

UTILIZATION OF MURUMURU RESIDUES FOR SULFONATED BIOCHAR IN VANILLIN SYNTHESIS

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ABSTRACT

Murumuru is an Amazonian fruit primarily valued for its butter, used in the cosmetic industry. The shells, constituting over half of the seed's weight, become agro-industrial waste once the almonds are extracted. Utilizing residual lignocellulosic biomass as precursors for acidic catalysts can reduce synthesis costs and provide beneficial characteristics like thermal stability, high porosity, and large surface area. This study aims to enhance catalytic reactions by anchoring active sites to the support to increase surface acidity. Sulfonic groups were employed on biochar supports from murumuru seed shells using concentrated sulfuric acid. The catalytic activity of sulfonated biochars was tested by oxidizing vanillyl alcohol to vanillin, a key flavoring agent widely used in the food, cosmetic, and pharmaceutical industries. Characterizations revealed that the synthesized catalyst contained sulfur and oxygen, indicating effective sulfonic group impregnation, and exhibited a surface acidity of $2.29 \text{ mmol H}^+\text{g}^{-1}$. The tests demonstrated excellent catalytic activity, achieving 100% conversion of the initial reagent in the first two reaction cycles, confirming its heterogeneous nature. Additional characterizations and further tests reducing reaction time are recommended to enhance conversion and selectivity for vanillin. This catalyst shows significant potential for use in acidic catalytic reactions, offering a sustainable alternative for vanillin synthesis.

Keywords: Murumuru residues. Biochar. Biorefinery. Heterogeneous catalyst. Vanillin synthesis.

1 INTRODUCTION

Murumuru is an Amazonian fruit, and its commercial value is primarily linked to the butter extracted from the almonds contained in the seeds, for application in the cosmetic industry¹. The shells represent a little more than half of the weight of the murumuru seeds and, after the almonds are removed, they become an agro-industrial waste². Residual lignocellulosic biomass as precursors for acidic catalysts are already widely used in the literature and, in addition to reducing synthesis costs, they can present beneficial characteristics derived from charcoal, such as good thermal stability, high porosity, and large surface area³. To enhance catalytic reactions, active sites are anchored to the support to increase surface acidity⁴. This study employs sulfonic groups on biochar supports from murumuru seed shells using concentrated sulfuric acid to optimize the reaction. The catalytic activity of sulfonated biochars was tested by oxidizing vanillyl alcohol to vanillin. Vanillin is the main component responsible for the aroma and taste of vanilla. Due to this, it is one of the most commercially used flavoring agents, being applied in various sectors such as the food, cosmetic, and pharmaceutical industries, among others². Studies on the vanillin molecule expand its applications, such as its use as a building block in polymers⁵. Therefore, it is expected that by 2025 the global vanillin market will reach \$724.5 million⁶. Heterogeneous catalysts, especially those derived from agro-industrial waste, present a promising, sustainable alternative for vanillin synthesis.

2 MATERIAL & METHODS

The preparation of the catalyst followed the procedure described by Corrêa *et al.* (3). Murumuru shells were crushed and passed through a 35-mesh sieve. The carbonization process took place in a tubular furnace at a temperature of 600 °C for 1 hour, with a heating rate of $10 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$ and an N_2 flow of $80 \text{ mL}\cdot\text{min}^{-1}$. The obtained biochar was sulfonated in a reflux system with concentrated sulfuric acid at a ratio of 1:10 w/v (biochar/acid) for 4 hours at a temperature of 200 °C. After this process, the content was diluted in 1 L of distilled water to reduce risks and then subjected to vacuum filtration. The biochar was washed with distilled water until the wash water reached a pH close to 7 and then dried in an oven at 110 °C. The catalyst characterizations were performed using energy dispersive spectroscopy (EDS) analyses, and the surface acidity of the samples was measured through acid-base back titration⁷.

The catalytic tests were conducted according to the method described by Saberi *et al.*⁸. A mixture of 0.77 g of vanillyl alcohol, 8 mL of acetonitrile, 1.2 mL of 50% H_2O_2 , and 0.1 g of catalyst, previously dried at 110 °C, was added to a reflux system for 1 hour at a temperature of 80 °C. Three reuse reactions of the catalyst were performed along with one blank test without the presence of the catalyst, following the same proportions. To evaluate the conversion percentage of vanillyl alcohol to vanillin, the reaction products were analyzed by Gas Chromatography with Flame Ionization Detector (GC-FID).

3 RESULTS & DISCUSSION

Energy Dispersive Spectroscopy (EDS) analysis was used to determine the elemental composition of the samples (Table 1). The biochar exhibited a characteristic composition of carbonaceous materials, with a predominant concentration of 87% carbon, resulting from the pyrolysis process, along with other common elements for this type of material. In the elemental composition of the catalyst, the appearance of sulfur, at 5.1%, is notable. Higher levels of oxygen were also observed, which can be mainly attributed to the sulfonic groups anchored to the material, as well as the carboxylic groups generated after sulfonation. In the catalyst obtained after the fourth reaction cycle, a decrease in the initial sulfur content from 5% to 1% can be observed, indicating a loss of catalyst efficiency due to the leaching of sulfonic groups from the material.

Table 1 Elemental Composition by EDS of the biochar and catalyst samples.

Sample	Elementary Composition				
	C	O	Si	Ca	S
Biochar	81.0	18.3	0.5	--	--
Catalyst	68.6	25.0	0.3	0.4	5.1
Catalyst - Cycle 4	72.4	25.8	0.2	0.3	1.0

Figure 1 shows the obtained surface acidity indices. The catalyst exhibited an acidity of 2.29 mmol H⁺ g⁻¹, a value higher than the acidity found in biochar, indicating that sulfonation indeed occurred. However, this value differs from the indices found in similar synthesis methodologies, where values of 4.19 mmol H⁺ g⁻¹ were observed for biochar sulfonated with sulfuric acid used in esterification reactions⁷. Nonetheless, the surface acidity found in catalyst proved effective for application in the oxidation reactions of vanillyl alcohol to vanillin.

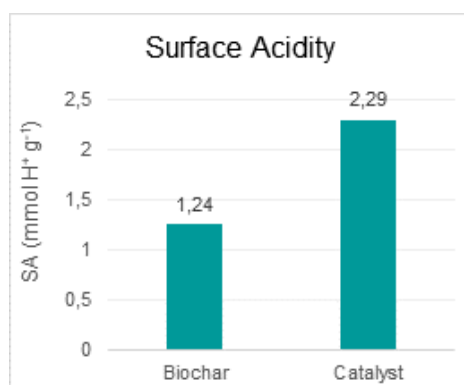


Figure 1 Surface acidity of the biochar and catalyst samples.

In the results of the GC-FID analysis, described in Figure 2, it can be observed that in the blank reaction the conversion of vanillyl alcohol to vanillin was 17.97% and the selectivity was 52.10%. The first reaction using the catalyst (cycle 1) shows a conversion and selectivity of 11.88%, both results lower than those obtained in the blank reactions. However, in Figure 3, it is possible to verify that vanillyl alcohol was completely converted in the reaction using the catalyst, while in the blank reaction only 34.49% of the reagent was converted. This indicates that vanillyl alcohol may have been converted to vanillin, but upon remaining in contact with the hydrogen peroxide present in the solution, the vanillin may have been further oxidized to methoxy hydroquinone. This phenomenon is referred to as vanillin superoxidation⁹, and the concentration of this byproduct identified in the first reaction by GC-FID, at 31.07%, supports the hypothesis.

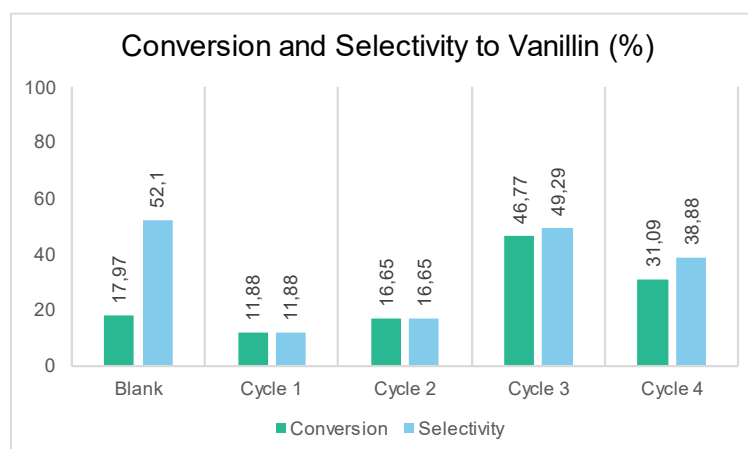


Figure 2 Percentage conversion and selectivity to vanillin in each reaction.

Another indicative factor of vanillin superoxidation is observed in figure 2, where the conversion to vanillin in cycle 4, where the catalyst is in its third reuse, is higher than that observed in the first cycle of catalyst use. This suggests that, with the loss of catalyst efficiency (observed in Figure 3 with the decline in the conversion of the initial reagent after the reactions), the catalyst converted vanillyl alcohol to vanillin more slowly than in the previous reactions, resulting in a shorter contact time of the produced

vanillin with hydrogen peroxide, consequently reducing superoxidation and achieving a higher conversion than in the first reaction cycle. The precursor vanillyl alcohol conversion results found in figure 3 corroborate with the results obtained by EDS, which indicate the leaching of sulfonic groups after the reactions and imply a reduction in catalyst efficiency.

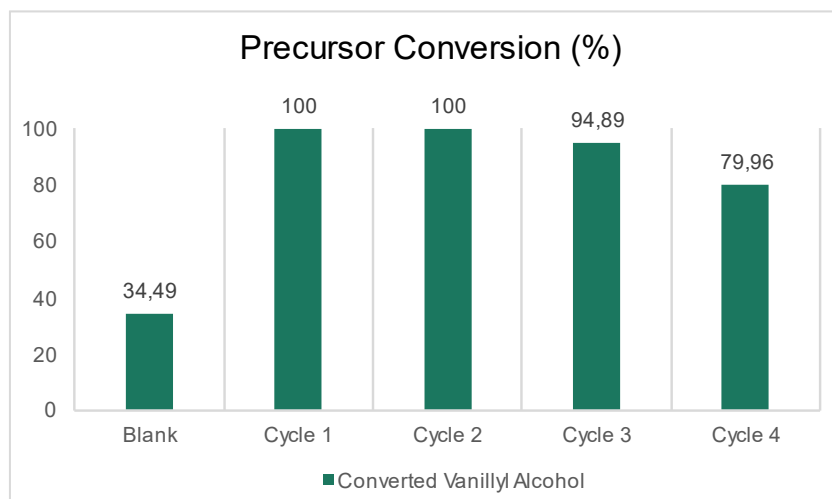


Figure 3 Percentage of vanillyl alcohol (starting reagent) converted during catalytic testing.

4 CONCLUSION

The characterizations performed indicated that the synthesized catalyst exhibited sulfur and oxygen content, demonstrating effective impregnation of sulfonic groups, as well as a surface acidity of $2.29 \text{ mmol H}^+\text{g}^{-1}$. The tests showed excellent catalytic activity, converting 100% of the initial reagent in the first two reaction cycles, confirming its heterogeneous nature. Additional characterizations of the catalyst and further tests reducing the reaction time should be conducted to achieve higher conversion and selectivity results for vanillin. Therefore, this catalyst shows great potential for use in acidic catalytic reactions.

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