



Estimate the impact of Plastic Waste Types and its Mixture on bio-oil Yield through Thermal pyrolysis.

A.Hafiz. A. Ali¹, Salah R.², and Seddik S.²

¹ Assis. Lecturer at the Higher Institute of Engineering and Technology, New Minya, Egypt.

²Emeritus Professor, Mechanical Engineering Department, Minya University, Egypt.

Abstract

Newly, many research studies have confirmed that the pyrolysis has gained significant importance as an effective technique in addressing the waste management crisis and as an alternative fuel to tackle the depletion of fossil fuels. The present study evaluated five different types of plastic waste, namely PP, PS, LDPE, PET, and HDPE, as well as two plastic blends PS/PET, and PWM. The study investigates the production of bio-oil through thermal pyrolysis at a range of temperatures from 400°C to 600°C, with increments of 50°C. The experiments were conducted using a 2.2 liters semi-batch reactor with 21.5°C/minute heat rate. The results revealed that PS yielded the highest amount of bio-oil (83% wt) at 450 °C optimum temperature. On the contrary, the lowest amount of oil recorded for PET type, but when mixed with PS type through co-pyrolysis process, the oil content increased for all concentrations. 25% PS recorded the highest positive synergistic effect (+4), and the oil content increased to 27% wt at 450 °C, PWM obtained the maximum bio-oil at 40%wt at 500 °C.

Key words: Pyrolysis, bio-oil, plastic waste, fuel.

Corresponding author : A. Hafiz A.A. Ali

Email: ali5.engstar@gmail.com

nomenclature list			
HDPE	High Density Polyethylene	LDPE	low Density Polyethylene
PET	Polyethylene Terephthalate	PP	Polypropylene
PS	Polystyrene	PWM	plastic waste mixture
SPW	solid plastic waste	PWF	Plastic waste feed

1. Introduction

Plastics are distinguished by unique properties such as light weightless, chemical stability, flexibility, durability, and low economical cost, which have made plastic a super material utilized in numerous engineering industries, including automotive, construction, healthcare, and household applications [1, 2], on the contrary, excessive plastic consumption, driven by population growth, industrial expansion, and poor solid waste management, has led to the accumulation of plastic waste. This has risen environmental and health concerns that jeopardize the lives of living organisms [2, 3].

Global plastic production reached about 370 million metric tons in 2019, representing a 2.5% increase over the previous year. However, in 2020, this percentage experienced a slight decrease due to the precautionary measures implemented to combat the COVID-19 pandemic [4]. Authors in [5, 6] their study showed that the mechanical recycling technique only addressed 9% of solid plastic waste (SPW), while 12% was incinerated and 79% was disposed of in landfills, waste dumps, and oceans. Furthermore, by the year 2050, a total of 12,000 million metric tons of plastic waste are projected to be destined for natural landfills if they are processed through conventional, low-efficiency methods.

On the other hand, excessive consumption and the monopolization of fossil fuels to meet population growth and industrial expansion have resulted in the exacerbation of the energy crisis, prompting researchers to search for new energy sources and alternatives to address the issue of fossil fuel depletion [7]

Recently, scientific research has revealed a new technique for converting solid plastic waste into high-value fuel. This technique is called pyrolysis, which involves the simple thermal decomposition of plastic in an inert atmosphere, away from oxygen, under temperatures ranging from 300 to 600 °C. Studies have shown that pyrolysis is one of the most important technologies for treating solid waste, in addition to producing fuel with properties similar to fossil fuels [8].

Numerous experimental studies have concentrated on various elements that influence the properties, amount, and quality of thermal pyrolysis outcomes In order to increase the efficiency of pyrolysis. These elements encompass the type of feedstock used, the design and operational features of the reactor, temperature conditions, reaction duration, heating rate, the type of catalyst material employed, and the system used for condensation [1, 10, 15, 17, and 22].

2. Material and Equipment.

2.1 Preparation of Feedstock.

The feedstock materials were obtained from various plastic waste products such as disposable plates, water containers, drinking water bottles, food containers, and grocery bags. These products represented the plastic types PS, HDPE, PET, PP, and LDPE respectively. In Egypt, these types of plastic products are the main sources of plastic waste. Additionally, a mixture of these five types of plastic waste, known as PWM (Plastic Waste Mixture), was prepared with equal weight ratios of each type. Initially, the feedstock was thoroughly washed and then crushed into small pieces measuring approximately 2 cm². This process aimed to achieve a uniform mixture, enhancing the chemical reaction during the pyrolysis process.

A small-scale pyrolysis reactor was employed to examine six different feedstocks for the conversion of plastic waste into liquid oil, gas, and char products, as illustrated in Figure (1). The reactor cylinder, made of cast iron with a thickness of 6 mm, had dimensions of 285 mm in height and 101.6 mm in diameter, providing a capacity of 2.2 liters (as presented in Table 1). It featured a 2.5-meter-long electric heater loop with a power capacity of 3 kW. To facilitate the process, the reactor was connected to a 20 mm diameter tube that passed through a condenser tube measuring 55 cm in length and 63.5 mm in diameter. The condenser tube was equipped with two openings, with the bottom functioning as the inlet and the top serving as the outlet for cooling water. The vapors generated from heating the plastic waste at high temperatures in the chamber were condensed within the condenser tube, resulting in the formation of liquid oil. The condensed liquid oil was collected in the oil collector tank situated at the system's base, while the uncondensed byproducts (gases) were expelled from the system, as depicted in Figure 1. The condenser tube received a continuous flow of water at a rate of 1.5 liters per minute.

2.2 Experimental set up

Throughout the entire series of experiments, a digital scale with a precision of 0.1 was employed to measure 60 grams of PWF for each plastic waste type. The pyrolysis reactor was gradually heated from room temperature using an electrical control unit, with a heating rate of 21.5°C/minute. During each experiment, various important parameters were recorded, including the time at which the first droplet of oil emerged, the time when the final droplet was observed, and the color of the generated gas. At the conclusion of the experiment, the mass of oil in the collector tank and the remaining char inside the reactor were determined using the digital scale, while the mass of bio-gas was calculated by applying the principle of mass balance.

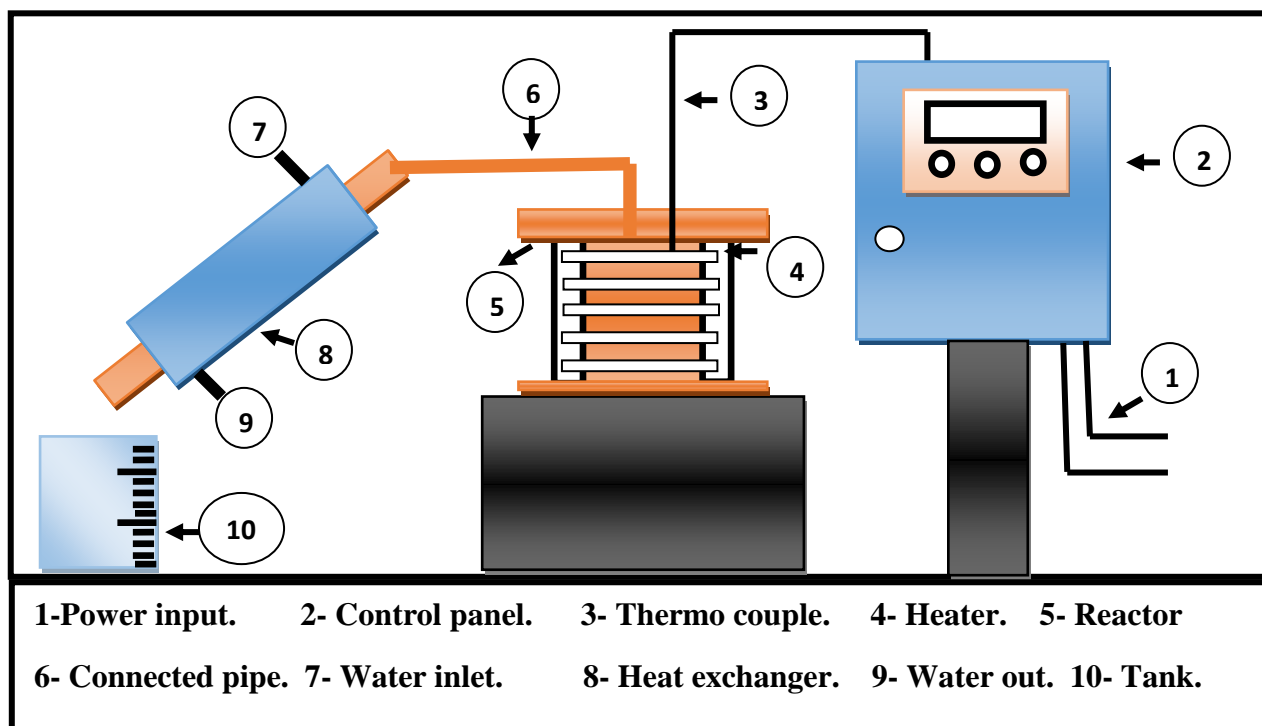


Fig.1.The schematic set up of the pyrolysis unit.

Table 1. components of pyrolysis unit.

Component		features
Reactor tank	Height	285 mm
	Out let diameter	101.5
	Thickness	6 mm
	Capacity	2.2 lit
Thermocouple		type K
Heater		2.5 m & 3 kW
condenser diameter		63.5 mm
condenser length		55cm

3. Results and discussion

3.1 Polystyrene (PS)

PS (C_8H_8)_n is composed of polymer chains consisting of repeating styrene molecules. It possesses several properties, as Transparency, Rigidity, Lightweight, Chemical resistance, and economical cost-effective, these make it suitable for various applications, as packaging materials, consumer products, disposable cutlery, CD cases, electronic components, insulation panels, disposable coffee cups, and food packaging that require insulation against temperature changes. It's important to note that PS plastic is not suitable for high-temperature applications as it has a relatively low melting point [9].

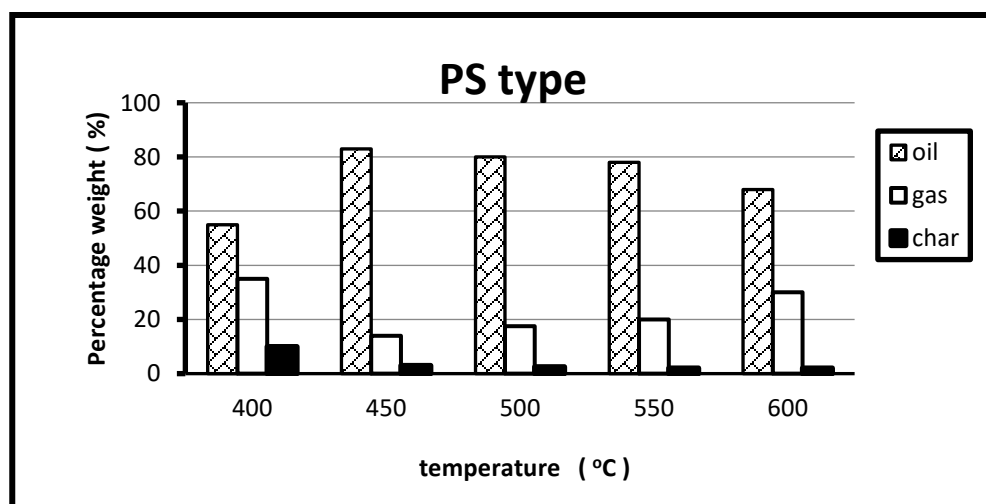


Fig. 2 products of PS pyrolysis verses temp.

During the PS pyrolysis experiment, the noticeable appearance of gases was observed at 375 °C. The first drop of oil was observed to fall at 383 °C. The highest amount of bio-oil was recorded at 450 °C (83%, 14%, and 3%) for oil, gas, and char yield respectively fig. (2). When the temperature increased to 600 °C, an increase in the quantity of gas and a decrease in the quantity of oil were observed. This can be attributed to the occurrence of secondary reactions that facilitated the formation of poly-aromatic bonds, which prevented gas condensation and consequently reduced the amount of oil [10].

Researchers in [11] their study has showed a strong convergence towards these results, it has recorded the highest oil yield (80.8%) at 450 °C, with 30 liter batch reactor and 10 °C/min heat rate.

3.2 Polyethylene terephthalate (PET)

PET ($C_{10}H_8O_4$)_n has a range of desirable properties as lightweight, Chemical Resistance, excellent mechanical strength this property makes PET a popular choice for packaging materials and containers that require durability. Transparency, This property is crucial for products like beverages, food items, and personal care products. Excellent barrier properties make it ideal for carbonated beverage bottles, food packaging, and pharmaceutical containers [12].

In figure (3), PET pyrolysis was showed an unusual behavior in the production of essential oil. The highest quantity of oil was recorded (5%) at 400 °C, and as the temperature increased, the oil nearly disappeared (2%) at 600 °C. Conversely, the gas recorded the highest yield (84%) at 600 °C.

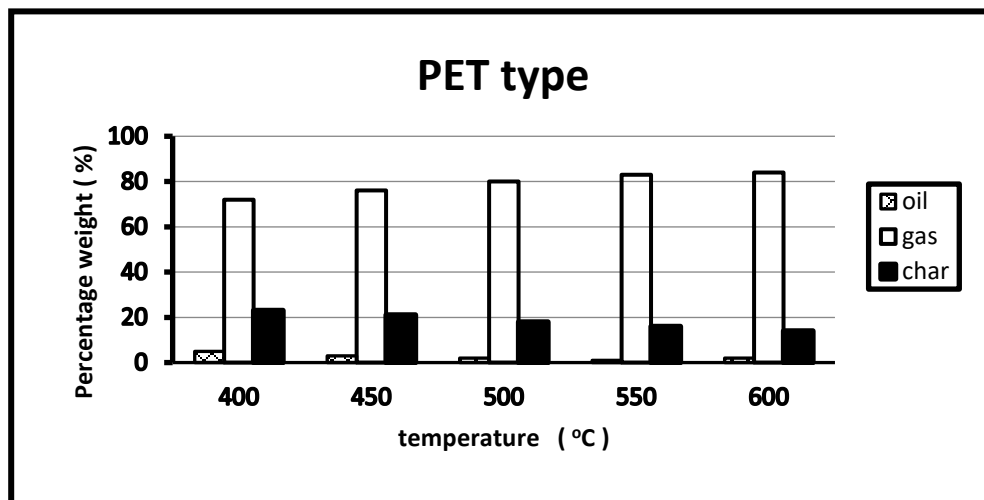


Fig. 3 products of PET pyrolysis verses temp.

These results completely agreed in this direction [13], as they recorded the oil, and gas yield about 1.4%, 70% respectively at 450 °C, 2500 W fixed bed. Furthermore, authors in [14] confirm this trend as well; their study recorded zero oil produced through 300 °C to 700 °C range. Study in [15] provided a scientific explanation for the significant decrease in the quantity of oil. They clarified that water bottles contain a lower percentage of volatile substances compared to other types of plastics.

3.3 PS/PET blend

Co-pyrolysis PS with PET, It is an experimental study to investigate the effect of different concentrations(25%,50%, and 75%) of PS weight on PET at optimum temperature 450 °C in order to obtain larger quantities of oil compared to the amount of oil produced from each type separately.

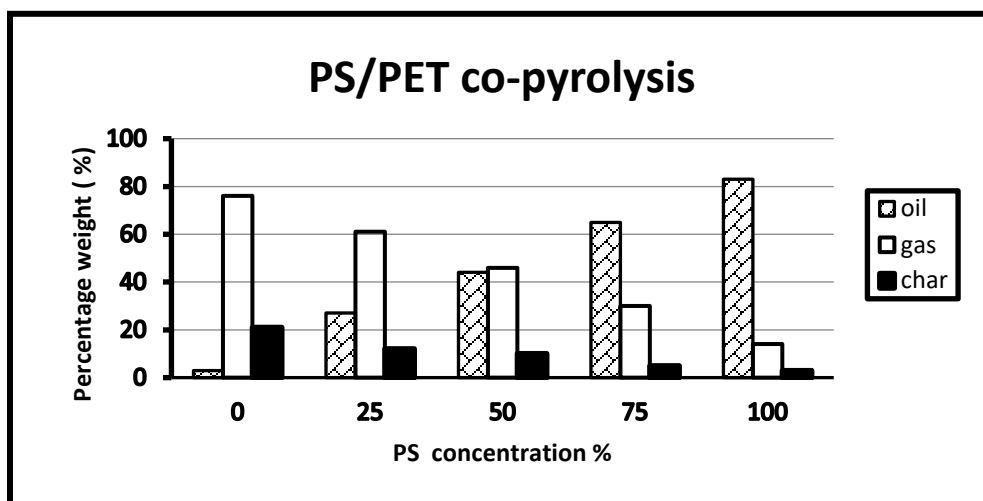


Fig. 4 products of PS/PET co-pyrolysis verses temp.

Figure (4) illustrates the effect of increasing the PS/PET ratio on the outcomes in the co-pyrolysis process. It showed the following: increasing the oil quantity is directly proportional to the increase in the PS ratio in the blend. A noticeable decrease in the coal quantity was observed at a concentration of 25%, followed by an approximate stability of the coal ratio for the remaining concentrations. To determine the impact of co-cracking on the oil quantity, it is necessary to know the synergistic effect.

Table 2 showed the synergistic effect PS/PET co-pyrolysis for oil yield to compare between experimental and calculated oil yield, the calculated values are determined by formula:
 $X_{cal} = M_{PET}Y_{PET} + M_{PS}Y_{PS}$ equ.(1)

M_{PET} / M_{PS} = relative mass.

Y_{PET} / Y_{PS} = oil yield.

$$\Delta Y = X_{\text{exp}} - X_{\text{cal.}} \quad (\text{Synergistic effect}) \quad \text{equ. (2)}$$

table 2. synergistic effect of bio-oil yield.

sample	Liquid fraction		ΔY
	$X_{\text{cal.}}$	X_{exp}	
PS plastic (100%)	83	83	0
PET plastic (0%)	3	3	0
25%PS+75%PET	23	27	+4
50%PS+50%PET	43	44	+1
75%PS+25%PET	63	65	+2

From table 2 showed that, co-pyrolysis has a positive effect at all concentrations, 25% PS has recorded the highest positive effect. Authors in [11] reported that, the inclusion of PS in the blend causes an increase in the oil content compared to individual types of plastics. This is due to the production of free radicals by PS, as well as the formation and presence of aliphatic and aromatic compounds.

3.4 High-Density Polyethylene (HDPE)

HDPE (C_2H_4)_n is a versatile and widely used thermoplastic polymer. HDPE is known for its excellent strength-to-density ratio, making it a popular choice for various applications, such as excellent resistance to a wide range of chemicals, its exceptional strength and durability, it is resistant to impact, abrasion, and weathering, lightweight despite its strength, and moisture resistance. These properties making it an ideal material for applications where packaging applications, including bottles, containers, and caps, pipes and fittings, geomembranes such as lining landfills, ponds, and canals, chemical tanks, corrosion-resistant pipes [9].

In the HDPE pyrolysis experiment, it was observed that at 400°C, dense gases were released, tending towards a brownish-yellow color, condensing on the base and wall of the collection tank to record 28% wax figure (5), the maximum oil/wax was obtained 64% at 550°C. The authors in [11] showed that the same phenomenon, they recorded 25% wax form at 450°C. Also the same trend in [16] it was recorded the highest oil/wax at 71% and 8% respectively at 550 °C, batch reactor 20 °C /min.

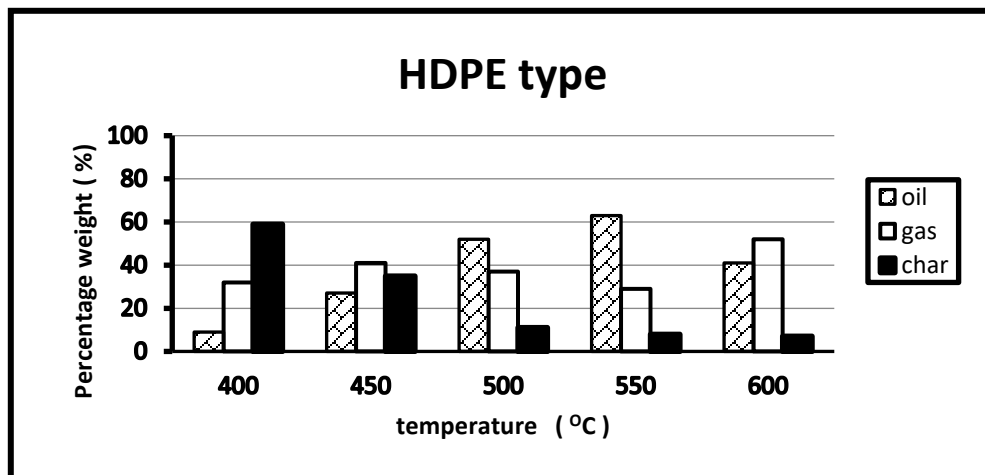


Fig. 5 products of HDPE pyrolysis verses

3.5 Low-Density Polyethylen (LDPE)

LDPE (C_2H_4)_n is a type of plastic that belongs to the polyethylene family. LDPE is characterized by several properties such as, flexibility and toughness, chemical resistance, high resistance to moisture, and good electrical insulator. These properties make LDPE the ideal material for many applications such as, packaging applications, including plastic bags, shrink films, and stretch films, wire and cable insulation, and medical applications, such as syringes, tubing, and prosthetic limbs [9].

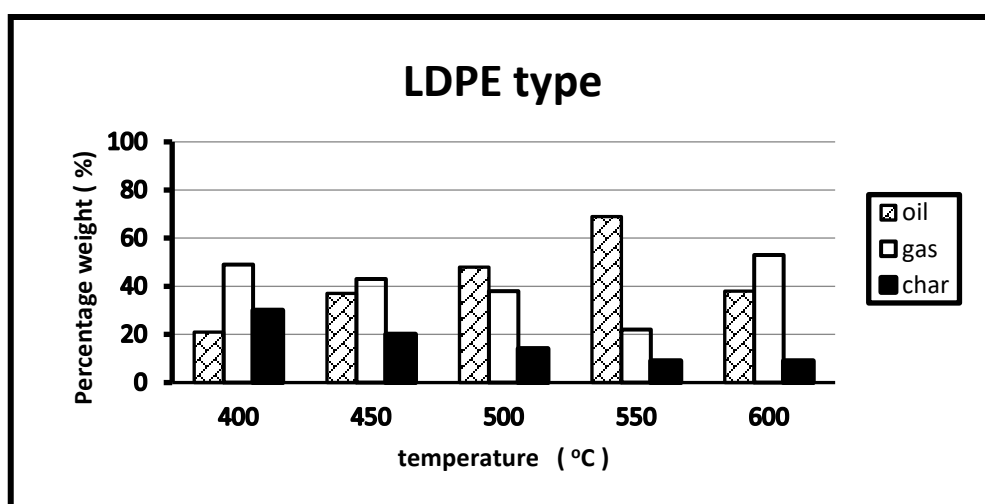


Fig. 6 products of LDPE pyrolysis verses temp.

In the detailed analysis of the graph in Figure (6), the following is evident: the quantity of oil produced gradually increases from a temperature of 400 °C (to a temperature of 550 °C (70%), yielding the highest oil yield at this temperature, with a sequential ratio of gas and coal (21%, and 9%) respectively. This behavior may be due to the fact that an increase in temperature leads to an increase in condensable gases. However, this trend is not observed at 600 °C, where the continued increase in temperature reveals secondary decomposition reactions to form non-condensable gases [17].

The authors in [18] their results are close to the previous ones, at optimum temperature 450 °C the bio-oil yield 74.7%, by using batch reactor 10 °C/min. Unlike, the study [19] has recorded the highest yield of oil is estimated (93.1%) at 550 °C and 5 °C min⁻¹ batch reactor, perhaps the reason for this increase is due to the size of LDPE particles powder 0.5 mm.

3.6 Polypropylene (PP)

PP (C₃H₆)_n is a linear hydrocarbon polymer with a high molecular weight. PP is produced through a polymerization process. Light weight, good mechanical strength and toughness, high chemical resistance, and excellent Heat Resistance. These previous characteristics are among the important distinguishing features of PP that make it suitable for many applications, such as, food packaging, beverage bottles, caps, and closures, manufacturing car interiors, such as dashboards, door panels, and trims, textiles and fibers, household products such as plastic furniture, storage containers, kitchenware, and toys [12].

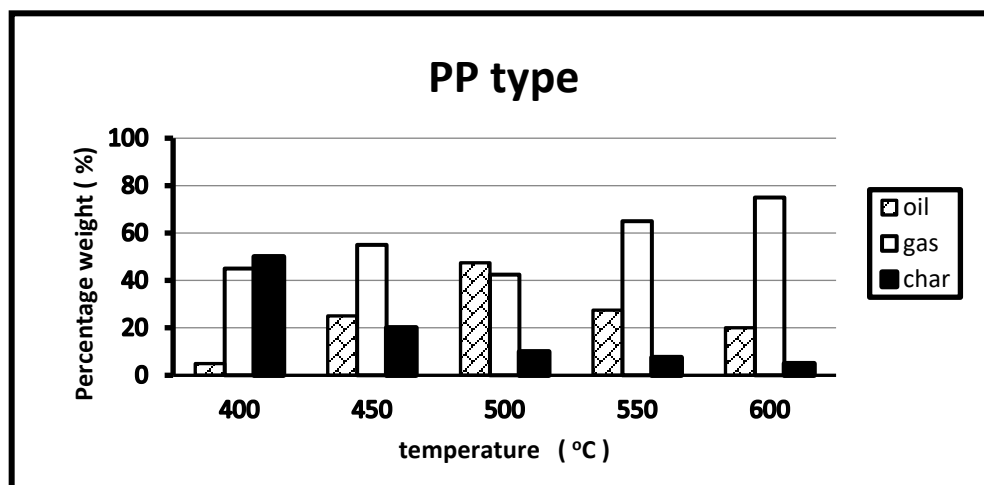


Fig. 7 products of PP pyrolysis verses temp.

Figure(7) showed the yield produced of the PP pyrolysis, at 400 °C yield of oil, gas, and char is 7%, 45%, and 48% respectively, the maximum oil was recorded 41% at 500 °C optimum temperature. On the same way the study in [20] it was showed the highest oil yield at 48.8% but another optimum temperature 740°C and 10 °C min⁻¹ batch reactor.

3.7 plastic waste mixture (PWM)

The plastic mixture has attracted the attention of researchers because it is an economically efficient technique that does not require sorting plastic waste.

The current work evaluated the production yield of the PWM pyrolysis, the study was showed that the yield of oil, gas, and char at 400 °C is obtained 6%, 44%, and 50% respectively, the largest oil yield 40% was recorded at 500°C fig.8.

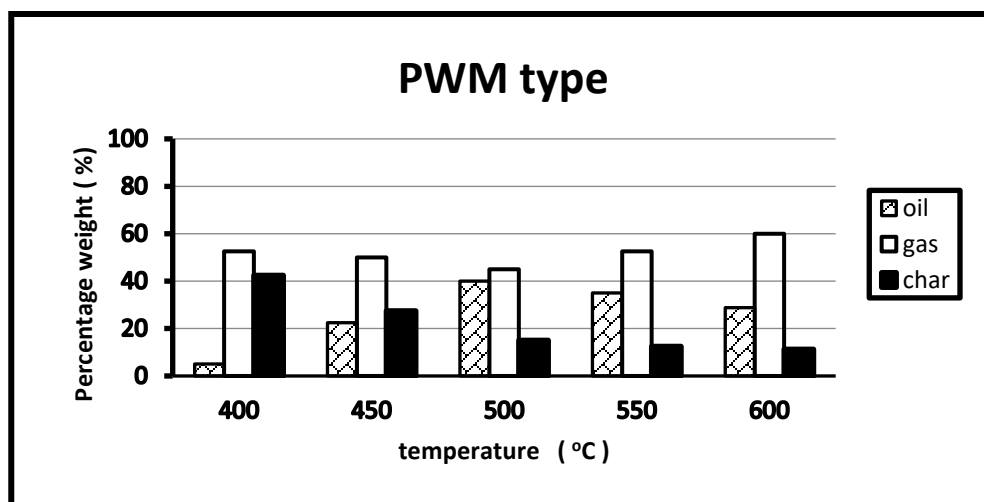


Fig. 8 products of PWM pyrolysis verses temp.

Very close to these results, the researchers in [21] they evaluated the effect of PWM (24% PP, 46% LDPE, and 30% HDPE) on pyrolysis production; they recorded the highest oil yield 48.4% at 650 °C using a fluidized bed reactor. Also the study in [11] it was showed that, the largest oil at 40% wt at 450 °C from PWM (40% PS, 20% PE, 20% PP, and 20% PET)

At another trend authors in [22] they obtained the maximum oil yield 84±4% at 500 °C and 17 °C/min scale batch from PWM (31.3% HDPE, 31.3% LDPE, 20% PET, 14% PP, and 2.5% PS).

5. Conclusion

The significance of utilizing the thermal pyrolysis process for energy recovery from SPW was highlighted in the present experimental study, and the subsequent conclusion was derived based on the study's findings.

1- PWP is a promising technique to eliminate solid plastic waste and convert it into fuel as a means to mitigate the landfill waste management crisis.

2- The temperature plays a crucial role in determining both the composition (oil, gases, wax, and char) and amount of the product obtained from the pyrolysis process. Generally, low temperatures favor the production of char, while high temperatures promote the generation of gases. The intermediate temperature range yields liquid oil.

3- Blends of pyrolytic oil and diesel fuel are examined in internal combustion engines due to the striking resemblance of the former to the latter, stemming from its production via the pyrolysis process.

4- The PS pyrolysis process yields the highest amount of pyrolytic oil, reaching 83%, when the optimum temperature of 450°C is maintained. On the other hand, in industrial applications that prefer gas fuel, PET is the most suitable for them, as it has recorded a very high yield of gases compared to other types.

5- co-pyrolysis PS/PET was obtained a positive synergistic effect for oil yield at all concentrations, 25%PS obtained the maximum positive synergistic.

Last but not least, researchers' efforts to further control the factors affecting the pyrolysis process are still ongoing, in order to achieve a larger quantity and better quality of bio-oil.

Conflict of interest. The authors of this study declare no competing interests and affirm that they are not affiliated or associated with any agency or organization that has any commercial or non-commercial stake in the materials or subject matter discussed.

References

- 1- S. M. Al-Salem, A. Antelava, A. Constantinou, G. Manos, A. Dutta, A review on thermal and catalytic pyrolysis of plastic solid waste psw, *Journal of Environmental Management* 197 (2017) 177-198. <http://dx.doi.org/10.1016/j.jenvman>.
- 2- A. Milbrandt, K. Coney, A. Badgett, and T. Beckham, “Quantification and evaluation of plastic waste in the United States”, *Resources, Conservation and Recycling*, Volume 183, August 2022, 106363. <https://doi.org/10.1016/j.resconrec>.
- 3- M. AlRayaan, Recent advancements of thermo chemical conversion of plastic waste to biofuel – A review, *Cleaner Engineering and Technology* 2(2021)100062, <https://doi.org/10.1016/j.clet>.
- 4- Association of Plastic Manufacturers Europe. An analysis of Europe an plastics production, demand and waste data. Belgium: European Association of Plastics Recycling and Recovery Organizations; from1950 to 2020.
- 5- Geyer, R., Jambeck, J.R., Law, K.L., 2017. Production, use, and fate of all plastics ever made. *Sci. Adv.* 3 (7), 1–5. [29\(3\):p 276-277, May 2018](https://doi.org/10.1126/sciadv.aag2487).

- 6- M. Saad Qureshi, A. Oasma, H. Pihkol, I. Deviatkin, A. Tenhunen, J. Mannila, H. Minkkinen, M. Pohjakallio, J. Laine- Ylijoki, Pyrolysis of plastic waste: Opportunities and challenges, *Journal of Analytical and Applied Pyrolysis* 148 (2020) 104804, <https://doi.org/10.1016/j.jaap.2020.104804>.
- 7- S. Wang, D. Alejandro, Kim, H., Kim, J.-Y., Lee, Y.-R., Nabgan, W., Hwang, B.W., Lee, D., Nam, H., Ryu, H.-J., 2022. Experimental investigation of plastic waste pyrolysis fuel and diesel blends combustion and its flue gas emission analysis in a 5 kW heater. *Energy*, Volume 247, 15 May 2022, 123408. <https://doi.org/10.1016/j.energy.2022.123408>.
- 8- F. Abnisa, P. Adeniyi Alaba, Recovery of liquid fuel from fossil-based solid wastes via pyrolysis technique: A review, *Journal of Environmental Chemical Engineering*, Volume 9, Issue 6, December 2021, 106593, <https://doi.org/10.1016/j.jece.2021.106593>.
- 9- C. Dorado, C.A Mullen, A. A. Boateng, H-ZSM5 Catalyzed Co-Pyrolysis of Biomass and Plastics. *ACS Sustain Chem Eng* 2014;2:301–11. <https://doi.org/10.1021/sc400354g>.
- 10- R. Miandad, A. S. Nizami, M. Rehan, M. A. Barakat, M. I. Khan, A. Mustafa, I. M. I. Ismail, J. D. Murphy, Influence of temperature and reaction time on the conversion of polystyrene waste to pyrolysis liquid oil, *Waste Management*, 58, (2016), 250 – 259, <http://dx.doi.org/10.1016/j.wasman.2016.09.023>
- 11- R. Miandad, M. A. Barakat, Asad S. Abu riazaza, M. Rehan, I. M. I. Ismail, A. S. Nizami, Effect of plastic waste types on pyrolysis liquid oil, *International Bio deterioration & Biodegradation*, 117(2017),239-252, <http://dx.doi.org/10.1016/j.ibiod.2016.09.017>.
- 12- L. Chen, S. Wang, H. Meng, Wu Z, Zhao J. Synergistic effect on thermal behavior and char morphology analysis during co-pyrolysis of paulownia wood blended with different plastics waste. *Appl. Therm. Eng* 2017;111:834–46. <https://doi.org/10.1016/j.applthermaleng.2016.09.155>.
- 13- E. Hartulistiyo, Febri A.P.A.G. Sigiro, and Muhamad Yulianto, Temperature distribution of the plastics Pyrolysis process to produce fuel at 450°C, *Procedia Environmental Sciences* 28 (2015), 234 – 241.
- 14- S. Merve, A. Gulnare, and Y. Isra, Comparative Study on Waste Plastics Pyrolysis Liquid Products Quantity and Energy Recovery Potential, *Energy Procedia* 118 (2017), 221–226, <http://dx.doi.org/10.1016/j.egypro.2017.07.020>
- 15- S. Dayana Anuar Sharuddin, F. Abnisa, W. Mohd Ashri Wan Daud, M. Kheir eddine Aroua, A review on pyrolysis of plastic wastes, *Energy Conversion and Management*, 115(2016)308–326, <http://dx.doi.org/10.1016/j.enconman.2016.02.037>.
- 16- S. Kumar and R. K. Singh, Recovery of hydrocarbon liquid from waste high density polyethylene by thermal pyrolysis, *Brazilian Journal of Chemical Engineering*, Vol. 28, No. 04, (2011), 659 – 667.

- 17- A. Jude. Onwudili, NagiInsura, T. Paul Williams, Composition of products from the pyrolysis of poly-ethylene and polystyrene in a closed batch reactor: Effects of temperature and residence time' journal of Analytical and Applied Pyrolysis, 86 (2009), 293 – 303, <https://doi:10.1016/j.jaap.2009.07.008>.
- 18- J. Aguado D. P. Serrano G. San Miguel M. C. Castro S. Madrid, Feedstock recycling of polyethylene in a two-step thermo-catalytic reaction system, , journal of Analytical and Applied Pyrolysis, 79, (2007), 415 – 425, <https://doi:10.1016/j.jaap.2006.11.008>.
- 19- A. Marcilla, M. I. Beltra'n, R. Navarro, thermal and catalytic pyrolysis of polyethylene over HZSM5 and HUSY zeolites in a batch reactor under dynamic conditions, Applied Catalysis B: Environmental, 86 (2009), 78 – 86, <https://doi:10.1016/j.apcatb.2008.07.026>
- 20- A. Demirbas, Pyrolysis of municipal plastic wastes for recoveryof gasoline-range hydrocarbons, Journal of Analytical and Applied Pyrolysis 72 (2004) 97–102, <http://dx.doi:10.1016/j.jaap.2004.03.001>.
- 21- P. Donaj, W. Kaminsky, F. Buzeto, and W. Yang, Pyrolysis of polyolefins for increasing the yield of monomers'recovery, Waste Management 32(2012)840–846, <http://dx.doi:10.1016/j.wasman.2011.10.009>.
- 22- C. Homer Genuino, M. Pilar Ruiz , Hero J. Heeres , R.A. Sascha. Kersten, Pyrolysis of mixed plastic waste: Predicting the product yields, Waste Management, Volume 156, 1 February 2023, Pages 208-215, <https://doi.org/10.1016/j.wasman.2022.11.040>.