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Synthesis and characterization of nitrostarch from jackfruit seed starch, a renewable energy source

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Abstract

The development of sustainable energetic materials is a huge challenge in propellant and pyrotechnic research. Conventional oxidizers such as nitrocellulose and perchlorates, are effective but create environmental and safety concerns [1]. Starch offers a natural and renewable alternative that can be chemically modified to form energetic derivatives. In this work starch was isolated from jackfruit seed (Artocarpus heterophyllus) an abundant and underutilized agricultural byproduct, and converted into nitrated starch using concentrated nitric acid and concentrated sulfuric acid at low temperature (0-5 ^{0}C). The product was washed with ice cold water, neutralized with sodium bicarbonate and recrystallized from ethyl acetate to obtain the purified compound. Nitration was confirmed by color tests, like diphenylamine test and diazotization test. Structural analysis was performed using Fourier Transform Infrared spectroscopy (FTIR) and Liquid chromatography-mass spectroscopy (LC-MS). The nitrated starch showed rapid burning, indicating its energetic behavior. These results demonstrate that jackfruit seed starch can be successfully modified into an energetic biopolymer. This study highlights the possibility of converting jackfruit seed starch into a nitrated derivative, establishing a foundation for future investigations into renewable nitrate-based materials.

Keywords: Jackfruit seed starch, nitrated starch, energetic material, bio- mass derivative, oxygen rich polymer

Introduction

Energetic materials are substances capable of rapidly releasing stored chemical energy in the form of heat, gas and pressure. They form the backbone of propellants, explosives and pyrotechnics with applications in military, space exploration, mining, and civilian uses such as firework and safety devices [2, 3]. A critical component of this formulation is the oxidizer, which provides the oxygen necessary for fuel combustion in environments where atmospheric oxygen is unavailable, such as in rockets engines or underwater systems. The efficiency of oxidizer is evaluated in terms of oxygen balance, heat of formation, decomposition pathway, thermal stability and environmental impact [4].

Historically inorganic oxidizers such as ammonium perchlorate (NH_4ClO_4) ammonium nitrate (NH_4NO_3), potassium chlorate ($KClO_3$) and potassium nitrate (KNO_3) have been employed extensively [5]. Ammonium perchlorate has dominated the field due to its high oxygen content and favorable decomposition profile. However, its combustion releases hydrochloric acid (HCl) and chlorine-containing species that are corrosive, toxic and ozone -depleting. Ammonium nitrate though less harmful environmentally, suffers from hygroscopicity and accidental detonation hazards, limiting its reliability [6]. These drawbacks have simulated a global research effort towards the development of green oxidizers. -alternatives that are high-performing, safer and less harmful to the environment. Such as Ammonium dinitride (ADN) and Hydrazinium Nitroformate (HNF), which decompose into mostly nitrogen, and oxygen and water. However, their cost of synthesis and limited scalability continue to restrict widespread adaptation [7].

One of the most promising strategies to overcome these limitations lies in renewable, biomass-derived energetic materials, particularly those based on polysaccharides. Cellulose and starch the two most abundant bio polymers in nature, they are attractive feedstocks due to their abundance biodegradability and molecular structures rich in reactive hydroxyl groups. Chemical modification of polysaccharides especially nitration has long been recognized as a mean to convert these natural polymers into energetic materials [8].

The most classical and successful example is nitrocellulose (also called guncotton), first discovered in the 19th century. Nitrocellulose revolutionized the field of propellants by providing a smokeless, renewable, and highly energetic alternative to black powder [9, 10]. The study of nitrocellulose provides a benchmark for exploring nitrated derivatives of other polysaccharides such as starch.

Starch differs from cellulose in being composed of two structurally distinct polysaccharides: amylose (a mostly linear polymer of α-1,4 linked D-glucose units) and amylopectin (a highly branched polymer with $\alpha -$1,4 and $\alpha - 1{,}6$ linkages).The ratio of amylose to amylopectin varies depending on botanical source and this ratio governs many physiochemical properties of starch, including granule morphology, solubility, swelling power and reactivity. Upon nitration starch's hydroxyl groups (OH) converted to nitro groups ($-ONO_2$), leading to enhanced oxygen content and energetic behavior. Prior studies on potato starch, maize starch, cassava starch and corn starch have confirmed the feasibility of starch nitration and reported promising results in terms of oxygen balance and combustion [11]. However, the field remains relatively underexplored compared to cellulose.

A Particularly interesting and underutilized starch is jackfruit seed starch (Artocarpus heterophyllus). Jackfruit is widely cultivated in tropical and subtropical regions, particularly in India, Bangladesh Sri Lanka and parts of south east Asia. While the fruit is widely consumed, but the seeds are often discarded as agriculture waste. These seeds contain 18-25% starch by dry weight, making them a valuable yet underutilized biomass resource [12]. Several studies have reported that jackfruit seed starch exhibits unique physiochemical properties such as: -

- Higher amylopectin content compared to maize and starch

- Distinct polygonal or oval granule morphology with smooth surface.
- Higher gelatinization temperature more than (260 °C), indicating stronger intermolecular bonding.
- Phosphorous-containing compounds naturally embedded, which may alter its chemical reactivity [13, 14, 15]

These characteristics suggest that jackfruit seed starch could behave differently during nitration compared to conventional starches, potentially producing nitrated products with unique energetic and combustion properties. Making use of jackfruit seed starch for energetic applications not only reduces agriculture waste but also aligns with the sustainability and circular economy.

In the present study, jackfruit seed starch was extracted, purified and nitrated using concentrated Nitric acid (HNO_3) and concentrated Sulfuric acid (H_2SO_4) in the ratio of 1:3. The reaction was carefully controlled under constant stirring and cooling to prevent uncontrolled degradation. The nitrated product was neutralized using sodium bicarbonate ($NaHCO_3$) to remove residual acidity and stabilize the product. For enhanced purity and crystallinity, recrystallization was performed using ethyl acetate, yielding a refined nitrated starch suitable for characterization [16].

To confirm the nitration, both classical qualitative tests and modern analytical techniques were employed. The diphenylamine test is used to detect nitrate groups by formation of a characteristic blue-green color· diazotization-coupling test with β-naphthol (also referred to as the Azo Dye Test) formation of dark green dye formation which confirms the presence of nitro group [17,18]. And also, modern analytical instrumental techniques like Fourier Transform Infrared spectroscopy (FTIR) to identify nitro functional group, while Liquid chromatography Mass spectroscopy (LC-MS) which provides the information on molecular weight distribution and substitution pattern. These methods together provide strong evidence for successful nitration of jackfruit seed starch.

In addition to spectroscopic and spectrometric characterization, the combustion behavior of nitrated starches is an important parameter in evaluating their suitability as energetic binders or oxidizers. Nitrated jackfruit seed starch, when subjected to a flame exhibits a rapid combustion with a bright flame and minimum residue, resembling the combustion pattern of classical nitrocellulose. This preliminary burning observation supports its potential role as a renewable energetic material.

This study thus contributes not only to the field of renewable energetic materials but also to the broader goal of designing high-performance propellants that balance efficiency, safety and environmental responsibility.

Materials and Method

1. Chemicals and Reagents

Concentrated Nitric acid LR (HNO_3,69-72%), Concentrated Sulfuric acid AR (H_2SO_4,98%), Sodium bicarbonate anhydrous LR ($NaHCO_3$) and Ethyl acetate AR ($C_4H_8O_2$) were used without further purification. Distilled water is used for washing and neutralization steps.

For the confirmation tests, Diphenylamine LR ($C_{12}H_{11}N$), Hydrochloric acid LR (HCL), 2-Naphthol LR ($C_{10}H_8O$), Sodium nitrite purified LR ($NaNO_2$), Sodium hydroxide flakes LR (NaOH), Tin granules were. used. which were all supplied by the s d fine chem Limited (Mumbai, India).

2. Isolation of Jackfruit Seed Starch

Fresh jackfruit (Artocarpus heterophyllus) seeds were collected from local sources. The seeds were peeled, washed thoroughly and cut into small pieces. These small pieces were grinded into a slurry. The slurry was filtered through muslin cloth and the filtrate was allowed to sediment for 6 hours. The settled starch was repeatedly washed with distilled water until the supernatant became clear. The starch was then air-dried at room temperature and stored in an air-tight container [19, 20, 21].

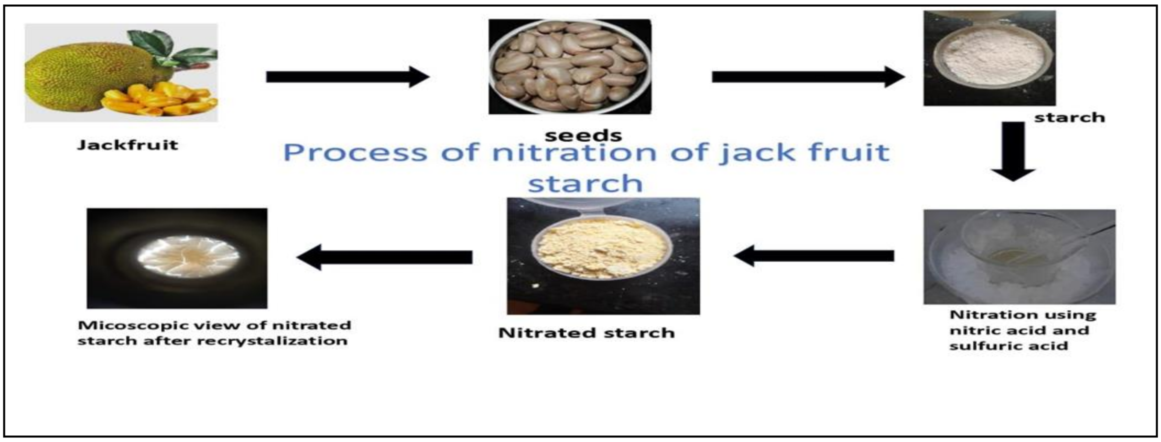
Nitration of Jackfruit Seed Starch

About 5.0 g of dried jackfruit seed starch was taken in a 250 ml beaker placed in an ice bath

(0-5 ^{0}C). To this 20 ml of concentrated nitric acid (HNO_3, 69-72%) was added gradually with constant stirring. Subsequently,30 ml of concentrated sulfuric acid (H_2SO_4, 98%) was added slowly maintaining the temperature 5 ^{0}C. The mixture is stirred for 30 minutes to ensure complete nitration. After completion of reaction the mixture was poured into ice cold water with constant stirring to quench residual acidity and recover the nitrated starch as a precipitate [16].

3. Neutralization and Purification

The crude nitrated product was filtered and washed thoroughly with chilled distilled water. It was then neutralized using sodium bicarbonate ($NaHCO_3$) solution until effervescence ceased, ensuring removal of residual acid. The neutralized product was again washed with distilled water and air dried. Recrystallization was done using ethyl acetate as solvent to obtain nitrated starch with improved stability. The purified material was stored in airtight container for further analysis.



Results and Discusions

1. Physical Appearance and Yield

The nitration of jackfruit seed starch produced 9.18 g pale yellow crystals after washing, neutralization and recrystallization. The product was brittle and slightly hydroscopic and soluble in polar organic solvent. Such as ethyl acetate. Recrystallization improved homogeneity and reduced colored impurities. Visual comparison with native jackfruit starch indicates a noticeable change in color and texture, suggesting successful chemical modification.

2. Qualitative Chemical Tests

Diphenylamine Test: A small sample of the nitrated jackfruit seed starch reacted with diphenylamine reagent and formed a green precipitate confirming the presence of nitrated group [18].

Diazotization Test: Treatment with diazotizing reagent yielded a green dye supporting the introduction of nitro functionalities [17].

3. Ftir Analysis

FTIR Spectrum of nitrated jackfruit seed starch showed a broad band at 3425.23 cm^{-1},1.44A (O-H stretching), reduced compared to native starch, indicating substitution by nitro groups. Strong new absorptions at 1650.57cm^{-1},2.1A NO_2 asymmetric stretch. 1429.87cm $^{-1}$, o.94A and 1383.75CM^{-1},1.08A NO_2 symmetric stretch, and 1281.10 cm^{-1},2.21A N-O stretch confirmed successful nitration. Peaks at 1155.21cm^{-1},1.28A to1010.71cm^{-1},1.64A indicated glycosidic C-O-C linkage [21,22]. The overall spectral features clearly demonstrate the incorporation of nitrate groups into the jackfruit seed starch.

4. Lc-Ms Analysis

The LC–MS spectrum of nitrated jackfruit seed starch displayed a dominant peak at m/z 333.5247, which corresponds to the potassium adduct [M+K] $^+$ of a nitrate starch fragment. The formation of such adducts is typical in carbohydrate mass spectrometry, as hydroxyl and nitrate groups exhibit strong affinity toward alkali metal ions such as Na^+ and K^+[23,24]. Potassium adduct formation has frequently been reported in polysaccharides due to multiple coordination sites, resulting in [M+K] $^+$ peaks that are more stable than protonated species [25, 26].

It should be noted that starch is a high-molecular-weight biopolymer composed of amylose and amylopectin, with varying degrees of polymerization; therefore, its exact molecular mass cannot be calculated. Instead, LC–MS analysis provides evidence through fragment ions and them adducts. The experimental m/z obtained in this study closely matched the calculated potassium adduct of the nitrated fragment, thereby confirming the successful incorporation of nitrate groups into the starch backbone [27].

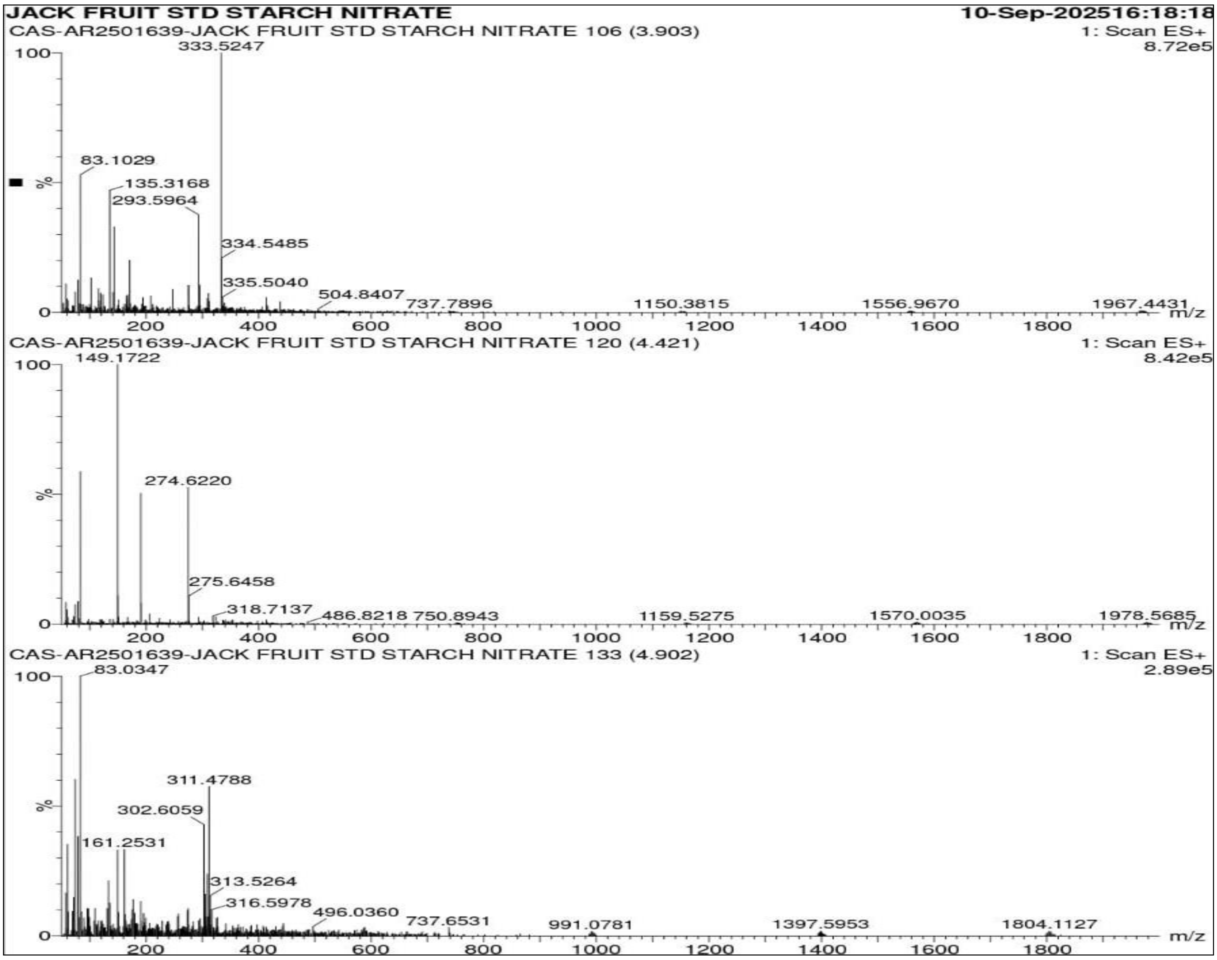


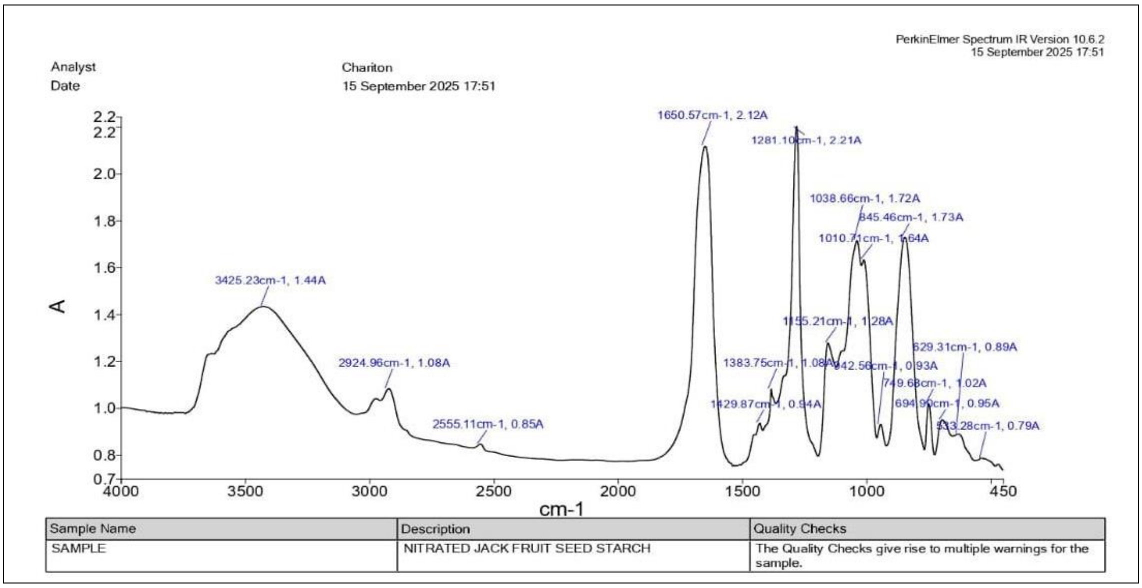
Fig 2: LC-MS Spectroscopy of nitrated jackfruit seed starch

5. Combustion Test

Controlled small-scale burning of the nitrated starch revealed rapid flame with minimum residue. The enhanced combustion behavior. Suggests the introduction of nitrate groups increased the starches oxygen content and energetic potential [28, 29].

6. Overall Discussion

The qualitative chemical tests, FTIR, LCMS and combustion observations confirms the successful nitration of jackfruit seed starch. The isolated product demonstrates that jackfruit seed starch can be converted into a nitrated derivative with preliminary energetic characteristics.



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Analyst Chariton
Date 15 September 2025 17:51

Sample Name	Description	Quality Checks
SAMPLE	NITRATED JACK FRUIT SEED STARCH	The Quality Checks give rise to multiple warnings for the sample.

Fig1: FTIR spectroscopy of nitrated jackfruit starch

Conclusion

This study demonstrates the successful nitration of jackfruit seed starch using an acid system. These findings suggest that jackfruit seed starch, a renewable biomaterial, can be converted into nitrated derivative with energetic characteristics, providing a foundation for future studies on starch-based nitrate esters.

Conflict of Interest

The authors declare that there is no conflict of interest regarding the publication of this research work

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