

Co-pyrolysis of Polyethylene and Sawmills Powder: Influence of Polyethylene on Pyrolysis Product Value

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Abstract

The aim of this study was to investigate the effect on plastics during co-pyrolysis with biomass. Pyrolysis of sawmills powders (SP), polyethylene (PE) and their mixtures was carried out in a semi-batch reactor with varying temperatures at 550 °C and 600 °C. This work is a preliminary study for the development of a co-pyrolysis process of plastic wastes with biomass with the aim to produce an alternative liquid fuel for industrial use. Experiments were carried out with plastics and biomass to highlight the interactions occurring between a plastic and a biomass during their co-pyrolysis. It appears that the main decomposition event of each component takes place at higher temperatures when the components are mixed than when they are alone, possibly because the two components stabilize each other during their co-pyrolysis. These interactions depend on the nature of the plastics and the biomass. In addition, co-pyrolysis experiments were led in a lab-scale reactor using a mixture of plastic wastes and biomass. The influence of some key operating parameters on the outcome of the process was analysed. Hence, this co-pyrolysis process could be economically viable, provided heat losses are addressed carefully when designing an industrial reactor. The maximum liquid product yields for the pyrolysis of SP and PE obtained were 35,17% and 61,00%, respectively, whereas the maximum liquid product yield for SP/PE co-pyrolysis was 46,05% at 550 °C with 1:1 blend ratio.

Keywords: Alternative Energy, Elemental Analysis, Pyrolysis, Waste Reduction.

Polietilen ve Kereste Tozlarının Ko-pirolizi: Piroliz Ürün Değeri Üzerinde Polietilenin Etkisi

Öz

Bu çalışmanın amacı biyokütlenin kopiroliz sırasında plastikler üzerindeki etkisini araştırmaktır. Kereste tozlarının (SP), polietilenin (PE) ve bunların karışımlarının pirolizi, 550 °C ve 600 °C değişen sıcaklıklarda yarı-kesikli bir reaktörde gerçekleştirildi. Bu çalışma, endüstriyel kullanım için alternatif bir sıvı yakıt üretmek amacıyla, biyolojik kütle ile plastik atıkların kopiroliz işlemini geliştirilmesi için bir ön çalışmadır. Bileşenlerin kopiroliz sırasında bir plastik ile bir biyokütle arasında meydana gelen etkileşimleri vurgulamak için, plastikler ve biyokütle ile deneyler gerçekleştirildi. Her bir bileşenin ana parçalanma olayı, bileşenlerin beraber olduğunda, yalnız olmalarına göre daha yüksek sıcaklıklarda gerçekleştiği görüldü ve bunun nedeninin iki bileşen kopiroliz sırasında birbirlerini dengelediği düşünüldü. Bu etkileşimlerin plastiklere ve biyokütleyle bağlı olduğu çıkarımı yapıldı. Ayrıca, biyokütle ve plastik atıkların karışımı kullanılarak laboratuvar ölçekli bir reaktörde piroliz deneyleri yapıldı. Bazı önemli işletme parametrelerinin sürecin sonucu üzerindeki etkisi de analiz edildi. Bu nedenle, bu kopiroliz işleminin, bir endüstriyel reaktör tasarlanırken ısı kayıplarına dikkat edilmesi koşuluyla ekonomik açıdan uygulanabilir olduğu görüldü. Elde edilen SP ve PE'nin pirolizi için maksimum sıvı ürün verimi sırasıyla % 35,17 ve % 61,00 iken, SP ve PE ortak pirolizi için maksimum sıvı ürün verimi 1:1 karışım oranında ve 550 °C'de % 46,05 sonucuna ulaşıldı.

Anahtar Kelimeler: Alternatif Enerji, Element Analizi, Piroliz, Atık Azaltma.

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1. Introduction

Plastic waste is discarded every day and most of it ends up in landfills. In recent years, concern about perceived garbage crisis has grown as landfill capacity diminishes and sites for new landfills become increasingly difficult to find. The plastics are mostly non-biodegradable and remain in the environment for hundreds of years [1]. Conventional recycling methods such as sorting and grinding can recycle only 15–20% of total plastic waste [2, 3]. The energy recovery technologies such as thermal and catalytic pyrolysis, gasification and plasma arc gasification are receiving more attention as alternative methods of plastic waste recycling [4]. Pyrolysis process converts plastic waste into liquid oil, solid residue and gases at high temperatures via thermal decomposition. The thermal pyrolysis of PE type plastics such as HDPE and LDPE along with PP are difficult to conduct due to their crossed chain hydrocarbon structures [5]. Therefore, catalytic pyrolysis is being developed to overcome the problems of thermal pyrolysis [6, 7, 8]. Pyrolysis is a tertiary recycling technique in which organic polymers are converted into liquid oil, char and gases at high temperatures via thermal decomposition [9]. Pyrolysis studies were carried out at different temperatures ranging from 550 to 600 °C, recommended that the typical optimum temperatures for plastic waste were around 500–550 °C [9]. In addition, researchers have used different retention times for pyrolysis process. For example, Lopez et al. (2011) carried out pyrolysis of plastic waste at retention times of 0–15, 30 and 120 min. Other similar studies used retention times of 40–70 min [10], 120 min [11] and 45 min [12]. However, there is a scope for further reduction of process temperature and retention time to optimize the overall process. The pyrolysis can be carried out via thermal and catalytic routes (Table 1).

Table 1. Thermal versus catalytic pyrolysis [4].

Catalyst used	Amount of catalyst	Feedstock used	Temp (°C)	Thermal Pyrolysis			Catalytic Pyrolysis			References
				Liquid	Gases	Char	Liquid	Gases	Char	
ZSM-5	10%	PE, P,PS,PET,PVC	450	79,3	17,7	3,0	56,9	40,4	3,2	[8]
ZSM-5	10%	PE,PP,PS,PET,PVC	400	79,3	17,7	3,0	56,9	40,4	3,2	[8]
Red Mud	10%	PE,PP,PS,PET,PVC	440	79,3	17,7	3,0	76,2	21,6	2,2	[8]
ZSM-5	10%	PE,PP,PS,PET,PVC	500	65,2	34,0	0,8	39,8	58,4	1,8	[8]
Red Mud	10%	PE,PP,PS,PET,PVC	500	65,2	34,0	0,8	57,0	41,3	1,7	[8]
Y-Zeolite	50%	Municipal plastic waste	450	58	28	14	52	36	12	[13]
Natural Zeolite	50%	Municipal plastic waste	450	58	28	14	50	34	16	[13]

Co-pyrolysis is the most promising technique which can meet the criteria, at the same time reducing the volume of the waste and environmental concerns as the waste is usually used as one of the feed. Many studies have shown improvement in the quality and quantity of bio-oil without any improvement in the process. The key feature of this technique is the synergistic effect between biomass and plastic which occurs during the process. Literature portrays cracking process of polymer waste into useful lower molecular weight compounds that could be utilized as fuels or chemicals [17,18]. Thus, co-pyrolysis of biomass and plastic produces a more stable and homogeneous pyrolysis oil than blending of individual oils, which is impractical as oil from biomass is polar in nature and the mixture of oil is found to be unstable since it undergoes phase separation after a short interval of time.

Table 2. Suitability of plastic [4].

Resin	Suitability	Remarks	References
Polystyrene (PS)	Very good and gives excellent fuel	Low temperature required as to PP and PE	[14]
		Produce less viscous oil as compared to PE and PP	[15]
Polyethylene (PE)	Very good for pyrolysis	Required temperature is high >500 due to its branched chain structure	[16]
		In thermal pyrolysis wax formation occurred on external site of catalyst further cracking of wax into gases liquid occurred in internal site of catalyst	[17]
Polyvinyl chloride (PVC)	Not suitable Only few studies were carried out by different scientists	Produce hazardous chlorine gas Dechlorination via low (250-320 °C) or physical or chemical adsorption	[7]
		In catalytic pyrolysis presence of chlorine and deposition of coke affect catalytic activity of catalyst	[8]
Polypropylene (PP)	Very good	Required high temperature After PE, it is difficult to degrade thermal pyrolysis of PP	[16]

Hugo et al., carried out slow pyrolysis and vacuum pyrolysis of bagasse [19]. They produced maximum char of highest calorific value by slow pyrolysis and bio-oil with less water content by vacuum pyrolysis. However, the HHV of bio-oil obtained from sugar- cane bagasse is 23.5 MJ/kg which is less than the HHV of petroleum fuels.

Montoya et al. studied the effect of temperature, biomass feed rate, carrier gas flow and feed particle size on the yield of products during fast pyrolysis of sugarcane bagasse [20]. The highest yield was obtained at 500 °C with nitrogen flow of 50 L/min and feed size range of 0.425 to 0.6 mm with 72.94% of bio-oil. They concluded that the yield increases due to heating severity and decreases due to entrainment of small particles. Nevertheless, the obtained bio-oil has low heating value due the presence of oxygen when inert particles of larger diameter are used.

Abnisa et al. showed that by adding the same ratio of polystyrene (PS) in the pyrolysis of palm shell the liquid yield was increased to about 61.63%, whereas for individual pyrolysis of palm shell the yield was obtained 46.13% [21]. Also, these authors stated that the heating value of co-pyrolysis oil increased to three times that of individual palm shell pyrolysis oil. Co-pyrolysis of pine cone with different plastics such as PP, LDPE, and PS has been proposed by Brebu et al. [22]. From their result, they concluded that the energy content of co-pyrolysis oil was comparatively more than that of single pyrolysis of pine cone alone. In addition, co- pyrolysis of biomass with bioplastic, also provides the positive contribution in pyrolysis product yield. Cornellsen et al. described the co-pyrolysis of willow with different bioplastics such as polylactic acid, polyhydroxy butyrate, corn starch, potato starch was used among them PHB showed great potential for improving the quality and quantity of co-pyrolysis oil [23]. Significance of plastic with biomass during co-pyrolysis makes the positive effect because plastic like polymer is a higher hydrogen rich product and the liquid product obtained from pyrolysis of plastic has a calorific value close to calorific value of conventional fuel which is around 40 MJ/kg [24].

2. Materials and Methods

Sawmills powder (SP) was obtained from the wood cutting plant. Polyethylene (PE) grains were obtained from Kalem Polymer Recycling Ltd. Before co-pyrolysis SP and PE were maintained in average size range. The compositional analysis of feedstock SP and PE was done based on proximate and ultimate analysis. Proximate analysis was carried out by standard procedure described by the ASTM D3172-07 a method to identify the moisture, volatile matter, fixed carbon and ash content of the feed. The percentage of carbon, hydrogen, nitrogen, and oxygen in the feedstock was determined using CHNSO Elemental Analyzer by Variael CUBE, Germany. The calorific values of the SP and PE, were obtained through a bomb calorimeter (Model: Parr 6100 EE digital bomb calorimeter). Pyrolysis experiments were carried out in a fixed bed pyrolysis reactor. The heating area of the electrically heated fixed bed reactor is 18x18x10 cm and made of stainless steel. Temperature measurement and control is provided by nickel-chrome thermal couple. The sample was placed in the sample chamber in the reactor. The reactor system consisted of a PID temperature controller with an adjustable heating rate for the furnace, a condenser with cold water circulation as the cooling medium at the outlet to condense the condensable gases. The raw materials were fed into the reactor and it was properly sealed; when the desired temperature reaches, the reaction starts. The inert atmosphere was created by flowing pure nitrogen gas at around 40 mL/min flow rate in replacement of the air present in the pyrolysis zone for avoiding unwanted oxidation of the sample. Co-pyrolysis of SP and PE was carried out in a laboratory scale semi-batch reactor. The liquid product collected after condensation consisted of a two-phase solution of heavy oil and light oil along with the water. The separation of pyrolysis liquid was conducted in a separating funnel and further analysis was carried out after removal of water from it. Pyrolysis char was also collected after the reactor became cooled. The yield of the pyrolysis product was determined by measuring the weight of pyrolysis oil and pyrolysis char. SP and PE were pyrolyzed individually in the temperature range of 550 °C and 600 °C, respectively. A mixture of feedstock with SP to PE ratio of 1:1 was pyrolyzed. The pyrolysis experiment was repeated three times to ensure the reproducibility. The features and codes of the samples and elementary analysis results were given in Table 3 and Table 4.

Table 3. Test samples features and codes

Sample number	Char code	Liquid code	Gases code	Content	Pyrolysis temp. (°C)	Heating Rate (°C/min)	Pyrolysis Time (hour)
N1	C1	L1	G1	40 g SP	550	5	2
N2	C2	L2	G2	40 g PE	550	5	2
N3	C3	L3	G3	20 g SP + 20 g PE	550	5	2
N4	C4	L4	G4	40 g SP	600	5	2
N5	C5	L5	G5	40 g PE	600	5	2
N6	C6	L6	G6	20 g SP + 20 g PE	600	5	2

Table 4. Elementary Analysis and properties of samples.

Material	Elementary Analysis (%) (w)					Humidity per. (%)	Volatile material (%)	Ash (%)	Thermal Value (kcal/kg)
	C%	H%	O%	S%	N%				
Sawmill powder	45.77	6.69	44.49	-	3.05	26.20	72,50	5,40	3445,44
Polyethylene	75.93	12.19	11.88	-	-	3.80	88,20	1,30	9282,76

To determine average pyrolysis rate of pre-pyrolysis materials, the average thermal value is determined, it is first calculated by using the upper thermal value Vondrake equation and the lower thermal value by using Kollmann equation. The data in Table 5 is used to calculate the upper and lower values. The average of these two values reveals the average thermal value.

$$\text{Vondrake Equation: } H_{upper} = [8100 \% C + 34000 (\% H - (\% O)/8) + 2500 \% S] \quad (\text{kcal/kg})$$

$$\text{Kollmann Equation: } H_{lower} = 1/(1+u) [H_{upper} - 600 (u + 9 \% H)] \quad (\text{kcal/kg})$$

$$H_{ave} = (H_{upper} + H_{lower})/2$$

H_{upper} : upper thermal value (kcal/kg)

H_{lower} : Lower thermal value (kcal/kg)

H_{average} = average thermal value (kcal/kg)

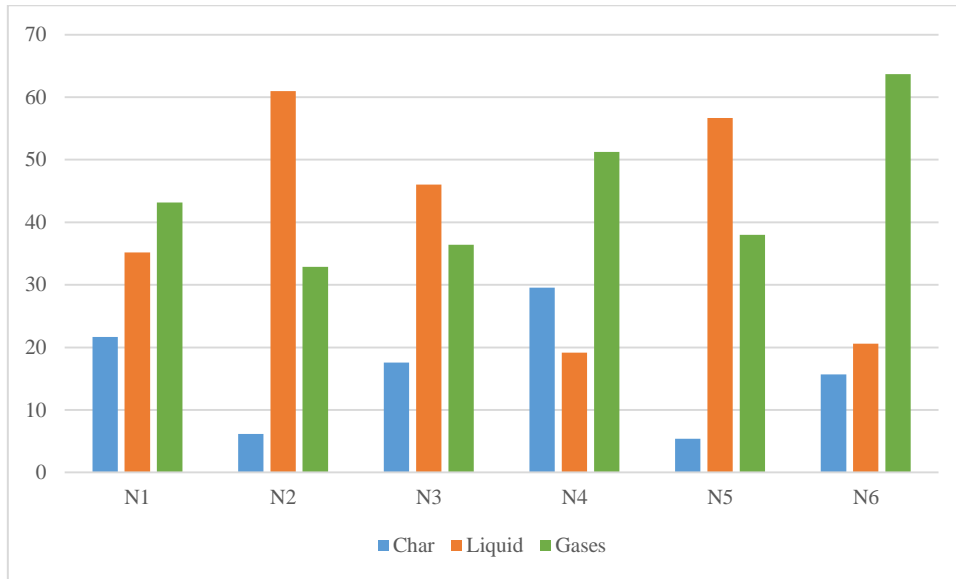


Figure 1. Effect of plastic waste on pyrolysis yield

The yield of pyrolysis products is shown in Fig. 1. From this figure, as the temperature increased from 550 °C to 600 °C, the yield of liquid product increased and reached to a maximum value of 61,00% and 46.05% for polyethylene and the mixture of polyethylene and sawmills powder at 550 °C. Several other studies have also reported similar observations stating that at this temperature strong cracking reaction takes place and secondary decomposition of char residue occurs since it maximizes the liquid yield. The gas yield increased over the whole temperature range, which is probably due to further decomposition of some small-chain liquid components into non-condensable gases. Several studies have reported that high temperatures, low heating rate and longer residence time favor the formation of more gaseous product. Also, decrease in the yield of char was observed with increasing temperature, which may be due to secondary reactions occurring at high temperatures. The result confirmed that the optimum temperature for the pyrolysis of PE is 550 °C as it maximized the yield of liquid product. Co-pyrolysis of SP: PE mixture was carried out at 550 °C and 600 °C with 1:1 with the aim of improving quality and quantity of pyrolysis oil. The result of the co-pyrolysis of SP: PE is shown in Fig. 2. All the experiments were performed in the absence of any catalyst, solvents or pressure.

Table 5. The calorific values of the liquid products obtained after pyrolysis (kcal/kg)

Char code	Lower heat value (kcal/kg)	Upper heat value (kcal/kg)	Average heat value (kcal/kg)
C1	296.06	8714.83	4505.44
C2	1937.09	10085.65	6011.37
C3	610.12	10504.12	5557.12
C4	25.40	7469.31	3862.35
C5	2026.56	10535.09	6280.82
C6	588.92	10122.41	5355.67

The average calorific values calculated as the result of the elemental analysis of the liquid products obtained after the pyrolysis process are shown in Table 5. The thermal values of the obtained products for the binary mixtures show that the heat value of C3 (SP + PE) is the highest (5557.12 kcal / kg) at 550 ° C. In addition, the values of C2 (PE) 6011,37 kcal / kg at 550 ° C and 6280.82 kcal / kg at C5 (PE) at 600 ° C were found to be the highest among the liquid products obtained after the pyrolysis of the samples. It has been seen that with the increase of the temperature, the pyrolysis resulted in an increase in the thermal values of the liquid products formed for polyethylene. This contrasts with the observed state of solid products resulting from pyrolysis.

3. Results and Discussion

The present study has shown that pyrolysis of SP mixed with PE has the potential to be a suitable method for producing high-grade pyrolysis oil, which produced a high yield of 52.75% with 1:1 ratio, at an optimum temperature of 550 °C. The temperature has a major effect on the production of pyrolysis yield. Further studies are also required to investigate the reaction condition of the blend composition to improve the applicability and feasibility of co-pyrolysis, which may be favourable for various advantages in waste treatment and utilization of bioenergy. In the study conducted, the use of waste as plastic and sawmills powders has led to the prediction that this work will be an alternative method to reduce the pollutant wastes in the future.

4. Acknowledgement

This article was presented at the International Conference on Civil and Environmental Engineering (ICOCEE - Cappadocia2017). Also the authors gratefully acknowledge the administrative bodies of Ondokuz Mayıs University for supporting Project OMU-BAP PYO.MUH.1904.13.003.

5. References

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