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Mini Review

Opportunities to Enhance the Pyrolysis of Biomass in The Production of Hydroxyapatite and Chemicals

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Abstract

The pyrolysis of calcium orthophosphates produces hydroxyapatite and chemicals. Additionally, pyrolysis proposes paths to manage animal-derived waste streams. As it happens in the pyrolysis of lignocellulosic biomass, operating variables like reactor temperature, reaction atmosphere, feedstock, and particle size affect the final product from animal-biomass. This review summarizes the characteristics of multiple pyrolysis methods to produce hydroxyapatite and chemicals. Finally, this short paper recommends opportunities to enhance the results by changing pyrolysis process variables, learning from lignocellulosic and animal-derived biomass experiences alike.

Keywords: Hydroxyapatite; Calcium Orthophosphates; Biomass; Pyrolysis; Combustion, Thermochemical Conversion; Bone meal; Ceramic Powder

Abbreviations: HAP: Hydroxy Apatite; COP: Calcium Ortho Phosphates; LCB: Ligno Cellulosic Biomass; COPB: Calcium Ortho Phosphate-Containing Biomass; TCB: Thermochemical Processing of Biomass; MBM: Meat and Bone Meal

Introduction

Calcium orthophosphates (COP) are the main inorganic constituent of hard tissue found in animals like bone, dental pieces, antlers, tendons, eggshells, seashells, and corals [1–5]. Moreover, COP is the precursor for synthesizing hydroxyapatite (HAp). There are multiple applications for HAp, including tissue engineering, bioactive and non-bioactive coatings, filtering media, heat generation, and production of upgradeable chemicals [2,3,6–11]. A plethora of methodologies is available in the literature to obtain HAp, which includes the use of chemical, mechanical, and thermal processes [12]. The raw material, biomass, to produce HAp can be bone specimens, bone particles or powder, or bone meal from the seafood, bovine, swine, poultry, and sheep food processing industry. COP usage and HAp applications involve multiple disciplines like medicine, dentistry, engineering, environmental remediation, and waste management.

Thermochemical processing of biomass is one route used to produce HAp. However, the literature on this topic predominantly covers lignocellulosic biomass (LCB) processing. These processes presented parallel development when using calcium orthophosphates (COPB) as the feedstock. In LCB processing, multiple projects have studied the effect of variables like reaction temperature, atmosphere reactiveness, catalyst usage, pressure, and solvents to increase the yield and properties of the products [13–15]. Moreover, the heating rates influence the distribution of products from processing LCB. For example, during the pyrolysis of LCB, slow heating rates favor the production of a solid charcoal-like product, meanwhile higher heating rates promote the production of room temperature condensable products, known as bio-oil. Moreover, heating rates are dependent mainly on particle size, reactor temperature, heat transfer mechanisms, and initial biomass properties [16–19].

Combustion and pyrolysis are among the literature reported thermal processes to obtain HAp [12,20–26]. Likewise, these methods can produce bone char, the solid product from bone processing, as well as liquid and gaseous products that can recover upgradeable organic materials for obtaining chemicals, pharmaceuticals, or energy carriers [27,28]. This review covers the basics of the thermochemical processing of biomass, and it compiles pyrolysis variables and trends to find opportunities for improving yields and product distribution when processing COPB into HAp and other value-added products.

Lignocellulosic Biomass Pyrolysis

Pyrolysis is the thermal decomposition of organic matter in the presence of an oxygen-poor or deprived atmosphere [29]. LCB pyrolysis yields room-temperature non-condensable gases, solid charcoal, and liquid bio-oil [30]. The latter is an attractive source of organic matter and has a variety of carbohydrate-derived compounds that are upgradable into fuels and chemicals. Multiple studies report that increasing heating rates, decreasing initial biomass particle size, and using proper reactor temperatures lead to higher bio-oil yields [31–34]. Fast pyrolysis of LCB uses reactor temperatures close to 500°C, particle residence times shorter than 2s, and heating rates larger than 10°C/s [35,36]. With high furnace temperatures, these heating rates are attainable when particles are in the millimeter-scale or smaller [37,38]. Also, stage fractionation of the bio-oil allows separating compounds, which helps their extraction or further upgrading [14,39]. Alternatively, these variables influence the properties of the solid product, promoting the release of volatile compounds from the biomass, leaving pores, and maintaining some of the initial structure [40].

These pyrolysis reactions are complex, and heat/mass transfer affects the preference of competing pathways. During the pyrolysis of LCB, the release of levoglucosan decreases in mass-transfer-limited cases. Since levoglucosan stays in the liquid phase, it thermally degrades instead of leaving as a volatile gas [31,41].

Pyrolysis of COPB in The Literature

Multiple examples of pyrolysis of COPB use different technologies, operating parameters, and feedstock to produce HAp and other chemicals. The feed stocks processed with pyrolysis are mainly meat and bone meal (MBM), raw food waste, eggshells, oyster shells, and COP solutions. The products from these pyrolysis experiments were bone char, HAp, and chemicals. Figure 1 summarizes these examples presenting reactor temperatures, reactor type, and reacting gas.

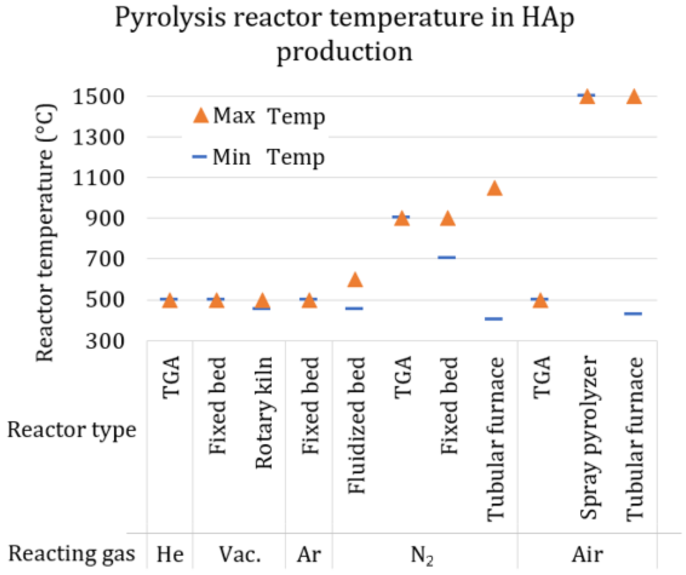

Figure 1: Summary of pyrolysis temperatures used in the production of HAp, organized by reactor type and reacting gas or vacuum (Vac.) [8,9,22,27,42-58,].

Figure 1 shows a variety of reactors that are also common in LCB processing. Thermogravimetric analyzer (TGA) is a powerful tool to perform controlled pyrolysis of milligram-scale samples, with insight on mass loss time evolution; however, this instrument has low heating rates close to 3°C/s (120°C/min) [59,60]. The furnace temperature ranges from 450 up to 150 °C in the projects reported. Not included in the summary, an arc plasma reactor reached temperatures close to 4200°C to treat oyster shells and food waste with disinfection and material recovery purposes [58]. Not all the projects reported heating rates. Even knowing reactor temperatures and particle size, the estimation of heating rates needs more input to be determined. However, reactors such as fluidized beds or preheated tubular furnaces with a high temperature and small feedstock particle size are useful to perform fast pyrolysis of LCB [61–63].

Regarding the reaction atmosphere, vacuum, argon, and nitrogen prevent oxidative reactions of the volatile compounds released during pyrolysis, allowing higher recovery of organic compounds in the bio-oil. Use of air as the carrier gas in some of the experiments with COPB usually promotes oxidation reactions when the organic volatiles are not the main goal of the process, but the production of clean bone char.

Products From COPB Pyrolysis and Their Relationship with Processing Variables

The projects summarized in Figure 1 mainly produced HAp, but some of them investigated the liquid products and the bone char. As in LCB pyrolysis, the projects with reactors capable of higher heating rates produced and collected bio-oil. [27] used a fluidized bed reactor to produce liquid yields of up to 43 wt.% of initial MBM at 550 °C. Since the biomass initially had fats and proteins, their bio-oil included fatty acids and fatty nitriles/amides. However, the most abundant were aliphatic compounds with functional groups involving either nitrogen or oxygen. [56], using a pilot-scale fluidized bed reactor, produced bio-oil that had the same main abundant products, but the maximum bio-oil yield was 30 wt.%. They also found chlorine-containing compounds that make the liquid product difficult to use as a fuel. Starting from bone, [55] produced bio-oil as well, in a vertical retort with a relatively low heating rate and much less initial organic material. The liquid yield was less than 5 wt.% and they found organic acids and asphaltenes as predominant products. These publications show a detailed product distribution with varying concentrations that present other chemicals like phenolic compounds, acids, and aromatics with downstream potential for separation or upgrading.

Looking at the solid products side, [46] produced nanosized HAp powder with regular spherical morphology using flame spray pyrolysis. Moreover, the stoichiometry was right for enhanced properties of densification, osseointegration, and bioreactivity. Flame pyrolysis, in general, presents high heating rates and high reaction temperatures. [51] produced HAp by pyrolyzing an aerosol. The used reactor was a 500 °C tubular furnace, much cooler than in the flame pyrolysis case. The product of the process were hollow spherical micrometer-scale particles with homogeneous chemical composition, but uneven crystal morphologies.

Further thermal treatment at 1050°C allowed obtaining changes in crystallite size and morphology. [8] slowly pyrolyzed specimens of porcine and bovine bone to understand various physical, mechanical, and electrical properties of the resulting solid product as a bone substitute in medical applications. In general, the products obtained were highly porous and with mechanical properties like those of human bones. Additionally, products from 950°C furnace pyrolysis reached close to stoichiometric HAp, Ca/P ratios similar to 1.67. [64] evidenced the changes in the crystalline structure of bone char when increasing the furnace pyrolysis temperature. With low heating rates in this type of reactors, the duration of the process provoked changes in the structure of the char. They report that the chemical structure did not change by pyrolysis. Additionally, they did not find HAp degradation, an idea commonly supported in the literature, except by [64,65].

Opportunities with The Pyrolysis of COPB

Optimization of pyrolysis process variables, mainly heating rates and furnace temperature, combined with a thorough grasp of feedstock properties, can open routes to increase quantity and quality of bio-oil from COPB. Moreover, using pyrolysis as a pretreatment of the HAp precursors, such as MBM, may lead to recovering organic chemicals from otherwise removed and rejected materials. Stage fractionation of bio-oil compounds obtained from COPB pyrolysis, especially the ones that carry fats and proteins, may improve the collection of value-added products, either directly or after upgrading steps. Understanding the effect of pyrolysis variables on stoichiometric composition, crystallinity, chemical structure, and morphology of HAp will allow tailoring the process to produce better materials for medical applications. Microgram-scale pyrolysis furnaces with high heating rates and short processing times will accelerate the study of pyrolysis conditions and products. Moreover, these reactors can input their gaseous product for compound identification and quantification into specialized analyzers.

Broadening the acceptable feedstock options and qualities for pyrolysis can expose pathways to manage wastes otherwise landfilled or poorly managed. Moreover, this may lead to adding value to the waste streams, consequently activating economic activity in the waste management sector. Techno-economic analysis of pathways to process biomass to obtain value-added products can reveal feasible projects that can promote their scalability and proliferation.

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