



DUAL-STAGE MODIFICATION OF STARCH EXTRACTED FROM HUNGRY RICE (*Digitaria Exilis*): SOAKING PRETREATMENT AND CITRIC ACID LINTNERIZATION EFFICACIES

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Abstract

Digitaria Exilis (Hungry rice) starch is an important promising functional ingredient in food and industrial systems, yet its native form often displays limitations in thermal stability, solubility, and processing performance. Lintnerization, a controlled acid hydrolysis technique, is widely applied to enhance starch functionality; however, the role of pretreatment prior to hydrolysis remains poorly understood. This study investigated the effect of soaking pretreatment on the citric acid modification of hungry rice (*Digitaria Exilis*). The modified starches were analyzed for swelling power, solubility, water holding capacity, paste clarity and the degree of substitution of the lintnerized starch and the characterization of the crude and modified starches were carried out using Fourier transform infrared (FTIR), scan electron microscope (SEM) and Energy dispersion microscope (EDX). Results revealed that pretreatment significantly influenced the degree of substitution, granule morphology, and overall functional properties of the resulting lintnerized starches. Variations were observed in the hydration properties, paste behavior and morphology, indicating that soaking alters granular structure interactions prior to acid modification. This study demonstrate that soaking can be used to tailor the properties of hungry rice starch for specific food and industrial uses. This study provides valuable insights needed to optimize starch modification techniques and expand the commercial utilization of hungry rice starch.

Keywords: *Climate-resilient Digitaria Exilis* (Hungry rice), Lintnerization, Nutrient-rich crops, Industrial applications

1. INTRODUCTION

Hungry rice, scientifically known as *Digitaria exilis* and locally referred to as acha, fonio, or hungry rice, is a tiny-grained cereal crop native to West Africa. It is considered one of the earliest cultivated grains in the region and plays a vital role in the traditional food systems due to its cultural, nutritional, and agronomic value. Despite its importance, it is still underutilized in large-scale commercial agriculture. *Digitaria exilis* is believed to have originated in the Sahel region and is mainly grown in countries like Nigeria, Guinea, Mali, Burkina Faso, and Senegal. The crop thrives in poor soils and dry conditions, making it

suitable for cultivation in areas with unpredictable rainfall

and low soil fertility (Adoukonou-Sagbadja et al., 2006). In West Africa, hungry rice is consumed during cultural festivals, rituals, and often used as baby food. The crop's potential to support food security and rural income in climate-vulnerable areas makes it an important economic resource. There is growing interest in climate-resilient and nutrient-rich crops like hungry rice, despite its benefits, this crop is largely underutilized and often considered a traditional or subsistence food.

Starch obtained from hungry rice is highly nutritious, especially in essential amino acids

such as methionine and cysteine, which are lacking in many staple cereals like maize and rice (Jideani and Jideani, 2011). It is naturally gluten-free and has a low glycemic index, making it ideal for people with celiac disease or those managing diabetes (Temple and Bassa, 1991). Hungry rice typically contains 70–80% carbohydrates, 7–10% protein, 1–2% fat, and 1–3% dietary fiber. It is also rich in micronutrients like iron, zinc, magnesium, and B vitamins (Vodouhe et al., 2006). However, its native starches often exhibit limitations which hinder their performance in many industrial processes. To overcome these limitations, various chemical, physical, and enzymatic modification techniques have been employed. Despite the functional importance of pretreatment, limited studies have systematically examined how soaking time affect the functional properties of lintnerized sweet potato starches. Understanding these effects is essential for tailoring starch characteristics for specific end-use applications, especially in food formulations where texture, stability, and processing behavior are critical. Evaluating how soaking time influences functional parameters such as swelling power, solubility, pasting clarity, water holding capacity and thermal transitions

will provide insights into optimizing lintnerization techniques for enhanced starch performance. Therefore, this study employed dual stage modification techniques of different soaking time and varied concentration of citric acid lintnerization with the aim of establishing relationships between pretreatment conditions, esterification behavior, and resulting functional properties of hungry rice starch. The outcomes will contribute to improved utilization of hungry rice starch in industrial applications.

2. MATERIAL AND METHODS

Sample Collection

Hungry rice (*Digilania exilis*), 1 kg was purchased from local farmers in Kawo market, Kaduna North Local Government Area of Kaduna State, Nigeria. Kawo is located at longitude 7°43'33" and latitude 10°05'16" in Kaduna State, Nigeria. The identification of the sample was done at Biology department's herbarium, Nigeria Defence academy Kaduna, with batch numbers NDA/BioH/2025 21.

Sample Preparation

The cereal grains were destoned and shafts was removed by handpicked before they kept in air tight container as shown in figure 1. The extraction of all the samples commenced immediately after the cleaning.



Figure 1. Sample Grains of Hungry Rice

Procedure for the extraction of Starch from Hungry Rice Samples

The procedure described by Amusan et al., (2026); Raugrusmee and Anal, (2019) was employed in the extraction of starch from the

cereal. Hungry rice grains (4.5 kg) were divided into three portions; the first portion was washed thoroughly in clean water at room temperature and ground (1:2 w/v) until a smooth slurry was formed in an electric food processor. The slurry was sieved in a 150 µm pore size Mushin cloth. The residual flesh on the sieve was further washed with water twice to remove the remaining starch. The filtrate was allowed to stand for 1 hr 30 mins to allow the starch sedimentation. The starch was separated by decantation and dried in an oven at 40°C for 48 hrs and allowed to cool. The dried starch cake was reground with a electric grounder in to a smooth powder, kept in an air tight container and labelled has U-Cs-HRS for further analysis (Figure 2) Amusan et al., (2026).

The second portion was soaked in water at room temperature for 24hrs, after which, the grain sample was washed thoroughly in fresh water before grounding with water (1:2 w/v) until a smooth slurry was formed. The slurry was sieved in a 150 µm pore size Mushin cloth. The residual flesh was further washed with water twice to remove the remaining

starch. The filtrate was allowed to stand for 1 hr 30 mins to allow the starch sedimentation. The starch was separated by decantation and dried in an oven at 40°C for 48 hrs and allowed to cool. The dried starch cake was reground with a electric grounder in to a smooth powder, kept in an air tight container and labelled has S₂₄-Cs-HRS for further analysis (Figure 2) Oyefeso et al., (2024).

The third portion was soaked in water for 48hrs at room temperature, followed by washing and grounding with water (1:2 w/v) until a smooth slurry was formed in a blender. The slurry was sieved and the residual flesh on the sieves was further washed with water twice to remove the remaining starch. The filtrate was allowed to stand for 1 hr 30 mins to allow the starch sedimentation. The starch was separated by decantation and dried in an oven at 40°C for 48 hrs. The dried starch cake was reground with a electric grounder in to a smooth powder, kept in an air tight container and labelled has S₄₈-Cs-HRS for further analysis (Figure 2) (Amusan et al., 2026; Raugrsmee and Anal, 2019; Torres *et al.*, 2020).



Figure 2. Hungry Rice Starch Samples

Lintnerization of Hungry Starch Samples (Esterification Method)

The three different pretreated hungry rice starches were Lintnerized (modified) by using citric acid at 1 M, 3 M and 5 M respectively, coupled with heat treatment method following the method employed by Kalu et al., (2022).

Procedure for 1 M Lintnerization

An accurately measured 50 ml of 1 M citric acid solution was transferred into a clean 250 ml beaker, the pH of the solution was adjusted to 3.0 using a pH meter by adding 10% NaOH and make up with water to 100 ml. Then 100 g of starch sample was added and stirred thoroughly until a smooth slurry is formed. The mixture was allowed to stand for 18 hrs and the starch suspension was then poured out into a flat tray and dried at 40°C until all the water was almost gone. After that the starch cake was super heated at 90°C for 1hr and then cooled to room temperature. the esterified starch was ground into powder, kept in an air tight container and labelled has U-M₁-HRS, S₂₄-M₁-HRS and S₄₈-M₁- HRS for further analysis (Kalu et al., 2022; Amusan et al., 2026).

Procedure for 3 M Lintnerization

An accurately measured 50 ml of 3 M citric acid solution was transferred into a clean 250 ml beaker, the pH of the solution was adjusted to 3.0 using a pH meter by adding 10% NaOH and make up with water to 100ml. Then 100 g of starch sample was added and stirred thoroughly until a smooth slurry is formed. The mixture was allowed to stand for 18 hrs. the starch suspension was then poured out into

a flat tray and dried at 40°C until all the water was almost gone. After that the starch cake was super heated at 90°C for 1hr and then cooled to room temperature. the esterified starch was ground into powder, kept in an air tight container and labelled has U-M₃-HRS, S₂₄-M₃-HRS and S₄₈-M₃- HRS for further analysis (Kalu et al., (2022).

Procedure for 5 M Lintnerization

An accurately measured 50 ml of 5 M citric acid solution was transferred into a clean 250 ml beaker, the pH of the solution was adjusted to 3.0 using a pH meter by adding 10% NaOH and make up with water to 100ml. Then 100 g of starch sample was added and stirred thoroughly until a smooth slurry is formed. The mixture was allowed to stand for 18 hrs. the starch suspension was then poured out into a flat tray and dried at 40°C until all the water was almost gone. After that the starch cake was super heated at 90°C for 1hr and then cooled to room temperature. the esterified starch is ground into powder, kept in an air tight container and labelled has U-M₅-HRS, S₂₄-M₅-HRS and S₄₈-M₅- HRS for further analysis (Amusan et al., (2026).

Physicochemical Properties of Crude and Lintnerized Starches

The physicochemical properties of the crude and Lintnerized starch samples were tested for water holding capacity, swelling power, solubility and paste clarity.

Determination of water holding capacity (WHC).

The water holding capacity of the starches was determined using the method of Yadav et al.,

(2018). The starch suspension was prepared by dissolving 1 g of starch in 15 ml distilled water, agitated for 2 mins and centrifuged at 1500 rpm for 10 mins. The supernatant was decanted and wet starch was weighed. The amount of water (g/g) absorbed by the sample was reported as water holding capacity as shown in equation 3.1.

$$\text{WHC} \quad (\text{g/g}) = \frac{\text{weight of wet starch} - \text{weight of dry starch sample (g)}}{\text{weight of dry starch sample (g)}} \quad 1$$

Determination of percentage water solubility

Solubility properties of the starches were determined according to the method described by Nuwamanya et al., (2011). Starch suspension (0.5 g) was dispersed in distilled water (10ml) and incubated in a water bath at temperatures of 90°C, with continuous stirring for 30 min. Subsequently, the sample was cooled to room temperature. After cooling, it was centrifuged at 1500 rpm for 15 mins, the supernatant was decanted and dried in an oven at 105°C for 2 hrs, and the weight of the sediment was also noted. The total amount of soluble starch was calculated using equation 3.2 (Nuwamanya et al., (2011)).

$$\text{Solubility (\%)} = \frac{\text{weight of soluble starch}}{\text{weight of dry sample}} \times 100 \quad 2$$

Determination of swelling power

The swelling power of the starch samples was determined following the Shrestha *et al.*, (2018) method as described by Raungrusmee, and Anal., (2019). The starch sample (1 g) was dispersed in distilled water (50 ml) in a centrifuge tube and heated in a water bath at 90°C for 30 min with continuous stirring. After cooling to room temperature, it was centrifuged at 1500 rpm for 15 mins, the

supernatant was decanted and the weight of the swollen starch was determined. The swelling power was calculated using the following equations (Raungrusmee, and Anal., (2019)).

$$\text{Swelling power (g/g)} = \frac{\text{weight of swollen starch(g)}}{\text{weight of dry sample (g)}} \quad 3$$

Paste clarity %of the Crude and Lintnerized Starches

Paste clarity of both crude and lintnerized starches were determined according to Kalu et al., (2022) and Nuwamanya, et al., (2011). A 1% aqueous solution of starch was boiled at 93°C with repeated shaking for 30 min. The solution was transferred into a cuvette after cooling and absorbance was measured using a UV spectrophotometer.

The paste clarity is calculated using equation 3.4:

$$10^{(-A)} \times 100 \quad 4$$

where A = absorbance of the aqueous solution of the starch.

Degree of Substitution

The degree of substitution of the crude and lintnerized starches was determined following the method describe by Amusan et al., (2026); kalu et al., (2022). A 1g of the starch sample was dissolved in 25ml distilled water, 25mls of 0.5M sodium hydroxide added and stirred thoroughly for homogeneity, then the solution was heated in a water bath at 60°C for 30 mins with continuous stirring. The solution was allowed to cool to room temperature. Then, 3 drops of phenolphthalein solution was added and the excess sodium hydroxide was titrated against 0.5 M HCl to colorless endpoint. The same procedure was repeated for the blank. The DS was calculated using the formula

$$\text{DS} = \frac{162 \text{ M(B-S)}}{1000 \text{ W}} \quad \text{Eqn. 5}$$

Where M is the Molarity of HCl (0.5 M), W is the weight of sample (1g), B is the volume of 0.5 M HCl in the blank (ml) and S the volume of 0.5 M HCl in the sample (ml). 162 stands for the molecular weight of anhydro glucose unit (AGU) of a starch molecule ($C_6H_{10}O_5 = 162$)

Characterization of the Crude and Lintnerized Sweet Potato and Cereal Starches

Crude and Lintnerized starches were characterized using Fourier transform Infrared (FTIR), Scan electron microscope (SEM), Energy dispersive microscope (EDX).

FTIR Analysis of Crude and Lintnerized Crude and Lintnerized Hungry Rice Starches.

Chemical Composition of the crude and lintnerized hungry rice starches was analyzed by using Fourier Transform Infrared (FTIR) spectrophotometer (Agilent Technology). Samples (0.5 g each) was pressed into a pellet for scanning with a FTIR spectrometer. The spectra were recorded for total scans between 4,000 and 400 cm^{-1} with resolution of 4 cm^{-1} .

Scanning Electron Microscope (SEM) Analysis of the Crude and Lintnerized Starches.

The granular morphology of the crude and lintnerized starches was analyzed using a scanning Electron Microscope (SEM). The starch sample (5mg) was placed on a microscopic slide and the slide will be observed under the light microscope at a magnification of 500 $\times$ (Ali et al., 2023)

RESULT AND DISCUSSION

Physicochemical Properties of Crude and Lintnerized Starches

Water Holding Capacity (WHC)

The result for the water holding capacity (WHC) of crude and lintnerized starches is presented in table 1. All the values are presented as mean $\pm$ SD (Standard deviation) of a triplicate measurement.

The crude starches have the WHC values of 1.28 $\pm$ 0.01 g/g, 1.24 $\pm$ 0.01 g/g, 1.02 $\pm$ 0.04 g/g for the unsoaked, (U-Cs-HRS), 24 hrs soaking (S₂₄-Cs- HRS) and 48 hrs soaking (S₄₈-Cs-HRS) respectively. While the values for 1 M citric acid lintnerization are; 1.12 $\pm$ 0.02 g/g, 1.00 $\pm$ 0.07 g/g, 1.15 $\pm$ 0.03 g/g for Unsoaked, (U-M₁- HRS), 24 hrs soaking (S₂₄-M₁- HRS) and 48 hrs soaking (S₄₈-M₁- HRS) respectively. The WHC values for 3 M citric acid lintnerization are 1.11 $\pm$ 0.03 g/g, 0.83 $\pm$ 0.02 g/g and 0.89 $\pm$ 0.06 g/g for Unsoaked, (U-M₃- HRS), 24 hrs soaking (S₂₄-M₃- HRS) and 48 hrs soaking (S₄₈-M₃- HRS) respectively. And the values for 5 M citric acid lintnerization are; 1.81 $\pm$ 0.09 g/g, 0.87 $\pm$ 0.11 g/g and 0.93 $\pm$ 0.09 g/g for Unsoaked, (U-M₅- HRS), 24 hrs soaking (S₂₄-M₅- HRS) and 48 hrs soaking (S₄₈-M₅- HRS) respectively. From the result obtained it was discovered that WHC value decreases with increase in concentration of citric acid modification.

The crude starches have a decrease in WHC with increasing soaking time. U-Cs-HRS drops from 1.28 $\pm$ 0.15 g/g to 1.02 $\pm$ 0.04 g/g for S₂₄-Cs-HRS. This suggest that prolonged soaking time may lead to loss of water-binding functional groups in the starch granule which can lead to rearrange that limits water uptake in most of the cereal starches. However, crude wheat starch shows an increase in WHC after 48 hours soaking (1.26 $\pm$ 0.61 g/g) compared to the unsoaked (1.09 $\pm$ 0.05g/g), suggesting the starch specific behavior.

Effect Of Citric Acid Lintnerization on the Water Holding Capacity of Hungry rice Starches

The Lintnerized hungry rice starches (M₁, M₃, M₅) exhibit lower WHC values compared to their respective crude starches. U-M₅-HRS has the lowest value (0.45±0.03 g/g) compared to all other lintnerized starches counterpart. The results of the WHC confirm that both soaking time and citric acid lintnerization significantly influence the water holding capacity of the starches. Lintnerization generally decreases WHC across starches treatment an effect attributable to the destruction of amorphous regions in the starch granule. The water holding capacity is the ability of starch to retain water within its structure when hydrated. It describes the interaction of starch with water under specified conditions (KarmvIr et al., 2018). This property of starch is a function of its crystallinity nature; starches with low crystallinity possess high WHC in comparison to those with high crystallinity and hence, it is dependent on the amylose content of starch (Ogunmolasuyi et al., 2017). The inter- and intra-granular forces in starch molecule are also important factors; the weaker the forces the higher the WHC (Aryee et al., 2006). Lintnerization of starch with citric acid reduce the ability of starch to absorb water and, therefore, the WHC of the acid modified starch reduced with respect to the concentration of acid applied (Lawal 2004 in Ogunmolasuyi et al., 2017). The variation in the WHC of acid treated starch could be attributed to the reduction of the amorphous region in the starch granule. This reduces the number of available binding sites for water in starch granules. (Lawal 2004 in Ogunmolasuyi et al., 2017). When starch is

treated with citric acid, the acid acts as a cross-linking and esterification agent which reacts with hydroxyl groups (-OH) on starch chains, forming ester bonds (-COO-) between different chains or within the same molecule. This reduces the number of free hydroxyl groups (which normally attract water). The cross-linked network reduces the availability of hydrophilic sites for water binding. And the internal hydrogen-bonding becomes stronger and less accessible to water molecules (Yadav et al., 2006). However, the extent of reduction depends on the concentration of citric acid (Kalu et al., 2022). Lower WHC in citric acid lintnerized starches Improves paste stability, gel firmness, and resistance to syneresis. Makes the starch more suitable for food and pharmaceutical applications that require controlled hydration (e.g., thickening agents, film-forming materials, or tablet binders).

Swelling Power (SP)

The result for the swelling power of crude and lintnerized starches at 90°C is presented in table 1. All the values are presented as mean ± SD (Standard deviation) of a triplicate measurement.

Crude starches have the SP values of 7.67 ±0.91 g/g, 7.64 ±0.39 g/g, 8.16 ±0.53 g/g for the unsoaked crude starch, (U-Cs-HRS), 24 hrs soaking crude starch (S₂₄-Cs- HRS) and 48 hrs soaking crude starch (S₄₈-Cs- HRS) respectively. While the values for 1 M citric acid lintnerization are; 8.90 ± 0.01 g/g, 8.87 ±1.15 g/g, 8.19 ±0.72 g/g for Unsoaked 1M lintnerized starch (U-M₁- HRS), 24 hrs soaking-1 M lintnerized starch (S₂₄-M₁- HRS) and 48 hrs -1 M lintnerized starches (S₄₈-M₁-HRS) respectively. The SP values for 3 M citric acid lintnerization are 7.76 ±0.57 g/g, 9.30 ±0.17 g/g and 9.36 ±0.73 g/g for

Unsoaked 3M lintnerized starch (U-M₃- HRS), 24 hrs soaking-3 M lintnerized starch (S₂₄-M₃- HRS) and 48 hrs- 3 M lintnerized starches (S₄₈-M₃- HRS) respectively. And the values for 5 M citric acid lintnerization are; 6.21 ±0.18 g/g, 6.23 ±0.23 g/g and 6.75 ±0.12 g/g for Unsoaked 5M lintnerized starch (U-M₅-HRS), 24 hrs soaking-5 M lintnerized starch (S₂₄-M₅- HRS) and 48 hrs -5 M lintnerized starches (S₄₈-M₅- HRS) respectively. From the result obtained it was discovered that the SP value decreases with increase in concentration of citric acid lintnerization. This result strongly suggests that the combination of 24-hour soaking time and the highest acid concentration (M₅) yields a highly cross-linked or tightly reinforced hungry rice starch

structure that offers maximum resistance to swelling. The varying effects of soaking on SP are explained by the interplay between water absorption and starch component leaching. Starch granules with initially high SP have weaker internal bonding and are more prone to amylose leaching during soaking. The loss of this soluble material reduces the mass available to swell, resulting in a lower SP. Starches with a stronger, more restrictive crude structure (low initial SP) require prolonged hydration (soaking) to fully overcome the internal forces (hydrogen and hydrophobic bonds). Soaking allows for water penetration and granule relaxation, increasing the SP.

Table 1. Physicochemical Properties of Crude and Lintnerized Hungry Rice Starch

Sample Treatment	WHC	SP	Solubility (%)	PC (%)
U-Cs- HRS	1.28±0.01	7.67 ±0.91	8.00±2.8	31
S ₂₄ -Cs- HRS	1.24±0.01	7.64 ±0.39	10.67±1.2	27
S ₄₈ -Cs- HRS	1.02±0.04	8.16 ±0.53	12.67±1.2	21
U-M ₁ - HRS	1.12±0.02	8.90±0.01	22.67±1.2	40
S ₂₄ -M ₁ - HRS	1.00±0.07	8.87 ±1.15	27±4.2	45
S ₄₈ -M ₁ - HRS	1.15±0.03	8.19 ±0.72	14.67±2.3	29
U-M ₃ - HRS	1.11±0.03	7.76 ±0.57	22.00±00	29
S ₂₄ -M ₃ - HRS	0.83±0.02	9.30 ±0.17	26.00±00	31
S ₄₈ -M ₃ - HRS	0.89±0.06	9.36 ±0.73	29.00±1.4	26
U-M ₅ - HRS	1.81±0.09	6.21 ±0.18	34.67±6.43	45
S ₂₄ -M ₅ - HRS	0.87±0.11	6.23 ±0.23	35.33±2.3	52
S ₄₈ -M ₅ - HRS	0.93±0.09	6.75 ±0.12	14.67±1.15	44

U = unsoaked, S₂₄ = 24 hrs soaking, S₄₈ soaking Cs = crude starch, M₁ = 1M Lintnerization, M₃ = 3 M Lintnerization M₅ = 5 M Lintnerization, HRS = hungry rice starch, SP = swelling Power (g/g), WHC = water holding capacity, PC = paste clarity (%).

Percentage Solubility (% S)

The result for the % solubility of crude and lintnerized hungry rice starches at 90°C is presented in Figure 3 All the values are presented as mean ± SD (Standard deviation) of a triplicate measurement. Crude starches have the % S values of 8.00 % ± 2.08,

10.67 % ± 1.2, 12.67 % ±1.2 for the unsoaked crude starch, (U-Cs-HRS), 24 hrs soaking crude starch (S₂₄-Cs-HRS) and 48 hrs soaking crude starch (S₄₈-Cs-HRS) respectively. While the values for 1 M citric acid lintnerization are; 22.67% ± 1.2, 27.00 % ± 4.2, 14.67% ± 2.3 for Unsoaked 1M

lintnerized starch (U-M₁- HRS), 24 hrs soaking-1 M lintnerized starch (S₂₄-M₁- HRS) and 48 hrs -1 M lintnerized starches (S₄₈-M₁-HRS) respectively. The % S values for 3 M citric acid lintnerization are 22.00 % $\pm$ 0.00, 26.00 % $\pm$ 0.00, 29.00 % $\pm$ 1.4 for Unsoaked 3M lintnerized starch (U-M₃- HRS), 24 hrs soaking-3 M lintnerized starch (S₂₄-M₃- HRS) and 48 hrs -3 M lintnerized starches (S₄₈-M₃-HRS) respectively. And the values for 5 M citric acid modifications are; 34.67 % $\pm$ 6.43, 35.33% $\pm$ 2.3, 14.67% $\pm$ 1.2 for Unsoaked 5M modified starch (U-M₅-HRS), 24 hrs soaking-5 M lintnerized starch (S₂₄-M₅-HRS) and 48 hrs -5 M lintnerized starches (S₄₈-M₅- HRS) respectively. From the results obtained, crude starches, (Unsoaked, 24 hrs, and 48 hrs soaking) all have low solubility, indicating that unmodified starch granules are relatively intact and have resistance to water dispersion. This implies that prolong soaking enhances water penetration, disrupting granules and increasing solubility. For 1 M lintnerized

starches, U-M₁ has high solubility (22.67%). S₂₄-M₁ increases to 27% but reduces in S₄₈-M₁ (14%). This implies that M₁ starch granules are more susceptible to acid hydrolysis after prolonged soaking, showing enhanced solubility across all fractions. S₂₄-M₃ values increases in HRS (26 %) while S₂₄-M₅ has the highest solubility over all (35 %). S₄₈-M₅ shows a sharp drop (14.67 %) which can be ascribe to operational error. The gradual increase in % solubility from crude to the lintnerized starches implies high concentration of citric acid enhances solubility. M₅ starches is highly soluble even without soaking, but prolonged soaking destabilizes the starch. The result of the analysis shows that soaking time increases acid accessibility, leading to greater cross linking and esterification and solubility. Acid concentration interacts with soaking: higher solubility values at S₂₄ suggest deeper hydrolysis, but in M₅, excessive soaking destabilizes the starch granules.

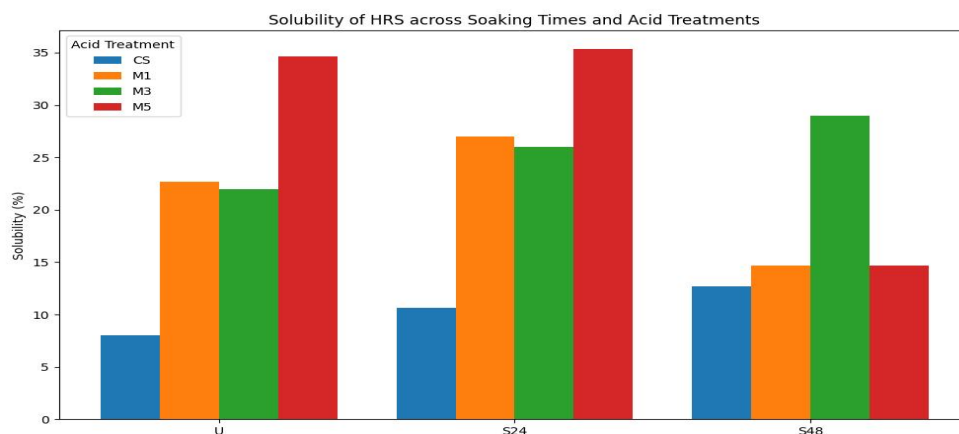


Figure 3. Effect of Citric lintnerization and Soaking Time on % Solubility of HRS

Paste Clarity (% PC)

The result of paste clarity (PC) is presented in Figure 4 From the result, unsoaked crude and lintnerized starch has % PC of 31%, 40%,

21%, 45%. For crude, 1 M, 3 M and 5 M respectively. While 24hrs. soaking have values of 27%, 27%, 31%, and 52% for crude, 1 M, 3 M and 5 M respectively, and 48 hrs. soaking

have values of 21%, 29%, 26%, and 44% for crude, 1 M, 3 M and 5M citric acid concentration respectively.

The unsoaked. Clarity of starch has a direct relationship with the concentration of citric acid treatment. From the result obtained, % paste clarity increases with the concentration of citric acid lintnerization. This was also reported by KarmvIr *et al.*, (2018). In his findings; chemical modification improves paste clarity of starch. Clarity characteristics of starches are dependent on the botanical

source of starch and the overall purity of the starch in case of cereal starches. However, paste clarity of starch is also influenced by the amylose and amylopectin content especially in cereal starches (Ogunmolasuyi *et al.*, 2016). To improve paste clarity of starch, chemical modification is usually a solution according to Zhang *et al.*, (2005). In this present study, starch clarity was achieved with citric acid modification and there was corresponding rise in clarity as the concentration of citric acid increases.

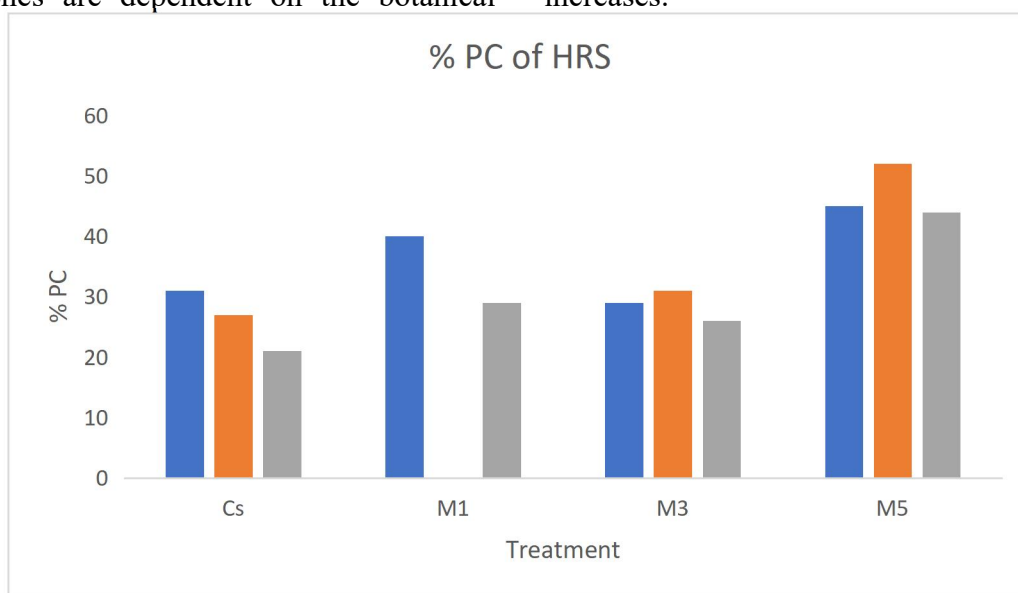


Figure 4. % PC of Hungry Rice Starch

Degree of Substitution

The degree of substitution (DS) of the lintnerized hungry rice starches under study was presented in Figure 4.16. The values for the degree of substitution ranges between 0.5427, 0.7047 and 0.7817 for 1M, 3M and 5M concentration of citric acid respectively. From the results obtained, it was discovered that the degree of substitution increases with increase in citric acid concentration. This is similar to the result presented by Kalu *et al.*, (2022) and Dastidar and Netraevali 2012. The DS of a starch is defined as the number of hydroxyl

groups substituted per d-glucopyranosyl ring (Dastidar and Netraevali 2012)). Since each ring possesses three hydroxyl groups, the maximum DS possible is 3. However, the primary hydroxyl group (C-6) is much more reactive than the two secondary hydroxyl groups (C-2 and C-3) due to steric hindrance (Mathew & Abraham, 2007). The DS is affected by various factors like source of starch, amylose and amylopectin content, reactant concentration, reaction time and temperature (Mathew & Abraham, 2007; Xu, Miladinov, & Hanna, 2004; Zhu, Zhang, &

Lai, 2007). Also, the DS is dependent on the extent of modification of starch which is

dependent on the end-user's applications.

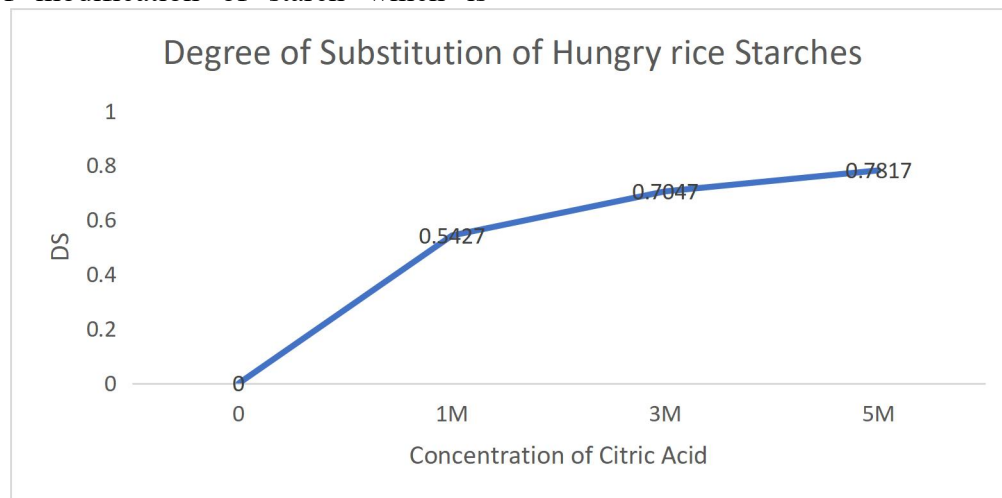


Figure 5. Degree of Substitution of Hungry Rice starches

FTIR Spectroscopy

The FTIR spectra of the crude and lintnerized starches are presented in table 2. From the FTIR spectra, it can be observed that all the crude starches have four specific absorption peaks; A broad peaks at 3385, 3302 3298 and 3300 cm^{-1} indicated the presence of a hydroxyl group in starch. (Na et al., 2021). while the aliphatic C–H stretch is observed as a sharp peak at 2929, 2827, 2933 and 2927, cm^{-1} (Dastidar and Netravali, 2012). The peak at 1636 cm^{-1} is assigned to the water adsorbed by starch molecules. and the peaks at 997 and 995 cm^{-1} are attributed to the glucopyranose ring C–O stretching vibrations. (Figure 6). Lintnerized starches have a disappearing band C–OH stretching absorption peaks at 3302 cm^{-1} , and an additional band at 1723 cm^{-1} (Figure 7) which is attributed to the C=O stretch of conjugated ester, another peak at 1220 cm^{-1} attributed to C–O–C stretch of ester (Dastidar and Netravali, 2012). The broad peak at 2117, 2089 cm^{-1} is attributed to the stretching of hydrogen bonded hydroxyl groups. Hydroxyl, O–H, deformations and C–O stretching modes

show peaks at 1420, 1388 cm^{-1} and 1340, 1302 cm^{-1} , respectively.

On comparing the spectra of crude and lintnerized starches, shown in figure 6 to figure 9), the presence of ester bond can be confirmed by the presence of carbonyl (C=O) peak in all the lintnerized starches that is observed at 1725, 1727 cm^{-1} . It was further noticed that the carbonyl stretching peak for lintnerized starches appeared at 1664 cm^{-1} . These results are similar to those observed by Sauperl and Stana-Kleinschek (2010) in which the carbonyl peak for unreacted 1,2,3,4-butanetetracarboxylic acid appeared at 1701 cm^{-1} and shifted to 1725 cm^{-1} after ester formation (Sauperl & Stana-Kleinschek, 2010; Yang, Lu, & Lickfield, 2002). Mathew and Abraham (2007) in Dastidar and Netravali, (2012) reported the esterification of crude starch with citric acid which showed the presence of carbonyl peak in the FTIR spectrum at around 1727 cm^{-1} which was absent in the FTIR spectra of the crude starches.

Table 2. FTIR Result for Crude and Lintnerized starches

Sample	Observed Peak	Interpretation
Crude	3265, 3267, 3280	O-H stretch of alcohols (broad band)
	2924, 2927, 2927	C-H stretch of aliphatic ring
	1418, 1638, 1653	C=C stretch
	997, 995, 997	C-O stretch of polysaccharide ring
1M	3293, 3298	O-H stretch of alcohols (narrow)
	2927, 2927	C-H stretch of aliphatic ring
	1725, 1727	C=O stretch of conjugated ester
	1220, 120	C-O-C stretch of ester
3 M	1149, 1149	C-O stretch of polysaccharides/starch
	997, 997	C-O stretch of polysaccharide ring
	3298, 3296	O-H stretch of alcohols
	,2822	C-H stretch of aliphatic ring
5 M	1727, 1723	C=O stretch of conjugated ester
	997	C-O stretch
	3300,	O-H stretch of alcohols
	2924	C-H stretch of aliphatic ring
5 M	1727	C=O stretch of conjugated ester
	1220	C-O-C stretch of ester
	995	C-O stretch

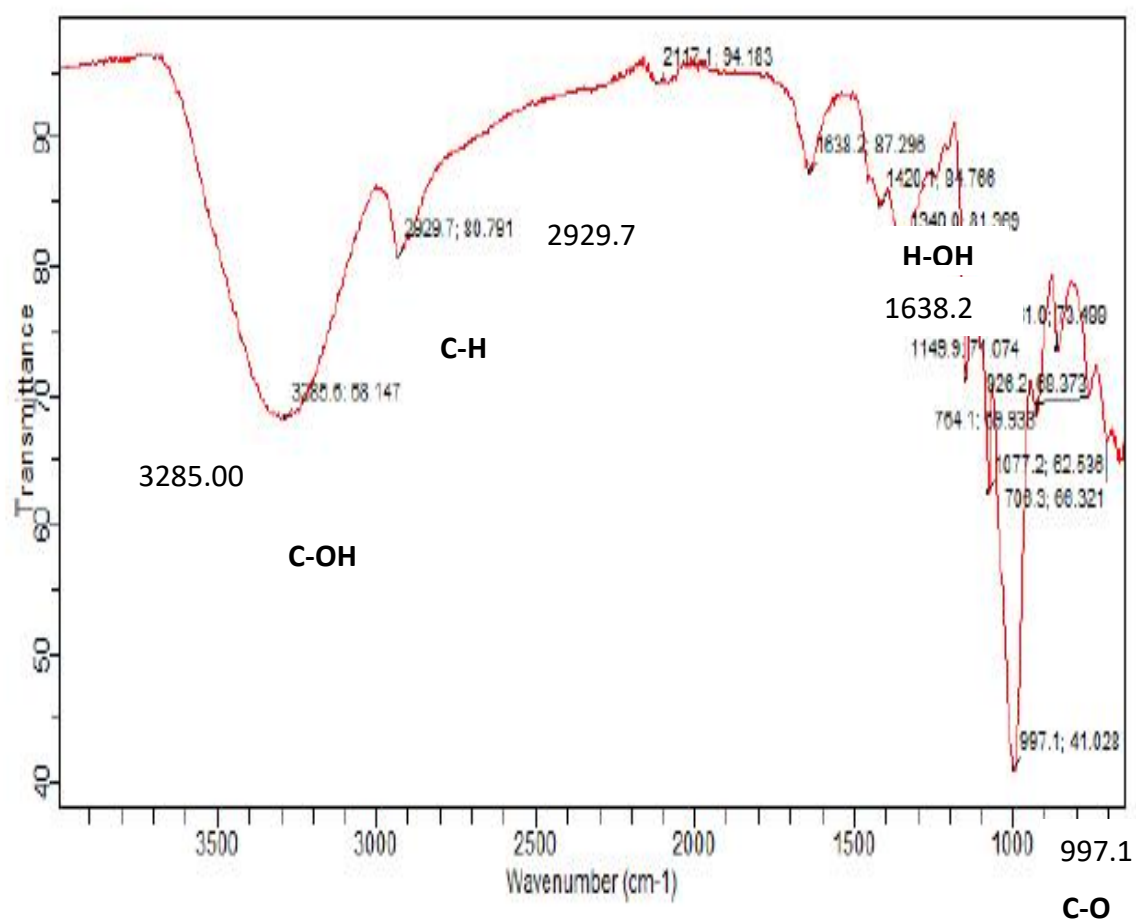


Figure 6. FTIR spectra of crude starch

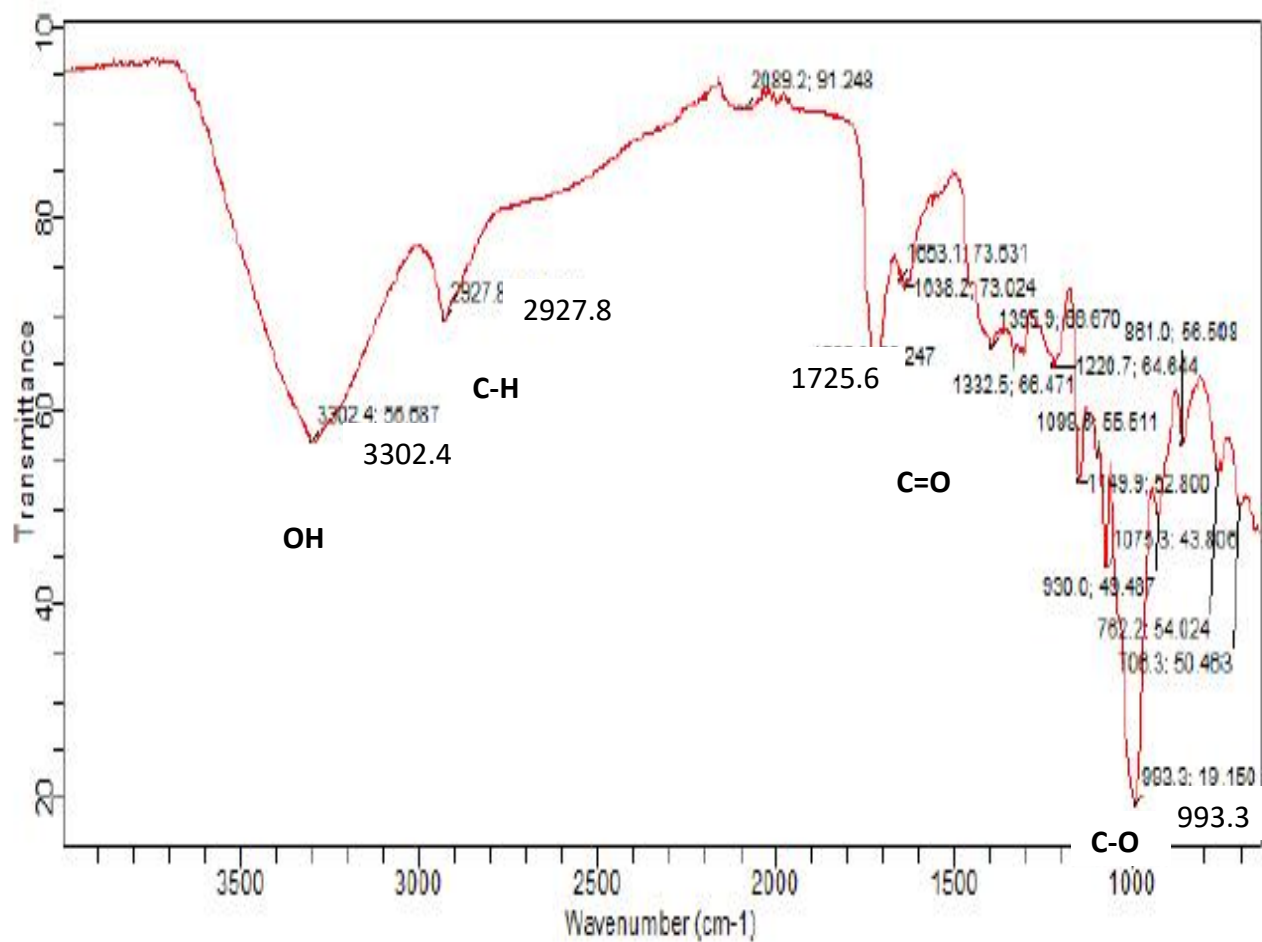


Figure 7. FTIR spectra of 1 M lintnerized starch

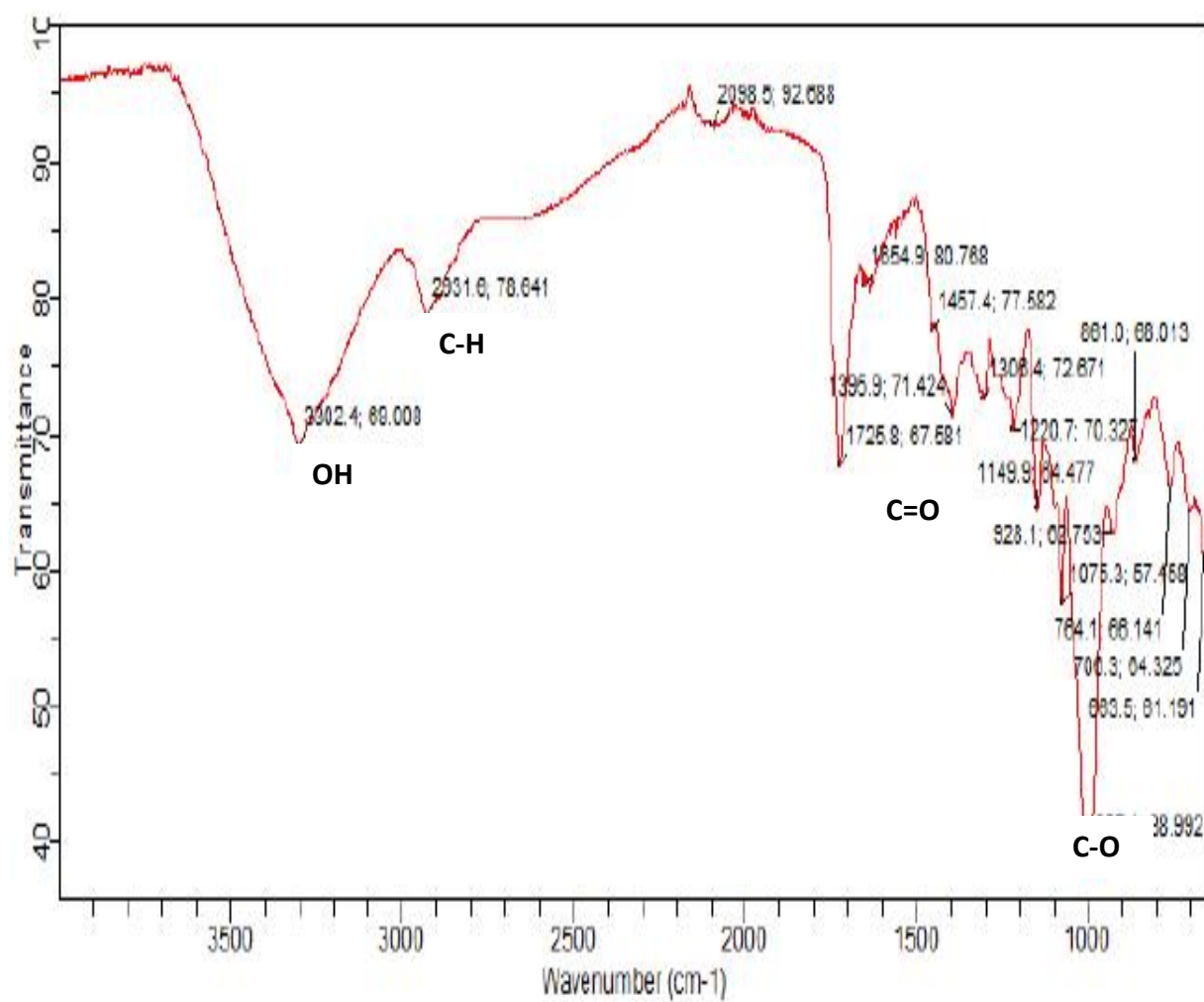


Figure 8. FTIR spectra of 3 M lintnerized starch

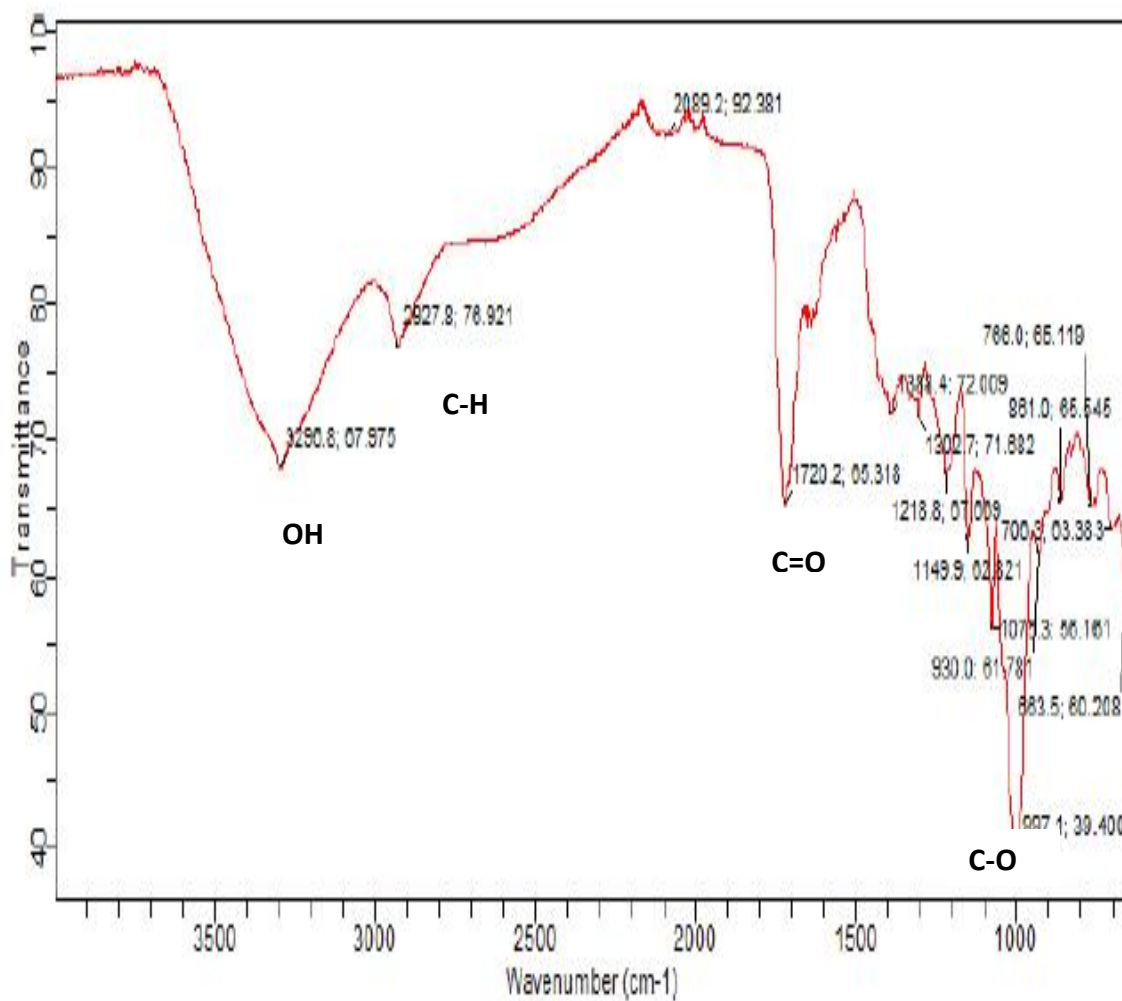


Figure 9. FTIR spectra of 5 M lintnerized starch

Thermogravimetry Analysis

The thermal decomposition of crude and lintnerized starches is presented in table 3. Initially, there was slight weight loss at 30-120 °C which was associated with evaporation of physically bond and absorbed water (Ali et al., 2023). The main degradation occurs at 200-350°C which was associated with the thermal scission of the starch molecule, corresponding to the breakdown of the starch polymer,

dehydration of the hydroxyl groups and depolymerization of glucose chains. Beyond 350°C, only a small decrease is observed, which signifying carbonization and structural reorganization of the starch molecule into a thermally stable carbon residue.

The result of the analysis shows that crude starches manifest excellent thermal stability, with minimal weight loss. While the lintnerized starches show higher total weight

loss and lower final residue. This can be attributed to the fact that citric acid treatment purifies the starch by removing non-starch components and breakdown less crystalline

regions, making the final cleaner (less inorganic ash) and making the degradation step more complete.

Table 3. Thermal Decomposition of crude and Lintnerized starches

S/N	Sample	Initial Weight loss (%) - Moisture	Stage II loss (%) - Pyrolysis	Stage III loss (%) - Carbonization	Total Weight loss (%)	Residual weight (%)
1.	U-Cs-OFSPS	2.0	82.9	3.4	88.4	11.6
2.	S ₂₄ -Cs-OFSPS	3.0	80.5	5.5	89.0	11.0
3.	S ₄₈ -Cs-OFSPS	4.0	84.0	3.0	91.0	9.0
4.	U-M ₅ -CFSPS	2.0	83.0	7.0	92.0	8.0
5.	U-Cs-HRS	2.0	80.0	7.0	89.0	11.0
6.	U-M ₁ -HRS	4.0	72.0	12.0	88.0	12.0
7.	U-M ₅ -HRS	4.0	82.0	5.0	91.0	9.0

HRS = hungry rice starch.

The 1 M Lintnerized samples exhibit a significantly higher initial weight loss (up to 11.4% for U-M₁-HRS). this indicates a substantial increase in the absorbed moisture or highly volatile compounds, suggesting that lintnerization process cause the material to be more hydrophilic and modifies the structural orientation of the starch.

Scan Electron Microscope (SEM) Analysis

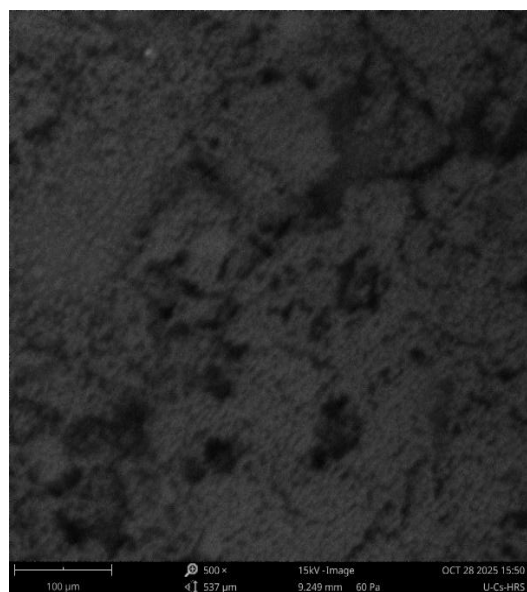
The SEM micrographs of crude and lintnerized starches as shown in Figure 10. The micrographs showed that the lintnerization process results into significant surface breakdown, rearrangement and aggregation of molecules in the morphology of lintnerized starches. The presence of cracks on the surfaces of all the lintnerized starches could be observed as the surfaces appear rougher than the crude starches. The M₁ lintnerized starches could be observed to be very smooth, continuous, featureless surfaces with linear pattern which serves as a near-

amorphous background. A significant shift in morphology occurs at the M₅ concentration, suggesting that a threshold was crossed where the acid's effect changed from localized aggregation to widespread structural breakdown and re-formation. The 3 M and 5 M starches appear to be more tightly packed and uniformly distributed as compared to the 1 M starch and crude starch. The presence of higher number of crosslinks (as observed from the higher lintnerized) could contribute to the tightly packed but uniform conformation. High concentration of citric acid causes rapid and extensive hydrolysis (breaking the starch chains) followed by intensive cross-linking and esterification (forming new bonds) upon drying.

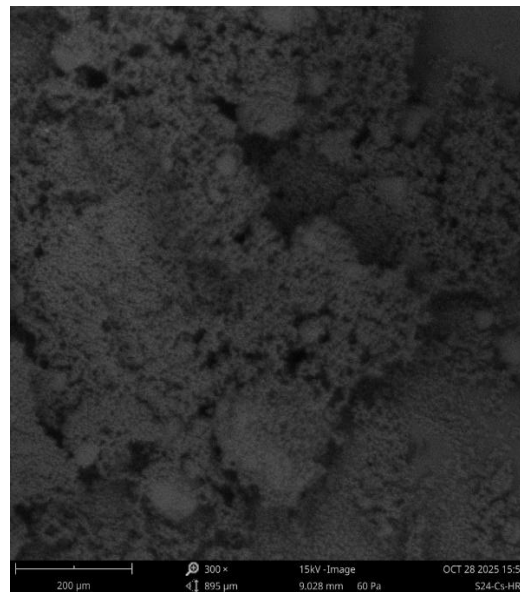
Comparing the S₂₄ and S₄₈ samples at the same concentration reveals the progression of the lintnerization reaction over time. Increasing soaking time (S₂₄ and S₄₈) Promotes particle growth and macro-

aggregation (clustering into larger spheres) at low and medium citric acid concentrations. Suggests slow, continuous rearrangement/cross-linking of partially lintnerized starch molecules. Increasing citric concentration (M3 and M5) Causes a dramatic switch from large aggregates to a fine, uniform, granular network which Indicates a shift from partial hydrolysis / aggregation to extensive hydrolysis and uniform cross-linking /re-precipitation of low molecular weight starch chains. The study demonstrates that citric acid concentration is a key factor controlling the final particle texture (aggregated spheres as against fine granular matrix), while soaking time influences the degree of coarseness and aggregation of starch morphology. The SEM results in this study are

similar to other reports including the cracks on the surface lining of citric acid crosslinked tapioca starch reported by Utomo et al., 2020 and the irregular shaped morphology of corn starch granules after crosslinking reported by Sudhakara and Parimalavalli, 2019. while another study observed that Cyperus starches appeared more uniform after crosslinking (Olayemi et al., 2021). Kalu et al., 2022 also reported that morphology of native starch is quite different from that of modified starches The micrographs show that the citric acid lintnerization had higher effect on the morphology of cream flesh sweet potato and hungry rice starches which further suggests that it might be better suitable for lintnerized starches for industrial applications.



U-Cs-HRS



S₂₄-Cs-HRS

Figure 4.24. SEM Images of Crude and Lintnerized Hungry Rice Starches

CONCLUSION

This study revealed significant changes in the physicochemical, functional properties as well

as structure of the crude and lintnerized starches from hungry rice. The effect of

pretreatment on the citric acid lintnerization was observed on the physicochemical properties. FTIR spectroscopy analysis also showed that there are substantial structural differences between the crude and lintnerized starches confirming esterification through the appearance of carbonyl and ester peaks. SEM revealed structural disruption of granules. The dua stage modification techniques have significant effect on functional and structural properties like water holding capacity, swelling power, Paste clarity of hungry rice starch. This proffers a promising balance of functional properties, positioning hungry rice starch as a viable gluten-free alternative in food industries.

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