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RESEARCH ARTICLE

Experimental mixed plastic waste pyrolysis in Iraq: Polymer composition, catalytic parameters, simulation, and Techno-Economic assessment

Ahmed H. Nahi*, Ali A. Jazie

Department of Chemical Engineering, Faculty of Engineering, University of Al-Qadisiyah, Al-Qadisiyah, Al-Diwaniyah, Iraq

***Corresponding author:** Ahmed H. Nahi, ahmedhassannhi878zwfqy@gmail.com

ABSTRACT

The accumulation of mixed Waste plastic represents an environmental challenge in Iraq. This study investigates the catalytic Pyrolysis of combined waste plastic composed of 30% LDPE, 30% HDPE, 15% PP, 20% PET, and 5% PS. Pyrolysis experiments were conducted using 250 g of Waste made of plastic per experiment at the temperature ranges from 400°C to 500°C under catalyst conditions. A CaO catalyst derived from eggshell waste was prepared and compared with a zeolite catalyst. The impact of temperature, reaction time, and catalyst type were evaluated. The optimal conditions resulted in the highest oil yield of 83.6 wt.% at 500°C, a reaction time of 90 minutes, and a 10% catalyst concentration. Experiments with individual plastic types showed the highest oil yields: 70.8% for LDPE using CaO, 63.2% for HDPE using CaO, 76% for PP without a catalyst, and 82% for PS without a catalyst. the pyrolysis oil was characterized by its density, viscosity, sulphur content, and fuel properties. GC-MS The analysis demonstrated the existence of valuable hydrocarbon compounds, particularly alkenes, alkanes, and aromatic compounds. The composition of the oil obtained from these experiments was incorporated into the Aspen Plus program for developing a 1000-ton/day industrial model. The techno-economic evaluation indicated a plant cost of approximately $25.88 million, with a payback period of 0.9 years and an income on investment of 111.4%, based on the assumed Iraqi market. This study provides an integrated pathway from catalytic pyrolysis experiments to industrial design and economic evaluation for sustainable Waste plastic management in Iraq.

Keywords: mixed plastic waste; catalytic pyrolysis; calcium oxide catalyst; pyrolysis oil characterization; techno-economic assessment

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1. Introduction

The environment is exposed to various sources of pollutants, produced in different ways Solid waste, particularly Waste made of plastic, is one of the most important causes of wide-ranging harm to ecosystems and human health[1]. The low cost of producing plastics has led to their fast production, making them an essential part of modern life and contributing to their widespread use. Furthermore, their light weight, strength, and versatility in various industrial, commercial[2].The global quantity of plastic waste generated has increased significantly as a result of domestic and industrial applications[3]. In the 21st century, the proliferation of plastic waste has emerged as a significant environmental issue, as it is disposed of in large quantities in landfills, open dumps, rivers, and oceans, causing widespread damage to aquatic ecosystems. Plastic waste can

decompose into fine particles known as "micro plastics" in water, and it can take hundreds of years to break down[4] . The OECD publication, titled Global Plastics Outlook: Policy Scenarios to 2060[5] , The data suggests that worldwide plastic waste would escalate significantly, projected to grow from 353 million tons in 2019 to around 1,014 million tons by 2060, see **Table 1** for details. The most common types of plastic waste include: water and soft drink bottles made of polyethylene terephthalate (PET), detergent and milk containers made of high-density polyethylene (HDPE), pipes and wires made of polyvinyl chloride (PVC), plastic bags and packaging made of low-density polyethylene (LDPE), food containers and lids made of polypropylene (PP), and foam cups and packaging made of polystyrene (PS), Numerous additional varieties are present, although these are regarded as the most important[6] . The administration and disposal of plastic mixed waste pose a significant challenge in numerous developing nations. International studies indicate that the issue of mixed plastic waste extends beyond merely the scale of global production, as developing countries are the most affected by this problem due to weak infrastructure for managing mixed Waste made of plastic and the absence of effective sorting and recycling systems. Therefore, these countries resort to burning and burying this Waste made of plastic, which exacerbates environmental pollution in the soil, water, and air[7] and[8] . Iraq is a clear example of this problem, as environmental reports indicate that solid waste management is still incomplete and relies mainly on burying and burning as the primary methods for disposing of Waste made of plastic[9] .The latest official data from the Iraqi Ministry of Environment, published by the Iraqi News Agency (INA), indicates that Iraq produces approximately 16,000 tons of plastic waste daily, That is approximately 5.84 million tons per year, reflecting a significant increase in plastic consumption This is a clear indicator of the environmental pressure resulting from the growing reliance on plastic products (Ministry of Environment, 2026). Due to the complex composition of these mixed Waste made of plastics, there is an urgent need to develop effective technologies to treat this waste and reduce their environmental impact Waste made of plastic treatment technologies are classified into two main types: mechanical recycling[10], and chemical or thermal pyrolysis recycling this[11] . In many countries, mechanical decomposition is the most common method, as it mainly depends on the presence of sorted and pure Waste made of plastic of one type. This process requires sorting, washing, and cutting the waste, so this process is costly, and its effectiveness decreases with mixed Waste made of plastic in countries that lack the infrastructure for the sorting process[12] , in Iraq, where the waste is a mixture of complex polymers of LDPE, HDPE, PP, PS, PET, and PVC and is mixed. Therefore, using and finding a promising method for disposing of this mixed plastic waste is necessary. Pyrolysis of plastic waste is a promising technology, as it relies on breaking down polymer chains in the absence of oxygen and converting them into valuable products such as hydrocarbon pyrolysis oil and combustible gases This method does not require sorting plastic waste, making it more suitable for countries with weak sorting and recycling systems[13]. Researchers Maddalena Lagiza, Silvia Fiori, and Franco Perotti performed a comprehensive review of the thermal transformation of plastic waste into fuels and chemicals, examining 195 scholarly articles that focused on raw materials, operational parameters, reactors, products, catalysts, and both environmental and economic viability. Their assessment determined that pyrolysis is a proficient method for transforming plastic waste into valuable products suitable for use as fuels and chemicals[14]. Numerous investigations have been conducted on plastic waste. In this study[15] a mix of plastic waste made up of polystyrene (PS), polyamide (PA), polyethylene terephthalate (PET), polypropylene (PP), and ethylene vinyl acetate (EVA) was tested at 500 °C in a batch reactor to see what effect it had on the products of thermal pyrolysis. The results showed that adding more PP and PE increased the percentage of oil, adding more PET increased the percentage of char and decreased the quality of the oil, and adding more PS increased the quality of the oil and decreased its viscosity. In another study. It was heated to between 340 and 440 °C and used with a mix of plastic waste. It was found that 425 degrees Celsius was the best temperature. At this temperature, the oil content was largest, at about 76-78%. This was followed by gases that couldn't be condensed and less

solid residue. The amount of energy in the oil was about 42.5 MJ/kg. This work also used catalytic pyrolysis[16] . Demonstrated a rise in oil output relative to traditional pyrolysis, a reduction in coal composition, and an enhancement in the calorific value of the oil for a blend of PP, PS, LDPE, and HDPE utilizing natural Zeolite. Moreover, simulation software was employed in the management of plastic waste. In this study[17]. The researchers used Aspen HYSYS v11 to design a full pyrolysis plant for a mix of plastic waste that was 45% PP, 8% PS, 1% PMMA, and 1% PVC. In this study, they thot that the result would be split into 70% oil, 20% gas, and 10% carbon. In a different study[18]. Researchers used the Aspen Plus program to find out how temperature changed a mix of plastics that included PE, LDPE, PS, and other plastics. The researchers raised the temperature from 350°C to 550°C and found that PS oil was 89% broken down at 450°C, PE oil was 85% broken down at 500°C, 60% oil from the plastic mixture was broken down, and 83% oil from LDPE was broken down. Therefore, this study is based on the creation of an integrated method that starts with lab experiments and ends with the design of an industrial plant in Iraq that will process plastic waste. Unlike other studies that only looked at one type of plastic or the process's theoretical performance, this one included real-life experiment, product analysis, simulations using Aspen Plus, and an economic analysis. Five different kinds of plastic waste were used, and some of them were studied on their own. A CaO catalyst was made locally from used eggshells[19] and was put up against a zeolite catalyst. Researchers looked into how temperature, catalyst type, and reaction time affect the amount and make-up of oil. A real GC-MS test was used to find the main hydrocarbon compounds, which were then added
to the Aspen Plus model. This made sure that the simulation was based on real experimental data and not on theories that had already been written down. After that, the model was used to plan a plant that could handle 1000 tons per day and to do a full cost analysis for an area like Iraq. This study gives a framework that connects experiments in the lab, use in industry, and an analysis of the cost-effectiveness of processing Iraqi plastic waste.

Table 1. OECD forecast for global plastic use.

Indicator	2019(Mt)	2060 Baseline (Mt)	Increase(Mt)	Increase%	rowth factor
Global Plastic use	460	1231	771	167.60%	2.68
Waste made of plastic	353	1014	661	187.30%	2.87
Mismanaged Waste made of stic	79	153	74	93.70%	1.94
Plastic leakage to environment	22	44	22	100%	2.0

2. Materials and methods

2.1. Feedstock collection and preparation

In this research, five types of Waste plastic were used: HDPE, LDPE, PP, PS, and PET, PVC was not included in the mixed plastic feedstock due to its potential release of corrosive HCl during thermal pyrolysis, which may cause corrosion problems in the reactor system and affect the quality of pyrolysis products[20]. These wastes were collected from various waste sources and manually sorted according to polymer type. They were then washed to remove contaminants such as dirt, dried, and shredded into small pieces ranging from 5 mm to 10 mm to ensure homogeneous thermal pyrolysis. Each type of waste was analyzed using FTIR spectroscopy to determine its chemical structure and functional groups. **Figure1** illustrates the five types of Waste made of plastic used as well as mixed plastic.

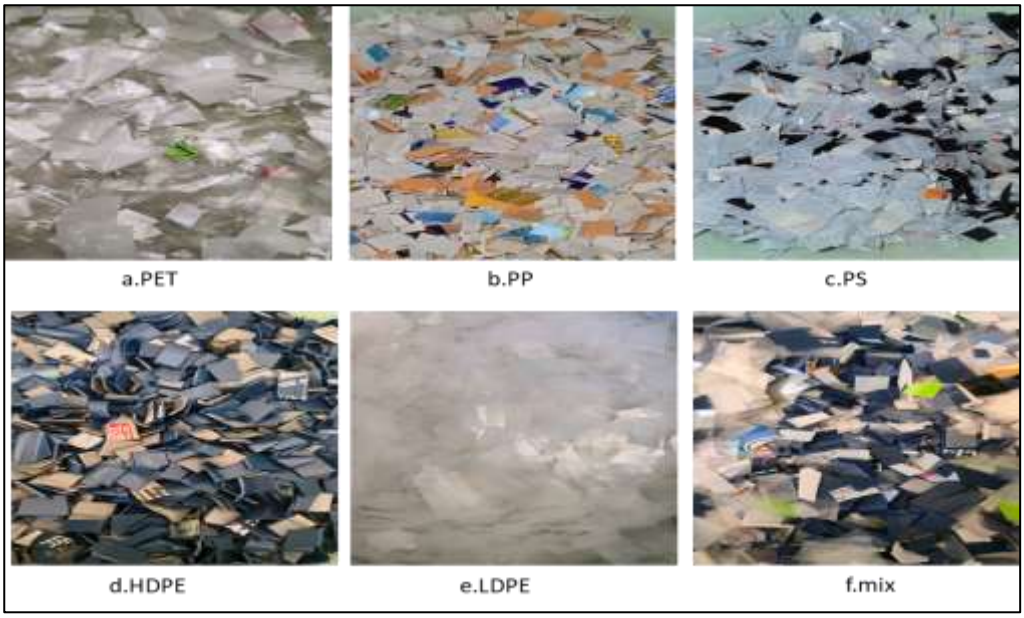


Figure 1. Illustrates the different types of plastic: a-PET, b-PP, c-PS, d-HDPE, e-LDPE, and f-mix.

2.2. Catalyst characterization and preparation

2.2.1. Preparation of calcium oxides (CaO)

A CaO catalyst was prepared from chicken eggshells as a low-cost alternative bio-source. The eggshells were collected and thoroughly washed with water to remove organic residues and surface pollutants. The shells were then dried until all moisture was removed **Figure 2** shows the preparation process. After that, the shells were ground using a laboratory mill to obtain a fine powder. The powder was then sieved using a 150µm sieve to ensure particle size homogeneity and improve calcination efficiency. The calcination process was carried out inside a thermal furnace at a temperature of 900°C for two hours. During this process, the calcium carbonate ($CaCO_3$) present in the eggshells decomposes into CaO, releasing CO_2 gas, according to the following equation

$$CaCO_3(s) \xrightarrow{\Delta} CaO(s) + CO_2(g) \quad (1)$$

After that, the catalyst was cooled and stored in a sealed container. The material was characterized before and after the calcination process using FTIR infrared spectroscopy to verify the structural transformation from $CaCO_3$ to CaO.

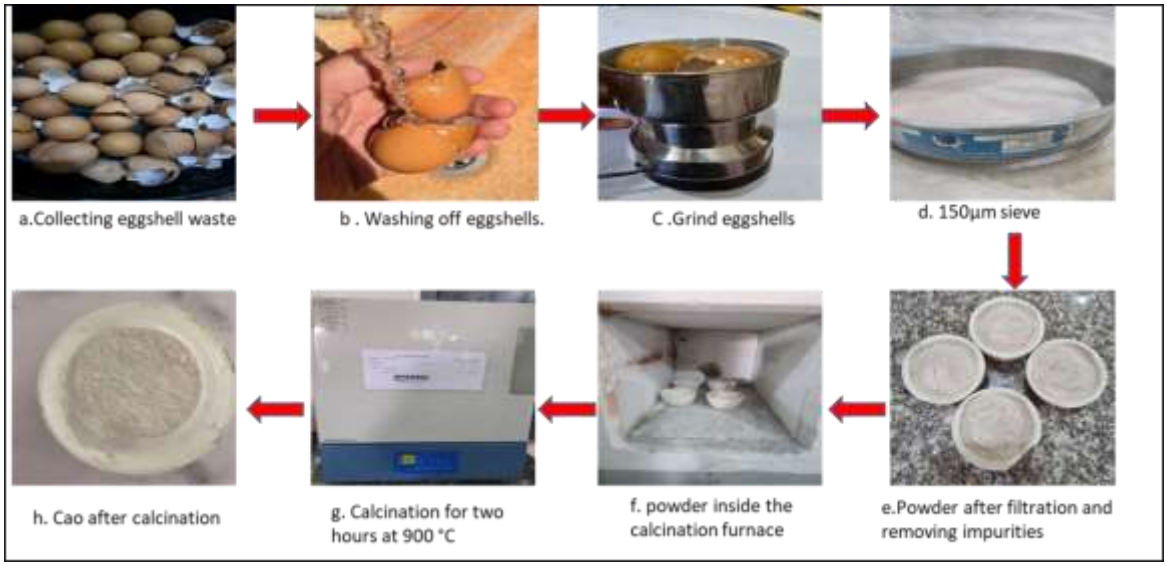


Figure 2. Illustrates the process of preparing the CaO catalyst.

2.2.2. Zeolite preparation of type A

Type A zeolite (13X molecular sieve) was used as a catalyst in the pyrolysis of Waste made of plastic. The commercial 13X molecular sieve used as a catalyst in this study was supplied by Hebei Runhuabang New Material Technology Co., Ltd., China. According to the manufacturer's specifications, the zeolite has a purity of 99% and comes in pellet form with an apparent density of 0.66 g/cm³ and a water adsorption capacity of 21.5%. Its chemical formula is $Na_2O{\cdot}Al_2O_32SiO_2{\cdot}9/21H_2O$, and its chemical registration number is CAS No. 63231-69-6. It was used as a catalyst and adsorbent due to its structural and porous properties, can aid in improving the efficacy of the pyrolysis procedure. **Figure 3** depicts the procedure for zeolite synthesis Before it was used in pyrolysis experiments, the catalyst was further examined with (FTIR) to verify the zeolite's structural composition and functional groups.

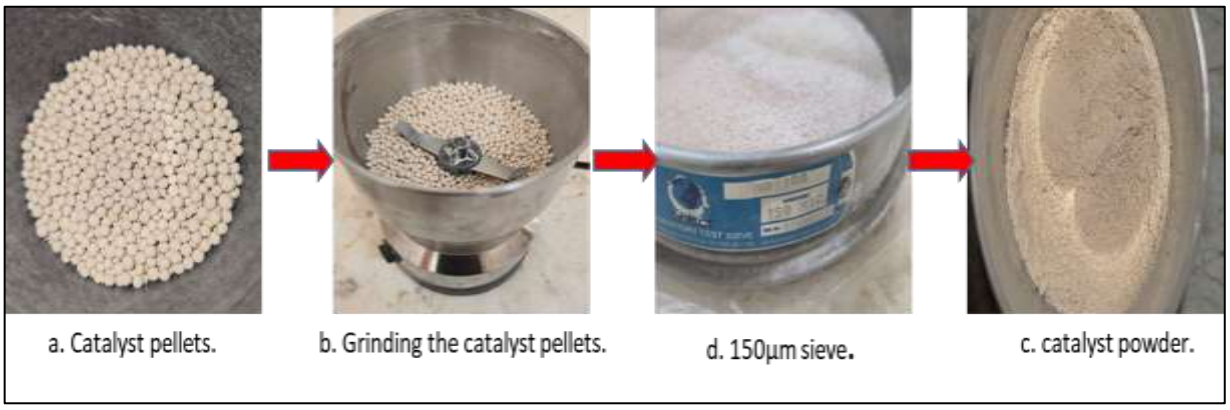


Figure 3. Illustrates the process of converting the zeolite catalyst from pellets to powder for use inside the reactor.

2.3. Pyrolysis reactor system

A batch-type pyrolysis reactor made of 4 mm thick stainless steel with an approximate capacity of 10 liters, a diameter of 20 cm, and a height of 30 cm was used. The reactor was designed to operate under oxygen-free conditions, and to improve the process of pyrolysis, the system was provided with an external heating source that uses LPG fuel to reach the required temperatures gradually and in a controlled manner. A nitrogen gas inlet was also added to maintain an inert environment and prevent oxidation reactions during operation. The vapors generated from the pyrolysis of the plastic mixture are transferred to the condensation unit, where the condensable portion is converted into liquid oil, while the non-condensable gases are released into the atmosphere. The solid materials remain inside the reactor after the process is completed until they are extracted.

2.4. Pyrolysis experimental procedure

A sequence of pyrolysis experiments was conducted utilizing a batch reactor for investigation. The Impact of Temperature, catalyst variation, and reaction duration on the pyrolysis outcomes of plastic waste. **Figure 4** shows stages of thermal pyrolysis, from the preparation of the Waste made of plastic mixture to the decomposition products. And, **Figure 5** shows the pyrolysis system used in this study. The study included 10 main experiments using a mixture of Waste made of plastic at a constant weight of 250 grams per experiment. The mixture consisted of 30% LDPE, 30% HDPE, 15% PP, 20% PET, and 5% PS, as detailed in **Table 2**, which outlines the experimental design and operating conditions for each case. In addition to the mixture experiments, individual experiments were performed for PS, PP, HDPE, and LDPE to evaluate the effect of polymer type on pyrolysis behavior. These experiments were done under constant temperature conditions, applying both catalyst-free (thermal pyrolysis) and CaO and zeolite catalysts to compare the catalyst performance for each polymer type. CaO was used at 5% and 10% loadings, while zeolite was used at 10% in

the comparison experiments. All experiments were performed at operating temperatures between 400 and 500 °C and reaction times between 60 and 90 minutes, according to the experimental design shown in **Table 2**. Before the start of each experiment, N_2 gas was introduced into the reactor at a low pressure of 0.1 bar to ensure an inert, oxygen-free environment. An external heating system supplied by LPG was used as the heat source, and the temperature was gradually increased until the required operating temperature for each experiment was reached. During the thermal process of pyrolysis, the polymer chains break down into hydrocarbon vapors, which are passed to the condenser using water as a cooling liquid. The condensible vapor is converted into liquid oil, which is collected in a specific vessel. The non-condensable gases are safely released into the atmosphere, while the solid residue remains inside the reactor. After the end of each experiment, the system is cooled to room temperature befo re opening. The weight of the oil and solids is then collected immediately, while the gas ratio is estimated using mass balance.

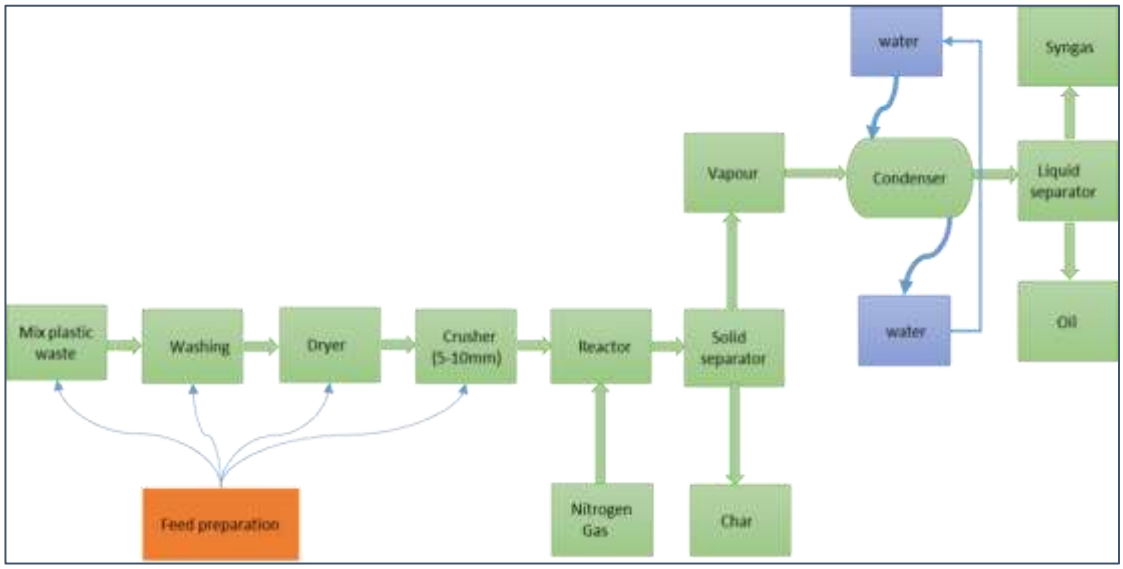


Figure 4. Process flow diagram for the treatment of waste plastic into pyrolysis products.

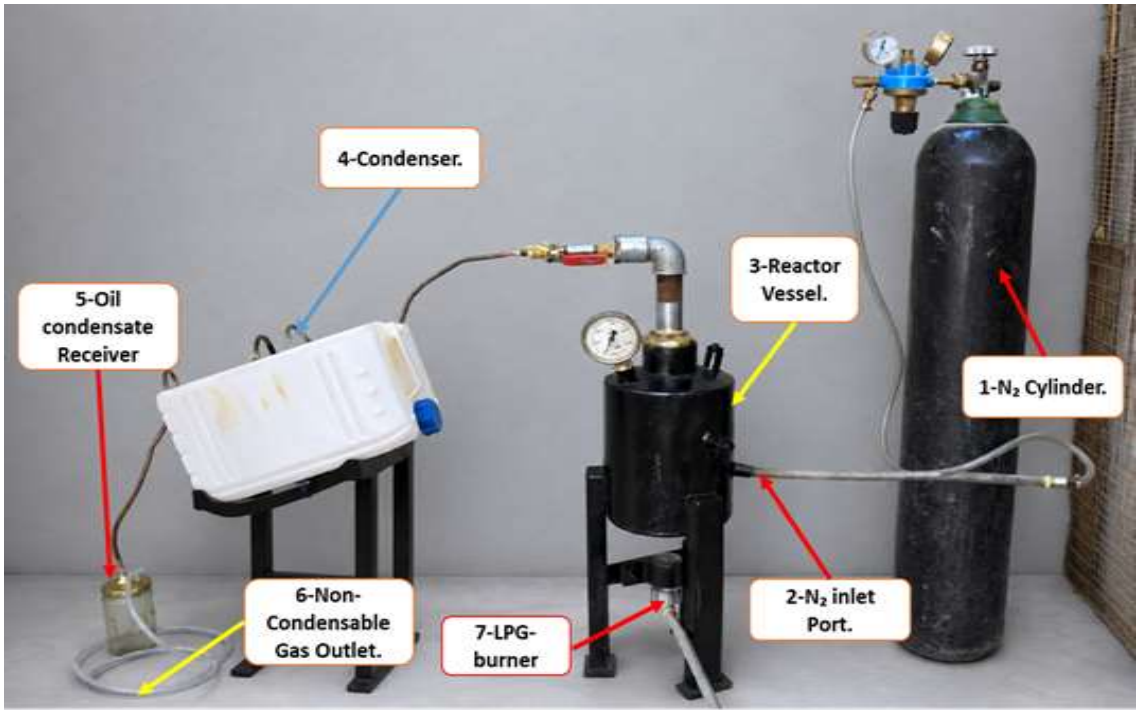


Figure 5. Laboratory-scale waste plastic pyrolysis system used in this study.

Table 2. Experimental design for thermal and catalytic pyrolysis of mixed and individual waste plastic.

Experiment number	Temperature (C°)	Time (min)	Catalyst (%)
1(MPW/CaO)	400	60	10
2(MPW/CaO)	450	75	5
3(MPW/CaO)	400	60	0
4(MPW/CaO)	500	60	10
5(MPW/CaO)	400	90	0
6(MPW/CaO)	500	60	0
7(MPW/CaO)	500	90	0
8(MPW/CaO)	450	75	5
9(MPW/CaO)	400	90	10
10(MPW/CaO)	500	90	10
EXP Zeolite MIX	450	60	10
EXP Zeolite MIX	450	90	10
HDPE without a catalyst	450	60	0
HDPE with (CaO)	450	60	10
HDPE with (Zeolite)	450	60	10
LDPE without a catalyst	450	60	0
LDPE with (CaO)	450	60	10
LDPE with (Zeolite)	450	60	10
PS without a catalyst	450	60	0
PS with (CaO)	450	60	10
PP without a catalyst	450	60	0
PP with (CaO)	450	60	10

2.5. Product recovery and yield calculation

After each pyrolysis experiment, the reactor was cooled to room temperature before product recovery. The liquid condensate from the condenser was collected and weighed as pyrolysis oil. The remaining solid residue inside the reactor was collected and weighed as solid carbon. The non-condensable gas was calculated using a mass balance between the input feedstock and the recovered oil and carbon.

Product yields were determined utilizing the subsequent formulae.

$$Y_{oil}\ (\%) = \frac{m_{oil}}{m_{feed}} \times 100 \quad (2)$$

$$Y_{char}\ (\%) = \frac{m_{char}}{m_{feed}} \times 100 \quad (3)$$

$$Y_{gas}\ (\%) = 100 - Y_{oil} - Y_{char} \quad (4)$$

Where $m_{oil,}$ m_{char} and m_{feed} represent the masses of liquid oil, solid residue and initial plastic feedstock, respectively.

2.6. Chemical and physical characterization of pyrolysis oil

A Chemical and Physical characterization was performed on pyrolysis oil produced from the pyrolysis of Waste made of plastic to evaluate its properties as a possible liquid fuel. The characterization included

measuring the density, kinematic viscosity, API gravity, and flash point of the oil under various operating conditions, including plastic mixture oil and individual polymer oils. The oil density was measured to determine the mass-to-volume ratio and assess the nature of the oil resulting from the process of pyrolysis. Kinematic viscosity was also measured to determine the oil's flow resistance and its suitability for transport and use in fuel applications. The API was calculated based on the density value according to the standard relationship used to evaluate the quality and lightness of petroleum products. In addition, the flash point was determined to evaluate the degree of oil safety during storage and handling and to determine its thermal behaviour compared to conventional fuels. All measurements were carried out using representative oil samples collected after the completion of the thermal pyrolysis experiments and under constant measurement conditions to ensure the accuracy and comparability of the results. The physical properties of the pyrolysis oils were determined using specialized analytical instruments. The kinematic viscosity measurements were carried out using a Kinematic Viscosity Bath (Koehler Instrument Company, Inc., USA, KV3000 Series) under controlled temperature conditions. The flash point measurements were performed using a Pensky–Martens closed-cup flash point tester (Koehler Instrument Company, Inc., USA), as shown in **Figure 12A**, and the corresponding flash point temperatures were recorded in °C. Density, specific gravity, and API gravity measurements were conducted under controlled conditions using calibrated instruments. All measurements were performed according to the applicable standard procedures, and the obtained values were used for evaluating the fuel characteristics of the pyrolysis oils.

2.7. GC-MS analysis of pyrolysis oil

The chemical composition of thermal pyrolysis oils derived from a blend of plastic waste and individual polymers was analyzed by gas chromatography-mass spectrometry (GC-MS) to ascertain the primary hydrocarbon constituents and to investigate the influence of feedstock type and catalyst on the oil's composition. Before the analysis, the oil samples were prepared by diluting them with n-hexane solvent of chromatographic purity to obtain a solution suitable for injection into the device. A dilution ratio of 1:50 (v/v) was selected, where one part of the thermal pyrolysis oil was mixed with 50 parts of the hexane solvent to obtain a suitable concentration for analysis and to improve the separation process within the chromatographic column. The examination was conducted with a Shimadzu GC-MS-QP2020 apparatus, which includes a GC-2010 Plus gas chromatography system and an AOC-20i automatic injection device. A 30-meter Rxi-5Sil MS (Restek) capillary column featuring an internal diameter of 0.25 mm and a fixed layer thickness of 1-micrometer was employed, utilizing a stationary phase composed of 5% diphenyl and 95% dimethyl polysiloxane Figure 6 shows the GC-MS device. Helium (He) gas served as a carrier gas to convey the elements of the vaporized sample thru the capillary column to the mass spectrometer, where the compounds are segregated according to their chemical and physical characteristics prior to detection and analysis. The chemical substances were recognized by contrasting the obtained mass spectra with the NIST Mass Spectral Library database. All oil specimens derived from the plastic amalgamation, together with oils from PS, PP, HDPE, and LDPE, were examined to ascertain the distribution of hydrocarbon constituents and to assess the influence of polymer classification and catalytic processing on the quality of the resultant oil.



Figure 6. Shows the GC-MS device used in the chemical analysis of thermal pyrolysis oil.

2.8. Aspen plus simulation

An industrial simulation model was developed using Aspen Plus V10 software to evaluate the process of converting mixed Waste made of plastic into liquid products useful as fuel. **Figure 7** shows the process flow diagram within Aspen Plus software. The Waste plastic mixture was fed at a rate of 1000 tons per day of Waste, equivalent to a feed rate of 41,667 kg per hour. The waste entered the drying unit at a pressure of 1 bar to remove the remaining moisture before the thermal process of pyrolysis. Nitrogen gas served as an inert medium at a flow rate of 1000 kg per hour, maintained at a temperature of 132°C and a pressure of 1 bar, to eliminate moisture and provide an oxygen-free atmosphere within the reactor. Following the desiccation phase, the plastic waste is introduced into the pyrolysis reactor, which was simulated using the RYield Reactor model at a temperature of 450°C and a pressure of 1 bar. The allocation of products in the simulation model was established according to the experimental findings derived from laboratory pyrolysis experiments. The chemical composition of the pyrolysis oil was introduced into Aspen Plus, informed by the findings of actual GC-MS analysis of samples obtained experimentally. The primary hydrocarbon compounds discovered from the investigation were chosen and incorporated as elements in the model. Upon the decomposition of plastic waste within the reactor, three by products are produced: liquid thermal oil, fumes, and solid residues. The solids are distinguished with the use of a separator. The vapours generated by the reactor flow into a condensing machine functioning at 12°C to transform the condensable vapours into liquid oil. The non-condensable gasses are subsequently isolated utilizing a separator 2, while the resultant oil is resulting in a collection tank. A simulation model was used to evaluate the process's performance at an industrial scale and compare the system's behaviour with experimental results. This contributes to studying the feasibility of applying thermal decomposition technology to treat large quantities of Waste plastic.

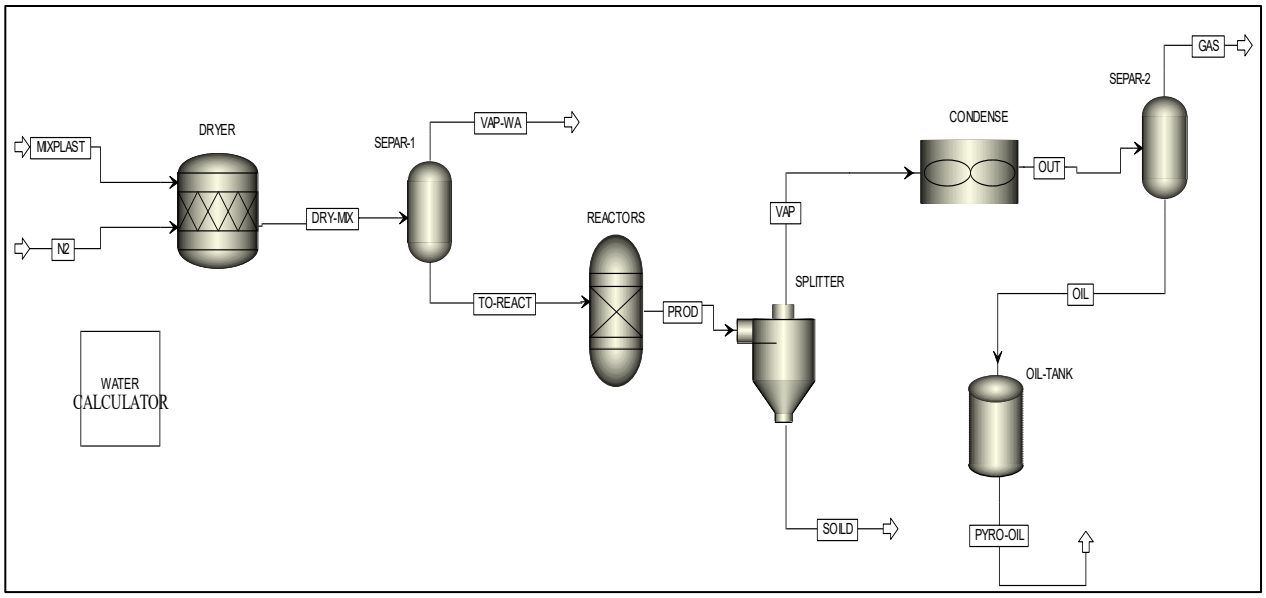


Figure 7. Aspen Plus simulation flow sheet of the proposed mixed waste plastic process of pyrolysis based on experimental GC-MS data.

2.9. Techno-economic analysis

The techno-economic analysis of the thermal process of pyrolysis of Waste plastic was done using the simulation results generated by the Aspen Plus software and the Aspen Process Economic Analyzer (APEA) tool, to estimate the economic requirements of the proposed plant with a processing capacity of 1000 tons per day of mixed Waste made of plastic. The economic evaluation was based on data from the main equipment used in the process flowchart, including the drying unit, pyrolysis reactor, condenser, separation units, and oil collection tank. APEA software was used to determine equipment costs, installation costs, and the total capital cost of the plant, based on equipment size and operating conditions. The project's capital cost (CAPEX) was calculated based on equipment purchase costs, installation costs, and indirect costs associated with setting up the plant. Annual operating costs (OPEX) were estimated based on process operating requirements, including energy, utilities, workers, maintenance, and general expenses. The economic returns of the process were assessed based on the products generated from pyrolysis. Pyrolysis oil produced from the process was considered a primary marketable product, as it can be sold in the market as an alternative fuel or industrial raw material. Its economic return was assessed based on market prices for similar products. The non-condensable gas produced from the process of pyrolysis was considered an internal energy source due to its combustible hydrocarbon content. It can be used as fuel to provide a portion of the heat energy required for the reactor and heating units, thus reducing external energy consumption and operating costs. The economic indicators for the proposed factory were calculated using the following equations.

$$CAPEX = C_{Equipment} + C_{Installation} + C_{Indirect} \quad (5)$$

$$OPEX = C_{Utility} + C_{workers} + C_{Maintenance} + C_{Raw\ Material} + C_{Other} \quad (6)$$

$$Annual\ Production = Annual\ Feed \times Product\ Yield \quad (7)$$

$$Adjusted\ CAPEX = CAPEX(Aspen) \times Correction\ Factor \quad (8)$$

$$Plastic\ Preparation\ Cost = Annual\ Feed \times Preparation\ Cost \quad (9)$$

$$Annual\ Revenue = (Oil\ Production \times Oil\ Price) + (Char\ Production \times Char\ Price) \quad (10)$$

$$Net\ Profit = Annual\ Revenue - OPEX \quad (11)$$

$$Payback\ Period = Adjusted\ CAPEX / Net\ Profit \quad (12)$$

$$ROI = (Net\ Profit/Adjusted\ CAPEX) \times 100 \quad (13)$$

3. Results and discussion

3.1. Characterization of feedstock and catalyst materials

3.1.1. FTIR characterization of Waste made of plastic feedstock

FTIR analysis was used to characterize the components of Waste plastic used as a raw material in the process of pyrolysis, which included PP, PS, PET, HDPE, and LDPE. The FTIR spectrum shows the presence of characteristic bands for each type of polymer, proving the chemical composition of the raw material before the process of pyrolysis. **Figure 8** shows the FTIR spectra of the five polymers.

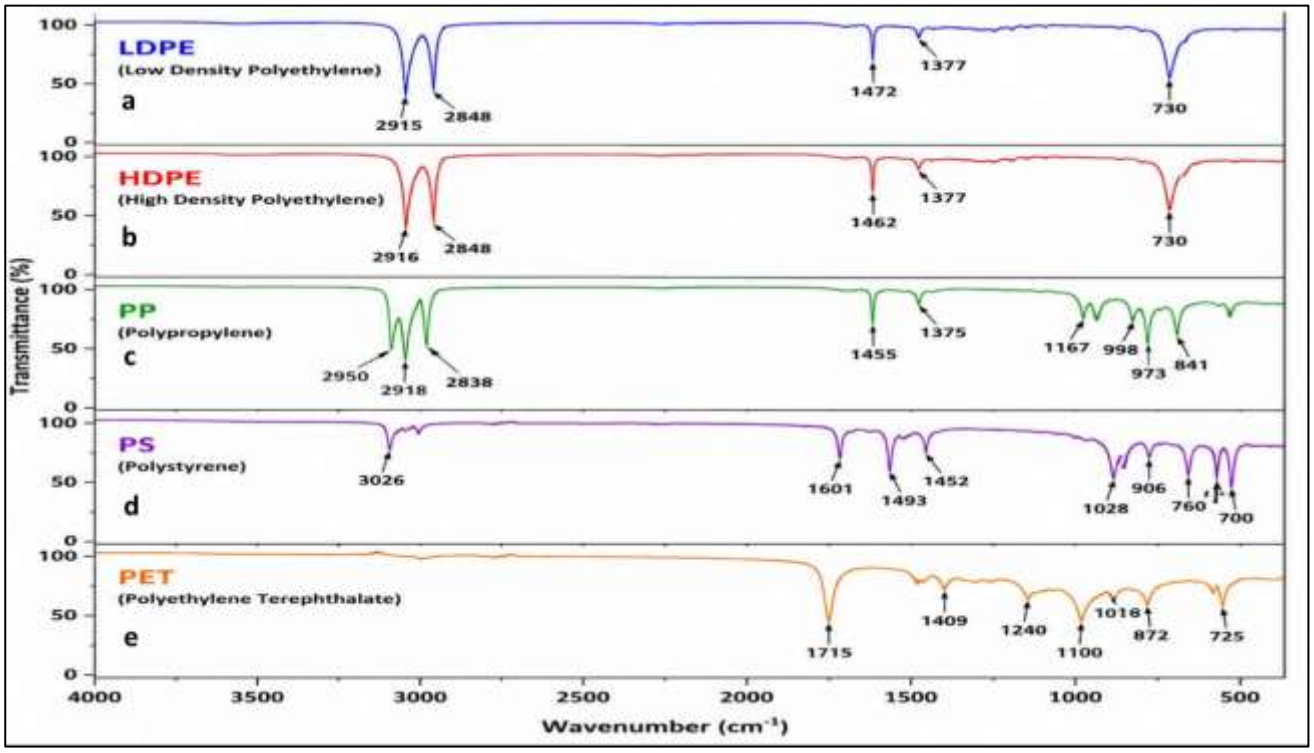


Figure 8. FTIR spectra of (a-LDPE) and (b-HDPE) and (c-PP) and (d-PS) (e-PET) waste made of plastic feedstock.

The spectra of HDPE and LDPE showed absorption peaks **Figure 8** at approximately 2915 and 2848 cm^{-1}, respectively, which are attributed to C-H bond vibrations in the methylene groups (CH_2). Peaks at 1470 cm^{-1} and 1377 cm^{-1} were associated with C-H bond bending, while the peak near 730 cm^{-1} indicated vibrations of the long methylene chains, a characteristic feature of polyethylene polymers. For PP, peaks appeared at 2950, 2918, and 2838 cm^{-1} due to C-H bond vibrations, while peaks at 1455 and 1375 cm^{-1} were attributed to methyl group (CH_3) vibrations. Additional bands appeared at 1167, 998, and 841 cm^{-1}, associated with structural vibrations of the polypropylene chain. FTIR testing of PS also showed special peaks **Figure 8** at 3026 cm^{-1} due to the vibration of aromatic C-H bonds, in addition to peaks at 1601, 1493, and 1452 cm^{-1} resulting from the vibration of aromatic ring bonds (C=C), while the peaks at 760 and 700 cm^{-1} indicate vibrations of the benzene ring, which confirms the presence of the aromatic structure of polystyrene. The FTIR for PET also showed special peaks at 1715 cm^{-1} due to the vibration of the C=O carbonyl group, in addition to the peaks at 1240 and 1100 cm^{-1} resulting from the vibration of C-O-C bonds and the peaks at 872 and 725 cm^{-1} associated with the aromatic structure, which are clear indicators of the presence of ester groups in the PET structure. In general, the FTIR results proved the presence of unique chemical fingerprints for each type of plastic used,

proving that the raw materials were correctly prepared and identified before being introduced into the pyrolysis reactor. The results also indicate differences in chemical composition between polymers, which is an important factor affecting the distribution of pyrolysis products such as oil, gas, and coal.

3.1.2. FTIR characterization of catalyst materials

FTIR analysis was done to determine the chemical changes in the catalyst used in the thermal process of pyrolysis and to ensure the formation of calcium oxides after calcination, in addition to determining the structural properties of the zeolite**. Figure 9** shows the FTIR spectra of CaO before calcination, CaO after calcination, and the zeolite used as the catalyst. in the case of CaO before calcination (**Figure 9a**), characteristic absorption bands of calcium carbonate ($CaCO_3$) were observed. A broad band was noted near -3419 cm^{-1}, referring to the vibration of O-H groups resulting from moisture adsorbed on the surface. A strong peak near -1427 cm^{-1} is associated with the vibration of carbonate CO_3 bonds. Other peaks appeared in the lower wavenumber region, related to the structural vibrations of the carbonate group, proving that the raw material before calcination was $CaCO_3$.After calcination at 900°C, the post-calcination CaO spectrum (**Figure 9b**) shown a clear change in spectral characteristics. The intensity of the carbonate peaks decreased due to the decomposition of $CaCO_3$ and the release of CO_2 gas. Additionally, absorption bands appeared in the lower region, approximately between 400 and 600 cm^{-1}, according to the vibration of Ca-O bonds. This indicates the possible formation of CaO after calcination. The disappearance or reduction of carbonate signals suggests the decomposition of $CaCO_3$ during calcination and the formation of CaO –related species. The zeolite spectrum (**Figure 9c**) only showed the characteristic aluminosilicate structure, with a band appearing near -990 cm^{-1}, attributed to the vibration of Si-O-Al bonds within the zeolite crystal structure. Bands also appeared in the lower region between -400 and -700 cm^{-1}, associated with the external vibrations of the aluminosilicate lattice. Additionally, the broad band near 3400 cm^{-1} indicates the presence of hydroxyl groups and water adsorbed within the zeolite pores. Overall, the FTIR results confirmed the chemical changes occurring during calcination and suggested the transformation of calcium carbonate into CaO after thermal treatment, while the zeolite retained its aluminosilicate structure. This makes it suitable for use in enhancing thermal decomposition reactions and improving the distribution of decomposition products.

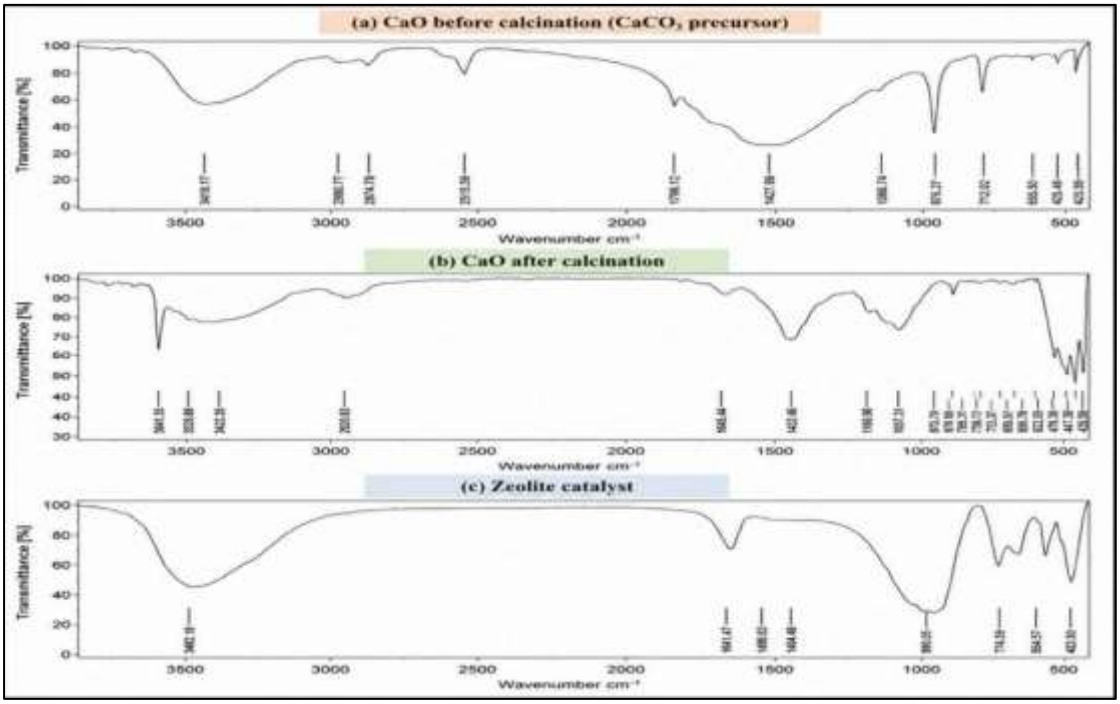


Figure 9. FTIR spectra of catalyst materials (a) CaO before calcination ($CaCO_3$ Precursor), (b) CaO after Calcination, Zeolite catalyst.

3.2. Pyrolysis product yield and distribution

The performance of the thermal pyrolysis process of mixed plastic waste was evaluated by calculating the distribution of the resulting products, including oil yield, gas yield, and solid residue. **Table 3** shows how temperature, reaction time, and the concentration of the catalyst affected the distribution of the products in the different tests. Overall, the tests showed that thermal oil was the main output, with amounts ranging from 53.2% to 83.6 wt%. Gas yield, on the other hand, varied from 10% to 39.6 wt%, and solid residue ranged from 3.2% to 15 wt%. This result is consistent approximately with Genuino et al[21]., who reported that mixed Waste made of plastic pyrolysis mainly produces pyrolysis oil, with oil yields of 70-85 wt%, gas yields of 10-25 wt%, and char yields of 2-10 wt%. It was found that Rising the temperature significantly affected product distribution, where higher temperatures lead to increased breakdown of polymer chains and their conversion into lighter hydrocarbon compounds[22]. Raising the temperature from 400°C to 500°C resulted in a change in the oil and gas yields due to increased thermal decomposition of the plastic materials. The **Table 3** also shows the effect of residence time, where extending the reaction time led to an increase in the secondary decomposition of the resulting vapors, which contributed to changing the proportion of oil produced and the transformation of part of the heavy compounds into non-condensed gases. As for the effect of the catalyst, the results showed that adding CaO and zeolite improved the thermal process of pyrolysis compared to experiments without a catalyst. The catalysts helped break the long bonds in the polymer chains and enhance the formation of liquid hydrocarbon compounds. In the case of the plastic mixture with CaO, the highest oil yield was recorded at 83.6% at a temperature of 500°C and a time of 90 minutes, and 10 wt%, indicating its effectiveness in improving the formation of liquid products and reducing carbon formation. For single polymers, the results showed a difference in behavior depending on the polymer type. HDPE and LDPE gave a high oil yield due to their structure rich in long-chain hydrocarbon bonds, while PS and PP showed a difference in product distribution due to the different structure of their polymer chains and their decomposition mechanism. It should be noted that replicate experiments (2 and 8) performed under identical operating conditions (450°C, 75 min, and 5 wt.% CaO catalyst loading) showed a variation in oil yield (56.8 and 69.2 wt.%). This difference is mainly attributed to the heterogeneous nature of the mixed plastic waste feedstock, where variations in polymer distribution, particle size, and local heat transfer within the reactor can affect the extent of thermal degradation and product formation. Moreover, differences in catalyst–feed contact and product collection efficiency may contribute to the observed variation. Such variations are commonly encountered in pyrolysis studies involving real waste-derived feed stocks.

Table 3. Effect of operating conditions and catalyst concentration on the distribution of pyrolysis products of mixed and Individual Waste made of plastic.

Experiment number	Temperature (C°)	Time (min)	Catalyst (%)	Oil yield (wt.%)	Solid Yield (wt.%)	Gas Yield (wt.%)
1(MPW/CaO)	400	60	10	60	13.6	26.4
2(MPW/CaO)	450	75	5	56.8	8	35.2
3(MPW/CaO)	400	60	0	65.6	15	19.4
4(MPW/CaO)	500	60	10	55.2	12.4	32.4
5(MPW/CaO)	400	90	0	67.2	11	21.8
6(MPW/CaO)	500	60	0	74	8	18
7(MPW/CaO)	500	90	0	75	8	17
8(MPW/CaO)	450	75	5	69.2	4.8	26
9(MPW/CaO)	400	90	10	53.2	7.2	39.6
10(MPW/CaO)	500	90	10	83.6	4.4	12
EXP Zeolite MIX	450	60	10	78	8	14
EXP Zeolite MIX	450	90	10	79	8	13
HDPE without a catalyst	450	60	0	60.8	3.2	36
HDPE with (CaO)	450	60	10	63.2	10	26.8
HDPE with (Zeolite)	450	60	10	58.4	13	28.6
LDPE without a catalyst	450	60	0	58.8	8.4	32.8
LDPE with (CaO)	450	60	10	70.8	4.8	24.4
LDPE with (Zeolite)	450	60	10	63.6	8	28.4
PS without a catalyst	450	60	0	82	8	10
PS with (CaO)	450	60	10	70	10	20
PP without a catalyst	450	60	0	76	3.2	20.8
PP with (CaO)	450	60	10	65	13	22

3.3. Effect of catalyst type on pyrolysis performance

3.3.1. Effect of calcium oxides (CaO).

The effect of CaO catalyst loading on the distribution of pyrolysis products was assessed using principal effect diagrams derived from factorial design analysis, which enhanced secondary cracking reactions of heavy hydrocarbons, transforming them into lighter gaseous products (**Figure10**). The findings indicated that the incorporation of the catalyst markedly influenced the allocation of oil, gas, and coke. **Figure 10a** demonstrates that elevating the CaO content from 0 to 10 wt% led to a reduction in the average oil output from 70.3 wt% to 62.9 wt%. In **Figure 10b**, gas yield increased from 19% wt. without a catalyst to 27.5% wt. with the addition of 10% CaO, indicating that CaO catalysed the cracking reactions and increased the formation of non-

condensable gases. As for solid coal, **Figure10c** shows a low decrease in solid coal production from 10.5% by weight to 9.4% by weight when the concentration of the catalyst was increased from 0% to 10%, which indicates an improvement in the conversion of carbon compounds into volatile products. In general, the use of the catalyst CaO led to a change in the distribution of thermal pyrolysis products leading to an increase in gas production with a relative decrease in liquid and solid products because of enhancing the catalytic cracking reactions.

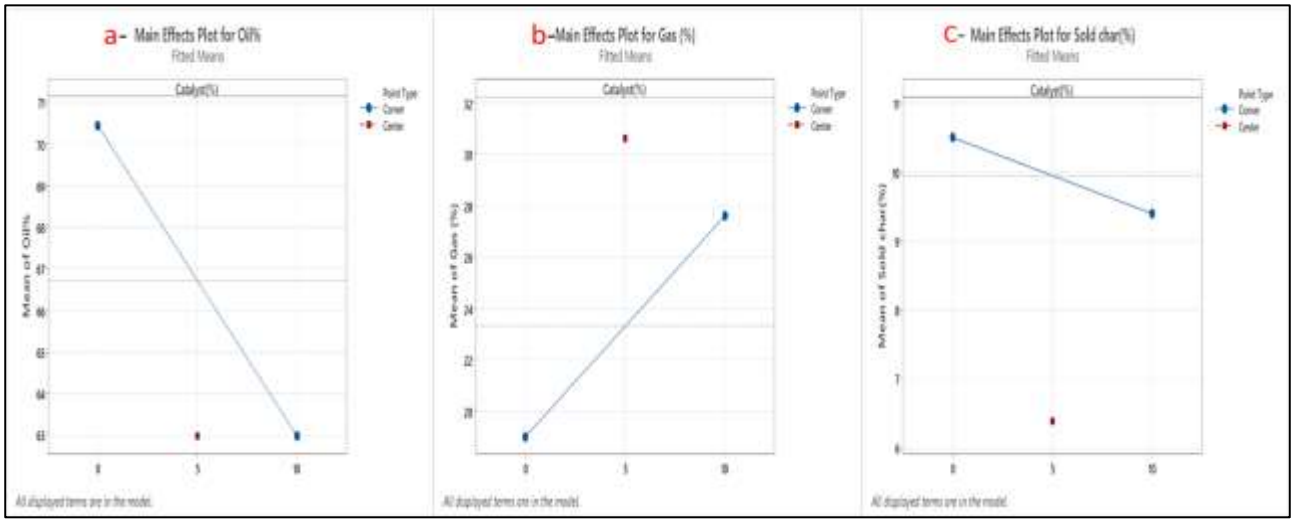


Figure 10. Shows the main effects plots illustrating the influence of catalyst loading on the distribution of pyrolysis products: (a) oil yield, (b) gas yield, and (c) solid char yield.

3.3.2. Effect of zeolite on pyrolysis product yield

The effect of zeolite on plastic mixes and individual plastics was evaluated at 450°C for 60 minutes. For plastic mixes, adding zeolite increased oil yield from 65.6% without the catalyst to 78% by weight, while decreasing char from 15% to 8% and gas content from 19.4% to 14%. Increasing the reaction time to 90 minutes additional raised oil yield to 79%. For individual plastics, the effect of zeolite varies depending on the polymer composition. In HDPE, oil yield decreased a little from 60.8% to 58.4%, with increased gas formation due to enhanced cracking reactions. In LDPE, zeolite improved oil yield from 58.8% to 63.6%. However, in PS, oil yield decreased from 82% to 70% due to the high cracking activity of zeolite and increased gas production. In the case of PP, oil production decreased from 76% to 65%, while gas formation increased. Overall, zeolites showed a positive effect on plastic mixes and LDPE by promoting the formation of liquid products, while their high cracking activity led to increased gas production in HDPE, PS, and PP.

3.4. Impact of temperature and residence time on pyrolysis product distribution

The main effect diagrams shown in **Figure 11** were used to look at how temperature and residence time affected the distribution of pyrolysis products. The figure shows how operating conditions, temperature, and time spent in the process can change the amount of pyrolysis oil, gas, and solid coke that is produced.

3.4.1. Impact of Temperature and Residence time on pyrolysis oil yield

Figure 11a shows how temperature and residence time change the amount of oil that comes out. What the researchers found was that weather had a bigger effect on oil production than residence time. When the temperature was raised from 400°C to 500°C, the average amount of oil produced went up from about 61.5% by weight to 72%. At higher temperatures, the polymer chains break down more quickly, creating more hydrocarbon fumes that can be condensed and turned into thermal pyrolysis oil. This is what makes the

improvement possible. Farjana Faisal and her friends[23] found that temperature and residence time are considered the most important factors in oil production from the thermal pyrolysis of mixed plastics. Their study showed that rising the temperature accelerates the decomposition of long polymer chains due to the increased thermal energy. Experimental results proved this pattern, with an even higher oil yield of 83.6% by weight achieved at a temperature of 500°C, a residence time of 90 minutes, and a 10% catalyst concentration. Furthermore, increasing the residence time from 60 to 90 minutes resulted in an average improvement in oil production due to the increased exposure time of the polymers to decomposition. However, temperature remained the most influential factor in controlling oil production.

3.4.2. Impact of temperature and residence time on gas yield

Figure 11b shows the Impact of Temperature and residence time on gas production. The results showed that rising the temperature from 400°C to 500°C led to a decrease in the average gas production from approximately 27% by weight to 20% by weight. This indicates that higher temperatures promoted the formation of liquid hydrocarbons rather than larger quantities of non-condensable gases under the study conditions. However, the experimental results showed that increasing the residence time could increase gas production due to the secondary cracking reactions of hydrocarbon vapors. The highest gas production, 39.6% by weight, was obtained at 400°C with a residence time of 90 minutes, resulting from the continued cracking of volatile compounds into lighter hydrocarbons and non-condensable gases. Overall, temperature had the greatest effect on gas production, while the effect of residence time was primarily related to the secondary cracking of the pyrolysis vapors.

3.4.3. Impact of temperature and residence time on solid char yield

Figure 11c shows the impact of Temperature and residence time on solid coal formation. Rising the temperature from 400°C to 500°C resulted in a decrease in the average solid coal yield from approximately 11.7% by weight to 8.2%. This decrease is attributed to the increased decomposition of plastic components and the conversion of the remaining solids into volatile products at higher temperatures. The lowest solid coal yield, 4.4% by weight, was obtained at 500°C, a residence time of 90 minutes, and a 10% catalyst concentration. Increasing residence time also contributed to a decrease in coal yield due to the continued decomposition of the remaining solids and improved conversion. However, the Impact of Temperature was greater than that of residence time in reducing solid coal formation.

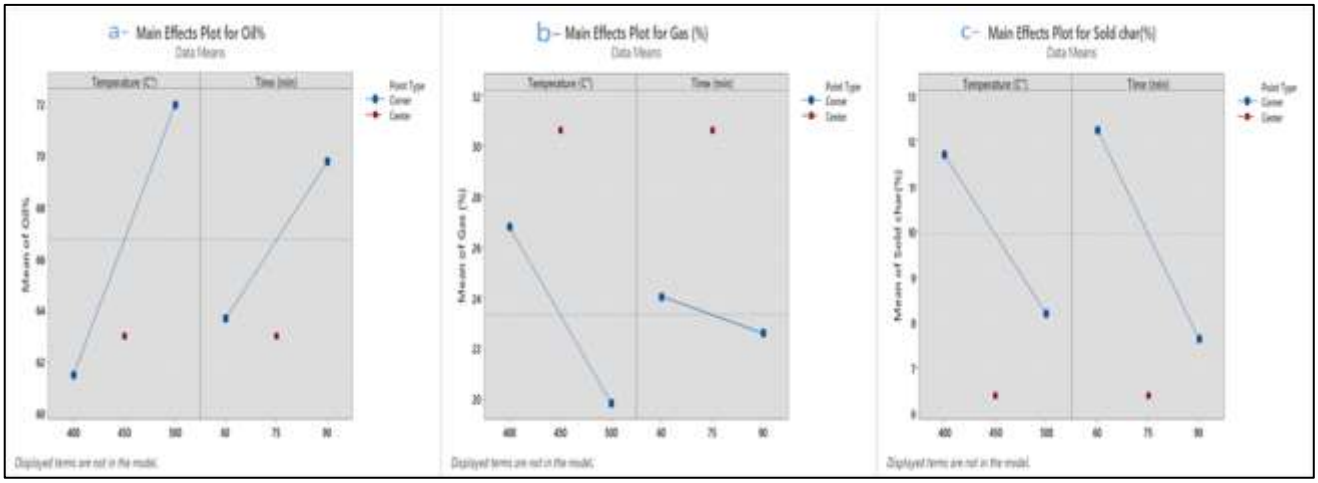


Figure 11. Shows the main effect graphs showing the impact of temperature and residence time on the productivity of pyrolysis products: (a) oil production, (b) gas production, and (c) solid char production.

3.5. Physicochemical and chemical characterization of pyrolysis products

3.5.1. Physical properties of pyrolysis oil

The Chemical and Physical properties of the resulting pyrolysis oils were evaluated to determine their fuel characteristics and suitability for energy applications. Tests included API gravity, density, specific gravity, viscosity, flash point, and sulfur content, which are important indicators for assessing fuel quality, flow behavior, storage requirements, combustion performance, and environmental impacts. Density and specific gravity measurements were performed at 15°C, while viscosity was measured at 40°C for all selected pyrolysis oil samples. These measurements were conducted using specialized instruments, as shown in **Figure 12A**. Figure a represents the viscosity meter, **Figure b** the API gravity meter, and **Figure12c** the flash point meter. In addition, the visual appearance and color of the pyrolysis oil samples obtained for different plastic materials, as shown in **Figure 12B**, reflect the differences in color, chemical composition, and hydrocarbon fractions of the oils produced. The Chemical and Physical properties of the pyrolysis samples are summarized in **Table 4**. The results showed that the resulting thermal pyrolysis oils have good fuel properties, as the relatively high API values indicate the formation of light hydrocarbon fractions with better fuel quality. The low density and specific gravity values show the presence of light oil components, and the low viscosity indicates good flow ability and ease of transport and handling. The measured flash point values of the pyrolysis oils indicate their ignition characteristics and provide important information about their potential handling and fuel applications. In addition, the low sulfur content indicates a reduction in environmental impact and a decrease in sulfur oxide emissions during combustion.

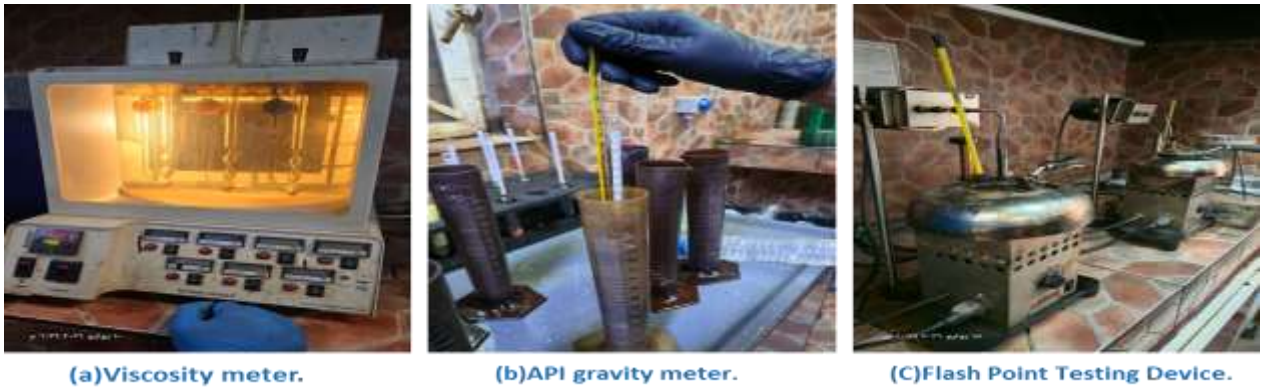


Figure 12A. Instruments used for the characterization of pyrolysis oil physical properties: (a)viscosity measurement, (b)API gravity meter, (C) Flash point device.

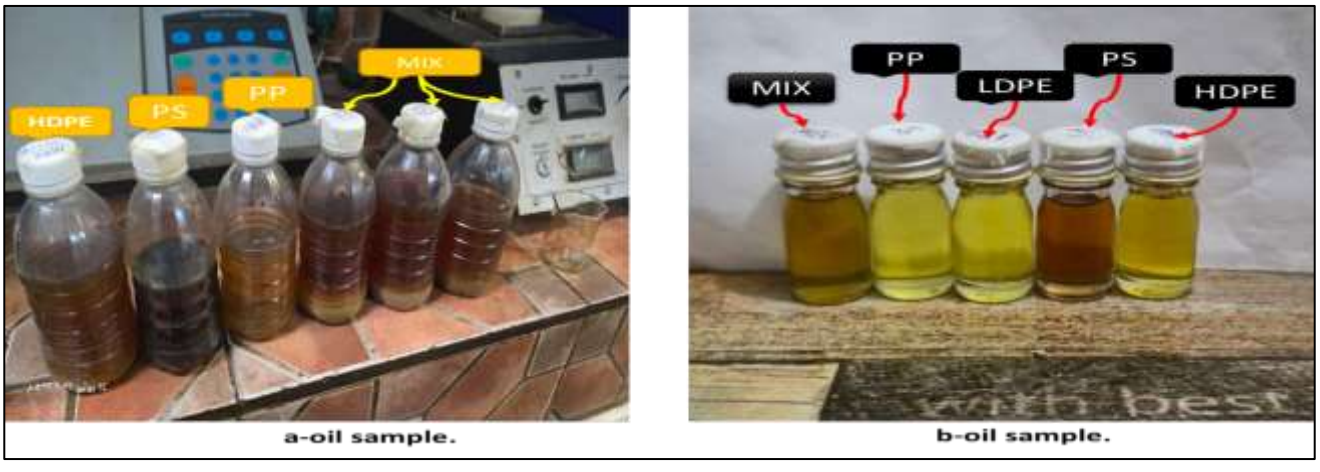


Figure 12B. Visual appearance and color variation of pyrolysis oil samples derived from different waste made of plastics.

The results of the current study are consistent with the review by Jia, Liew, Chai, and others[24] indicated that the physical properties of pyrolysis oil depend primarily on the type of plastic and operating conditions. The studies they reviewed showed that the oil's density ranges from 780 to 860 kg/m³, while its kinematic viscosity at 40°C ranges from 1 to 5 cSt. The API gravity value ranges from 35 to 55°, indicating that the oil is relatively light and has properties similar to diesel fuel. The review also showed that the sulfur content is very low when using polyolefin plastics such as HDPE, LDPE, and PP. The researchers concluded that pyrolysis oil possesses promising physical properties that qualify it as a potential alternative to diesel fuel; however, it requires further processing and improvement before commercial use.

Table 4. Chemical and Physical properties of selected and representative thermal pyrolysis oil samples.

Pyrolysis oil sample	API gravity	Specific gravity (15C)	Density(Kg/m^3) at 15°C	Viscosity (cSt)at40°C	Flash Point °C	Sulfur content(PPM)
Mix plastic with CaO	45.8	0.7891	797.7	1.7	31	19.6
Mix Plastic with Zeolite	46.6	0.7945	794.1	1.67	30	19.3
Mix Plastic without catalyst	44.7	0.8031	802.7	1.857	34	19.4
PP	51.6	0.7728	772.5	1.6	27	0.0
PS	30.4	0.8740	873.5	1.3	21	0.0
HDPE	48.1	0.7879	787.5	1.8	30	23.9
LDPE	47	0.8130	781.0	1.78	26	12.6

3.5.2. GC-MS analysis of Pyrolysis Oil

1) GC-MS analysis of mixed plastic pyrolysis oil

GC-MS analysis was done to determine the chemical composition of the pyrolysis oils produced from mixed Waste plastic under different catalytic conditions. **Figure 13** shows the total ion chromatography (TIC) plots of the pyrolysis oil produced using a CaO catalyst (**Figure 13a**), without a catalyst (**Figure 13b**), and using a zeolite catalyst **(Figure 13c**). The identified compounds showed that most of them fall under the alkenes, alkanes, and oxygenated hydrocarbon compounds, indicating the breakdown of polymer chains and their conversion into liquid hydrocarbon fractions. **Table 5** also shows the main compounds identified in these oils, in addition to their chemical formulas, molecular weights, chemical classification, range of carbon atoms, and area percentage for each compound. Thermal pyrolysis oil using CaO showed the majority of long-chain olefin compounds, mainly octadecene (C18H36)-1 at 6.27% and nonadecene (C19H38)-1 at 5.11% within the major carbon range C17-C21, indicating the formation of long-chain hydrocarbon fractions. As for the oil produced without a catalyst, it showed the presence of similar main compounds, with 1-octadecene reaching about 5.68% and 1-nonadecene about 5.65%, with a carbon range from C15 to C22. This indicates random thermal pyrolysis of the polymer chains due to the absence of a catalyst. While the oil produced using zeolite showed the presence of compounds such as octadecane-1 at a rate of 5.59%, pentadecane-1 at a rate of 5.13%, and tetradecane-1 at a rate of 4.13%, in addition to cetene at a rate of 5.13%, the appearance of compounds with shorter carbon chains indicates that zeolite enhanced secondary cracking reactions, which led to the production of lighter hydrocarbon compounds. In general, the GC-MS results, **Figure 13** and **Table 5** show that the type of catalyst clearly affects the distribution of hydrocarbon compounds in the thermal pyrolysis oil,

as CaO led to an increase in the formation of long-chain olefins, while zeolite contributed to enhancing catalytic cracking and the formation of lighter hydrocarbon fractions.

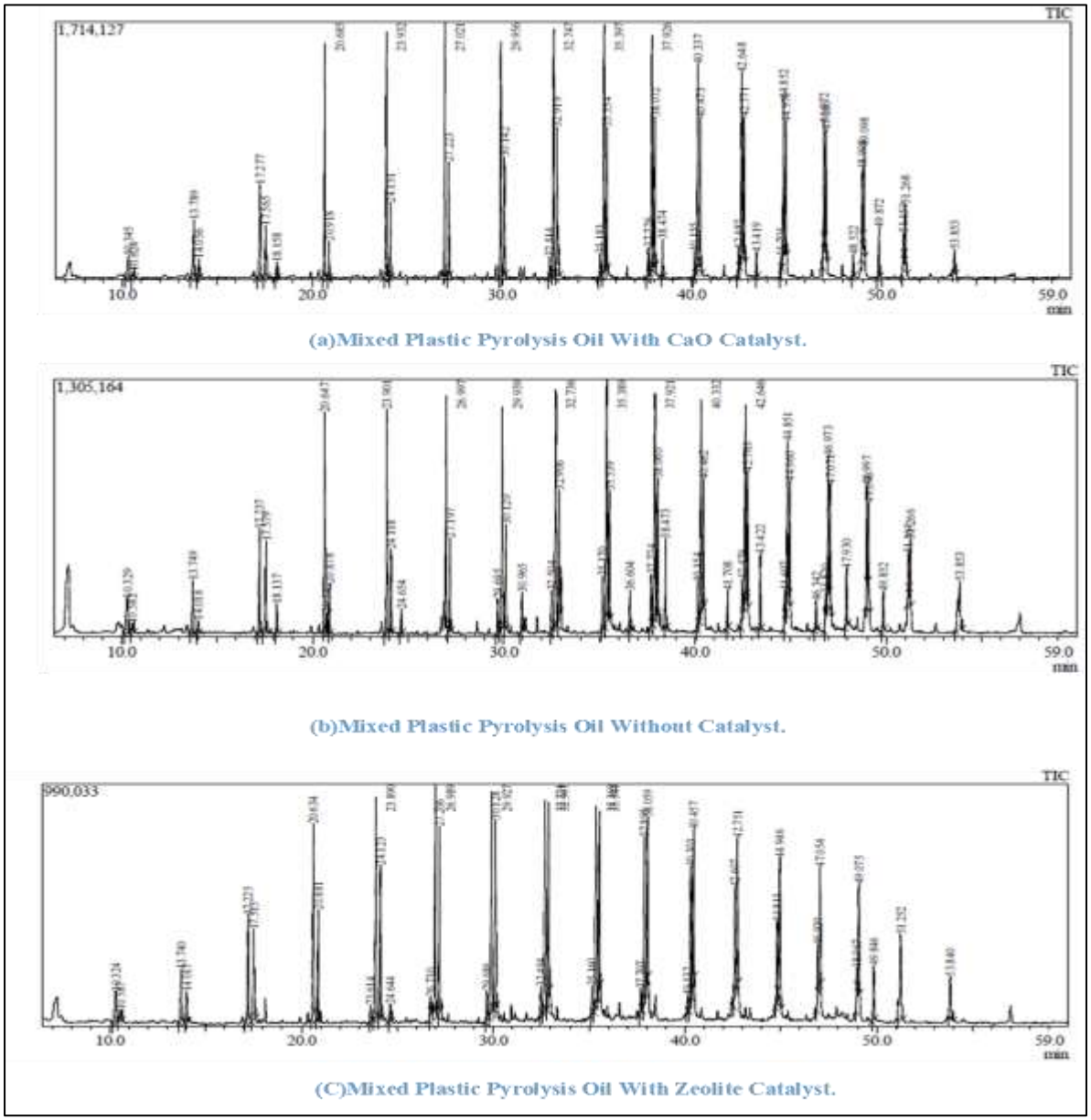


Figure 13. GC-MS chromatograms of pyrolysis oil obtained from mixed Waste plastic under different catalytic conditions: (a) pyrolysis oil with CaO catalyst. (b) pyrolysis oil without catalyst (c) pyrolysis oil with zeolite catalyst.

2) GC-MS analysis of individual polymer pyrolysis oil

GC-MS chromatograms of the resulting pyrolysis oils from individual plastic polymers are shown in **Figure 14** and **Figure 15,** while the identified major compounds and their corresponding chemical properties are summarized in **Table 5.** The results show that the polymer structure has a major effect on the chemical composition and distribution of hydrocarbons in the resulting pyrolysis oils. **Figure 14a** shows the GC-MS chromatogram of the pyrolysis oil produced from HDPE. The chromatogram shows most linear aliphatic hydrocarbons, primarily classified as alkenes. According to **Table 5**, the identified compounds include pentadecene-1 (C15H30), tetradecene-1 (C14H28), tridecene-1 (C13H26), and octadecene-1 (C18H36). These compounds fall within an approximate carbon range of C10 to C24. The formation of these long-chain

hydrocarbons is attributed to the linear structure of HDPE, where the random break-up of polymer chains during pyrolysis leads to the formation of olefinic compounds with properties like the original chain. **Figure 14b** represents the GC-MS analysis of the pyrolysis oil of LDPE without a catalyst. Compared to HDPE, the resulting oil mainly contained alkenes, but with a different distribution of hydrocarbon compounds due to the branching in the LDPE structure. According to **Table 5**, the main compounds were tetradecene-1, cetene (hexadecene-1), tridecene-1, heptadecene-1, and octadecene-1, within a carbon range from C10 to C24. These results indicate the occurrence of efficient pyrolysis of the LDPE chains and the formation of liquid hydrocarbon fractions. In addition, the thermal pyrolysis oil of LDPE was analyzed in **Figure 14c** using the CaO catalyst, where the chromatogram showed a difference in the distribution of compounds compared to the sample without the catalyst. However, alkenes remained the predominant compounds, as compounds such as pentadecene-1, tetradecene-1, tridecene-1, and octadecene-1 appeared, as shown in **Table 5**. The presence of CaO enhanced the secondary cracking reactions, which led to a modification of the hydrocarbon distribution while maintaining the olefinic nature of the resulting oil. With respect to PP and PS, **Figure 15a** shows a GC-MS chromatogram of PP thermal pyrolysis oil. The structure of PP oil differs from that of polyethylene oils due to the presence of methyl side chains in the polymer structure. According to **Table 5**, the main compounds were undecyl trifluoroacetate and 1-decanol, 2-hexyl, with surface area percentages of 17.82% and 13.21%, respectively. The formation of branched and oxygen-containing compounds is attributed to the nature of PP thermal pyrolysis, which results in a more complex molecular structure. As shown in **Figure 15b**, the GC-MS chromatogram of PS thermal pyrolysis oil shows a high percentage of aromatic compounds, compared to polyethylene and polypropylene oils, due to the presence of benzene rings in the polymer's main structure. According to **Table 5**, α-Methylstyrene (C10H10) was the primary compound at 25.73%, followed by 1,2-Diphenyl-1-isocyanoethane (C15H13N) at 14.89%. These compounds support the characteristic decomposition behavior of PS, where the breakdown of the polymer chain leads to the formation of styrene-derived compounds. In general, the results of the GC-MS analysis shown in **Figure 14** and **Figure 15** and summarized in **Table 5** show that the chemical composition of the thermal pyrolysis oil depends mostly on the type of original polymer, as polyethylene polymers mainly produced linear olefin hydrocarbons, while polypropylene produced more branched compounds and contained oxygen. Polystyrene decomposition led to the formation of aromatic compounds due to its aromatic molecular structure.

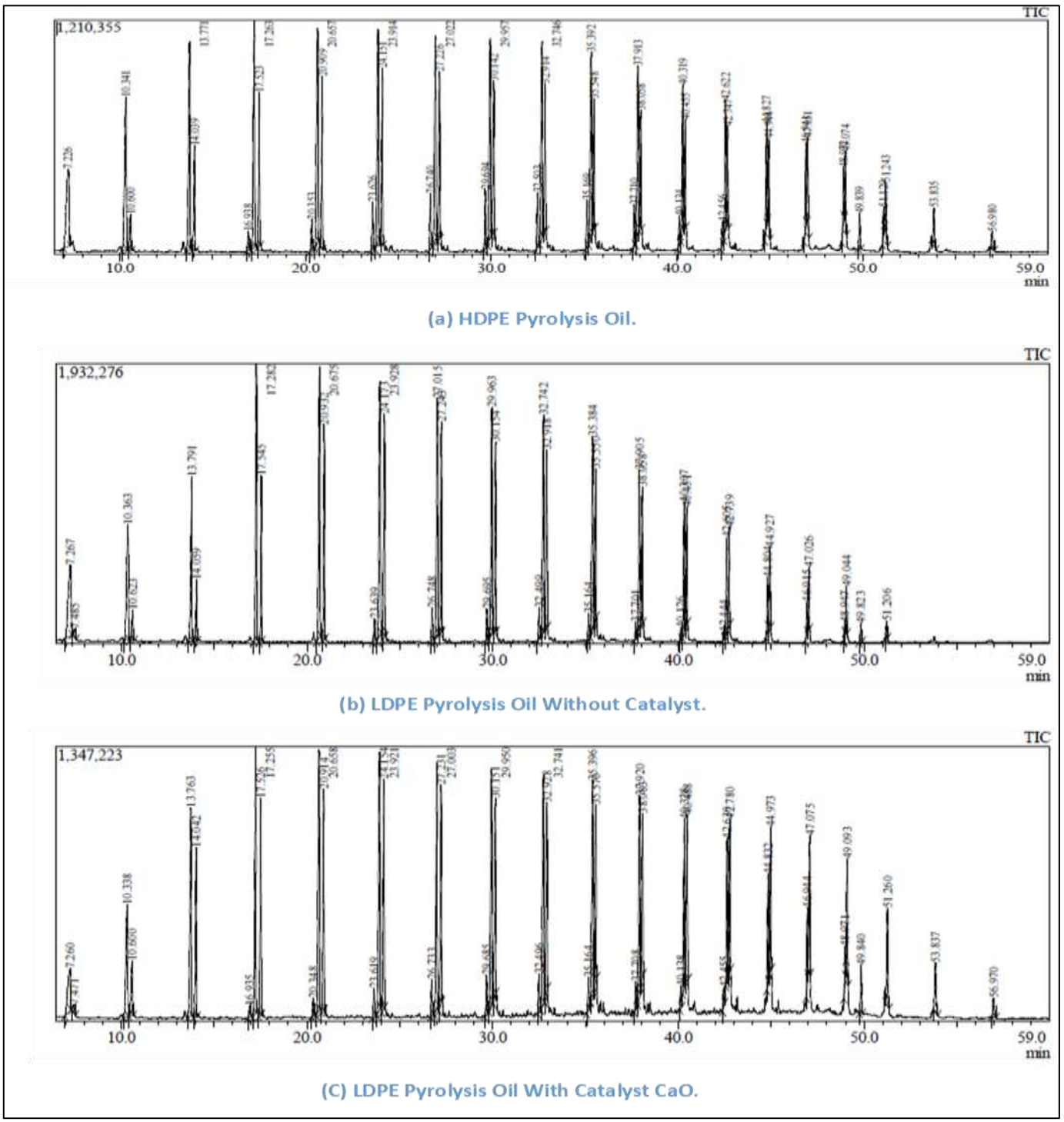


Figure 14. GC-MS chromatograms of individual polymer pyrolysis oils: (a) HDPE Pyrolysis oil (b) LDPE pyrolysis oil (C) LDPE pyrolysis oil with catalyst.

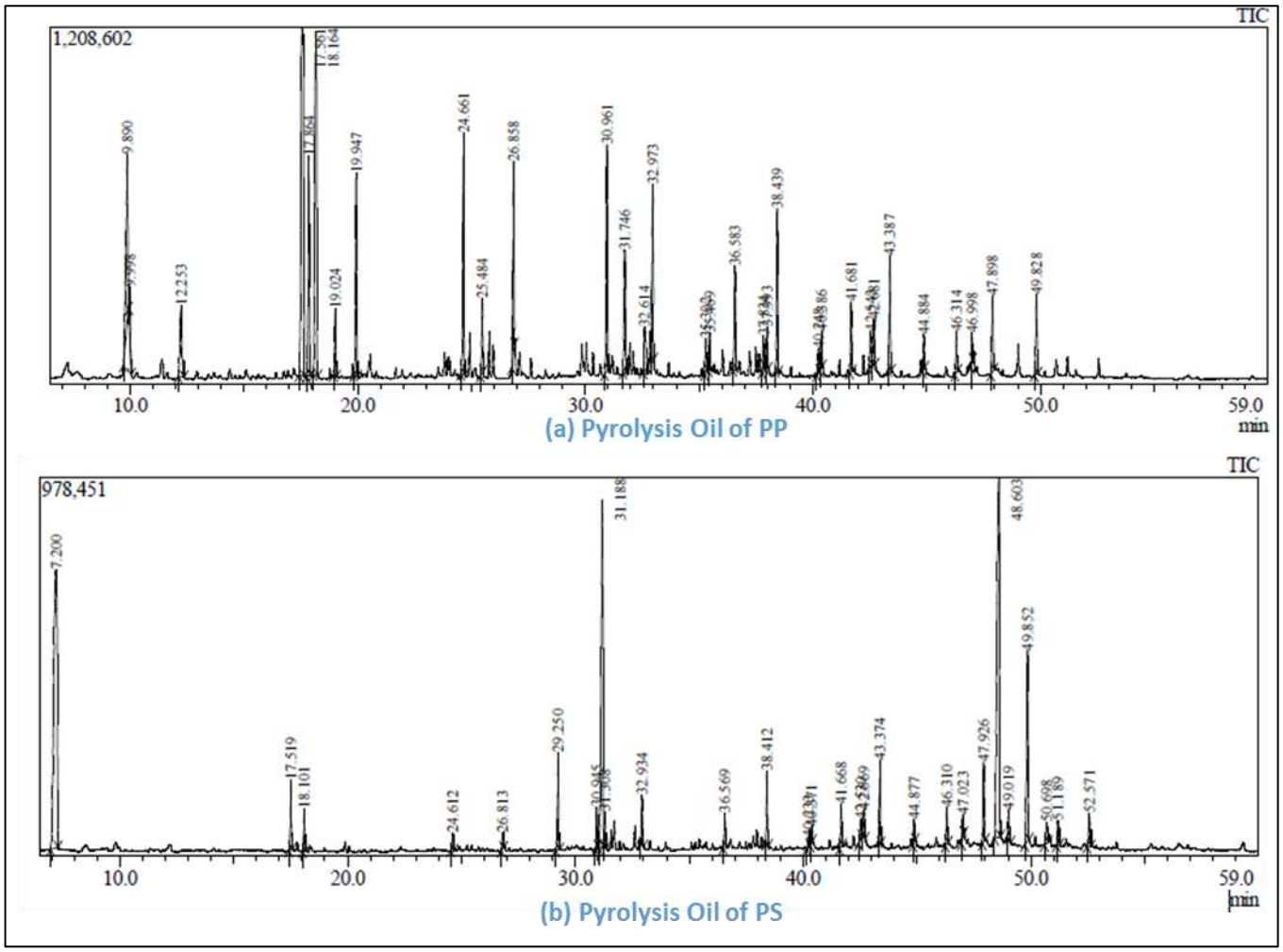


Figure 15. GC-MS chromatograms of individual polymer pyrolysis oils: (a) pyrolysis oil of PP (b) pyrolysis oil OF PS.

Table 5. GC-MS identification of major compounds, chemical classes, and carbon distribution in mixed plastic and individual polymer pyrolysis oils.

Sample	Compound name	Chemical formula	Molecular weight (g/mol)	Chemical class	Carbon range	Area (%)
Mixed plastic + CaO	1-Octadecene	C18H36	252.48	Alkene	C17–C21	6.27
	1-Nonadecene	C19H38	266.50	Alkene		6.05
	1-Heptadecene	C17H34	238.45	Alkene		5.11
	Octadecyl trifluoroacetate	C20H39F3O2	368.51	Oxygenated compound		5.76
Mixed plastic without catalyst	1-Octadecene	C18H36	252.48	Alkene	C15–C22	5.68
	1-Nonadecene	C19H38	266.50	Alkene		5.65
	1-Pentadecene	C15H30	210.40	Alkene		4.25
	1-Heptadecene	C17H34	238.45	Alkene		4.60
Mixed plastic + Zeolite	1-Octadecene	C18H36	252.48	Alkene	C14–C19	5.59
	1-Pentadecene	C15H30	210.40	Alkene		5.13
	1-Tetradecene	C14H28	196.37	Alkene		4.13
	Cetene (1-Hexadecene)	C16H32	224.43	Alkene		5.13
HDPE	1-Pentadecene	C15H30	210.40	Alkene	C10–C24	6.00
	1-Tetradecene	C14H28	196.37	Alkene		5.92
	1-Tridecene	C13H26	182.35	Alkene		5.34
	1-Octadecene	C18H36	252.48	Alkene		4.61
LDPE	1-Tetradecene	C14H28	196.37	Alkene	C10–C24	7.33
	Cetene (1-Hexadecene)	C16H32	224.43	Alkene		7.68
	1-Tridecene	C13H26	182.35	Alkene		5.69
	1-Heptadecene	C17H34	238.45	Alkene		5.55
LDPE + catalyst	1-Pentadecene	C15H30	210.40	Alkene	C10–C24	5.36
	1-Tetradecene	C14H28	196.37	Alkene		5.26
	1-Tridecene	C13H26	182.35	Alkene		4.68
	1-Octadecene	C18H36	252.48	Alkene		4.50
PP	1,13-Tetradecadiene	C14H26	194.36	Unsaturated hydrocarbon (diene)	C14	4.35
	1-Decanol, 2-hexyl-	C16H34O	242.44	Alcohol		13.21
PS	α-Methylstyrene	C10H10	130.19	Aromatic hydrocarbon	C10–C20	25.73
	Benzene, 1,1'-(1,3-propanediyl)bis.	C15H16	196.29	Aromatic hydrocarbon	C15	2.93

3.5.3. FTIR analysis of solid char

FTIR analysis was used to characterize the functional groups and chemical bonding characteristics of the solid char produced from the process of pyrolysis. The FTIR spectrum of the carbon produced from a Waste plastic mixture was chosen as a representative model because the carbon produced from different types of Waste made of plastic showed similar carbonaceous properties, as shown in **Figure 16**. The spectrum showed the presence of carbon-based structures, mainly represented by C-H and C=C bonds. The absorption bands observed at approximately 2922 and 2851 cm^{-1} are attributed to C-H bond vibrations in the aliphatic structures, while the band at approximately 1439 cm^{-1} is attributed to C-C bond vibrations associated with aromatic carbon structures. These results suggest the formation of a carbonaceous solid residue resulting from the decomposition of polymer chains and secondary carbonation reactions during the process of pyrolysis.

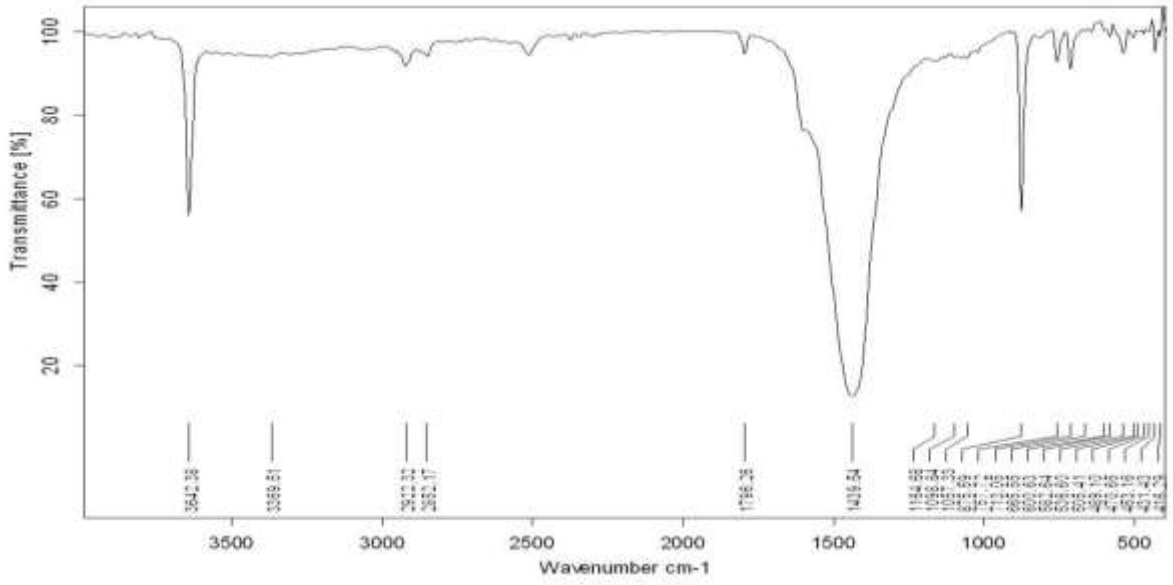


Figure 16. FTIR spectrum of solid char obtained from mixed plastic process of pyrolysis.

3.5.4. Expected composition of non-condensable gases

During the thermal Pyrolysis of combined waste plastic, a part of the resulting volatile compounds are converted to a gaseous phase and remain non-condensable. Due to the limitations of the experimental setup, these gases were not collected and analyzed in this study. However, according to previous studies, the gases produced by the thermal pyrolysis of plastics consist primarily of light hydrocarbons, Zhang et al.[25] explained in their review that non-condensable gases consist mainly of light hydrocarbons resulting from the breakdown of polymer chains, and including methane (CH_4), ethane (C_2H_6), ethylene (C_2H_4), propane (C_3H_8), and propylene (C_3H_6), in addition to small amounts of H_2 and CO. As Abdullah and others[26] have pointed out These gases are mainly produced as a result of secondary cracking reactions of the thermal pyrolysis vapors, where long hydrocarbon chains are broken down into lighter gaseous molecules. The composition and productivity of non-condensable gases are highly affected by operating conditions, especially temperature, residence time, and the presence of a catalyst. The researchers added that polyolefin plastics such as HDPE, LDPE, and PP tend to produce larger quantities of lighter hydrocarbons, while the presence of oxygen-containing polymers such as PET can lead to the formation of oxygen-containing gases like CO and CO_2. Because these gases contain a high percentage of combustible compounds, the researchers suggested they could be used as an energy source to provide the heat needed for the pyrolysis reactor, thus improving energy efficiency and the sustainability of the process.

3.6. Aspen plus simulation results

The outcomes of the Aspen Plus simulation for the thermal pyrolysis of mixed waste plastic are summarized in **Table 6,** while the process schematic is illustrated in **Figure 6**. The table contains the most important flows resulting from the simulation, including operating conditions, mass flow rates, densities, and composition of products resulting from the industrial expansion process. The simulation was conducted with an industrial feed capacity of 1000 tons per day of mixed plastic waste. The findings indicated that the pyrolysis reactor functions at a temperature of 450°C and a pressure of 1 bar, yielding three primary products: pyrolysis oil, non-condensable gasses, and charcoal. The simulated oil production was 704.689 tons per day, accounting for almost 70.5% by weight, while gas production reached 245.33 tons per day, or 24.5% by weight, and charcoal production was 50 tons per day, constituting 5% by weight. The oil generated in the simulation exhibited a density of 752.409 kg/m³, signifying the creation of a light hydrocarbon liquid appropriate for prospective fuel uses. The gaseous emission had a diminished density of 0.917 kg/m³ attributable to light hydrocarbons generated from polymer chain degradation, but the solid coal demonstrated a density of 2274.28 kg/m³, affirming the emergence of a carbon-dense portion. The allocation of compounds in Aspen Plus was derived from the GC-MS analysis results of the oil generated from practical experiments, which predominantly comprised hydrocarbons within the carbon range of C11 to C22, whereas the gas stream encompassed lighter compounds including CH_4, C_2H_4, C_2H_6, C_3H_8, H_2 gas, CO, and CO_2. In the absence of a mechanism for gathering and examining gasses during practical tests, the composition of indeterminate gasses within the Aspen Plus software was derived from earlier published research to ascertain the gasses generated from plastic waste. The existence of CO_2 and CO signifies restricted secondary reactions linked to the decomposition of carbon molecules throughout the pyrolysis procedure. These gasses are regarded as secondary products resulting from the thermal breakdown of polymer chains. In contrast to conventional plastic waste disposal techniques like open burning or unregulated landfilling, pyrolysis presents a more sustainable solution by transforming around 1,000 tons of plastic waste daily into valuable hydrocarbon products while minimizing direct atmospheric emissions. Moreover, the resultant gasses can be captured and utilized as supplementary fuel in the process, so reducing environmental repercussions and enhancing the overall energy efficiency of the system. The Aspen Plus findings further demonstrate the model's capacity to forecast the product distribution and mass balance of the process of pyrolysis for plastic waste when implemented on an industrial scale. The high percentage of oil obtained supports the possibility of using this technology to convert plastic waste into valuable liquid hydrocarbons.

Table 6. Aspen Plus simulation results showing operating conditions, mass flow rate, densities, and the product compositions of the mixed Waste made of plastic process of pyrolysis.

Stream Name	Units	MIXPLAST	TO-REACT	PROD	VAP	GAS	SOILD	OIL
Temperature	C	25	150	450	450	13.25	450	13.25
Pressure	bar	1.01353	1.01353	1	1	1.01	1	1.01
Mass Density	kg/cum	546.162	546.162	1.12838	1.07199	0.917302	2274.28	752.409
Mass Flows	tons/day	1000	1000	1000	950	245.311	50	704.689
Mass Fractions								
H2O		0	0	0	0	0	0	0
MIXPLAST		1	1	0	0	0	0	0
N2		0	0	0	0	0	0	0
H2		0	0	0.005	0.00526316	0.0203779	0	1.51E-06
CH4		0	0	0.06	0.0631579	0.244097	0	0.000170649
C2H4		0	0	0.05	0.0526316	0.202186	0	0.000569582
C2H6		0	0	0.035	0.0368421	0.140939	0	0.000604591
C3H8		0	0	0.025	0.0263158	0.0972829	0	0.0016112
C4H8		0	0	0.015	0.0157895	0.0511725	0	0.00347218
CO		0	0	0.01	0.0105263	0.0407362	0	9.85E-06
CO2		0	0	0.05	0.0526316	0.202051	0	0.000616878
C11H22		0	0	0.035	0.0368421	5.13E-05	0	0.0496495
C11H24		0	0	0.025	0.0263158	0.000119496	0	0.0354351
C12H24		0	0	0.045	0.0473684	0.000921153	0	0.0635373
C12H26		0	0	0.03	0.0315789	4.43E-05	0	0.0425566
C14H28		0	0	0.07	0.0736842	2.95E-06	0	0.0993336
C14H30		0	0	0.035	0.0368421	5.06E-06	0	0.0496656
C15H30		0	0	0.07	0.0736842	9.72E-06	0	0.0993313
C15H32		0	0	0.04	0.0421053	1.86E-06	0	0.056762
C16H34		0	0	0.065	0.0684211	1.08E-06	0	0.0922389
C17H34		0	0	0.09	0.0947368	4.31E-07	0	0.127716
C18H38		0	0	0.035	0.0368421	6.06E-08	0	0.0496673
C19H38		0	0	0.07	0.0736842	5.11E-08	0	0.0993346
C19H40		0	0	0.025	0.0263158	1.51E-08	0	0.0354767
C20H42		0	0	0.035	0.0368421	6.31E-09	0	0.0496673
C22H46		0	0	0.03	0.0315789	8.48E-10	0	0.042572
CHAR		0	0	0.05	0	0	1	0

3.7. Economic evaluation results of the plastic waste pyrolysis process

The techno-economic assessment of the pyrolysis procedure for plastic waste was conducted utilizing simulation outcomes from Aspen Plus V10 software and the Aspen Plus Economic Analyzer (APEA) tool, as

outlined in the methodology. The economic evaluation was performed on a proposed industrial unit with a processing capacity of 1000 tons/day of mixed Waste made of plastic. The evaluation included the main units used in the pyrolysis system, including the drying unit, pyrolysis reactor, condenser, separation units, and oil collection tank. The analysis also included estimating the capital cost, operating cost, and economic performance based on the simulation results. The capital cost was determined based on the cost of purchasing equipment, installation costs, and indirect costs associated with building the pyrolysis plant. **Table 7** shows the estimated cost of the main equipment in the process.

Table 7. Capital cost estimation of the main process equipment.

Equipment	**Equipment cost (USD)**	**Installed cost (USD)**
Dryer unit	342,900	532,500
Flash separation unit (SEPAR-2)	296,400	1,247,100
Condenser	291,900	1,716,500
Pyrolysis reactor	1,806,600	4,263,700
Splitter unit	357,600	558,700
Oil storage tank	1,195,600	1,482,900
Flash separation unit (SEPAR-1)	226,100	1,263,000
Total	4,517,100	11,064,400

Table 7 indicates that the pyrolysis reactor represents the highest contribution to equipment cost, with a cost of $4.26 million after installation. This is due to its large production capacity and operating conditions at high temperatures. The condensation and separation units also contributed significantly to the investment cost due to the heat transfer and product separation requirements. The economic parameters of the designed pyrolysis plant are summarized in **Table 8**, which shows the main capital and operating costs generated by the Aspen Process Economic Analyzer software.

Table 8. Summary of capital and operating costs of the pyrolysis plant.

Economic parameter	Cost (USD)
Equipment purchase cost	4,517,100
Total installed equipment cost	11,064,400
Total capital cost (CAPEX)	17,252,200
Annual operating cost (OPEX)	1,777,490/year
Utility cost	534,190/year

Table 8 shows that the total capital expenditure (CAPEX) for the proposed plant is approximately $17,252,200, including equipment purchase costs, installation costs, and indirect costs required for plant construction. The annual operating expenditure (OPEX) is approximately $1.78 million, primarily related to energy consumption, auxiliary services, maintenance, workers, and other operational requirements. The cost of auxiliary services constitutes a significant portion of the operating costs due to the high energy demand of the process of pyrolysis. Economic performance of the process was evaluated based on the output products, which include pyrolysis oil, non-condensate gases, and solid waste. Pyrolysis oil was considered the primary product of economic value due to its potential use as an alternative fuel or industrial feedstock. The gases produced internally can be used as an energy source, reducing external fuel consumption and improving the overall economic success of the process. The economic evaluation of pyrolysis requires assessing the market value of the resulting products, particularly pyrolysis oil and charcoal. Several previous studies have indicated varying economic values for pyrolysis oil and charcoal depending on their properties and quality. Kulas, Zolghadr et al[27] reported a minimum selling price of pyrolysis oil produced from the pyrolysis of Waste made

of plastic at US$561 per ton. Hosseiny and Shi[28] reported a minimum selling price of US$420 per ton. Also, Hasan and Rasul[29] stated that the minimum selling price (MSP) for the liquid product was US$302.50/ton. Due to the absence of reliable commercial data on pyrolysis oil and coal prices in Iraq, conservative economic assumptions were adopted. A price of $170 per ton for pyrolysis oil and $80 per ton for coal was assumed. The plant was assumed to operate for 330 days per year. Based on Aspen Plus results, the annual production volume was estimated at 232,650 tons/year of pyrolysis oil and 16,500 tons/year of coal. Non-condensable gases were used as a heat source within the plant and were not included in the revenue. Furthermore, the capital cost generated by the Aspen Process Economic Analyzer was adjusted using a correction factor of 1.5 to account for the uncertainties associated with implementing a large-scale industrial project. The adjusted capital cost was thus $25,878,300. A cost of $30 per ton was also used for collecting, sorting, transporting, and processing Waste made of plastic, amounting to an annual cost of $9.9 million. The total annual revenue from pyrolysis oil and coal reached 40.87 million US, while the total operating cost was 12.03 million US per year, resulting in a net annual profit of 28.84 million US. The capital recovery period was approximately 0.9 years (11 months), with a return on investment of 111.4%. These results indicate the promising economic viability of the proposed process of pyrolysis within the Iraqi market conditions. In comparison with other studies, Almohamadi et al[30] indicated that a plant for processing 1000 tons/day of Waste made of plastic, simulated using Aspen Plus, costs approximately 118 million US dollars to construct. The reason for the high cost of constructing the plant is that it includes a power generation unit from the produced gas, in addition to a hydrogen production reactor and other equipment. Meanwhile, the annual operating costs were estimated at approximately 27 million USD, which demonstrates the possibility of achieving economic feasibility for producing hydrocarbon fuel from Waste made of plastic, assuming a selling price of 200 USD/ton of pyrolysis oil from Waste plastic.

4. Conclusion

This study proved the feasibility of converting mixed Waste plastic into valuable hydrocarbon products through catalytic pyrolysis. Experimental results showed that the type of catalyst, temperature, and reaction time significantly influence the distribution of the resulting products. Furthermore, locally prepared calcium oxide (CaO) catalysts derived from eggshell waste and zeolite catalysts showed distinct effects on the pyrolysis behavior, contributing to improved hydrocarbon conversion and product composition change. The maximum oil yield of 83.6 wt.% was achieved under optimal operating conditions, indicating the effectiveness of catalytic thermal pyrolysis in increasing the production of liquid products. Analysis using GC-MS proved the presence of important hydrocarbon compounds in the resulting oil, including alkenes, alkanes, and aromatic compounds, indicating its ability to use as an alternative fuel source. Mixing the experimental GC-MS results with the Aspen Plus simulation led to the development of a realistic industrial process model based on the actual oil composition. Furthermore, the economic evaluation of the proposed 1000-ton/day plant under Iraqi conditions provided a practical indication of the process's feasibility on an industrial scale. In general, this study presents an integrated approach, from laboratory experiments to industrial process design and economic evaluation, making it a promising solution for the sustainable management of Waste plastic in Iraq.

Nomenclature

LPG	Liquefied petroleum Gas	APEA	Aspen Process Economic Analyser
ROI	Return on Investment	MPW	Mixed Plastic waste
OPEX	Operating Expenditure	PVC	Polyvinyl Chloride
TEA	Techno-Economic Assessment		
CAPEX	Capital Expenditure		

CaO	Calcium Oxide
PS	Polystyrene
PET	Polyethylene Terephthalate
PP	Polypropylene
HDPE	High-Density Polyethylene
GC-MS	Gas Chromatography–Mass Spectrometry
LDPE	Low-Density Polyethylene

Conflict of interest

The author declares no conflict of interest.

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