

Thermal degradation of emerging pollutants in municipal solid wastes and agro wastes: effectiveness of catalysts and pretreatment for the conversion of value added products

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Abstract

In this study, emerging soil pollutants in the form of municipal solid waste (MSW) and agricultural waste were converted into biofuel via thermal degradation process. Among various waste-to-energy conversion processes, the pyrolysis of biomass is considered the most significant due to its maximum biofuel yield than other conversion techniques. Individual and co-pyrolysis of MSW and sugarcane residue (SR) as well as its treated variant (TSR) were performed in a lab-setup fixed-bed reactor with and without catalyst. The effect of acid pretreatment and catalytic effects on the pyrolysis process was assessed in terms of product yields and characterization. The acidic pretreatment of SR and catalyst in the pyrolysis process alters the process yield and its composition. The maximum oil yield of 50.5 wt% was achieved by catalytic co-pyrolysis of MSW + TSR + HZSM5, whereas the maximum gas yield of 38.1 wt% was achieved by catalytic co-pyrolysis of MSW + SR + HZSM5. This suggests that intrinsic minerals present in the biomass and MSW, particularly alkali and alkaline earth metals, have a catalytic effect on the devolatilization of organic material and the char cracking event. The pretreatment of biomass showed considerable improvement in the properties of the produced pyrolysis oil and char. Compared to the pyrolysis oil and char obtained from MSW + SR, the oil and char obtained from MSW + TSR + HZSM5 showed a small increment in their heating values. Pretreatment and the catalytic co-pyrolysis process influenced the structure of the pyrolysis oils, increasing the production of phenolic compounds and aromatic hydrocarbons. The amount of gas components in pyrolysis gas, such as CH₄, CO₂, and CO also changed more according to the feedstock used for the process. Overall, the HZSM-5 catalyst and co-pyrolysis of MSW with pretreated SR enhanced the pyrolysis conversion of waste municipal solids and agricultural wastes into energy-rich products.

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Article Highlights

- Pretreatment of SR reduced the ash content by 17.4% and increased the volatile matter by 11.0%.
- The maximum pyrolysis oil yield of 50.5 wt% was obtained from the catalytic co-pyrolysis of MSW + TSR.
- Pyrolysis of MSW + TSR + HZSM5 produced 19.6% more pyrolysis oil than individual pyrolysis.

Keywords Waste treatment · Acid pretreatment · Pyrolysis · Fixed bed · Biofuel

1 Introduction

Global production of MSW is estimated to be 2.01 billion tons per year [1] and by 2050, the production may reach 3.40 billion tons per year [2]. MSW is a mixture of different solid wastes produced by human activities. Food waste, wood, glass, rubber, textiles, and, micro- and nano-level plastics are the main parts of MSW. As per the report published by Sharifah et al. [3], the MSW contains approximately organic components (46.94%), plastics (20.28%), paper waste (17.89%), metals (4.31%), glass materials (2.6%), inorganic elements (0.17%), and other elements (such as rubber and wood) (7.81%). Among all other wastes, plastics in MSW are considered a main threat to global sustainability. In general, MSW contains 12% plastic, and when it burns in an open atmosphere, it releases toxic gases such as dioxins, furans, and mercury into the atmosphere. Particularly, the burning of PVC emits hazardous halogens [4]. The properties of wastes present in MSW vary greatly based on a number of factors, including recycling rates, environmental conditions, and the type of collection region (rural, urban, or industrial) [5]. The most popular way to dispose of MSW is in a landfill; in India, around 50% of MSW is disposed of by the land filling method. Many nations, like India, USA, and UK, imposed strict regulations to stop landfilling and also offered incentives to develop more environmentally friendly technology for treating MSW. Incineration is the next alternative option for landfilling. Compared to incineration, landfilling is typically less expensive. Environmental experts have shown over time that landfills actually produce higher net CO₂ emissions [6]. The primary aim of employing incineration technology is to decrease its volume. The direct incineration reduces its volume by up to 95% [7]. But the process is mostly done in a poorly controlled manner that has no pollution control systems. Uncontrolled bringing of MSW poses a risk for non-point emissions, which is particularly concerning in developing nations like India. One of the main obstacles to an appropriate MSW management system in India is the ignorance of the public. In rural areas, they do not have awareness about the environmental impact of open burning [8]. However, the usage of these incinerators has recently ended because of the higher operating costs associated with the higher moisture, which also led to higher fuel prices and inadequate knowledge about incinerator maintenance [3].

The need to reduce environmental stress caused by managing growing volumes of MSW has sparked researchers to turn into renewable energy sources. Thermal pyrolysis is an effective technique to treat MSW that breaks down complex organic materials into fuel with the aid of external energy input. The vast amount of published work related to the treatment of MSW is focused primarily on the pyrolysis of MSW [9, 10]. The thermal pyrolysis process is categorized as slow, fast, and flash pyrolysis. These classifications are based on the respective heating rate. MSW is typically treated in huge quantities and processed with higher moisture content, and the material with higher moisture content is always preferred for the slow pyrolysis process [11]. During pyrolysis, the components of MSW can produce a variety of intermediary molecules, and they may interact to produce synergistic pyrolysis [12]. The synergistic interactions quicken the process of pyrolysis and favor yield products. Numerous parameters involved in the process affect the yield and composition of the biofuel, such as the properties of the feedstock, reactor type, and reaction [13]. Waste-to-energy is a method of recovering energy from waste materials like MSW to fuel, heat, and electricity in an environmentally friendly and commercially feasible way [14]. It has been suggested that pyrolysis oil and gas obtained from MSW can be utilized as fuel for industries, oil refining processes, ammonia production and feedstocks for the synthesis of fine chemicals [15]. Biochar is the solid byproduct. It has been utilized as a soil amendment, carbon sink, catalyst, and electron conductor in anaerobic digestion processes and energy production [16].

Co-pyrolysis is a viable and effective method for producing bioenergy and products from biomass. It is a simple and effective technique to produce high-grade pyrolysis oil [17]. In this process, two or more different materials are used as feedstock. Numerous studies have demonstrated that co-pyrolysis can be used to enhance the properties of pyrolysis oil, such as increasing the oil yield, lowering the water content, and increasing the heating value of the oil [18]. It has been demonstrated that combined feedstock pyrolysis has a beneficial synergistic interaction that improves oil quality and

offers a secure and reliable waste management system. It has been suggested that co-pyrolysis of plastics and biomass is a successful upgrading technique that will increase oil production as well as its heating value [19]. Zhou et al. [20] report that the interaction of biomass and plastics during co-pyrolysis increases the yield and quality of the pyrolysis oil. When MSW was being co-pyrolyzed, there was little interaction between the components of the same origin, such as paper and wood, but the interaction between polymers and biomass was significant [21]. Co-pyrolysis of biomass and mixed plastics has gained more attention. Polymers present in MSW can be co-pyrolyzed with biomass components to produce a variety of chemicals and fuels.

Catalytic pyrolysis is a process that aims to increase conversion efficiency. Numerous research studies have documented the impact of catalysts during pyrolysis. Catalysts were employed to enhance the yield of pyrolysis production by decreasing the intermolecular interactions within the polymeric chain [22]. The catalysts for the pyrolysis can be added in three different ways: the first category, known as the primary catalyst group, is added straight with feedstock [23]. In second category, the catalysts are allowed inside the secondary reactor. It is generally called a downstream catalyst [24]. The catalysts in the third group are placed directly inside the reactor, which allows the evolved vapors, solids, and tar to come into direct contact with the catalyst [25]. A variety of catalysts, such as metal oxides, have the ability to speed up the breakdown of hydrocarbons and facilitate the easy decomposition of tar [26]. The food waste catalytic pyrolysis process was carried out by Liu et al. [27] using different types of metal oxides, such as MgO, Fe₂O₃, and MnO₂ and two types of chlorine salts (CuCl₂, NaCl). Due to the catalytic effect, the yield of gas increased with decreased oil yield. Xie et al. [28] investigated the catalytic pyrolysis of sludge. The catalysts in the process decreased oil yield and a considerable reduction in nitrogen and oxygen-carrying compounds. Fang et al. [29] used GC/MS to analyze the co-pyrolysis of paper sludge containing 10%, 30%, and 50% combined with MSW in the presence of an MgO catalyst. The investigation was done to find the properties of pyrolysis yield, process emissions, chemical kinetics and chemical composition. In this process, emissions of aliphatic hydrocarbons were reduced with increased percentage of paper sludge. The pyrolysis process without a catalyst produces more oxygenated elements, whereas adding catalyst results in decrease in residue mass and oxygenated elements [30].

The study concluded that MSW with 30% paper sludge and MgO may have the ideal ratio for co-pyrolysis. The intrinsic elements present in the feedstock demonstrated catalytic activity in accelerating degradation pathways. Alkali and alkaline earth metals present in the lignocellulosic biomass have a major impact on the distribution of pyrolysis products and their physical and chemical characteristics [31]. For instance, some agricultural wastes, such as rice husk and cereal straw, are Si-rich and can be cultivated in contaminated soils. The effect of these heavy metals on the biomass conversion process is typically neglected due to their lower concentration in the biomass, however, when zeolite-based catalysts are utilized, the transfer of these metals to the condensable fractions and char leads to environmental issues [32]. Among the different catalysts used for pyrolysis, HZSM-5 is considered the most effective, particularly for the production of aromatic hydrocarbons [33]. Williams and Nugranad conducted a pyrolysis experiment on rice husks using HZSM-5 catalyst and produced more polycyclic aromatic hydrocarbons at higher temperatures [34]. The presence of HZSM-5 catalyst in this study reduced the formation of oxygenated compounds in the bio-oil. In another study, pyrolysis of microalgae in a fixed-bed reactor with HZSM-5 produced bio-oil with a lower oxygen level and a higher heating value of 32.7 MJ/kg compared to a non-catalytic reaction [35]. According to Zhang et al. [36], catalytic pyrolysis of maize cobs with HZSM-5 reduced the oxygen content in the pyrolysis oil by up to 25%. When HZSM-5 was used, the aromatic hydrocarbon content in the oil increased significantly.

Pretreatment of biomass is usually carried out to enhance enzymatic saccharification. There are several pretreatment methods used by various researchers and reported. The results of the speciation can be affected by the techniques used to prepare the solid material samples. Pretreatments can be categorized as chemical, biological or physical based on their operation [37]. Each pretreatment process has its own merits and disadvantages. For example, water washing eliminates certain metal elements from biobased feedstocks [38]. On the other side, acid washing is used to eliminate large quantities of metals. The pretreatment process improves the feedstock in a number of ways, including breakdown the structure, lower the oxygen content, increasing energy content and increasing the C/O molar ratio [39]. Liu et al. [40] produced hydrocarbons and ammonia through the catalytic process of sewage sludge with acid pretreatment. The authors developed acid pretreatments, such as infusion and washing, to increase the yield. Although both methods increased the production, acid infusion produced more hydrocarbons than acid washing. Vijayan et al. [41] conducted a slow pyrolysis process utilizing pretreated automotive shredder residues collected from MSW. The feedstock sample in this study was pretreated by heating it to 200 °C in a furnace. Finally, the pretreated samples were sieved to certain microns. After pretreatment, the estimated heating rate for residual pyrolysis was 2 °C/min to progress in a reactor. The physicochemical characteristics of the woody and non-woody biomass show significant variations and that should be

consistent to produce optimal conversion conditions. In order to produce high-quality pyrolysis oils via pyrolysis process, biomass formulations can aid in meeting the specifications [42]. Pretreatment of biomass may occasionally be required to produce biofuels. Torrefaction, steam explosion and leaching are commonly used techniques that have been demonstrated to increase oil yield. Hakeem et al. [43] claimed that removing inorganics with acidic pretreatment may improve the standards of the feedstock and yield. According to Shankar Tumuluru et al. [44], hydrothermal carbonization improves the conversion efficiency of biomass. Acidic pretreatment is the most popular traditional technique. It is carried out with the use of sulfuric acid, dilute acid, and dicarboxylic acid. Sulfuric acid is the most common commercially used acid for treating lignocellulosic biomass. Previously, it was widely used for the pretreatment of switchgrass, corn stover, spruce, and poplar [45]. Acidic pretreatment of lignocellulosic biomass is considered a conventional approach due to its lower cost. Acidic pretreatment enhances the breakdown of biomass during pyrolysis and increases the rate of levoglucosan formation. Pittman et al. [46] employed 2% sulfuric acid to treat corn stalks, demonstrating a rise in the organic fraction up to 30%, decrease in the water content up to 41% with an increased pyrolysis oil yield from 35 to 51 wt%.

As mentioned above, an abundance of research has been done on the co-pyrolysis of MSW and biomass in different operating conditions. However, there is no evidence in the literature regarding the effect of combined biomass pretreatment and catalysts during co-pyrolysis of MSW and SR. This is a clear research gap in knowledge, given that the role of acidic pretreatment in SR processing is well established. Therefore, the purpose of this work is to examine the co-pyrolysis behavior of the pretreated SR and MSW in the presence of HZSM-5 catalysts. This study aimed to determine the impact of pre-treatment and catalyst on the following specific outcomes: (i) physicochemical properties of feedstock (ii) thermal degradation behavior of the feedstocks (ii) distribution of co-pyrolysis product yield and (iv) composition of the products.

2 Materials and methods

2.1 Feedstock

The MSW samples were collected from a local panchayat union in Coimbatore, India. The samples have different kinds of waste materials, such as plastic (with a majority of PVC, PET and PS), cloth, wood, rubber, paper, glass, food, and fruit waste. The metal, glass, and food wastes were separated and the sand particles were removed from the collected samples by water washing. After separation and cleaning, the samples were mixed thoroughly and cut into uniform pieces of diameter less than 5 mm. The mass percentage of the material present in the collected MSW is listed in Table 1. The SR used for this work was collected from a nearby sugarcane juice center in Coimbatore, India. Pith, fiber, and rings are the three primary components of the residue. In general, pith makes up about 5 wt%, fibers account for 73%, and rings make up 22% [47]. The residues collected for the tests had an initial moisture content of > 30% which was reduced to less than 10% after natural drying in open sunlight for five days. After drying, the SR particles were cut into small pieces with a diameter less than 3 mm. Both feedstocks were cut by a ball mill (Dharani ball miller) and sieved using a sieve shaker (Jayant Scientific, Mumbai, India).

2.2 Biomass pretreatment

In this study, the SR was treated with sulfuric acid (98%) to create pretreated SR (TSR). For this, 10 g of SR and 200 ml of a 0.1 M sulfuric acid solution were combined to create acid-washed SR. After 4 h of processing, the mixture was stirred at room temperature. Further, residues were rinsed using deionized water till the water turned neutral after the solution was filtered. The dried residue was then placed in a furnace and allowed to dry for 24 h at 50 °C. For making the acid-infused SR, 15 g of deionized water were used for diluting the sulfuric acid, which accounted for 4% of the total weight of the

Table 1 Composition of MSW

| Component | Weight by % |
|--------------|-------------|
| Cloth | 13.3 |
| Wood | 25.7 |
| Plastic | 34.5 |
| Rubber | 14.6 |
| Fruit wastes | 11.2 |

SR. After that, 5 g of SR was mixed with the acid solution. The residue was stirred for three hours at ambient temperature and then allowed to dry for 12 h in the oven. For the pretreatment process, the procedure outlined by Kuzhiyil et al. [48] was used to determine the acid infusion concentration.

2.3 Pyrolysis experiment

The experiments were conducted in a laboratory scale. The individual and co-pyrolysis experiments were conducted by keeping the material directly inside the reactor. For each experiment, 30 g of material were loaded. For all experiments, the product yield was assessed by keeping the temperature at 500 °C. To carry out non-catalytic pyrolysis, equal amounts of MSW and SR were combined and added to the active zone. 10% (wt%/wt% of feedstock) of zeolite HZSM-5 catalysts were added to the combined feedstock for catalytic pyrolysis. The catalysts are blended into the reactor system in situ (blended with feedstocks). The blending of different feedstocks and catalysts was done manually. In those preliminary tests, the catalyst-to-biomass ratio was selected at arbitrary only to demonstrate the possibility of generating more liquid oil and it will need to be optimized in later stages of the process development. For individual and co-pyrolysis experiments, a total of six feed samples were used: (i) MSW, (ii) SR, (iii) MSW + SR, (iv) MSW + SR + HZSM5, (v) MSW + TSR and (vi) MSW + TSR + HZSM5. Each sample was tested in a pyrolysis system by fixing the reactor at a temperature of 500 °C. Each experiment at the selected temperature was conducted three times, and the average was considered for the analysis. For individual pyrolysis, MSW and SR were loaded in the reactor and pyrolysis experiments were conducted. For co-pyrolysis experiments, equal weights of MSW, SR and TSR were blended thoroughly and loaded into the reactor. For the catalytic co-pyrolysis process, the blended feedstocks were mixed with 10% HZSM-5 and loaded into the reactor. At the end of each experiment, the reactor is allowed to cool to a normal temperature. After reaching atmospheric temperature, the reactor is cleaned every time. The char produced at each run is collected from the bottom of the reactor. The collected char is weighed using an electronic weighing machine to analyze the product distribution. Condensable volatiles released during the process were converted into oil and collected separately. For every sample, the procedure was repeated two times and average value was taken for the analysis. Table 2 shows constituent of each feedstock. Equations 1, 2 and 3 were used to find the percentage of individual product yield.

$$\text{Pyrolysis oil}(wt\%) = \frac{\text{Weight of pyrolysis oil}}{\text{Weight of feedstock}} \times 100 \quad (1)$$

$$\text{Pyrolysis char}(wt\%) = \frac{\text{Weight of pyrolysis char}}{\text{Weight of feedstock}} \times 100 \quad (2)$$

$$\text{Pyrolysis;gas}(wt\%) = 100 - \text{pyrolysis oil}(wt\%) - \text{pyrolysis char}(wt\%) \quad (3)$$

2.4 Reactor set up

A lab-scale fixed-bed reactor was used for the pyrolysis tests. This section provides more explanation of the reactor utilized in the current study, which is the same as the reactor used in previous literature [49]. The reactor core was stainless steel tubes and heated outside using an electrical heater. The outer layer of the heater is surrounded by insulating material (generally mineral wool). The reactor had an outer diameter of 60 mm and an effective length of 150 mm. The reactor was separated into a heating zone and a normal temperature zone. The temperature of the

Table 2 Constituent of feedstock

| Feedstock | Constituent |
|-------------------|-------------------------------|
| MSW | 100% MSW |
| SR | 100% SR |
| MSW + SR | 50% MSW + 50% SR |
| MSW + SR + HZSM5 | 45% MSW + 45% SR + 10% HZSM5 |
| MSW + TSR | 50% MSW + 50% TSR |
| MSW + TSR + HZSM5 | 45% MSW + 45% TSR + 10% HZSM5 |

reactor was measured along the axis direction in both zones using two K-type thermocouples. The most crucial factor to consider is its internal temperature, which is extremely hard to determine precisely due to the large temperature gradients between the reactor wall and feedstock due to their lower thermal conductivity. The temperature of the reactor can be referred to as the temperature of the process since it reflects the temperature change of the feedstock. The reactor is coupled to a water-cooled condenser, with surplus ice water flow maintained at 5 °C. Figure 1 shows the schematic view of the pyrolysis reactor.

2.5 Feedstock and product characterization

Pyrolysis oil and char gaseous components are generally examined using a variety of analytical methods. The methods used for analyzing raw materials are also applied to char components. Proximate analysis of the raw material and char provides total values of volatile matters, fixed carbon, moisture and ash. The ultimate analysis provides details about C, H, N, S, and O. Both analyses were carried out as per ASTM protocols. The fixed carbon and O content are found by the following equation:

$$\text{Fixed carbon (wt\%)} = 100 - (\text{VM} + \text{Ash} + \text{Moisture}) \text{wt\%} \quad (4)$$

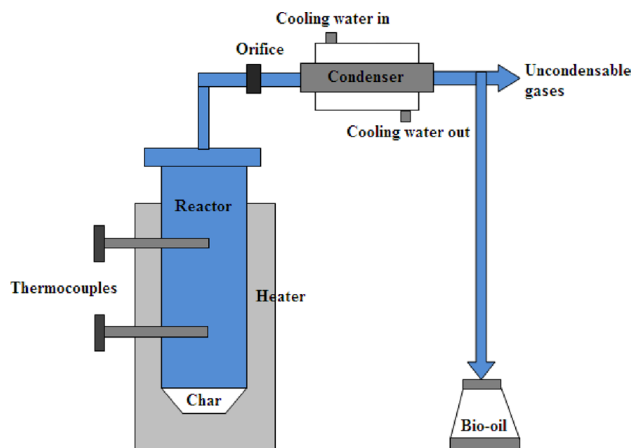
$$\text{O (wt\%)} = 100 - (\text{C} + \text{H} + \text{N} + \text{S}) \text{wt\%} \quad (5)$$

The method employed by Madhu et al. [50] was utilized for calculating the lignocellulosic content of SR, which includes celluloses, hemicelluloses, and lignin. TGA (thermogravimetric analysis) and DTG (derivative thermogravimetry) of the feedstock are very essential before conducting pyrolysis experiments. It shows material behavior as a function of temperature and time. With the aid of TGA701 analyzer, the analysis was carried out under nitrogen environment by heating the sample up to 600 °C at a heating rate of 15 °C/min and 25 °C/min. The HHV of the feedstock, pyrolysis oil and char were found by Dulong method outlined in Eq. (6) mentioned in the literature [51].

$$\text{HHV}_{\text{dry}} = \frac{338.2 * C + 1442.8 * (H - \frac{O}{8})}{1000} \left(\frac{\text{MJ}}{\text{kg}} \right) \quad (6)$$

Apart from the HHV, the physical characteristics of the pyrolysis oil were analyzed using various instruments, such as Cleveland open-cup flash point apparatus, redwood viscometer and digital pH meter. The functional groups existing in the feedstock, pyrolysis oil, and char were analyzed using FT-IR analyzer (BRUKER Optik GmbH TENSOR 27). The analyses for all the samples were carried out in transmittance mode with 4 cm⁻¹ resolution in the 4000–400 cm⁻¹ range. A Thermo Scientific Trace GC Ultra with DSQ II GC/MS was used to analyze the volatile compounds released during pyrolysis processes. For the analysis, helium was utilized as a purging gas and allowed to flow at a rate of 10 mL/min with a 50:1 split ratio. The GC was maintained at 280 °C after holding at 40 °C for 4 min. A capillary column

Fig. 1 Reactor set up



measuring 30 m in length and 0.25 mm in diameter was coated with a 0.25 μm film of DB-35. The gas fractions acquired from pyrolysis processes were analyzed using a Shimadzu GC-2014 gas analyzer.

3 Results and discussion

3.1 Characterization of feedstock

3.1.1 Proximate and ultimate analysis

Table 3 lists the proximate, ultimate, and other characteristics of MSW, raw and treated SR. In comparison to MSW, raw SR has lower ash content. But the moisture content was found to be higher. Naturally, SR has higher cellulose and hemicellulose content. Moreover, SR is a readily accessible and most promising environmentally benign raw material for the biofuel industry [52]. This easily accessible biomass is disposed of as waste after harvest and is burned in the agricultural sector. After sugarcane is harvested, farmers usually burn the residue in an open atmosphere to minimize residue. It may be a cost-effective method, but it affects the quality of air and the lives of all living organisms. The proximate analysis of both MSW and SR revealed higher volatile concentration of 75.15 wt% and 73.22 wt% respectively. The degradation of the hemicellulose existing in the feedstock was the primary cause of these higher volatiles, which promote the formation of condensable gases. Higher volatile matter, along with a lower ash and sulfur content, is one of the primary criteria for the pyrolysis process since it offers higher volatility and reactivity, facilitating the formation of liquid fuel [53]. The solid residue left over after the volatilization process is called fixed carbon. It originates primarily from lignin and promotes the production of char components. The high fixed carbon percentage (> 10%) suggests that the pyrolysis process yields high carbon products [54]. Ash present in the feedstock affects the pyrolysis conversion and the higher ash in the feedstock inversely affects the yield of liquid products [55]. Compared to MSW, the selected SR has a lower ash content of 5.29 wt% which favors oil yield. The carbon and hydrogen content showed that MSW is similar to SR. Furthermore, SR is environmentally benign because it contains very little sulfur and nitrogen. Pretreatment of SR had a little impact on the final feedstock compositions. During pretreatment, the volatile matter of the feedstock was increased from 73.32 to 81.31 wt% whereas the fractions of fixed carbon, moisture, and ash level were reduced.

Table 3 Properties of MSW and SR in wt%

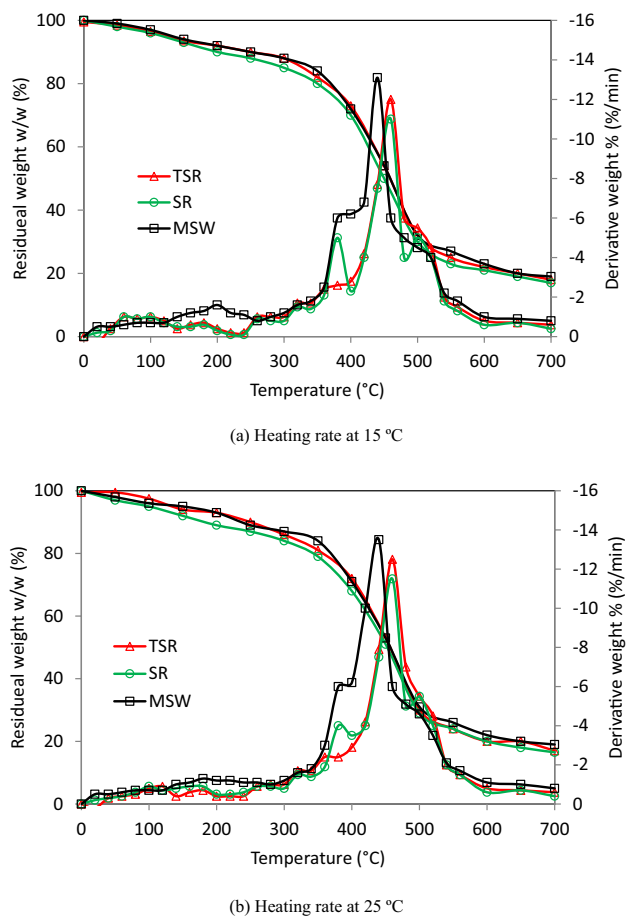
| Content in (wt%) | MSW | SR | TSR | MSW+SR | MSW+TSR |
|---|-----------------|-----------------|-----------------|-----------------|-----------------|
| <i>Proximate analysis</i> | | | | | |
| VM | 75.15 \pm 2.1 | 73.22 \pm 2.3 | 81.31 \pm 2.4 | 74.98 \pm 1.8 | 79.01 \pm 2.0 |
| FC* | 11.09 \pm 0.9 | 12.19 \pm 1.1 | 7.05 \pm 0.9 | 11.92 \pm 0.7 | 9.05 \pm 0.7 |
| MC | 6.42 \pm 0.6 | 9.30 \pm 0.8 | 7.27 \pm 0.7 | 6.91 \pm 0.6 | 6.91 \pm 0.7 |
| A | 7.31 \pm 0.8 | 5.29 \pm 0.6 | 4.37 \pm 0.7 | 6.33 \pm 0.5 | 5.92 \pm 0.6 |
| <i>Ultimate analysis (ash free basis)</i> | | | | | |
| C | 53.10 \pm 1.5 | 44.72 \pm 1.6 | 46.30 \pm 1.7 | 49.04 \pm 1.2 | 50.0 \pm 1.4 |
| H | 6.33 \pm 0.3 | 6.50 \pm 0.5 | 7.25 \pm 0.5 | 6.44 \pm 0.4 | 6.81 \pm 0.5 |
| N | 1.84 \pm 0.1 | 0.36 \pm 0.1 | 0.34 \pm 0.1 | 1.0 \pm 0.1 | 0.98 \pm 0.1 |
| S | 0.88 \pm 0.1 | 0.04 \pm 0.01 | 0.58 \pm 0.1 | 0.89 \pm 0.1 | 0.72 \pm 0.1 |
| O* | 33.85 \pm 0.9 | 48.38 \pm 1.6 | 45.53 \pm 2.0 | 41.31 \pm 0.8 | 39.75 \pm 1.0 |
| <i>Lignocellulosic composition</i> | | | | | |
| Lignin | # | 24.5 | # | # | # |
| Cellulose | # | 41.9 | # | # | # |
| Hemicellulose | # | 32.7 | # | # | # |
| Extractives | # | 0.9 | # | # | # |

FC and O obtained by difference, #- Not analyzed

3.1.2 Thermal degradation profile

TGA provide a relationship between temperature and weight loss. Figure 2 signifies the TGA and DTG curves of the selected three feedstocks obtained at different heating rates of 15 °C/min and 25 °C/min. From both the TG and DTG thermograms of all feedstock, it can be understood that there are three distinct stages in the breakdown process. In SR, a tiny peak appeared in the beginning, representing the evaporation of moisture, which lasted from the atmospheric temperature to 95 °C. According to Anand et al. [35], these losses were caused by the removal of moisture (7 wt%) and light volatile vapors. This loss reflects the evaporation of moisture from biomass. The breakdown of hemicellulose starts at about 215 °C. The subsequent temperature peak occurs at about 350 °C due to cellulose breakdown. The degradation of cellulose and hemicelluloses continued up to the end of the process [56]. The mass loss appeared between 360 and 430 °C, showed the highest possible breakdown rate. The breakdown of cellulose and hemicellulose released the maximum possible condensable volatiles. The final stage of decomposition is attributed to the breakdown of lignin, which starts at 530 °C and continues until 700 °C represents the formation of solid residues [57]. The pretreatment of SR has a little impact on the thermal degradation process. Pretreatment moved the primary and maximum breakdown temperatures to the right (higher temperatures). The final decomposition stage was identified as the same for both raw and treated SR. The maximum possible rate of decomposition for TSR was raised to 21.3%/°C. The peak attributed to hemicellulose degradation was altered by pre-treatment and nearly vanished in TSR, indicating hemicellulose solubilization. The TGA analysis of MSW showed quick weight loss compared to lignocellulosic biomass degraded into two stages. The initial stage, accounted for 62.5% of the mass loss, appeared between 275 and 425 °C through degradation of light organic molecules. The next stage belongs to the degradation of strong hemicellulose, lignin and plastic materials between 550 and 700 °C [58, 59]. After reaching 550 °C, some residues remained for all feedstock, which represents the presence of ash content in the samples [60]. With the use of the thermal decomposition characteristics data for the selected feedstock, the temperature for the pyrolysis process was fixed at 500 °C.

Fig. 2 TG and DTG curves of MSW, SR and TSR



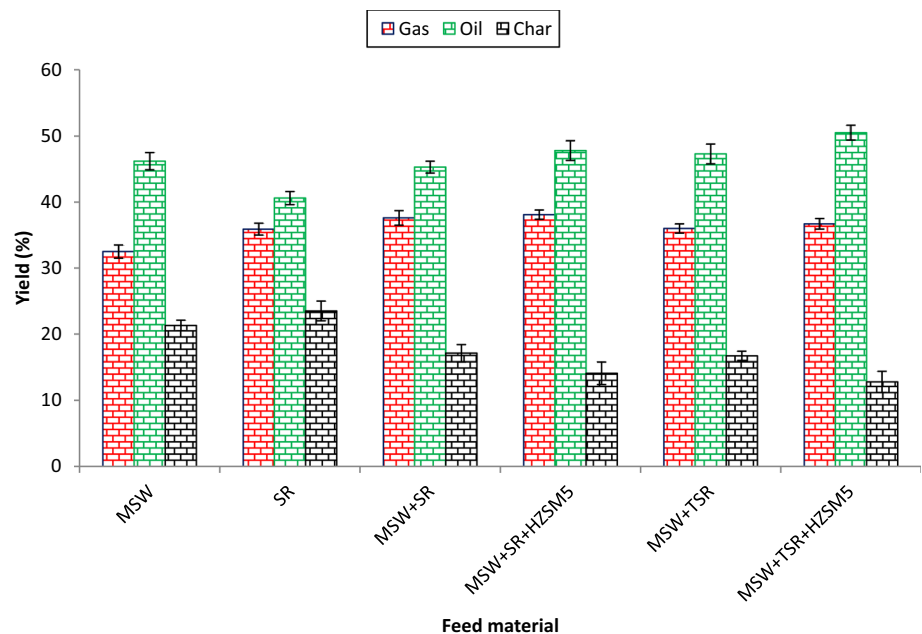
3.2 Co-pyrolysis product distribution

To analyze the effects of pyrolysis synergy, pretreatment and catalytic effect, the experiments were conducted in five different modes. Initially, individual pyrolysis experiments were conducted on MSW and SR. Further co-pyrolysis experiments were performed under different combinations, such as MSW + SR, MSW + RS + HZSM5, MSW + TSR and MSW + TSR + HZSM5. For all experimental works, the temperature of the reactor was kept at 500 °C. Since then, the majority of biomass and plastic wastes have been chemically degraded between 450 and 550 °C [55, 59]. During individual pyrolysis of MSW, the oil, char and gas yield was recorded at 46.2 wt%, 21.3 wt% and 32.5 wt% respectively. Pyrolysis of SR produced 40.6 wt% of pyrolysis, 23.5 wt% of char and 35.9 wt% of gas. Compared to SR, MSW produced more pyrolysis oil and gaseous products. The reason for maximum pyrolysis oil yield from MSW is the presence of polymers and rubbers. The presence of plastic wastes results in an increase in conversion and, thus, in the amount of condensable gas products [61]. The oil production via individual pyrolysis of MSW was higher than that of SR pyrolysis, which is also revealed during the co-pyrolysis process. The oil yield increased with respect to the addition of MSW. During individual pyrolysis of SR, the yield of oil and gas was 40.6 wt% and 35.9 wt% respectively. The addition of MSW with SR increased the yield of oil and gas up to 45.3 wt% and 37.6 wt% respectively. Rather than biomass, the presence of maximum volatiles in MSW is the cause of higher oil output in relation to the addition of MSW. Polyolefin polymers present in the MSW will function as an ideal hydrogen donor and create the radical interaction to produce maximum oil and gas yield [62]. The higher pyrolytic conversion in MSW was caused by a higher volatile matter in comparison to SR. The combined benefits of co-pyrolysis make it an accepted low-cost method of effectively improving the standard of bio-oil. Different materials have different synergy principles. Certain components from one material might influence the results of another material through co-pyrolysis. However, carbon- and hydrogen-rich materials can serve as a source of hydrogen for other feedstocks during the co-pyrolysis process. So the majority of the co-pyrolysis process is established by combining plastic waste and biomass. The co-pyrolysis process produced less char compared to individual pyrolysis processes. This could be the cause of the maximum production of oil products with the least amount of solid phase. In general, polyolefin polymers present in MSW typically serve as good hydrogen sources, which improve oil conversion [63]. As demonstrated by [61], the synergistic effect of MSW + SR pyrolysis was found by comparing experimental and theoretical values. Compared to individual pyrolysis, the combination of MSW + SR showed synergistic improvements in co-pyrolysis. The higher oil production could be related to the interaction between the H radicals derived from HDPE and SCB. This interaction prevented the development of lower-molecular-weight vaporous products and form oil containing higher-molecular-weight compounds, leading to a significant amount of pyrolysis oil [64]. The co-pyrolysis of MSW + SR produced 45.3 wt% of oil, 17.1 wt% of char and 37.6 wt% of gas fractions. Compared to the individual pyrolysis of SR, the combination of these two materials produced 11.58% more pyrolysis oil.

In comparison to the traditional pyrolysis method, the catalytic pyrolysis process delivers better liquid fuel quality and is more convenient since the reaction is carried out in a catalyst environment. The catalysts are used to advance the degradation of the pyrolysis feedstock. Adding zeolite additives resulted in a considerable modification in the pyrolysis behaviour of the co-pyrolysis of MSR and SR. The addition of catalysts reduced the mass of the pyrolysis residue by 17.54% compared to co-pyrolysis of MSR + SR without catalysts. The reduction of solid residue may be the reason for the complete degree of reaction. The gas yield increased from 37.6 to 38.1 wt% with the introduction of catalysts. The evolved volatiles in the pyrolysis region entered the catalytic region, where they contacted HZSM-5 and endured further cracking, which increased the yield of gas fractions than non-catalytic co-pyrolysis [65, 66]. It can be witnessed that the pyrolysis process yield is improved up to 47.8 wt% due to the catalytic effect. The increment in yield compared to non-catalytic pyrolysis was observed at 5.23%. Zeolite catalysts affect the degradation process, increase the production of condensable gases, and produce a higher concentration of liquid fuels.

Acid pretreatment has been considered to be the most successful in improving the quality and production of pyrolysis oil since it modifies the composition and structure of biomass [67]. According to Neupane et al. [68], hydroxyl acids are produced after an acid treatment, which eliminates the hemicellulosic carbohydrates in the biomass. Further, as reported in Table 3, an acid pretreatment enhances the qualities of the pyrolysis oil by reducing the ash content of the biomass feedstock. It has also been observed that acid pretreatment enhances the biomass component by breaking the ester and glycosidic bonds in the lignin structure. Figure 3 illustrates individual, catalytic, and non-catalytic co-pyrolysis product distributions. The figure shows that there was a considerable increase in oil output. Compared to MSW + SR pyrolysis, co-pyrolysis of MSW + TSR produced a maximum pyrolysis oil yield

Fig. 3 Individual, catalytic and non-catalytic co-pyrolysis product distributions



of 4.23%. Due to pretreatment, the char yield reached a low value of 16.7 wt%. This is explained by the fact that the acid pretreatment helps to reduce the amount of ash and inorganics in the biomass. By pre-treating the SR, the ash content was reduced by around 17.39% and the volatile matter was increased by 11.05%. These improvements in turn improved the pyrolysis conversion of TSR, ensuing in an increase in pyrolysis oil output and a 2.34% drop in char output. In order to increase pyrolysis oil production, the pre-treatment influence on organic matter devolatilization rather than demineralization was more pronounced. According to Zhang et al. [69], this finding implies that the demineralization influence on the dispersion of pyrolysis products is minimal at lower pyrolysis temperatures, but it is recognized to be profoundly greater at elevated temperatures where secondary char cracking is faster. Though inorganic matter mainly ends up in the char residue, it has been shown that the improvement in organic matter devolatilization brought about by pretreatment, which removes mineral matter from the biomass [70]. Pre-treated samples enhanced the formation of higher volatile gases, leading to higher yields of liquid products [71]. Since the reactants are close to the acid sites, pre-treatment has increased the catalytic activity. Lee et al. [72] observed similar outcomes from the catalytic co-pyrolysis of polypropylene and torrefied cellulose. Utilizing pretreated torrefied cellulose, their findings revealed increased aromatic liquid products. Additionally, studies using greater pore catalysts have shown positive synergistic effects on the catalytic co-pyrolysis of plastic and biomass [73, 74]. The findings of Muhammad and Manos also showed increased synergy between linear low density polyethylene and cellulose, thereby pretreatment of cellulosic biomass enhanced the yield of liquid products (55 wt%) [71]. The acid pretreatment of the biomass allowed the particles to expand. It also simplifies the degradation of lignin, which is considered the most challenging component during pyrolysis. According to Misson et al. [75], the pretreatment reduced the lignin content in biomass. Figure 3 also illustrates the product distribution of the pyrolysis of MSW + TSR + HZSM5. The figure shows a higher yield of pyrolysis of 50.5 wt% compared to other combinations. At 500 °C the char and gas yield was identified as 12.8 wt% and 36.7 wt% respectively. Comparing the pyrolysis of MSW, SR, MSW + SR, MSW + SR + HZSM5 and MSW + TSR, pyrolysis of MSW + TSR + HZSM produced 5.3% to 19.6% more pyrolysis oil.

3.3 Characterization study

3.3.1 Analysis of char

Table 4 presents the elemental composition of the char obtained from different process settings. From the analysis, it can be understood that the presence of volatile matter, fixed carbon, ash, and moisture contents are in the range of 18.2–26.7%, 41.6–58.5%, 0.9–1.5%, and 16.0–39.3%, respectively. In comparison to the feedstock that was used to produce the char, the proximate analysis of the char reveals the presence of reduced moisture content. The decreased

Table 4 Effect of catalysts and pretreatment on char properties

| Content in (wt%) | Individual and co-pyrolysis char | | | | | |
|---|----------------------------------|-----------|-----------|------------------|-----------|-------------------|
| | MSW | SR | MSW + SR | MSW + SR + HZSM5 | MSW + TSR | MSW + TSR + HZSM5 |
| <i>Proximate analysis</i> | | | | | | |
| VM | 18.2±0.7 | 22.9±0.9 | 20.3±0.8 | 21.5±0.7 | 26.7±1.0 | 25.5±0.9 |
| FC* | 41.6±1.1 | 58.5±1.7 | 49.0±1.6 | 49.9±1.8 | 55.1±2.0 | 57.2±1.2 |
| MC | 0.9±0.1 | 1.5±0.1 | 1.2±0.1 | 1.0±0.1 | 1.4±0.1 | 1.3±0.1 |
| A | 39.3±0.6 | 17.1±0.5 | 29.5±0.4 | 27.6±0.6 | 16.8±0.5 | 16.0±0.3 |
| FC/VM | 2.28 | 2.55 | 2.413 | 2.320 | 2.063 | 2.243 |
| <i>Ultimate analysis (ash free basis)</i> | | | | | | |
| C | 51.2±1.0 | 67.0±1.1 | 58.6±0.9 | 59.1±1.3 | 59.3±1.2 | 60.3±1.9 |
| H | 1.9±0.1 | 2.9±0.1 | 2.3±0.1 | 2.3±0.2 | 2.2±0.1 | 2.4±0.2 |
| N | 3.4±0.2 | 1.1±0.1 | 2.7±0.2 | 2.6±0.2 | 2.4±0.1 | 2.4±0.1 |
| S | 0.4±0.1 | 0.03±0.02 | 0.38±0.1 | 0.39±0.1 | 0.33±0.1 | 0.36±0.1 |
| O* | 43.1±0.9 | 28.9±0.8 | 36.0±0.9 | 35.6±1.0 | 35.7±1.0 | 34.5±0.9 |
| Molar H/C | 0.442 | 0.515 | 0.467 | 0.463 | 0.442 | 0.474 |
| Molar O/C | 0.631 | 0.324 | 0.461 | 0.452 | 0.452 | 0.430 |
| HHV | 12.28±0.3 | 21.62±0.6 | 16.64±0.5 | 16.88±0.5 | 16.77±0.6 | 17.62±0.6 |

*FC and O obtained by difference

moisture content is an indication of the dehydration reaction brought on by the heating of the feedstock [76]. When it comes to ash content, it is simple to say that it will increase following pyrolysis process. The char obtained from MSW pyrolysis has higher ash content of 39.3 wt% compared to other feedstocks. On the other side, the char produced by co-pyrolysis of MSW + TSR with the presence of HZSM5 catalyst showed a minimum ash percentage of 16.0 wt%. The lower ash level improved the carbon in the resilience of char for oxidation, encouraging C–C=C bonds and showing increased aromatization of the co-pyrolysis char produced from MSW + TSR + HZSM5 [77]. It can be shown that the presence of natural minerals accelerated the thermal breakdown of the carbon structure, impeded the carbonization process, and reduced the oxidation resistance of char [78]. The acid pretreatment of the SR improved the volatile fraction and reduced ash content in the char due to prior removal of ash-forming components. There is a considerable correlation between the co-pyrolysis impact and the proximate components of the char derived from the parent feedstock. Char is mostly made of carbon, irrespective of the kind of feedstock used for the pyrolysis process, which became more aromatic [79]. In the MSW + SR based char, the carbon content increased by 19.5% during pyrolysis, whereas for both MSW + TSR, it increased by 18.5%. Except for the char produced from MSW, the amounts of hydrogen and oxygen in the char have dropped considerably compared to the feedstock. These findings are consistent with the char produced by the pyrolysis of maize stalk [80], wood pallets, and food waste [79]. The char produced by SR has a higher carbon and lower oxygen level of 67 wt% and 28.9 wt% respectively. The presence of catalyst for pyrolysis and pretreatment of RS increased the carbon content of the produced char. For example, the char made from MSW + SR has 58.6 wt% of carbon content. However, for the char made from MSW + TSR, the value rose to 59.3 wt%. On the other side, the char made from MSW + SR + HZSM5 and MSW + TSR + HZSM5 has 59.1 wt% and 60.3 wt%, respectively. The pretreatment and catalyst also reduced the nitrogen and sulfur content in the char. For example, the char made from MSW + TSR and MSW + TSR + HZSM5 has a nitrogen content of 2.6 wt% and 2.4 wt% and sulfur content of 0.39 wt% and 0.36 wt% respectively.

In addition to that, the remaining char obtained from TGA analysis and the pyrolysis process was compared to identify the characteristics differences. For SR, cellulose pyrolysis is concentrated in TGA at a higher temperature range, whereas lignin decomposes at a very small mass loss rate until the end of the process. The pyrolysis of cellulose produces bio-oil with moderate yields. Pyrolysis of hemicellulose yields higher gas and liquid products. The yield of solid residue is shown by the lignin present in the biomass, which also yields a high-phenolic liquid. Considering gas composition, lignin yields more H₂ and CH₄, whereas cellulose and hemicellulose yield higher CO₂ and CO. Understanding this process could be of importance in a pyrolysis process for the efficient use of biomass [81]. The char obtained from both TGA analyses had the same H/C ratios and volatile matters. These indices were noteworthy only when applied to the char obtained from the same feedstock.

3.3.2 Analysis of pyrolysis oil

3.3.2.1 Physical analysis Determining the viability of pyrolysis oil as a liquid fuel mostly depends on its physical qualities. Table 5 signifies the different physical characteristics of pyrolysis oil obtained from all samples. The pyrolysis oils are light to dark brown in colour and have a smoky odor. The density of the produced pyrolysis oil is between 1023 and 1056 kg/m³, which are comparable to other types of pyrolysis oils made from various biomass sources [82, 83]. All pyrolysis oils are found to be denser than conventional diesel (~830 kg/m³). The structure and function of the fuel injection system are significantly influenced by the viscosity of the fuel. Compared to diesel, the pyrolysis oil exhibits a higher kinetic viscosity of up to 13.10 cSt. The higher density of the liquid fuel affects the fuel atomizer and combustion quality [84]. Therefore, additional refinement and upgrading are needed to achieve the desired quality, which is comparable to that of gasoline and diesel. The higher flash point of the pyrolysis oil (~95 °C) provides confidence to store it in normal temperature. The low pH of (2.15–2.75) indicates that the pyrolysis oils are acidic in nature due to the presence of phenols, hexadecanoic, octadecenoic and tetradecanoic acids. Due to their lower pH value, the pyrolysis oils become more corrosive to machine components made of aluminium and steel [49]. The HHV of the oils was found to be 20 MJ/kg, which is lower than diesel fuel. The pyrolysis oil obtained from MSW + TSR + HZSM5 shows HHV of 20.95 MJ/kg which is higher than all other types of pyrolysis oil. However, the unsuitable physical character of the oil can be improved through various upgrading techniques.

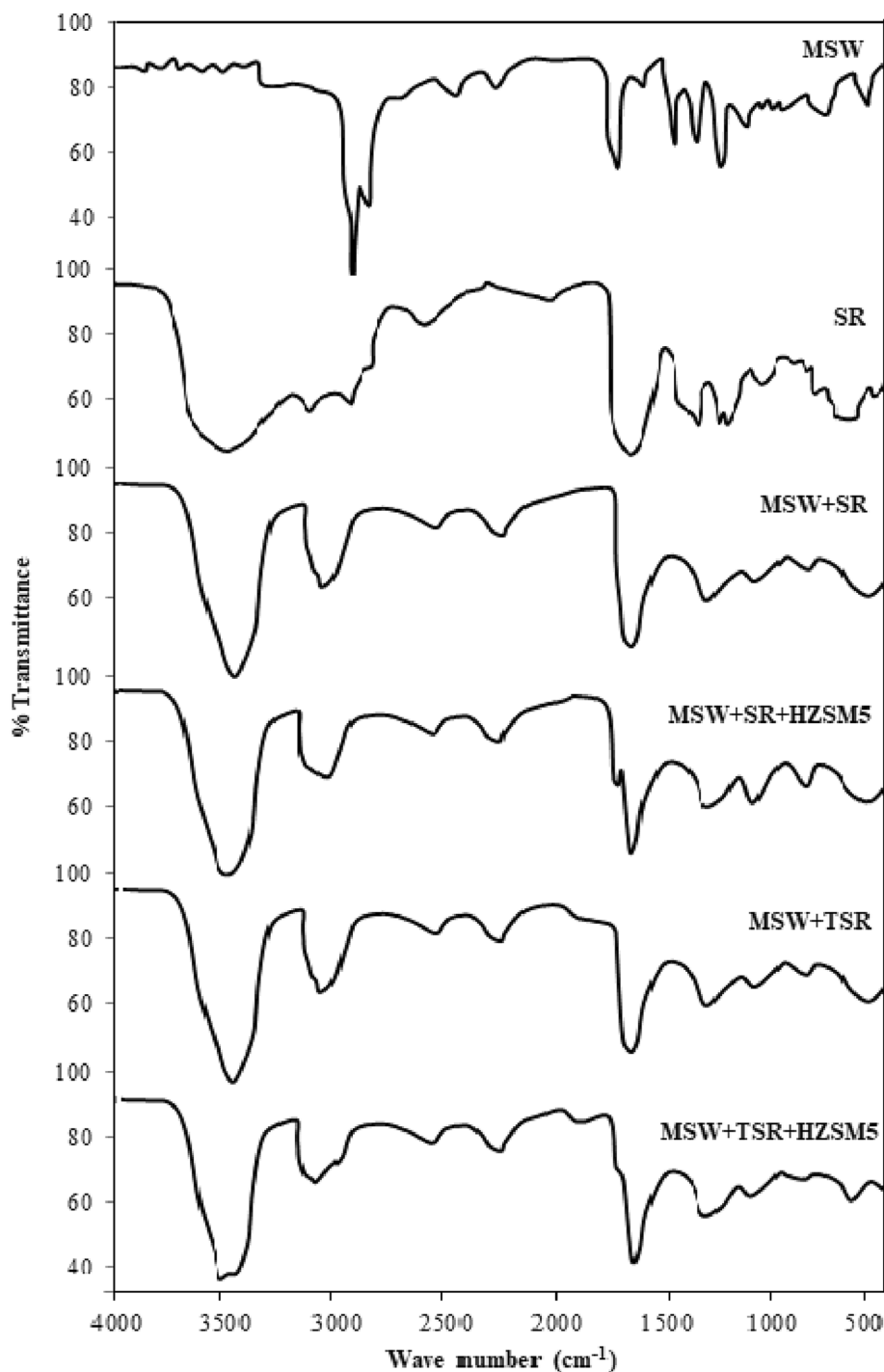
3.3.2.2 FT-IR analysis The pyrolysis oil is analyzed using FT-IR spectroscopy to identify the basic functional groups. The FT-IR spectra of the pyrolysis oils acquired using different feedstocks are displayed in Fig. 4. In pyrolysis oil produced from MSW, the maximum absorption is detected at 2918.5 cm⁻¹ illustrate the existence of hydrocarbon stretching group (C–H). The presence of C=O-stretching carbonyl groups is shown by the lower peak at 1733.3 cm⁻¹. The presence of medium-level carbonyl and aromatic ring groups is identified by the peaks looking at 1470.5 cm⁻¹ and 1376.6 cm⁻¹, respectively. Furthermore, the peaks at 1162.8 cm⁻¹ and 770.7 cm⁻¹ show aliphatic amines (C–N) and aromatic ring alkanes in the oil. Overall, the FTIR analysis of the MSW oil shows the presence of alkanes, alkenes, and carbonyl groups in MSW pyrolysis oil, due to the high organic content of the feedstock [85]. While analyzing SR pyrolysis oil, alcohols and phenols (O–H) were identified by the broad peak that appeared at 3486.3 cm⁻¹ [86]. The presence of alkanes is indicated by the light peaks at 2954.9 cm⁻¹ that are caused by C–H vibration. The strong peaks at 1656.3 cm⁻¹ are caused by C–O stretching vibrations, which indicate the presence of aldehydes, carboxylic acids, and ketone. The existence of alkenes and aromatics (C–H) is indicated by the peak appearing at 1447.0 cm⁻¹. The figures show the occurrence of alcohol, phenols, and carboxylic acids in the co-pyrolysis oil. The high viscosity of the pyrolysis oils is mostly attributed to intra- and intermolecular hydrogen-bond hydroxyl groups [87]. Apart from that, the pyrolysis oils contain many different chemical components, including acids, aldehydes, ketones, and furans, etc. [88].

3.3.2.3 GC–MS analysis This work used GC/MS analysis to assess pyrolysis oil compositions obtained from individual and co-pyrolysis of MSW and SR, with and without catalyst and pretreatment. Figure 5a–f shows the GC–MS analysis of the produced pyrolysis oils and Table 6 displays the comprehensive component analysis, which includes the chemical name, formula and peak area. According to the results, more than 50 chemicals were found for each sample and the main peaks representing a higher probability of detection (≥ 80%) were chosen and reported in the table. Owing to the complexity of oil nature, it is impossible to distinguish each peak with clarity. The percentage area of the chemical peaks was used in a semi-quantitative analysis to ascertain the dispersion of chemicals in pyrolysis oils. The oils contain mainly alcohol, aliphatic, aromatic, and cyclic hydrocarbons. In the petrochemical sector, these elements are important raw material. The

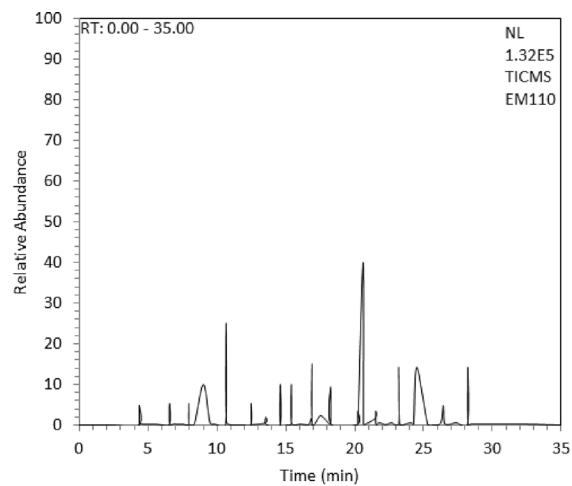
Table 5 Physical analysis of pyrolysis oil

| Feedstock | Density kg/m ³ | Viscosity cSt | pH – | Flash point °C | Heating value MJ/kg |
|-------------------|------------------------------|------------------|---------|-------------------|------------------------|
| MSW | 1023 | 7.04 | 2.27 | 85 | 18.86 |
| SR | 1037 | 13.10 | 2.15 | 95 | 20.72 |
| MSW + SR | 1025 | 10.25 | 2.50 | 94 | 20.04 |
| MSW + SR + HZSM5 | 1042 | 10.84 | 2.45 | 96 | 19.30 |
| MSW + TSR | 1056 | 10.33 | 2.62 | 96 | 20.58 |
| MSW + TSR + HZSM5 | 1035 | 10.89 | 2.75 | 95 | 20.95 |

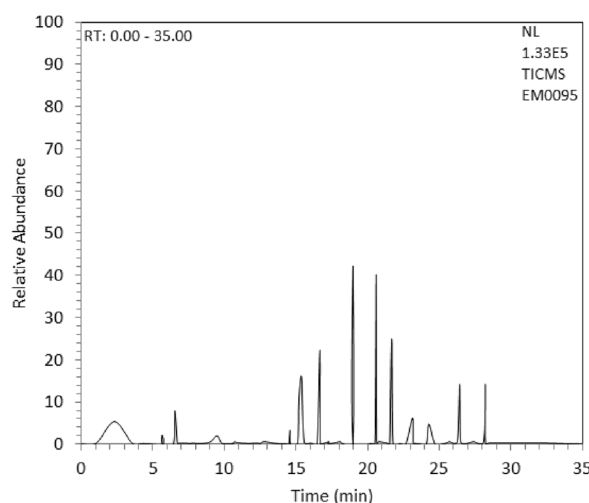
Fig. 4 FT-IR analysis of the pyrolysis oil obtained using different feedstocks



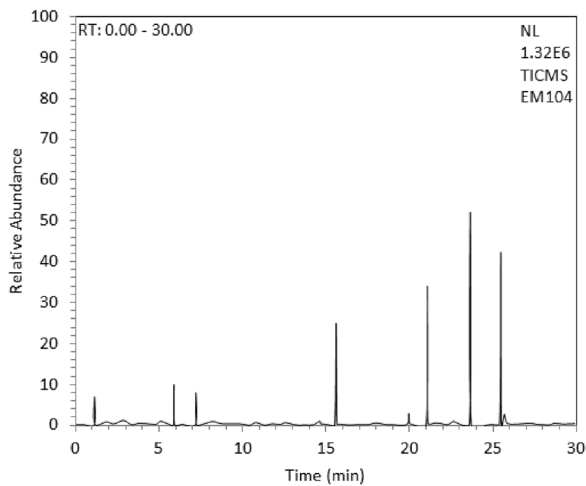
spectrum of polymer breakdown present in the MSW is greater than that of lignocellulosic biomass due to its complex structure. The pyrolysis oil produced from SR has a majority of alcohols, aldehydes, ketones, furfural, and furan due to cellulose and hemicellulose breakdown [76, 89]. The breakdown of lignin is the cause of the existence of aromatics, creosol, and phenol-based chemicals in pyrolysis oil [90]. Phenol identified in this analysis is a significant chemical component used nowadays in the manufacture of many beneficial products. 4-Ethyl-2-methoxyphenol, 2-Methoxyphenol, 5-Methyl-2-nitrophenol, 3-Furanmethanol, 4-ethyl-2-methoxyphenol identified in pyrolysis oil are utilized in polymer, wood, and automobile based industries. The results of FTIR analysis also clearly show the presence of phenolic compounds. Cyclo-tetrasiloxane, octamethyl, Cyclopentasiloxane, decamethyl, n-Hexadecanoic acid, Octadecane, Terephthalic acid, di(2-chloroethyl) ester, 4-Ethylphenol, Bis(2-ethylhexyl) phthalate, and Hexacosane are the important chemicals identified



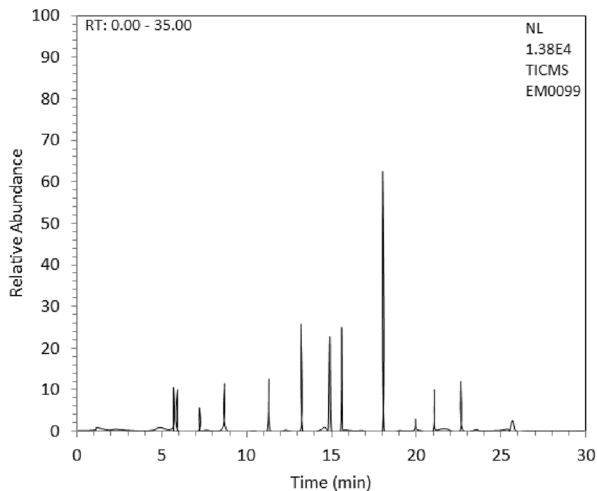
(a) MSW



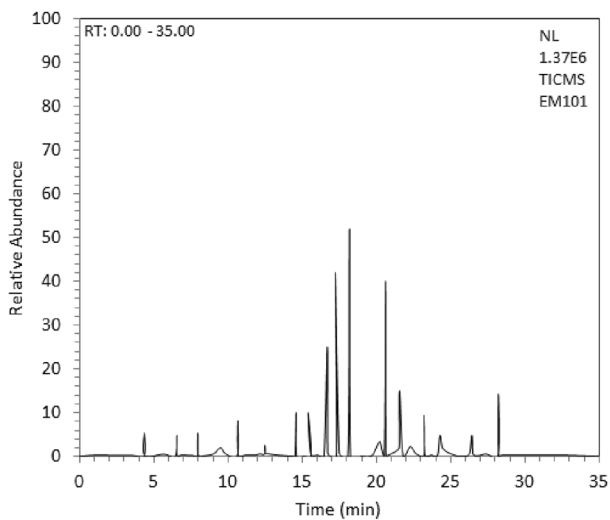
(d) MSW+SR+HZSM5



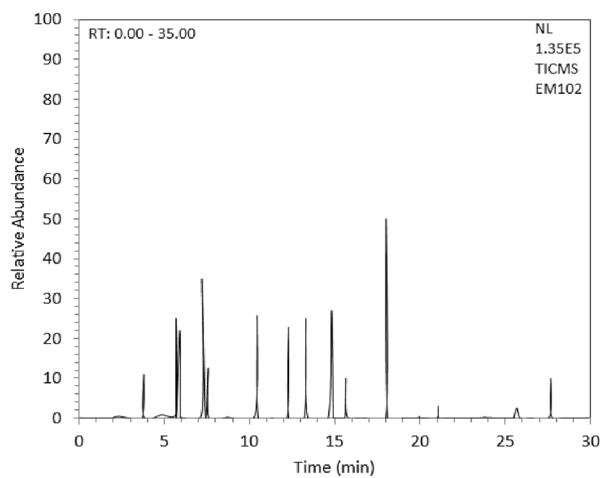
(b) SR



(c) MSW+TSR



(e) MSW+SR



(f) MSW+TSR+HZSM5

Fig. 5 GC-MS analysis of the produced pyrolysis oil

Table 6 GC–MS analysis of pyrolysis oil

| Compound name | Formula | Area % | | | | | |
|--|--|--------|------|----------|------------------|-----------|-------------------|
| | | MSW | SR | MSW + SR | MSW + SR + HZSM5 | MSW + TSR | MSW + TSR + HZSM5 |
| 2,6-Dimethoxyphenol | C ₈ H ₁₀ O ₃ | 1.74 | 5.81 | 2.11 | 2.54 | 3.48 | 2.99 |
| Cyclopentanone | C ₅ H ₈ O | – | 0.83 | 0.76 | – | 0.81 | – |
| 4-Ethyl-2-methoxyphenol | C ₉ H ₁₂ O ₂ | 1.33 | 5.35 | 2.27 | 2.84 | 1.51 | 3.30 |
| Cyclotetrasiloxane, octamethyl- | C ₈ H ₂₄ O ₄ Si ₄ | 3.52 | – | 1.18 | 1.38 | 0.94 | 0.72 |
| Furfural | C ₅ H ₄ O ₂ | – | 8.15 | 3.37 | 3.30 | 1.82 | – |
| 2,4-Dimethyl-1-heptene | C ₉ H ₁₈ | 0.98 | – | 0.64 | – | 0.50 | – |
| 4-Methyl-1,3-heptadiene | C ₈ H ₁₄ | 1.44 | 1.82 | 1.20 | 1.11 | 1.06 | 0.85 |
| Cyclopentasiloxane, decamethyl- | C ₂ H ₆ O ₅ Si ₅ | 4.55 | – | 1.58 | 0.84 | 0.24 | 0.57 |
| 2-Methyl-2-hexanol | C ₇ H ₁₆ O | – | 3.50 | 1.26 | 1.17 | 1.23 | 0.98 |
| 4-Ethylpyridine | C ₇ H ₉ N | 2.11 | 2.75 | 1.28 | 2.50 | 2.75 | 2.80 |
| 2-Ethylphenol | C ₈ H ₁₀ O | – | 1.83 | 0.77 | 0.36 | 0.34 | 0.29 |
| n-Hexadecanoic acid | C ₁₆ H ₃₂ O | 11.01 | 4.25 | 3.88 | 4.01 | 3.97 | 3.50 |
| Octacosane | C ₂₈ H ₅₈ | 3.83 | – | 1.14 | 0.58 | – | – |
| 1-Hydroxy-2-methoxy-4-methylbenzene | C ₈ H ₁₀ O ₂ | – | 0.58 | – | – | – | 0.24 |
| Creosol | C ₈ H ₁₀ O ₂ | – | 4.09 | 2.10 | 1.57 | 1.19 | – |
| 2-Methylnaphthalene | C ₁₁ H ₁₀ | – | 0.67 | – | – | – | – |
| Z-5-Nonadecene | C ₁₉ H ₃₈ | 1.05 | – | 0.58 | – | – | – |
| Azulene | C ₉ H ₈ | 3.22 | – | 0.83 | 0.72 | – | 0.37 |
| Octadecane | C ₁₀ H ₈ | 3.48 | – | 1.58 | 0.58 | 3.22 | 3.24 |
| Naphthalene, 2-methyl- | C ₁₁ H ₁₀ | 2.52 | 0.65 | 1.27 | 0.94 | – | – |
| 3-Decyne | C ₁₀ H ₁₈ | – | 0.70 | – | – | – | – |
| 5-Methylfuran-2-carbaldehyde | C ₆ H ₆ O ₂ | – | 2.51 | 0.83 | – | 0.84 | – |
| beta.-iso-Methyl ionone | C ₁₄ H ₂₂ O | 1.47 | – | 1.44 | 1.28 | 1.59 | 2.01 |
| 2-Furancarboxaldehyde,-5-Methyl | C ₆ H ₆ O ₂ | – | 1.28 | 1.01 | 1.04 | 0.58 | 1.25 |
| 2-Methoxy-4-nitroaniline | C ₇ H ₈ N ₂ O ₃ | 0.83 | – | – | – | – | – |
| 6-Octadecenoic acid | C ₁₈ H ₃₄ O | 3.25 | – | 1.20 | 1.98 | 1.84 | 1.77 |
| Benzaldehyde, 4-hydroxy-3-methoxy | C ₈ H ₈ O ₃ | – | 1.24 | 0.28 | – | 0.36 | – |
| Phenol | C ₆ H ₆ O | 2.38 | 8.77 | 5.27 | 5.35 | 4.20 | 4.45 |
| 1,2-Diphenylcyclopropane | C ₁₅ H ₁₄ | 2.33 | 1.28 | 0.85 | – | – | – |
| 9-Octadecenamide, (Z)- | C ₁₈ H ₃₅ NO | 1.95 | – | 1.23 | 0.84 | 0.83 | – |
| Heptacosane, 1-chloro- | C ₂₇ H ₅₅ Cl | 2.47 | – | 2.30 | 2.97 | 2.00 | 1.99 |
| Stearic acid, methyl ester | C ₁₉ H ₃₈ O ₂ | – | 3.07 | 1.87 | 1.92 | 1.28 | 1.00 |
| 5-Methyl-2-nitrophenol | C ₇ H ₈ NO ₃ | 1.36 | – | 0.39 | 0.40 | 0.51 | – |
| Eicosane | C ₂₀ H ₄₂ | 0.98 | – | 0.50 | 0.55 | – | 0.47 |
| Pyrene, 1-methyl- | C ₁₇ H ₁₂ | 0.25 | – | – | – | – | – |
| 4-Pyridinol | C ₅ H ₅ NO | – | 0.99 | 0.65 | 0.28 | – | – |
| 3-Methylcyclopentane-1,2-dione | C ₆ H ₈ O ₂ | – | 4.29 | 3.44 | 3.88 | 3.25 | 3.57 |
| 2,2-Dimethylcyclopentane-1,3-dione | C ₇ H ₁₀ O ₂ | 0.38 | 1.11 | 1.02 | 0.58 | – | 0.34 |
| Dibenzo[a,e]cyclooctene | C ₁₆ H ₁₂ | 0.55 | – | – | – | – | – |
| 2-Methoxy tetra hydro furane | C ₅ H ₁₀ O ₂ | – | 0.28 | – | – | – | – |
| Terephthalic acid, di(2-chloroethyl) ester | C ₁₂ H ₁₂ Cl ₂ O ₄ | 3.61 | – | 2.75 | 2.58 | 2.80 | 1.98 |
| Tetradecanoic acid | C ₁₄ H ₂₈ O ₂ | – | 1.29 | 0.44 | 0.25 | – | – |
| 1,2-Benzenediol, 3-methoxyl | C ₇ H ₈ O | – | 3.22 | – | – | – | – |
| 4-Ethylphenol | C ₈ H ₁₀ O | 10.05 | – | 6.28 | 6.23 | 2.99 | 2.94 |
| Ethisterone | C ₂₁ H ₂₈ O ₂ | – | 0.82 | – | – | – | – |
| 3-Furanmethanol | C ₅ H ₆ O ₂ | – | 1.26 | 0.92 | 0.82 | 0.80 | 0.88 |
| Bis(2-ethylhexyl) phthalate | C ₂₄ H ₃₈ O ₄ | 7.14 | – | 6.21 | 6.25 | 6.00 | 5.83 |
| 2-Methoxyphenol | C ₇ H ₈ O ₂ | 5.28 | – | 3.33 | 3.10 | 3.81 | 2.27 |

Table 6 (continued)

| Compound name | Formula | Area % | | | | | |
|--------------------------------------|--|--------|------|----------|------------------|-----------|-------------------|
| | | MSW | SR | MSW + SR | MSW + SR + HZSM5 | MSW + TSR | MSW + TSR + HZSM5 |
| 5-Isopropyl-2,4-imidazolidinedione | C ₆ H ₁₀ N ₂ O ₂ | – | 0.93 | – | – | – | – |
| Butyrolachone | C ₄ H ₈ O ₄ | 0.82 | – | – | 0.81 | – | 0.44 |
| Carbazole | C ₁₂ H ₉ N | 0.95 | – | 0.86 | 0.55 | – | – |
| Hexacosane | C ₂₆ H ₅₄ | 3.20 | 3.01 | 2.28 | 2.95 | 2.66 | 2.47 |
| Toluene | C ₇ H ₈ | 1.28 | – | – | – | – | – |
| Benzaldehyde | C ₇ H ₆ O | – | 0.34 | – | – | – | – |
| 3-Methyl-1-phenyl-1H-indene | C ₁₆ H ₁₄ | 1.28 | – | 0.88 | 0.34 | 0.29 | – |
| 2-(2-propenyl)furan | C ₇ H ₈ O | 0.95 | 7.33 | 3.90 | 3.28 | 3.17 | 3.30 |
| 1,4-Benzenedicarboxylic acid | C ₂₄ H ₃₈ O ₄ | 1.19 | – | – | – | – | – |
| 2-Isopropyl-2,5-dihydrofuran | C ₇ H ₁₂ O | – | 1.80 | 1.11 | 1.23 | 0.94 | 0.96 |
| Cresol | C ₇ H ₈ O | – | 0.85 | 0.41 | 0.38 | 0.33 | 0.93 |
| 3-Cyclopentene-1-acetaldehyde, 2-oxo | C ₇ H ₈ O ₂ | – | 0.39 | – | – | – | – |

in MSW pyrolysis oil. On the other side, 2,6-Dimethoxyphenol, 4-Ethyl-2-methoxyphenol, Furfural, n-Hexadecanoic acid, Creosol, Phenol, Stearic acid, methyl ester, 3-Methylcyclopentane-1,2-dione, 1,2-Benzenediol, 3-methoxyl, and 2-(2-propenyl)furan were identified as the majority in the pyrolysis oil derived from SR. Compared to MSW, SR-generated pyrolysis oil has a greater oxygen content with lower monoaromatic hydrocarbons, and larger amounts of oxygenated chemicals.

3.3.3 Analysis of gas

When biomass is pyrolyzed, gaseous products are released in the form of non-condensable gases. These gases are mainly contains H₂, O₂, CO, CO₂, CH₄, and light hydrocarbons. Table 7 shows various gas fractions obtained from the individual and co-pyrolysis of different feedstocks. H₂ and CO present in the gas are used for liquid fuel production. In addition to that, H₂ is also used for improving of pyrolysis oil [86]. CO₂ was found more in the pyrolysis gas produced by the individual pyrolysis of MSW. However, CO was found more in SR pyrolysis gas. The breakdown of the feedstock constituents and secondary cracking reactions of the primary products are the main reasons for the yield of gaseous components [87].

4 Conclusion

The objective of this work was to improve the quality and yield of biofuel from biomass and municipal solid waste. For this, sugarcane residue was used to represent biomass and combined with MSW. Individual and co-pyrolysis experiments were performed by combining MSW, SR, and TSR in catalytic and non-catalytic modes. Acid pretreatment of SR has diverse effects on the co-pyrolysis process and alters the yield of pyrolysis products. The experiments were conducted with six different combinations of MSW, SR, MSW + SR, MSW + SR + HZSM5, MSW + TSR, MSW + TSR + HZSM5, and the products obtained under each process were evaluated. The maximum pyrolysis oil yield of 50.5 wt% was obtained with MSW + TSR + HZSM5 combination, whereas the maximum gas yield of 38.1 wt% was obtained with MSW + SR + HZSM5.

Table 7 Component analysis of non-condensable gas fractions

| Feedstock | Components in % | | | | |
|-------------------|-----------------|-----------------|----------------|-----------------|------|
| | H ₂ | CH ₄ | O ₂ | CO ₂ | CO |
| MSW | 5.1 | 10.6 | 0.9 | 53.2 | 28.6 |
| SR | 6.4 | 12.3 | 1.2 | 36.3 | 42.1 |
| MSW + SR | 5.5 | 12.9 | 1.0 | 46.8 | 31.7 |
| MSW + SR + HZSM5 | 5.7 | 11.1 | 1.6 | 46.5 | 31.3 |
| MSW + TSR | 5.7 | 11.5 | 1.3 | 46.3 | 33.2 |
| MSW + TSR + HZSM5 | 5.9 | 12.1 | 1.5 | 45.8 | 32.0 |

The char yield was considerably decreased by pretreatment and catalytic effect. In co-pyrolysis, pretreatment improved the devolatilization of organic matter and raised the production of pyrolysis oil. The heating value of the pyrolysis oil obtained in this study was in the range of 18.86–20.95 MJ/kg. Though the heating value of the char obtained in this study was not significantly affected by pretreatment, the process altered the composition of the char. The volatile matter and fixed carbon of the char produced from pretreated biomass increased significantly. The ash content of the char decreased more during the co-pyrolysis of pretreated biomass. The produced pyrolysis gas contains H₂, O₂, CO, CO₂, CH₄, and light hydrocarbons. The higher percentages of CO₂ and CO in the gas components are related to the available oxygen content in the feedstock. From the characterization analysis, it can be concluded that the pretreatment of biomass improved the phenolics and aromatic hydrocarbons and decreased nitrogen and oxygen-based components. The pyrolysis oil had significant amounts of organic mixtures and it can be used as a fuel for furnaces and feedstock for chemical industries. The pyrolysis gas can be used as a gaseous fuel and the char obtained in this study has an acceptable volatile matter and fixed carbon content. Hence, it has a higher potential for use as fuel, fertilizers and carbon sink.

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Author contributions GC: Data Collection and investigation. NA: Data Collection and investigation. RP: Conceptualization and supervision. PM: Writing, editing and investigation. LV: Conceptualization and investigation. SV: Investigation and supervision. AP: Reviewed the writing. AB: Helped in editing. JJRL: Writing and editing.

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Data availability The data generated or analyzed during this study are available within the article.

Declarations

Ethical approval All experimental and laboratory tests were performed in accordance with the relevant guidelines and regulations.

Consent to publication All authors gave their consent to publish this article.

Competing interests The authors declare no competing interests.

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