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# Thermal treatments affect breakage kinetics and calcium release of fish bone particles during high-energy wet ball milling

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ABSTRACT

Effects of thermal treatments on breakage and calcium release of fish bone particles during high-energy wet ball milling were investigated. Heating temperature (55–130 °C) showed much more obvious influences on the breakage and calcium release than heating time (20–60 min). As heating temperature increased from 55 °C to 120 °C, fish bone matrix became more porous, and mechanical parameters of fish bone remarkably decreased ($p < 0.05$). Furthermore, particle size of the fish bone after milling reached a limit (approximate 110 nm) in a shorter time and calcium release was enhanced. Regardless of heating time, size of the fish bone particles was not significantly different ($p > 0.05$) between the samples treated with 120 °C and 130 °C during milling, while calcium release was higher for the latter sample. Breakage kinetics and calcium release of fish bone particles were fitted with the first-order exponential decay function and the Higuchi equation, respectively.



## 1. Introduction

Discards or by-products from global aquatic production reached over 20 MT per year (FAOSTAT, 2014). These by-products, which are rich in proteins, lipids, minerals and other nutrients, are still mostly used as raw materials for fish meal production with low economic value. Fish bone is the main solid by-product from fillet and surimi processing, which accounts for 10–15% of the total fish biomass and is mainly composed of minerals (21–57%), organic matter (35–73%) and water (3–8%) (Toppe et al., 2007). Moreover, previous researches have shown that calcium from fish bone possesses high bioavailability (Malde et al., 2010). Thus fish bone may be considered as a potential dietary calcium supplement in food.

In order to incorporate fish bone into calcium-fortified food, it should be converted into an edible form by softening its structure or diminishing it to extremely small particle size. As a two-phase interpenetrating and staggered composite material, bone tissue is composed of an inorganic phase (mainly including hydroxyapatite crystals) and an organic phase (mainly including highly organized collagen fibers) (Olszta et al., 2007). Hence, bone tissue shows both high stiffness and toughness (Gao, 2006), which leads to the extreme difficulty to break natural fish bone. Adding fish bone powders with coarse particle size (commonly micro-scale) to food contributes to grittiness and decreases food sensory quality (Yin et al., 2014).

As one of the most commonly used nano-milling techniques (Peltonen and Hirvonen, 2010), high-energy wet ball milling is capable of grinding materials into nanometer scale in a relatively short time by viscous friction, collision and squeezing particles between high-speed rotating balls (Eskin et al., 2005). Yin and Park (2014) obtained nano-scaled fish bone (NFB) particles with an average size of 110 nm by high-energy wet ball milling. Furthermore, they found that calcium ions from NFB induced endogenous transglutaminase to catalyze myosin cross-linking reaction, resulting in the enhancement of surimi gel strength (Yin and Park, 2014). In addition, appropriate thermal treatment induces the degradation of organic matrix and therefore efficiently weakens the mechanical strength and breaking resistance of bone (Fantner et al., 2004), which facilitates the processing of fish bone.

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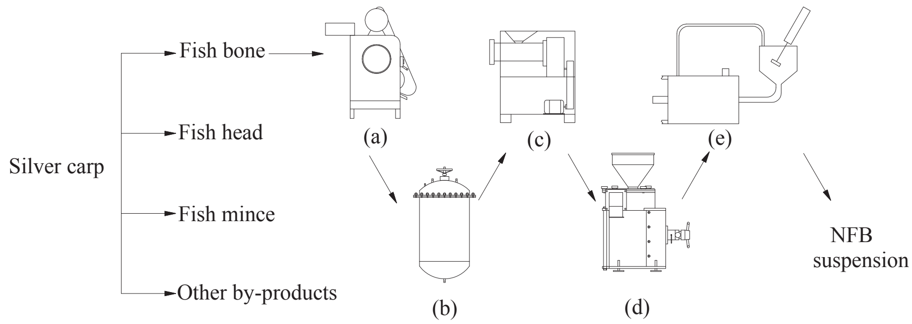


**Fig. 1.** The schematic diagram of the production process of fish bone particles suspension. The involved equipments: (a) roll-type meat separator, (b) pressure cooker, (c) mincing machine, (d) bone grinding machine and (e) high-energy wet ball mill.

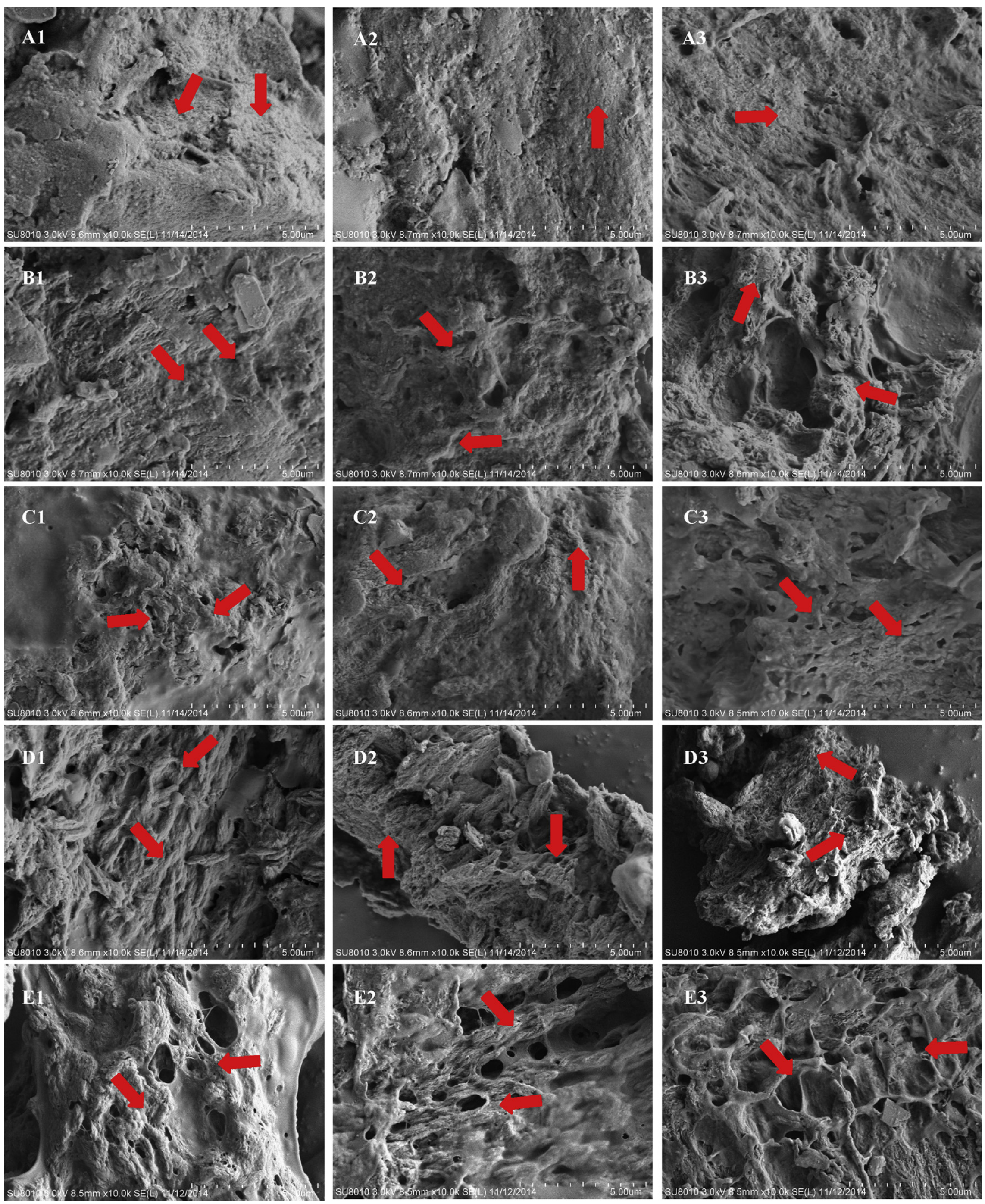


**Fig. 2.** Effects of thermal treatment on the surface morphology of fish bone. A, B, C, D and E represent 55 °C, 100 °C, 110 °C, 120 °C and 130 °C, respectively. 1, 2 and 3 represent 20 min, 40 min and 60 min, respectively. Arrows show the structural changes in density and consecutiveness.