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Title: Developing process and procedures for the refinement of surfclam and ocean quahog shells into calcium carbonate ($CaCO_3$)

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Statement of Problem: Calcium carbonate is one of the most used raw materials in various industries, such as construction materials, food supplement, pharmaceutics, animal feed, plastic production, and others. Mussel shell represents about 32% of the mussel weight used in cannery and processing installations. The shell is considered a composite biomaterial, which calcium carbonate, accounts for 95–99% by weight while the remaining 1–5% represents an organic matrix. Therefore, calcium carbonate can be exploited from these shells to be used for a wide range of applications. The very high content of calcium carbonate in surfclam and ocean quahog shells, which is typically around 95%, makes them ideal candidate for being used as a source of bio-originated and food safe $CaCO_3$. Biogenic carbonates show unique properties that make them interesting for possible industrial applications. The chemical composition of the shell is different in each type of the seashells. Table 1 shows the composition of the shell materials for surfclam, quahog, and oyster compared to the composition of the Aragonite. Also the specific gravity of the shell is different in each type for example the density of oyster was reported 2.65 while for the clam it is 2.71.

Table 1. Chemical composition of surfclam, quahog, and oyster shell compared to aragonite

Seashell	Ca	Mg	Si	Al	Cl	K	Na	P	S	$CaCO_3$	$MgCO_3$
Surfclam	36.3	0.03	NA	NA	0.12	0.08	0.69	0.01	0.1	92	5.7
Quahog	38.5	0.02	NA	NA	0.06	0.07	0.53	<0.01	0.1	96	4.2
Oyster	35.3	0.39	0.56	0.43	0.01	NA	1.06	0.08	NA	96	NA
Aragonite	39.1	0.17	NA	NA	0.10	0.08	0.33	<0.01	0.1	96	3.5

However, there were few challenges for calcium carbonate production from shells especially the environmental issues. For example, lack of proper washing step resulted in high emission levels of the treated effluents (total nitrogen). In addition, lack of optimization in calcination process and targeted particle size (choosing right end-use application) could potentially add to the cost of the process.

Deliverables: This project uses the clam and quahog shells and will focus on producing high quality $CaCO_3$ for higher revenues including, but not limited to, animal feed, as filler and coating pigment for paper production, and biomedical applications. Selection of the proper particle size, purity, whiteness and consistency are key parameters for the animal feed and nutrition application. We propose a characterization method in order to tailor-made the produced $CaCO_3$ for target applications such as animal feed (bioavailability), paper production (size and porosity), and biomedical applications (cytotoxicity). The calcium carbonate production from shell waste includes the collection, transport, cleaning (elimination of salt, soil and remaining meat), drying, grinding, micronizing, sieving, and, most importantly, characterization of the product(s). We propose a thorough characterization in order to analyze the produced $CaCO_3$ to target any desire applications. Characterization of the products, help us to optimize the calcination process; control of the polymorph and size of the $CaCO_3$ from clam and quahog shells. We will develop a standard operating procedure for product characterization. These are the list of deliverables for this project:

- Best cleaning method for the special feed shells,

- Optimized calcination process in terms of product properties and process cost,

- Control of the polymorph and size of the $CaCO_3$ form the clam and quahog shells,

- Detailed characterization methods as quality control,

- Development a standard operation procedure for product characterization.

Status relative to deliverables:

Efficient washing/cleaning of the shells: different chemicals and procedures have been used to find the best cleaning procedure.

Coarse grinding: we used coarse grinding before washing the shells, in which we figure it helps better in terms of washing step.

Calcination: the furnace heating can produce a persistent gray color as well as loosing CO_2 from $CaCO_3$ at 500 °C and higher temperature. We found that by heating washed and/or cleaned samples acceptable results in terms of color and remaining organic matter can be obtaining.

Micronizing and sieving: we used ball-mill for grinding samples both before and after heating in furnace to compare the particle size, morphology and color.

Characterization: we used ATR-FTIR for structural comparison of samples with pure $CaCO_3$. Thermogravimetric analysis (TGA) was also done for samples prepared via different washing/cleaning/thermal procedure and the results were compared with pure $CaCO_3$ from Sigma. We have used X-ray diffraction (XRD) in order to characterize the polymorph of the $CaCO_3$ from different samples. Scanning electron microscopy (SEM) has been also used to analyze the size and morphology of the samples. Also we used the energy dispersive X-ray analysis (EDX) to investigate the elemental composition and elemental map of the samples. We are preparing samples for performing X-ray fluorescence (XRF) as a precise elemental and chemical analysis method.

Summary of results relative to deliverables:

- The coarse grinded shell should be washed with hot water (~95 °C) in order to be ready for next step which can be chemical cleaning or oven heating.

- We realized that if a chemical procedure for cleaning is needed, a 5 w% NaOH solution, a 5 w% H_2O_2, or even a 5 w% bleach solution can be use at high temperature (~75 °C). Acid wash (HCl and H_2SO_4) was found not useful in terms of whitening and/or removing the organic matter.

- We use a high temperature electrical furnace to heat the samples in order to remove the remaining organic matter. Both 350 °C and 500 °C was used for both samples and we found that heating samples for 10 h at 500 °C can generate a persistent gray color. The 350 °C heating, however, does not have the severe coloring effect on the samples. Furthermore, it is known that by heating the calcium carbonate higher than 500 °C, it decomposed to CO_2 and CaO. Therefore, heating samples for long time at 500 °C and higher might have deterioration effect on their compositions.

- We use a high speed, vibrating ball-mill for grinding and micronizing the washed and/or oven-treated samples. Our SEM study shows that the samples are fine-grind to a level of micron and sub-micron size which is a requirement for many applications.

- The ATR-FTIR showed structurally comparable results with $CaCO_3$. Thermogravimetric analysis (TGA) was also confirm the thermal stability of the final samples and showed the importance of the washing/cleaning/heating steps. We have used X-ray diffraction (XRD) and our results showed that the polymorph is in agreement with the commercial $CaCO_3$ from Sigma. Scanning electron microscopy (SEM) of the ball-milled samples confirmed the presence of micronized $CaCO_3$ and submicron particles. The energy dispersive X-ray analysis (EDX) also shown the presence of Ca, C, O and trace Na (likely due to wash with NaOH) in the weight percentage that almost matched the weight fractions of $CaCO_3$. We are preparing samples for performing X-ray fluorescence (XRF) as a precise elemental and chemical analysis method.

Challenges to project completion and recommendations addressing the same:

- The XRF analysis needed to be done for detail elemental analysis of the samples;

- Samples are quite white, however, for making them even whiter for especial applications e.g. paper production, extra processing might be needed;

- The bioavailability of the prepared $CaCO_3$ samples should be assessed;

- The cost of each step of the process need to be evaluated.