Synthesis of Precipitated Calcium Carbonate (PCC) Nano-Particles using Turbo-Mixing Reactive Precipitation

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TABLE OF CONTENTS

CHAPTER 3: RESEARCH METHODOLOGY

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Materials
CSD	Crystal Size Distribution
FE-SEM	Field Emission Scanning Electron Microscopes
GCC	Ground Calcium Carbonate
ISO	International Standards Organization
M	Molar
nano-PCC	nano-sized Precipitated Calcium Carbonate
OFN	Oxygen free Nitrogen
PC	Personal computer
PCC	Precipitated Calcium Carbonate
PAA	Phenylacetic acid
RPB	Rotating Packed Bed Reactor
SEM	Scanning Electron Microscopes
TEM	Transmission Electron Microscopes
TMRP	Turbo-Mixing Reactive Precipitation Reactor
XRD	X-ray diffraction
XRF	X-ray fluorescence

LIST OF SYMBOLS

Å	Angstrom
α	Alpha
β	Beta
γ	Lambda
(a)	Aqueous form
(g)	Gasses form
(l)	Liquid form
(s)	Suspension form
Al_2O_3	Aluminum oxide
Ca or Ca^{2+}	Calcium
$CaCl_2$	Calcium chloride
$CaCO_3$	Calcium carbonate
$CaMg(CO_3)_2$	Carbonate mineral (Dolomite)
CaO	Calcium oxide
$Ca(OH)_2$	Calcium hydroxide
CO_2	Carbon dioxide
CO_3^{2-}	Carbonate
Fe^{2+}	Iron
Fe_2O_3	Iron (Tribble et al.) oxide
hkl	Crystallography
H_2O	Water
LaB_6	Lanthanum hexaboride
Mg	Magnesium
MgO	Magnesium oxide

N_2	Nitrogen
Na_2CO_3	Sodium carbonate
NH_4	Ammonium
Ni^{2+}	Nickel
N_2O	Nitrous oxide
O_2	Oxygen
pH	Power of Hydrogen / potential of Hydrogen
P_2O_5	Phosphorus pentoxide
SiO_2	Silicon dioxide
SO_3	Sulfur trioxide
SrO	Strontium oxide
Zn^{2+}	Zinc

Sintesis Partikel Nano Mendakan Kalsium Karbonat (PCC) Yang Menggunakan Penyebatian Turbo Reaktif Pemendakan

ABSTRAK

Kalsium karbonat ($CaCO_3$) adalah sebatian kristal yang banyak terdapat dalam bahan semulajadi kebanyakannya dalam batuan sedimen yang terdiri lebih daripada 4% kerak bumi di seluruh dunia. Kalsium karbonat merupakan salah satu sebatian organik yang dikaji secara meluas kerana kepentingannya dalam pelbagai bidang. Dalam beberapa dekad, pengeluaran konvensional mendakan kalsium karbonat (PCC) hanya berjaya menghasilkan zarah bersaiz tidak kurang dari 200 nm. Dalam laporan ini, satu kaedah inovatif dan reka bentuk dalam pemprosesan yang dikenali sebagai penyebatian turbo reaktif pemendakan (TMRP) yang dicadangkan sebagai alternatif kepada pengeluaran konvensional mendakan halus kalsium karbonat (nano-PCC) dalam keadaan pencampuran turbo. Dalam proses TMRP, nano-PCC yang dihasilkan menggunakan sistem gas-cecair-pepejal (pengkarbonan) yang melibatkan pengkarbonan kalsium hidroksida terampai ($Ca(OH)_2$) atau lebih dikenali sebagai "susu batu kapur" dalam tangki reaktor yang dikacau. Gas karbon dioksida dan nitrogen dimasukkan ke dalam tangki melalui semburan ke dalam "susu batu kapur" dalam tangki reaktor. Matlamat penyelidikan ini adalah untuk meneroka kaedah baru dan pengoptimuman pembolehubah yang mempengaruhi pengeluaran nano-PCC dengan menggunakan teknik TMRP. Hasil ujikaji menunjukkan bahawa kalsium oksida yang paling reaktif boleh diperolehi dengan pembakaran pada 1100 °C selama 60 minit untuk sampel bersaiz julat antara -30+20 mm. Purata saiz $CaCO_3$ zarah-nano sekitar 26.79 nm berjaya diperolehi dengan 15 ℓ/min kadar semburan CO_2 gas dan N_2 tanpa O_2 gas, 0.60 M kepekatan awal likatan $Ca(OH)_2$ dan 900 rpm kelajuan putaran penyebatian pada suhu penyebatian yang rendah (10 ±5 ºC). Kajian ini mendedahkan bahawa sifat-sifat bahan nano-PCC dan reka bentuknya dapat dipertingkatkan dengan menggunakan teknik TMRP. Namun, penambahbaikan persediaan alatan dan peningkatan kaedah pencirian kimia permukaan mineral diperlukan. Seterusnya, kerja-kerja dimasa akan datang juga perlu bertumpukan kepada pembolehubah terhad lain yang mempengaruhi produk mendakan perlu disiasat, untuk mengoptimumkan proses rekabentuk.

Synthesis of Precipitated Calcium Carbonate (PCC) Nano-Particles Using Turbo-Mixing Reactive Precipitation

ABSTRACT

Calcium carbonate ($CaCO_3$) is a crystalline compound appear abundantly in nature substance mostly in sedimentary rocks which comprise more than 4% of the earth's crust throughout the world. Calcium carbonate is one of the most extensively studied inorganic compounds because of its importance in the various fields and industrial processes due to its large range of applications. In recent decades, conventional productions of the precipitated calcium carbonate (PCC) only manage to produce particle size not less than 200 nm. In this thesis, an innovative and novel technology method of processing called Turbo-Mixing Reactive Precipitation (TMRP) design proposed as an alternative to this current processing or conventional productions of fine precipitated calcium carbonate (nano-PCC) in turbo-mixing conditions. In the TMRP process, nano-PCC is fabricated using gas-liquid-solid systems (precipitation) of the calcium hydroxide slurry ($Ca(OH)_2$) or better known as "milk of lime" in a stirred tank batch reactor system. Carbon dioxide and nitrogen gas is introduced into the tank through bubbled into the "milk of lime" in the reactor tank. The key research of this study explored new methodologies and optimization the influence parameters in the production of nano-PCC using TMRP technique. The experimental result indicated that the most reactive of quicklime can be obtained by calcined at 1100 °C with 60 minutes of soaking time for sample sized range between -30+20 mm. An average particle size approximately 26.79 nm of $CaCO_3$ nanoparticles was successfully produced by the 15 ℓ/min flowing rate of CO_2 gas and O_2-free N_2 gas, 0.60 M concentrations of $Ca(OH)_2$ slurry and 900 rpm stirring rotation speed at low precipitation temperature (10 ±5 ºC). This research revealed that the production of nano-PCC characteristics and morphological can be enhanced by using the TMRP technique. However, improved experimental setup and enhance methods for characterizations mineral surface chemistry needed to be applied. Nevertheless, it is suggested to focus on other restricted parameters that influenced the precipitated products, in order to optimize the design process in the near future.

CHAPTER 1

INTRODUCTION

1.1 Research Background

Calcium Carbonate ($CaCO_3$) has been a vital role and were used widely as building construction material since ancient world throughout history. In the modern world, calcium carbonate mainly used in the civil engineering, either as a building material or road construction, in the purification process of iron from iron ore, and more. In recent decades, it is now becoming used in other industries as filler materials and increasingly important used for the paper production, plastics and pharmaceutical industries, in personal care and cosmetics, food and beverages, nutritional supplements, adhesives, and sealants (Kemperl & Macek, 2009).

PCC is especially utilized as a part of extensive amounts in the mash and paper making industry as a paper filler and in coatings to provide properties such as good opacity, excellent brightness and enhanced printability due its great ink receptivity. Such industrial applications require well-defined PCC particles with narrow size distribution, uniform shape, and definite crystal structure. These characteristics play a crucial role in PCC properties and their control is closely related with the method of its production and the process parameters (Xiang et al., 2002). Calcium carbonate also has been used as a model mineral in biomimetic research, leading to increased understanding of biogenic control over mineral orientation, morphology, and polymorph (Meldrum & Colfen, 2008).

There are various types of PCC grades, but the purity of PCC is usually over 99% with a density of 2700 kg/m^3. For filler pigments 70% of the carbonate particles are smaller than 2 μm. The particle size affects paper smoothness, gloss and printing characteristics. Printing characteristics are also related to particle distribution and shape, which also affects the consumption of chemical additives in papermaking.

This is due to the brightness of PCC filler pigments is larger than 93%, and the pH of 1 Mol/ℓ in an aqueous solution is 9. As a coating pigment, its average particle size is 0.4-2.0 μm with a refraction index of 1.49-1.67. The high refraction index and narrow particle size distribution of PCC promotes sheet light scattering. The ISO brightness for a PCC coating pigment is 95%, which requires a very pure limestone as raw material (Teir et al., 2005).

The polymorphs of calcium carbonate is generally classified three anhydrous crystalline phases (rhombic calcite, needle-like aragonite and spherical vaterite, which have the crystal system of rhombohedral, orthorhombic and hexagonal), two hydrated ones (monohydrate and hexahydrate), and amorphous calcium carbonate (Lopez-Periago et al., 2010). The thermodynamic stability of the three polymorphs at atmospheric temperature and pressure is in the order calcite>aragonite>vaterite. Because the morphology and physicochemical properties such as solubility and density depend on each polymorph, the polymorph control of calcium carbonate ($CaCO_3$) crystal is very important in a crystallization process. Therefore, a considerable amount of attention and effort has been devoted to elucidate the relationship between the precipitation condition and the particle morphology (Jiang et al., 2012; Jung et al., 2000; Matsumoto et al., 2010).

The typical morphologies of the different $CaCO_3$ modifications already enable morphogenesis by choosing the precipitation conditions for one modification, which is kept stable. However, a much better morphology control is possible by either choosing soluble additives which control the crystallization or superstructure formation of nano-particles or by using macroscopic templates or matrices which can act as a mold (Colfen, 2003). Nano-PCC with particle sizes less than 100 nm have shown many unique properties compared to regular PCC particles (1-3 µm) (Tran et al., 2010).

$CaCO_3$ particles with specific properties are usually prepared under carefully controlled conditions (Wen et al., 2003). The synthesis of the high quality of PCC has mostly been done by using the high impurities of $CaCO_3$ carbonate rocks. However, some common carbonate rocks contain dolomite as a prominent rock forming mineral. This foreign impurity subsequently affects the quality of the PCC produced due to the difficulties in the separation of Ca and Mg components in carbonate rocks, which is the low solubility of both materials (Mantilaka et al., 2013). Some of the researchers also concerned with the usage of inorganic additives (Fe^{2+}, Ni^{2+}, and Zn^{2+} etc.) onto the properties of synthesized calcium carbonate. The controllable synthesis of $CaCO_3$ polymorphs is still a practical challenge due to the remaining problems as the complex processes, the expensive reactants and the coexistence of the irregular byproduct, etc. (Chen & Xiang, 2009).

1.2 Problem Statement

PCC is one of the most extensively studied inorganic compounds because of its importance in the various fields and due to its large range of industrial applications

(Isopescu et al., 2010; Kirboga & Oner, 2013). In the present day of industrial or laboratory manufacturing scale, PCC is normally manufactured using gas-liquid-solid systems (precipitation) in the stirred tank batch reactor system. However, precipitation is a complex system due to its various process variables involved such as initial concentration, rotating speed, reaction temperature, pH, time and else. These proses variables are interrelated with each other and difficult to control as compared with the other systems.

Numerous precipitation synthesis techniques have been developed by various researchers such as double injection method (Chen & Xiang, 2009; Chen et al., 1997), rotating continuous stirred tank reactors called a Couette-Taylor reactor (Jung et al., 2010; Jung et al., 2000), double-wall Pyrex reactor with a double-blade vertical shaker (Carmona et al., 2003a, 2003b), bubble column with a radiate-shaped sparger nozzle, a rectangular stirrer and a two-blade stirrer (Tran et al., 2010; Wen et al., 2003), rotating packed bed (RPB) reactor (Wang et al., 2004), three phase stirred reactor tank (Teir et al., 2005), vapor diffusion method (Yang et al., 2010), and many more with identical attempt which is to produce uniform nano-sized of PCC, morphological controlled and yet not fully achieved.

Involvement of chemicals additives in the previous work to enhance or better controlled onto PCC production which is expensive and can be harmful to human life or deleterious to the environment. Common chemicals additives used such as strong acids or polyphosphates, citric acid, sucrose, calcium lignosulfonate, sodium dodecyl sulfate, polyethylene glycol, triethanolamine, calcium sulfate, aerosol (OT) and others (Alimi et al., 2009; Fathi et al., 2006).

However, conventional or industrial productions method of PCC only manage to produce particle size not less than 200 nm. In the meantime, the problem is how to get produced nano-sized of PCC with controlled and uniform particle size distribution, and control shape of the particle morphology. Thus, to achieve the objective of synthesizing the nano sized of PCC, optimum parameter that affects the production should be determine.

In this research, an innovative and novel technology method called Turbo-Mixing Reactive Precipitation (TMRP) reactor is proposed as an alternative to this current processing or conventional productions. It is designed to overcome the inability of current industrial technique to produce nano-sized particles with the narrow size distribution of morphology by its tremendous mass transfer and great homogeneous mixing. The key of this research is to explore a new approach (TMRP technique) in the synthesizing of nano-PCC by gas-liquid-solid systems (precipitation process) without the usage of any organic or inorganic additives.

1.3 Research Objectives

The main target of this research is to investigate and explore new methodologies in developing this target-oriented product (nano-PCC) compared to the other existing conventional or industrial routine practice via batch-wise methods.

This study embarks on the following objectives:

i. To investigate the influences of various calcination temperatures, calcination times and limestone sizes onto quicklime reactivity produced.

ii. To evaluate the effect of experimental operating variables ($Ca(OH)_2$ slurries, stirring speeds, CO_2 gas flow rates, and initial reaction temperatures) onto PCC nanoparticles morphology.

iii. To determine the optimum parameter to produce finest PCC nanoparticles using TMRP reactor.

1.4 Scope of the research

This thesis is presented in five separated chapters, including of Introduction, Literature Review, Research Methodology, Results and Discussion, and Conclusions. In this research, there were three major phases involved in preparing the precipitated calcium carbonate through precipitation process using TMRP reactor.

Phase one specifically into raw materials preparation procedures; including of the calcination process of raw limestone at various calcination temperatures (900-1200 ºC), soaking times (30-120 minute) and sizes (-10+5 and -30+20 mm) then followed by slaking test to evaluate the quicklime reactivity corresponding to the standard of American Society for Testing and Materials (ASTM C110)(International, 2011).

Phase two strictly involves of hydration process which is preparation of various molarity concentration of $Ca(OH)_2$ slurry and precipitation process using TMRP reactor with four experimental operating variables; i.e., $Ca(OH)_2$ slurries, stirring speeds, CO_2 gas flow rates and initial reaction temperatures. The focus onto the influence of various concentrations of $Ca(OH)_2$ slurries (0.1-1.0 M), stirring speeds (700-1200 rpm), CO_2 gas flow rates (5-20 ℓ/min) and initial reaction temperatures (10 ±5, 30 ±5, and 50 ±5 °C) towards precipitated calcium carbonate behavior are evaluated.