OXIDATION OF PHENOL USING SILICA NANOPARTICLE FROM RICE HUSK ASH AS A CATALYST; EFFECT OF TEMPERATURE

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2023

DECLARATION

I declare that this thesis entitled oxidation of phenol using silica nanoparticle from rice husk ash as a catalyst; effect of temperature is the results of my own research except as cited in the references.

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ABSTRACT

Rice husk, often overlooked as agricultural waste, harbours significant potential across diverse industries, serving as a source of silica, biofuel, animal bedding, construction materials, soil amendment, water filtration media, insulation, and biodegradable products. The surplus of rice husk (RH) poses a significant global concern due to its underutilization. Often, RH is disposed of through open burning, resulting in adverse environmental and health effects. Phenol is a common industrial chemical used in the production of plastics, resins, and other synthetic materials. Phenol can be released into the environment through industrial processes, waste disposal, and accidental spills. It can have adverse effects on aquatic life, particularly fish, and can contaminate soil and groundwater. Rice husk was treated by Sodium Hydroxide and Hydrochloric Acid as a leaching agent and undergo solvent extraction method. Several characterizations have been done to analyse the chemical properties of rice husk such as FTIR, XRD, SEM/EDX and GCMS for product of oxidation of phenol. The objectives of this study are to extract the silica from rice husk by using the sol-gel method, to characterize the catalyst produced by FTIR spectroscopy, Powder X-ray Diffraction (XRD) and scanning electron microscopy (SEM), to study the catalytic activity of silica on the oxidation of phenol by using different temperatures. This study proves that 75 °C is the optimum temperature for the catalyst to interact with the oxidation of phenol.

Keyword: Rice husk, Sodium Hydroxide, Hydrochloric acid, Silica, Phenol

ABSTRAK

Sekam padi, sering diabaikan sebagai sisa pertanian, menyimpan potensi penting di pelbagai industri, berperanan sebagai sumber silika, bahan api bio, alas haiwan, bahan pembinaan, pindaan tanah, media penapisan air, penyerapan bunyi, dan produk biodegradasi. Kelebihan sekam padi (RH) menjadi kebimbangan global yang signifikan kerana penggunaannya yang kurang berkesan. Sekam padi dibuang melalui pembakaran terbuka, menyebabkan kesan buruk kepada alam sekitar dan kesihatan. Fenol adalah bahan kimia industri yang biasa digunakan dalam pengeluaran plastik, resin, dan bahan sintetik lain. Fenol boleh dilepaskan ke alam sekitar melalui proses industri, pelupusan sisa, dan tumpahan tidak sengaja. Ia boleh memberi kesan buruk kepada hidupan akuatik, terutamanya ikan, dan boleh mencemari tanah dan air bawah tanah. Sekam padi dirawat dengan Natrium Hidroksida dan Asid Hidroklorik dalam usaha untuk menghasilkan silika. Beberapa pencirian telah dilakukan untuk menganalisis sifat kimia jerami padi seperti FTIR, XRD, SEM/EDX, dan GCMS untuk mengenalpasti produk oksidasi fenol. Objektif kajian ini adalah untuk mengekstrak silica dari sekam padi dengan menggunakan kaedah sol-gel, untuk mencirikan pemangkin yang dihasilkan oleh spektroskopi FTIR, Pembezaan Sinar-X Serbuk (XRD), dan mikroskopi elektron pengimbasan (SEM), untuk mengkaji aktiviti pemangkin silica dalam oksidasi fenol dengan menggunakan suhu yang berbeza. Kajian ini membuktikan bahawa suhu optimum bagi pemangkin silika berinteraksi dengan oksidasi fenol adalah 75 °C.

Kata kunci: Sekam padi, Natrium Hidroksida, Asid hidroklorik, Silika, Fenol

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1 INTRODUCTION

1.1 Background of study

Paddy has become an important staple food crop in Malaysia, producing rice as well as rice husk, which is utilised in a variety of industries. (RH). Figure 1.1 depicts global rice production projections for 2021/2022 per nation. (M. Shahbandeh et al., 2023). After burning rice husks, the residual components are 20% carbon dioxide, 80% air and 20% ash. Rice husk ash may be used to produce silica gels and particles at a reasonable cost. (RHA Silica). Silica accounts for approximately 60% of RHA, making it the most prevalent component. RH is one of the agricultural wastes that has gained popularity due to its several benefits, including low cost, absence of rivalry with food supply, reduced reliance on nonrenewable energy, and the ability to reduce greenhouse gas emissions.

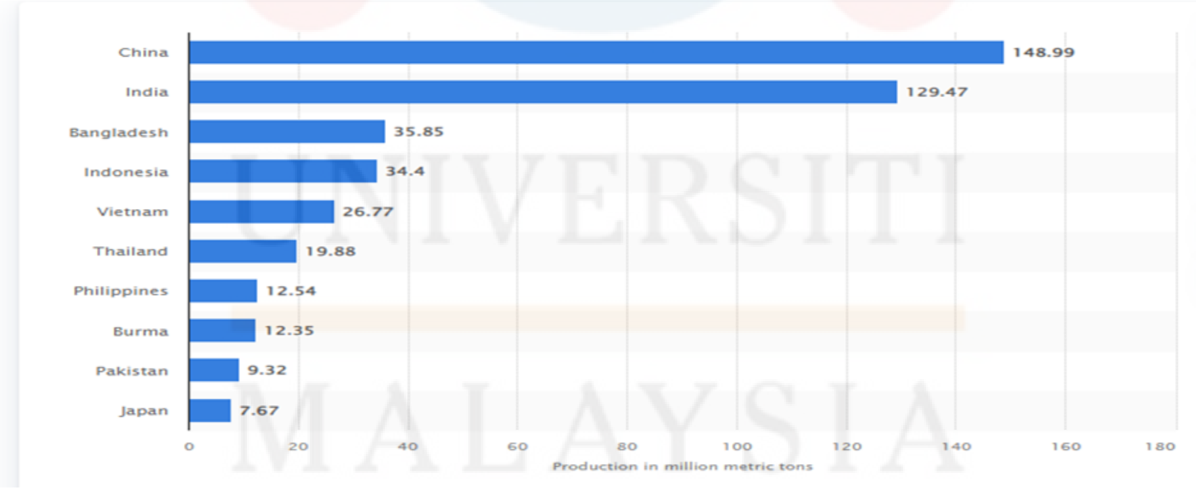


Figure 1.1: Milled rice production in year 2021/2022

Published by M. Shahbandeh, Mar 17, 2023

Figure 1.2: Rice husk.

Published by Adam Duckett, 1st February 2023

The components of RH include cellulose, hemicellulose, lignin, and ash. Furthermore, this biomass waste has distinct features, such as a high silica content, which is an inorganic chemical component of ash. Rice husk ash (RHA) is made by burning rice husks (RH) at high temperatures, where most of the RH is slowly burned away and the predominant residue is silicates. RH has around 20% silica, but RHA is around 90% silica, has a highly porous structure, is lightweight, and has a high specific surface area. Rice husk is the outer covering of the rice grain that is separated during the milling process.

It is a hard, protective layer that surrounds the edible part of the rice grain. Rice husk is typically light brown in color and has a dry and fibrous texture. Rice husk is a valuable by-product of the rice milling industry, and it has several practical uses. It is often used as a fuel in boilers to generate steam for power generation and as a source of heat for drying purposes. It can also be used as a substrate for the cultivation of mushrooms and as a raw material for the production of biofuels, building materials, and animal feed. Rice husk has many advantages, including its low cost, high availability, and renewability.

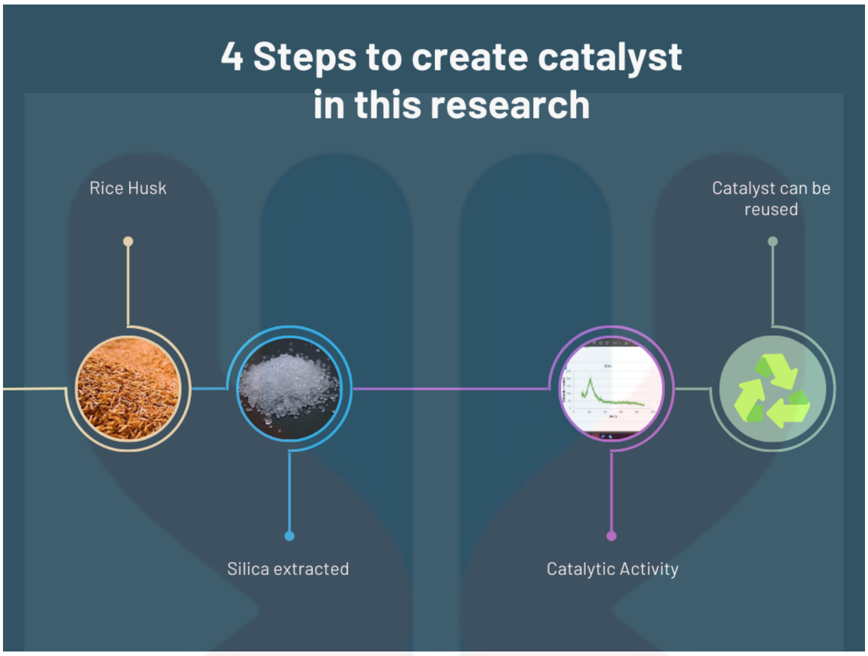


Figure 1.3: The flow of catalyst produced and used in this research.

Figure 1.3 depicts the flow of this work, in which silica extracted from RH was took oxidation of phenol. This catalyst will aid in increasing the oxidation process's reaction rate, reducing reaction time, and increasing yield output. Phenol, having the chemical formula C_6H_5OH, is a dangerous and destructive pollutant that is commonly found in wastewater from industrial, agricultural, and residential activities, hence phenol levels must be lowered before disposal into the environment. The usage of phenol in industry contributes to pollution of the environment. The goal of the catalyst generated is to produce phenol byproducts that are less harmful to the environment and may also be utilised in other applications such as photographic chemicals, polymerisation inhibitors, antioxidants, and flavouring agents.

1.2 Problem statement

Due to the high silica content in creating silica base material and identifying their importance or need, a large number of researchers are employing RH as their study material. As previously said, it has been utilised in a specific location, for example, as fuel for parboiling paddy in rice mills, although in certain areas it is field burned as a local fuel. In such instances, RH combustion is incomplete, and partial combustion adds to air pollution. Excess RH may also be a major issue for the entire globe since it is not adequately utilised. RH is frequently disposed of by open burning, which has a detrimental impact on the environment and health. Due to undesired qualities such as resistance to breakdown, low nutritional value, and high ash content, RH waste utilisation is extremely low. The rice husks will be either burnt or buried, both of which will produce large CO_2 emissions. It's a serious situation, yet companies have little motivation to assist in getting rid of agricultural trash. Because rice husks are burnt, most of them are unworkable and cause severe environmental damage. Due to its low density, there is still considerable scepticism regarding the practicality of transporting and processing agricultural waste. The commercial use of rice husk provides a solution to the disposal problem.

Phenol is considered harmful to the environment due to its toxic and corrosive properties. Phenol is a common industrial chemical used in the production of plastics, resins, and other synthetic materials. It is also used as a disinfectant and in the manufacturing of some pharmaceuticals. Phenol can be released into the environment through industrial processes, waste disposal, and accidental spills. It can have adverse effects on aquatic life, particularly fish, and can contaminate soil and groundwater. In addition, phenol can react with other pollutants to form toxic compounds, such as dioxins and furans, which are persistent and can bioaccumulate in the environment.

In humans, exposure to phenol can cause skin irritation, respiratory problems, and damage to the central nervous system. Long-term exposure to phenol can increase the risk of cancer. Therefore, it is important to handle and dispose of phenol properly to prevent harm to the environment and human health. Proper storage, handling, and disposal procedures must be followed, and spills or releases must be promptly reported and cleaned up. Because phenol is one of the most dangerous compounds, many applications of it may release an elevated amount of phenol into the environment, affecting the ecosystem's quality and causing problems with nutrient cycling and biological ecosystems.

1.3 Objectives of the study

1) To extract the silica from rice husk by using the sol-gel method.

2) To characterize the catalyst produced by FTIR spectroscopy, Powder X-ray Diffraction (XRD) and scanning electron microscopy (SEM).

3) To study the catalytic activity of silica on the oxidation of phenol by using different temperatures.

1.4 Research scope

The research scope of this study is to address the oxidation of phenol with the assistance of a catalyst generated, which is the immobilisation of silica extraction from RH. Because it is made of silica extract from RH, the catalyst is ecologically benign. This research will begin by extracting silica from RH and immobilising it with silica to produce a catalyst. The catalyst will next be characterised and tested on phenol oxidation with a temperature parameter. The outcome of phenol oxidation will define the catalytic activity and condition of the catalyst required to realise their maximum potential when interacting in a process.

1.5 Significance of study

The silica collected from the RH is used in this study to build an organic catalyst in performance to convert phenol to their product via an oxidation process, preventing the phenol from damaging the quality of water or the environment that affects humans. The manufactured catalyst is ecologically benign and aids in increasing the pace of reaction and product yield. With the suggested strategy, the RH may be completely exploited without negatively impacting the environment. This research is critical for the environment and humans to maintain a healthy and stable ecosystem.

There are many methods that have been tried before, burning rice husk waste is still practised today to reduce rubbish accumulation. Uncontrolled combustion processes, on the other hand, have the potential to accelerate global warming and climatic changes by spewing greenhouse gases into the environment. Burning rice husks emits carbon dioxide (CO2), which can be harmful to the environment and people's health. Traditional techniques are now obsolete in light of these difficulties. Farmers that follow the traditional way may be able to recycle their trash into something beneficial. One possibility for the material is rice husk. Rice husk, whether raw or burnt, has a variety of useful purposes.

In this research, the effect of temperature will be the determined in order to get the most suitable temperature for the oxidation of phenol. The temperature plays a crucial role in catalytic oxidation reactions using silica nanoparticles from rice husk ash as a catalyst.

Reaction Rate. Generally, an increase in temperature enhances the reaction rate in catalytic oxidation reactions. Higher temperatures provide more thermal energy, leading to increased molecular collision frequency and higher activation energy for the reaction. This results in a faster conversion of phenol to the desired oxidation products.

Catalyst Activity. The catalytic activity of silica nanoparticles derived from rice husk ash can be temperature dependent. The surface chemistry and catalytic sites on the silica nanoparticles may exhibit different reactivity at various temperatures. Optimal temperatures can maximize the catalyst's activity and efficiency for the phenol oxidation reaction.

Stability. The stability of the catalyst can be influenced by temperature. Higher temperatures may promote catalyst deactivation or degradation, leading to a decrease in catalytic activity over time. It is important to consider the temperature range that maintains the stability of the catalyst during the oxidation reaction.

Overall, the oxidation of phenol utilising rice husk ash-derived silica nanoparticles as a catalyst depends critically on temperature, which influences the reaction rate, catalytic activity, stability. To obtain the desired reaction results, the temperature must be carefully optimised while considering the unique properties of the catalyst and reaction system.

1.6 Expected outcomes

The expected outcome of the oxidation of phenol using silica nanoparticles from rice husk ash as a catalyst is the conversion of phenol into more environmentally friendly compounds. Phenol is a toxic and persistent organic pollutant that can have harmful effects on human health and the environment. By using silica nanoparticles as a catalyst with hydrogen peroxide, the oxidation of phenol can result in the formation of less harmful products such as water, carbon dioxide, and other organic compounds. This method can be an effective and efficient way to treat phenol-containing wastewater, reducing the environmental impact of industrial processes and improving the overall health and safety of communities. Additionally, the use of rice husk ash as a source of silica nanoparticles provides a sustainable and cost-effective solution for catalytic applications.

2 LITERATURE REVIEW

2.1 Rice Husk

Rice husk (RH) refers to the protective outer covering of the rice grain, derived from the grass species Oryza sativa. It serves the purpose of safeguarding the seed throughout its growth cycle. RH is an agricultural byproduct found abundantly in rice-producing countries, resulting from rice cultivation and production. The highest rice production globally is concentrated in Asian countries such as China, India, Bangladesh, Indonesia, Thailand, Myanmar, and Vietnam. With rice being a staple food for a significant portion of the world's population, the annual rice production surpasses 700 million tonnes (Bhupinder, 2018), and RH constitutes more than 10% of the grain's weight.

Malaysia, among other countries, is actively involved in rice production, considering its importance as a staple food source. The production of paddy and rice in Malaysia has been steadily increasing over the years. According to data from the Department of Agriculture Malaysia, rice production experienced a slight increase from 2018 to 2020, contributing 2.5% to the country's agricultural sector. Consequently, the production of RH has also seen a proportional rise as rice production expands. RH finds various applications such as fertilizer, improving soil quality as a planting medium, insulation material, and fuel. It is commonly burned to obtain its ash, which has further used.

To obtain silica, the RH undergoes a burning process to produce rice husk ash (RHA). RHA is produced by subjecting the RH to moderate temperatures, resulting in white RHA that typically contains about 80-98% silica content. RHA is a valuable raw material rich in silica, particularly high-grade amorphous silica, which meets the demands of various industries utilizing silica as a raw material. The silica extracted from RH is typically in an amorphous form with minimal metallic impurities, which can vary depending on the treatment process. Common impurities found in RHA include calcium oxide, magnesium oxide, manganese oxide, iron II oxide, aluminum oxide, among others, with percentages below 3%, while silica content exceeds 90%.

2.2 Silica

Silica can be sourced naturally from various origins, including sand, plants, sponges, and animals. Supersaturated solutions of silica can be produced in certain hot spring areas. Plants, such as grasses, grains, and rice, have the ability to absorb silica, depositing it as characteristic microscopic amorphous opaline particles within their tissues. These particles can later be found in the soil and the intestinal tracts of grazing animals. While silica can be collected in small quantities from seashore sand or quartz, the dissolution rate is slow, occurring only in small parts per million. Biochemical processes carried out by diatoms, sponges, and plants continuously remove silica from seawater, with the deposited silica within these organisms being eliminated. Amorphous silica may be more soluble in deep seawater due to the higher pressures present.

2.3 Phenol

Phenol (C6H5OH) possesses a distinctive aromatic ring structure with a hydroxyl (-OH) group attached. At room temperature, it appears as a colorless crystalline compound and exhibits slight solubility in organic solvents, displaying hygroscopic properties when in contact with water. Phenol finds extensive application in chemical manufacturing processes involving xylenols, oils, plastics, plasticizers, drugs, aspirin, detergents, oil refining, antiseptics, pharmaceuticals, explosive dyes, dye production, chemical analysis reagents, as well as leather and wood preservatives. Additionally, phenol plays a role in the production of herbicides, insecticides, algaecides, bactericides, molluscicides, and fungicides (Ansah, 2012; Nguyen et al., 2003) (reference: journal book "Liquid Phase Oxidation of Phenol in the Industry").

The diverse range of applications involving phenol may result in the release of elevated phenol levels into the environment, posing a significant risk to ecosystem quality. This can disrupt nutrient cycling and negatively impact biological ecosystems, as phenol is recognized as one of the most hazardous chemicals.

3 MATERIALS AND METHODS

3.1 Materials and chemicals

In this study, the materials used are rice husk ash, hot plate, glass stirrer, 200ml beaker, pH meter, funnel, ash-less filter paper, digital analytical balance, aluminium foil, and dropper, Scanning Electron Microscopy (SEM), X-ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR) and Gas chromatography/mass spectrometry (GC/MS) while the chemicals used are Sodium Hydroxide (NaOH), Hydrochloric acid (HCl), Phenol and Hydrogen Peroxide (H_2O_2).

3.2 Methods

3.2.1 Removing contaminants of RH.

First of all, the rice husk was soaked for a while in a container with tap water. The needed sample of rice husk stayed at the bottom of the container. Then, it was washed repeatedly with tap water to remove the dirt like soil and dust, and the final rice husk was rinsed with distilled water. The sample then dried at room temperature.

3.2.2 Treatment of RH

180 g of sample (RH) was weighed, divided into 3 beakers, and stirred with 1.0 M of hydrochloric acid (HCl) for about 24 hours. The rice husk was stirred in HCl, then rinsed with distilled water until the pH of the rinsed was constant (~5.00). The sample dried in the oven for 24 hours at 100±1 ºC and burned in a muffle furnace at 800 ºC for 6 hours with a heating rate of 10 ºC/min to obtain white rice husk ash (RHA).

3.2.3 Preparation of sodium silicate solution

According to 10.0 g of RHA mixed with 1M of NaOH in a plastic bottle, the preparation of sodium silicate solution was carried out, and the mixture stirred continuously for 1 hour. Then it was cooled to room temperature. The mixture was filtered using filter paper no.1. a clear liquid solution, sodium silicate solution, was obtained. Drop 1M of hydrochloric acid into the solution until the pH drops less than 10. When the pH drops less than 10, the solution turns into white gel. The sample dried for 24 hours to obtain white powder.

3.5.1 Reaction methods of RHA in the oxidation of phenol

A 250mL double-necked round bottom flask fitted with a liebig condenser. In a typical run, phenol 20 mmol was dissolved in 20 ml of acetone. The catalyst was activated at 100 ºC for 24 hours in order to remove any adsorb water molecules and cool in a desiccator to minimise moisture content. The mixture was transferred into a round bottom flask containing 0.1g of activated catalyst which was immersed in a temperature-controlled oil bath at 75 ºC. Once the reaction temperature stabilised, hydrogen peroxide (H2O2), 20mmol, was added dropwise to the vigorously stir (600rpm) reaction mixture. The reaction was carried out for 3 hours. 0.5 mL of aliquot was withdrawn and filter at each hour by using a syringe. The catalytic reaction then was conduct with a parameter by using different temperature. The identities of the respective products were confirmed by Gas Chromatography Mass Spectrometry (GC-MS).

The products were further confirmed by comparing the GC of the respective pure hydroquinone. Phenol conversion and selectivity of the products was calculated respectively by using the equation below.

$$\text{Selectivity (\%)} = \frac{\mathit{Area\ of\ peak\ GCMS}}{\mathit{Total\ Area}} \times 100$$

$$\text{Conversion (\%)} = \frac{\mathit{Starting\ compound} - \mathit{Initial\ starting\ compound}}{\mathit{Starting\ compound}} \times 100$$

4 RESULTS AND DISCUSSION

4.1 Characteristic of catalyst

The results are divided into 5 sections which is X-ray diffraction (XRD), Fourier transformed infrared spectroscopy analysis (FTIR), Thermogravimetric Analysis (TGA), Scanning Electron Microscopy (SEM) with Energy Dispersive X-Ray Analysis (EDX), Gas chromatography–mass spectrometry (GC–MS).

4.1.1 XRD result

The X-ray diffraction (XRD) instrument displayed the pattern for silica obtained from rice husk. The types and relative amounts of crystalline phases contained in the silica sample can be ascertained by researchers by comparing the measured diffraction peaks with reference patterns for known crystal structures. This data is necessary to customise the material's characteristics for particular uses, such strengthening composites' mechanical strength, increasing soil fertility for farming, or creating cutting-edge materials for nanotechnology, (Shaohua Li, Yuxuan Chen, H.J.H. Brouwers, Qingliang Yu, 2023).

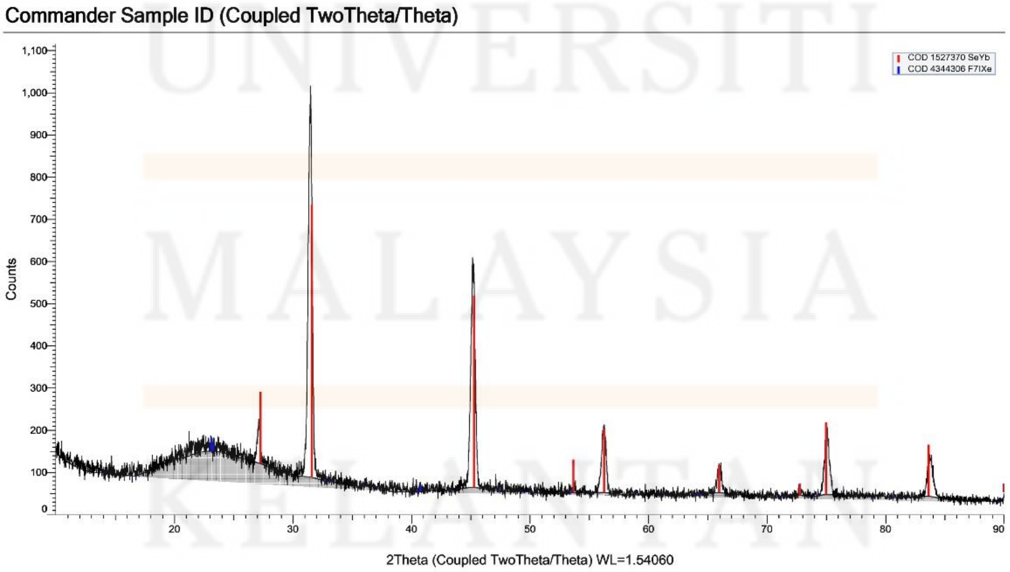


Figure 4.1: The X-ray diffraction pattern for RHA.

Table 4.1: The percentage of amorphous and crystalline of silica RHA

SAMPLE	AMORPHOUS (%)	CRYSTALLINE (%)
RHA	43.4	56.6

The silica powder obtained from the resultant ash was treated with a sodium hydroxide (NaOH) solution, followed by titration with hydrochloric acid (HCl) solution. It was established using XRD analysis, as showed in the figure, that the silica powder that had been removed was amorphous. The amorphous form of silica is preferable for the production of silicon-based compounds since it is the form in which silica becomes active, (Antonio Comite, 2017), Active form of silica. The term active in this context implies that the amorphous form of silica is more chemically reactive or readily participates in chemical reactions compared to its crystalline counterparts, (Jian-Qiang Zhong, Hans-Joachim Freund, 2022). This reactivity is often attributed to the disordered and reactive surface structure of amorphous silica.

Figure 4.1 illustrates X-ray diffraction patterns obtained from hydrochloric acid treatment, confirming the authenticity of SiO_2 samples. The peak displays a large, flat top with no discernible structure. In the XRD pattern, the amorphous peak is observed at 2θ-31°. Table 1.0 indicates that the amorphous silica content was approximately 43.4%, while the crystalline silica content was around 56.6%. Amorphous silica, comprising SiO_2 tetrahedra sharing corners, exhibits polymorphs such as cristobalite and tridymite, wherein SiO4 tetrahedra are arranged in two-layer (tridymite) or three-layer (cristobalite) structures (Ma. del Carmen Gutiérrez-Castorena, 2018). The relatively open structure of cristobalite and tridymite compared to quartz allows for some incorporation of other elements into the crystal structure. Due to the absence of a coherent structure, SiO_2 tetrahedra form a continuous but random network in amorphous silica. Given its amorphous nature, characterized by random molecular clusters, the XRD pattern of hydrochloric acid-treated silica RHA lacks a distinct crystalline structure. Typically, in crystalline materials, peaks are sharp, whereas in amorphous materials, peaks appear broader and lack identifiable features, the extent of which depends on the proportion of amorphous materials (Masaeli, Mohamad, 2023).

As a result, amorphous silica required to be extracted from rice husk ash during the silica extraction process. This is due to the fact that amorphous silica is more dynamic than crystalline silica (P.U. Nzereogu a, A.D. Omah, 2023). Amorphous silica outperforms crystalline silica in non-distractive testing and has greater mechanical characteristics. To put it another way, crystalline silica outperformed amorphous silica.

4.1.2 Fourier transformed infrared spectroscopy analysis (FTIR)

Figure 4.2 shows that the isolated and surface functional O-H groups of (Si-OH) in the silica and adsorbed water molecules on the silica surface are responsible for the observed bandwidth between 3750.27cm^{-1} (RHA).

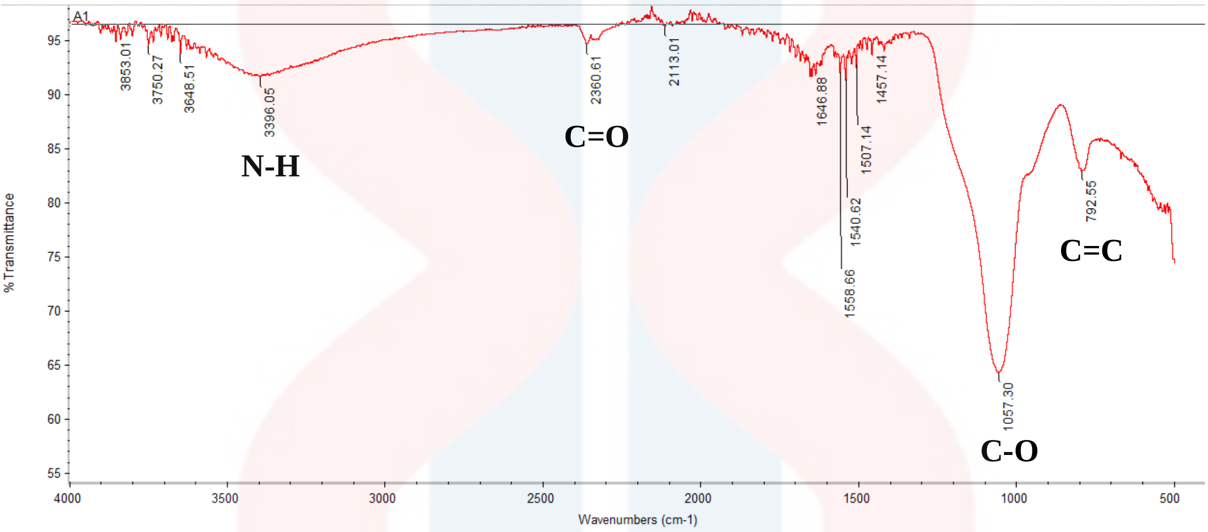


Figure 4.2: The FT-IR spectra of RHA

Absorption band centered at 3396.05cm^{-1} as N-H group demonstrates the presence of adsorbed water molecules between 3500 and 3000cm'. With a C=O wavenumber of 2360.61cm^{-1}, RHA is a rare-earth halide. Performance peaks occurred at 2113.01cm^{-1}', which is between 2500 and 2000cm^{-1}. Peaks were played at 1540.62cm^{-1} before 1500cm^{-1}. The bands at 1057.30 cm^-1 in Figure 4.2 spectra are attributed to asymmetric stretching vibration, symmetric stretching vibration, and bending vibration of the Si-O-Si bond. Additionally, the band at 792.55 cm^-1 corresponds to the formation of C=C in the spectra.

On another research, high-purity nano silica powder from rice husk using a simple chemical method**.** In addition, the major chemical groups present in the nano silica powder at 2 and 2.5 N NaOH purification treatments have been identified from the FTIR spectra. Figure 4.3 shows the FTIR spectrum of nano silica powder at 2 N NaOH purification treatment.

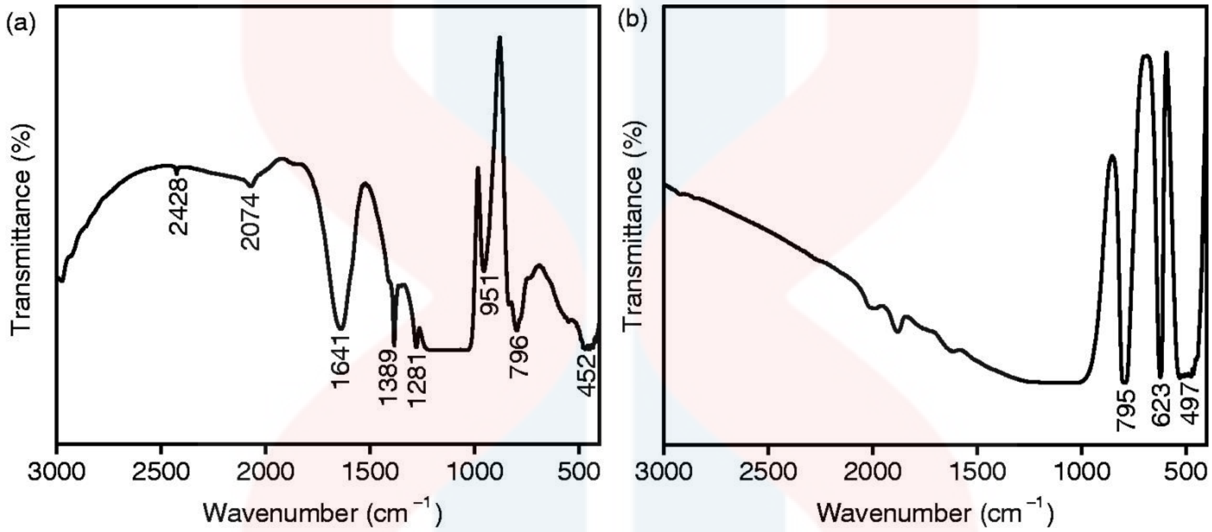


Figure 4.3: FTIR spectra of silica powder (a) 2 N and (b) 2.5 N NaOH purification treatment.

The broad absorption peaks between 452 and 951 cm^{-1} are because of the silica structures and the other peaks observed in the range of 1281–2428 cm^{-1} are because of impurities such as carbonate and sodium groups. On the other hand, at 2.5 N NaOH treatment, the sodium and carbonate groups were absent in the FTIR spectrum of pure nano silica powder, as is evident from Figure 4.3 (b). The strong absorption peaks absorbed at 497, 623 and 795 cm^{-1}, respectively, indicate Si–O–Si bending, Si–H and symmetric Si–O–Si stretching modes of vibrations. Thus, it is confirmed that one can produce a highly pure nano silica powder from RHA using 2.5 N NaOH purification treatment. The review confirms that rice husk is an excellent source for the production of high-grade amorphous bulk silica powder. In recent years attempts have been made to prepare nano silica powder from rice husk, (Tzong-Horng Liou, Chun-Chen Yang, 2011)

4.1.3 Thermogravimetric Analysis (TGA)

TGA was performed on RHCL Form (sample weight 0.0026 g) using a Mettler Toledo 851° TGA/SDTA at a heating rate of 10°C/min from 40 to 600°C in pin-holed aluminum crucibles.

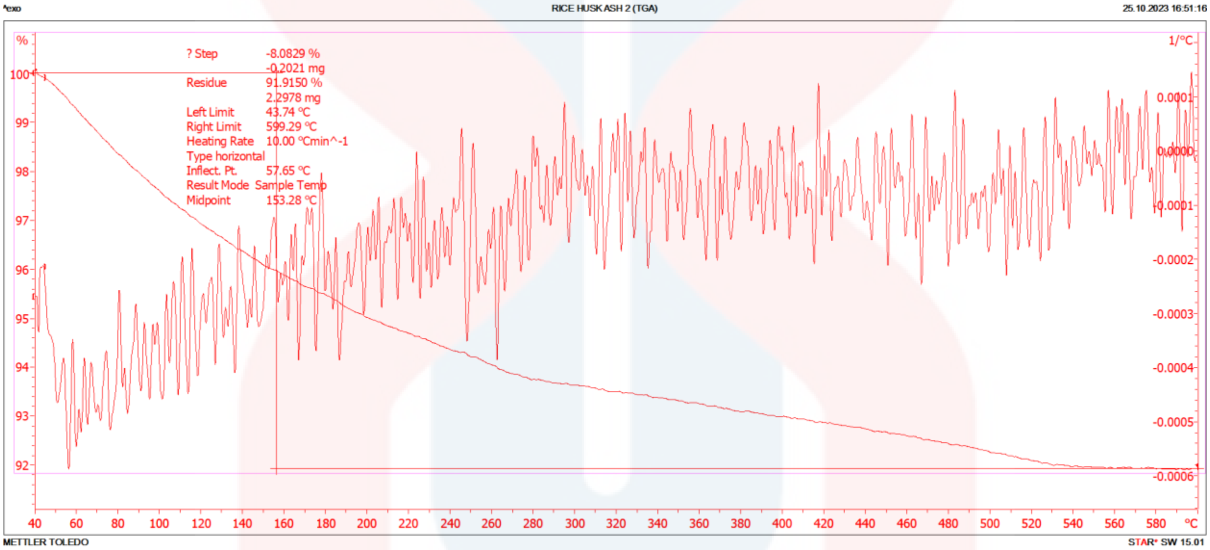


Figure 4.3: TGA thermogram of RHA.

The TGA thermogram of RHCI revealed weight reductions. At 43.74 °C, RHA begins to melt, resulting in an 8.0829% mass loss. Before the temperature began to melt, there was no sign of dehydration. Figure 4.3 shows a decreasing curve. Such a curve can be generated when there is an increase in weight for the sample due to surface oxidation reactions occurring in a reactive atmosphere.

For another research, Development of photoluminescent glass derived from rice husk. Simultaneous thermogravimetric analysis (TGA/DSC) was carried out to determine the combustion temperatures for RH in air as shown in Figure 4.4. Three stages of weight loss were observed in the TG curve of raw RH. The initial weight loss of 8.54% at temperatures below 100 °C was ascribed to the evaporation of adsorbed water, which was trapped physically on as received RH, (Siqueira EJ, Yoshida IVP, Pardini LC, Schiavon MA, 2009).

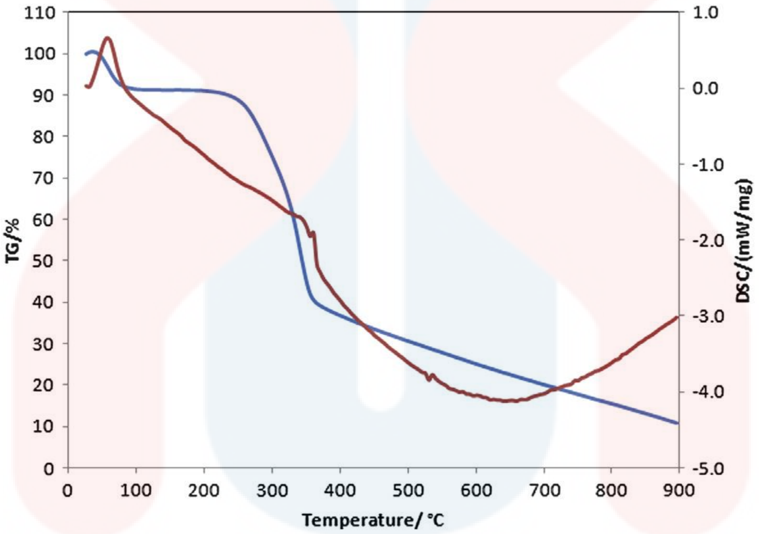


Figure 4.4: Simultaneous thermogravimetric analysis (TGA/DSC) for rice husk powder.

This phenomenon was also observed in the DSC graph as an endothermic peak at 55 °C. A sharp drop in weight (50.32%) was observed in the temperature range from 210 °C to 360 °C. This phenomenon was caused by thermal decomposition of hemicellulose and cellulose of the RH, (Zhao Q, Zhang B, Quan H, Yam RCM, Yuen RKK, Li RKY, 2009). Beyond 360 °C, the weight of RH decreased gradually (29.74%) until 900 °C. This was due to the degradation of lignin, which had lower decomposition rates throughout a wider temperature range as compared to cellulose and hemicellulose.

Two exothermic peaks were observed at 355 °C and 530 °C in the DSC graph. These results showed that rice husk achieved its pyrolysis around 355 °C, and more volatile components were burnt while the carbonized fraction was burnt at a higher temperature around 530 °C. For this reason, the rice husk can only be combusted under the condition of temperatures above 600 °C, (Brebbia CA, Marinov AM, Safia CA, 2013).

4.1.4 SEM/EDX analysis

The morphology of the rice husk ash (RHA) has been examined using scanning electron microscopy (SEM). Figure 4.5 presents SEM micrographs of the RHA at various magnifications.

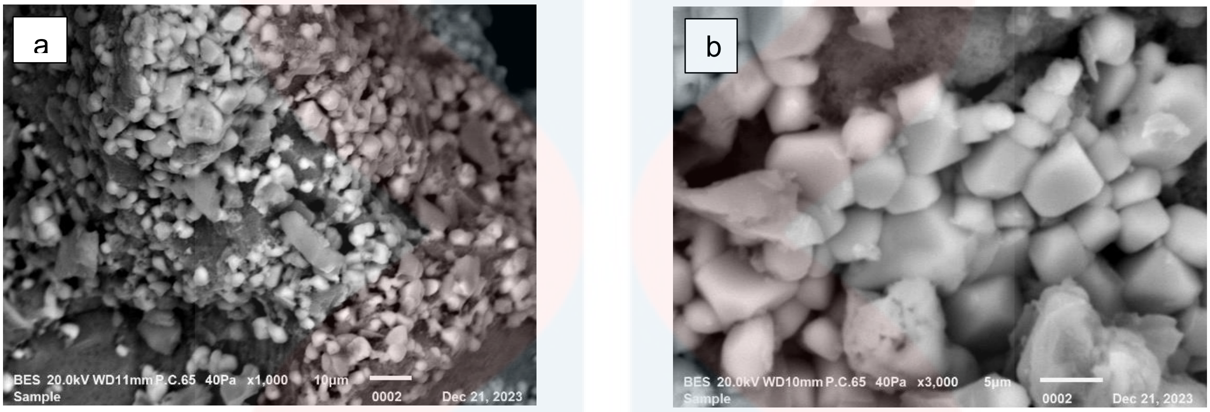


Figure 4.5: SEM image of RHA silica with magnification (A) 1000k (10µm) and (B) 3000k (5µm)

Under low magnification, the topology of RHA is composed of agglomerate and spherical surface particles. The surface reveals that it is made up of small particle sizes randomly organised with irregular morphologies. Uneven rock-like particles are randomly distributed on the surface at a magnification of 3000k. Presenting extensive porosity and microcracking. Extensive porosity and microcracking may result in composites more susceptible to the main deterioration mechanisms, (de Souza Rodrigues, C., Ghavami, K. & Stroeven, 2010).

On the other research, high-purity amorphous silica from rice husk: Preparation and characterization, by Nguyen Nguyen Ngoc, Le Xuan Thanh, La The Vinh, Bui Thi Van Anh, (2018). Figures 4.6a and 4.6b show the surface morphology (SEM images) of silica samples produced through alkaline-extraction and SiO_2-precipitation routes, respectively.

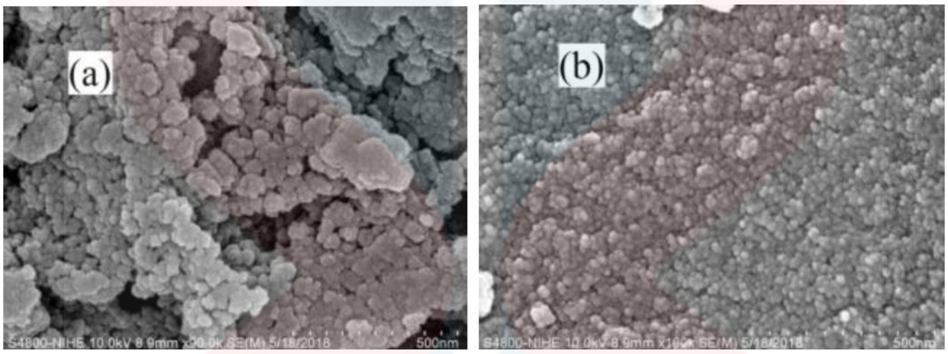


Figure 4.6: SEM images of silica produced from alkaline-extraction (a) and SiO2-precipitation methods (b)

Silica products exist as clusters composed of primary particles. Despite having larger primary particles (approximately 50 nm) compared to SiO2-precipitated silica (about 25 nm), the alkaline-extracted silica displays voids and pores, as evidenced by SEM images. This observation is consistent with the measured BET surface areas of 186.5792 and 68.2269 (m²/g) for alkaline-extracted and SiO2-precipitated silica, respectively.

RHA elemental analyses were examined by the EDS at the selected location in the SEM micrograph shown in Figure 4.7 and 4.8.

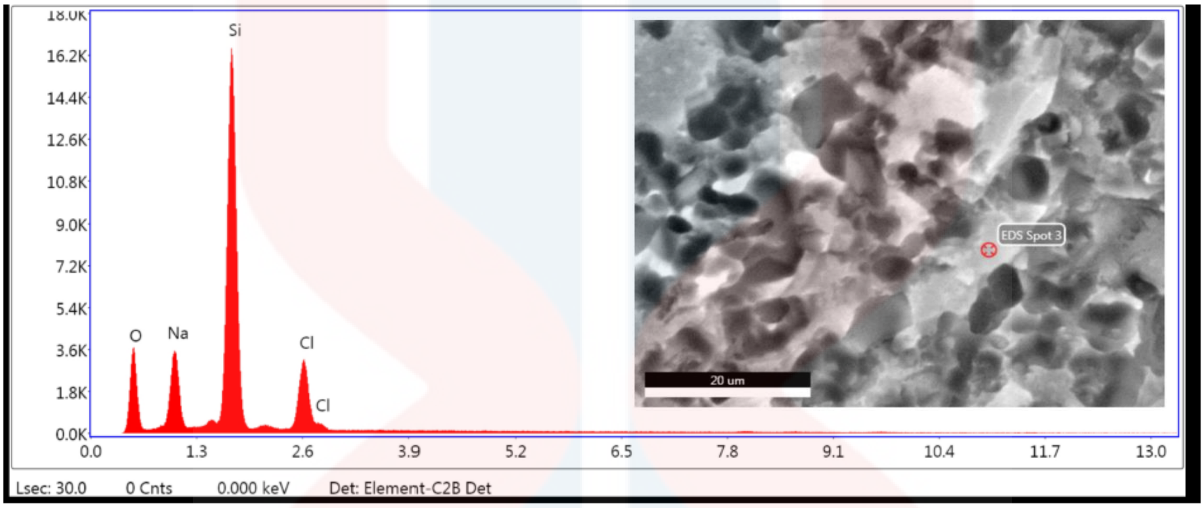


Figure 4.7: EDX profile of RHA at spot 3.

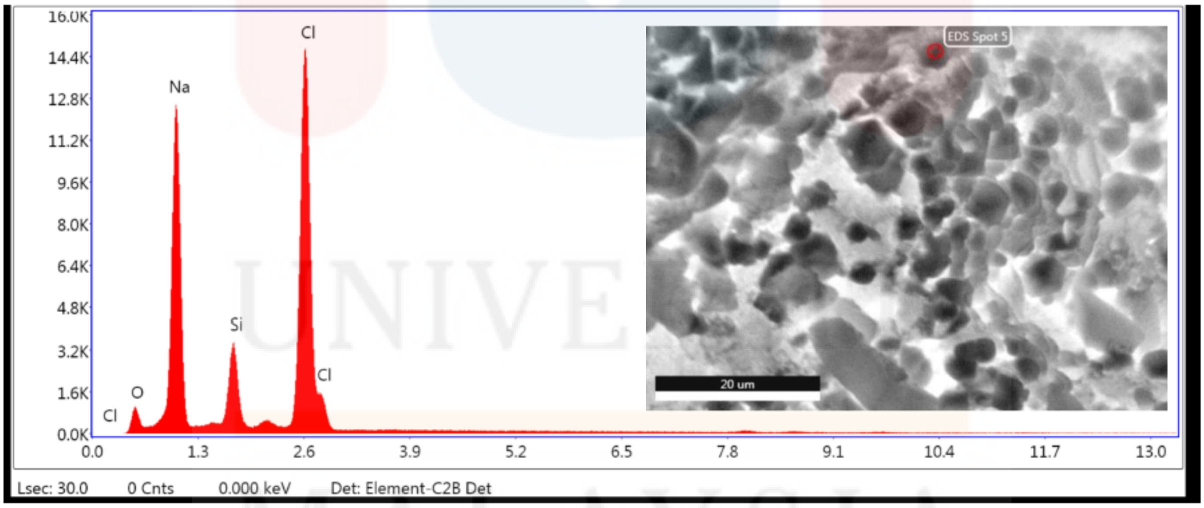


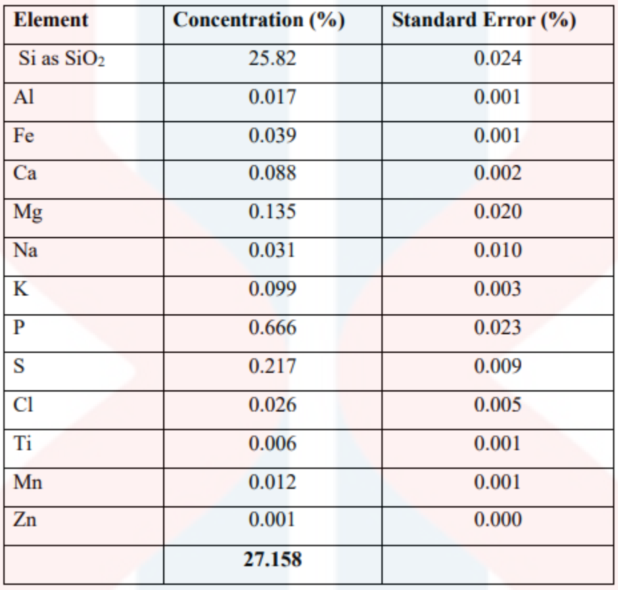
Figure 4.8: EDX profile of RHA at spot 5.

Table 4.2: Shows the percentage of element content regarding figure 4.7 and 4.8.

Element	RHA	
	Spot 3 (Weight %)	Spot 5 (Weight %)
O K	25.42	6.06
Na K	15.23	39.80
Si K	45.54	8.83
Cl K	13.81	45.31

Spot 3 displays a higher weight percentage for silicon (Si) and oxygen (O) at 45.54% and 25.42%, respectively, whereas spot 5 exhibits lower values at just 8.83% and 6.06%. Sodium (Na) and chlorine (Cl) elements are also detected, showing percentages of 39.80% and 45.31%, respectively. The remaining portion consists of impurities, primarily originating from ion adsorption onto SiO2 precipitates during the precipitation process from aqueous solutions. Due to the amorphous nature of SiO2 precipitates, the adsorption of ions tends to be strong, making it difficult to remove these adsorbed ions through washing processes (Le Xuan Thanh, La The Vinh, Bui Thi Van Anh, 2018).

Previous research, Elemental Analysis of Rice Husk Using Proton Induced X-Ray Emission (Pixe) Spectrometry, (Clementina D. Igwebike-Ossi, 2017). Figure 4.9 shows the Elemental Components of Rice Husk using PIXE technique.

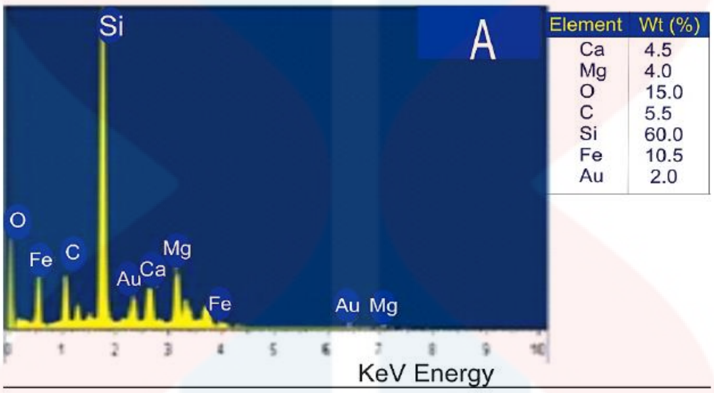


Element	Concentration (%)	Standard Error (%)
Si as SiO_2	25.82	0.024
Al	0.017	0.001
Fe	0.039	0.001
Ca	0.088	0.002
Mg	0.135	0.020
Na	0.031	0.010
K	0.099	0.003
P	0.666	0.023
S	0.217	0.009
Cl	0.026	0.005
Ti	0.006	0.001
Mn	0.012	0.001
Zn	0.001	0.000
	27.158	

Figure 4.9: Elemental Components of Rice Husk using PIXE technique.

The concentration value obtained for silicon present in the form of silica (ash) is appreciably higher than some literature values of 15-20% but close to some (22-29%), (Maeda, N, Wada, Kawakami, M, Ueda, T and Pushpalal, G.K.D, 2001). Some of these thirteen elements detected in rice husks using the PIXE technique have been reported by other X-ray emission analytical techniques such as X-ray fluorescence (XRF). The elements reported are Fe, Ca, K, Cl, Mn and Zn, (Omatola, K.M and. Onojah, 2009). The elements not detected by PIXE but have been reported to be present using the XRF technique are Cr, Ni, Cu, Sr, Br, I, and while those detected by PIXE but not found using XRF are Al, Mg, Na, P, S, and Ti. This variation in the elemental components of rice husks can be attributed to a number of factors such as rice variety, soil chemistry, use and type of fertilizer, climatic conditions as earlier enumerated, (Chandrasekar, S Satyanarayana and Raghavan, 2003).

From research article Development and Characterization of Rice Husk Ash-based Photocatalyst for Degradation of Methylene blue, (Olusegun Ayoola Ajayi, Oluwafunto Oyinkan Okeniyi, Ojo Adefela Adekunle, Yahaya Muhammad Sani, 2021). The composition of the products was determined using Energy Dispersive X-ray spectroscopy (EDS). The spectrums and the summarized results are shown in figure 5.0.



Element	Wt (%)
Ca	4.5
Mg	4.0
O	15.0
C	5.5
Si	60.0
Fe	10.5
Au	2.0

Figure 5.0: Element percentage in RHA.

The EDX of the rice husk ash showed high content of silicon, followed by magnesium, calcium, iron, and presence of other oxides which recorded the weight percent of the significant elements as silicon (60wt.%), oxygen (15.0 wt.%), carbon (5.5 wt.%), the other elemental compositions might be due to pre and post treatment process effect of the rice husk ash.

4.1.5 Catalytic activity of RHA in oxidation of phenol.

In this section, the catalytic activity of the synthesized catalysts was evaluated using a Gas Chromatography-Mass Spectrometry (GC-MS) instrument. RHA was tested using several temperatures and hydrogen peroxide as the oxidising agent to oxidise phenol. The factors of the reaction that have been studied include the response to the impact of different temperatures. Upon oxidation, the major molecule formed is phenol, 4-phenoxy- or known as hydroquinone monophenyl ether and phenyl ester, acetic acid, Tricyclo [4.3.1.1(3,8)] undecan-1-amine occasionally showing up as a minor by-product.

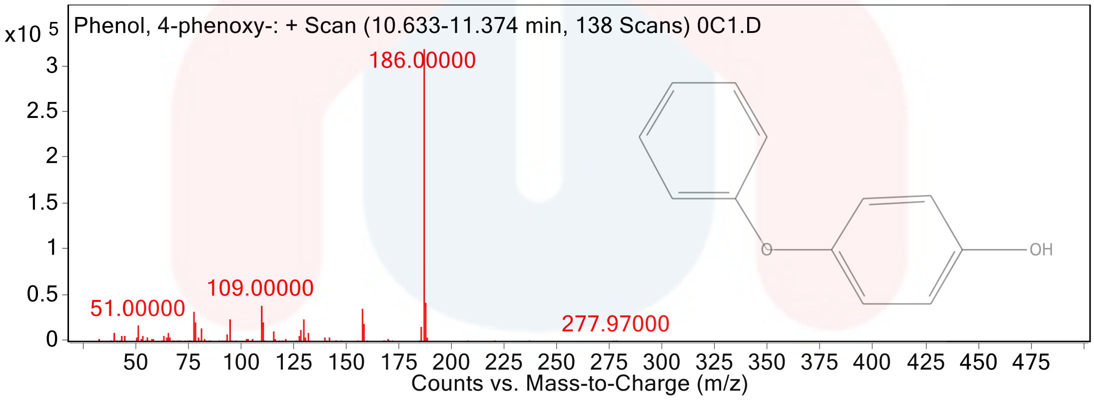


Figure 5.1: Shows the major molecule formed.

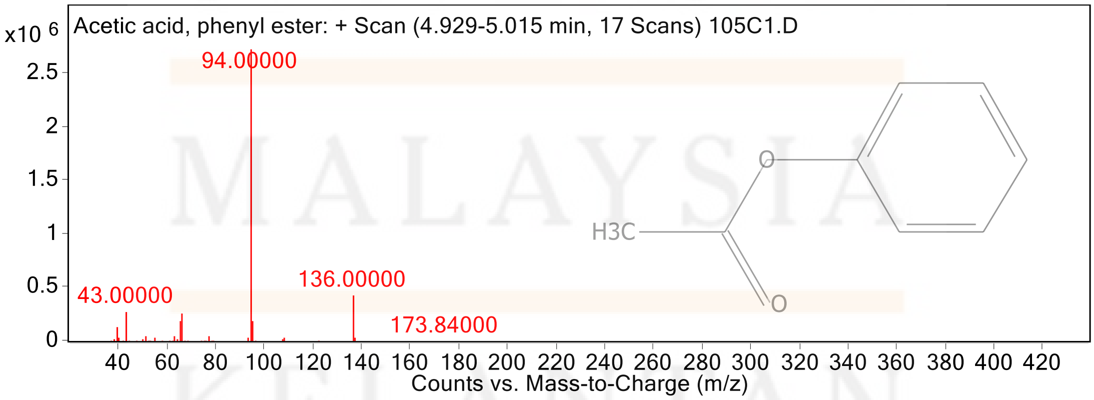


Figure 5.2: Shows the minor by-product formed.

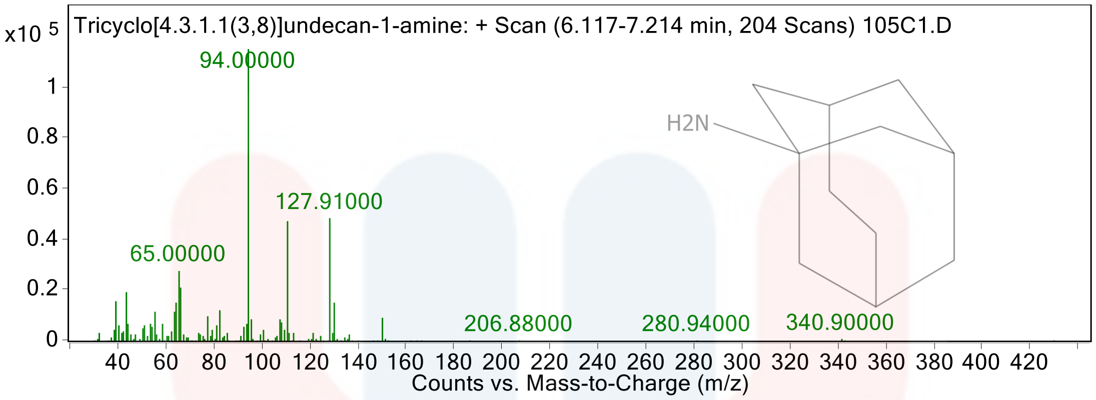


Figure 5.3: Shows the minor by-product formed.

The reaction was examined at temperatures ranging from 35 °C to 105 °C while the other parameters were kept constant (0.10 g of RHA, a 1:1 molar ratio of phenol to H2O2, and a 3-hour reaction).

The primary compound formed is phenol, specifically 4-phenoxy- or hydroquinone monophenyl ether. This molecule serves as a polymerization inhibitor in the production of acrylic acids, playing a significant role in manufacturing acrylic fibers, paints, inks, adhesives, and super absorbent polymers. Additionally, it finds utility in the production of methacrylic and other acrylates, vinyl acetate monomer (VAM), styrene monomer, and unsaturated polyesters. Hydroquinone cream is a widely recognized depigmentation or skin lightening agent, commonly employed clinically to address dyschromia issues such as melasma, chloasma, solar lentigines, freckles, and post-inflammatory hyperpigmentation (Chelsea Schwartz; Arif Jan; Patrick M. Zito, 2023).

A minor by-product observed is phenyl ester. The stability of the phenyl ester function during typical chain extension manipulations allows for its selective removal by treatment with one equivalent of hydrogen peroxide at pH 10.5 in various solvents such as 80% acetone, dimethylformamide, hexamethylphosphoramide, or trifluoroethanol (I.J. Galpin, P.M. Hardy, G.W. Kenner, J.R. McDermott, R. Ramage, J.H. Seely, R.G. Tyson, 2011).

Tricyclo [4.3.1.1(3,8)] undecan-1-amine occasionally showing up as a minor by-product at 105°C reaction. It is an organic compound with a unique structure consisting of three fused rings and nine carbon atoms. It is a colorless to pale yellow liquid with a pungent odor. The compound is of interest to scientists due to its wide range of applications in organic synthesis and medicinal chemistry, (PE Aldrich, EC Hermann, WE Meier- *Journal of Medicinal*, 1971)

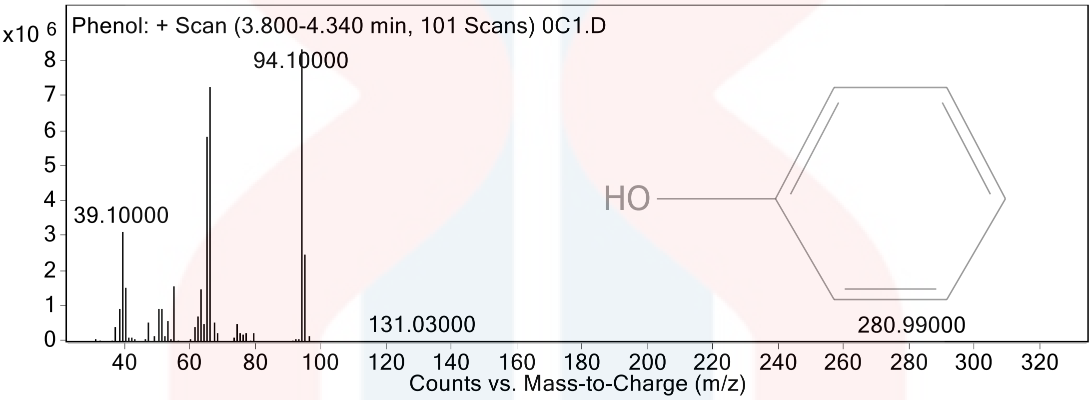


Figure 5.4: Shows mass-to-charge ratio (m/z) at 0°C reaction.

The tallest peak at m/z 94.1000 indicates that the most abundant ion detected has a mass-to-charge ratio of 94.1000. There are also other peaks present, such as the one at m/z 39.10000 and another at m/z 131.03000, which represent ions with those respective mass-to-charge ratios. The peak at m/z 94.1000 could represent the molecular ion of phenol (C6H5OH) with a molecular weight of 94.

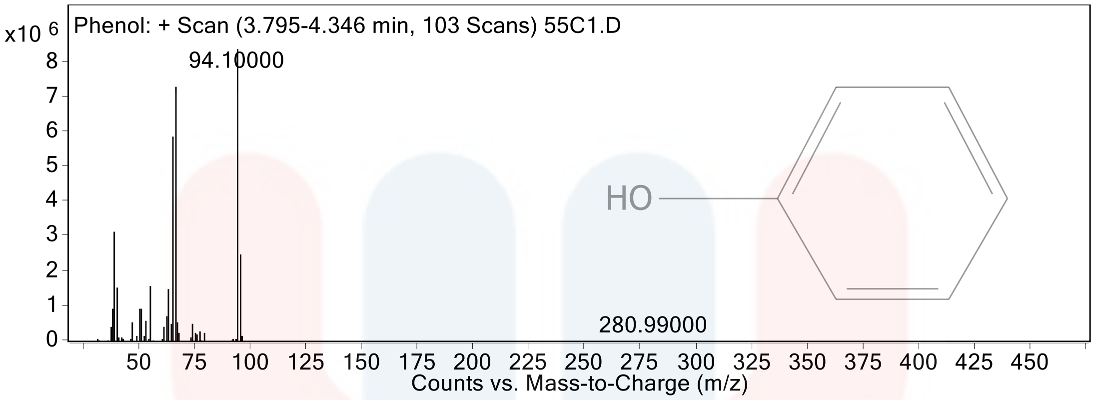


Figure 5.5: Shows mass-to-charge ratio (m/z) at 55°C reaction.

The peak at m/z = 94 corresponds to the molecular ion of phenol (C6H5OH). This is the base peak and represents the intact phenol molecule that has been ionized without fragmentation. The molecular weight of phenol is 94 g/mol, which matches the m/z value of this peak.

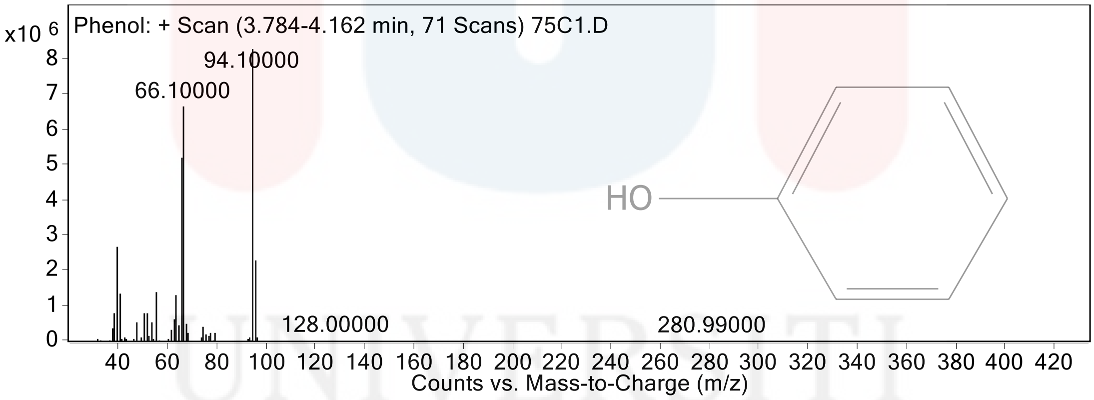


Figure 5.6: Shows mass-to-charge ratio (m/z) at 75°C reaction.

The peak at m/z 94 could correspond to the molecular ion of phenol itself, which has a molecular weight of 94 g/mol. This suggests that some unreacted phenol may be present in the sample. The peak at m/z 66 might represent a fragment of an oxidation product or a smaller organic compound that could be formed during the oxidation process. The peak at m/z 128 is more difficult to assign without further information. It could represent a dimer or an oxidation product with a higher molecular weight than phenol.

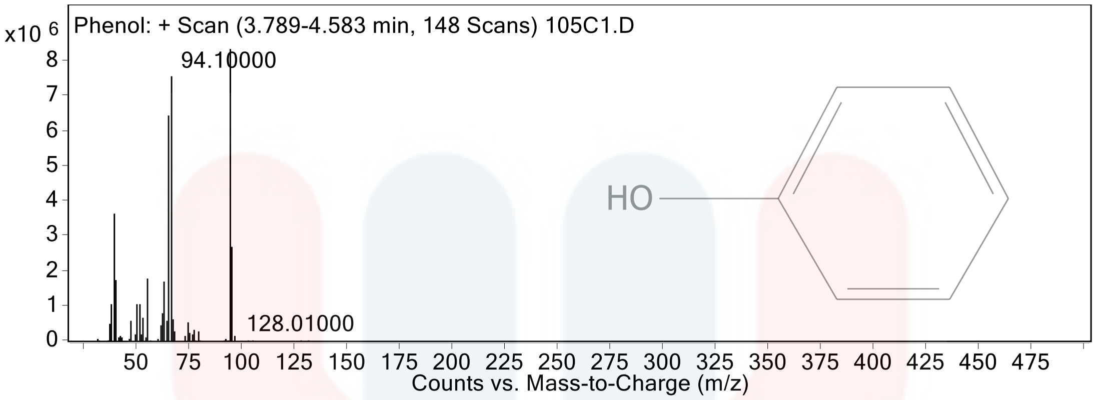


Figure 5.7: Shows mass-to-charge ratio (m/z) at 105°C reaction.

The first part of the Figure indicates the specifics of the scan performed for phenol. It mentions the time range during which the scan was conducted (3.789-4.583 min) and the number of scans performed (148). This information suggests that a detailed analysis of phenol was carried out within the specified time frame, potentially yielding insights into its molecular composition or characteristics.

The second part features a graph showing the counts versus mass-to-charge (m/z) ratio for mass values ranging from 75 to 475. This graph likely represents the mass spectrum of the analyzed substance, displaying the distribution of ions based on their mass-to-charge ratio. Such data is crucial in identifying the compounds present in the sample and determining their molecular weights, offering valuable insights into the composition and structure of the substance under investigation.

4.1.6 The influence of reaction to different temperatures.

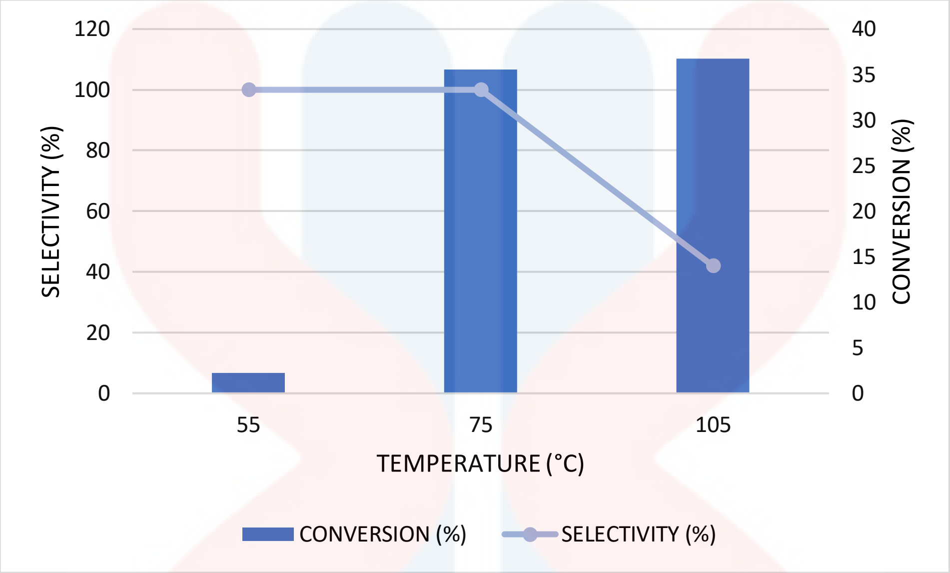


Figure 5.8: The percentage conversion and selectivity to hydroquinone at different reaction temperatures in the oxidation of phenol.

The highest phenol conversion was achieved using 0.10 g of catalyst and a 1:1 molar mass ratio of phenol to hydrogen peroxide for a duration of three hours at 75°C. Within a temperature range of 65 to 75°C, all phenol removal rates reached 36%. Initially, the solution was colorless, but after some time, it developed a yellow hue, transitioning subsequently from orange to brown, and eventually, the color began to fade. During this color change process, aromatic intermediates and organic acids resulting from phenol oxidation were detected. Figure 5.8 shows that the conversion of phenol also rises with temperature, reaching a maximum of about 37% at 105 °C. Although phenol is converted at 105 °C with the best efficiency, it has a low selectivity compared to 75 °C. According to (Santos A, Yustos P, Quintanilla A, 2004), hydroquinone and p-benzoquinone are 3 and 2 orders of magnitude more toxic than phenol, respectively, and catechol shows a toxicity value 2-fold that of phenol.

Thus, considering the environmental perspective, the elimination of phenol remains detrimental to the environment, necessitating its complete oxidation into CO2 and H2O. Achieving the full removal of all toxic compounds requires a significantly longer duration, as noted by WANG Pan, BIAN XiuFang, and LI YanXin in 2011.

In summary of the effect on different temperatures, in comparison to 105 °C, 75 °C has the highest conversion 37% and 36% and the highest selectivity of hydroquinone monophenyl ether. Since it has the highest selectivity, this proves that 75 °C is the optimum temperature for the catalyst to interact with the oxidation of phenol. The best temperature for this reaction is 75 °C, which has a high selectivity compared to 55 and 105°C. While 36% removal was achieved, the transformation of phenol into highly toxic intermediates emphasizes the need for prolonged reaction times to ensure complete mineralization and mitigate environmental harm.

5. CONCLUSION

The demand for products that are natural, organic, or environmentally friendly nowadays draws the attention of researchers. Heterogeneous catalysts are one of the products which have benefits that can be regenerated. In this study, a green chemical product known as a catalyst is created by utilising rice husk from agricultural waste as a source of silica. The sol-gel method has successfully extracted silica from rice husks. Still, most of them employ a metal element that is not a renewable resource to boost the catalyst activity. Rice husk ash (RHA) can serve as an effective catalyst in various chemical processes due to several advantages including abundant and renewable resource, high silica content, thermal stability, and environmental sustainability.

A few analyses from the XRD, SEM, EDX, FTIR, and TGA were used to characterise the formation of RHA in order to learn about their shape characterisation. The XRD diffractogram at two thetas demonstrates the samples are in the crystalline form. In addition, the surface structure of the sample is shown in the SEM image before and after the incorporation of an organic substance with agglomerate, spherical particles and some irregular, rock-like particles.

One parameter was used to test the synthesised RHA catalyst in the oxidation of phenol utilising hydrogen peroxide as the oxidising agent. The most prevalent product in the reaction is hydroquinone. The outcome, however, showed that the selectivity to hydroquinone only had a mediocre transformation. Without the catalyst, the phenol oxidation continued for 4 hours with no product being produced, and the catalyst created a product while it was active only for 0 hours. This demonstrates how the RHA catalyst can speed up the reaction's yield. The maximum phenol conversion was obtained using 0.10 g of catalyst and a 1:1 molar mass ratio of phenol to hydrogen peroxide for three hours at 75 °C.

5.1 RECOMMENDATION

This research has developed a catalyst derived from rice husk, where the application of heat during the catalyst synthesis process is crucial for achieving optimal effectiveness. Varying temperatures have been shown to influence the catalyst's morphology, encompassing its structure, surface characteristics, pore configuration, shape, and other pertinent attributes. These alterations could potentially impact the catalyst's active sites. Therefore, ensuring the appropriate static temperature setting is imperative. The conclusion presented in this thesis is finalised. Yet further research can be carried out as described below:

- Ensure that the catalyst is devoid of absorbed water prior to usage.
- Use another different parameter such as times.
- Burn the rice husk direct into furnace.
- Rinsed the rice husk completely after acid treatment.

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APPENDIX A

Figure A (a) : Shows the first step of washing rice husk from dirt.

Figure A (b): Shows the drying of rice husk outdoor.

APPENDIX B

Figure B (a): Shows the acid treatment on rice husk.

Figure B (b): Shows the rice husk rinsed with distilled water until pH 5.

APPENDIX C

Figure C (a): Shows burning of rice husk in the furnace 900°C.

APPENDIX D

Figure D (a): Shows the preparation of sodium silicate.

Figure D (b): Shows the crushed silica.

APPENDIX E

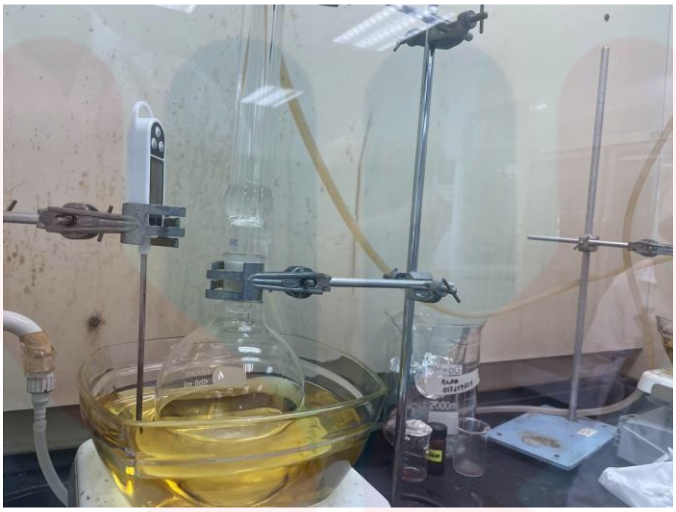

Figure E (a): Shows the oxidation of phenol process.

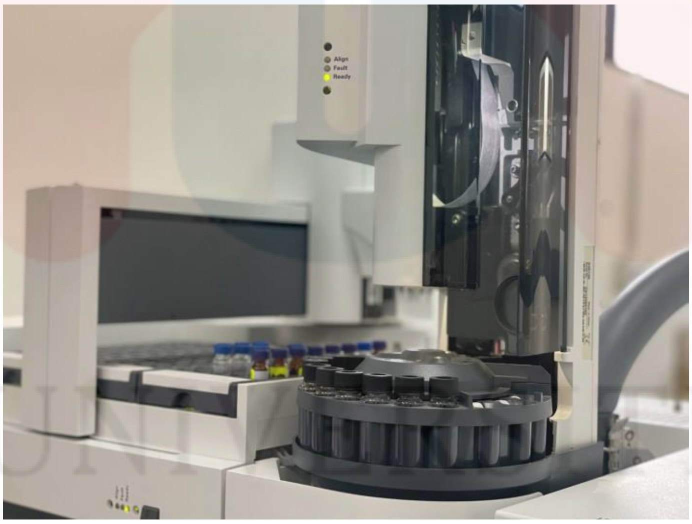

Figure E (b): Shows the sample were run by GCMS.