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Article

Fast Catalytic Pyrolysis of Tamarind Pulp over Green HZSM-5 Zeolite

Dirléia dos Santos Lima ¹, Lucas Capello ^{1,2,*}, Manuela de Santana Santos ³
and Maria do Carmo Rangel ^{3,*}

¹ Chemical Engineering Department, University of Rio Grande do Sul, Porto Alegre, Brazil

² Chemistry Department, University of Rio Grande do Sul, Porto Alegre, Brazil

³ Dinah Gonçalves State College, Salvador, Brazil

* lucas.capello@ufrgs.br (L.C.); maria.rangel@ufrgs.br (M.d.C.R.)

Abstract

Aiming to obtain chemicals from renewable sources to mitigate global warming, the catalytic pyrolysis of tamarind pulp, obtained from juice industries, was studied. Catalysts based on HZSM-5 zeolite prepared from rice husk ash using ultrasound, microwaves, and a combination of both were employed. The catalysts were characterized by elemental analysis, X-ray diffraction, specific surface area and porosity measurements, scanning electron microscopy, and acidity measurements. The specific surface areas and the micropore volumes were slightly affected by the treatments, microwave alone or combined with ultrasound, having the strongest effect. The number of acid sites increased, and the relative number of strong sites decreased with the treatments. The relative amount of Bronsted to Lewis sites was increased by ultrasound and decreased by microwave, alone or combined. These catalysts decreased oxygenated products and increased BTEX production during tamarind pulp pyrolysis. The product distribution was similar for all cases, meaning that HZSM-5 with the following characteristics are selective catalysts to BTEX in tamarind pulp pyrolysis: specific surface area= 310-347 m²/g; micropore volume= 0.099-0.105 cm³/g; acidity= 327 to 571 μmol NH₃/g_{cat} and Bronsted to Lewis acid sites ratio= 0.034 to 0.044.

Keywords: HZSM-5; tamarind; fast pyrolysis; benzene; toluene; ethylbenzene; xylenes; BTEX

1. Introduction

Since the Industrial Revolution, the human-environment relationship has focused on maximizing commodity production for providing a comfortable life to society. However, industrialization and fossil fuels severely stress global ecosystems via atmospheric emissions and indiscriminate waste disposal. This disrupts critical biogeochemical processes, causing significant climatic alterations, notably the rise in global mean temperature [1]. The petroleum industry has been historically identified as a major contributor to environmental pollution. Fossil fuel combustion releases carbon monoxide and carbon dioxide, the latter exacerbating the greenhouse effect, in addition to producing nitrogen oxides (NO_x) and sulfur oxides (SO_x), which contribute to acid rain and photochemical smog [2]. Restoring climate balance critically requires reducing energy dependence on petroleum-derived fuels and promoting greater use of renewable energy sources such as wind, solar, hydropower and biomass [3].

Biomass is considered a 100% renewable resource since its chemical energy is solar-derived through photosynthesis [4,5]. It can be converted into energy via thermochemical processes to yield heat and electricity (cogeneration), synthesis gas (syngas), and valuable chemical products, including biofuels [6]. Among these processes, pyrolysis emerges as a major route, because of its economy, flexibility and simplicity [7]. The most advanced regime, flash pyrolysis, is distinguished by achieving virtually instantaneous heating by introducing the biomass directly into a pre-heated reactor. This approach represents the optimal condition for achieving the highest bio-oil yield [8,9].

However, the major constituents of biomass pyrolysis oil encompass a diverse array of oxygenated organic compounds, including carboxylic acids, ketones, phenols and their derivatives, furans, sugars, aldehydes, and alcohols [10]. This intrinsic compositional complexity and high oxygen content critically confer undesirable properties to bio-oil, specifically low heating value, chemical instability, and high corrosivity [10,11]. Consequently, comprehensive upgrading processes are mandatory for effective utilization as a fuel source or as a platform chemical feedstock.

An effective strategy to overcome these drawbacks is the in situ application of heterogeneous catalysts to directly hydrodeoxygenate the pyrolysis vapors. This approach yields a higher-quality bio-oil enriched in hydrocarbons, demonstrating superior product selectivity compared to conventional non-catalytic thermal pyrolysis [10,12]. The most widely employed catalysts used in pyrolysis are zeolites, favored for their exceptional characteristics such as high specific surface area, well-defined microporous structure, and significant Brønsted and Lewis acidity, properties indispensable for promoting the key hydrodeoxygenation (HDO) reaction pathways [12].

Keeping these ideas in mind, this work deals with the convergence of two residual biomass valorization strategies for obtaining high value-added products. While rice husk ash is a sustainable silica source for catalytic zeolite synthesis, tamarind pulp (*Tamarindus indica* L.) is the biomass feedstock for pyrolysis.

Tamarind, a widely cultivated tropical fruit, yields a significant agro-industrial residue, as its pulp (a byproduct of the juice industry), constitutes approximately 30% of the fruit mass [13]. Several studies have investigated the potential of tamarind seed husks for producing value-added chemicals. Keder et al. [14], for instance, performed tamarind seed pyrolysis at different temperatures and obtained the maximum bio-oil yield of 45 wt.% at 400 °C. Moreover, Makhairas and Pugazhivadivu [15] used microwave pyrolysis of tamarind seeds to extract high quality bio-oil (36%) with higher calorific value than the bio-oil produced by traditional pyrolysis.

Tamarind seed husk biomass has been explored to study its slow pyrolysis behavior and potential for bio-oil and biochar production. The first study on slow pyrolysis of seed husk of tamarind with detailed characterization of pyrolysis products and in-depth investigations into the breaking pathways during pyrolysis was carried out by Kaur et. al. [16], from 300 to 450 °C. They concluded that 400 °C is the optimized temperature for bio-oil production (yield= 38.8 wt.%; conversion= 67.1%). Furthermore, ketones, aldehydes, carboxylic acids, furans, phenolics and N-containing functionalities are the main products and thus bio-oil can be a source of functional chemicals. However, as far as we know, no work has been reported on catalytic pyrolysis of seed husk of tamarind. The use of catalysts can provide the control of reactions towards the desirable products, for instance, high value benzene, toluene, ethylbenzene and xylenes (BTEx).

On the other hand, the demand for high-purity silica in zeolite synthesis is a significant cost driver. Therefore, utilizing rice husk ash as a silicon precursor emerges as a robust strategy for circular economic implementation and process cost reduction. Brazil, being one of the largest rice producers outside Asia, generates this agro-industrial byproduct on a massive scale [17]. Due to its high calorific value, rice husk is primarily valued in thermal power plants for bioenergy generation. The ash resulting from this thermal combustion can achieve purity exceeding 90%, meeting the reactivity requirements for the synthesis of zeolites, such as ZSM-5 [18,19].

2. Materials and Methods

2.1. Biomass Preparation and Characterization

The tamarind pulp residue (TP) was dried at ambient conditions, for 15 days, subsequently ground to fine powder by pestle and mortar and sieved to 100 mesh. The resulting material was characterized by elemental analysis of carbon, hydrogen and nitrogen (CHN), in a 2400 Series II Perkin Elmer equipment and by thermogravimetry in a TGA (Q50 V.67 Build 203) Exapro equipment, from 25 to 700 °C at a heating rate of 5 °C/min under nitrogen flow.

2.2. Catalysts Preparation

The samples were synthesized according to the methodology adapted from Bortolini et al. [20], using crystallization seeds and rice husk ash (RHA) as a silica source, without any organic template. The RHA was obtained by burning rice husks in a fluidized bed during the rice processing and industrialization companies in Rio Grande do Sul, Brazil.

During zeolite preparation, an acidic aqueous solution containing aluminum sulfate and sulfuric acid was slowly dropped on a basic aqueous solution of sodium hydroxide and the silica source (RHA) under vigorous stirring. The mixture was then kept under constant stirring at 25 °C, for 60 min, to form the hydrogel. The hydrogel was transferred to a Teflon vessel containing ZSM-5 zeolite seeds (CBV 2314, Zeolyst) and autoclaved. This system was kept in an oven at 190 °C, for 24 h. The solid was then vacuum filtered and washed with deionized water until the conductivity was less than 50 $\mu\text{S/m}$. The sample was dried at 80 °C for 12 h to get the Z sample.

Other samples were treated with ultrasound (NI1201D, Nova Instruments) and microwave (ME044, Electrolux) to improve the dissolution and homogenization of the reactants. In order to obtain the ZU sample, the basic solution was kept under an ultrasonic bath for 10 min before the addition of the acidic dispersion. The remaining subsequent steps followed the same methodology. For preparing the ZM sample, the resulting gel was kept for 30 s under microwave (760 W), followed by the same steps described. Another sample (ZUM) was got by using both treatments, under the same conditions already described.

The acidic form of the zeolites was obtained by ion exchange, using a heated ammonium nitrate solution (80 °C) and keeping the dispersion under stirring, for 2 h. Subsequently, the material was vacuum filtered and washed with deionized water until an electrical conductivity of less than 50 $\mu\text{S/m}$ was obtained. The samples were then dried at 80 °C, for 12 h and then calcined for 2 h, at 600 °C to obtain the zeolites in their acidic form (HZ, HZU, HZM, and HZUM samples).

2.3. Rice Husk ash Characterization

The rice husk ash used as a source of silica was characterized by X-ray fluorescence (XRF), X-ray diffraction (XRD), specific surface area (S_g) measurements, scanning electron microscopy (SEM), and temperature programmed desorption of ammonia (NH_3 -TPD).

The chemical composition of the ash was determined by the X-Ray Fluorescence technique (XRF), using a WD-FRX model RIX 3100 Rigaku Dengui equipment. Quantitative analysis was performed using the fused sample technique with a calibration curve from rock patterns and artificial patterns for the most found element (manganese). The loss on ignition (LOI) was performed by heating 2 g of the sample to 1000 °C, the value being obtained by the difference in sample mass before and after being heated to 1000 °C.

2.4. Catalysts Characterization

The silicium and aluminum contents of the catalysts were determined by X-ray Fluorescence (XRF) technique, using the S2 Puma XRF model Bruker equipment. The analyses were carried out using a sample cup for XRF and 6 μ Mylar Film in a Helium atmosphere.

The X-ray diffractograms were obtained in a D2 Phaser Bruker equipment, using Cu-K α radiation. The specific surface area and porosity measurements were carried out in a NOVA 4200e model Quantachrome apparatus. Prior to experiments, the sample was heated at 300 °C, for 3 h, under vacuum. The specific surface area (S_g) was calculated using the BET method and the micropore volume (V_{micro}) was obtained by t-plot method. The morphology of the samples was observed by scanning electron microscopy (SEM). An EVO 10 model Zeiss equipment working at a 10 kV accelerating voltage was used. Before the analysis, the samples were placed on aluminum brackets with carbon tape and metalized with gold.

The acidity of the samples was measured by temperature-programmed desorption of ammonia (NH_3 -TPD) using a QME 200 model Pfeiffer quadrupole mass spectrometer. First, the sample was

heated at 550 °C for 60 min, under helium flow (60 mL.min⁻¹). Then, adsorption of NH₃ was performed under a flow (60 mL.min⁻¹) of 4 vol% NH₃/He mixture, at 70 °C, for 30 min. Before heating, the sample was purged by helium flow for 60 min. Then, the temperature was raised up (20 °C. min⁻¹) to 800 °C, under helium flow.

The Bronsted and Lewis acid sites of the catalysts were identified by Fourier transform infrared (FTIR) spectroscopy on samples previously adsorbed with pyridine. The catalyst (around 10 mg) was exposed to pyridine vapor for 15 h, dried at 100 °C for 18 h, cooled at room temperature and then analyzed in a FT-IR/NIR model Frontier equipment. The spectra were deconvoluted to calculate the Bronsted to Lewis acid sites ratio.

2.5. Catalyst Evaluation

The catalysts were evaluated in the fast pyrolysis of tamarind pulp residue, using an EGA/Py-3030D model Frontier equipment coupled to a QP2010-Ultra Shimadzu gas chromatograph-Mass Spectrometer (GC/MS). Non-catalytic pyrolysis was also performed. For each run, a mixture of 0.88 mg of biomass and 4.4 mg of catalyst (catalyst/biomass ratio= 5:1) was used. Pyrolysis was performed at 550 °C for 1 min, under helium (99.999% purity) flow a (100 mL · min⁻¹). Condensable vapors were fed to the GC/qMS via an injector port at 280 °C, operating in split mode (1:30). For separation, an SH-5MS capillary column (30 m x 0.25 mm x 0.25 µm Crossbond 5% diphenyl/95% dimethyl polysiloxane) was used. All experiments were performed in duplicate. The compound identification was tentatively achieved via retention indices and mass spectral data. Semi-quantitative analysis was performed by determining the chromatographic peak area percentage for each compound.

3. Results and Discussion

3.1. Biomass Characterization

The elemental analysis showed that the tamarind pulp is made of 43.26% carbon, 5.10% hydrogen, and 1.35% nitrogen, the remaining 50.29% being attributed to oxygen. This composition immediately highlights the high oxygen content and the notably low H/C ratio of approximately 0.12, which is characteristic of biomass [21,22].

The thermogravimetric curve (Figure 1) shows two weight losses. The first one, up to 110 °C, is attributed to the loss of volatiles adsorbed on biomass, corresponding to a weight loss of 6.85%. The second event is associated with the successive degradation of hemicellulose, cellulose, and lignin. The final residue (27.9%) is related to the ash content and fixed carbon generated during analysis.

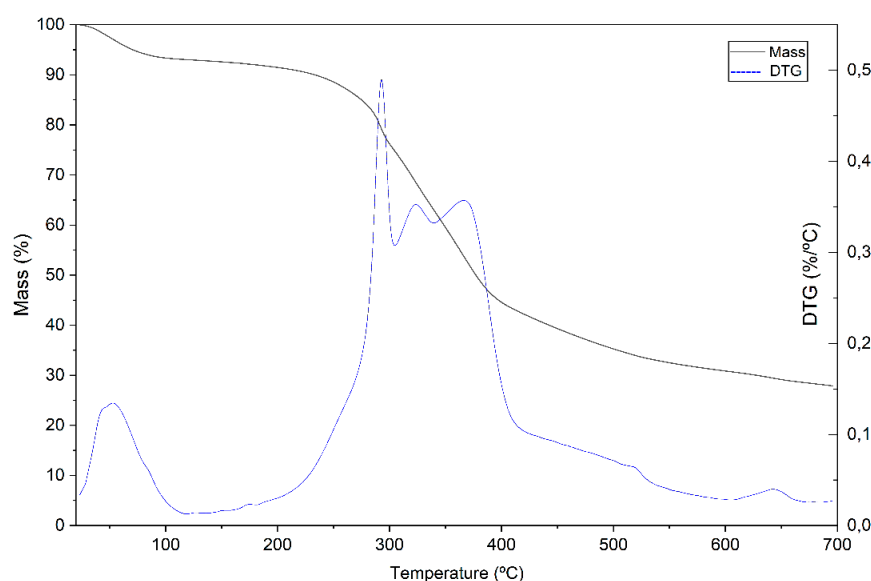


Figure 1. TG and DTG curves of tamarind pulp.

3.2. Rice Husk Ash Characterization

Table 1 presents the RHA composition obtained through XRF analysis. It is observed that it has high silica content, small amount of alumina, and few impurities. Similar results for rice husk ash were observed by Dey et al. [23] and Khoshbin & Karimzadeh [24]. Because of the high silicon content, RHA was used directly in the synthesis of ZSM-5 zeolite, without any prior treatment.

Table 1. Rice husk ash (RHA) composition determined by XRF analysis.

Composition	SiO ₂	Al ₂ O ₃	TiO ₂	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	LOI
%	93.49	1.36	nd	nd	0.3	0.12	0.33	Nd	1.5	0.18	1.54

3.3. Catalyst Characterization

3.3.1. Si/Al Ratio Results

Table 2 shows that the Si and Al content remained similar across all zeolites. However, ultrasound and microwave treatments slightly reduced the Si/Al ratio. The combined treatment (ultrasound plus microwave) sample exhibited the lowest Si/Al, ratio.

Table 2. Si/Al ratio (w/w) values of zeolite-based catalysts. HZ: HZSM5 zeolite without any treatment; HZU: HZSM5 zeolite treated with ultrasound; HZM: HZSM5 zeolite treated with microwave; HZUM: HZSM5 zeolite treated with ultrasound and microwave.

Samples	Elements (% w/w)		Si/Al
	Si	Al	
HZ	94.2	3.5	27
HZU	93.8	3.8	25
HZM	93.8	3.9	25
HZUM	93.7	4.1	23

3.3.2. X-Ray Diffraction Results

Figure 2 shows the X-ray diffractograms for the samples. For all cases, the characteristic pattern to the HZSM-5 [25] was found. The diffraction pattern is characteristic of the MFI (Mobil Five) framework type, which crystallizes in an orthorhombic system and belongs to the pentasil type zeolite.

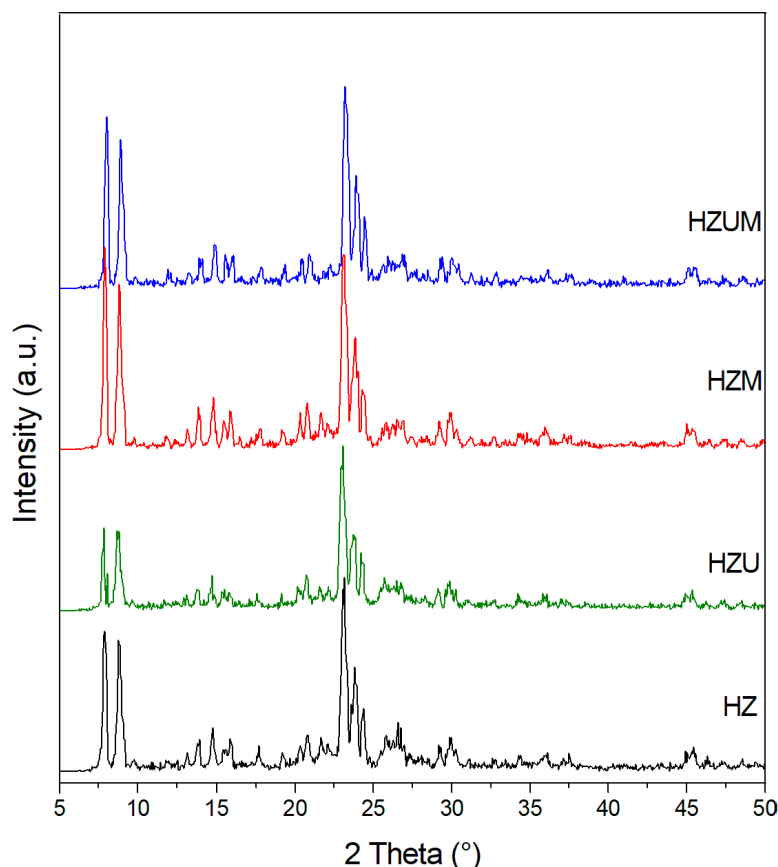


Figure 2. X-ray diffractograms of the catalysts. HZ: HZSM5 without any treatment; HZU: HZSM5 zeolite treated with ultrasound; HZM: HZSM5 zeolite treated with microwave; HZUM: HZSM5 prepared using both ultrasound and microwave.

3.3.3. Textural Properties Results

The nitrogen adsorption-desorption isotherms for the synthesized samples are shown in Figure 3. All samples show Type I isotherms, which are characteristic of zeolites and other primary microporous solids. Some interparticle mesopores were also observed at higher pressures. The values of specific surface area range between 310 and 347 $\text{m}^2\cdot\text{g}^{-1}$, which are also typical of ZSM-5. One can see that the different treatments change micropore volumes, the samples treated with microwave showing the highest values, in accordance with previous work [26,27]. However, the treatment with ultrasound alone slightly decreased the micropore volume, as found previously [28].

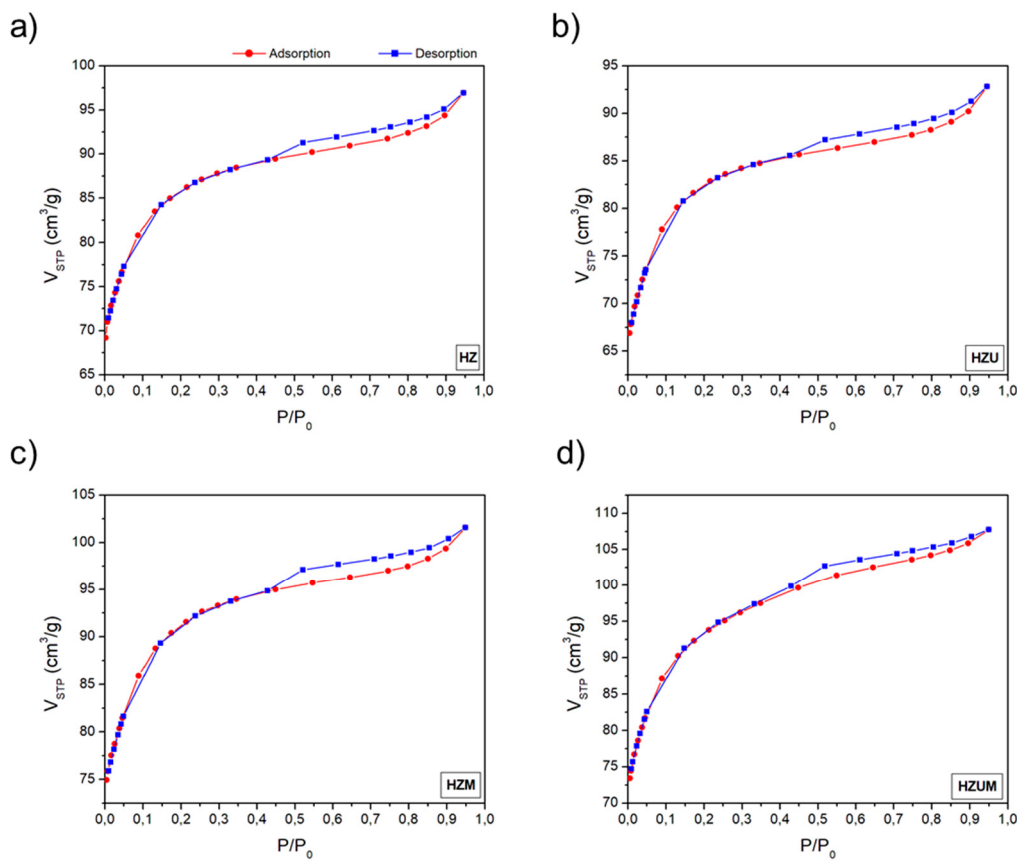


Figure 3. Nitrogen adsorption and desorption curves of HZSM5 zeolite-based catalysts. (a) HZ: HZSM-5 zeolite without any treatment; (b) HZU: HZSM-5 treated with ultrasound; (c) HZM: HZSM-5 treated with microwave; (d) HZUM: HZSM-5 treated with both ultrasound and microwave.

Table 3. Textural properties of zeolite-based catalysts. HZ: HZSM-5 zeolite without any treatment; HZU: HZSM-5 treated with ultrasound; HZM: HZSM-5 treated with microwave; HZUM: HZSM-5 treated with both ultrasound and microwave.

Samples	S _g (m ² /g)	V _{micro} (cm ³ /g)
HZ	322	0.099
HZU	310	0.096
HZM	342	0.105
HZUM	347	0.100

3.3.4. Acidity Results

Figure 4 presents the NH₃-TPD curves for the samples. All catalysts exhibit two desorption peaks, the first one centered at around 250 °C, related to weak acid sites. The second peak, with a maximum around 450 °C, is related to moderate and strong acid sites [29]. After deconvolution of the curves by the Lorentzian method, the number of weak, moderate, and strong acid sites was calculated, and the values are shown in Table 4. Weak, moderate and strong acid sites were considered those between 150 and 250 °C; 250 and 400 °C, and 400 and 600 °C, respectively.

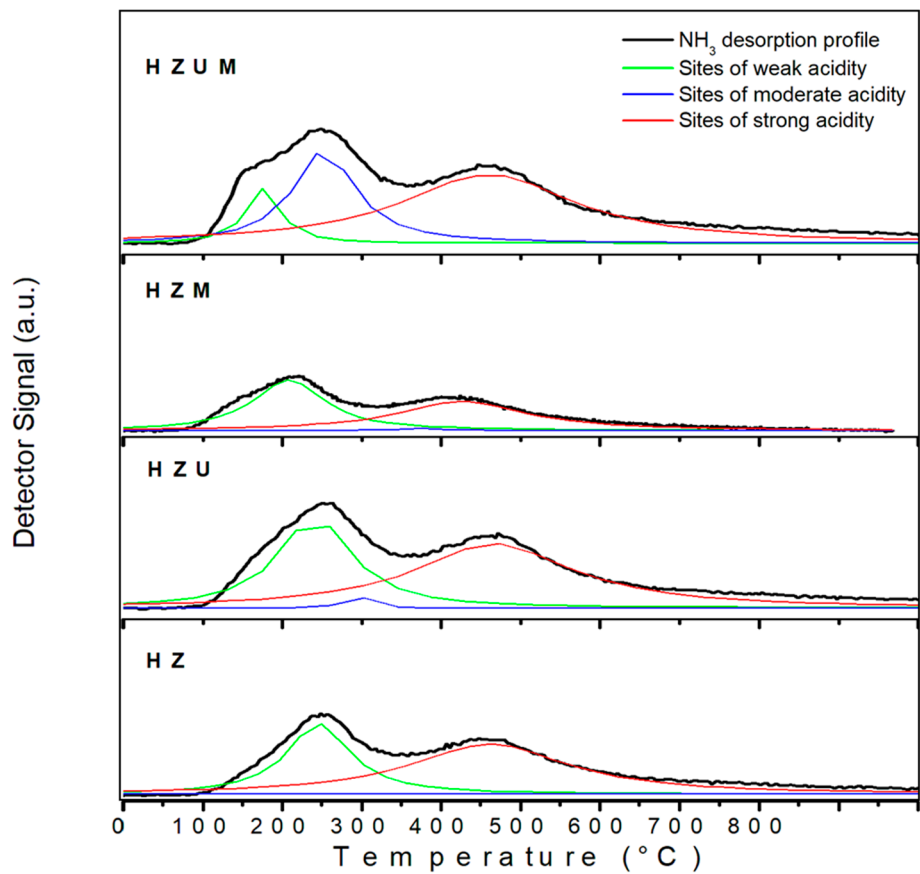


Figure 4. Curves of NH₃-TPD for the samples. HZ: HZSM-5 zeolite without any treatment; HZU: HZSM-5 treated with ultrasound; (c) HZM: HZSM-5 treated with microwave; (d) HZUM: HZSM-5 treated with both ultrasound and microwave.

Table 4. Acidity of the samples obtained by NH₃-TPD. HZ: HZSM-5 without any treatment; HZU: HZSM-5 treated with ultrasound; HZM: HZSM-5 treated with microwave; HZUM: HZSM-5 treated with both ultrasound and microwave.

Samples	T (maximum) (°C)			Relative amount of acid sites (%)			Total acidity (μmol NH ₃ /g _{cat})
	1° peak	2° peak	3° peak	Weak acidity	Moderate acidity	Strong acidity	
HZ		246	350	36.0	0.2	63.8	327
HZU	241	294	467	36.7	1.7	59.6	480
HZM	208	375	426	47.8	1.7	50.5	392
HZUM	175	253	460	9.5	29.0	61.5	571

It can be noted that the different treatments markedly changed the strength and amount of acid sites. The total acidity decreased in the order: HZUM > HZU > HZM > HZ, indicating that the treatments increased the number of acid sites, ultrasound alone or combined with microwave being the most effective. However, it is observed that the use of ultrasound alone does not significantly alter the relative amount of acid sites with different strengths, while microwaves increase the relative amount of weak acid sites and decrease the strong acid sites. The combined treatment decreases the weak acid sites and increases the moderate ones. Furthermore, it is noted that ultrasound shifts the peak of moderate acid sites to lower temperatures, while the microwave does the opposite. The combined treatment led to major changes, the HZUM sample showing mostly moderate and strong

acid sites. The majority of the samples (HZ, HZU, and HZUM) presented strong acid sites (> 59%), HZ showing the highest relative amount (63.8%). As a whole the treatments decreased the relative amounts of strong acid sites and increased the moderate sites. The relative amount of Bronsted to Lewis acid sites in the catalysts was also affected by the treatments, as shown in Table 5. In a general tendency, ultrasound increases the relative amount of Bronsted sites while microwave, alone or combined, does the opposite.

Table 5. Bronsted and Lewis acid sites of the samples. HZ: HZSM-5 without any treatment; HZU: HZSM-5 treated with ultrasound; HZM: HZSM-5 treated with microwave; HZUM: HZSM-5 treated with both ultrasound and microwave.

Sample	BAS (a.u) 1545 (cm ⁻¹)	LAS (a.u) 1445 (cm ⁻¹)	BAS/LAS
HZ	0.00031	0.0073	0.042
HZU	0.00032	0.0073	0.044
HZM	0.00029	0.0075	0.038
HZUM	0.00028	0.0082	0.034

3.3.5. SEM Results

The SEM images of the catalysts is displayed in Figure 5. All catalysts predominantly exhibit a coffin-shaped morphology characteristic ZSM-5 zeolite [30], indicating that the treatment does not alter the particles shape. However, microwave caused certain “hole-like” imperfections in the formed crystals, which may be associated with the increased mesopore volume among the particles, as noted for HZM and HZUM samples.

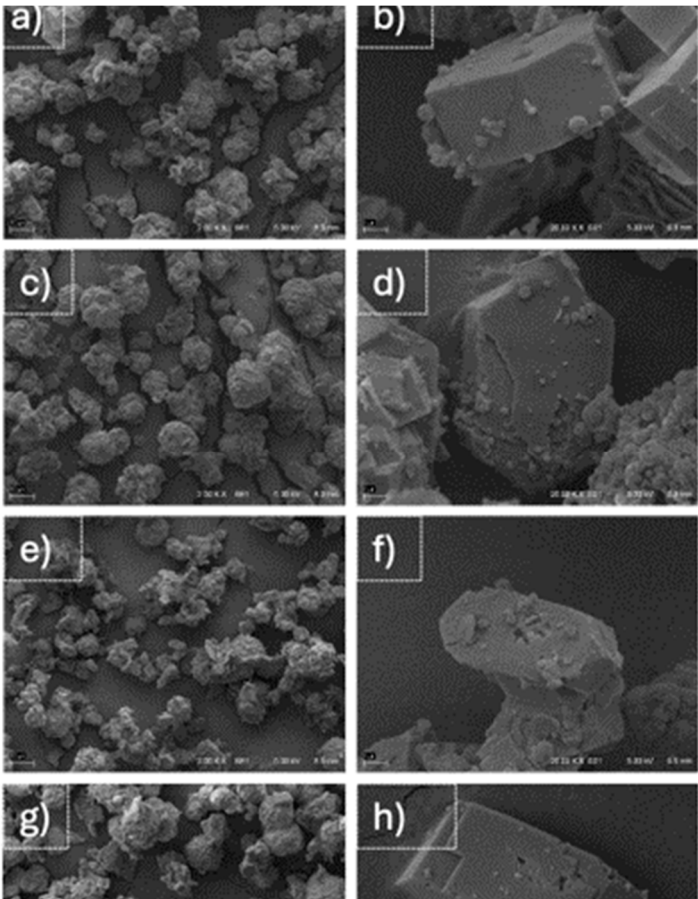


Figure 5. Scanning electron micrographs for HZ (HZSM05 without any treatment): a) 2000x, b) 20000x; for HZU (HZSM-5 treated with ultrasound): c) 2000x, d) 20000x; for HZM (treated with microwave: e) 2000x, f) 20000x and for HZUM (treated by both ultrasound and microwave): g) 2000x, h) 20000x.

3.3.6. Catalytic Evaluation Results

Table 5 shows the compounds obtained from tamarind pyrolysis. High concentration of oxygenated compounds and a low content of hydrogenated compounds were found in bio-oil. This is expected, since biomasses typically exhibit a low H/C ratio and high oxygen content, as shown by CHN analysis. This concentration of oxygenated compounds ($78.1 \pm 1.3\%$) is similar to previous works on the pyrolysis of tamarind [16] and other lignocellulosic materials [31,32]. A drastic catalytic effect was observed for all samples. The catalysts caused an increase of hydrogenated fraction up to 89.7% and 92.3%, while simultaneously reducing the oxygenated fraction to values between 7.5% and 9.0%.

Table 5. Compounds formed during the catalytic and non-catalytic pyrolysis of tamarind bagasse. TP: tamarind; HZ: HZSM5 without any treatment; HZU: HZSM5 treated with ultrasound; HZM: HZSM5 treated with microwave; HZUM: HZSM5 treated with both ultrasound and microwave.

Compounds	TP	TP + HZ	TP + HZU	TP + HZM	TP + HZUM
Hydrogenated	$19.4 \pm 1.2\%$	$89.7 \pm 1.3\%$	$91.3 \pm 0.0\%$	$92.3 \pm 0.1\%$	$92.0 \pm 0.6\%$
Oxygenated	$78.1 \pm 1.3\%$	$9.0 \pm 1.1\%$	$8.3 \pm 0.1\%$	$7.5 \pm 0.2\%$	$7.6 \pm 0.7\%$
Nitrogenous	$2.6 \pm 0.1\%$	$1.2 \pm 0.3\%$	$0.4 \pm 0.0\%$	$0.3 \pm 0.0\%$	$0.4 \pm 0.6\%$

Figure 6 shows the distribution of compounds in bio-oil produced from catalytic and non-catalytic pyrolysis. The non-catalytic biomass pyrolysis (TP) resulting bio-oil which is dominated by unstable oxygenated compounds, primarily phenols, sugars, ketones, and others (furans, fatty acids, alcohols). These findings are typical of biomass pyrolysis, according to previous works [16,31,32]. Furthermore, the BTEX fraction is very low ($4.7 \pm 0.9\%$) and the undesirable polyaromatic hydrocarbons (PHA) are not produced under these conditions.

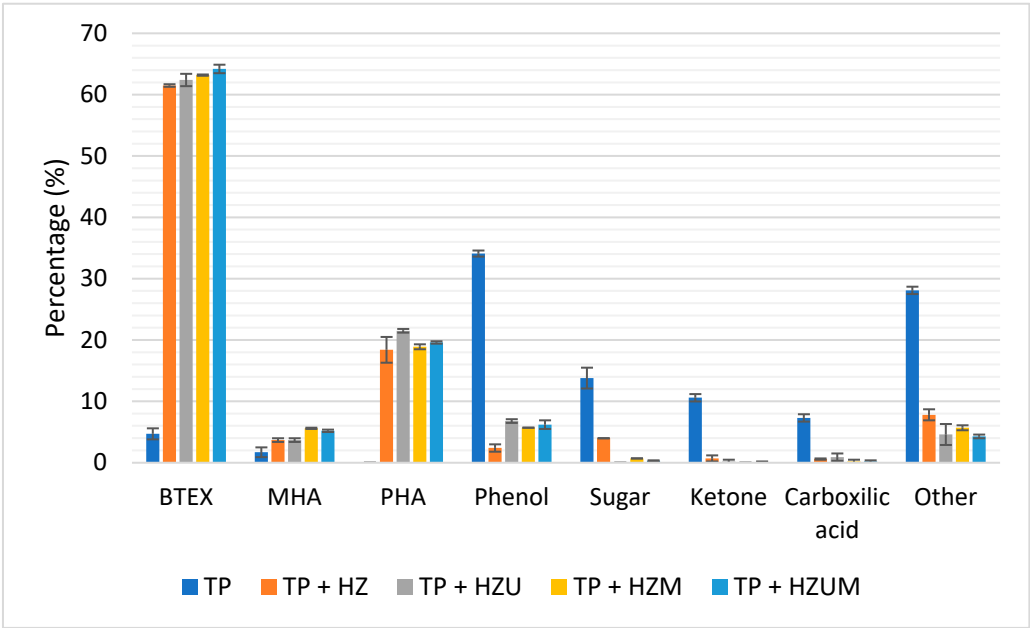
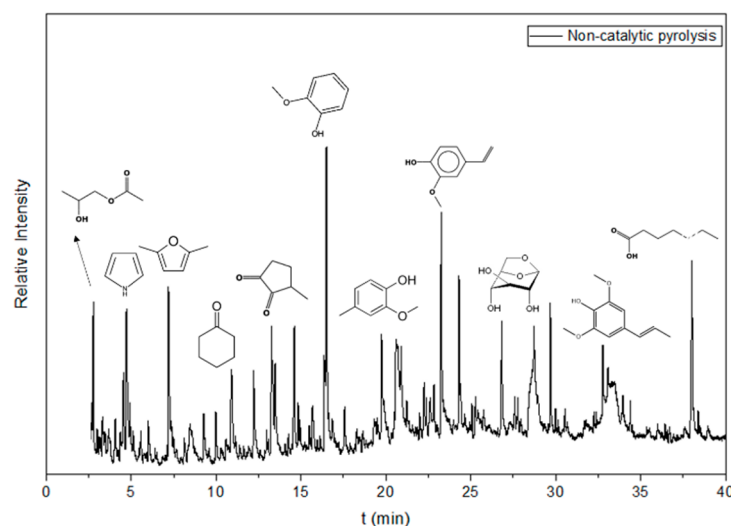


Figure 6. Distribution of products obtained during non-catalytic pyrolysis and catalytic pyrolysis. TP: tamarind pulp); HZNT: HZSM-5 without any treatment; HZU: HZSM-5 treated with ultrasound; HZM: HZSM-5 treated with microwave; HZUM: HZSM-5 treated with both ultrasound and microwave.

The introduction of the catalysts promotes a massive conversion of oxygenated compounds into monoaromatic hydrocarbons (BTEX and other MHA), thus indicating a drastic increase in bio-oil quality. The bio-oil composition becomes dominated by BTEX (ranging from 61.5 to 64.2%) and PHA (ranging from 18.4 to 21.5%). Furthermore, there is a sharp reduction in undesirable compounds: phenol drops to 2.4–6.8%; sugars are nearly eliminated, especially with HZU, HZM, and HZUM and ketones and carboxylic acids are drastically reduced to less than 1.0%.

Considering BTEX production, HZUM ($64.2 \pm 0.7\%$) is statistically superior to HZM and HZU, and also to HZ ($61.5 \pm 0.2\%$), although the difference was not remarkably expressive. The PHA is primarily composed of naphthalene, which is toxic and acts as coke precursors, despite having market value. Among the catalysts, HZU produced the highest amount of PHA ($21.5 \pm 0.3\%$), with this value being statistically superior to the others.

Figure 7 illustrates the differences found in chromatograms of non-catalytic and catalytic pyrolysis. Non-catalytic pyrolysis produces predominantly oxygenated compounds and some nitrogenated species. Conversely, catalytic pyrolysis produces mainly BTEX and naphthalenes. This is a valuable result, since these compounds are crucial feedstocks for the production of various chemical and petrochemical products. They are utilized in the synthesis of polymers, including polystyrene, nylon, polyurethane, synthetic rubbers, and polyester; they function as solvents in paints, adhesives, and coatings; and they serve as high-value gasoline additives [33]. The commercial importance and value of these products are evident in market projections: the estimated production volume for BTEX is expected to reach approximately 143 Million Tons in 2025, generating revenues of USD 269.1 billion, with an anticipated Compound Annual Growth Rate (CAGR) exceeding 7% [34].



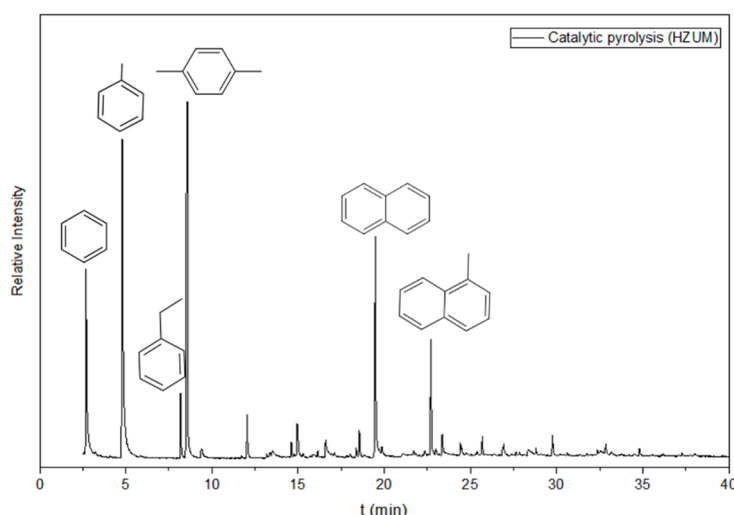


Figure 7. Chromatograms of (a) non-catalytic pyrolysis (TP), and (b) catalytic pyrolysis over HZUM (HZSM-5 treated with both ultrasound and microwave).

The results show that HZSM-5 is an efficient catalyst to produce BTEX from tamarind pulp, regardless of the use of ultrasound and microwaves or their combination. These treatments cause changes in specific surface area, micropore volume, strength and distribution of acid sites and Bronsted to Lewis acid sites ratio but these changes are not enough to affect significantly the selectivity of the catalysts to BTEX. Therefore, it can be stated that HZSM-5 samples with specific surface area ranging from 310 to 347 m²/g, micropore volume from 0,099 to 0,105 cm³/g, acidity from 327 to 571 $\mu\text{mol NH}_3/\text{g}_{\text{cat}}$ and Bronsted to Lewis acid sites ratio from 0,034 to 0,044 are efficient catalysts to produce BTEX.

5. Conclusions

Green HZSM-5 type zeolites were successfully obtained using rice husk ash and employing different treatment conditions, namely ultrasound, microwaves, and a combination of both. The different treatments slightly affect the specific surface area and the micropore volume, the samples treated with microwave alone or combined with ultrasound showing the highest values. As a whole, the treatments increase the number of acid sites and decrease the relative number of strong sites, the combined treatment causes a large decrease in weak sites. Ultrasound increases the relative amount of Bronsted to Lewis sites while microwave, alone or combined, does the opposite. These catalysts largely affect tamarind pyrolysis by decreasing oxygenated compounds and increasing BTEX production. However, no significant difference in the products distribution was found. It means that the HZSM-5 with the following characteristics are selective catalysts to BTEX in tamarind pulp pyrolysis: specific surface area from 310 to 347 m²/g, micropore volume from 0,099 to 0,105 cm³/g, acidity from 327 to 571 $\mu\text{mol NH}_3/\text{g}_{\text{cat}}$ and Bronsted to Lewis acid sites ratio from 0,034 to 0,044.

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Abbreviations

The following abbreviations are used in this manuscript:

RHA	Rice Husk Ash
Z	ZSM5 zeolite without any treatment
ZU	ZSM5 zeolite treated with ultrasound
ZM	ZSM5 zeolite treated with microwave
ZUM	ZSM5 zeolite treated with ultrasound and microwave
HZ	HZSM5 zeolite without any treatment
HZU	HZSM5 zeolite treated with ultrasound
HZM	HZSM5 zeolite treated with microwave
HZUM	HZSM5 zeolite treated with ultrasound and microwave
NH ₃ -TPD	Temperature Programmed Desorption of Ammonia
S _g	Specific Surface Area
SEM	Scanning Electron Microscopy
FTIR	Fourier Transform Infrared Spectroscopy
HDO	Hydrodeoxygenation reaction
BTEX	Benzene, Toluene, Ethylbenzene, and Xylenes
PHA	Polyaromatic Hydrocarbons
MHA	Monoaromatic Hydrocarbons
Py-GC/MS	Fast Catalytic Micropyrolysis

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