SYNTHESIS AND CHARACTERIZATION OF RANKINITE FROM RICE HUSK ASH AND EGGSHELLS

PRISCILLA TONG SHUEN

UNIVERSITI SAINS MALAYSIA
2022

SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING

UNIVERSITI SAINS MALAYSIA

SYNTHESIS AND CHARACTERIZATION OF RANKINITE FROM RICE HUSK

ASH AND EGGSHELLS

by

PRISCILLA TONG SHUEN

Supervisor : Assoc. Prof. Ir. Ts. Dr. Hasmaliza Mohamad

Dissertation submitted in partial fulfillment

of the requirements for the degree of Bachelor of Engineering with Honours

(Materials Engineering)

Universiti Sains Malaysia

AUGUST 2022

DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled 'Synthesis and Characterization of Rankinite from Rice Husk Ash and Eggshells'. I also declare that it has not been previously submitted for the award of any degree and diploma or other similar title of this for any other examining body or University.

Name of Student   : Priscilla Tong Shuen

Date   : 17/8/2022   Signature :

Witness by

Supervisor   : Associate Professor Ir. Ts. Dr Hasmaliza Bt Mohamad

Date   : 17/8/2022   Signature :

ACKNOWLEDGEMENT

First of all, I would like to express my appreciation to Universiti Sains Malaysia for providing opportunities for me to complete my research.

This endeavor would not have been possible without support from the School of Materials and Mineral Resources Engineering for providing the equipment and materials.

My honest appreciation to Profesor Ir. Dr. Mariatti Jaafar, Dean of School of Materials and Mineral Resources Engineering, Universiti Sains Malaysia, Engineering Campus for the supports and opportunities given this research.

I would express deepest gratitude and sincere appreciation to my supervisor, Associate Professor Ir. Ts. Dr Hasmaliza Bt Mohamad for her patient guidance and regular supervision and encouragement in successfully completing this research.

Apart from that, I would like to deliver my appreciation to all the lecturers, technicians and staffs of School of Materials and Mineral Resources Engineering for providing the facilities and supports during the final year project.

Last but not least, my grateful thanks to all my family members and friends for their constant support.

**SINTESIS DAN PENCIRIAN RANKENIT DARIPADA ABU SEKAM PADI
DAN KULIT TELUR**

ABSTRAK

Rankenit telah lama digunakan dalam penghasilan bahan binaan disebabkan suhu pengkalsinan yang rendah dan lebih kurang penggunaan bahan api daripada OPC. Rankenit selalunya disintesis daripada kalsium oksida dan silika. Oleh itu, rankenit akan disintesis daripada sekam padi dan kulit telur sebagai sumber silika dan kalsium oksida. Tujuan projek ini adalah untuk menentukan kesan daripada nisbah komposisi $CaO:SiO_2$ dalam 3:2 dan 1:1 serta suhu pensinteran dalam 950 ℃, 1050 ℃ dan 1150 ℃ terhadap sistesis rankenit. Silika dan kalsium oksida diektrak daripada sekam padi dan kulit telur melalui rawatan haba. Selepas itu, silika dan kalsium oksida ditimbang dalam nisbah mol, dikisar dan dipadatkan kepada pelet. Bahan mentah telah dianalisis dengan menggunakan pembelauan sinar-X (XRD), pendarflour sinar-X (XRF) dan analisis saiz zarah (PSA). Campuran sampel rankenit dianalisis melalui XRD, spektrometri transformasi inframerah Fourier (FTIR), mikroskop imbasan elektron (SEM), PSA, ujian pengecutan linear, ujian ketumpatan dan keliangan serta ujian pemampatan. Rankenit telah berjaya disintesis melalui nisbah komposisi $CaO:SiO_2$ (3:2 dan 1:1) dan semua suhu persinteran. Dengan peningkatan suhu persinteran, ketumpatan dan kekuatan tegangan diametral meningkat manakala kekerasan berkurangan. Nisbah komposisi $CaO:SiO_2$ dalam 3:2 menunjukkan ketumpatan, kekuatan tegangan diametral dan kekerasan yang lebih tinggi berbanding dengan nisbah komposisi 1:1. Secara keseluruhan, rankenit yang disintesis pada nisbah komposisi 3:2 dan disinter pada 1150 ℃ menunjukkan sifat-sifat yang paling relevan kepada OPC. Oleh itu, ia adalah rankenit yang paling sesuai untuk menggantikan OPC sebagai klinker.

SYNTHESIS AND CHARACTERIZATION OF RANKINITE FROM RICE HUSK ASH AND EGGSHELLS

ABSTRACT

Rankinite has been used in production of building materials such as cement or concrete because of its lower calcination temperature and less fuel consumption than OPC. Rankinite is usually synthesized from calcium oxide and silica. Therefore, rankinite is synthesis from rice husk ash and eggshells as source of silica and calcium oxide, respectively in this work. The aim of this study is to determine the effect of composition ratio $CaO:SiO_2$ of 3:2 and 1:1 and sintering temperature of $950°C$, $1050°C$ and $1150°C$ towards the rankinite synthesis from rice husk ash and eggshells. Silica and calcium oxide are first extracted from the rice husk and eggshells. The silica and calcium oxide are then calculated by mole ratio, milled and pressed into pellets. The raw materials were analysed with X-ray diffraction (XRD), X-ray fluorescence (XRF) and particle size analysis (PSA). The mixing sample of rankinite is analysed via XRD, Fourier-transform infrared spectrometry (FTIR), Scanning electron microscope (SEM), PSA, linear shrinkage test, density and porosity test and compression test. After characterization, rankinite was synthesized successfully via both composition ratio $CaO:SiO_2$ (3:2 and 1:1) and all sintering temperature. Density and diametral tensile strength are directly proportional to sintering temperature while hardness shows inversely proportional to the sintering temperature. Composition ratio $CaO:SiO_2$ at 3:2 shows higher density and porosity, higher diametral tensile strength and higher hardness compared to composition ratio 1:1. Overall, rankinite synthesized at composition ratio 3:2 and sintered at 1150 °C shows most relevant properties with OPC hence most suitable to replace as clinker.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

˚	Degree
˚C	Degree Celcius
cm^{-1}	Per centimeter
g	Grams
g/cm^3	Grams per cubic centimeter

LIST OF ABBREVIATIONS

CSC   Calcium Silicate Cement

DTS   Diametral Tensile Strength

ES   Eggshells

FTIR   Fourier-transform Infared Spectroscopy

HAp   Hydroxyapatite

OPC   Ordinary Portland Cement

PPG   Polypropylene Glycol

PSA   Particle Size Analyzer

PVA   Polyvinyl Alcohol

RH   Rice Husk

RHA   Rice Husk Ash

SEM   Scanning Electron Microscope

XRD   X-ray Diffraction

XRF   X-ray Fluorescence

CHAPTER 1

INTRODUCTION

1.1 Background

In recent years, greenhouse gas emissions have been becoming a serious issue causes climate change. One of the greenhouse gases is carbon dioxide (CO_2). The high carbon footprint has been contributed by different sectors of human activities. One of the activities is construction. Production of building materials required in construction sector such as cement uses Ordinary Portland Cement (OPC) as binder or clinker. As shown in Figure 1.1, global cement production has been rising rapidly as well as global fossil energy production. Pacheco-Torgal *et al.* (2011) has predicted that the demand for OPC in cement production will increase 200 % by 2050.
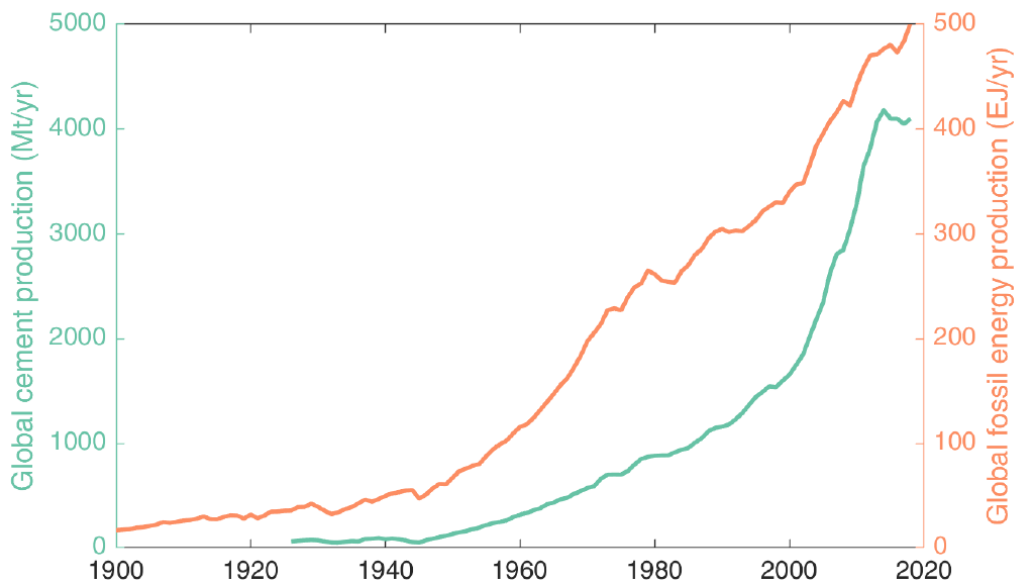
Figure 1.1   Global cement and fossil energy production (Andrew, 2021).

OPC contains large quantity of calcium oxide, silica, alumina and iron oxide as chief chemical constituent. Its manufacturing process includes carbonates decomposition and fuel burning which will release CO_2 gases. Carbonates from the

raw materials are very likely to decompose and emit CO_2 gases as by-products when burned at high temperature around 1500 ˚C (He *et al.*, 2019). Besides, fuel used during the high temperature burning reacts with oxygen in the surrounding to form carbon dioxide.

According to Smigelskyte et al., (2020) current production of concrete or cement using OPC clinker has caused greenhouse effect due to the emission of carbon dioxide (CO_2) gases during the high temperature heating. The occurrence of this situation is due to production of 1 ton of OPC releases 0.54 ton of CO_2. (Antunes *et al.*, 2022) The large emission of CO_2 has created strong impact to environment. This can be seen in Figure 1.2 where the CO_2 emissions increasing continuously annually.
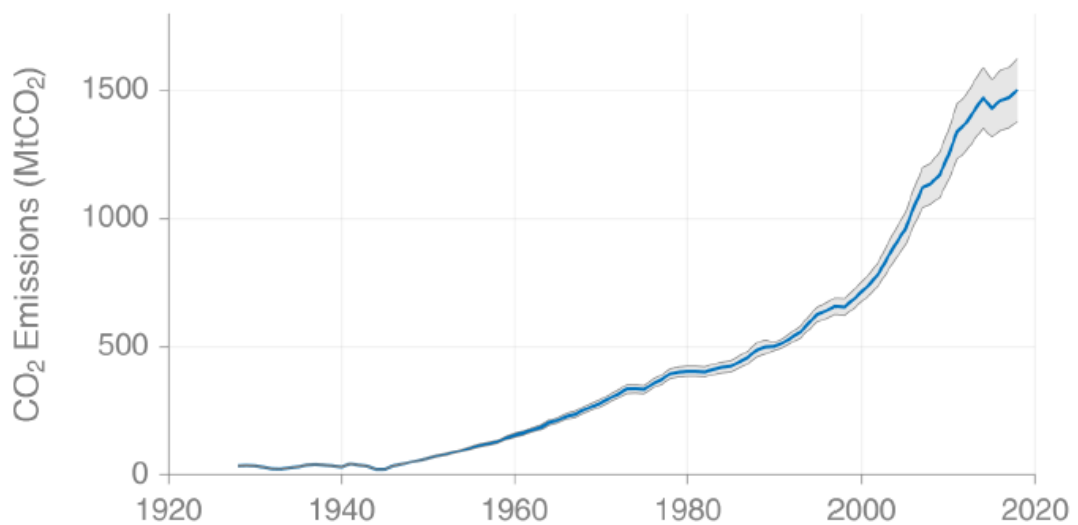
Figure 1.2   Global CO_2 emissions from cement manufacturing with 95% confidence interval (Andrew, 2021).

Shah, Huseien & Xiong (2020) suggest that the amount of CO_2 emissions from OPC manufacturing is approximately 6 % - 7 % over total CO_2 emission from all sectors. This situation has urged the researchers to explore a new method of producing OPC to lower the CO_2 emissions. High demands in development of other types of cementitious system which produce lower CO_2 footprint to replace OPC has been

droved. Low-lime calcium silicate or calcium silicate cement (CSC) is one of the approaches.

CSC contains non-hydraulic lime which absorbs carbon dioxide to harden. During the carbonation process, carbon dioxide released from the carbonate's decomposition process is absorbed by the lime, thus lower the carbon footprint in the cement. Besides, CSC is produced at lower temperatures around 1200 ˚C – 1400 ˚C which is about 200 ˚C – 300 ˚C lower than OPC manufacturing temperature (Ashraf, Olek & Sahu, 2019). This results in lesser amount of CO_2 is released as well as lower energy and fuel is used due to the low manufacturing temperature. Amount of limestone or calcium carbonate required for CSC is also lower than those required in OPC. This results in lower CO_2 emissions from the carbonation process.

There are several CSC systems proposed recently, for example wollastonite ($CaO.SiO_2$) and rankinite ($3CaO.2SiO_2$). In general, raw materials to produce CSC are limestone and silica, mostly taken from calcareous rock mostly consist of calcium or calcium carbonate and argillaceous rock which containing clay like component, respectively. To produce CSC in a more environmentally way, Choudhary *et al.* (2016) has proposed a new concept of raw materials which is produce CSC from waste materials. As raw materials of CSC synthesis, silica and calcium oxide are feasible to obtain from agricultural waste. This For example, silica can be obtained from rice husk or rice straw while calcium oxide can be obtained from seashells and eggshells (Ismail & Mohamad, 2021; Laohavisuti *et al.*, 2021).

1.2   Problem Statement

Calcium silicates have various applications due to its large range of properties. The variation in chemical composition of the raw materials which are silica and

3

calcium oxide can change the properties of calcium silicate-based materials. One of the calcium-silicate based materials is rankinite ($Ca_3Si_2O_7$) which used as building materials. Current cement production is using Ordinary Portland Cement (OPC) which requires high temperature and high energy to produce. Its production also releases similar ratio of carbon dioxide (CO_2) as by-product which is 1:1. Hence, rankinite is proposed to be used in cement production due to its lower temperature and energy required. To synthesis rankinite, rice husk ash (RHA) and eggshells are proposed as silica and calcium oxide source, respectively. These two raw materials are considered as agricultural waste which can cause environmental pollution if do not dispose properly. By utilizing them, 3R principle is implemented where the waste is reduced, reused in rankinite synthesis and recycle them in producing building materials.

1.3   Objectives

1. To determine the effect of sintering temperature on the physical and mechanical properties of rankinite synthesized using rice husk ash (RHA) and eggshells (ES).

2. To determine the effect of composition ratio of calcium oxide (CaO) and silica (SiO_2) on the physical and mechanical properties of rankinite using rice husk ash (RHA) and eggshells (ES).

1.4   Scope of Research

The aim in this research is to fabricate and characterize rankinite synthesized from rice husk ash (RHA) and eggshells (ES). The raw materials used are rice husk (RH), eggshells, calcium oxide (CaO) and silica (SiO_2). RH is calcined at 850 ˚C for 6 hours while ES is calcined at 900 ˚C for 2 hours with heating rate of 10 ˚C/min each. The RHA and ES powder are determined existence of SiO_2 and CaO, respectively

4

through X-ray diffraction (XRD) and X-ray fluorescence (XRF) analysis. Particle size analysis (PSA) is also conducted.

The RHA and ES powders are mixed homogenously at 300 rpm for 2 hours. The parameter that will be varies are the composition ratio of CaO to SiO_2 which are 3:2 and 1:1. The powder mixture is then sintered at different temperatures (950 °C, 1050 °C, 1150 °C) for 2 hours with heating rate 10 °C/min. The sintered powder is then mixed with binder solution which is PVA solution and pressed into pellet size.

The rankinite pellets with different composition ratios and sintering temperatures are characterized by X-ray diffraction (XRD), X-ray fluorescence (XRF), Particle size analysis (PSA), Fourier Infrared Spectrometry (FTIR) and scanning electron microscope (SEM), respectively. Mechanical properties such as diametral tensile strength will be determined by compression test. Physical properties such as density, porosity, particle size and linear shrinkage will be analysed as well. Figure 1.3 shows the flowchart of the overall process for rankinite synthesis and characterization method.

```
┌─────────────────────────────────────┐
│   Extraction of SiO₂ from RHA        │
│                                       │
│                &                      │
│                                       │
│   Preparation of CaO from ES          │
└─────────────────────────────────────┘
                    │
                    ▼
┌─────────────────────────────────────┐
│   Characterization of raw materials   │
│                                       │
│     •  X-ray diffraction (XRD)        │
│     •  X-ray fluorescence (XRF)       │
│     •  Particle size analysis (PSA)   │
└─────────────────────────────────────┘
                    │
                    ▼
┌─────────────────────────────────────┐
│        Synthesis of rankinite         │
│                                       │
│     Composition ratio (3:2 & 1:1)     │
│                                       │
│  Sintering temperature (950°C,        │
│  1050°C & 1150°C)                      │
└─────────────────────────────────────┘
                    │
                    ▼
┌─────────────────────────────────────┐
│        Characterization method        │
│                                       │
│     •  X-ray diffraction (XRD)        │
│     •  Fourier infrared spectrometry  │
│        (FTIR)                         │
│     •  Scanning electron microscope   │
│        (SEM)                          │
│     •  Particle size analysis (PSA)   │
│     •  Linear shrinkage test          │
│     •  Density and porosity test      │
│     •  Compression test               │
└─────────────────────────────────────┘
```

Figure 1.3   Flowchart of overall process for rankinite synthesis and characterization method

CHAPTER 2

LITERATURE REVIEW

2.1   Calcium Silicate (CS)

Calcium silicate (CS) is a natural occurring mineral composed of calcium oxide (CaO) and silicon oxide or silica (SiO_2). It is also known as larnite and formulated as Ca_2SiO_4 or $2CaO.SiO_2$. The phases of CS can be transformed into others by changing the ratio of CaO and SiO_2 (Taylor, 1941). Generally, ratio CaO to SiO_2 or C/S ratio suitable to be use as Portland Cement (PC) are in range of 1.3 to 2.1 (Tajuelo Rodriguez *et al.*, 2017). Within this range, there are different phases of CS can be formed. For example, wollastonite (C/S = 1), rankinite (C/S = 1.5), belite (C/S = 2) and alite (C/S = 3) (Freitas *et al.*, 2015).

Calcium silicate (CS) is an essential component in various field for its excellent properties to wide range applications. It can be used as building materials such as cement, refractories and fire protection, pharmaceutical and cosmetics uses such as binder or stabilizer as well as drug delivery (Durgun *et al.*, 2012). CS is used in manufacturing building materials due to its strengthening method. It can be hardened to a high strength material after carbonation (Goto, Kenzo & Takeshi, 1995). This unique strengthening mechanism resulted in excellent properties of CS including high tensile characteristics and excellent thermal resistance which make it useful for building materials.

Apart from the application above, CS is also getting more well known in bone tissue regeneration applications. Comparing to CS, bulk ceramic is unable to be used in medical implant due to the poor mechanical properties. Based on Venkatraman *et al.*'s research on 2021, calcium and silicon are the most essential elements of bone mineralization, growth and development especially during the initial stages. In CS

7

system, the calcium ions tend to dissolution in the biomimetic solution and at the same time, silica-rich interlayer will be formed simultaneously which makes CS system a good replacement for medical implant (Bao, Zhao & Liu, 2012). In general, there are various types of bioceramics include wide range of calcium-based due to its suitability to use in bio-implant (Kumar *et al.*, 2019). Figure 2.1 shows the types of bioceramics.
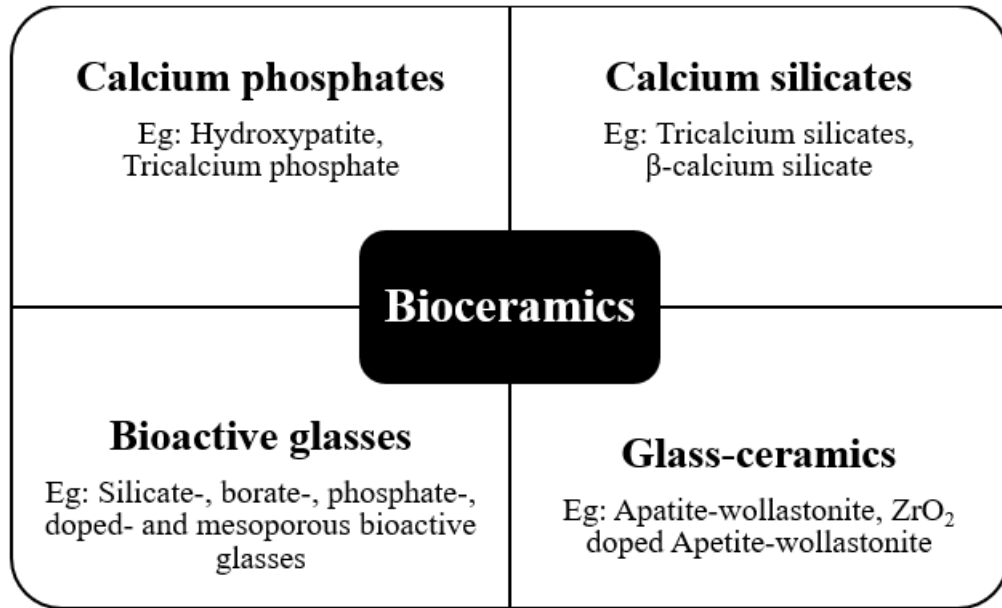
Figure 2.1   Schematic diagram of different types of bioceramics (Kumar *et al.*, 2019)

New perspectives have been proposed by Martinez, Izquierdo-Barba & Vallet-Regi, (2000) that CaO-SiO$_2$ system is opened for study the limits of bioactivity in this system. In 2014, Wang, Lu and Zreiqat has mentioned that in order for a ceramics to be classified as bioceramics in bone tissue generation, some criteria must be meet. The bioceramics must be free from toxicity, carcinogenic, allergy and inflammatory. They are also must be biocompatible and biofunctional. This can be seen from wollastonite (CaSiO$_3$) or which has been studied broadly due to its ability of bone mineralization and ability to repair damaged bone tissue. However, studies show that variation in chemical composition can create huge differences in properties of calcium silicate-

based materials either in structural, chemical, biological or mechanical form. This can be represented by larnite (Ca_2SiO_4) which shows twice the calcium concentration than wollastonite and was reported to have better bioactivity than wollastonite (Gou, Chang & Zhai, 2005). The high contribution of Ca-O which provides stability in the crystal system effectively inhibits the degradation of bioceramics (Choudhary, Koppala & Swamiappan, 2015; Collin *et al.*, 2021). This also agreed by Meiszterics *et al.*, (2010) that the calcium silicates system is suitable for biomedical applications due to its properties such as low porosity and high mechanical strength.

2.2 Rankinite

Rankinite or tricalcium disilicate formulated as $3CaO.2SiO_2$ or $Ca_3Si_2O_7$ is a type of mineral can be obtained from natural melt rocks. It is very rare as natural C_3S_2 has slightly different composition compared to the pure C_3S_2 (Smigelskyte *et al.*, 2020). This causes the purity of C_3S_2 from natural melt rocks is very low which can be considered as only impurities.

2.2.1 Crystal structure of rankinite

In C_3S_2 crystal arrangement, the silicates are arranged in silicon-oxygen tetrahedron as shown in Figure 2.2. The calcium (Ca) atoms and the silicate groups are arranged parallel to the z-direction. Meanwhile, the angle between Ca atoms and oxygen (O) atoms are in the range of 60° to 87°. The silicon and oxygen atoms are arranged in sorosilicate $[Si_2O_7]^{-6}$ groups or known as disilicate where there is a central oxygen atom connecting two SiO_3 units as shown in Figure 2.3. Sorosilicate groups have similar shape as silicates where the angle between silicon and oxygen atoms is ranging from 106° to 115° (Kusachi *et al.*, 1975).
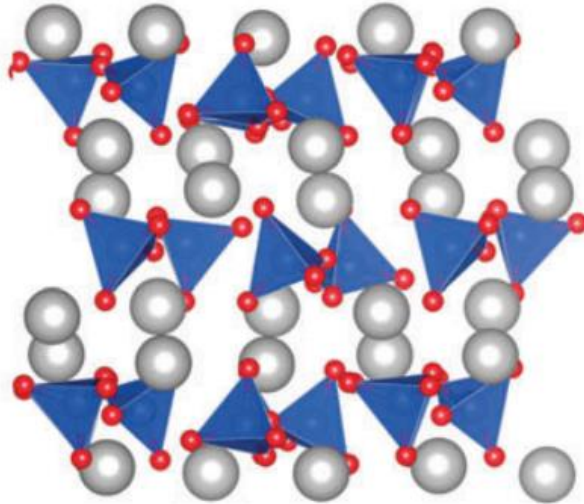
Figure 2.2   Crystal structure of rankinite using Molecular Dynamics (MD) Simulation. Calcium, silicon and oxygen atoms are depicted as grey, blue and red spheres, respectively (Freitas *et al.*, 2015).
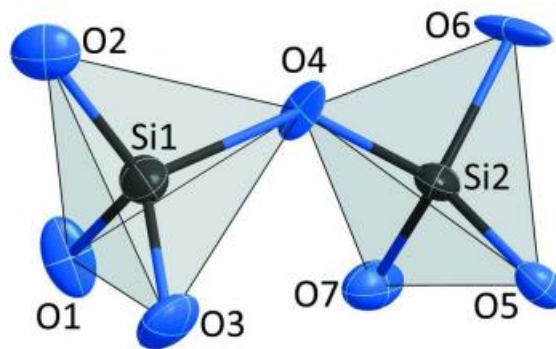
Figure 2.3   Crystal structure of disilicate (Schäfer, Hartenbach & Schleid, 2013).

2.2.2   Application of rankinite

Rankinite has high calcium and silica content which is suitable in production of building materials, for instance concrete or cement. The presence of silica is blocking the porosity and inhibits the reducing gases flow in (Mandal & Sinha, 2015). Like OPC clinker, C_3S_2 can be manufactured from the similar calcareous and siliceous raw materials (Šmigelskytė, 2019). However, its C/S ratio is nearly twice lower than OPC clinker. Since its calcination temperature is lower than OPC around 200 ˚C – 250 ˚C, the fuel and energy consumption is also lower. Besides, Šmigelskytė also proposed at 2019 that tricalcium silicate (C_3S) or alite is absent in C_3S_2 and this makes less

sensitivity to cooling rate. Hence, C_3S_2 does not require rapid cooling where the heat loss from cooler is ignorable and reducing the additional energy. Moreover, C_3S_2 has non-hydraulic nature where it is not prone to hydration. This nature has given benefits to itself as it does not require a set-controlling component for hardening process such as gypsum. Its high durability of the atoms makes it does not require special storage arrangements resulting C_3S_2 has a rapid hardening process in presence of CO_2 (Smigelskyte *et al.*, 2020). Apart from these pros, studies has also shown that carbonation of rankinite enhances corrosion resistance of concrete as well as improves initial strength of concrete and makes waste building materials or used concrete recyclable (Zhang *et al.*, 2018).

2.2.3   Properties of rankinite

Since rankinite is well-known to be used as binder in production of building materials, the properties of rankinite are investigated to determine whether it is competitive to replace OPC. Table 2.1 shows the properties of rankinite and OPC. From Table 2.1, it shows that rankinite has lower density than OPC (Mursky & Thompson, 1958; Panditharadhya *et al.*, 2018). However, rankinite has higher hardness than OPC, at the same time able to withstand higher compressive stress. Besides, rankinite requires shorter initial and final setting time.

Table 2.1   Properties of rankinite and OPC

Properties	Rankinite	OPC	Reference
Density (g/cm^3)	2.96 – 3.00	3.12	Mursky & Thompson, 1958; Panditharadhya *et al.*, 2018
Hardness (Mohs)	5.5	5	Hill & Antrim, 1941; Il'Ina, Gichko & Mukhina, 2016
Compressive strength (MPa)	62.5	55	Panditharadhya *et al.*, 2018; Wang, Ren & Yang, 2018
Initial setting time (min)	36	50	Gandolfi *et al.*, 2009; Panditharadhya *et al.*, 2018
Final setting time (min)	70	390	Gandolfi *et al.*, 2009; Panditharadhya *et al.*, 2018

2.2.4   Synthesis of rankinite

In C_3S_2 synthesis, CaO and SiO_2 are the main starting materials. Hence, binary phase diagram of CaO-SiO_2 as shown in Figure 2.4 is used as reference to determine the mole ratio and temperature where C_3S_2 will form. Based on the Figure 2.4, C_3S_2 can be formed at approximately 50 % to 65 % of CaO and temperature range 800 °C to 1464 °C but there are other calcium silicates formed at the range as well. However, at around 60 % CaO, pure C_3S_2 is formed.
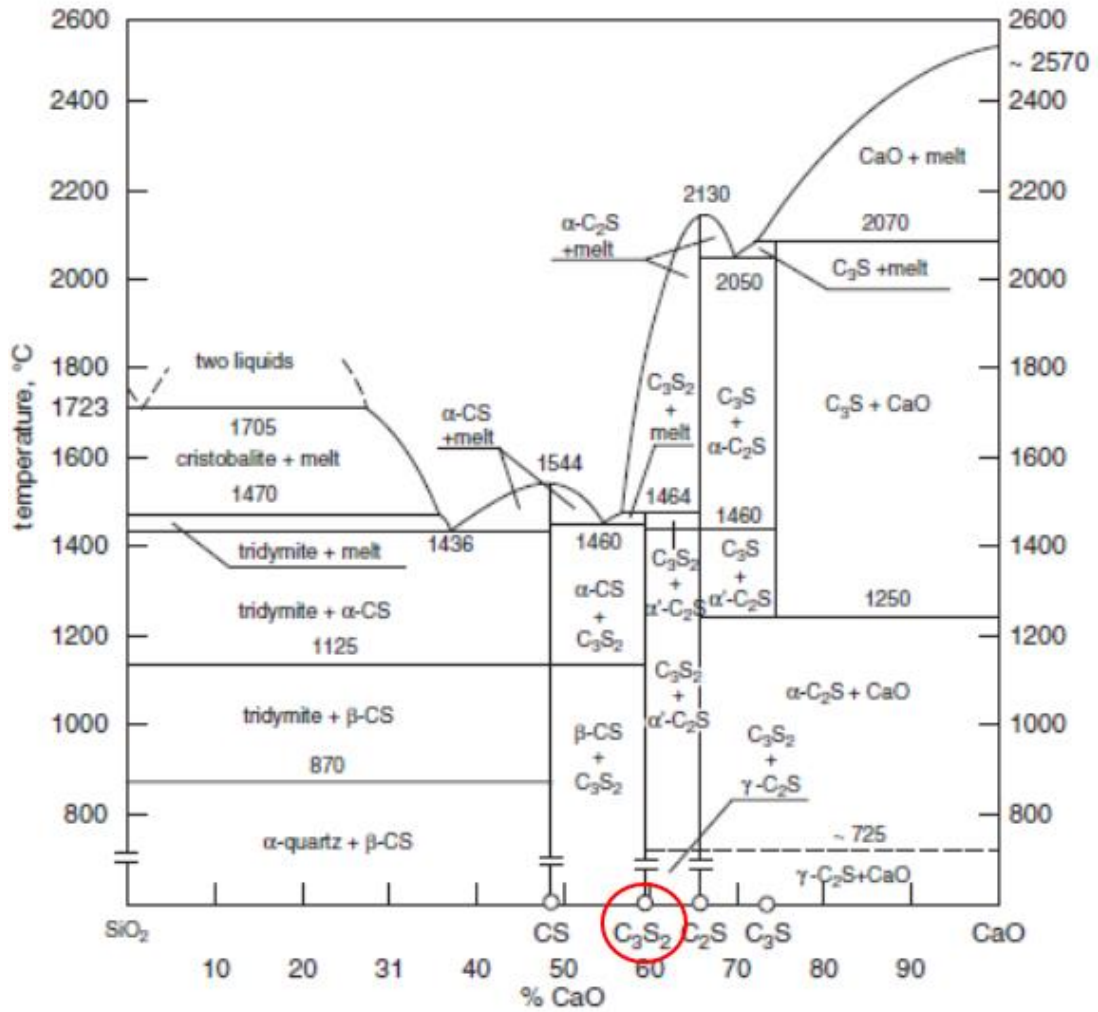
Figure 2.4   Phase diagram of CaO-SiO₂ system (Hermansson, 2020)

2.3   Agricultural waste

Agricultural wastes are known as unwanted waste produced from agricultural activities such as vegetables, fruits, meat, dairy products and crops (Obi, Ugwuishiwu & Nwakaire, 2016; Ramírez-García, Gohil & Singh, 2018). The waste might be beneficial in other way, but the extra cost of collection, processing and transportation are higher than its economic values. Agricultural waste can be in the form of solids, slurry, or liquids.

Recently, issue of disposing the agricultural waste or biowaste is getting more serious. This is due to when the wastes are not well managed, they are causing health and environmental risks. These wastes are usually disposed through combustion or

dumped into landfills which may causes environmental pollution especially greenhouse effect (Van Wyk, 2011). According to Brosseau & Heitz (1994), landfill gases generated consists of five major components which are methane, carbon dioxide, hydrogen, oxygen and nitrogen. There is minor trace compound such as hydrocarbons and sulphur compounds as well. These components contribute to acid deposition along with nitric acid which posing threats to human health (Lacaux *et al.*, 1992).

To reduce the negative impact brought by agricultural waste or biowaste, the wastes are utilized. Table 2.2 shows effort taken to utilize agricultural waste.

Table 2.2   Agricultural waste utilization (Nagendran, 2011)

Waste	Utilization
Rice husk ash and carbon	Additive in cement Water glass manufacture Active carbon
Rice husk	Electricity production
Banana peel and sugarcane fibers	Paper making pulp
Bagasse	Mushroom cultivation
Bagasse or banana fruit reject	Ethanol production Animal feed
Onion skin or groundnut husk	Heavy metal removal
Sunflower stalk or corn stalk	Thermoplastics reinforcement
Animal waste	Compost Fertilizer

2.4   Rice husk ash

Rice as the major staple, its agricultural crop covers more than one-third countries globally especially in Asian nations. In the 2020/2021 crop year, a total of 507.24 million metric tons of rice have been produced worldwide while China has the highest productivity of 148.30 million metric tons as shown in Table 2.3.

Table 2.3   Production of Milled Rice in 2020/2021 Crop Year (Shahbandeh, 2022).

Country	Production (million metric tons)
China	148.30
India	122.27
Indonesia	35.30
Bangladesh	34.6
Vietnam	27.38
Thailand	18.86
Burma	12.6
Philippines	12.42
Pakistan	8.42
Brazil	8

During the rice milling process, the products obtained contain 78 % of rice, broken rice and bran while another 22 % is husk. The husk will then contribute as fuel in rice mills to generate power and be converted into ash during the combustion process which is rice husk ash (Venkatraman *et al.*, 2021). By burning rice husk gradually from room temperature to the range of 700 °C and 1000 °C with a heating rate of 10 °C / minute, RHA with different purity can be obtained (Azmi *et al.*, 2016). In recent, rice husk has been utilized for energy and biofuels production as well as used as solid fuels in power plants due to its high calorific values up to 15.84 MJ/kg (Mirmohamadsadeghi & Karimi, 2020).

Figure 2.5 (a) shows raw rice husk while (b) shows burned rice husk or rice husk ash (RHA). Unburned rice husk is usually brownish yellow in colour while RHA is white in colour if it is fully burned as shown in Figure 2.5 (c). Figure 2.5 (b) shows RHA in black colour is due to unburned carbon which not fully burned and not yet

transform into CO_2 as by-product. Figure 2.6 shows schematic diagram of silica extraction process proposed by Mirmohamadsadeghi & Karimi, (2020).

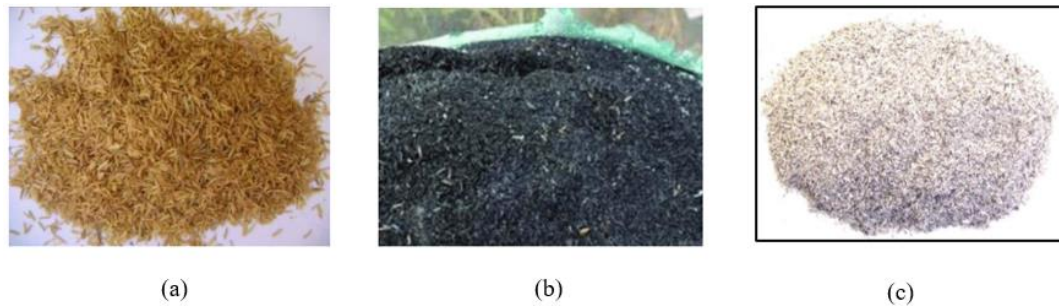Figure 2.5 (a) Rice husk (b) Rice husk ash (RHA) (Tambichik *et al.*, 2018) (c) Completely burned rice husk ash (RHA) (Kizhakkumodom Venkatanarayanan & Rangaraju, 2015)
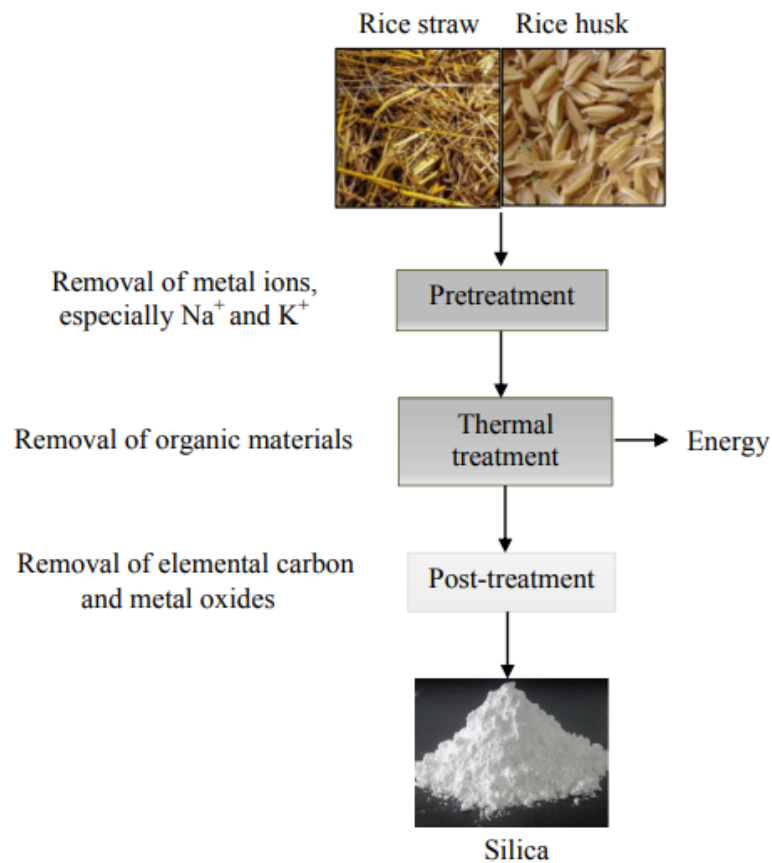

Figure 2.6 Flowchart of silica production process (Mirmohamadsadeghi & Karimi, 2020)

According to Table 2.4, RHA contains large amounts of silica which is one of the main components of calcium silicates. Therefore, many studies were focusing on

synthesis of silica from RHA. The structure of silica is based on SiO_4 with a tetrahedron shape where a central silicon atom is connected to four oxygen atoms by covalent bonds. Each oxygen atom is bounded to two silicon atoms forming a functional group named siloxane group (Si-O-Si). Another functional group which exists on the surface of silica is silanol group (Si-OH) (Mirmohamadsadeghi & Karimi, 2020).

Table 2.4   Chemical composition in rice husk ash (Zhang & Malhotra, 1996; Bui, Hu & Stroeven, 2005)

Constituent	Percentage (%)	
	Vol, 2015	Mohseni *et al.*, 2016
Silicon dioxide (SiO_2)	99.36	91.15
Phosphorus pentoxide (P_2O_5)	0.16	0.00
Calcium oxide (CaO)	0.15	0.41
Sulphur oxide (SO_3)	0.10	0.62
Sodium oxide (Na_2O)	0.06	0.05
Potassium oxide (K_2O)	0.05	6.25
Magnesium oxide (MgO)	0.04	0.45
Aluminium oxide (Al_2O_3)	0.03	0.41
Ferrous oxide (Fe_2O_3)	0.03	0.21
Loss of ignition (LOI)	0.01	0.45

2.4.1   Thermal treatment

To obtain silica, thermal treatment is the most main key stage where no pretreatment or post treatment is needed. The composition, purity and structure of silica is totally depending on the temperature of thermal treatment. By adjusting the parameter, the crystallinity of silica will be altered. At temperature range 600 ˚C to 800 ˚C, silica undergoes phase transformation from amorphous to crystalline. At

17

temperature below 800 ˚C, amorphous silica is produced. Meanwhile, at temperature above 800 ˚C, crystalline silica is formed in the form of cristobalite and finally transform into tridymite at temperature above 1000 ˚C (Mirmohamadsadeghi & Karimi, 2020). The transformation of phase of silica and thermal treatment methods is shown in Figure 2.7.
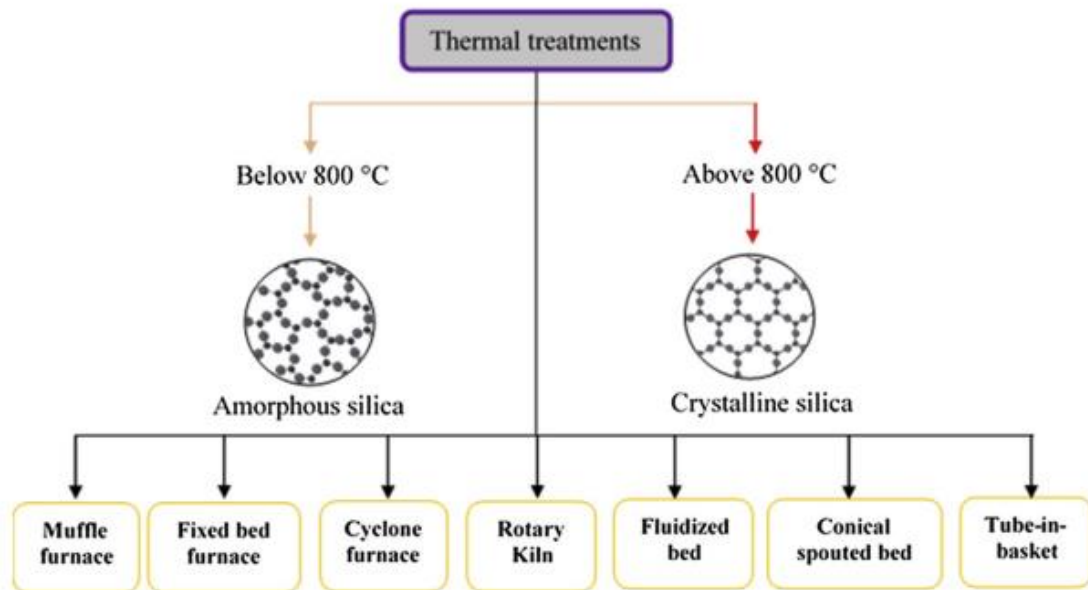
Figure 2.7   Thermal treatment applied for producing silica from rice straw / husk (Mirmohamadsadeghi & Karimi, 2020).

Generally, thermal treatment of rice husk contains low silica content due to presence of metallic impurities which may accumulated during the thermal treatment process. For example, potassium has high tendency to react with silica and form a eutectic system which results in reducing melting point of silica (Mirmohamadsadeghi & Karimi, 2020). This causes silica particles are melting at low temperature and aggregate. Thus, decreasing the total surface area and reactivity of silica (Real *et al.*, 1997).

2.4.2   Pretreatment

To reduce the heavy metal content in rice husk, various types of pretreatment is introduced to ensure the purity of silica. Figure 2.8 shows pretreatment used for producing silica from rice husk or rice straw. Pretreatments can be categorized into physical, chemical, biological and physiochemical (Tu & Hallett, 2019).
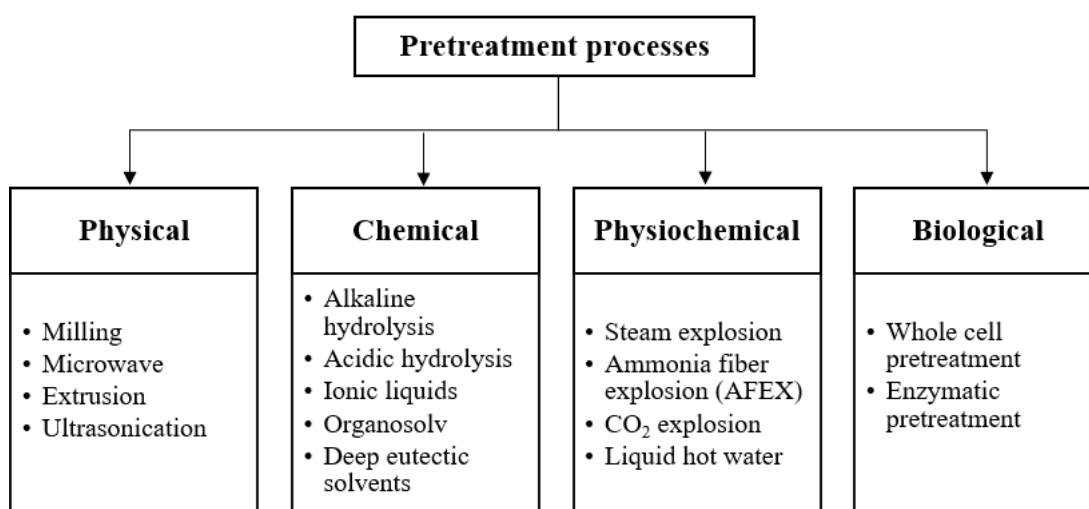
Figure 2.8   Pretreatment processes used for producing silica from rice straw / husk (Baruah *et al.*, 2018).

2.4.2(a)   Physical pretreatment

Physical pretreatments are usually applied prior chemical or biological pretreatment. The rice husk is subjected to heating process at temperature range between 180 ˚C and 240 ˚C with an addition of mechanical shear mixing (Shirkavand *et al.*, 2016). During physical pretreatment, the size and crystallinity of particle is reduced with increasing surface area (Nauman Aftab *et al.*, 2019). By reducing the size and increasing the surface area, hydrolysis of rice husk can be done more efficiently. This is agreed by Zadeh *et al.* (2020) where it was stated that smaller particle size leads to better and uniform heat transfer due to lower heat resistance. In the other hand, larger particle size with smaller surface area is not preferred as its poor heat transfer

affects the yield of rice husk (Mosier *et al.*, 2005; Lu *et al.*, 2010). Physical treatments are generally environmentally friendly and free from toxic material (Shirkavand *et al.*, 2016).

2.4.2(b)   Chemical pretreatment

Chemical pretreatments can be categorized into acid pretreatments, alkali pretreatments, organic solvent and ionic liquid pretreatments (Shirkavand *et al.*, 2016). They are usually conducted after the particle sizes reduced and surface area increased through physical pretreatment. This leads to more surface contact between the rice husk particle and the solution. According to Baruah *et al.* (2018), acid pretreatment can be applied as dilute or concentrated acids. At acid concentration higher than 30%, the steps are conducted at temperature lower than 100 °C while at acid concentration lower than 10%, the steps are required to conducted at temperature around 100°C to 250 °C. Based on research, concentrated sulphuric acid is the most common used acid as it can accelerate the process at least 90 % (Shirkavand *et al.*, 2016). However, concentrated acid is usually toxic and corrosive which required high operational cost to resist the corrosiveness.

Alkali pretreatment can be conducted at lower temperature and pressure as comparing to other pretreatment methods. Although lower temperature is needed, the low solubility in between the rice husk particles can increasing the surface area as well as reduce the crystallinity and degree of polymerizations (Baruah *et al.*, 2018). Alkali pretreatment can be also carried out at high temperature and pressure but with longer duration as an additional step is needed to remove the inhibitors such as lignin (Rezania *et al.*, 2017). In 2016, Shirkavand *et al.*has proposed that sodium hydroxide is the most common used alkaline solvent and it has resulted in a 71 % yield of rice husk.

2.4.2(c)   Biological pretreatment

Biological pretreatment is carried out by using microorganisms and bacteria to alter the chemical composition or structure of rice husk. Its principle is works on enzymatic digestion or hydrolysis to degrade the lignin in rice husk and remove unwanted substances. In 2020, Zadeh *et al.* has proposed that biological pretreatment has high efficiency as it can be performed under ambient conditions without presence of chemicals or usage of energy.

2.4.2(d)   Physiochemical pretreatment

Physiochemical pretreatment is a combination of physical and chemical processes of degradation of lignin and hydrolysis of rice husk cellulose. Some well-known physiochemical pretreatment methods are steam-explosion and liquid hot water. Steam-explosion is carried out at high temperature (190 ˚C – 270 ˚C) and high pressure (0.5 - 4.8 MPa) with rapid depressurization system in a short duration (Brodeur *et al.*, 2011). The explosive decompression of rice husk has disrupted the fibrils resulting increases in water retention, pore size and surface area which can yield maximum rice husk concentration (Bensah & Mensah, 2019). Like steam-explosion, liquid hot water pretreatment employs water at high temperature (160 ˚C – 240 ˚C) and high pressure to ensure the water is maintained at its liquid form. This is to promote degradation and separation of lignin matrix in rice husk (Brodeur *et al.*, 2011). Table 2.5 shows the advantages and disadvantages of different types of pretreatment method.

Table 2.5   Advantages and disadvantages of pretreatment method

Pretreatment Method	Advantages	Disadvantages	References
Physical	- Free from chemical - Increase surface area - Uniform heating	- High energy consumption - Require additional pretreatment steps afterwards	Shirkavand *et al.*, 2016; Zadeh *et al.*, 2020
Chemical	- High production yield - Reduce crystallinity - Reduce degree of polymerization	- High operational cost - Long operational duration - Large amount of water required for washing - Corrosive resistant equipment required	Rezania *et al.*, 2017; Zadeh *et al.*, 2020
Biological	- Can be conducted at ambient temperature - Degradation of lignin - Free from chemical - Low energy consumption	Low hydrolysis rate	Shirkavand *et al.*, 2016; Zadeh *et al.*, 2020
Physiochemical	- Cost effective - Hydrolysis of rice husk cellulose - Degradation of lignin	Formation of inhibitors	Brodeur *et al.*, 2011; Zadeh *et al.*, 2020

2.4.3 Disposal of rice husk

Some typical disposal methods of rice husk are open burning and dumping. During open burning, the rice husk decomposes, and the silica ash is left as primary residue where other volatile components have been evaporated. The silica ash is usually disposed in rivers nearby rice milling factory which leads to elevating of riverbed level and indirectly causing flash flood. There are also some countries which disposed the burned rice husk or RHA on agricultural land where the silica content will destroy the fertility of the soil (Chakraborty *et al.*, 2020). In some areas, large amount of RHA is treated as waste and disposed at landfill site which frequently leads to air and water pollution. Besides, due to the light weight of RHA, the disposal of bulky RHA has contributed to a problem. The airborne particles from RHA are also harmful to human and causing respiratory disease. By reusing the rice husk in rankinite synthesis, it is benefits in protect environment from pollution as well as minimize threat to human health.

2.5 Eggshells

Eggshells are one of the most used food processing and manufacturing field by-products. Eggshells are readily available as waste product and usually can be collected in large quantity. Approximately 250,000 tons of eggshells are produced from food processing industry globally which also can be known as industrial waste (Husain, Permitaria & Haryanti, 2019). For instance, hatcheries, farms, restaurants and domestic source from home.

2.5.1   Egg structure

The outermost layer of an egg is called eggshells which has weight 10 to 11 % of a total weight of an egg (Mittal *et al.*, 2016). Figure 2.9 shows the egg and eggshells membrane. The outer layer of eggshells consisted of cuticle, inner shell membrane and outer shell membrane (Gaurang, 2020). Based on Belyavin & Boorman, cuticle of eggshell can be removed by immersing in weak acid and followed by washing with water. After removing the cuticle, the inner and outer shell membrane consisted inorganic limestone substance are used for extraction (Gaurang, 2020).
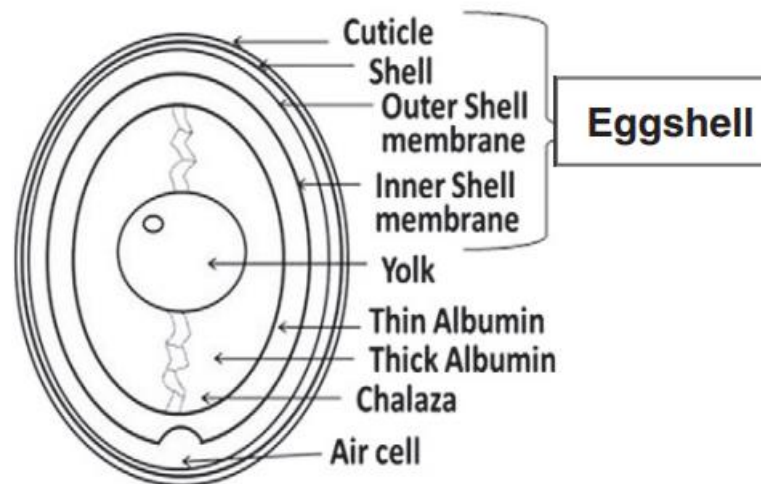

Figure 2.9   Egg and eggshells membrane (Mittal *et al.*, 2016)

2.5.2   Chemical composition of eggshells

Eggshells contain approximately 94 % of calcium carbonate ($CaCO_3$), 1 % magnesium carbonate ($MgCO_3$), 1 % calcium phosphate ($Ca_3(PO_4)_2$) and the remaining 4 % is organic matter (Tsai *et al.*, 2006). Calcium oxide (CaO) in eggshells powder form can be extracted from calcium carbonate when the eggshells undergo calcination at temperature above 700 °C (Witoon, 2011). Besides, by extracting calcium oxide from