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# Microwave co-pyrolysis of Agro–Waste rubber Tire: Char and Oil Characterization

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## Abstract

*The purpose of this study is to investigate the feasibility of using waste rubber tires (WRT) in conjunction with rice straw (RH) and sugarcane bagasse (SCB) for microwave-assisted co-pyrolysis in order to recover char and oil. While co-pyrolyzing SCB: WRT and RH: WRT blends, the impacts of temperature profiles, and average heating rates are carefully investigated in the study. In addition to comparing and contrasting products, it delves into the ways in which char, oil, and gas yields change when subjected to varying feedstock blends and catalysts. Both the KOH and NaOH catalysts improved the oil and char yields at a SCB: WRT ratio of 2.5:17.5. With a 1:1 RH: WRT ratio, the char yield was raised by more than 34% with KOH and NaOH, while the gas output was increased by 42.66% with CaO. While NaOH kept a larger percentage of oxygenated chemicals, KOH was better at deoxygenating and aromatising liquid goods to improve their quality, contrarily, gasification was promoted by CaO. The SCB: WRT combination increased oil yield by 37.72%, which is somewhat less than the RH: WRT combination's 37.05%, thus, the analysis concludes that SCB: WRT is the optimal mix for increasing total product production. In addition, KOH facilitated the production of hydrocarbon-rich oil with lower oxygen concentration and a char structure that was more fragrant. According to XRD examination, the char matrix contained highly crystalline potassium and sodium salts as a result of a reaction between silica in rice husk ash and alkali catalysts (KOH and NaOH). The results show that catalyst selection is the most important factor in controlling the distribution of renewable energy products produced by microwave-assisted co-pyrolysis, which is a strong and highly adjustable method for processing complex waste streams.*

Keywords: SCB; RH; WRT; Microwave catalytic co-pyrolysis; Pyrolysis oil and char.

## 1. Introduction

The effective management of agro-industrial waste plays a pivotal role in mitigating various forms of pollution. Sustainable treatment is necessary for sugarcane bagasse (SCB), a large biomass waste product of the sugar industry following cane juice extraction [1]. Wet sugarcane bagasse is used as fuel in some sugar mills, but most of the time it's piled up and burnt on-site, creating a very combustible biomass that is bad for both the industry and the environment [2]. The energy potential of biomass is significant in a variety of agricultural and forestry waste products, including straw, bagasse, coffee husks, rice husks, wood chips, sawdust, and bark [3-5].

Out of the 500 Mt of crop residues produced annually, 60 Mt is generated in Uttar Pradesh, 51 Mt in Punjab, and 46 Mt in Maharashtra, according to the National Policy for Management of Agricultural Residues. Of this, about 92 Mt are burnt in the open fields. The two staple grains that produce the most excess produce are wheat and rice [6-8]. The Ministry of New and Renewable Energy (MNRE) reported that India's installed biomass power capacity was 10,205.6 MW as of October 2022. The capacity to generate electricity from biomass in India is over 18,000 MW. Industries have been pushed to meet their energy needs through the adoption of biomass wastes by the government through its laws [9].

After biomass devolatilization, scientists have found that turning agricultural waste into biochar is an efficient way to harness energy, thus they've set out to solve this problem. The conversion of biomass into charcoal, biogas, and biofuel products with added value is a topic of scholarly interest. To counteract stubble burning in agricultural areas, one key technique to waste management is the thermochemical conversion of crop wastes into biochar [6]. In India, the potential production of biochar from 517.82 MT of agricultural residues might reach 212.04 ± 44.27 million metric tonnes, which would result in a market value of $500 billion. An effective technique being used to achieve a circular economy is the valorisation of crop leftovers for possible uses such as organic manure, compost, biochar amendment in soil, and renewable solid fuel [10-11]. In order to avoid polluting the environment, the present method of managing rice husks involves either mass burning or direct disposal into soil. Therefore, it is necessary to transform rice husks into by-products with additional value (Zhang et al., 2018).

Conversely, WRT is a waste product that originates from fossil fuels. According to Naveed Ahmed et al. (2018), the global production of tires is approximately 1.5 billion units per year [12-13]. Unfortunately, WRT is also utilised for direct combustion heat generation, which has a greater effect on air quality despite the tiny increase in energy gained [14-15]. Due to their petrochemical nature, the hydrocarbon solids (char), liquids, and gases that are formed during the subsequent breakdown of polymers are considered fuel grade [16-19].

Biomass and tyre debris can be transformed into useful bioproducts through a process known as thermochemical and biochemical conversion [20-21]. Microwave pyrolysis has recently attracted the attention of researchers due to its potential to outperform traditional pyrolysis methods in terms of heating efficiency and the quality of fuel and chemical compounds produced. The use of microwaves to heat materials accelerates and uniformises the pyrolysis process. Because it is more efficient, requires less energy, and can be controlled more precisely, microwave heating has surpassed traditional heating methods [22-23]. It is possible to produce less complex chemicals by heating long-chain polymer molecules and using a catalyst. Pyrolysis and co-pyrolysis procedures that make use of microwave heating systems can boost product yield, enhance product quality, and slow down reaction times. By manipulating the pyrolysis processes with microwaves, product distribution and yield can be improved. The fast and effective heating capability of microwave-assisted pyrolysis makes its commercialization feasible. By providing a more environmentally friendly and cost-effective alternative, this technology has the potential to revolutionize pyrolysis. Selective material heating, increased automation, and safety are a few further benefits of microwave processing [22].

The oil that results from pyrolysing lignocellulosic biomass is acidic, has a low calorific value, and contains a lot of moisture, which makes it unstable in both heat and storage. Crucially, a large need for hydrogen develops due to the oil's high oxygen concentration. By encouraging synergistic interactions between the intermediates generated from the two feedstocks, co-pyrolyzing biomass with hydrogen-rich polymers is one way to improve oil quality. The high carbon content and heating potential of the scrap tyre make it an ideal candidate for co pyrolysis [21].

The possibility of catalytic co-pyrolysis and co-pyrolysis to increase the yield and quality of pyrolysis oil has recently attracted a lot of interest. Several studies have found that catalytic co-pyrolysis improves the oil's characteristics and yield, which could be due to the synergistic effects of two materials used in the pyrolysis process (Ahmed et al., 2018; Shah et al., 2019). Waste tyres and biomass pyrolysis byproducts have radical interactions, which are associated with the upgrading process. Also, the new bio-oils are more stable since the number of aldehydes and phenolic chemicals is greatly reduced when waste tires are added to the feedstock mix [21- 26].

Using a fixed-bed reactor, Ahmed et al. (2018) investigated the co-pyrolysis of sugarcane bagasse (SCB) and tyre waste (WRT) [12]. Results showed that pyrolysis oil yield was 49.7 weight percent when using an optimized ratio of WRT to SCB of 1:3, compared to 42.1 weight percent when using SCB as a single feedstock. The calorific value of the oil reached 41.0 MJkg 1 (WRT /SCB; 1:3), a considerable increase from 19.1 MJkg 1 (SCB) after adding WRT to SCB.

The purpose of this research was to examine the effects of catalytic co-pyrolysis of SCB and RH with WRT on the yield of liquids and char, both in terms of quality and quantity. This study is anticipated to contribute significantly to the current body of knowledge regarding the synergistic effects of co-pyrolysis, which are contingent upon the composition and combination of the feedstock. Up until now, no research has examined the production of oil and char through catalytic co-pyrolysis of this particular feedstock combination, so it is important to fill this gap.

## 2. MATERIALS AND METHODS

### 2.1. Materials

In this study, source for rice husk feedstock was a nearby mill in the Indian city of Visakhapatnam, in the state of Andhra Pradesh. A nearby sugarcane processing company supplied the sugarcane bagasse, which is a byproduct of sugarcane juice extraction. A carbon-rich polymeric waste, was obtained from a local tyre recycling facility. Industrial grade graphite powder (Fe 98.5% pure, ~50 μm), procured from Sisco Research Laboratories Pvt. Ltd., India, and was used as a susceptor. The borosilicate flask was protected by a ceramic wool thermal insulation muffle, which had a shallow cylindrical shape. A sturdy base for the reactor was constructed by wrapping the insulation muffle with Teflon® tapes. Additionally, the condensation, thermocouple, and oil collection system's joints were sealed using Teflon® tape.

### 2.2. Experimental Methodology

A modified microwave oven was used to conduct pyrolysis tests. The top side of the microwave oven cavity was machine drilled to provide a circular opening. To hold the mixture of feedstock and susceptor, a 500 mL borosilicate flask was utilized. This was accomplished by means of a K-type thermocouple in particular. In order to keep track of the feedstock temperature during the pyrolysis process, this sturdy sensor is made of two different metal alloy wires, Chromel and Alumel, which are connected at a sensing junction. A condensation network was attached to the flask in order to condense the pyrolysis vapours. The feedstock mixture also included ambient oxygen, therefore nitrogen gas was used to purge it. Direct measurement and mass balance were used to determine the gas, oil, and char yields. For every experiment, the feedstock combinations of SCB: WRT and RH: WRT were combined with 10 g of graphite and 5 g of KOH catalyst; the identical procedure was repeated with other catalysts. A large number of studies were conducted to determine the microwave catalytic co pyrolysis of RH and SCB with WRT.

### 2.3. Product Collection and Quantification:

The solid (biochar) and liquid (bio-oil) byproducts were measured and collected once the reaction was finished. Here are the formulas that were used to determine the yields of char, oil and gaseous products:

$$\text{Char Yield (wt\%)} = \frac{Mass\ of\ Char\ (g)}{Initial\ Mass\ of\ Feedstock\ (g)} \times 100\% \quad (1)$$

$$\text{Oil Yield (wt\%)} = \frac{Mass\ of\ Oil\ (g)}{Initial\ Mass\ of\ Feedstock\ (g)} \times 100\% \quad (2)$$

$$\text{Gas Yield (wt\%)} = 100\% - (\text{Char Yield \%} + \text{Oil Yield \%}) \quad (3)$$

### 2.4.Product (char & oil) Analysis

The characterization of bio-oil included FTIR, NMR and GC-MS analyses while that of bio-char included XRD, BET and SEM analyses. The analysis was performed using a Bruker TENSOR II FTIR spectrometer. Spectra were observed in the wavenumber range of 4000 to 400 $cm^{-1}$. The carbon structures present in the liquid bio-oil can be determined using Nuclear Magnetic Resonance (NMR) spectroscopy. Specifically, $^{13}C$ NMR spectra was observed on a Bruker Avance III 400 MHz instrument. The pyrolysis-oil fraction obtained from microwave pyrolysis experiments were analyzed by using GC/MS (Agilent 7890, 5975C) for organic composition. The column used for the separation of pyrolysis vapors was HP-5MS (30 m length × 0.25 mm i.d. × 0.25µm film thickness). Ultra-high pure helium (99.9995%) was used as the carrier gas at a flow rate of 0.8 mL $min^{-1}$.

Regarding the product of solid char, using a PANalytical Empyrean diffractometer with Cu Kα radiation ($\lambda$ = 1.54 Å), X-ray diffraction (XRD) was performed to investigate the crystalline structure, phase composition, and any changes to its graphitic nature. The surface area, pore volume, and pore size distribution of the solid char obtained from microwave co-pyrolysis experiments were analyzed using BET (Brunauer-Emmett-Teller) analysis. The surface morphology of the solid char obtained from microwave co-pyrolysis experiments was examined using Scanning Electron Microscopy (SEM). The analysis was performed using a JEOL JSM-IT200 InTouchScope™ Scanning Electron Microscope.

## 3. Results and discussion

### 3.1. Temperature profiles observed during microwave-assisted co-pyrolysis of RH: WRT::1:1 and SCB: WRT::2.5 : 17.5

The purpose of the co-pyrolysis tests was to examine the effects of WRT on SCB and RH (Rice Husk). The temperature-time patterns displayed in Figure 1 clearly demonstrate that the overall pyrolysis time can vary between 4 and 13 minutes. There is a clear upward trend in the SCB:WRT temperature-time profile compared to the RH:WRT profile. Additionally, it was noted that RH:WRT had a more linear relationship with an upward tendency. In comparison to traditional heating methods, microwave pyrolysis was discovered to exhibit a distinct non-linear property. Low dielectric losses at room temperature cause biomasses like RH and SCB to heat slowly at first until they reach the critical temperature or moisture content. That was the only reason susceptors like graphite were used as microwave absorbers. In around 4 min, it was seen that the RH:WRT and SCB:WRT plots were linear, and this region is known as the initial drying phase. From around 4 to 10 min, a steep upward slope was observed in the SCB:WRT plot. This phase is known as the rapid heating phase. In this phase, the decomposition of the materials takes place with the formation of pyrolysis-oil and gas over char. The slope of the graph rapidly increased in this region, indicating the decomposition followed by the formation of products. As in the previous works mentioned earlier, DV Suriapparao et al. (2022) plotted and studied the graphs for temperature-time data for the various feedstock ratios [25].

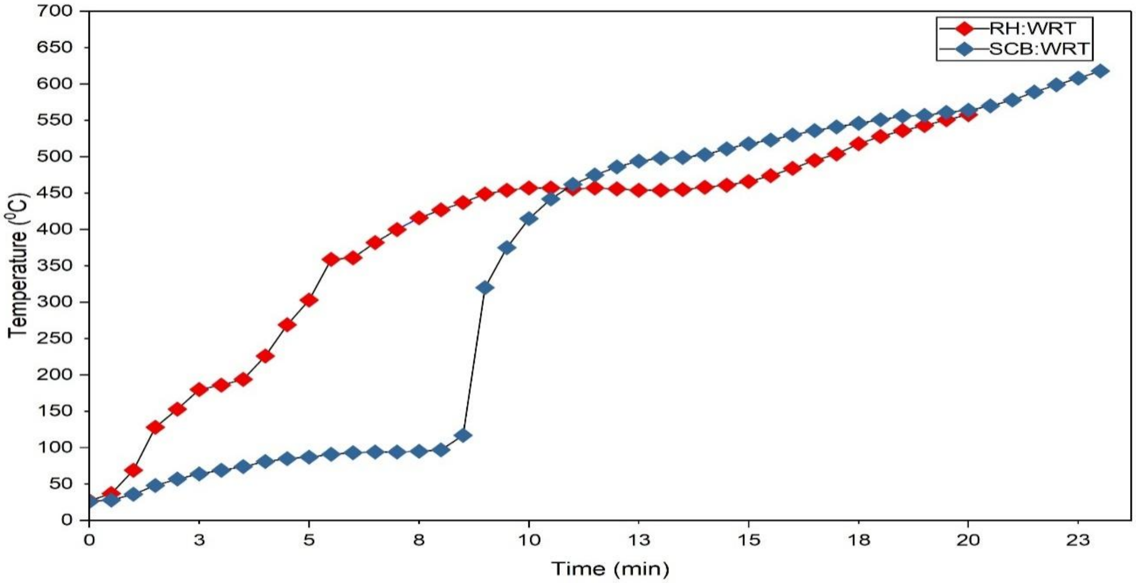

**Figure 1 Temperature profile of co pyrolysis of RH: WRT and SCB: WRT**

Susceptor play an important role in microwave pyrolysis by converting incident microwave energy into thermal energy. The converted microwave energy into heat energy is associated with frictional resistance offered by materials in the microwave field. Kinetic energy associated with vibrational, rotational and translational movement of valence electrons is responsible for the generation of thermal energy. Graphite was used as a susceptor as it was a promising susceptor owing to high average heating rate, thermal stability and high heating rates achieved in the initial phase of pyrolysis. With high sample heating rate, the higher yields of oil and lower yields of non-condensable gases and solid char were obtained. While sample heating rate proved to be an important criterion in microwave pyrolysis, there were other factors that determined the quantity and quality of oil. The essential nature or chemical structure of the susceptor, the type of catalyst and susceptor to feed ratio also played significant roles in the microwave pyrolysis reaction.

### 3.2. Product yields at different feedstock combination of RH: WRT::1:1 and SCB: WRT::2.5 : 17.5

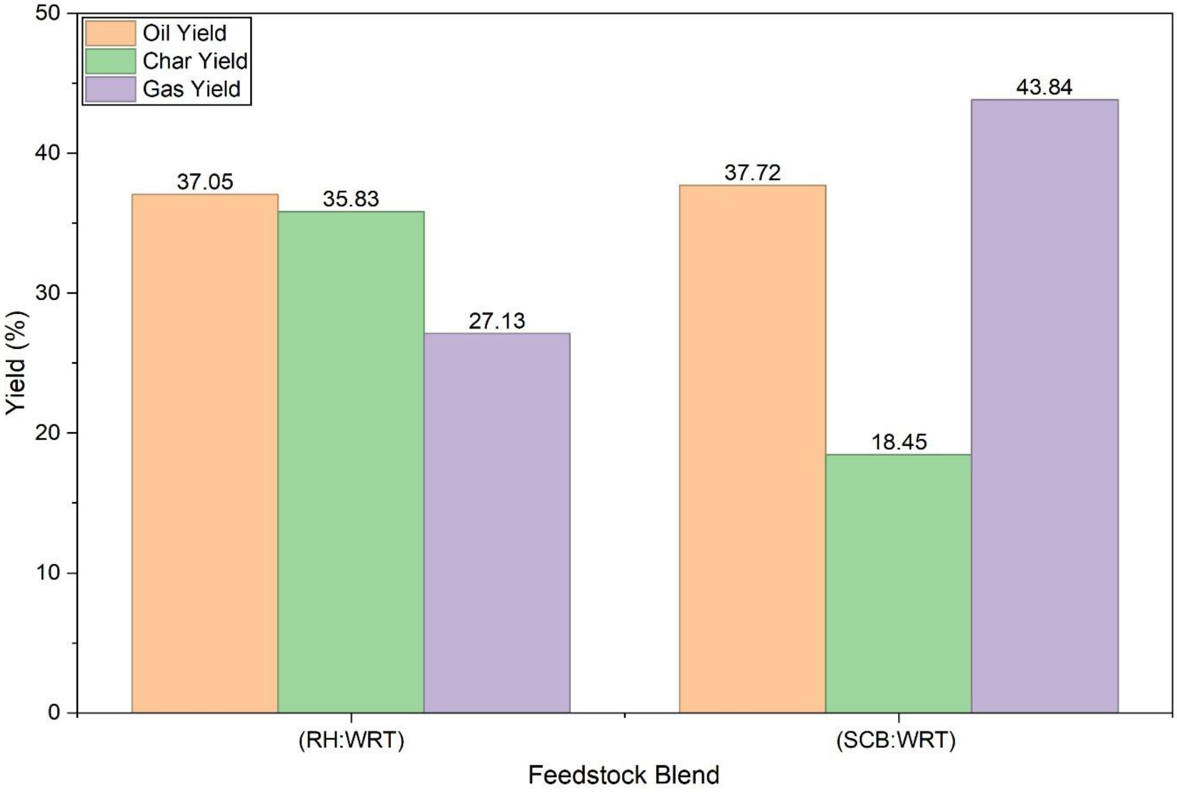

**Figure 2. Product yields for different feedstock combinations**

**Figure 2** predicts the percentage yields of char, oil, and gas, obtained from the combinations of RH:WRT and SCB:WRT with the KOH catalyst, at the microwave power of 450 W.  It was observed that the oil yield for RH:WRT was 37.05%, whereas the oil yield for the SCB:WRT was 37.72%. The reason for slight increase in oil yield in the SCB:WRT mixture was due to the formation of more hydrocarbons as the end product and also due to the high synergistic effect of the feed mixture rather than the RH:WRT mixture. The char yield for the co-pyrolysis of RH:WRT was found to be 35.83%, and that of the SCB:WRT it was 18.45%. The formation of char in the SCB:WRT mixture was lower than in the RH:WRT mixture; this indicated that the biomass content in the RH was higher than that of SCB. But when the gas yield was analyzed, it was observed that in the RH:WRT mixture it was 27.13% and in the SCB:WRT mixture it was 43.84%. The SCB:WRT mixture showed a significantly higher gas yield, indicating that therewere more volatiles in the SCB:WRT mixture than in the RH:WRT mixture.

Overall, the data depicted that feedstock combinations significantly influences product distribution, with moderate energy inputs favoring oil yields and higher consumption driving gas production, necessitating tailored optimization for desired outcomes.

### 3.3. Average heating rates during the co-pyrolysis of RH: WRT::1:1 and SCB: WRT::2.5 : 17.5

Higher heating rates achieved at higher microwave powers (450 W) are due to sustained generation of microplasmic spots. The microplasma spots were generated due to the ejection of elctrons from the valence shell of the susceptor at high microwave power level. In both of the mixtures RH:WRT and SCB:WRT , the higher microwave powerof 450 W helped in generating huge amount of energy, the temperature rise or heating rate was steady at 14±8 $^{0}$C min$^{-1}$in time period of around 20 minutes. But it was observed that heating rates in the initial 5 min or above of microwave irradiation increased to 118 $^{0}$C min$^{-1}$ in RH:WRT and 406 $^{0}$C min$^{-1}$in SCB:WRT respectively. Because of the synergistic effect of SCB:WRT, the average heating rate peaked to a very high value, indicating the initial boost of tempearature led to uncontrollled or excessive cracking of long chain polymer an results in the production of light hydrocarbons (**Figure 3**). The formation of products and the profile trend suggested that with catalyst there was increased thermal energy transfer, driving rapidcracking and deoxygenation while the decline correlates with the observed yield variation with higher gas yields with slow initial rates and increasing gas yields. Similar report was also studied by Suriapparao, & Vinu (2015) [25].

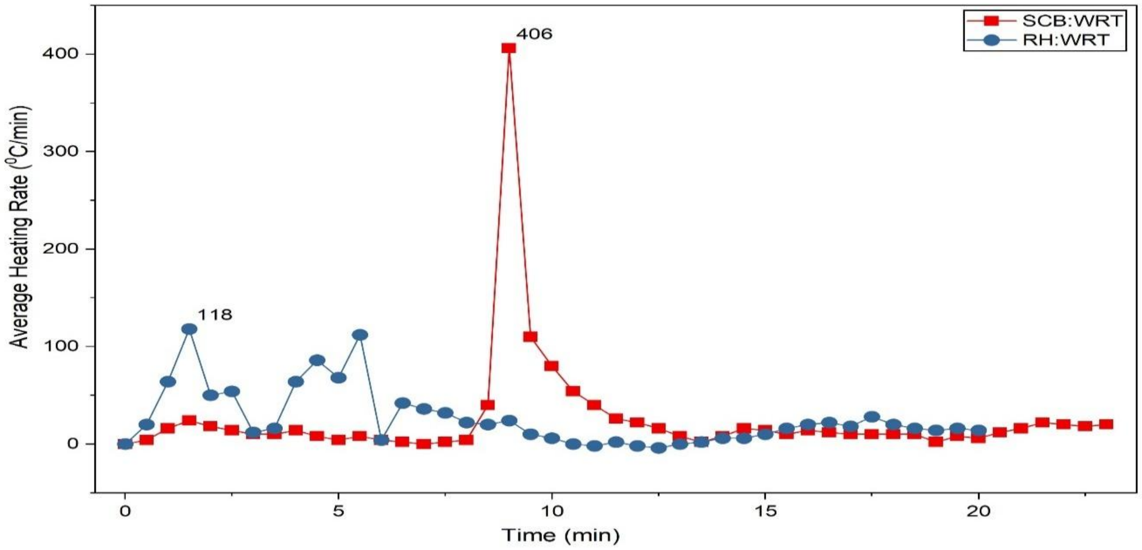

**Figure 3 Average heating rates of co pyrolysis of RH: WRT and SCB: WRT**

### 3.4. Product yield of co pyrolysis of RH: WRT::1:1 and SCB: WRT::2.5 : 17.5 at different catalysts

**Figure 4.,** shows the changes in char, oil and gas yields from the microwave co pyrolysis of RH:WRT and SCB:WRT at different catalysts. It was observed that the highest yield percentage of oil, char and gas respectively for RH:WRT was 37.05%, 35.83% and 65.6% and that for SCB:WRT was 37.72%, 34.14% and 43.84%.

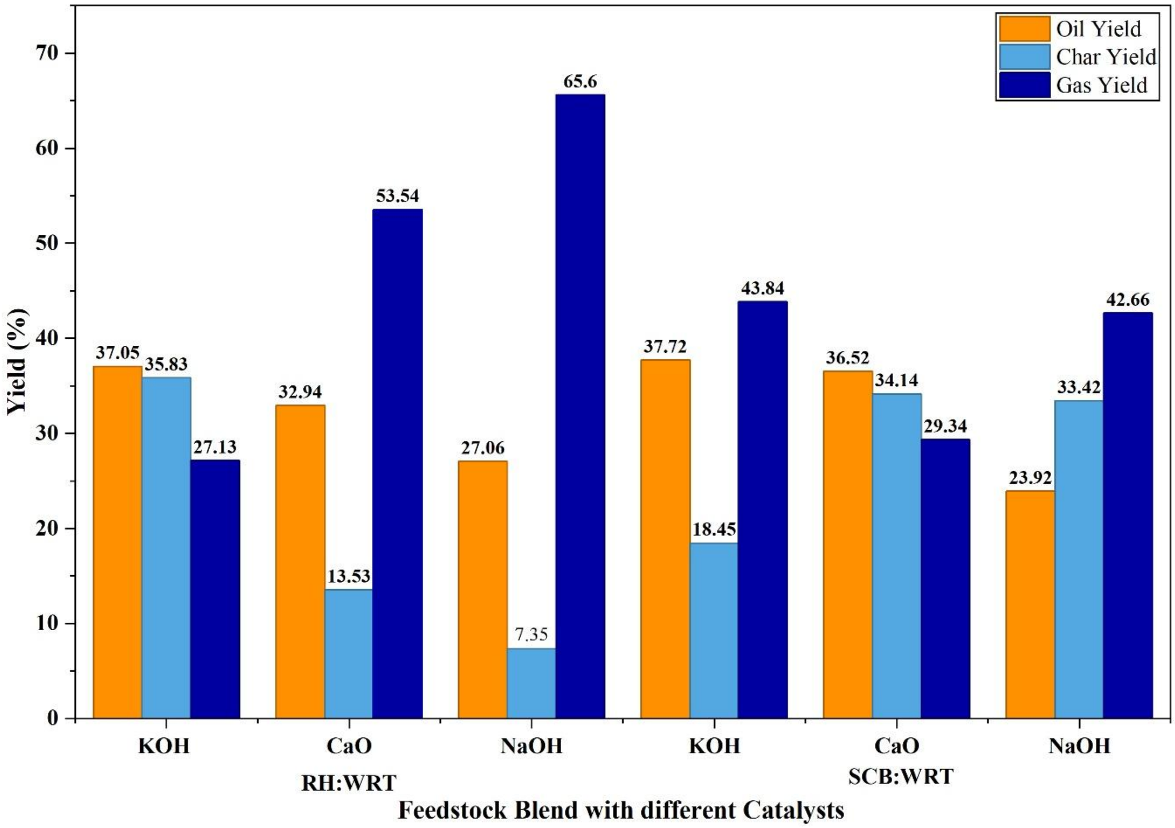

**Figure 4 Effect of catalysts on feedstock blend**

The introduction of KOH significantly modified the product distribution in both the feed mixtures RH:WRT and SCB:WRT. The oil yield continued to rise steadily with catalyst loading. This trend indicates that lower amounts of KOH and NaOH effectively catalyze reactions that favor the formation of condensable volatiles. The oil yield showed a progressive increase with less catalyst loading and higher loadings resulted in a decreasing oil yield. This indicated that higher concentrations of NaOH intensify catalytic dehydration and decarboxylation reactions, converting condensable hydrocarbons into solid and gaseous products. In contrast to the alkali hydroxides, the catalytic activity of CaO favored gasification and charring reactions over oil production across all tested loadings. Even the smallest addition of CaO resulted in a low oil yield continued to decrease progressively. This confirms that CaO is a strong catalyst for decarboxylation and reforming reactions, converting potential oil vapors directly into non-condensable gases, leading to gas yields consistently above 42 wt%. From this study it was concluded that all catalysts were effective in altering the product distribution, their impact on oil yield was highly dependent on type and concentration. Both KOH and NaOH showed optimal performance at a 5 g loading for maximizing liquid oil yield. However, at higher dosages, all catalysts promoted excessive cracking and gasification, thereby lowering the total oil recovery.

### 3.5. Characterization of char

### 3.5.1. X-ray diffraction (XRD) studies:

The XRD results provided critical insight into how catalyst-induced structural evolution in char governs the overall thermochemical environment, linking solid-phase transformation with liquid product selectivity [28-29].

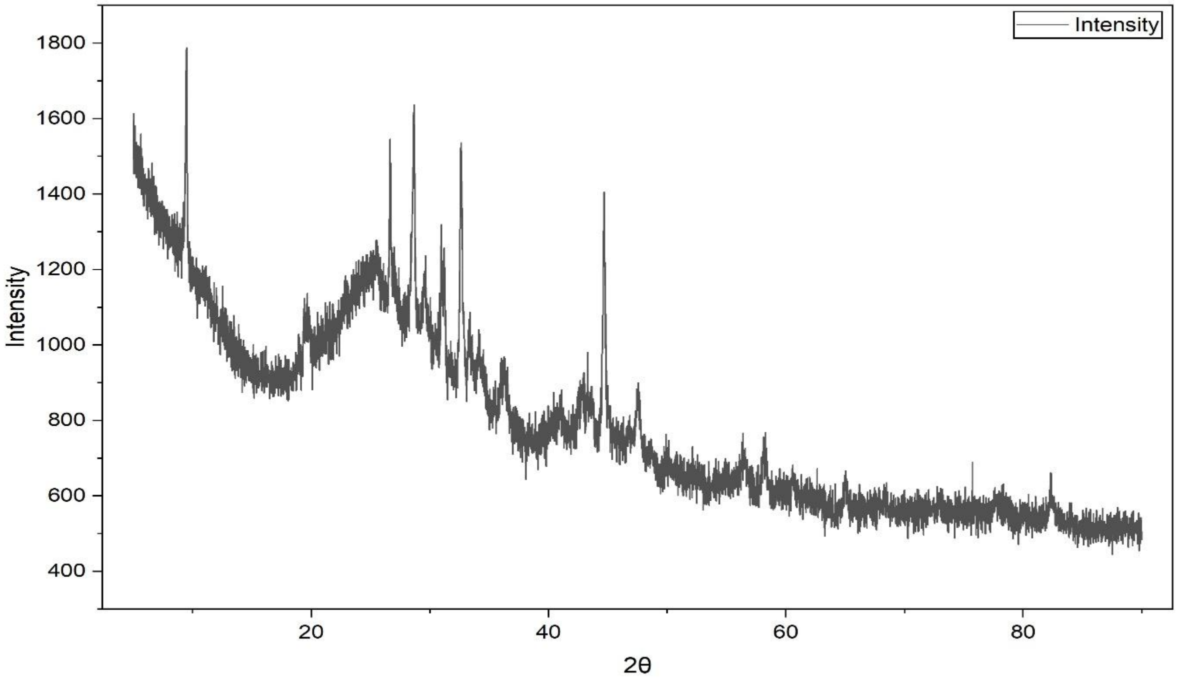

**Figure 5 (a) XRD spectrum of char from co-pyrolysis of SCB: WRT::2.5 : 17.5 with KOH catalyst**

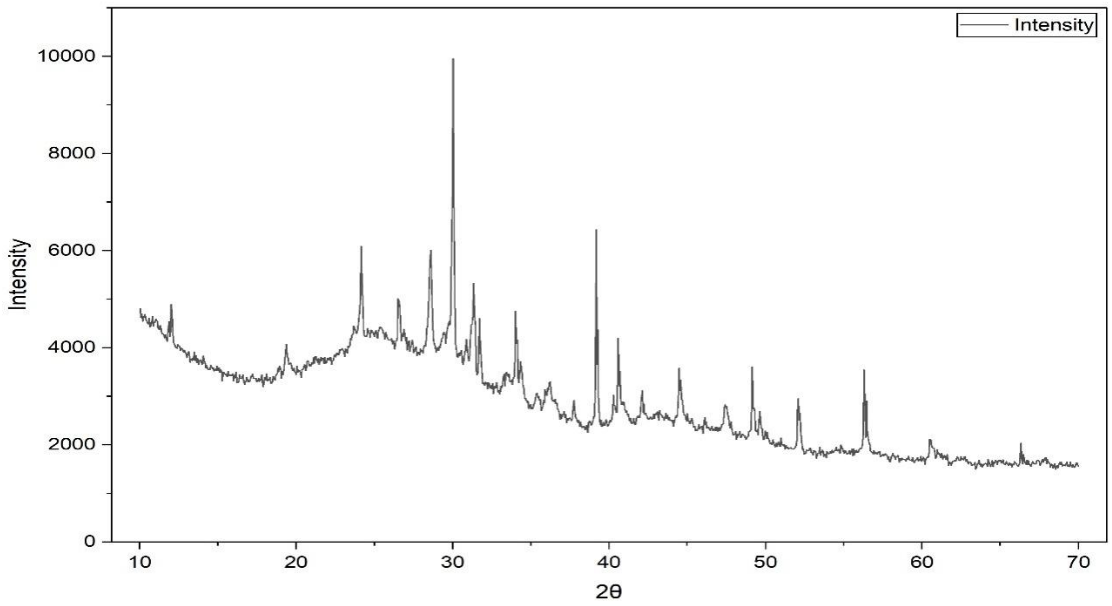

**Figure 5 (b) XRD spectrum of char from co-pyrolysis of RH: WRT::1:1 with KOH catalyst**

The phase composition and crystallinity of the solid char generated by microwave co-pyrolysis of SCB:WRT and RH:WRT, with a KOH catalyst, were examined using X-ray diffraction (XRD) analysis and were shown in **Figure 5 (a&b).** It was noticed that in SCB:WRT mixture, there was an amorphous halo in the background, suggesting of amorphous carbon and silica, the crystalline signals predominate. A prominent peak at approximately 26.5° (2θ), corresponding to the graphite (002) plane, remains discernible, likely reflecting the carbonization of rubber tyre components under microwave heating. However, the most striking features are the dense clusters of sharp peaks within the 20°–40° range, with notable intensities around 28°–30° and 35°–38°, characteristic of crystalline potassium compounds formed at high temperatures. But in the RH: WRT mixture, the susceptor's strong peak at around 26.5° (2θ), which corresponds to the graphite's (002) plane, is still discernible. The new, dense clusters of sharp peaks in the 20°–40° range, however, are the most noticeable features. These peaks are typical of different high-temperature-formed crystalline potassium salts. Additional minor peaks, such as those near 50°–60°, may indicate potassium oxides or residual char phases.

Besides this it was found that both the mixtures had formed major new phases that were most likely potassium carbonate ($K_2CO_3$), formed from the reaction of the catalyst with $CO_2$, and various forms of potassium silicates (e.g., $K_2Si_2O_5$), formed from the reaction between KOH and the abundant silica. Finally, the XRD analysis confirms that the KOH catalyst acted as a chemical reactant, converting the char into a highly crystalline composite of amorphous carbon/silica, residual graphite, and newly formed potassium salts, suggesting potential applications in catalysis or as a value-added material. These peaks are also reported for multi-walled carbon nanotubes [30].

### 3.5.2. Scanning Electron Microscopy (SEM):

The Scanning Electron Microscopy (SEM) analysis of the char produced from microwave co-pyrolysis of SCB: WRT utilizing 450 W microwave power, 5 g KOH catalyst, and 10 g graphite susceptor, provides detailed insights into its surface morphology and structural characteristics. The SEM micrographs **Figure 6 (a&b)** reveal a highly porous and heterogeneous surface, with a network of irregular pores ranging from micro- to mesopore sizes. The presence of these pores, likely formed through KOH-catalyzed etching and thermal decomposition of the biomass and rubber components, suggests an enhanced surface area, which supports potential applications in adsorption or catalysis. The char exhibits a rough texture with distinct particle agglomerates, indicative of the carbonization of rubber tyre components and the interaction of silica from bagasse ash with KOH. Small, spherical particles scattered across the surface may represent residual catalyst residues or carbonized residues, while the absence of large, smooth domains points to minimal graphitization. The porous structure and heterogeneous composition reflect the synergistic thermal effects of microwave heating, with KOH facilitating deoxygenation and cracking, contributing to the stable 18.45 wt% char yield. Overall, the SEM analysis highlights the char's potential as a value-added material, with its morphology optimized under the optimum conditions. A similar surface morphology was also observed in microwave pyrolysis char from *P. juliflora* biomass by Nair and Vinu 2016 [31].

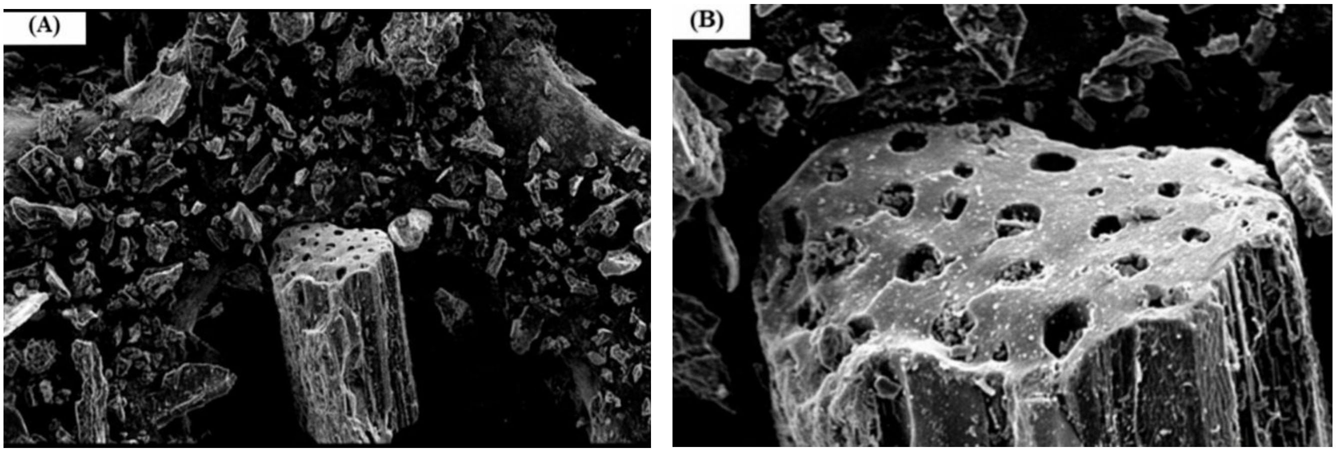

**Figure 6 (a&b) SEM images of the char from co-pyrolysis of SCB: WRT with KOH catalyst**

### 3.6. Charaterization of oil

### 3.6.1. FTIR Analysis of pyrolysis oil:

For SCB:WRT mixture the FTIR Analysis was performed and it was found that there was intense C–H stretching vibrations are observed at 2957, 2926, and 2855 $cm^{-1}$, which are diagnostic of aliphatic $CH_2$ and $CH_3$ groups (**Figure 7(a)).** These assignments are further corroborated by deformation vibrations at 1457 and 1377 $cm^{-1}$, confirming the prevalence of saturated aliphatic moieties. A distinct but relatively weak band at 1709 $cm^{-1}$ indicates the presence of carbonyl (C=O) functionalities, suggesting a minor fraction of oxygenated species within the matrix. The fingerprint region provides additional structural information. Absorptions at 886, 728, and 695 $cm^{-1}$ are assigned to out-of-plane C–H bending vibrations of aromatic rings,The absence of a strong carbonyl band and broad O-H signal, along with an increase in aliphatic C-H stretching and bending modes (2924–2958 $cm^{-1}$, 1451, and 1375 $cm^{-1}$) and distinct aromatic out-of-plane bending peaks (886, 728, and 695 $cm^{-1}$), indicate a significant decrease in oxygenated functional groups in the KOH-catalyzed spectrum. This implies improved aromatization and deoxygenation under KOH.

For RH:WRT mixture the FTIR Analysis was performed and it was observed that in **Figure 7(b)**,the high sharp peaks on the graph between 2958 and 2924 $cm^{-1}$ were indicated by Aliphatic C-H stretching. These were further confirmed by C-H bending peaks at 1451 and 1375 $cm^{-1}$. Out-of-plane C-H bending vibrations in the fingerprint region, notably at 886 $cm^{-1}$, 728 $cm^{-1}$, and 695 $cm^{-1}$, indicating the presence of aromatic chemicals. Importantly, the spectrum shows a low concentration of alcohols, phenols, and carbonyl compounds because it lacks a strong carbonyl (C=O) peak around 1700 $cm^{-1}$ and a noticeable broad O-H band around 3300 $cm^{-1}$. There may be trace amounts of free O-H or N-H groups, or overtones, responsible for the abrupt, faint peaks at 3676 $cm^{-1}$ and 3916 $cm^{-1}$(Wang et al., 2017). All things considered, the spectrum indicates an oil that is rich in hydrocarbons and has a notable aliphatic character [32]. It was concluded that the KOH catalyst effectively enhances deoxygenation and aromatization, resulting in a hydrocarbon-dense oil with significantly reduced oxygenated functionalities. It is proven that SCB:WRT produced better results than RH:WRT in the formation of bio-oil.

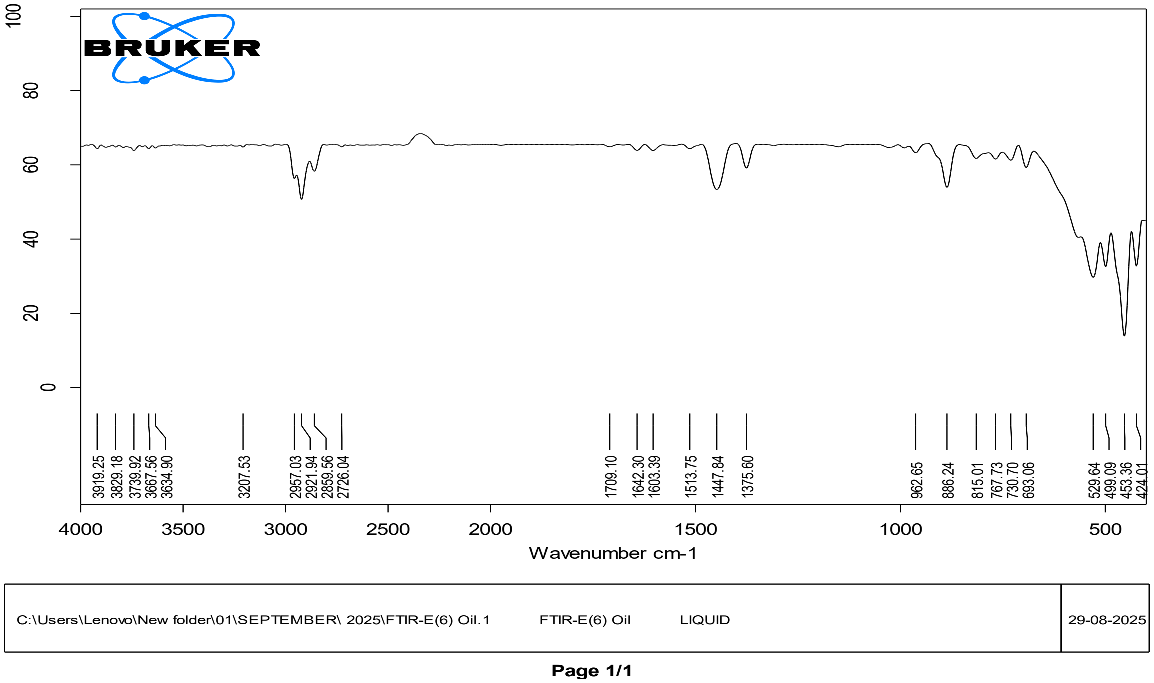

Fig 7(a) FTIR analysis of SCB:WRT mixture with KOH as catalyst

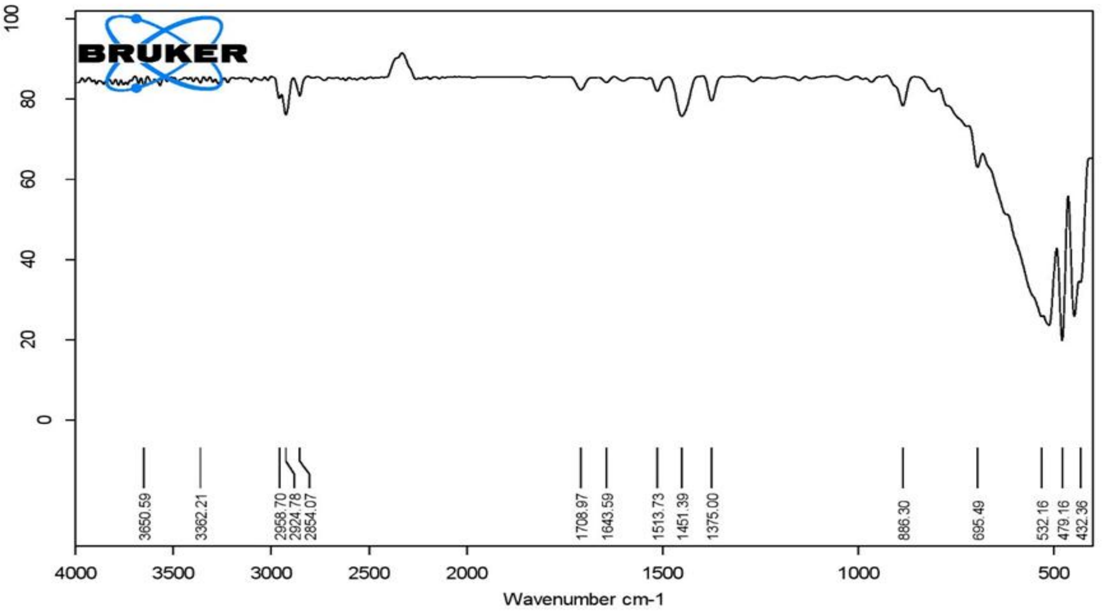

Fig 7(b) FTIR analysis of RH:WRT mixture with KOH as catalyst

### 3.6.2. Gas Chromatography- Mass spectrometry (GC-MS) Characterization of oil:

The GC-MS analysis of the microwave co-pyrolysis oil from SCB:WRT revealed a complex mixture dominated by cyclic hydrocarbons (e.g., Cyclobutane, 1,2-bis(1-methylethyl)-, trans-at 49.05%) and aromatic compounds (e.g., 1,3,5-Trimethylbenzene and naphthalene derivatives) **(Figure 8).** These findings indicates a pyrolysis oil with potential applications in fuel production or as a source of aromatic chemicals, though further processing may be needed to mitigate PAH and impurity levels. The results underscore the effectiveness of microwave co-pyrolysis in producing a hydrocarbon-rich oil, offering insights for optimizing process conditions or upgrading strategies. This was also verified in a study by (Ahmed et al. 2018) during microwave pyrolysis of SCB.

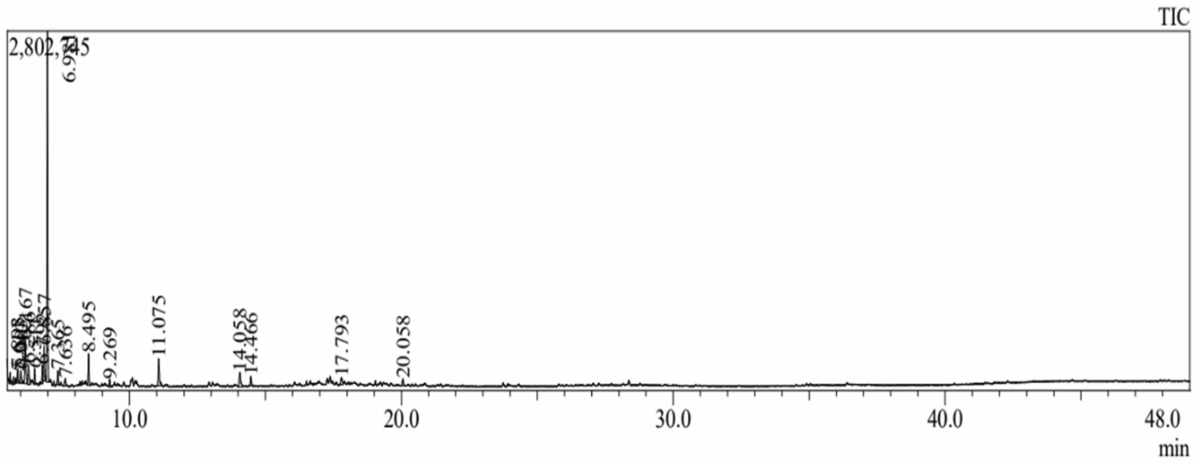

**Figure 8 GC-MS spectrum of the oil from co-pyrolysis of SCB:WRT:: 2.5:17.5 with KOH Catalyst**

## Conclusion

The present study demonstrates that microwave-assisted catalytic and non-catalytic co-pyrolysis is an effective valorization route for converting agricultural wastes rice husk (RH) and sugarcane bagasse (SCB) with waste rubber tires (WRT) into valuable products such as liquid oil, char, and combustible gases. At an SCB:WRT ratio of 2.5:17.5, both KOH and NaOH catalysts enhanced char and oil yields. KOH was more effective in upgrading liquid products through deoxygenation and aromatization, whereas NaOH retained a higher proportion of oxygenated compounds. In contrast, CaO favored gas production.

At a 1:1 RH:WRT ratio, KOH and NaOH increased char yield to over 34%, while CaO enhanced gas yield up to 42.66%. A slightly higher oil yield (37.72%) was obtained with SCB:WRT compared to RH:WRT (37.05%), indicating SCB:WRT as the more effective blend. The temperature–time profile of SCB:WRT showed a steeper rise than RH:WRT, reflecting a higher heating rate due to synergistic interactions. This rapid heating led to excessive cracking of long-chain polymers, producing lighter hydrocarbons.

Catalyst performance strongly depended on type and dosage. KOH and NaOH showed optimal performance at a 5 g loading for maximizing oil yield, whereas higher dosages promoted excessive cracking and gasification, reducing oil recovery. XRD analysis revealed that KOH acted as a chemical reactant, converting char into a crystalline composite of amorphous carbon/silica, residual graphite, and potassium salts, indicating potential value-added applications.

Overall, KOH proved most effective in enhancing deoxygenation and aromatization, resulting in hydrocarbon-rich oil with reduced oxygenated compounds. GC–MS analysis of SCB:WRT-derived oil confirmed the presence of cyclic hydrocarbons and aromatic compounds. These findings establish SCB:WRT as the optimal feedstock blend for improved bio-oil production.

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## References

[1] O'Connor, D., Peng, T., Zhang, J., Tsang, D.C., Alessi, D.S., Shen, Z., Bolan, N.S., Hou, D., 2018. Biochar application for the remediation of heavy metal polluted land: A review of in situ field trials. Science of The Total Environ. 619, 815-826.

[2] Giwa, A.S., Xu, H., Wu, J., Li, Y., Chang, F., Zhang, X., Jin, Z., Huang, B., Wang, K., 2018. Sustainable recycling of residues from the food waste (FW) composting plant via pyrolysis: thermal characterization and kinetic studies. J. Clean. Prod.

[3] Optimization studies of microwave-induced co-pyrolysis of empty fruit bunches/waste truck tire using response surface methodology, Rubia Idris a,b, Cheng Tung Chong c, Jahimin A. Asik a, Farid Nasir Ani, Journal of Cleaner Production 244 (2020) 118649. https://doi.org/10.1016/j.jclepro.2019.118649.

[4] Shah, S.A.Y.,Zeeshan,M., Farooq,M.Z.,Ahmed,N., Iqbal,N.,2019.Co-pyrolysisof cottonstalkandwastetyrewithafocusonliquidyieldquantityandquality. Renew.Energy130,238e244. Bhuvaneshwari S, Hettiarachchi H, Meegoda JN (2019) Crop resi due burning in India: policy challenges and potential solutions. Int J Environ Res Public Health 16(5):832

[5] Feng, Q., Lin, Y., 2017. Integrated processes of anaerobic digestion and pyrolysis for higher bioenergy recovery from lignocellulosic biomass: A brief review. Renew. Sustain. Energy Rev. 77, 1272-1287.

[6] Bhuvaneshwari S, Hettiarachchi H, Meegoda JN (2019) Crop resi due burning in India: policy challenges and potential solutions. Int J Environ Res Public Health 16(5):832

[7] Anand A, Kumar V, Kaushal P (2022) Biochar and its twin benefits: crop residue management and climate change mitigation in India. Renew Sustain Energy Rev 156:111959.

[8] Iwuozor KO, Emenike EC, Ighalo JO, Omoarukhe FO, Omuku PE, Adeniyi AG (2022) Review on the thermochemical conversion of sugarcane bagasse into biochar. Cleaner Materials 6:100162

[9] Microwave-assisted co-pyrolysis of rice straw pellets and plastic packaging wastes for value-added products and energy recovery, Mahendra Tiwari., Ravikrishnan Vinu, Process Safety and Environmental Protection. Volume 190, Part B, October 2024, 606-621. https://doi.org/10.1016/j.psep.2024.08.033

[10] Porichha GK, Hu Y, Rao KTV, Xu CC (2021) Crop residue man agement in India: stubble burning vs. other utilizations including bioenergy. Energies 14(14):4281

[11] Shinde R, Shahi DK, Mahapatra P, Singh CS, Naik SK, Thombare N, Singh AK (2022) Management of crop residues with special reference to the on-farm utilization methods: a review. Ind Crops Prod 181:114772

[12] Naveed Ahmed, Muhammad Zeeshan, Naseem Iqbal, Muhammad Zohaib Farooq, Syed Asfand Yar Shah, Investigation on bio-oil yield and quality with scrap tire addition in sugarcane bagasse pyrolysis, Journal of Cleaner Production jclepro.2018.06.142 (2018), doi: 10.1016/j.jclepro.2018.06.142

[13] Effective and green tire recycling through microwave pyrolysis Yu-zhe ZHANG1, Ting-ting BIAN1, Yi ZHANG1, Xu-dong ZHENG1, Zhong-yu LI†‡1,2,3. Zhang et al. / J Zhejiang Univ-Sci A (Appl Phys & Eng) 2018 19(12):951-960

[14] Farooq, M.Z., Zeeshan, M., Iqbal, S., Ahmed, N., Shah, S.A.Y., 2018. Influence of waste tire addition on wheat straw pyrolysis yield and oil quality. Energy 144, 200-206.

[15] Martínez, J.D., Veses, A., Mastral, A.M., Murillo, R., Navarro, M.V., Puy, N., Artigues, A., Bartrolí, J., García, T., 2014. Co-pyrolysis of biomass with waste tyres: upgrading of liquid bio-fuel. Fuel Process. Technol. 119, 263-271.

[16] Joglekar SN, Tandulje AP, Mandavgane SA, Kulkarni BD (2019) Environmental impact study of bagasse valorization routes. Waste Biomass Valor 10:2067–2078

[17] Rahman MA, Jahiruddin M, Kader MA, Islam MR, Solaiman ZM (2022) Sugarcane bagasse biochar increases soil carbon sequestra tion and yields of maize and groundnut in charland ecosystem. Arch Agron Soil Sci 68(10):1338–1351

[18] Saini K, Biswas B, Kumar A, Sahoo A, Kumar J, Bhaskar T (2021) Screening of sugarcane bagasse-derived biochar for phenol adsorp tion: optimization study using response surface methodology. Int J Environ Sci Technol 19(9):1–14

[19] Niju S, AjiethKanna SK, Ramalingam V, Satheesh Kumar M, Bala jii M (2023) Sugarcane bagasse derived biochar–a potential hetero geneous catalyst for transesterification process. Energy Sources, Part A: Recover Utilization Environ Effects 45(4):9815–9826

[20] Sikarwar, V.S., Zhao, M., Fennell, P.S., Shah, N., Anthony, E.J. 2017. Progress in biofuel production from gasification. Progress in Energy and Combustion Science, 61, 189-248

[21] Lan R, Eastham SD, Liu T, Norford LK, Barrett SR (2022) Air quality impacts of crop residue burning in India and mitigation alternatives. Nat Commun 13(1):6537

[22] Husam Talib Hamzah, Suhair Abdulhadi Mahdi, Sridevi Veluru, Thamer Adnan Abdullah, " Microwave-Assisted Pyrolysis and Co-Pyrolysis: Oil, Char, and Gases-A Technological Review", El-Cezeri Journal of Science and Engineering, Vol: 11, Iss:2, (2024), pp.(186-198). DOI : 10.31202/ecjse.1386535

[23] H. T. Hamzah, V. Sridevi, and D. V. Surya. Conventional and microwave-assisted acid pre-treatment of tea waste powder: analysis of functional groups using ftir. Environmental Science and Pollution Research, 2023.

[22]H.TalibHamzah,V.Sridevi,M.Seereddi,D.V.Suriapparao,P.Ramesh,C.SankarRao,R.Gautam, F.Kaka,andK.Pritam. The role of solvent soaking and pre-treatment temperature in microwave-assisted pyrolysis of waste tea powder: Analysis of products, synergy, pyrolysis index, and reaction mechanism. Bioresource Technology, 363:127913, 2022.

[23] Suriapparao, D. V., Kumar, D. A., & Vinu, R. (2022). Microwave co-pyrolysis of PET bottle waste and rice husk: effect of plastic waste loading on product formation. *Sustainable Energy Technologies and Assessments*, *49*, 101781.

[24] Fan, S., Zhang, Y., Cui, L., Maqsood, T., & Nižetić, S. (2023). Cleaner production of aviation oil from microwave-assisted pyrolysis of plastic wastes. *Journal of Cleaner Production*, *390*, 136102.

[25] Suriapparao, D. V., & Vinu, R. (2015). Resource recovery from synthetic polymers via microwave pyrolysis using different susceptors. *Journal of analytical and applied pyrolysis*, *113*, 701-712.

[26] Shen, Y. (2025). Microwave-assisted pyrolysis of biomass and plastic wastes for hydrogen production. *Green Chemistry*, *27*(35), 10402-10422.

[27] Prajitno, H., Subagjo, S., & Park, S. E. (2021). The effects of NaOH and KOH as activating agents on the characteristics and adsorption performance of rice husk-based activated carbon. *Journal of the Indian Chemical Society*, *98*(12), 100244.https://doi.org/10.1016/j.jics.2021.100244

[28] Keiluweit, M., Nico, P. S., Johnson, M. G., & Kleber, M. (2010). Dynamic molecular structure of plant biomass-derived black carbon (biochar). *Environmental Science & Technology*, *44*(4), 1247–1253. https://doi.org/10.1021/es9031419.

[29] Prajitno, H., Subagjo, S., & Park, S. E. (2021). The effects of NaOH and KOH as activating agents on the characteristics and adsorption performance of rice husk-based activated carbon. *Journal of the Indian Chemical Society*, *98*(12), 100244.https://doi.org/10.1016/j.jics.2021.100244

[30] Yao, Y., Huang, Z., Xie, P., Lacey, S.D., Jacob, R.J., Xie, H., *et al.* (2018) Carbothermal Shock Synthesis of High-Entropy-Alloy Nanoparticles. *Science*, 359, 1489-1494. https://doi.org/10.1126/science.aan5412

[31] Nair, V., & Vinu, R. (2016). Peroxide-assisted microwave activation of pyrolysis char for adsorption of dyes from wastewater. *Bioresource technology*, *216*, 511-519.

[32] Wang, G., Dai, Y., Yang, H., Xiong, Q., Wang, K., Zhou, J., & Wang, S. (2020). A review of recent advances in biomass pyrolysis. *Energy & fuels*, *34*(12), 15557-15578.