary requirements like GMP/GLP, FDA, Pharma-, Food-, Nuclear-, Chemistry- or other Industrial-Standards.

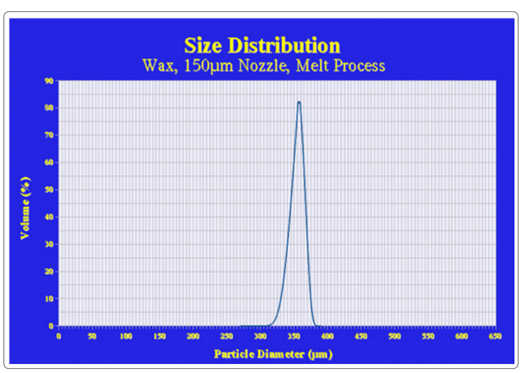

Figure 3: Typical size distribution with a 150µm nozzle for BRACE Microsphere units

Depending on the application and the raw materials to be used, the processes vary in details, e.g. if a heating chamber of a furnace is installed or not. The basic principle can be seen in figure where the melt process is shown exemplary: A liquid feed is pumped from a feed tank (3) to the nozzle head (5) where the vibrating device (2) induces the breakup of the flow into uniform droplets. These are formed into spheres by the surface tension of the feed. The droplets are solidified during falling (9). This can be realized depending on the materials and/or coagulation system used by cooling, chemical reaction or drying. The head of the Microsphere unit can be placed in a heating chamber (6), the visual control of the process can be either done by a stroboscopic lamp or with a camera set for remote control. The electronic cabinet (1) controls the Microsphere unit and can be integrated in existing control systems. Such processes where a melt is processed are build with heating chambers up to 1500°C to process e.g. Silicon for solar cell applications. In other processes were powders are processes, e.g. for proppants production, the process is run at room temperature and the resulting droplets are solidified in a reactive solution. Other materials as metal solutions for various applications from catalyst carriers to nuclear fuel make use of a sol-gel reaction where the metal solution is solidified during the fall with a gas reaction.

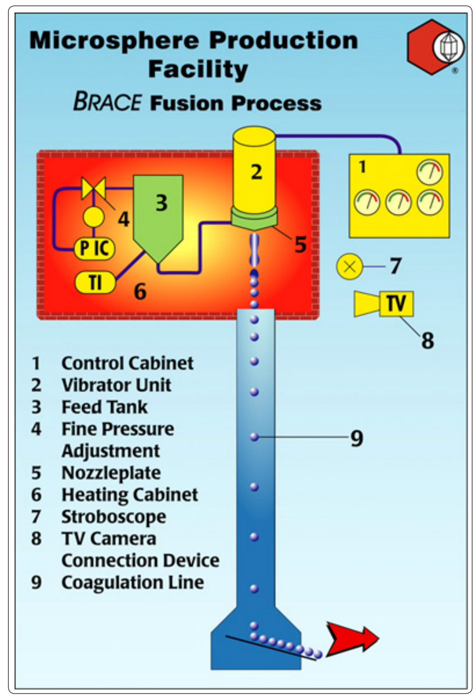

Figure 4: BRACE Microsphere Process (Fusion Process)

Ceramic applications

Ceramics are used in a variety of applications. For example densely sintered ceramics such as Al_2O_3, ZrO_2, HfO_2 or mixtures are used as grinding material to prepare fine powders that are used then in other fields or applications. While there are many ways to produce grinding balls, the BRACE processes offer an outstanding low energy approach, to produce high yield, high dense, monomodal size distributed grinding balls. This increases the grinding yield, lowers energy costs both for production and use as well as reduces waste and additive use in the process.

More sophisticated processes use catalyst carriers, filter materials and even hollow ceramic spheres to enhance reactions, filter efficiently materials from liquids and gases, use them as porous carrier for fluid bed reactions or even as insulation materials (see figure).

Figure 5: Aluminiumsilicate hollow spheres

Food and Feed Applications

As replacement of Antibiotics a raising number of products make use of plant extracts, such as extracts from herbs that have similar properties as antibiotics. Such oils are however highly volatile, tend to trigger allergic reactions and damage the mucus layer in the stomach. To reduce and remove those effects, these materials are encapsulated in enteric formulations, making them readily available where effective. Such capsules are used in feed additives, as anti-diarrhea formulations for companion animals, as additives for meat producing animals like cattle, pig or poultry. In food applications such capsules and spheres are used as nutrients to deliver such important dietary providers as fish oils, vitamins or minerals.

For encapsulation of such actives as well as for e.g. probiotics for both nutrient, feed and pharmacological applications, natural and sustainable polymers are used. This offers a full "green" product, without the need of using artificial materials in processing (see figure).

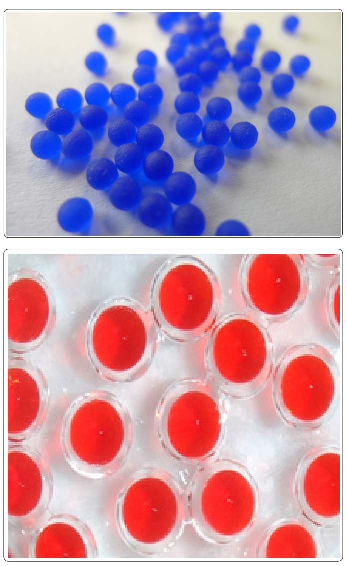

Figure 6: Essential oil filled capsules (red capsules, before drying) in alginate shell for companion animal products, menthol oil filled capsules (blue capsules, dried) for use in human food application

With many other similar applications in the agricultural field, such as biopesticides, enhanced encapsulation of fertilizers etc. Microencapsulation offers means of reducing or even eliminating synthetic or toxic materials from many processes.

While the replacement with natural, sustainable materials is often possible, there are applications were it is desired to process materials without any additives. For example in the production of instant drinks and instant coffee etc., mostly the "pure" material is used. Traditional processes often have drawbacks as low yields (classical freeze drying process) or substantial changes in taste (spray drying). With the BRACE Instant processes it is possible to produce high quality, natural tasting instant products, as yields close to 100%.

Solar Cell Applications

Solar cells are produced in a variety of processes. The majority of solar cells available on the market are however solar cells made via a metallurgic route. This route is cheap, simple and – inefficient. The resulting solar cells are usually rather for the "good feel" than for a real environmental effect. In some countries, e.g. in Germany, it is possible to profit from an economical effect, as electricity generated by solar energy is highly subsidized.

Figure 7: Laboratory unit for Silicon sphere production

There are however a number of concepts that eliminate the biggest drawbacks of solar cells. One of those drawbacks is certainly the necessity of flat panel solar cells to be tracked according to the angle of the sunlight to have optimum performance. Another drawback is the thick an inefficient way flat solar cells are of today packed into layers and layers of polymers, glass and other boxing and protecting housings, which reduces the energy yield even further and brings up increasing problems of recycling. A possible solution to those problems is the use of spherical solar cells.

Here, a single round sphere is a solar cell. The round shape renders it independent of the angle of the sunlight - any angle will do for high energy efficiency. In addition, such spherical particles are highly resistant to mechanical stress, so they do not have to be protected. As a result a tough, highly efficient and light solar panel can be generated by "just" using the right process. The "right" process is here of course a BRACE melt process, preparing monomodal size distributed silicon Microspheres from a silicon melt. By choosing the optimized cooling parameters it is even possible to generate mono crystalline or close-to-mono crystalline Microspheres, which reduces downstream processing costs dramatically.

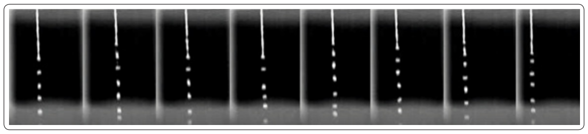

Figure 8: Drip casting of molten Silicon in a BRACE Unit

In figure the drip casting of silicon Microspheres can be seen. As the silicon has only to be molten "once" as opposed to ribbon or tube-pulling processes, where the ribbon/tube is pulled from a melt of Silicone, the purity of the silicon is very high. The spherical shape of the particles and their robustness makes it even possible to use continuous handling processes that are efficient and fast. Converting close to 100% of the raw material used into Microspheres reduces in-process recycling costs to before unseen values.

Conclusion

Those applications are but a small selection of uses of the BRACE Microspheres and Microcapsule processes, that offer to reduce energy and ressources to build better products and processes. BRACE offers formulation and product development, contract manufacturing and machinery and equipment, from desktop to large scale facilities of 20 t/h and more, to its customers, to provide for tomorrow [1-25].

The advantages that the Microspheres and Microcapsules, with there outstanding sphericity, monomodal and tight size distribution and low energy processes offer, render the presented processes the first choice for any current technology.

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