Study on Citric Acid Leaching Method to Eliminate Impurities in Rice Husk

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LIST OF ABBREVIATIONS

RH	Rice husk
RHA	Rice husk ash
LRH	Leached rice husk
LRHA	Leached rice husk
RH-Glass	Rice husk-glass
$C_6H_8O_7$	Citric acid
HCL	Hydrochloric acid
HNO_3	Nitric acid
H_2SO_4	Sulfuric acid
NaOH	Sodium hydroxide
$KAlSiO_8$	Feldspar
SiO_2	Silicon dioxide
Fe_2O_3	Iron oxide
K_2O	Potassium oxide
Na_2O	Sodium oxide
SEM	Scanning electron microscopy
XRD	X-ray diffraction
XRF	X-ray fluorescent
ICP-MS	Inductively couple plasma spectroscopy

LIST OF SYMBOLS

2θ	Diffraction angle
^{o}	Degree
μ	Micron

Kajian Tentang Kaedah Asid Sitrik untuk Menghilangkan Bendasing di Dalam Sekam Padi

ABSTRAK

Tujuan tesis ini adalah untuk mengkaji kesan kaedah asid organik untuk menghilangkan bendasing dalam sekam padi (RH) untuk mendapatkan silika berketulenan tinggi (SiO_2) bagi penghasilan kaca sekam padi (RH-kaca). Parameter-parameter yang terlibat dalam proses tersebut adalah kepekatan larutan asid sitrik, masa larut lesap, dan masa kisaran. Penghasilan RH-kaca dari ketulenan SiO_2 yang tinggi telah dihasilkan dengan memperkenalkan rawatan asid larut lesap dengan menggunakan asid sitrik ($C_6H_8O_7$) diikuti dengan pembakaran. Ketulenan silika dalam sekam padi telah dianalisis dengan menggunakan analisis pendarfluor sinar-x (XRF) dan dengan peratusan SiO_2 berketulenan tinggi melebihi >99%. Peratusan SiO_2 meningkat >99% seiring dengan peningkatan kepekatan larutan asid sitrik, masa larut lesap, dan masa kacau. SiO_2 yang berketulenan tinggi dapat diperolehi walaupun RH telah terlarut lesap pada parameter minimal iaitu pada 0.1 M larutan asid sitrik, dengan suhu 40 ºC selama 1 jam. Penghapusan bendasing elemen ferum (Fe) dianalisis dengan menggunakan spektrometri jisim plasma (ICP) yang digabungkan secara induktif plasma. Kandungan unsur Fe yang dinyahcaskan ke dalam larutan asid sitrik semasa proses pengurasan asid didapati meningkat dengan peningkatan kepekatan larutan asid sitrik. Fasa silika di dalam abu sekam padi (RHA) telah terhasil selepas dibakarkan pada suhu 1000 ºC selama 5 jam. Pembelauan sinar-x (XRD) menunjukkan bahawa silika wujud dalam keadaan amorfus dan dikesan pada $2\theta = 22^{\circ}$. Walau bagaimanapun, struktur fasa RH-kaca boleh berubah menjadi hablur kerana silica mempunyai suhu lebur yang tinggi. Warna abu sekam padi berubah sepenuhnya dari hitam menjadi abu putih. Mikrostruktur silika dicerapkan menggunakan Mikroskop Imbasan Elektron (SEM) dan menunjukkan mikrograf fasa yang homogen dan bentuk yang tidak teratur. RH-kaca yang lutsinar dapat dihasilkan dengan membakar SiO_2 yang berketulenan tinggi pada suhu 1560 ºC selama 12 jam.

Study on Citric Acid Leaching Method to Eliminate Impurities in Rice Husk

ABSTRACT

The aim of this thesis is to investigate the effect of citric acid leaching method to eliminate impurities in rice husk (RH) in order to obtain high purity silica (SiO_2) for the production of rice husk glass (RH-glass). The process parameters involved are citric acid solution concentration, leaching time, and stirring time. The production of RH-glass from high purity SiO_2 was prepared by introducing acid leaching treatment by using citric acid ($C_6H_8O_7$) followed by combustion. The purity of silica in rice husk were analyzed by using X-ray Fluorescence (XRF) analysis and proven to be high purity by percentage of >99 wt% SiO_2. With increasing of citric acid solution concentration, leaching time, and stirring time, the percentage of SiO_2 was increased to >99 wt%. High purity of SiO_2 was achieved even when the RH was leached at minimal parameter of 0.1 M citric acid solution, temperature of 40 ºC for 1 h. The elimination of iron (Fe) element impurities was analyzed by using Inductively Coupled Plasma Mass Spectrometry (ICP). It was found that content of Fe elements discharged into the citric acid solution during the acid leaching process gradually increases with increasing molarity of citric acid solution. Phase of silica in rice husk ash (RHA) was obtained after heated at 1000 ºC for 5 hours. X-ray Diffraction (XRD) shows that the silica exist in amorphous phase and was detected at $2\theta=22^{o}$. However, the phase structure of the RH-glass was observed to be crystalline due to the high melting temperature of silica. The color of rice husk ashes completely changed from black to white ashes. The microstructure of silica as observed using Scanning Electron Microscope (SEM) and the micrograph shows the homogenous phases and irregular shape of particles. A clear RH-glass was produced by heating the high purity SiO_2 at 1560 ºC for 12h.

CHAPTER 1

INTRODUCTION

1.1 Rice husks

Rice husks are the hard protective covering which forms on the rice grains during their growth. Rice husks is part of the main agricultural wastes in South-east Asia and have high potential to be used as useful renewable resources in attempted to provide energy and high-purity silica, SiO_2. This is because they contain about 70% organics such as cellulose or hemi-cellulose, and 20% amorphous SiO_2 (Umeda & Kondoh, 2008). Since last four decades lot of study and research has been conducted to utilize the rice husk wastes. However, there is still plenty of abundant ash, rice husk ash (RHA) that remain as an agricultural waste in open burning to dispose the husk but causing air pollution.

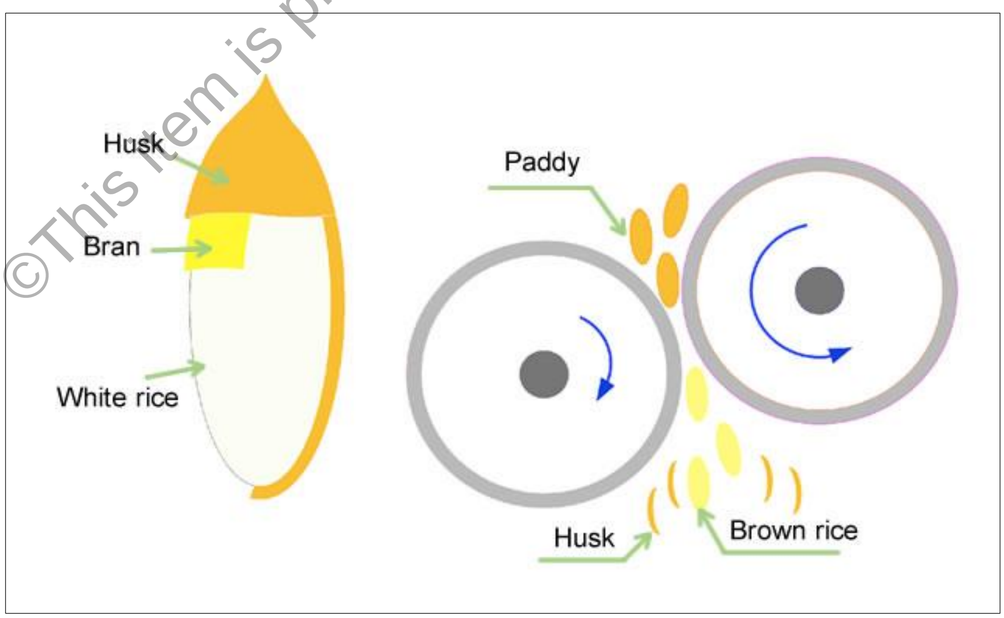

Figure 1.1: Paddy grain (left) and its products after husking (Rice husk, 2017).

Rice husks are one of the largest abundantly available but most less utilized biomass resources, being an ideal fuel for generation of electricity (Onyenanu et al., 2015). It is essentially and readily free as waste material from agriculture field and forest wastes. Utilization of these wastes can resolve the disposal problem and lessen the cost of waste treatment. Rice husk ash is the ash obtained from when rice husk is combusted (Kumar, 2013). Rice husk is remarkably high in ash compared to other biomass fuels close to 20% (Adylov et al., 2003). The ash contains 92 – 95% silica, highly porous and light weight, with a very external surface area (Rozainee et al., 2008). Thus, it becomes economical to extract silica with such a large ash content and silica content in the ash.

1.2 Rice husk ash

The generation of rice husk is mainly available where the abundant of rice crops are found. Rice husk ash is produced from the burning of rice husk. After the burning process of rice husk, cellulose and lignin are removed and remains behind silica ash. Rice husk ash could be purple, grey or white, which depends on the burning conditions and also the impurities present in rice husk. As rice husk burnt in open field or in conditioned where combustion environment is uncontrolled, the ash will mostly remain non-reactive due to the undesirable mineralogical composition (Ugheoke & Mamat, 2012). Rice husk ash that burned partially contains carbon, and thus gives away black colour. The rice husk ash consists of amorphous or crystalline silica, which is controlled by the manner it is burned and cooled. If the ash is produced in open field burning or in uncontrolled combustion surroundings, it will possess a massive distribution of un-reactive silica in the form of cristobalite and tridymite (Siddique & Khan, 2011).

Among all the plant residues, raw rice husk (RRH) and rice husk ash (RHA) contains the highest proportion of silica practically 20% of silica in amorphous form. Under controlled combustion conditions, this by-product can obtain an amorphous silica with high reactivvc ity. Since then, more study and research have been done to explore the benefits of RRH/RHA. The benefits are the usage of RHA as a filler or additive in cement and concrete (Ganesan et al., 2008; Kishore et al., 2011; Kulkarni et al., 2014). Research to corporate the RHA as a filler to produce an insulating materials have been done by few researchers (Goncalves, 2007; Bhatti et al., 2011). RHA also shows the ability to produce glass product (white ware, biomedical glass, optical glass etc.) (Lee et al., 2013).

Yet, the purity of rice husk ash is reduced by the remains of both carbon contents originated in organics and original metallic impurities such as K, Na, Ca, P, Al, Fe etc. Previous research had done many attempts in order to purify SiO_2 content and reduce impurities which cause production of low quality RH-glass.

The chemical composition of RH had been found to differ from sample to sample. Any of the differences in type of paddy, soil chemistry, climatic and geographical conditions, crop year, sample preparation, or method of analysis could be a reason for this variation. In consequences of this compositional variation, the compatibility of rice husk silica for any given application will therefore be mostly dependent on the purity level needed and if it is not compatible from the beginning for a given application, then a purification process will be performed to reduce or eliminate unwanted impurities (Ugheoke & Mamat, 2012).

These impurities somehow may lead to serious issue over their benefits in various applications such as the production of colorless or optical glass, optical fibers and high purity ceramics. In glass production, the usage and place of floated material are determined by the iron content (Fe_2O_3) of quartz sand as investigated by (Farmer et al. 2000). For example, quartz used for glass production in plain glass quality and in glassware glass items should be consisted <0.05% Fe_2O_3 content and <0.02% Fe_2O_3 content, respectively (Ay et al., 2000).

1.3 Acid leaching treatment

A pre-treatment method of acid leaching is commonly used to reduce or remove metallic impurities in attempt to increase the probability of obtaining higher purity silica (Matori et al, 2009). In previous studies, strong acid leaching treatment was used to remove organics and metallic impurities originated in rice husk. Strong acid such as sulphuric acid (H_2SO_4), hydrochloric acid (HCl), and nitric acid (HNO_3) solutions are used commonly in acid leaching treatment. However, these acids are somehow significantly hazardous to the environment as well as humans. In addition, strong acid leaching treatment also has an economical issue due to the use of expensive materials with corrosion resistance to the strong acids, water rinsing of rice husks, and also disposal treatment of used strong acids (Umeda & Kondoh, 2008).

Thus, for an environmental friendly, economical and harmless to humans citric acid ($C_6H_8O_7$) solution is used to replace the strong acids. Silica with very high purity (>99.5%) from rice husk was achieved from pretreatment it with citric acid leaching (Umeda & Kondoh, 2010). The chemical composition of the husk will be affected by acid leaching but will not affect the structure, whether crystalline or amorphous of the silica obtained (Ugheoke & Mamat, 2012).

1.4 Problem statement

The annual global production of rice is more than 650 million tons and each tons of paddy rice yields approximately 220 kg of rice husk (FAO, 2006). Rice husk (RH) is an agricultural waste which had been utilized as useful renewable resources to produce energy with high-purity silica (SiO_2) contents. The large availability of rice husk makes it becomes economical for industrial applications.

However, problem arises from the metallic impurities content originating from the rice husk ash which will influence the quality of the end-product. For example, usage of rice husk in various applications such as the production of colorless or optical glass, optical fibers and high purity ceramics. The usage and place of floated material for glass production are determined by the iron content (Fe_2O_3) in quartz sand (Farmer et al., 2000).

Therefore, citric acid leaching method to eliminate impurities in rice husk is introduced in this study. It is believed can increase and upgrade the production of high purity silica. This can be achieved by controlling the parameters of acid leaching treatment which are concentration of citric acid solution, leaching temperatures, and stirring times. High-purity amorphous silica with 99.5-99.77 mass% was produced from rice husks via citric acid leaching treatment conducted to remove metallic impurities (Umeda & Kondoh, 2010). At the same time, the pollution problems from husks and their ashes burned in the agriculture field are reduced.

1.5 Objectives

The objectives of this study are:

i. To extract silica from rice husk by using citric acid leaching method.
ii. To determine the effect of reaction conditions i.e: acid concentration, leaching temperature, and stirring time in producing high-quality silica from rice husk
iii. To determine the effect of impurities towards the properties of silica in rice husk ash.

1.6 Scope of study

In the preparation of raw material, raw rice husk was grinded to a fine powder form (particle size of ≤ 75 μm). The grinded rice husk was analysed to know its exact composition. The composition of fine raw rice husk powder has been used as reference to be compared afterwards with experimental samples. The washed-leached rice husk powder has been combust in a furnace at 1000 ºC for 5 h at heating rate of 5 ºC/min to prepare husk ash (RHA). For the application of RHA, the glass was produced by melting the RHA in top loading furnace for 12 h at heating rate of 5 ºC/min and then quenched in a bucket of ice water. The process parameters of this study are concentration of citric acid solution, leaching time and leaching temperature that are controlled to optimize the elimination of impurities. Concentrations of citric acid solution chosen were 0.1 M, 0.3 M, 0.5 M, 0.7 M and 1.0 M. The leaching time chosen were 1 h, 3 h, 6 h, 9 h, and 12 h whilst the leaching temperatures were 40 ºC, 50 ºC, 60 ºC, 70 ºC, and 80 ºC. Then, it was characterized via various analyses which include phase analysis, morphology study, and composition.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Rice is an important primary food source for approximately half of the population worldwide (Slayton & Timmer, 2008). About 1% of the earth's surface is covered with paddy field and ranks as the second over wheat in terms of area and production. Over than seventy countries mainly China, India, Indonesia, and also Malaysia are producing rice. Globally, approximately 600 million tons of rice is produced each year, and for per 1000 kg of milled paddy, about 220 kg of rice husk (RH) is produced which is about 22 %. Rice husk (Figure 2.1) is one of the most abundant by-products produced from rice processing. The by-product from rice agricultural includes rice husk, rice straw, and plant material. Rice husk is an agricultural crop that is either burnt or dumped as waste (Saudi, 2015).

Figure 2.1: Image of rice husk (Saudi, 2015)

The amount of RH produce in Malaysia is more than 2 million tons annually. The primary constituents of RH are lignin, cellulose, and ash which are high compared to other biomass fuels. The actual composition is variable, typically: ash (20%); lignin (22%); cellulose (38%); pentosans (18%); and other organics (2%) (Matori et al., 2009). The major mainly consist of silica and some metal impurities (Umeda & Kondoh, 2008). When rice husk is combusted, the ash obtained is called rice husk ash (RHA) (Kumar et al., 2013).

There are a lot of research done to study the usage of RHA as a filler or additive in cement and concrete (Cordeiro et al., 2012; Raman, 2011; Kishore et al., 2011). Research to incorporate the RHA as a filler to produce an insulating materials have been done (Goncalves, 2007; Bhatti, 2011). Some other research is to produce glass product such as white ware, biomedical glass and optical glass (Lee et al., 2013).

Yet, the purity of rice husk ashes is reduced of both carbon content originating from organics and original metallic impurities such as K, Na, Ca, P, Al, and Fe (Umeda & Kondoh, 2008). Attempts had made by researchers in purifiying SiO_2 content and reducing impurities contained in the RHA that in future will affect its industrial application in various ways (Kumar et al., 2012; Chandrasekar et al., 2004). These impurities somehow cause serious problems during their use in various applications such as the production of colorless or optical glass, optical fibers and high purity ceramics. In the production of high purity silica from rice husk, pretreatment methods have been used generally (Ugheoke & Mamat, 2012). A pretreatment method of acid leaching is commonly used where metallic impurities are reduced or removed in order to increase the probability of gaining silica with high purity. Leaching is an extraction of certain materials from a carrier into a liquid or removes the impurities of the materials by dissolving them away from the solids.