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Characterisation and gas chromatography–mass spectrometry analysis of products from pyrolysis of municipal solid waste using a fixed-bed reactor

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ABSTRACT

A comprehensive understanding of the properties of pyrolysis oil made from municipal solid waste (MSW) is essential for advancement in pyrolysis technology research. Optimizing bio-oil production conditions effectively necessitates a thorough analysis of the resulting product composition. This study aims to assess the potential of converting MSW into pyrolytic oil through the pyrolysis process. MSW samples were collected from the Urta Chirchik landfill in the Tashkent region and utilized as the primary feedstock. Proximate and elemental analyses were utilized for studying at the MSW's physical and chemical characteristics. The findings revealed that the moisture content of the MSW was 13.05 wt% (dry basis), volatile matter (VM) was 51.64 wt%, ash content was 30.53 wt%, and fixed carbon (FC) content was 4.78 wt%. The ultimate (chemical) analysis was conducted using CHS and XRF fluorescence analyzers, and found the following results: 39.81% carbon (C) content, 23.92% hydrogen (H_2), 0.27% Sulphur (S), 0.84% nitrogen (N_2), 44% oxygen (O_2), and 38.79 MJ/kg of higher heat value (HHV). The MSW mixture was pyrolyzed in a vertical batch-type reactor at temperatures and time ranging from 200 to 600 °C and 20 to 60 minutes. The thermal decomposition of municipal solid waste (MSW) generated three primary products: a liquid fraction (pyrolytic oil), solid residue (char), and a gaseous mixture. The study demonstrated that the composition of the pyrolytic oil was significantly influenced by changes in both pyrolysis temperature and processing duration. The pyrolytic liquid was further refined (purified) using a distillation apparatus. The upgraded oil obtained from this process was then analyzed for its composition and characterized using gas chromatography–mass spectrometry (GC–MS). The GC–MS analysis identified approximately 28 major chemical compounds in the oil derived from the MSW mixture. The most abundant components identified were ethanone and 2-furancarboxaldehyde, followed by benzene, 1-ethyl-3-methyl; 1-undecene; 3-dodecene; benzene, 1,2,4-trimethylbenzene; and 1,2,4-trimethylcyclohexene. The energy value analysis results showed that upgraded pyrolytic oil's HHV is increased (40.6 MJ/kg). The findings emphasize the potential of pyrolysis as an effective approach for transforming MSW into valuable oil-based resources. The characterization of these compounds using GC-MS techniques gives useful information for further optimizing and utilizing MSW-derived pyrolysis oils.

Keywords: pyrolysis, municipal solid waste, pyrolytic oil, chemical composition.

INTRODUCTION

High energy demand and air pollution have become critical global challenges in recent years. According to the statistics, currently, more than eighty percent of world power demand is supplied through finite energy sources and fossil fuels. The excessive use of fossil fuels generates significant CO_2 emissions, which are strongly linked to the greenhouse effect and may contribute to global climate change (Yue et al., 2023). In addition, global waste production has been consistently increasing, fueled by the growth of the population, urban development, also expanding global economy and industry-based activities. Although many attempts have been made to tackle this problem, managing the vast amounts of waste produced remains a significant challenge for humanity. For instance, waste produced in the world reached to 2.02 bln tons in 2016, followed by forecasts suggesting that this amount is expected to grow up to 2.59 bln tons till 2030, also 3.4 bln tons by 2050 (Awogbemi & Kallon, 2022). According to The World Bank, solely MSW itself will be generated 2.2 bln tons by 2025, equivalent to 1.42 kilograms per person per day (Tokmurzin et al., 2020).

In light of these challenges, adopting renewable energy for diverse applications presents a practical solution to mitigate the adverse environmental consequences associated with the extraction, refining, and consumption of fossil fuels (Awogbemi & Kallon, 2022). Bioenergy is one of the reliable option due to its abundant resources, wide variety of secondary value-added products and their multifunctional use. Bioenergy refers to energy obtained from various sources of biomass (Adams et al., 2018), which comprises organic or biological substances originating from living organisms. These materials are generated through either direct or indirect conversion processes (Nachenius et al., 2013). Biomass can be systematically subdivided into distinct groups: forest-derived resources, agricultural residues and post-harvest crop remnants, wood-derived products, and waste materials from both animal and human sources, including municipal solid waste (Inayat et al., 2022). Municipal solid waste (MSW) impacts the environment and human well-being both directly and indirectly. Direct impacts include material damage, diminished aesthetic value, and adverse effects on human health, leading to considerable socio-economic repercussions. Indirect impacts, often long-term, involve alterations to ecosystem structure and function, contributing to climate change, which subsequently affects regional socio-economic stability and sustainability (Tursunov & Abduganiev, 2020).

Uzbekistan, with a population exceeding 33 mln, is the most populous country in Central Asia, generating significantly more MSW) than its neighbors like Kazakhstan, Tajikistan, Turkmenistan, and the Kyrgyz Republic. Proper solid waste management remains a serious issue both in Uzbekistan and globally. As reported by State Statistics Committee, Uzbekistan generates 35 mln m^3 of MSW annually. Furthermore, approximately 100 mln tons of waste from industries and municipalities are deposited in landfills each year, resulting in a cumulative total waste of over 2 bln tons are collected in landfills to date (Tursunov et al., 2023a).

Although municipal wastes are generated in substantial quantities and are often considered unusable, leading to environmental pollution, they represent a valuable secondary energy resource. The energy obtained by these types of discarded materials have a potential for utilization of heat or electrical power generation. Moreover, integrating MSW into the energy sector not only helps tackle critical environmental pollution challenges in urban areas but also offers an additional source of energy (Tursunov and Abduganiev, 2020). The waste-to-energy (WtE) approach represents an effective strategy for managing municipal solid waste. This technique significantly decreases the amount of Urban waste while simultaneously producing sustainable energy and useful chemical derivatives. Various WtE technologies, such as pyrolysis, gasification and incineration are employed for the treatment of MSW (Chicaiza-Ortiz et al., 2024).

Pyrolysis technique involves thermo-chemical decomposition of organic matter which happens within a temperature range of 300÷650 °C under oxygen-free conditions. During this process, biomass undergoes thermal decomposition, converting into liquids (pyrolysis oils), gases, and char (a solid product). Primary pyrolysis outputs are pyro-oils, gases, and semi-coke (char) (Abduganiev et al., 2020). Applying pyrolysis for processing MSW effectively reduces corrosion and emissions by capturing hazardous substances, such as alkali and heavy metals (excluding mercury and cadmium), sulfur and chlorine, present in residual by-products of the process. It also prevents the formation of harmful compounds like

PCDD/Fs and lowers thermal NOx emissions due to reduced temperatures. Therefore, applying pyrolysis to MSW avoids these issues and shows promising potential for waste-to-energy applications (He et al., 2010).

Pyrolysis oil is regarded as a renewable resource because it can be converted into fuels, chemicals, and energy (Muzyka et al., 2023). Liquid product of pyrolysis, which named differently on literatures: bio-crude oils, wood fluids, wood oils or bio-oils, are liquid compounds produced through the condensation of vapors released during the thermal breakdown and depolymerization of biomass constituents, including cellulose, hemicellulose, and lignin, under oxygen-free conditions. The pyrolysis process encompasses a wide range of chemical reactions, such as hydrolysis, dehydration, isomerization, hydrogenation, aromatization, condensation, coking. These reactions contribute to the highly complex composition of pyrolysis oils, which consist of approximately 300 different compounds, including: water, alcohols, carboxylic acids, hydrocarbons, aldehydes, ketones, sugars, esters, phenolic substances, and furan derivatives (Van Nam et al., 2020). Several factors significantly influence bio-oil chemistry and properties. These factors include: class of pyrolysis vessel used, reaction conditions, and specific characteristics of the feedstock, such as its content of lignin, hemicellulose, cellulose, minerals, and extractable compounds (Chen et al., 2024; Van Nam et al., 2020). Bio-oils mainly consist of oxygenated hydrocarbons, with compounds such as ketones, phenols, acids, aldehydes and esters (Chen et al., 2024). Comprehensively analyzing of resulting bio-oils is vital for optimizing their production conditions, otherwise, optimization will not be achieved (Grams, 2020).

Gas Chromatography-Mass Spectrometry (GC-MS) analysis is crucial for understanding complex chemical composition of bio-oils derived from pyrolysis fuels. Due to the numerous compounds with varying properties and concentrations present in bio-oils, detailed compositional analysis is vital for optimization of pyrolysis conditions, also subsequent upgrading steps. Compound identification and quantification, along with determination of specific functional groups total content, pose significant challenges that GC-MS can effectively address. Conducting GC-MS analysis offers several advantages. It enables simultaneous achievement of important tasks such as feedstock and product characterization, optimization of the pyrolysis process, process monitoring and quality control, and product development and valorization (Chen et al., 2024). By analyzing thermal breakdown behaviour of different biomass materials via pyrolysis-GC/MS (Py-GC/MS), researchers are able to gain a deeper insight into the impact of additives, assess improvements, and identify products formed during different forms of pyrolysis (Chen et al., 2024). Py-GC/MS also enables the comparative analysis of various feedstocks and the differences in the products generated during pyrolysis. Moreover, understanding the composition of bio-oil present in biomass-derived waste materials through GC-MS analysis provides vital information for creating predictive models (Muzyka et al., 2023). Investigating the characteristics and chemical composition of bio-oils aids in determining appropriate methods for their production, processing, storage, and utilization (Van Nam et al., 2020).

The aim of this study is to investigate the properties of pyrolytic oil samples extracted from MSW. Detailed chemical composition of the pyrolytic oil is determined using an Agilent 7890A GC–MS system. A comprehensive analysis of the oil's composition will improve its characterization and offer valuable insights for refining the pyrolysis process.

MATERIALS AND METHODS

Biomass characterization

Sampling

Sampling of MSW followed European PN-EN and ASTM 5231 standards. About 100 kg of waste, comprising 10 components (wood, kitchen waste, plastics, textiles, glass, rubber, and ferrous materials) (see Figure 1), was collected from Urta Chirchik landfill and analyzed at TIIAME National Research University. The waste was sorted, crushed, and sieved into 2–3 mm particles for the experiments. A more detailed information can be found on (Tursunov et al., 2023b).

Proximate and ultimate analysis

Measurements of moisture, volatile matter, fixed carbon, and ash contents were performed in compliance with the PN-EN 14774–3:2010 and ASTM-E871 standards, employing an Eltra TGA Thermostat analyzer. The CHS (carbon, hydrogen, sulfur) content in municipal solid waste (MSW) was determined using an Eltra CHS-580 analyzer. Higher heating value, also known as high calorific value, was tested by Leco AC calorimeter.

Pyrolysis experiments

In this study, a pyrolytic reactor developed by Tursunov and Abduganiyev was used to convert the mixture of MSW to pyrolysis oil. Figure 1 illustrates a schematic diagram of the pyrolysis reactor. The main working part of the pyrolysis device – the reactor (2), has a 3 kg capacity, 10 mm thickness, 65 mm inner diameter, and 300 mm overall length. If the biomass has 200 kg/m³ density and 20% moisture content, then, 3 kg of raw material with optimal size of 3.5 cm can be loaded into the reactor. A 2 kW electric heating source (1) was used to provide necessary temperature for processing the biomass feedstock. When reactor internal temperature reaches 200–600 °C, the loaded solid waste samples undergo a reaction, and the resulting vapor-gas mixture begins to exit due to internal pressure. The heavy hydrocarbons present in the vapor-gas mixture accumulate in the first container (4). The remaining mixture is cooled through a condenser (5), and the resulting liquid fuel is collected in the second container (6). The vapor-gas mixture that has not condensed into liquid passes through a filter (7) and is collected in the gas collector (8). The internal temperature of the reactor was measured using a K-type thermocouple.

The following equation applied for determination of pyrolysis oil yield generated through slow pyrolysis of MSW (Song et al., 2018):

$$Y_0 = \frac{m_o \times 100\%}{m_f} \quad (1)$$

where: Y_o represents the yield in %, which is depicted as a ratio of pyrolytic oil mass (m_o, in kg) to the total mass of shredded municipal solid waste (m_f, in kg) used as raw material in each experiment.

Product analysis

Distillation of pyro-oil

In order to identify specific functional groups, mitigate coelution issues, and increase the detection sensitivity for a wide range of compounds,

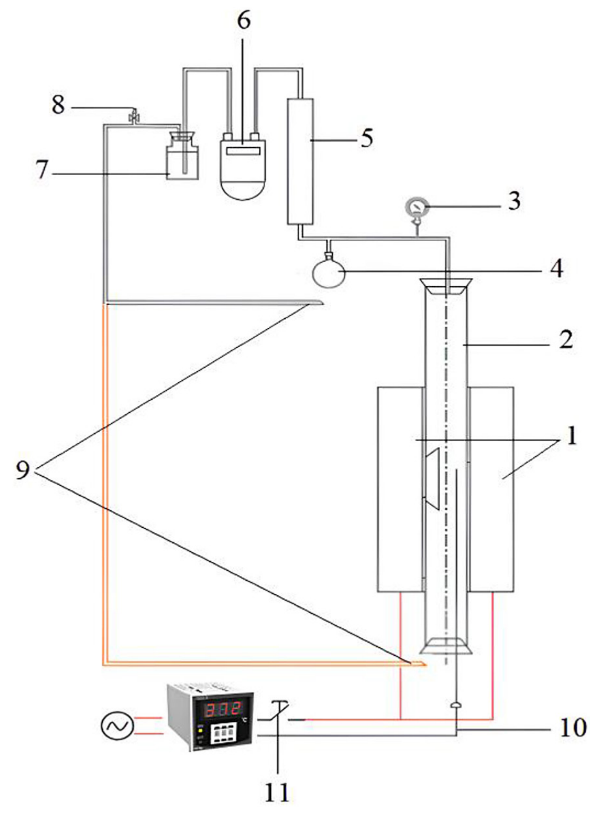


Figure 1. Pyrolysis reactor scheme. 1 – electric heating source; 2 – reactor; 3 – pressure gauge; 4 – first product (heavy hydrocarbons); 5 – condensate; 6 – gas analyzer and second product (biofuel); 7 – water (filter); 8 – gas collection vessel; 9 – gas; 10 – thermocouple; 11 – temperature control unit

pre-treatment steps are frequently required prior to GC-MS analysis due to the complex nature of the compound mixtures present in pyrolysis bio-oil and its high water content (Staš et al., 2020).

The purification (distillation) of the pyrolysis oil obtained from the experiments was carried out at the Uzbekistan Forestry Research Institute laboratory using an experimental apparatus, as described by da Mota et al. (2014). The laboratory distillation apparatus is depicted in Figure 2. The laboratory setup comprises a heater, distillation flask, distillation head, thermometer, condenser, distillation adaptor, receiving flask. The pyrolytic oil with volume of 400 ml was poured into the re-boiler and then heated at temperatures between 70-180 °C with 1.5 hours of operation. Over the course of 1.5 hours, the temperature was monitored every minute. Distillate volume and time from the first drop were recorded, followed by time for each of the 40 ml of distillate for 1.5 hours. After that, the distillate was stored in a glass container in a cool environment.

GC-MS analysis

In this study, the chemical compounds present in pyro-oil were determined by GC-MS analysis (Agilent Technologies 7890A). The analysis was done at "Plant Substances Chemistry" scientific research institute under Uzbekistan Academy of Sciences. The GC-MS analysis utilized the following optimized parameters: helium (99.999% purity) served as an inert gas, operating in constant flow mode at 1.2 mL per min rate (linear velocity of 27.9 cm/s) and an initial inlet pressure of 348 kPa. 1 µL sample was supplied through a split-mode injector by 1:20 split ratio at 280 °C temperature. A non-polar capillary column, Rxi-5Sil MS (inner diameter and film thickness are 60 m × 0.18 mm and 0.10 µm respectively) was utilized.

The temperature setting in GC oven was configured as follows: 40 °C initial temperature was kept constant 5 minutes, followed by 104 °C gradual rise (0.7 °C/min rate). Next, a subsequent rise to 280 °C (10 °C/min rate), which was held for an additional 5 minutes. The MS transfer line was maintained at 280 °C, and the system operated in full scan mode, covering a range of 35 to 350 m/z with a 4.5 scans/s scan rate and a standard electron ionization energy of 70 eV. The electron multiplier voltage was set to 1188 V. For selective ion monitoring, one quantifier ion and two qualifier ions were recorded. During the experiments, the temperature of Mass Spectrometer source was maintained at 230 °C, and the quadrupole temperature was maintained at 150 °C consistently.

RESULTS AND DISCUSSION

MSW Sampling

Figure 3 illustrates the outcomes of the sorting procedure and the amount of each distinct MSW component at Urta-Chirchik landfill. As shown in Figure 3, the majority of the waste produced at Urta-Chirchik landfill is MSW, which includes materials like wood, textiles, food and organic waste, and film plastics. The high amount of wood waste can be attributed to the Urta-Chirchik region's geographical location,

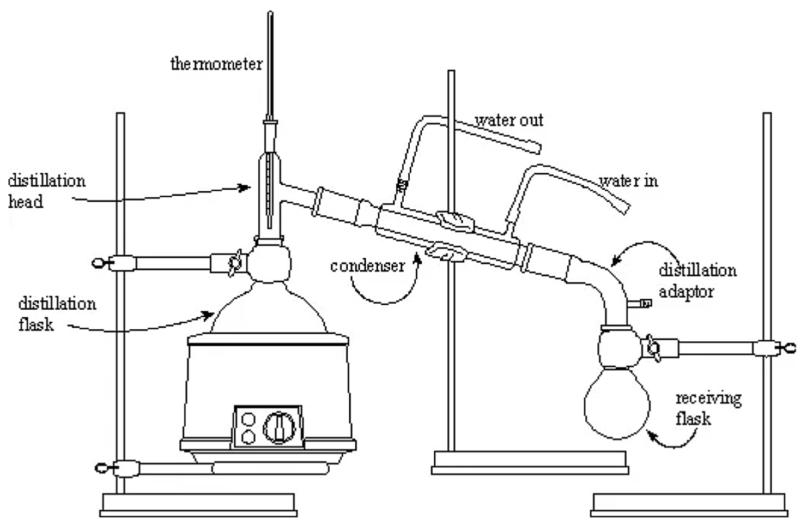


Figure 2. A schematic diagram of the distillation unit, adopted from (Shahriar, 2013)

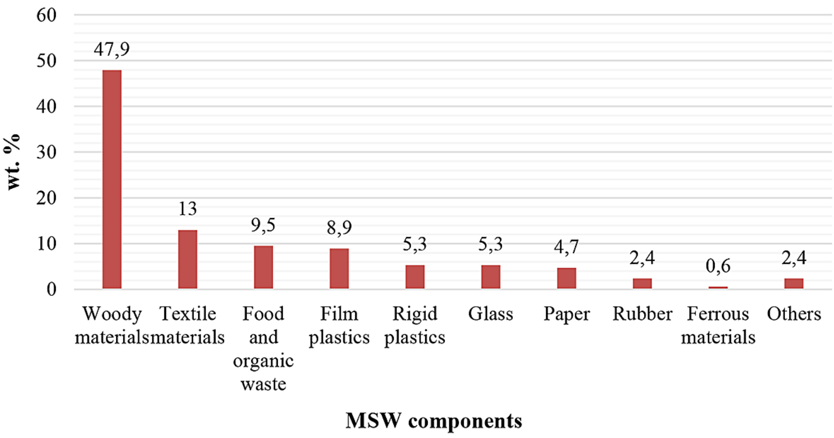


Figure 3. Composition of MSW

which lacks towering building apartments and is more of a suburban region with people living in ground-floor residences. One more reason for the larger percentage of woody materials among the other components of MSW is that the collecting method occurred in January, soon after the fall harvesting, construction, and gardening seasons. It should be noted that the fall season in Uzbekistan begins late. The waste materials collected during these seasons from homes and municipalities were simply mixed with other sorts of wastes and dumped in landfills.

The main reason for the increase in MSW quantity could be population growth and increasing industrialization over the last few years. Only a small percentage of the MSW at the disposal site is composed up of ferrous materials and other wastes. The high proportion of recyclable materials shows that Urta-Chirchik's landfill has a lot of potential for recovery facilities, such as pyrolysis.

Proximate and ultimate analysis

A valuable insight on the characteristics of MSW feedstock were gathered from proximate and ultimate analyses, also the interactions which, feedstock properties have on pyrolysis processes and final pyro-oil product. Proximate, ultimate and HHV tests results of MSW samples are presented in Table 1. The analysis revealed the following composition: carbon (C) at 39.81%, hydrogen (H) at 23.92%, sulfur (S) at 0.27%, nitrogen (N) at 0.84%, and oxygen (O) at 35.14%. These findings help clarify how the properties of MSW affect pyrolysis efficiency and bio-oil quality. The bio-oil's potential for a high calorific value is shown by its high hydrogen and carbon content (Kumar and Strezov, 2021). An excessive amount of oxygen may affect pyrolysis oil quality by binding with hydrocarbon molecules during pyrolysis process and creating oxygenated chemicals. Hence, higher-quality bio-oil is produced from biomass with less oxygen. Furthermore, the low sulfur and nitrogen content in the MSW suggests that the generated pyrolytic bio-oil is less likely to emit toxic gases SO_x and NO_x to the environment (Zheng et al., 2020).

The proximate analysis of the MSW sample revealed the following composition: 13.05% moisture, 51.64% volatile matter, 4.78% fixed carbon, and 30.53% ash. Additionally, the sample exhibited 38.79 MJ·kg^{-1} heating value on a dry basis. These results provide critical information about the thermal behavior and energy

Table 1. Proximate, ultimate, and HHV testing results of MSW (dry matter basis)

Tests	MSW
Proximate analysis (%wt.)	
Moisture content	13.05
Volatile matter	51.64
Ash content	30.53
Fixed carbon	4.78
Ultimate analysis (%wt.)	
C	39.81
H	23.92
S	0.27
*N	0.84
**O	35.14
Higher heating value (HHV, MJ*kg^{-1})	38.79

Note: *N was determined by X-ray fluorescence analysis, and **O by difference.

potential of the MSW during the pyrolysis process. This supports the accuracy of the elemental analysis results by demonstrating a high degree of agreement with the theoretical HHV determined from the Dulong equation. Pyrolysis-oil quality can be impacted by a high water content in biomass since it can cause in a low heating value (Solantausta et al., 2012; Zhuang et al., 2023). Additionally, bio-oil yield during pyrolysis is significantly influenced by the volatile matter of MSW. The volume produced of bio-oil increases with the percentage of volatile matter in biomass. Heat can convert this volatile material into vapor, which condenses to produce pyrolysis-oil (Shrivastava et al., 2021; Adegoke et al., 2021). The presence of ash and fixed carbon in municipal solid waste (MSW) also influences bio-oil production. A higher ash content tends to lower bio-oil yields, though it can enhance the production of biochar (Li et al., 2017). Similarly, a high fixed carbon may also enhance the generation of char yield. Consequently, MSW is appropriate for the pyrolysis process of producing bio-oil due to its moderate ash and low fixed carbon content.

According to the obtained results from proximate and ultimate analyses, it is possible to conclude that MSW has great potential for the pyrolysis-based production of bio-oil by comparing the outcomes of the proximate and final studies of the MSW.

Product yields in pyrolysis: Effect of temperature and time

In this research, a pyrolytic reactor developed by the authors was used to obtain liquid fuels from the pyrolysis of MSW, and practical experiments were conducted. In the experiment, MSW pyrolysis was conducted at 200÷600 °C temperatures ranges. The highest resulting biofuel (38.3%) was observed at the temperature of 430 °C, gas, and bio-char constituted 26.7%, and 35% respectively. A comparative analysis of the experimental results with those of other researchers is presented in Table 2.

Pyrolytic oil, solid char, and gas were the end products of the pyrolysis process. It was discovered that the liquid had a single phase with dark brown-light black color. The results of several studies showed that pyrolysis conditions affected yields of solid char and liquid product from pyrolysis. The temperature of 430 °C and time of 45 minutes produced the highest liquid yield (38.3 wt%). The rise in pyrolytic liquid production is linked to the extended secondary reaction period, which enhances the decomposition of lignin into hydrocarbon compounds (Qureshi et al., 2021). At temperatures under 430 °C, the production of char increased, while the yield of liquid decreased. However, at temperatures above 450 °C, the gas yield was found to be higher while the char and liquid yield were found to be lower. The reduced liquid production at lower temperatures could be due to insufficient temperature rise

Table 2. Product distribution of MSW pyrolysis and its comparison with other results

No.	Temperature, °C	Catalyst	Bio-fuel, %	Gas, %	Bio-coal, %	Reference
1	200–600, highest yield at 430 °C	–	38.3	26.7	35	Present study
2	450–550	–	51.3	37	11.7	Velghe et al., 2011
3	400 (inert gas – nitrogen)	Natural zeolite	15.2	48.2	34.6	Gandidi et al., 2018
4	200–750 (inert gas – nitrogen)	–	21.72	39.91	38.36	Tursunov, 2014

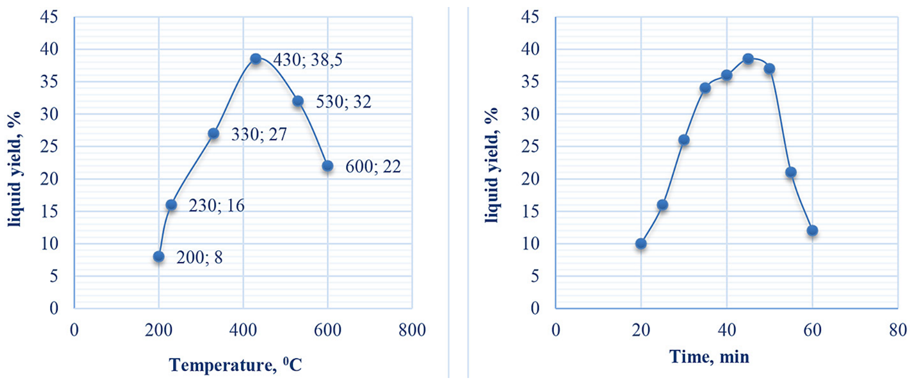


Figure 4. The influence of pyrolysis temperature (a) and time (b) on liquid products

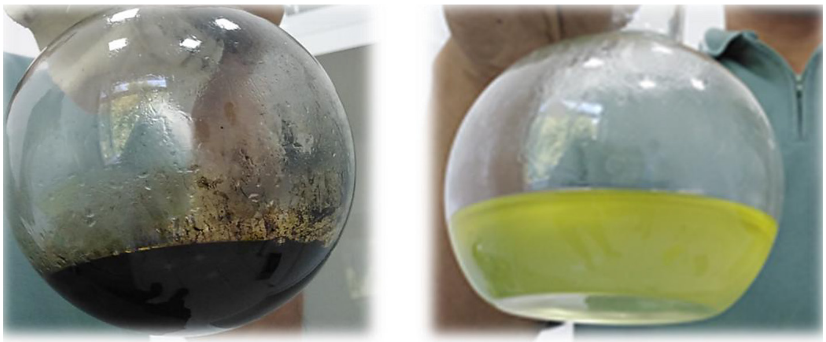
enabling for complete pyrolysis, resulting in less liquid and more solid char. At higher temperatures, however, additional breakdown reactions to lighter gaseous products may occur, resulting in decreased liquid and char yields. Figure 4a depicts the temperature-dependent change in pyrolysis liquid yields.

The product obtained increased with time, however after 45 minutes, the liquid yields did not considerably increase and dropped rapidly after 50 minutes. Figure 4b illustrates the effect of time on pyrolysis liquid yields between 200 and 600 °C.

Distillation results

Researchers have used distillation to enhance the characteristics of the pyrolysis oil produced from MSW. The heavy residue can be separated from the light fractions by distillation (Yang et al., 2024). Following distillation, MSW pyrolytic oil's density and viscosity decreased, and its characteristics resembled those of gasoline and diesel fuel. Light distillation temperature allows for the separation of mid-distillate and heavy fractions, whereas higher temperature increases the volume of distillation (Limayem and Ricke, 2012). The distillation results and the comparative analysis of the energy value of the resulting upgraded pyrolytic oil with other petroleum products are presented in Figure 5 and Table 3, respectively.

As shown in Table 3, the higher heating value (HHV) of the upgraded pyrolytic oil, derived from the distillation of pyrolysis oil produced from municipal solid waste, is 40.6 MJ/kg. This energy value is comparable to that of conventional petroleum products such as gasoline and diesel. This finding suggests that the upgraded



a) *b)*

Figure 5. Pyrolysis oil (a) and the upgraded pyrolytic oil obtained from distillation (b)

Table 3. Distilled pyrolysis oil energy content and its comparison with other fuels

No.	Fuel type	Heating value, MJ/kg	Reference
1	Upgraded pyrolytic oil	40,6	Current study
2	Diesel	43,0	Ghazali et al., 2015
3	Gasoline	46.0	Ghazali et al., 2015

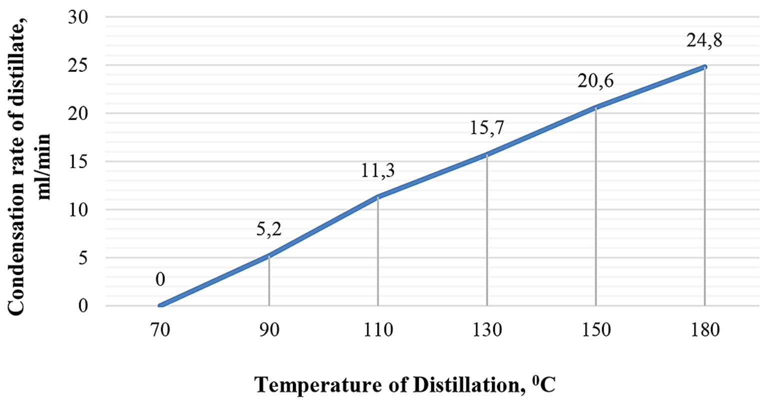


Figure 6. Variation of the condensation rate of distillate over temperature

pyrolytic oil obtained from the experimental process has the potential to serve as a viable alternative to gasoline and diesel.

Figure 6 shows that by increasing the distillation temperature, the overall distillation rate was also raised. For three-four days, the distillate at each distillation temperature remained unchanged and was clear and uniform with no contaminants.

GC-MS of pyrolysis oil distillate

Pyrolysis is a process of thermal decomposition that breaks down lignocellulosic biomass in the absence of oxygen, typically in an inert environment. The basic chemical reaction is a multi-step process that is quite complex. The final products of biomass pyrolysis include gases, charcoal, and bio-oil. Drying the sample is the initial phase, which entails removing moisture and light organic matter including alkaloids, terpenes, and waxes. There are four basic processes in pyrolysis, which are shown in Figure 7.

Cellulose, hemicellulose, and lignin are the primary components of biomass decomposed into smaller compounds like water, tar, and organic matter as the pyrolysis temperature was continuously raised. According to Mishra et al. (2024) and Rahman et al. (2020), depending on the process circumstances, cellulose and hemicellulose broke down to produce carboxylic acids, aldehydes, furans, ketones, and water. The bulk of the tar compounds and phenols were formed by the thermal breakdown of lignin (Fabri et al., 2023; Li et al., 2024). The second stage of the pyrolysis process consists of the secondary thermal decomposition of the primary pyrolysis products, which is affected by the residence time and the temperature at which the liquid and gaseous components are retained in the reactor's heated zone. This stage produces a range of aromatic hydrocarbons, such as polycyclic aromatic hydrocarbons (PAHs), toluene, benzene, xylenes, and styrene (Yaman, 2004). Furthermore, this phase influences the product distribution, resulting in a rise in gaseous product yields accompanied by a reduction in liquid product yields. Secondary processes, such as steam gasification and biochar formation, also play a role, particularly when water is involved in the reactions.

GC/MS is an extremely useful analytical technique for determining the chemical composition of pyrolytic oil. It not only identifies the chemical compounds within the oil but also quantifies their concentrations.

A detailed analysis of the pyrolysis oil's chemical composition was conducted using gas chromatography-mass spectrometry (GC-MS). Figure 8 presents the total ion chromatogram for the pyrolysis oil, organized by carbon numbers, under the specified experimental conditions. The chromatogram illustrates the relative abundances of the compounds as a function of their retention times, providing insights into the distribution and identity of the chemical components in the oil. In Table 4, a list of the various components found in the pyrolysis oil is provided, showing that the liquid product comprises nearly 30 major compounds present in different concentrations. As shown in Table 4, the majority of compounds are alkenes (1-Undecene; Cyclohexene; Styrene; 3-Dodecene; Cyclohexene,

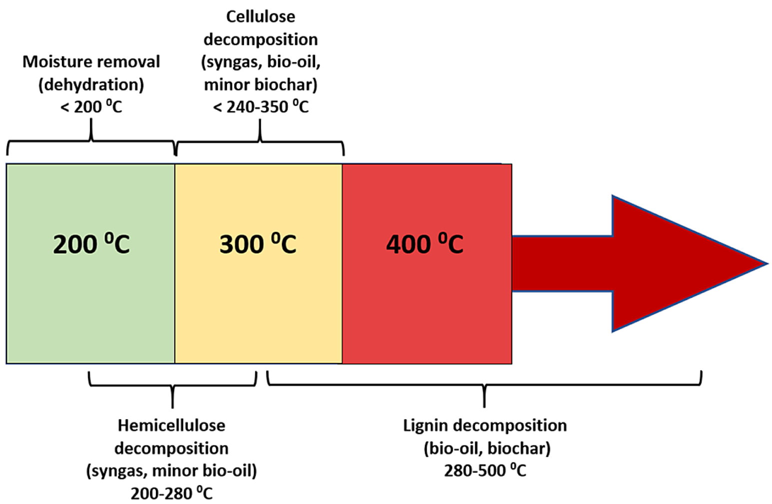


Figure 7. Biomass decomposition behaviour of constituents at different temperature

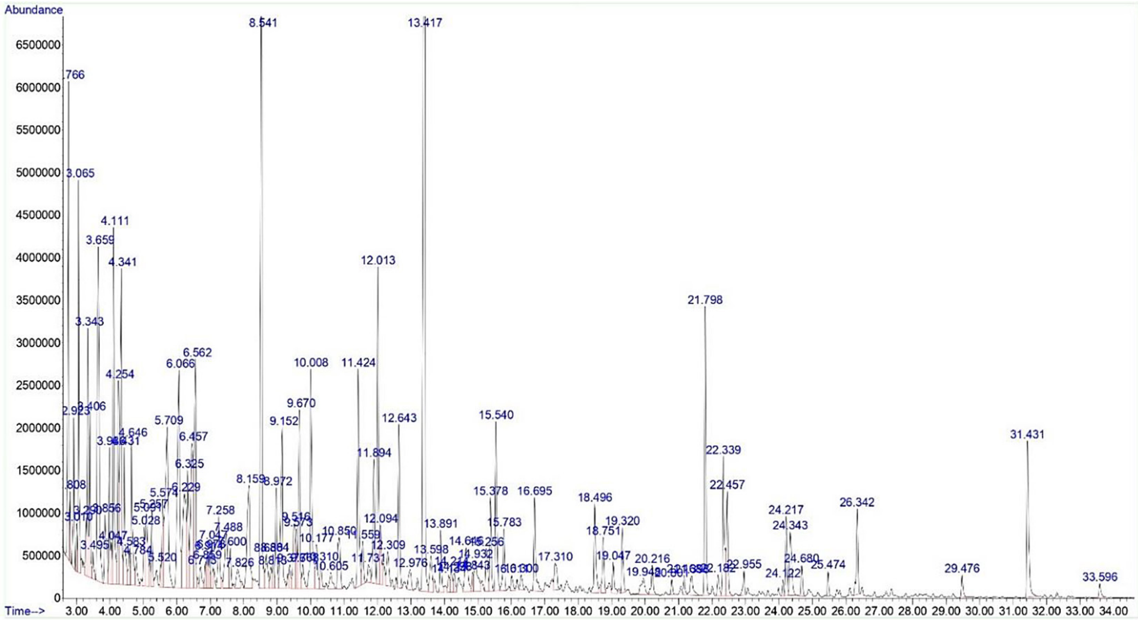
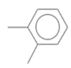
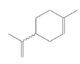
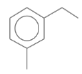
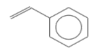
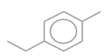
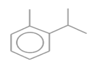
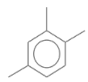
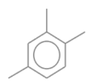
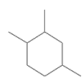
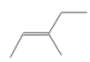
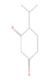
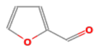
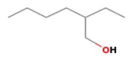
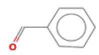
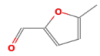
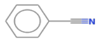
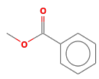
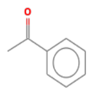
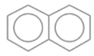
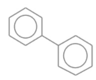
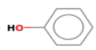
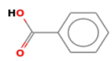


Figure 8. Total ion chromatogram of the pyrolysis oil distillate derived from MSW

Table 4. Major compounds in distillated pyrolysis oil from MSW

Peak No	Retention time, min	Compound	Mol. Weight, g/mol	Formula	Structure	Group*	Area, %
1	2.768	1-Undecene	154.29	$C_{11}H_{22}$		Alkene	2.80
2	3.066	Benzene	106.16	C_8H_{10}		Aromatic hydrocarbon	2.08
3	3.344	Cyclohexene	136.23	$C_{10}H_{16}$		Cyclic alkene	1.36
4	3.661	Benzene, 1-ethyl-3-methyl	120.1916	C_9H_{12}		Aromatic hydrocarbon	3.72
5	4.114	Styrene	104.1491	C_8H_8		Aromatic alkene	2.19
6	4.256	Benzene, 1-ethyl-4-methyl	120.1916	C_9H_{12}		Aromatic hydrocarbon	1.22
7	4.340	3-Dodecene	168.319	$C_{12}H_{24}$		Alkene	2.61
8	4.430	Cymene	134.2182	$C_{10}H_{14}$		Aromatic hydrocarbon	1.06
9	4.644	1,2,4 - Trimethyl	120.1916	C_9H_{12}		Aromatic hydrocarbon	1.20
10	5.711	Benzene, 1,2,4 - Trimethylbenzene	120.1916	C_9H_{12}		Alkylated aromatic hydrocarbon	2.78
11	6.067	Cyclohexene, 1,2,4 - Trimethyl	126.2392	C_9H_{18}		Alkene	2.80
12	6.229	2-Pentene	84.1595	C_6H_{12}		Alkene	1.73

Cont. Table 4

13	6.455	4-Isopropyl – 1. 3 - cyclohexanedione	154.21	$C_9H_{14}O_2$		Cyclic diketone	2.03
14	6.565	1-Tridecene	182.3455	$C_{13}H_{26}$		Alkene	2.01
15	8.156	Tetradecane	198.388	$C_{14}H_{30}$		Alkane	1.66
16	8.538	2 – Furancarboxaldehyde	96.0841	$C_5H_4O_2$		Aldehyde	6.15
17	9.153	1-Terradecene	196.3721	$C_{14}H_{28}$		Alkene	1.70
18	9.670	2 Ethyl Hexanol	130.2279	$C_8H_{18}O$		Alcohol	1.40
19	10.006	Benzaldehyde	106.1219	C_7H_6O		Aldehyde	2.14
20	11.423	2-Furancarboxaldehyde	110.1106	$C_6H_6O_2$		Aldehyde	1.84
21	11.895	1-Tridecene	182.3455	$C_{13}H_{26}$		Alkene	1.18
22	12.012	Benzonitrile	103.1213	C_7H_5N		Nitrile	2.37
23	12.646	Benzoic Acid	136.1479	$C_8H_8O_2$		Carboxylic acid	1.28
24	13.415	Ethanone	120.1485	C_8H_8O		Ketone	9.98
25	15.537	Naphthalene	128.1705	$C_{10}H_8$		Polycyclic aromatic hydrocarbons (pahs)	1.51
26	21.799	Biphenyl	154.2078	$C_{12}H_{10}$		Aromatic hydrocarbon	2.26
27	22.336	Phenol	94.1112	C_6H_6O		Aromatic alcohol	1.38
28	31.431	Benzoic acid	122.1213	$C_7H_6O_2$		Carboxylic acid	1.60

1,2,4 – Trimethyl; 2-Pentene; 1-Tridecene; Tetradecane; 1-Terradecene and 1-Tridecene) and aromatic hydrocarbons (Benzene; Benzene, 1-ethyl-3-methyl; Benzene, 1-ethyl 4-methyl; Cymene; 1,2,4 – Trimethyl; Benzene, 1,2,4 – Trimethylbenzene; Naphthalene and Biphenyl). It can be observed that the most abundant components are ethanone and 2 – furancarboxaldehyde followed by Benzene, 1-ethyl-3-methyl; 1-Undecene; 3-Dodecene; Benzene, 1,2,4 – Trimethylbenzene and Cyclohexene, 1,2,4 – Trimethyl. This may be explained by the breakdown of lignin and hemicellulose. N-containing compounds like C_7H_5N was also recorded due to the decomposition of protein.

It is challenging to clearly distinguish each peak due to the intricacy of oil nature. A semi-quantitative assessment was performed to evaluate the distribution of chemical compounds in the pyrolysis oils by analyzing the relative percentage area of the chromatographic peaks. The results revealed that the oils primarily consist of alcohols, aliphatic hydrocarbons, aromatic hydrocarbons, and cyclic hydrocarbons, which together make up the majority of the chemical composition. These components are crucial raw materials used in the petrochemical industry and synthesis, where separation of such compounds may produce value-add chemicals and high-quality bio-oils. This implied that the pyrolytic byproducts of MSW had a significant energy value and thus the potential to be harnessed.

CONCLUSIONS

This study involved the slow pyrolysis of municipal solid waste (MSW) in a fixed-bed reactor, operating at temperatures between 200 and 600 °C with a residence time of 5 minutes. Multiple analytical techniques, including elemental analysis, physicochemical property assessment, and GC–MS, were employed to characterize both the MSW as a raw material and the pyrolysis oil produced. MSW sample exhibited an acceptable moisture level and an elevated carbon content, suggesting its suitability for the pyrolysis process. A maximum pyrolysis oil yield of 38.3% was obtained at a temperature of 430 °C and a residence time of 45 minutes. An Agilent 7890A GC-MS analyzer was utilized to thoroughly investigate the chemical composition of hydrocarbon oils produced from the pyrolysis of MSW at temperatures ranging from 200 to 600 °C. The GC–MS analysis revealed that the pyrolysis oil consists of 28 major components, with alkenes and aromatic hydrocarbons being the predominant compounds. These findings highlight the aromatic and carbon-rich nature of the pyrolysis oil generated in this study. Pyrolysis of MSW could be a viable substitute source of chemical compounds and liquid hydrocarbon fuels in the future. To find ways to use the liquid as fuel for boilers, internal combustion engines, or as value-added chemicals, more characterization research on the liquid products of pyrolysis from the solid wastes should be carried out.

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