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Effect of Solvent Pre-Treatment and Catalyst on Microwave-Assisted Pyrolysis of Rice Straw

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ABSTRACT

The microwave-assisted pyrolysis (MAP) application of rice straw as feedstock is the primary focus of this research. Some of the solvents that were utilized for soaking feedstocks included benzene, acetone, and ethanol. These solvents were used to pre-treat the rice straw. Through the use of solvents, yields were increased, reaction times were decreased, and the pyrolysis index was improved. KOH catalyst increased the amount of gaseous products produced by 47.5 wt%. When rice straw was prepared with benzene, the average heating rate decreased to 21.8 °C/min, significantly increasing the amount of oil and char produced. Rice straw that had been prepared with acetone had a much lower energy consumption in MAP (283 kJ) when compared to fresh rice straw, which had a different energy consumption (418 kJ). In the process of pyrolysis, it is demonstrated that solvent soaking occupies a significant position. The recovered bio-oil also included mono-aromatics, poly-aromatics, and oxygenated compounds.

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1. INTRODUCTION

The cultivation of rice is widespread in South and Southeast Asia, making rice straw a major agricultural byproduct internationally. The world produces almost 550 million tons of wasted rice straw annually [1]. The high expense of collecting and transporting straw forces farmers to let it decay in paddy fields after harvest or burn it openly to make way for new crops [1]. When mixed with soil, anaerobic decomposition of rice straw could significantly increase CH4 greenhouse gas emissions [2]. Burning of rice in open fields releases many pollutants, such as CO2, CO, CH4, NOx, and SO2 [3]. When burnt, it often releases some pollutants as well as emissions, such as polychlorinated dibenzofurans (PCDFs) and aromatic polycyclic aromatic hydrocarbons (PAHs), which are harmful to the environment and can cause disease [4,5]. In addition to contributing to local climate change-induced climate change, unburned carbon and particulate matter from rice burning can significantly affect human health [6]. Indirect consequences on the national economy remained unclear [4]. It is, therefore, of the utmost importance to find long-term, environmentally friendly, and economically viable solutions to this problem. In Asia and the Americas, where rice is grown extensively, rice straw can be used as feedstock for biorefineries to produce high-value fuels and chemicals. The use of acid and alkaline pre-treatment processes to improve cellulose quality for efficient and sustainable fuel production has grown in popularity due to its accessibility and affordability. There are various other approaches as well. In most cases, these techniques are employed to remove lignin, break the crystalline structure of cellulose, and soften the material [7,8]. Conducting pyrolysis studies using two chemical additive solutions containing ammonium sulfate (AS) and diammonium phosphate (DAP) for rice straw pre-treatment involved varying concentrations (0.1, 0.2, and 0.5 mol/L), dwell durations (30 and 60 min), and pyrolysis temperatures (300, 400, 500, and 600°C). Treatment of RS resulted in lower temperatures for mass loss, slower breakdown, and higher char output than untreated RS [9]. The primary focus of the currently ongoing research is the utilization of microwave-assisted pyrolysis (MAP) to decompose feedstock materials such as fresh and torrefied waste tea powder. The feedstocks must be soaked using solvents, including ethanol, benzene, and acetone. By increasing the feedstock torrefaction temperature to 150 °C and soaking it in the solvent, MAP's oil and char yields were increased from 39.8 to 45.3%. The production of gaseous products increased from 4.7% to 20.1% weight percent due to co-pyrolysis synergy. Typical heating rates ranged from 5 to 25 °C/min [10]. Researchers have sought ways to valorize waste rice straw by combining microwave-assisted pyrolysis (MAP) with supercritical carbon dioxide (ScCO2) extraction. A 0.7% dry weight yield of lipophilic molecules was achieved by extracting ScCO2 from rice straw at elevated temperatures of 65°C and pressures of 400 bar. The lipid composition of the wax extracted by scCO2 is comparable to the wax extracted by Soxhlet with the potentially harmful solvent n-hexane. This compound comprises steroid ketones, phytosterols, n-alkanes, fatty alcohols, aldehydes, and fatty acids [1]. Produced high-quality biochar pellets from pelleted rice by torrefaction and pyrolysis using microwave heating, and optimized the energy consumption with microwave heating. Microwave power and final temperature were carefully monitored effects resulting from materials of different yields and types [11]. Reducing solid waste through pyrolysis using microwaves is a highly effective method. Pelletizing paraffin wax (PW) and rice straw (RS) using microwave-assisted catalytic co-pyrolysis allowed for extracting valuable byproducts such as char, gas, and oil. As for the catalyst, it was potassium hydroxide, and the susceptor was graphite. A feedstock blend of RS and PW, with a ratio ranging from 0 to 10 g [12]. Producing bio-oil that meets fuel specifications requires strict adherence to process parameters, one of which is the employment of a catalyst. At varying reaction temperatures, basic (MgO and CaO) and acidic (ZSM-5 and Y-zeolite) catalysts were used to catalytically rapidly pyrolyze rice straw (RS) and wheat straw (WS). It was discovered that various feed compositions exhibited distinct reactions when exposed to different catalysts. The pyrolysis byproducts were classified into three classes of hydrocarbons: aromatic, carbonyl, and phenolic. Under non-catalytic conditions, carbonyls were the most abundant chemicals [13].

This research seeks to examine the effects of chemical pre-treatment on the MW-assisted pyrolysis of rice straw for the production of oil, gas, and char. The pre-treatment includes the use of acetone, ethanol, benzene, and potassium hydroxide as catalysts. The outcomes will be evaluated in terms of pyrolysis index, yields, composition, temperature profile, heating rate profile, average heating rate, high heating value, energy consumption, and processing time.

2. METHODS

The rice straw originates from a farm in Andhra Pradesh, Visakhapatnam, India (**Figure 1a**). The rice straw from the farm Simi dried, then dried extensively in a hot air oven for 30 min after being sliced into little pieces at 80°C to remove any sign of the remaining trace. Finally, it was ground into a fine powder using a grinder machine (**Figure 1b**). The surface area of the resultant powder was increased by grinding it into a fine powder. The powder had an average particle size of 150 micrometers after being passed through some laboratory sieves. Before continuing the experiments, the dehydrated RS was sealed in polythene containers with zip-lock closures to keep out any outside air. Rice straw was pre-treated by soaking in solvents (Acetone, Ethanol, benzene) for 24 hours at room temperature.

Figure 1. Dried (a) and ground rice straw to get a fine powder (b).

Grinding rice straw into a fine powder is an essential step in preparing it for soaking in organic solvents such as benzene, acetone, and ethanol. The process begins by thoroughly drying the straw to remove moisture. It is then ground using an electric grinder to produce a fine powder that increases the surface area exposed to the solvent. The finer the powder, the more effective it is at breaking down lignin due to the increased interaction between the material and the solvent. After grinding, the powder is placed in glass containers and immersed in a selected solvent to study the solvent's effect on the straw. Benzene is used to extract non-polar compounds, while acetone and ethanol are suitable for polar and semi-polar compounds. The soaking process continues for several hours to enhance the breaking and extraction of certain straw compounds. This is often done to extract active organic compounds such as lignin, phenols, or vegetable waxes, making the cellulose more easily thermally broken down in the microwave [14].

2.1. Calorific Value

The amount of energy generated when a sample is burned under standard conditions is known as its calorific value, which applies to feedstocks and products. You might think of this as a measure of the energy content of the feedstock or product. Calorific value can be expressed in two ways: higher heating value (HHV) and lower heating value (LHV). When the latent heat of vaporization of water is considered, the notation HHV indicates the maximum amount of heat that may be extracted from fuel after combustion. The latent heat of vaporization is not taken into account while calculating LHV. The LHV is always lower than the HHV because the products are cooled to room temperature before the assessment. Here, we detail the conventional method of testing a bomb calorimeter's heating value. Hydrocarbon polymers, oil, biomass, and other components' HHVs were calculated using this method [15].

2.2. FTIR Analysis

A Fourier transform infrared spectrometer (Nicolet iS5, Thermo Fisher, Waltham, MA, USA) was used to analyze organic functional groups using an attenuated transmittance and reflectance (ATR) mode. The spectra were recorded using a 4 cm-1 resolution, with 32 scans between 4000 and 700 cm-1. After every experiment, the ATR crystal was quickly cleaned with acetone solvent and tissue paper. Plotting the acquired transmittance data versus wavenumber allowed us to display the results of the functional group analysis [16].

2.3. GC-MS Analysis

The bio-oil fraction's organic composition obtained from microwave pyrolysis experiments was assessed using gas chromatography/mass spectrometry (Agilent 7890, 5975C). With a film thickness of 0.25 micrometers and an internal diameter of 0.25 millimeters, the HP-5MS column measured 30 meters in length. It was used to separate pyrolysis vapors in 69 steps. The carrier gas used was 0.8 mm/s of ultra-high-purity helium, with a purity level of 99.9995 percent. The chemical components in bio-oil were identified by comparing each peak's mass spectra with the NIST library. Multiple groups were formed from the organic compounds with a match factor of 85% or greater. To round out the mass balance, the chemicals that were either not detectable or had a low match factor were incorporated into the diverse group of other substances. Next, the proportion of peak area attributable to each chemical was adjusted according to the bio-oil output. From time to time, relative selectivity is also used to display the peak area (%) [17].

3. RESULTS AND DISCUSSION

According to **Table 1**, the feedstock utilized in our studies had a high heating value. Before and after soaking for 24 hours, the rice straw was treated with acetone, ethanol, and benzene, three of the most common solvents. The bomb calorimeter was used to verify the high heating value of all RS samples before and after pre-treatment. The results of HHV are shown in **Figure 2**.

Table 1. The high heating value of rice straw powder before and after pre-treatment.

Biomass	HHV (MJ/Kg)
Rice straw powder (RS), untreated	14.8
Rice straw powder soaked in benzene (RS-B)	15.7
Rice straw powder soaked in acetone (RS-A)	15.5
Rice straw powder soaked in ethanol (RS-E)	15.4

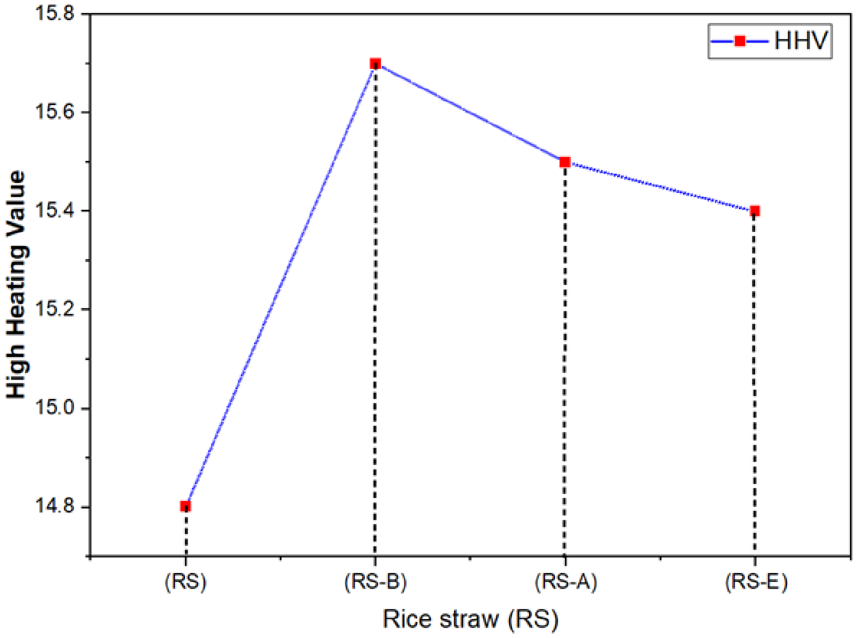


Figure 2. The HHV of rice straw powder before and after pre-treatment.

Table 1 shows the results of a bomb calorimeter analysis of the high heating value of pre-treated and untreated rice straw. Before microwave-assisted pyrolysis, rice straw can be pre-treated in solvents (i.e. benzene, acetone, ethanol) for 24 hours. Which increases the calorific value of the oil, char, and gases produced, reduces reaction time, and improves the overall efficiency of the process. As well as increasing the product and saving energy. The calorific value was increased according to the following sequence: Rice straw powder soaked in benzene (RS-B) 15.7 MJ/Kg > Rice straw powder soaked in acetone (RS-A) 15.5 MJ/Kg > Rice straw powder soaked in ethanol (RS-E) 15.4 MJ/Kg > Rice straw powder (RS) 14.8 MJ/Kg.

Table 1 and **Figure 2** show the changes in the high heating value (HHV) of rice straw powder before and after soaking in different organic solvents such as benzene, acetone, and ethanol. The HHV of untreated rice straw powder was 14.8 MJ/kg, while it increased after soaking in solvents to 15.7 MJ/kg when treated with benzene, 15.5 MJ/kg when treated with acetone, and 15.4 MJ/kg when treated with ethanol. This increase in HHV is due to the removal of some undesirable compounds present in the straw, such as lignin, moisture, ash, and polar or non-polar compounds that do not contribute to improving the heating value. For example, benzene, as a non-polar solvent, dissolves waxes, fats, and hydrocarbons, which may be low-combustibility or flame-retardant substances. While acetone and ethanol, as polar solvents, remove compounds such as phenols and some soluble sugars, resulting in a greater concentration of high-energy carbon compounds. This improved HHV means that rice straw, after processing, becomes a more thermally efficient fuel, making it a better choice for use in thermal applications, as an alternative fuel, or for biodiesel production, enhancing its value as an energy source [18,19].

3.1. FTIR analysis of Rice straw pre-treated by various solvents (Acetone, Ethanol, and Benzene)

The predominant components of rice straw, a rice crop waste product, include lignin, cellulose, and hemicellulose. However, it contains several functional groups and compounds that can undergo modification or observation when exposed to various solvents. In this section, we will examine the functional groups of three samples of rice straw that were subjected to multiple solvents: acetone (sample S1), ethanol (sample S2), and benzene (sample S3). **Figure 3** shows that benzene is an appropriate solvent for the aromatic chemicals found in rice straw; therefore, the improvement in this range could indicate that these compounds have been dissolved or extracted. After treating sample S1 with acetone, the infrared spectra of the rice straw show many modifications. The presence of hydroxyl (-OH) groups, characteristic of cellulose and hemicellulose, is indicated by a prominent peak in the 3250 - 4000 cm^{-1} range [7,8]. These functional groups appear to have remained unchanged after being treated with acetone. An additional peak at 2350 cm^{-1} may be a carbonyl group (C=O). The carbonyl group may be derived from acetyl groups, as acetone can acetylate hydroxyl groups in rice straw.

After ethanol treatment of sample S2, the infrared spectra of the rice straw do not exhibit a significant peak at 1600 cm^{-1}, which indicates that functional groups absorbing in this range were either deleted or altered during the ethanol treatment. If there isn't a prominent peak, it can mean that the C=C bonds aren't as intense, which could mean that the lignin content is lower. Ethanol can separate plant components into their parts, removing lignin while preserving cellulose and hemicellulose. Thus, it is possible that the rice straw sample was partially delignified after being treated with ethanol [11,12,20]. The infrared spectra show an improvement in the 1250-1800 cm^{-1} range when rice straw (sample S3) is treated with benzene. This enhancement indicates functional group modifications or removals brought about by benzene treatment. It is possible to detect aromatic rings in rice straws in the 1250–1800 cm^{-1} region, which is generally linked to aromatic chemicals [1,12].

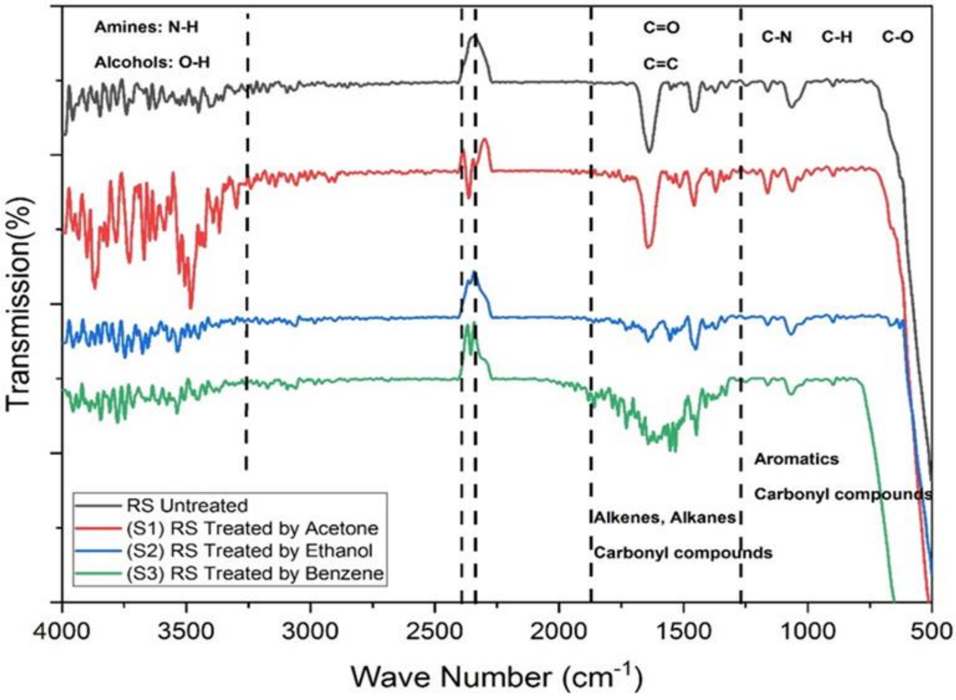


Figure 3. FTIR spectra of (RS) Pre-treatment with solvents (RS untreated, S1, S2, S3).

Figure 3 shows the FTIR spectrum of rice straw powder before treatment (black) and after treatment with three different organic solvents: acetone (red), ethanol (blue), and benzene (green). FTIR analysis relies on infrared absorption spectroscopy to identify functional groups in the sample, thus demonstrating the structural changes resulting from solvent treatment. In the untreated sample (RS untreated), we observe prominent peaks at 3400–3200 cm^{-1}, indicating N-H amine groups and O-H alcohols. Other peaks at 1700–1600 cm^{-1} indicate C=O carbonyl bonds, and others at 1600–1500 cm^{-1} indicate C=C double bonds in aromatic compounds. After treatment, some peaks are reduced or partially disappear, particularly in the green spectrum (RS treated with benzene), indicating the removal of certain compounds, such as organic acids or aromatic compounds. Gasoline, as a nonpolar solvent, dissolves waxes and hydrocarbons, so the decrease in the C-H and C=C peaks reflects its effectiveness in removing these components. Meanwhile, acetone and ethanol remove polar compounds such as alcohols and phenols, which explains the decrease in the intensity of the O-H and C=O peaks. Thus, the figure demonstrates that solvent treatment induces significant structural changes that contribute to the improvement of the physical and chemical properties of rice straw powder, such as increased calorific value and improved combustibility [8,21].

3.2. Microwave Pyrolysis of Rice Straw

The results of pyrolyzing the feedstocks independently at 450 W microwave power with a 20:10 (feedstock: graphite) ratio are shown in **Table 2**. With graphite as the susceptor, the reactant temperature reached 450-700°C after 9.5-20 min. Although the average heating rates for the rice straw trials ranged from 21 to 62 °C/min, the following feedstocks were heated at a quick pace: In this order, S2, S1, S3, N1, N2, and N3 took 9.5; 10.5; 15.5; 17; and 20 min, respectively. The bio-oil produced by pyrolyzing rice straw with the help of microwaves is displayed in **Figure 4**. Here is a breakdown of the bio-oil yields from rice straw: N1 (41.4 wt%), S3 (40 wt%), S2 (34.69 wt%), N3 (34.15 wt%), and finally, S1 (32 wt%). The highest oil yields were in the experiment (sample N1) of MW-assisted pyrolysis of rice straw without a KOH catalyst and the experiment (sample S3) of rice straw pyrolysis after pre-soaking in benzene. In contrast to the experiment (sample S1), rice straw pyrolysis after pre-soaking in acetone produced the lowest oil yields. As shown in **Table 2**, the char yield is 33.6% from the S3 method for benzene-pretreated rice straw, and the gas yield is 47.5% from the N3 method for MW pyrolysis of rice straw using a KOH catalyst [22].

Table 2. Microwave-assisted Pyrolysis of Rice Straw results.

Sample	RS (g)	KOH Catalyst (g)	Soaking in solvent	Average heating rate (AHR) (°C/min)	Oil yield (wt%)	Gas yield (wt%)	Char yield (wt%)	Conv. (wt%)	Heating value (MJ/kg)	Pyrolysis time (min)	MW Energy (kJ)
N1	10	No	No	42.38	41.40	32.78	25.82	74.18	34.80	15.50	418
N2	10	2	No	39.17	34.15	47.50	18.35	81.65	35.40	17.00	459
S3	10	No	Benzene	21.80	40.00	26.40	33.60	66.40	35.20	20.00	540
S2	10	No	Ethanol	62.00	34.69	43.40	21.88	78.09	34.90	9.50	256
S1	10	No	Acetone	61.00	32.00	39.70	28.19	71.70	35.00	10.50	283

Figure 4. Microwave-assisted pyrolysis of Rice straw oil samples.

The oil yields reported in **Table 2** are depicted in **Figure 5**. The fund with the highest oil yield in N1 and S2, the recovered bio-oil, included mono-aromatics, poly-aromatics, and oxygenated compounds. On the other hand, the highest gas yield was obtained from experiments N2 and S2, while the highest char yield was reached in experiment S1 (28.19 wt%), which involved the rice straw being pre-treated with acetone. The conversion rate represents the percentage of gas and oil products resulting from thermal decomposition with microwave assistance. The highest conversion rate was found when KOH was used in microwave-assisted pyrolysis and when rice straw was pre-treated by ethanol before microwave-assisted pyrolysis, as the conversion rate was 81.65 and 78.09 wt%, respectively. Because of their impact on breaking the large molecules into the simplest molecules that are easy to break down in thermal pyrolysis, this explains the percentage of high gas products [10].

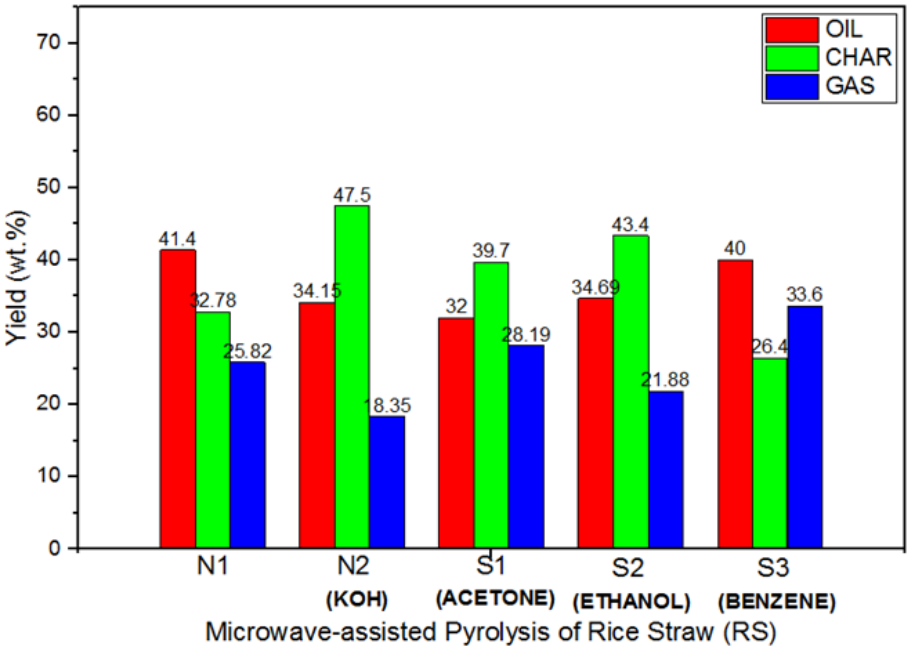


Figure 5. Yields of Microwave-assisted pyrolysis of Rice straw.

Table 2 and **Figure 5** show details of five different experiments (i.e. N1, N2, S3, S2, and S1) using 10 grams of rice straw. The catalyst and solvent-soaking conditions were varied. Experiment N1, without catalyst or soaking, produced only 25.82% oil, with the highest char content (Char) of 32.78%. When KOH was added (experiment N2), the overall conversion increased to 81.65%, and the char yield decreased, indicating the catalyst's effectiveness in promoting the decomposition of organic compounds. In experiments S1-S3, the feedstock was soaked in different solvents. Ethanol (sample S2) and acetone (sample S1) significantly improved oil yield to 62% and 61%, respectively, while benzene (sample S3) reduced oil yield to 21.8%. This indicates that the solvent type affects the cleavage potential of rice straw when exposed to microwaves [23].

3.3. Temperature and Heating Rate Profiles of MW-assisted pyrolysis of Rice straw

The temperature profiles corresponding to microwave pyrolysis of Rice straw soaked in different solvents and without soaking with solvent, as well as with KOH catalyst and without catalyst, are depicted in **Figure 6** in the order mentioned in **Table 2**. Temperature profiles were achieved when feedstock was pyrolyzed at a microwave power of 450W; in experiment N1 regarding rice straw without soaking or catalyst, and experiment S3 regarding rice straw soaked with benzene, the oil yield was highest, heating value 34.8 MJ/Kg and 35.2 MJ/Kg respectively, the average heating rate was 42.38 and 21.8 °C/min, respectively. Experiments involving MW-assisted pyrolysis of rice straw showed the following trend in terms of average heating rate: S2 (62 °C/min) > S1 (61 °C/min) > N1 (42.38 °C/min) > N2 (39.17 °C/min) > S3 (21.8 °C/min). The AHR of MW-assisted pyrolysis of rice straw that was pre-treated by soaking for 24 hours with Ethanol (sample S2) and Acetone (sample S1) was the highest, with high gas yield (43.4 and 39.7 wt%, respectively). In the MW-assisted pyrolysis of rice straw that was pre-treated by soaking for 24 hours with benzene (sample S3), the AHR was the lowest (21.8 °C/min) with the lowest gas yield (26.4 wt%) and highest char yield (33.6 wt%). The heating rate profiles in **Table 3** show that graphite is a promising susceptor owing to the high average heating rate, thermal stability, high heating rates achieved in the initial pyrolysis phase, and the pre-treatment by soaking with Ethanol and Acetone [10,24].

Table 3. Temperature and heating rate Profiles of MW pyrolysis.

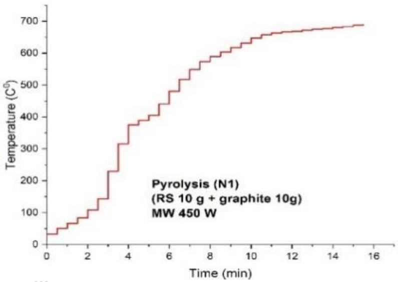
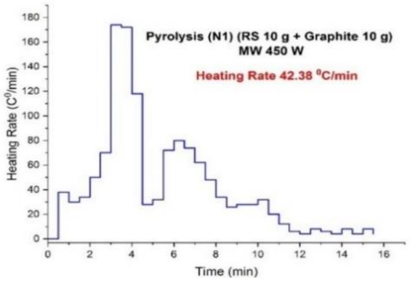
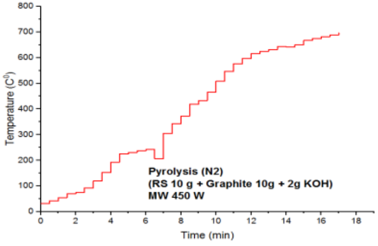
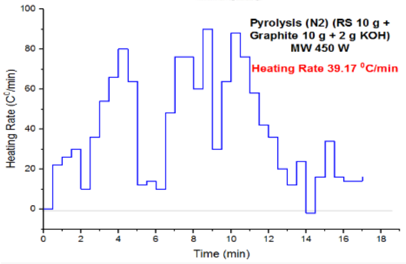
Sample	Temperature	Heating rate
10 g RS + 10 g Graphite		
10 g RS + 10 g Graphite + 2 g KOH		

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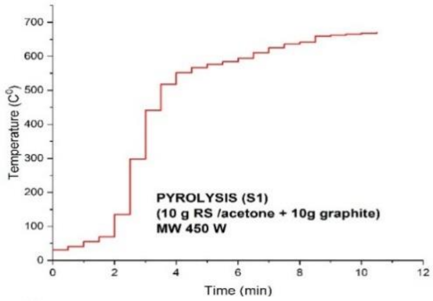
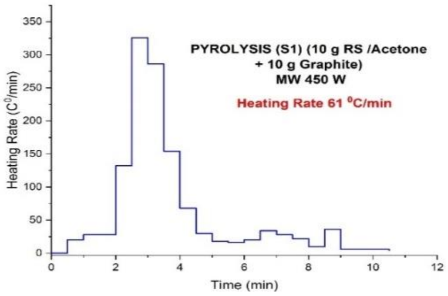
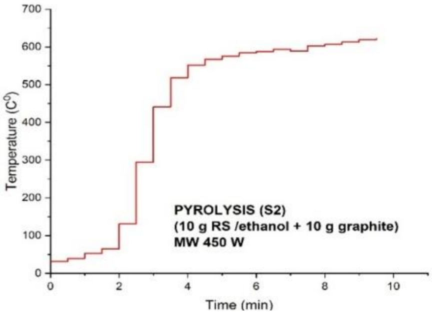
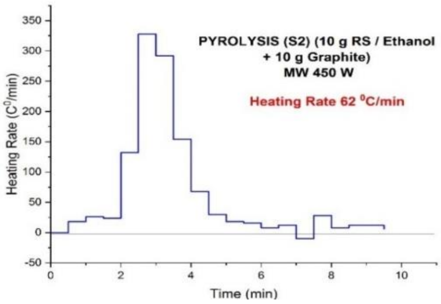
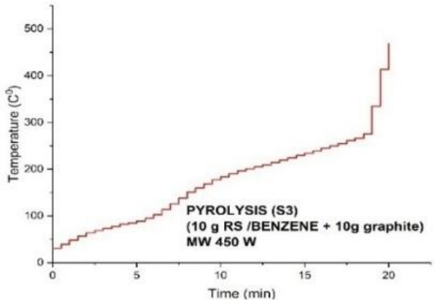
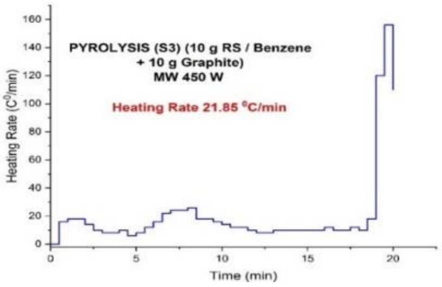
Table 3 (continue). Temperature and heating rate Profiles of MW pyrolysis.

Sample	Temperature	Heating rate
10 g RS/acetone + 10 g Graphite		
10 g RS/ethanol + 10 g Graphite		
10 g RS/benzene + 10 g Graphite		

3.4. Microwave energy consumed and Higher Heating Values of MW-assisted pyrolysis Oil of Rice Straw

Bomb calorimeter experiments were performed on oil samples to ascertain the higher heating values of MW-assisted pyrolysis of Rice Straw (RS) and MW-assisted pyrolysis of pre-treated rice straw with solvents, as shown in **Table 2**. A specific range of combustion times in minutes was used for all the trials. The HHV of Pyrolyzed RS without a catalyst is 34.8 MJ/kg, and Pyrolyzed RS with a KOH catalyst is 35.4 MJ/kg. The HHV values increased using a KOH catalyst [25]. The trends of HHV of MW-assisted pyrolysis of soaked Rice Straw with solvents are as follows: S3 (35.2 MJ/kg) > S1 (35 MJ/kg) > S2 (34.9 MJ/kg), benzene, Acetone, Ethanol, respectively. The microwave energy required is calculated using Equation (1) [10]:

$$Microwave\ energy = \text{MW Power } (450\ W) \times Total\ pyrolysis\ time\ \text{(min)} \tag{1}$$

3.5. Pyrolysis index

The mass, heating value, pyrolysis time, conversion, and pyrolysis energy consumption of the feedstock are some of the variables that determine the performance of PI. Its value can be anywhere from 0 to ∞, with higher values indicating more effective pyrolysis. The pyrolysis index was determined using Equation (2):

$$Pyrolysis\ index\ (PI) = F_m * F_{HHV} * F_X \,/\, P_{EC} * P_t \tag{2}$$

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Where P_t, P_{EC}, F_m, F_X, F_{HHV} are pyrolysis time (s), pyrolysis energy consumption (J/s), the mass of feedstock (g), conversion of feedstock (%), and the higher heating value of feedstock (J/g), respectively [10,26].

In **Table 4** and **Figure 7**, it displays the solvents' effect on RS's PI values when RS pyrolyzed separately effect of no catalyst, KOH catalyst, and soaking in solvents; their respective PI values are 46.97 when soaking for 24 hours in ethanol and 39.27 when soaking for 24 hours in acetone, respectively. On the other hand, PI recorded for RS varies in the following order: ethanol (46.97) > acetone (39.27) > KOH Catalyst (26.32) > without catalyst and solvents (26.26) > benzene (22.71). Furthermore, the pyrolysis index has an inverse relationship with the pyrolysis time, except for N2 (17 min), due to the high conversion rate attributed to the catalyst's effect. The trend is as follows: ethanol (9.5 min) > acetone (10 min) > without catalyst and solvents (15.5 min) > benzene (20 min). An improvement in PI is due to a shorter pyrolysis time and a higher conversion rate [27]. A few key factors that significantly impact the PI values include the feedstock type, feedstock characterization, pyrolysis reaction time, conversion percentage, and energy consumption during pyrolysis [10,24,26].

Table 4. Pyrolysis index of MW-assisted pyrolysis of RS under the effect of catalyst and solvents.

Sample	RS (g)	KOH Catalyst (g)	Soaking solvent	Oil yield (wt%)	Gas yield (wt%)	Char yield (wt%)	Pyrolysis time (min)	Pyrolysis index
N1	10	NO	No	41.4	32.78	25.82	15.50	26.26
N2	10	2	No	34.15	47.50	18.35	17.00	26.32
S3	10	NO	Benzene	40.00	26.40	33.60	20.00	22.71
S2	10	NO	Ethanol	34.69	43.40	21.88	9.50	46.97
S1	10	NO	Acetone	32.00	39.70	28.19	10.50	39.27

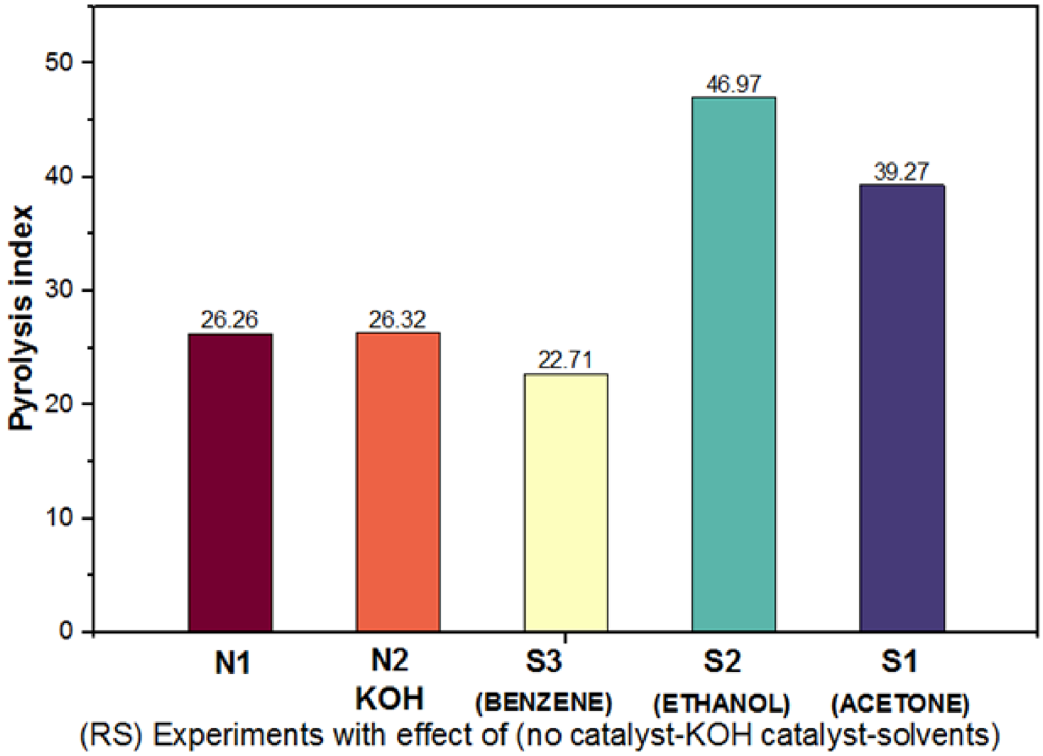

Figure 7. Pyrolysis index of microwave-assisted pyrolysis of rice straw.

Figure 7 and **Table 4** show the pyrolysis index (PI) of rice straw using microwaves under the influence of catalysts and solvents. The Pyrolysis Index (PI) is a measure used to evaluate the efficiency of the pyrolysis process. In experiments N1 and N2, no solvents were used; the first was without a catalyst, and the second was with KOH. Both showed low PIs (26.26 and 26.32, respectively), indicating that the effect of the KOH catalyst on the process efficiency was limited in the absence of a solvent. Experiments S1, S2, and S3 relied on soaking the feedstock in various organic solvents. Experiment S2 (ethanol) achieved the highest PI (46.97), reflecting ethanol's effectiveness in improving the quality of the pyrolysis process by enhancing gas and oil production and reducing the pyrolysis time (only 9.5 min). Experiment S1 (acetone) ranked second with an index of 39.27, while experiment S3 (benzene) was the least effective (22.71) despite its high oil content. These results demonstrate that solvent type plays a crucial role in improving the thermal decomposition of rice straw using microwaves. Polar solvents such as ethanol and acetone help break down organic bonds more efficiently compared to non-polar benzene. Reducing decomposition time also enhances energy efficiency and lowers operating costs, reinforcing the importance of selecting optimal processing conditions to achieve better results in biofuel production [28].

3.6. Specific surface area analysis

Surface area analysis was performed to determine the surface area of the solid residues created by microwave pyrolysis of rice straw at 450 W power. There was a range of 175.76–284.49 m^2/g for the BET surface area (SBET), 243.88–382.11 m^2/g for the Langmuir surface area (SL), and 140.93–206.10 m^2/g for the mesopore surface area (Smesopore). The specific surface area could be increased during the MW-pyrolysis experiment on fresh rice straw using a different pre-treatment solvent and a KOH catalyst. The KOH catalyst produced a higher gas yield of 47.5%. Additionally, the rice straw that was pre-treated with ethanol and acetone resulted in a high gas yield of 43 weight percent and 39 weight percent, respectively, with a high average heating rate of 63 °C/min. as well as the trends of total pore volume (VT) and mesopore volume (Vmesopore), which, when combined, imply a more specific surface area with a higher heating rate profile and a higher temperature. Given that 4VT/SBET calculated the average pore diameter (Dave) to be between 24 and 25 Å, it may be concluded that there was a negligible difference in diameters when subjected to various soaking solvents [26,27,29].

3.7. Analysis of Oil and Gas Yields

Following the extraction of the oil yield from the microwave pyrolysis of rice straw using dichloromethane, the oil was analyzed using GC/MS. A semi-quantitative study was carried out by determining the relative proportion of chromatographic area occupied by each chemical. The primary chemicals that are included in the liquid product can be classified into three distinct groups:

(i) alkanes, which range from carbon 12 to carbon 32;
(ii) polar structure, which includes phenol and its derivatives; and
(iii) polycyclic aromatic hydrocarbons (PAHs), which consist of two to three rings and their derivatives [30].

As a result, the liquid product had a composition that was extensively alkylated and oxygenated, and the amount of potentially harmful PAHs was significantly lower. Due to the complexity of the liquid product's composition, additional refinement will be required before it can be put to any practical use. During microwave-assisted pyrolysis, a significant amount of hydrogen is created, demonstrating that the microwave pyrolysis of rice straw can produce a fuel gas rich in hydrogen. In addition, to calculate the caloric value of the gas, approximately half of the percentage of hydrogen 55 vol.%, carbon dioxide, carbon monoxide, and methane from the rice straw sample was converted to gases 17, 13, and 10 vol.%, respectively. Three gases, H_2, CO, and CH_4, with high heating values (HHV), were used. The calorific value of the gaseous product was calculated to be approximately 9.83-11.54 MJ/Nm^3, which is higher than the values obtained from the gasification process, which range from 4–7 MJ/Nm^3 [31,32].

4. CONCLUSION

Production and energy consumption vary considerably according to the type of solvent and whether MW is catalytic or non-catalytic. The RS was pre-treated with ethanol and acetone to obtain a high pyrolysis index. The yields of bio-oil, gas, and char produced by the rice straw soaked in the solvent differed from those produced by the fresh feedstock. The maximum gas output was observed when MW-assisted pyrolysis of untreated RS was performed with a KOH catalyst. By pre-treating rice straw with ethanol and acetone, the time required for pyrolysis was cut down, and the energy consumed was lowered. Benzene was used to pre-treat rice straw, which decreased the average heating rate to 21.8 °C/min and increased the amount of oil and char produced. As a result of the transformation of approximately half of the rice straw sample into hydrogen-rich fuel gas, the percentages of hydrogen, carbon dioxide, carbon monoxide, and methane were (55; 17; 13; and 10 vol.%), respectively. With high heating value gases. There was a significantly lower concentration of potentially hazardous PAHs in the condensable portion of the product, which was strongly alkylated and oxygenated. The use of solvents to pre-treated the RS before the thermal decomposition with the assistance of the microwave showed many benefits compared to the previous studies, as it showed reducing the time of reaction, reducing energy consumption, and increasing the percentage of products, as well as raising the thermal value of the oil products and gases resulting from microwave-assisted pyrolysis of rice straw. In light of this, microwave pyrolysis would make it possible to recover the resources and energy inside rice straw. It is necessary to conduct additional research to determine whether or not this technology is feasible and whether or not it can be implemented.

5. AUTHORS' NOTE

The authors declare that there is no conflict of interest regarding the publication of this article. The authors confirmed that the paper was free of plagiarism.

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