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(54) **Title:** DEVELOPMENT OF CHARACTERIZATION AND SYNTHESIS OF NATURAL FISH BONE ACTIVATED CARBON AND HYDROXYAPATITE THROUGH HEAT TREATMENT

RESULT OF ANALYSIS:

Test Parameters	Unit of Measurement	to*** Fishbone-After Treatment	LOR	Test Method References
Calories,total	kcal/100g	1000.69	0.01	Calculation
Calories from fat	kcal/100g	<0.01	0.01	Calculation
#Fat,total	g/100g	<0.01	0.01	AOAC 996.06
Carbohydrate	g/100g	57.85	0.01	Calculation
Protein	g/100g	1.92	0.01	AOAC 920.152
Sugar,total	g/100g	<0.01	0.01	In-House based on AOAC 925.05 & 923.09
#Dietary fiber,total	g/100g	16.59	0.01	AOAC 985.29
Saturated Fat	g/100g	<0.01	0.01	In-House based on AOAC 996.06 and Operation Manual of Agilent Technologies
Trans Fatty Acid	g/100g	<0.01	0.01	In-House based on AOAC 996.06 and Operation Manual of Agilent Technologies
#Cholesterol	mg/100g	<0.01	0.01	In-House Method based on Journal of Food Composition and Analysis 16 (2003) 147-153
#Vitamin A as Retinol Acetate	g/100g	<0.01	0.01	In-House based on AOAC 2002.06 by HPLC
#Vitamin C	g/100g	0.06	0.01	In-House based on Report Analysis of water soluble vitamin by HPLC
Calcium,Ca	g/100g	0.07	0.01	In-House method based on AOAC 999.08
Iron,Fe	g/100g	<0.01	0.01	In-House method based on AOAC 999.08
Sodium,Na	mg/100g	3.21	0.01	In-House method based on AOAC 999.08

Remarks:
AOAC : Association of Official Analytical Chemists
#Test Parameter : Not SAMM Accredited
mg/100g: milligram per hundred gram of sample
kcal : kilo calories of sample
g/100g : gram per hundred gram of sample
LOR:Limit of Reporting

Figure 6 illustrate the nutrition contain in Hydroxyapatite.

(57) Abstract: The natural (1) fish bone activated carbon and hydroxyapatite powder can be obtain by involving process of separated part of fish, boiling (2), drying (3), grinding (4), heat treatment method (5), mixing (6) and compressed (7).

WO 2016/080825 A1

Title:

DEVELOPMENT OF CHARACTERIZATION AND SYNTHESIS OF NATURAL FISH BONE ACTIVATED CARBON AND HYDROXYAPATITE THROUGH HEAT TREATMENT

Technical Field

This present invention discloses generally about development of characterization and synthesizing natural hydroxyapatite and activated carbon originated from Tamban fish bone waste through heat treatment method.

Background Art

Fish bone waste is a waste that possesses economic value that has been abundant by the community of fish processing in Malaysia. Researchers have undertaken many studies regarding the benefits of fish bone which is one of the bioorganic sources, and one of the most potential ceramic compound in the fish bone is Hydroxyapatite $Caio(P0_4)6(OH)2$. Hydroxyapatite is a thermodynamically most stable crystalline phase of calcium phosphate in body fluid, good chemical homogeneity, possesses the most similarity to the mineral part of bone. Looking at available of manmade Hydroxyapatite have been recently limited, expensive and using manmade chemical as one of the method in producing Hydroxyapatite, natural hydroxyapatite will be an important sources of calcium phosphate in the future. From this innovation, The result show that the bioactivity in Hydroxyapatite makes it has a lot of functionality such as heavy metal remover, bacterial growth inhibitor and etc.

Summary of invention

The present invention realizes that the fish processing community has not been the recipients of clear and sufficient information about what they can obtain from the fish bone waste. Thus, community participation in the transfer of knowledge has to be encouraged to provide the correct information about the harnessing of fish bone waste.

First Phase

Fish bone waste collected by fish processing community and being cleaned first, separate from unused part such as head, tail and scale. After that, the fish bone are then boiled to separate fish bone from organic compound such as protein, fat, college and

gelatin, leaving only inorganic compound. The boiling process is repeated several times, preferably five times, until the organic compound gone. Next, the boiled fish bone dried under sunshine or drying them in an oven at 100°C-200°C for the totally dried.

Second Phase

The dried fish bones then passed grinding process using grinder (juicer commercial) until become powder. After that, the powder filtered using sevier machine until the powder size become under 50 microns.

Third Phase

In the form of powder, the heat treatment applied to the fish bone powder. During this phase, two main products will be produce; the first one (in the form of powder) is Activated Carbon which is burned inside a furnace machine for at 300°C-600°C in 15 minutes. Secondly is Hydroxyapatite which is burned for an hour at 1000°C to 1300°C. The order in heat treatment divided into two steps. The first step objective is to terminate organic compound in the fish bone which is heat-treated applied at 600 °C. After that, 15 minutes will apply as soaking hour. The second step is continue the heat treatment begin at 600°C until 1300°C. The second product is Hydroxyapatite and Activated Carbon in granule form. To produce Activated Carbon granule, the process begins with mixing the fish bone powder with clay material with 60:40 portions. After that, the mixing portion compressed using compaction machine with 15 tan momentums into granule balls with having ll-13mm sizes. Separate the granule ball into two groups. The first group is burned inside furnace machine at 500°C for one hour (carbonization process) and it will continue for activate the carbon using heat treatment at 700°C for an hour and the end product is granule activated carbon. The second group is burned inside a furnace machine at 1000°C until 1300°C for an hour to get granular hydroxyapatite. The order in heat treatment divided into two steps. The first step objective is to terminate organic compound in the fish bone which is heat-treated applied at 600 °C. After that, 15 minutes will apply as soaking hour. The second step is continue the heat treatment begin at 600°C until 1300°C

Fourth Phase

All the created AC and HA will having characterization of the sample using TGA, DTA, XRF, XRD, SEM EDS and FTIR test to make sure it's safe to consume.

TGA and DTA result showed the removal organic proportion from Tamban fish bone.

SEM result show picture of contain porous structure of the raw fish powder.

FTIR result showed the amount of component in Hydroxyapatite.

XRF / XRD result show diffraction patent of Hydroxyapatite.

This product may be used inside a conventional cartridge water filter as the properties to eradicate the odor and dissolve heavy metal in the water and create clean and high calcium water. The AC and HA in powder is also safe to be used in chocolate to create a high calcium chocolate.

Description of Drawing and the Best Mode for Carrying Out the Invention

In order that the invention may be more readily understood and put it into practical effect, a preferred illustrated compound and process also specific result of the invention will now describe with references to the accompanying drawing. In which:

Figure **1** illustrates Natural Hydroxyapatite and Activated Carbone process flow

Figure 2 illustrate TGA and DTA result showed the removal organic proportion from Tamban fish bone.

Figure 3 illustrate SEM result show picture microstructure of the raw fish powder.

Figure 4 illustrate FTIR result showed the amount of component in Hydroxyapatite.

Figure 5 illustrate XRF / XRD result show diffraction patent of Hydroxyapatite

Figure 6 illustrate the nutrition contain in Hydroxyapatite.

Claims

1. The NATURAL (1) FISH BONE ACTIVATED CARBON AND HYDROXYAPATITE powder can be obtain by involving process of separated part of fish, boiling (2), drying (3), grinding (4), heat treatment method (5), mixing (6) and compressed (7).

2. The NATURAL FISH BONE ACTIVATED CARBON AND HYDROXYAPATITE powder according to claim 1, preparation of Hydroxyapatite particle obtain without using any solvent or manmade chemical by allowing the fish bone powder to react with heat treatment.

3. The NATURAL FISH BONE ACTIVATED CARBON AND HYDROXYAPATITE powder according to claim 2, characterised in that fish bone are then boiled to separate fish bone from organic compound such as protein, fat, college and gelatin, leaving only inorganic compound. The boiling process is repeated several times, preferably five times, until the organic compound gone.

4. The NATURAL FISH BONE ACTIVATED CARBON AND HYDROXYAPATITE powder according to claim 3, characterised in that boiled fish bone dried under sunshine or drying them in an oven at 100°C-200°C for the totally dried.

5. The NATURAL FISH BONE ACTIVATED CARBON AND HYDROXYAPATITE powder according to claim 4, characterised in that dried fish bone grinding process using grinder (juicer commercial) until become powder. After that, the powder filtered using sevier machine until the powder size become under 50 microns.

6. The NATURAL FISH BONE ACTIVATED CARBON AND HYDROXYAPATITE powder according to claim 5, characterised in that during this phase, two main products will be produce; the first one (in the form of powder) is Activated Carbon which is burned inside a furnace machine for 1 hour at 300°C-600°C in 15 minutes. Secondly is Hydroxyapatite which is burned for an hour at 1000°C to 1300°C. The order in heat treatment divided into two steps. The first step objective is to terminate organic compound in the fish bone which is heat-treated applied at 600 °C. After that, 15 minutes will apply as soaking hour. The second step is continue the heat treatment begin at 600°C until 1300°C. Separate the granule ball into two groups. The first group is burned inside furnace machine at 500°C for one hour (carbonization process) and it will

continue for activate the carbon using heat treatment at 700°C for an hour and the end product is granule activated carbon. The second group is burned inside a furnace machine at 1000°C until 1300°C for an hour to get granular hydroxyapatite. The order in heat treatment divided into two steps. The first step objective is to terminate organic compound in the fish bone which is heat-treated applied at 600 °C. After that, 15 minutes will apply as soaking hour. The second step is continue the heat treatment begin at 600°C until 1300°C

7. The NATURAL FISH BONE ACTIVATED CARBON AND HYDROXYAPATITE powder according to claim 6, characterised in that process begins with mixing the fish bone powder with clay material with 60:40 portions

8. The NATURAL FISH BONE ACTIVATED CARBON AND HYDROXYAPATITE powder according to claim 7, characterised in that mixing portion compressed using compaction machine with 15 tan momentums into granule balls with having ll-13mm sizes

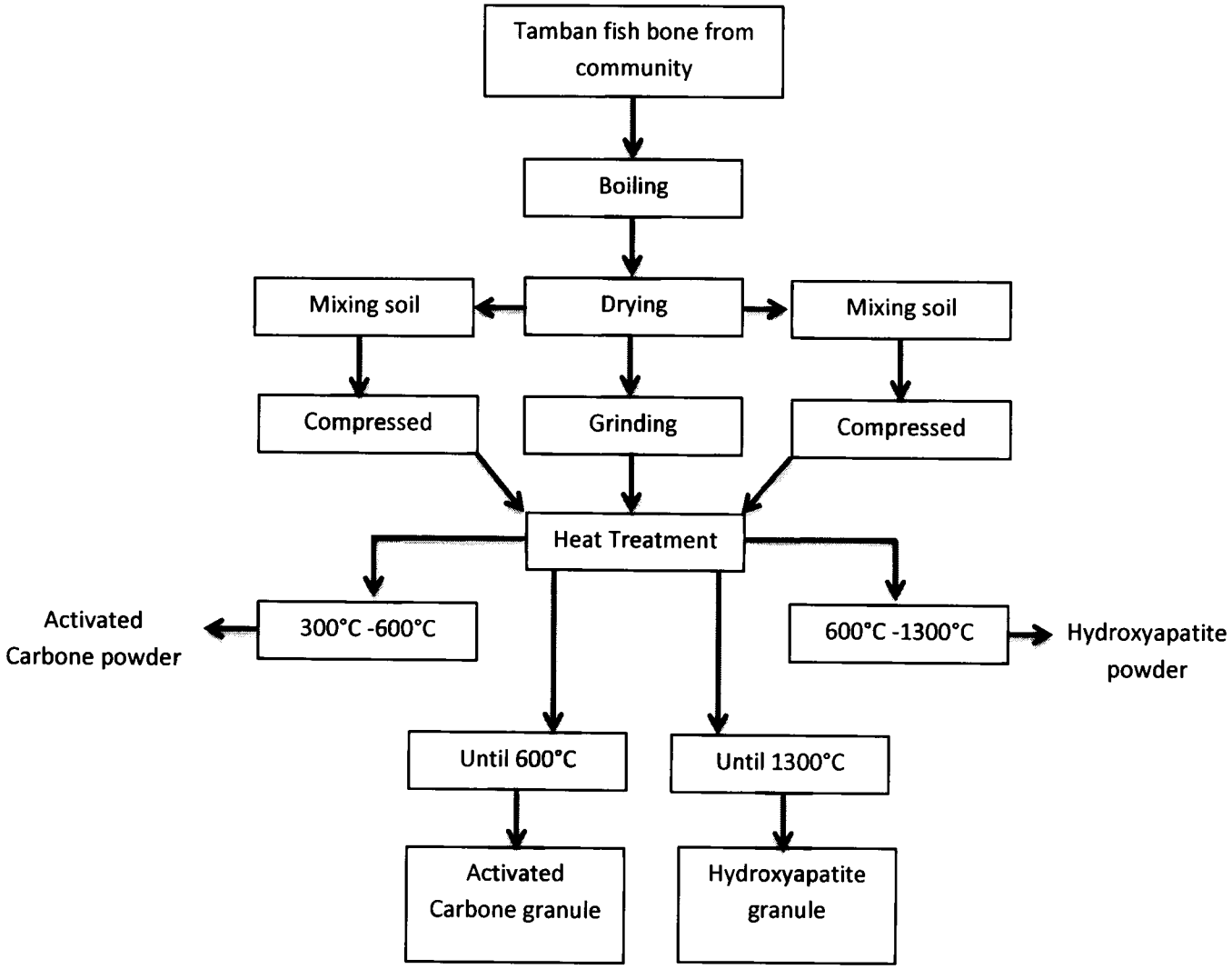
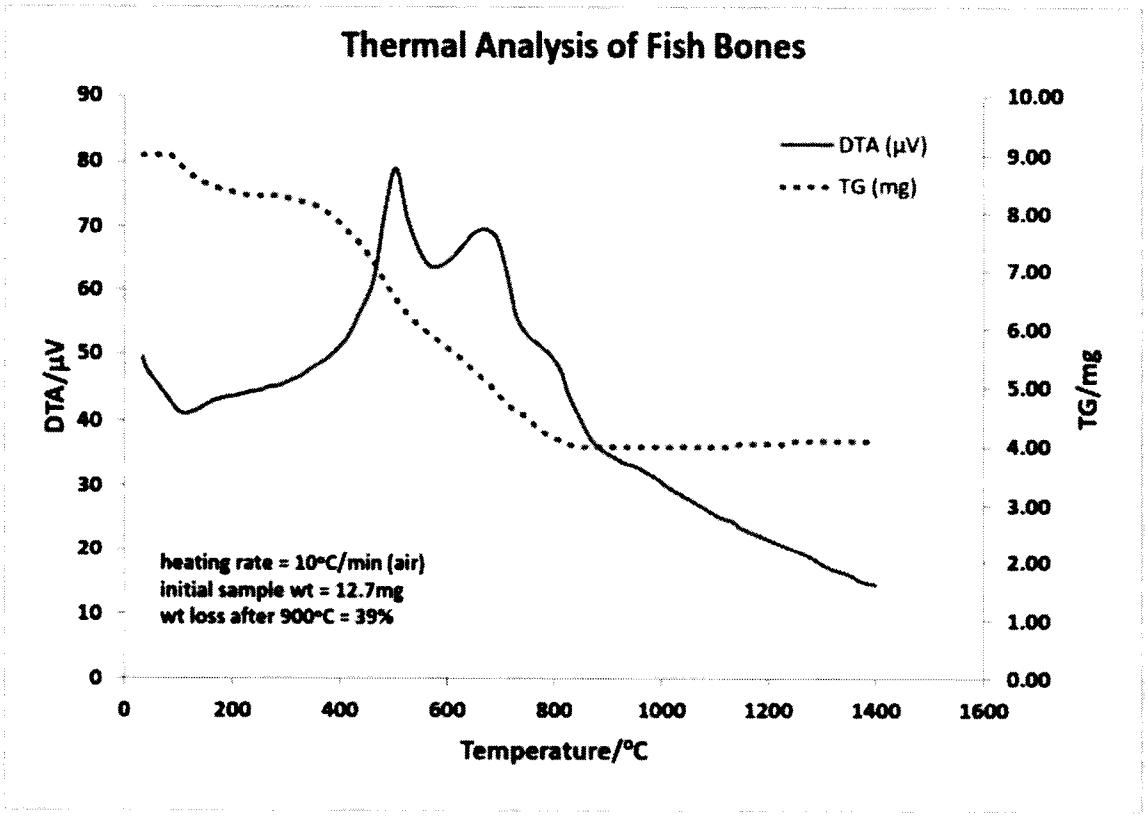


Figure 1: Natural Hydroxyapatite and Activated Carbone process flow



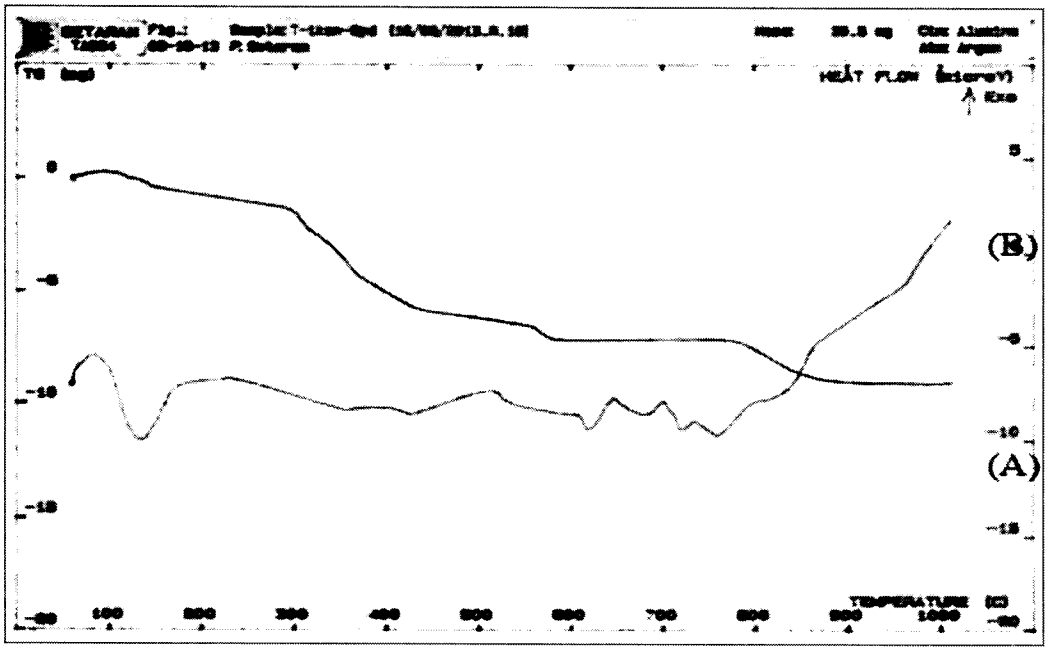


Figure 2 : TGA and DTA result showed the removal organic proportion from Tamban fish bone.

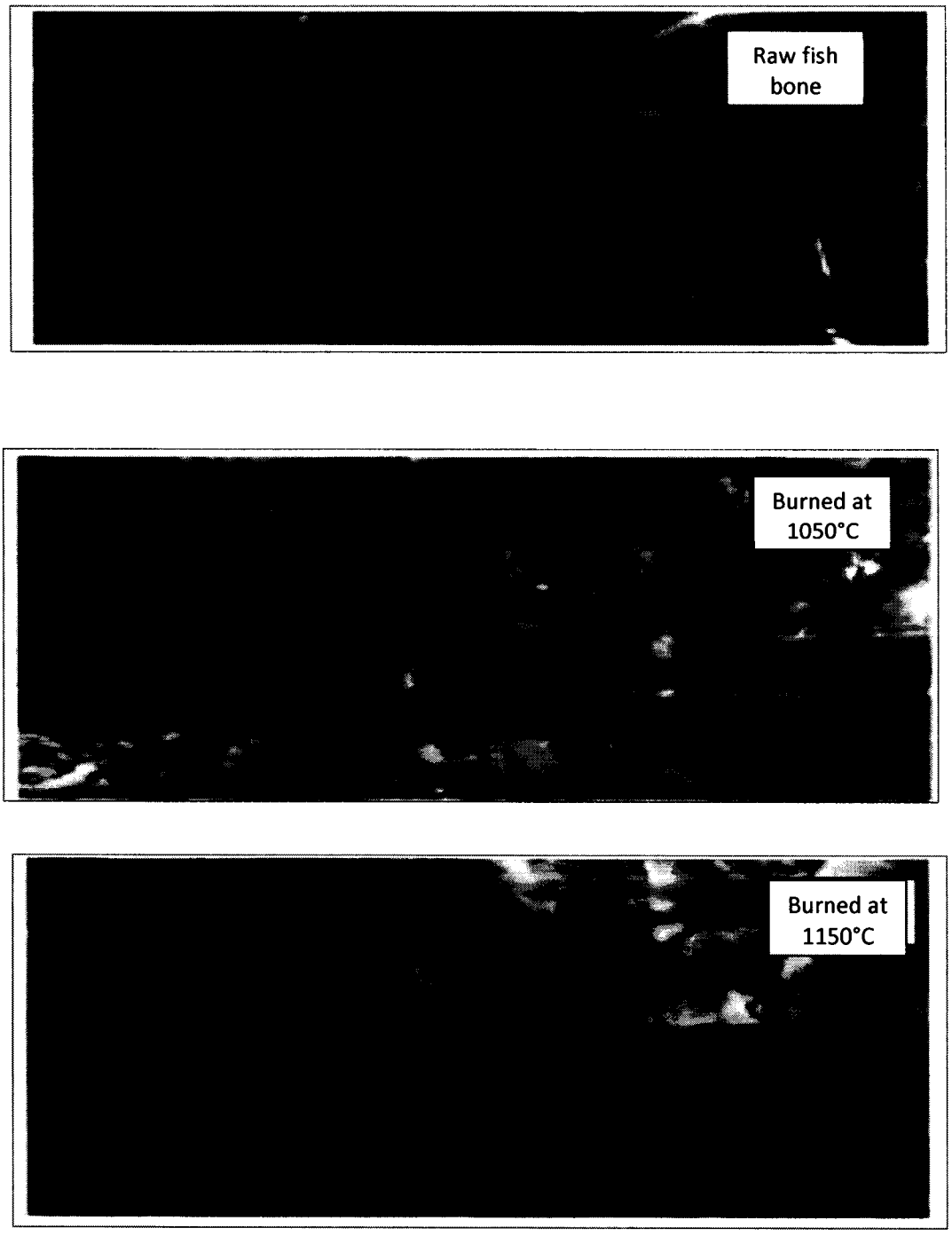
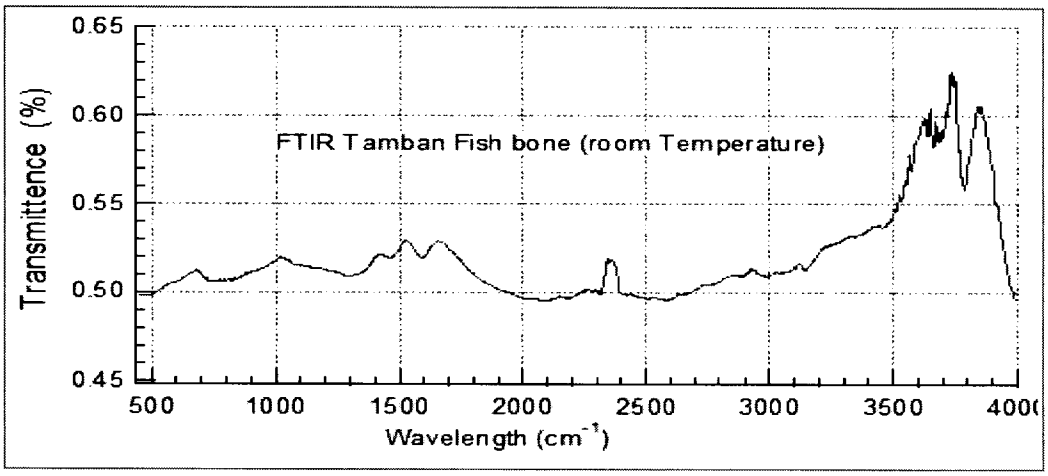


Figure 3 illustrate SEM result show microstructure of the raw fish powder.



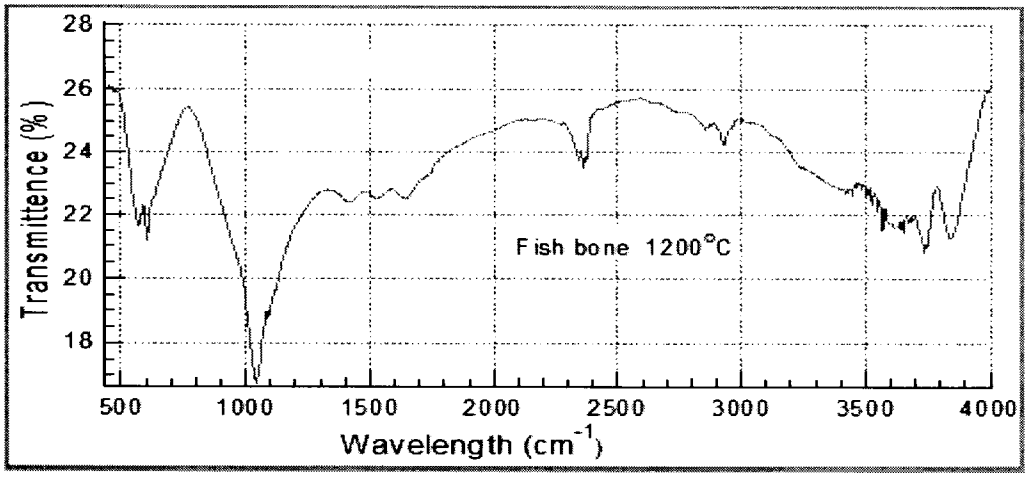
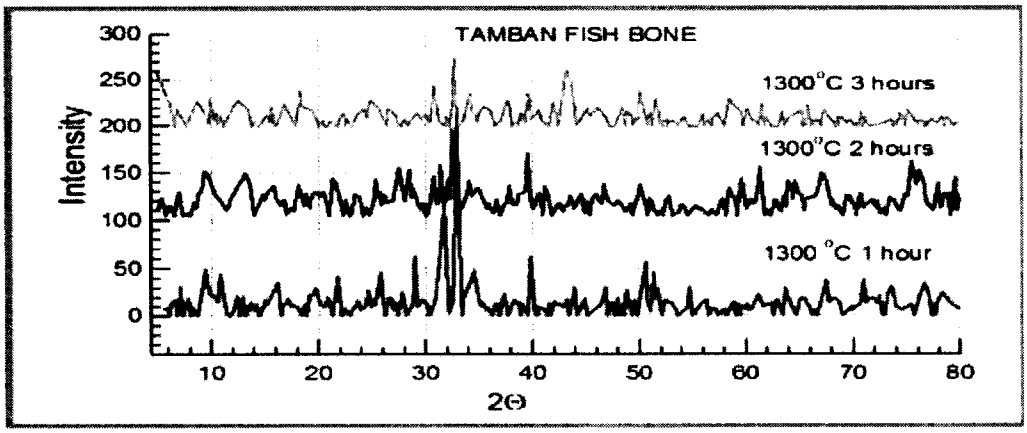
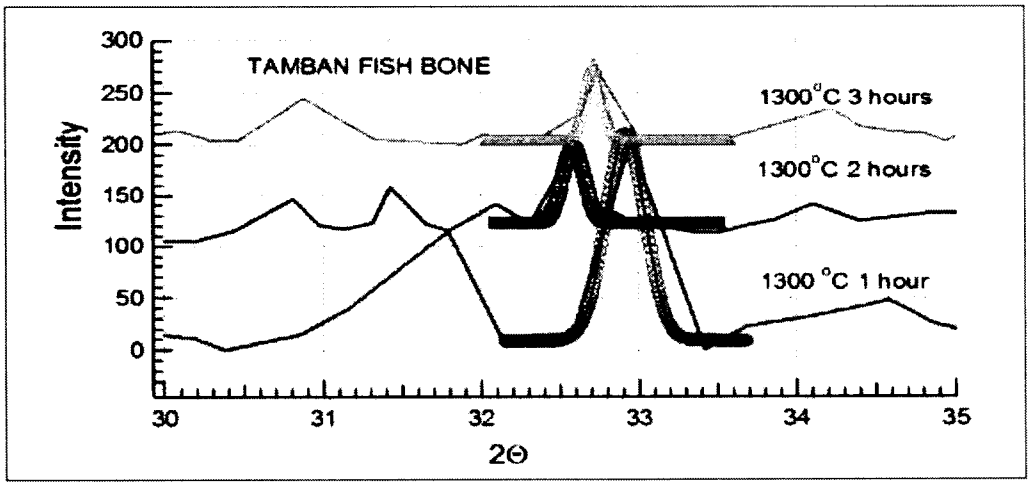


Figure 4 illustrate FTIR result showed the amount of component in Hydroxyapatite.





Material	Peak	2Ξ	FWHM	Crystal size D(nm)	Intensity (count)
Fish bone 1300°C 1 hour	peak 1 hour	32.915	0.1761	90	209.960
Fish bone 1300°C 2 hours	peak 2 hours	32.587	0.0970	160	91.277
Fish bone 1300°C 3 hours	peak 3 hours	32.720	0.0784	190	76.796

COMPOUND	P	S	K	Ca	Mn	Fe	Cu	Zn	Sr	Yb	Re
CONC	12.20	0.59	0.20	85.41	0.087	0.19	0.082	0.17	0.58	0.45	0.07
UNIT	%	%	%	%	%	%	%	%	%	%	%

Figure 5 illustrate XRF / XRD result show diffraction patent of Hydroxyapatite

RESULT OF ANALYSIS:

Test Parameters	Unit of Measurement	Result	LOR	Test Method References
		Fishbone-After Treatment		
Calories,total	kcal/100g	1000.69	0.01	Calculation
Calories,from fat	kcal/100g	<0.01	0.01	Calculation
#Fat,total	g/100g	<0.01	0.01	AOAC 996.06
Carbohydrate	g/100g	57.85	0.01	Calculation
Protein	g/100g	1.92	0.01	AOAC 920.152
Sugar,total	g/100g	<0.01	0.01	In-House based on AOAC 925.05 & 923.09
#Dietary fiber,total	g/100g	16.59	0.01	AOAC 985.29
Saturated Fat	g/100g	<0.01	0.01	In-House based on AOAC 996.06 and Operation Manual of Agilent Technologies
Trans Fatty Acid	g/100g	<0.01	0.01	In-House based on AOAC 996.06 and Operation Manual of Agilent Technologies
#Cholesterol	mg/100g	<0.01	0.01	In-House Method based on Journal of Food Composition and Analysis 16 (2003) 147-153
#Vitamin A as Retinol Acetate	g/100g	<0.01	0.01	In-House based on AOAC 2002.06 by HPLC
#Vitamin C	g/100g	0.06	0.01	In-House based on Raport Analysis of water soluble vitamin by HPLC
Calcium,Ca	g/100g	0.07	0.01	In-House method based on AOAC 999.08
Iron,Fe	g/100g	<0.01	0.01	In-House method based on AOAC 999.08
Sodium,Na	mg/100g	3.21	0.01	In-House method based on AOAC 999.08

Remarks:

AOAC : Association of Official Analytical Chemists

#Test Parameter : Not SAMM Accredited

mg/100g: milligram per hundred gram of sample

kcal : kilo calories of sample

g/100g : gram per hundred gram of sample

LOR:Limit of Reporting

Figure 6 illustrate the nutrition contain in Hydroxyapatite.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/MY2015/050003

A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl. C01B31/08 (2006.01)i, C01B25/32 (2006.01)i, B09B3/00 (2006.01)n

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int.Cl. C01B31/08, C01B25/32, B09B3/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Published examined utility model applications of Japan 1922-1996
Published unexamined utility model applications of Japan 1971-2015
Registered utility model specifications of Japan 1996-2015
Published registered utility model applications of Japan 1994-2015

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

JSTPlus/JST7580(JDreamIII)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 9-278425 A (KABUSHIKI GAISHA ADOBANSU) 1997.10.28, claim 1; column 2, lines 28-30; column 3, lines 31-40; Figure 3 (Family: none)	1-8
Y	JP 3-164411 A (TAIYO KAGAKU KOGYO KABUSHIKI GAISHA) 1991.07.16, page 2, upper left column, line 19 - upper right column, line 1; Example (Family: none)	1-8
Y	JP 2-6306 A (FUJITA, Sanai) 1990.01.10, claim 1; page 3, upper left column, line 10 - upper right column, line 2 & US 5047255 A & US 5397499 A & US 5487844 A & US 5254285 A	1-8

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
14.05.2015	26.05.2015

Name and mailing address of the ISA/JP	Authorized officer
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