

A review: Catalytic Pyrolysis of Municipal Plastic Waste

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Abstract

Plastics without any doubt have been proved to be the most important derivatives of fossil fuels. Besides their useful impacts on today's advanced scientific world regarding their comprehensive uses, they still are a threat to nature and the environment. In Pakistan, 2.7 million tons of annual plastic waste is generated and most of the plastic is directly burnt, releasing toxic gases like Dioxins and Furans to the ambient air. The rest of the waste is either dumped into the open atmosphere or thrown into the sea. A derivative called Bisphenol is added into the plastics to make them more supple and durable. At very high or very low temperatures the additive has the capability to leach into the atmosphere, posing serious threats to the lives. Plastics can be recycled but recycling is not feasible either economically or regarding green engineering due to higher labor costs and huge amounts of water contamination. Therefore, scientists have classified pyrolysis of plastic as an effective method of treating municipal plastic waste, ultimately producing useful fuels with high heating values (HHV). This paper has reviewed the pyrolysis of two basic types that are: Thermal Pyrolysis, Catalytic pyrolysis and the main parameters that influence the whole process. These parameters include temperature, retention time, heating rate, and feedstock composition.

Key words: Pyrolysis, Municipal waste, Combustion, Retention time

Introduction

Plastic is one of the greatest inventions of the 21st century meanwhile it is a malediction too. Due to its higher demands, the production of plastic has increased with very limiting sources of its recycling or decomposition. There existed only two ways to handle the Municipal Plastic

Waste earlier. One was to dump it into landfills and sea. Plastics on average take around 300 years on average to fully degrade as a result keeps contaminating the air on land and marine waters, exerting a carcinogenic effect. The 2nd way is to burn them in the open air, it could help get rid of the plastic, leaving a relatively lower amount of residue behind, but contaminates the atmosphere with toxic gases as well as the microparticles of non-combusted plastics. With the passage of time, the demand for plastics is increasing due to its portability, tensile strength and lightweight. There is an immediate need to resolve the issues caused by municipal plastic waste to the environment and comprehensive steps are needed to be taken if we don't want Plastic to ruin our natural atmosphere and environment.

Karachi is the 8th largest city in the world, and the largest of Pakistan with a population of around 22 million people, covering an area of around 3780 km².

Karachi is a mega-giant when it comes to businesses and industries but along with comes the great challenge of disposing-off large amounts of plastics. The estimated production of municipal waste of Karachi is ranged near 12000 TPD. The rate of collection is around only 35-45% which is disposed-off to landfills while the rest 55-65% remains uncollected on open space, streets, and vacant plots. In this waste around 10.8% is estimated to be plastic and its derivative related waste. Causing a disrupt in a natural environment and way of living and promoting various diseases. [1]. With our project we can help the government (especially of Karachi) go get rid of the plastic waste and convert it into combustible fuels in an economically profitable way.

Methods of waste Handling

I. Incineration (combustion)

A few methods have been developed for the removal of plastic waste. Incineration is one of them in which combustion i.e. burning in the presence of oxygen takes place [2]. From incineration, the municipal solid waste or plastic waste may generate energy that could be used for industrial purposes such as electricity generation [3].

Highlight

- It's a combustion of plastic waste for the generation of heat.
- It produces carbon dioxide, carbon monoxide, NO_x & SO_x.

II. Gasification

Solid waste may also be reduced through gasification with a moderate amount of energy supply to produce “syngas” which has a high heating value [4]. It is a demanding process for the industry but is not economic and environmentally friendly.

Highlight

- The controlled amount of oxygen is to be supplied for the process.
- Controlling of process is difficult as compare to other methods.

III. Pyrolysis

It is the conversion of municipal solid waste or biomass into the pyrolytic oil (bio-fuel), coke, and gaseous fractions by heating the municipal solid waste in an oxygen-free environment [5]. This paper mainly focuses on the process of pyrolysis and the discussions about the variation in product distribution caused because of usage of different catalysts, heating rates, temperatures, and compositions.

Highlight

- Pyrolysis is the cracking of long chains of hydrocarbons into shorter chains in the absence of oxygen.
- Catalysts can increase the cracking reactions, but we require the discovery or maybe manufacturing of a suitable catalyst for a better optimization.

Factors Affecting Pyrolysis Process

I. Retention time

Moving on to the most important factors involved in pyrolysis, we've studied the critical effects of each one of them in detail and then tried to present them in a more comparative way for a better understanding. It is very much crucial to understand the close relation of these factors with pyrolysis. Since it was observed that both retention-time and temperature play an important role in the product distribution. The data observed for different reaction times and temperature from a study is given in the following table. Since in the following observation we limit our analysis to these two factors only provided the fact that an overall combination of all the factors can influence each other but the general trend of each individual factor would be the same as mentioned here.

However, a better understanding of all the factors individually could lead to better optimization of these factors collectively.

Table 1 Different composition produced in different retention time

Temperature (F)	Time (min)	Max. observed pressure (atm)	Distribution of Product (wt-fraction)		
			Gas	Pyrolytic Oil	Solid
703	15	0.98	0.087	0.903	0.01
	37.5	5.42	0.142	0.848	0.01
	60	5.78	0.189	0.801	0.01
733	15	9.37	0.191	0.799	0.01
	37.5	15.54	0.388	0.595	0.017
	60	15.75	0.464	0.507	0.029
763	15	20.62	0.593	0.374	0.033
	37.5	18.93	0.606	0.345	0.049
	60	17.54	0.669	0.266	0.065

It was observed that the most desirable product distribution was attained at a temperature of 430°C with a reaction-time of 60 mins which gave around 80.1% of Pyrolytic Oil and 18.9% of Gases with 1% of Carbonaceous Residue, and also at a temperature of 460°C and reaction-time of 15 mins where 79.9% of Pyrolytic Oil, around 19.1% of Gases, and almost 1% of Carbonaceous residue was obtained [6].

Highlights

- By increasing the Retention time, the yield of gaseous products is increased.
- Optimization of retention-time to minimum values could play a vital role for efficient consumption of fuel in furnace and in the production of liquid oil.

II. Feedstock composition

Feedstock composition is important in predicting the product composition. An individual type of plastic can yield specific products (fixed percentage compositions of liquid oil, gases, and solid residues). However, when charged with a mixed composition, the overall yield can be changed. Rashid Miandad et al. executed pyrolysis of municipal plastics of different types namely PE, PS,

PP, and PET as these are the prime source of plastic used in daily life products including bottles, shopping bags, packaging materials, disposable glasses, etc. The reaction was carried out in a batch of 1000gm of plastic at a time, where Natural Zeolite (Acid Activated (AA)/Temperature Activated (TA)) was used as a catalyst in the ratio of 1:10 for every batch of plastic feed. Optimum temperatures were taken as 450°C with a heating rate of 10 °C/min. Different compositions of the above-mentioned types of plastics were used for each individual test, which is given as follows [7] :

Table 2: Different Feedstocks with Catalyst

Feedstock type	Feedstock quantity (kg)	Catalyst Quantity (kg)	Feedstock Ratio (%)
PS	1	0.1	100
PE	1	0.1	100
PP	1	0.1	100
PS/PE	1	0.1	50/50
PS/PP	1	0.1	50/50
PP/PE	1	0.1	50/50
PS/PP/PE	1	0.1	50/25/25
PS/PP/PE/PET	1	0.1	40/20/20/20

These tests were carried out in a pilot-scale reactor with a capacity of 20L and having a maximum safe working temperature of around 600°C. The characterization of the obtained PO was made by GC-MS, TGA, and Bomb Calorimeter.

Each type of plastics was analyzed individually and the following rate of decrease in weight was seen on TGA analysis with the increase in temperature at a rate of 10 °C/ min [7].

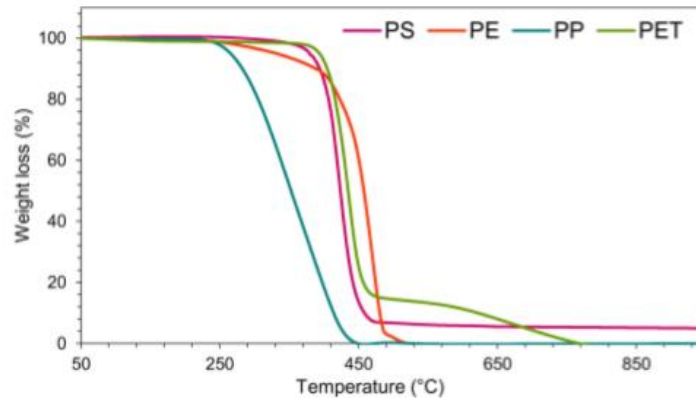


Figure 1: Thermogravimetric Analysis (TGA) of PS, PE PP, and PET plastic waste.

The degradation of plastic took place in two steps. First, as the temperature reached around 385°C a steep decline in weight was observed. The 2nd decline was observed at around 550°C where around 95% of plastic was degraded. PE & PET contain volatile impurities such as filler which can cause the initial degradation of these plastics. The degradation temperature of these plastics is high because of the presence of a long-chained branched structure in PE. The degradation occurred as a random chain scission [8]. But for PET, the degradation was carried out by the formation of Oligomers because of ester-linked random scission [9].

The yields for each of the mentioned sample were analyzed individually and in a mixed composition, and the following data was obtained [7]:

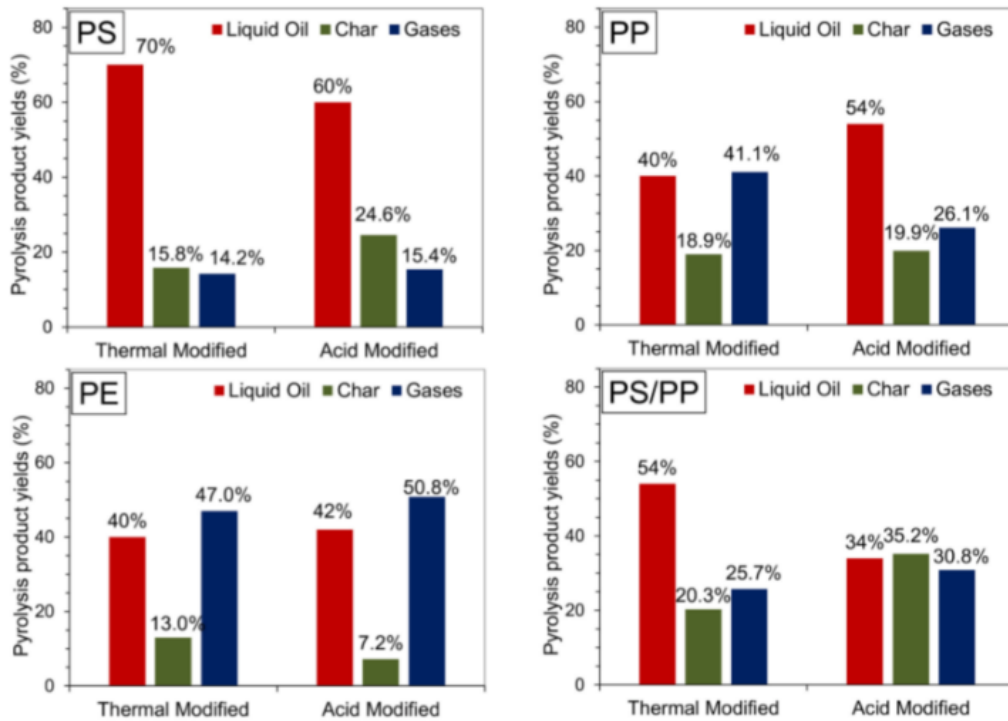


Figure 2: Percentages of Product in different feedstock composition (PS,PP,PE,PS/PP)

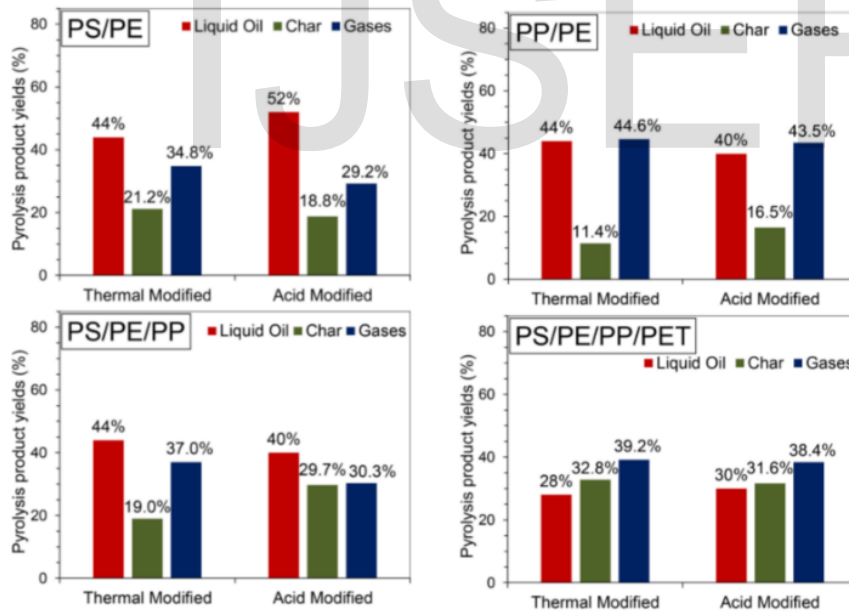


Figure 3: Percentages of Product in different feedstock (PS/PE,PP/PE,PS/PE/PP, PS/PE/PP/PET)

Since the results clearly indicate that the yield of Pyrolytic Oil varies with the different arrangements as well as the compositions of plastics. As the most favorable results were obtained

by the distinct pyrolysis of PS sample which gave around 70% of Pyrolytic Oil, 14.2% of Gases, including 15.8% Char in presence of Natural Zeolite (TA) and around 60% Pyrolytic Oil, 15.4% Gases including 24.6% Char in presence of Natural Zeolite (AA). On the other hand, the least favorable results were obtained by the sample containing PS/PE/PET/PP around 28% Pyrolytic Oils and 39.2% gases while producing around 32.8% of Char in presence of Natural Zeolite (TA), while around 30% PO, 31.6% Gases and 38.4% Char in presence of Natural Zeolite (AA).

Highlight

- Different feedstock has a distinct melting point, i.e., degradation temperature, so the product composition varies according to the feedstock composition.
- The catalyst can influence the product yield, provided that regeneration of catalyst is a very difficult task.

III. Moisture content

Moisture can be very detrimental in bringing the impurity to the product, and in the fuel's consumption while achieving the desired temperatures. However, we have presented here a study that would help in comprehending its undesirable effects. Quezada et al. took the plastic samples from municipal waste and performed a pyrolysis process using different retention times, temperatures, and heating rates to determine the influence of these factors on the final product distribution. The temperature presets were taken to be 450, 500, 550°C with residence time presets of 40, 80, and 120 mins, while they took the heating rates to be 20, 35, 50°C/min. The data chart is given as [10]:

Table 3: Effect on heating rate from moisture content in Feedstock

Sample	Temperature (°C)	Heating rate (°C/min)	Time (min)
P1	500	35	80
P2	550	50	120
P3	550	50	40
P4	550	20	120
P5	450	50	120
P6	550	20	40

P7	450	50	40
P8	450	20	120
P9	450	20	40
P10	550	35	80
P11	450	35	80
P12	500	50	80
P13	500	20	80
P14	500	35	120
P15	500	35	40

By the product analysis the decline in weight of 3 samples p11, p1 and p10 is given as, [10]

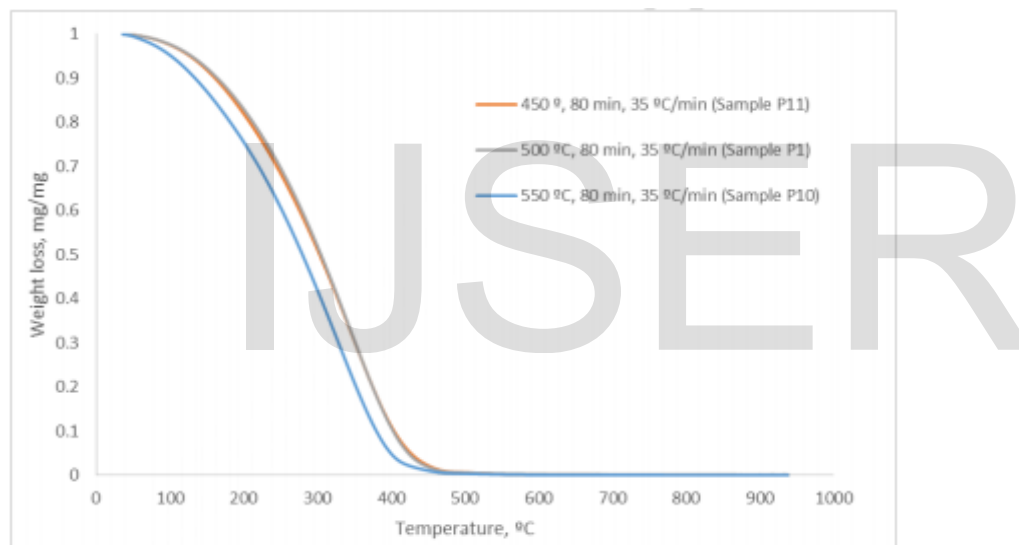


Figure 4 thermogravimetry analysis of oil (sample P11, P1 and P10)

The degradation of plastic took place in 2 stages, 1st was between temperatures of 0-100°C where the volatilization of the lighter products took place, while the 2nd stage had temperature ranges of 100-550°C where cracking took place. The product got was tested in TGA, FTIR, DSC, GC-MS and the following results were obtained [10]:

Table 4: Elementary Analysis of Feed at different percentage of moisture content in Feedstock

Sample	Elemental Analysis (fraction)	
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	Carbon (C)	Hydrogen (H)	Nitrogen (N)	Sulfur (S)	Oxygen (O)	Water content
P1	0.78	0.145	0.0004	0	0.075	0.0232
P2	0.796	0.129	0.0036	0	0.0719	0.0224
P3	0.834	0.144	0.0106	0	0.0113	0.0386
P4	0.829	0.128	0.0004	0	0.0218	0.0315
P5	0.777	0.146	0.0005	0	0.0766	0.0282
P6	0.817	0.148	0.0004	0	0.035	0.0273
P7	0.821	0.153	0.0006	0	0.0258	0.0154
P8	0.823	0.149	0.0004	0	0.0273	0.0163
P9	0.814	0.151	0.0007	0	0.0342	0.0185
P10	0.8	0.149	0.0004	0	0.0503	0.048
P11	0.814	0.151	0.0003	0	0.0349	0.0245
P12	0.828	0.151	0.0004	0	0.0212	0.0165
P13	0.819	0.149	0.0002	0	0.0316	0.0202
P14	0.807	0.152	0.0001	0	0.0417	0.0124
P15	0.827	0.138	0.0007	0	0.0338	0.0212

Highlight

We can deduce the following results by the study presented above:

- High amount of moisture consumes an outrageous amount of fuel in the furnace. Since moisture can delay the achieving of the desired temperature.
- Moisture content disturbs the purity of product because of the undesirable reactions taking place.

IV. Heating rate

We have discussed the effects of temperature and retention time in section (I) of the factors affecting the pyrolysis process. But here is an important terminology “Heating Rate” which is the amount by which we increase the temperature regarding time. It can be 10 degrees Celsius/min, 7 degrees Celsius/min, or whatever, since it depends on the observer’s ease or comfort. This heating

rate can have implications that can't be ignored. To understand this, we've again presented a study in which tests were performed.

by the students of NIT Durgapur India in which a semi-batch reactor with a capacity of 500g of sample per batch was used. A Thermogravimetric Analyzer was used to study the effect of different heating rates on mass-loss and the degradation reactions. The sample was experimented on heating rates of 5, 10, 20, and 40 °C/min to analyze the degradation behavior of plastic. Figure "a" showed the mass-loss at different heating rates while figure "b" represented the reaction rate of degradation at different heating rates.

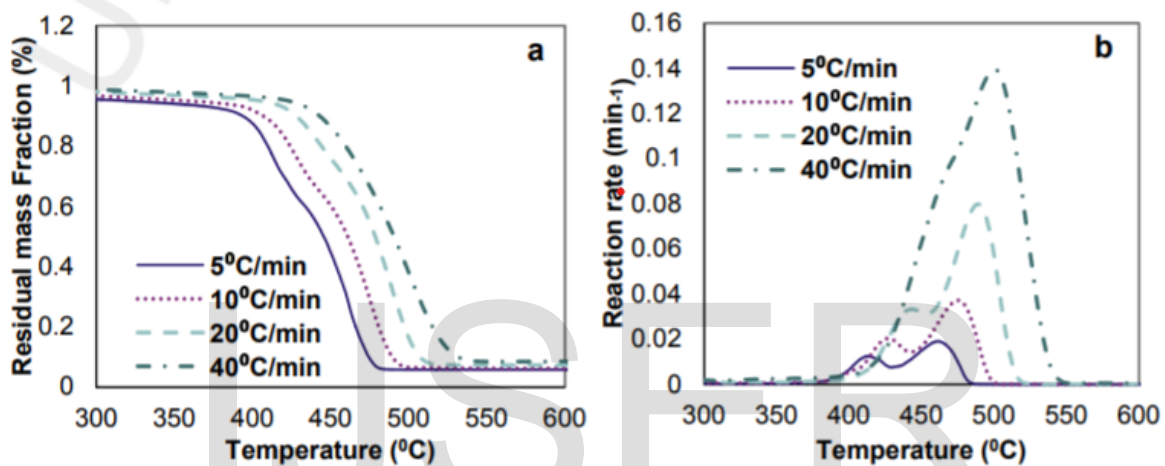


Figure 5: (a) Mass loss of Feed in different heating rate (b) Degradation rate

It can be concluded from the figures that higher heating rates decreased the reaction time which ultimately leads to the production of less residues. Heating rate also has an impact on the temperature at which decomposition of a particular type of plastic takes place which was further covered in the details of this study. However, we can limit our findings to the fact that heating rate influences the production of residues as well as degradation temperature.

Highlight

- Higher heating rates increase the temperature at which decomposition for a particular feedstock or type of plastic starts.
- At higher heating rates the residence time is less so the production of solid residues decreases.

Role of Catalyst in the pyrolysis process

So far, we have focused on the important parameters which can affect the product yields in pyrolysis, irrespective of the type of pyrolysis (Thermal or Catalytic) used. However, we can achieve better optimization regarding the temperatures at which decomposition takes place (by a reduction in fuel composition) and in terms of the product purity by using catalytic pyrolysis. In this section, we will analyze the behavior of catalyst in Pyrolysis in detail for which we have reviewed different studies found in the literature and analyzed them. A study was carried out by Mohan, A, Dutta in which untreated fly-ash was used as a catalyst in the co-pyrolysis of plastics and scrap tires. The process was run at the temperature of 300°C at the different proportions of tire and thermoplastics commonly known as polypropylene. It used a high amount of tire in the ratio of reactant like 40%-60% at 500°C at the normal pressure. The batch reactor was used for this experiment. Almost every time temperature was maintained at 300°C and increased by 10°C/min [11].

Since, 20wt% fly-ash (catalyst) was used that improved the quality of the oil, as compared to the thermal pyrolysis. Fly ash consists of the multi-compounds like oxides of silica, alumina, iron, aluminum, magnesium, and calcium [11].

On the other hand a similar study showed that if activated carbon was used as a catalyst, it promoted the aromatization reactions because of its strong acidity, large pore volume, and a low percentage of micropores also resulting in the production of high-quality hydrocarbons, as shown in the following table [12]:

Table 5: Product composition at different ratio of Activated Carbon Catalyst

Commercial Activated Carbons (CAC) type						
Products yields (wt%)	CAC 1	CAC 2	CAC 3	CAC 4	CAC 5	CAC 6
Liquid	73.1	70.4	61.6	64.7	65.1	66.5
Gas	24	25.5	25.9	29.7	29.5	30.0
Coke	2.9	2.5	2.5	4.6	5.4	3.5

Another study was carried out by Yayun & Dangle in which they converted Low-Density Polyethylene into the Jet fuel with the use of activated carbon as a catalyst. They observed the overall process parameters and their effects on the product yield by using different catalyst to

reactant ratios. The table given below shows the distribution of product yield. ‘The catalyst to reactant ratio’ and ‘the catalytic temperature’ were the independent quantities. In this study, the temperature was kept between 430 to 570°C and a mass ratio of activated carbons to LDPE were 0.6 to 2.71 [13].

Table 6: test run at different parameters

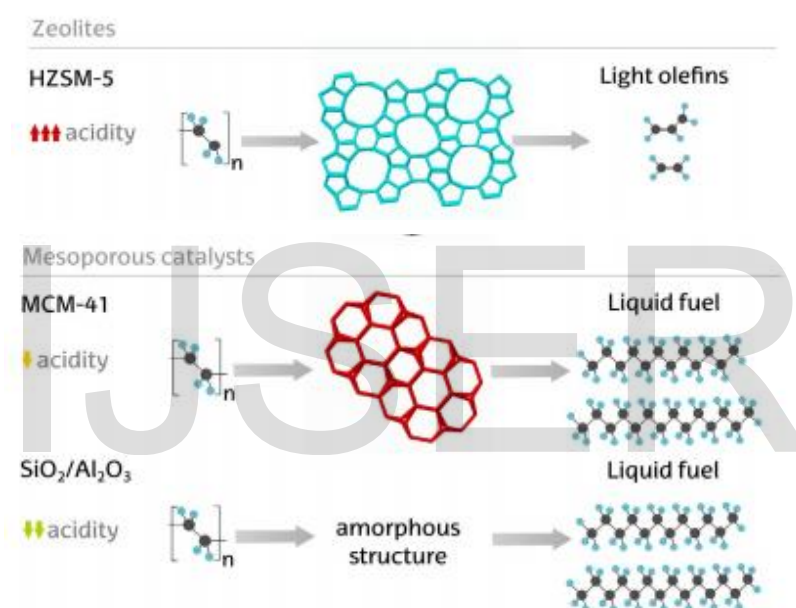
Run	Catalytic temperature (°C)	Catalyst/reactant mass ratio	Yield (wt fraction)		
			Liquid	Gas	Coke
R-1	703	2	0.43	0.109	0.461
R-2	723	2.5	0.385	0.122	0.493
R-3	723	1.5	0.515	0.11	0.375
R-4	773	2	0.708	0.253	0.039
R-5	773	2.71	0.711	0.247	0.042
R-6	773	2	0.725	0.235	0.04
R-7	773	2	0.72	0.237	0.043
R-8	773	2	0.715	0.245	0.04
R-9	773	2	0.711	0.248	0.041
R-10	773	1.3	0.73	0.238	0.032
R-11	823	1.5	0.644	0.333	0.023
R-12	823	2.5	0.581	0.388	0.031
R-13	844	2	0.54	0.448	0.012
	773	Without Catalyst	0.905	0.095	-

The use of activated carbon in pyrolysis produced a maximum yield of (44.8wt%) of the gaseous product at a temperature of 571°C. In this set of parameters, the production of solid residue was considered to be almost zero, due to the complete decomposing of the solid at the current pyrolysis temperature. However, we can't ignore the fact that 571 °C was comparatively a high temperature. Since the production of solid residue in the catalytic process can influence the catalyst's performance and also makes it difficult to regenerate the catalyst [12].

Goertzen and Maite have discussed some catalysts in their review paper interpreting that different catalysts comprise unique structures and properties. Among those catalysts, zeolite is the most reliable one because of its rich acidic site, unique and uniform porous structure and produces low carbon chain products. It gives the liquid fuel instead of the non-condensable gaseous fuel, since the most valuable product in pyrolysis is liquid [14].

Figure 6 Main products obtain form polyolefins on different acid catalyst.

The economic feasibility is also a concern when we talk about pyrolysis. There are some less costly catalysts being discussed previously. But when choosing the catalyst, we should keep



the desired product composition in mind. Supattra & Andrew used a cheap catalyst (bentonite) for the catalytic pyrolysis of waste plastic. The bentonite made the process economical. It has the same composition compared to kaolin and Red Mud.

The chemical compositions of kaolin were Al₂O₃ 46.07 wt%, SiO₂ 43.12 wt%, TiO₂ 0.74 wt%, CaO 0.03 wt% while red mud had Fe₂O₃ 36.5 wt%, Al₂O₃ 23.8 wt%, TiO₂ 13.5 wt%, SiO₂ 8.5 wt%, CaO 5.3 wt%, Na₂O 1.8 wt%. so, the ratio of SiO₂/Al₂O₃ gives information about the acidity of the catalyst. It easily predicts the acidic nature of the bentonite catalyst. The total pore volume of the bentonite clay catalyst is 0.13 cm³, and the BET surface area is found to be 47 m²/g [15].

The results of their study as shown in the following table indicated that the increased percentage of catalyst, didn't influence the yield of oil to a great extent but it increased the calorific value of the oil.

Table 7: Liquid Quality at different Feedstock

Plastic	Catalyst to plastic ratio (by weight)	Oil yield (wt%)	Calorific value (kJ/kg)	Density (g/cm ³)	Viscosity (cP)	Flash point (°C)	Pour point (°C)	Reference
Without Catalyst								
PS	-	86.4	43550	0.855	2.0	48	19	[15]
PP	-	89.5	43695	0.905	2.3	40	15	
LDPE	-	85.6	43390	0.911	2.5	45	24	
HDPE	-	86.9	43646	0.916	2.5	50	24	
With Catalyst (5 wt%)								
PS	0.05	88.5	44547	0.843	1.8	51.2	17	[15]
PP	0.05	90.2	44659	0.906	2.0	44	15	
LDPE	0.05	86.6	44121	0.905	2.0	57	21	
HDPE	0.05	88.7	44191	0.910	2.5	59	24	
With Catalyst (20 wt%)								
PS	0.2	88.2	44769	0.842				[15]
PP	0.2	89.9	44896	0.904				
LDPE	0.2	87.6	44436	0.893				
HDPE	0.2	88.7	44750	0.901				

Xiaona & Zhang conducted pyrolysis of Wood Polypropylene (WPP) and Polypropylene (PP) at 600°C, maintained for 60 seconds at 600°C using GC-MS. The main components detected in GC-MS from the pyrolysis of PP were branched aliphatic hydrocarbons (range from C₅ to C₃₁). But if the process was carried out without any catalyst, the products of WPP contained oxygenated compounds, where the oxygen was the part of compounds that helped in the complete combustion in the engine and its products had less soot [16].

At the same parameters of pyrolysis, the PP products were aliphatic hydrocarbons, like the straight-chain, branched and unsaturated. As compared to WPP, PP had slow pyrolysis feedstocks, and the presence of PP also decreased the contents of oxygenated compounds [16].

Kaltume & Mohamad Anas Nahil conducted an experiment without any catalyst, producing liquid products of 70 wt% and a gas yield of 21 wt%. But the introduction of the Y-zeolite catalyst in the pyrolysis of plastic increased the yield of gas to 36 wt% and accordingly the yield of oil was decreased. However, there were no deposits of carbon on the catalyst [17].

After that experiment, they used the composition of catalysts like Ni-Y-zeolite, Mo-Y-zeolite, Fe-Y-zeolite, Ga-Y-zeolite, Ru-Y-zeolite, and Co-Y-zeolite and found different results which are presented in the following table [17].

Table 8: Product wt% produce at different catalyst

	Pyrolysis	Y-zeolite (5 wt%)	Ni-Y-zeolite (5 wt%)	Mo-Y-zeolite (5 wt%)	Fe-Y-zeolite (5 wt%)	Ga-Y-zeolite (5 wt%)	Ru-Y-zeolite (5 wt%)	Co-Y-zeolite (5 wt%)
Gas yield (wt%)	21	36	36	36	38	37	31	40
Oil yield (wt%)	69	45	43	35	30	29	43	30
Carbon (wt%)	-	10	18	20	22	24	20	26

Since we have reviewed an adequate number of catalysts and now, it is possible for us to present the conclusion of our study regarding this section. So, we have categorized our findings as a table given below to make it easy for analysis.

Table 9: Mixture of feedstock with different ratio of Catalyst

Material	Type of Catalyst	Amount of Catalyst (wt%)	Temperature °C	Gas wt%	Liquid wt%	Solid wt%	Reference
Low-Density Polyethylene	Without catalyst	-	500	9.5	90.5	-	[13]
Tire Polypropylene	+ Activated Carbon 1	20	500	24	73.1	2.9	[12]
Tire Polypropylene	+ Activated Carbon 2	20	500	30.0	66.5	3.5	[12]

HDPE	CuCO ₃		390	14.7	85.0		[18]
Mix	Ni-Y-zeolite	5		36	45	10	[17]
HDPE	Bentonite	20			88.7		[15]
PP	Bentonite	20			89.9		[15]
PE	Ultra-Stable Zeolite Y	50	450	26.8 wt%	71.0 wt%		[19]

Highlight

- Catalysts are used for the optimization of process.
- Catalysts help in reducing the consumption of fuel as they tend to decrease the decomposition temperature.
- Regeneration of catalyst is a difficult task for the process of pyrolysis.

Analysis of Products in Catalytic Pyrolysis

I. Pyrolytic Gas fuel

We cannot neglect the importance of the production of gases in the pyrolysis of plastic. Since the gases produced have a high heating value (HHV), which can be exploited for the generation of power. These gases can also serve as energy inputs to make the process more economical and self-sustainable.

An experimental study on fuel gas generation by the pyrolysis of plastic was conducted in Durgapur, India [20]. The plastic used for pyrolysis was taken according to the proportions as 58.8% Polyethylene which comprised both HDPE and LDPE, 26.9% PP, 8.7% PS, and 5.6% PET. The reaction was carried out in a single step batch-reactor with a sample mass of 200 g. They analyzed that increasing the temperature had increased the yield of gas. The gases obtained were hydrogen, methane, propane, and n-butane. The percentage of gases as per the weight percent of the feed introduced was obtained to be 10-15% at a reactor temperature between 450-600°C. Since the analysis of the products obtained by the pyrolysis of plastic reveals the production of oil, char, and gases but because of the low residence time at a higher temperature, the cracking occurs rapidly, resulting in the decreased yield of oil with an increased amount of the production of gases [21]. An increased temperature during the pyrolysis of PS favors the secondary reactions (which may involve the cracking of propane and butane) to occur resulting in the production of gaseous components up to 13.7 wt% at 600°C [22].

A study carried out regarding the waste plastic treatment in Indonesia [23] suggested that the pyrolysis of polyethylene bags collected from the waste deposits can have impurities like moisture and biomass along with them which could enhance the yield of gaseous products along with the production of solid residue. However, pre-treatment of the plastic can minimize those factors. Various studies which have been carried out so far, suggest that certain parameters including temperature, pressure, types of reactors used, catalyst and retention time influence the type of products yield. One can optimize these parameters and manipulate them to get the desired yield [24].

Highlight

- The range of hydrocarbons in gaseous products was mostly of Methane and LPG.
- We can use these gases in the furnace to make pyrolysis more economical.

II. Pyrolytic Oli

With the growing consumption of fossil fuels, it has been an important task for us to find some alternate energy resources. The standing of liquid oil as a fuel cannot be abandoned. The excess product yield in the pyrolysis is of liquid oil and in cases of gases which can be further optimized and shifted towards the desired side by bringing in more innovations in the process. In a study conducted in KSA [25], majority of the household plastic waste was used for the pyrolysis which included, PS, HDPE, LDPE, PP, and PET. The experiments were conducted in a small pilot-scale pyrolysis reactor with a maximum heating temperature up to 450°C and a retention time of 75 minutes. The feedstock consisted of individual components as well as a mixture. The following results were obtained.

Table 10: Product fraction at variety of feedstock

Feedstock Types	Liquid oil (fraction)	Gases (fraction)	Char (fraction)	Wax (fraction)
PS	0.808	0.13	0.062	--
PP	0.42	0.545	0.035	--
PE	-	0.62	0.13	0.25
PS/PP	0.25	0.699	0.051	--
PS/PE	0.54	0.383	0.077	--
PP/PE	0.24	0.512	0.248	--
PS/PP/PE	0.49	0.471	0.039	--

PS/PP/PE/PET	0.4	0.42	0.18	--
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The maximum yield of the liquid oil as shown above, was obtained by the individual pyrolysis of polystyrene, which if used with other types of plastics in different ratios can alter the overall yield.

We have already discussed how an increased temperature decreases the yield of liquid oil by favoring the secondary reactions to occur. However, the use of different catalysts can increase the amount as well as the quality of liquid oil obtained. Since the accessibility of the catalyst allows the decomposition and cracking of the long-chain polymers which increases the volume of condensable gases in the product ultimately increasing the amount of liquid oil [15]. Catalysts can serve both the causes, to minimize the heat input and to enhance the quality of liquid oil by post-treatment [26]. For an instance, zeolite as catalyst has the capability of adsorbing certain impurities and heavy hydrocarbon molecules to enhance the quality of liquid oil [27]. Another study on reverse engineering of plastic wastes [28] was conducted which showed that in the presence of silica-alumina as catalyst increased the gaseous fractions in the product and the liquid oil yield is maximum in thermal pyrolysis using a batch-reactor which occurs at higher temperatures.

The retention time also affects the vintage of liquid oil depending upon the instance at which it is elevated respective of the temperature on which the process is going on. If the residence times are kept between 1 hour to 2 hours, the yield of liquid oil could be maximized. And on further increasing the residence time the yield of liquid oil is lowered [29].

Highlight

- The liquid pyrolytic oil may contain C₇ to C₂₀ hydrocarbons, mainly saturated chain.
- The aromatic hydrocarbons can also be produced but the percentage of aromaticity vary by using different catalysts.

III. Solid Fuel

The definitive aim of pyrolysis is to produce valuable products that can serve an alternate source to fuel. Still, wax and sometimes the char is also produced during the pyrolysis of plastic. It doesn't mean that these products have no importance, as they are used for several purposes. The production of either wax or char depends upon the retention time, type of process, types of reactors and temperature [30]. Char has the capability to serve as an energy source and is used as an adsorbent in wastewater conduct. [31]. The calculated calorific value of char obtained by the

pyrolysis of HDPE was found to be 4500 Cal/g which can generate an evaporation rate of 1.04kg/h in the water [32].

Yuan Xue and Patrick Johnston [33] conducted experiments by using a Tandem micro-pyrolizer which comprised of two furnaces 5 cm apart from each other, each having the capability of making a temperature up to 900°C. A very small amount of the feedstock, about 250 micrograms of PE was premixed with 250 micrograms of PET or PS. Then the feed was injected into the first furnace. The vapors were transmitted to the downstream catalyst-bed which exited through the second furnace. He or hydrogen was used as carrier gas which minimized the residence time of pyrolysis vapor less than 1 second. The final analysis of the experiment showed that an amount of 15.86% of carbon as a solid residue was obtained.

Highlight

- The solid carbon is accumulated in the bottom of reactor. It mainly contains carbonaceous content.
- We can vary the amount of solid residue by changing the operating parameters or by catalytic cracking.

Challenges and Prospects

Although pyrolysis is a green engineering process, there are still some challenges that require more research to be carried out to further bring the process into workable ranges.

In thermal pyrolysis, the oil obtained is crude, which needs refining, ultimately increasing the total cost for the final product. For catalytic pyrolysis, the cost of the catalyst is usually very high. So, there is an immediate need for cost-effective catalysts to be discovered or invented. The catalysts used are difficult or sometimes impossible to regenerate in a simple batch-reactor. The ores of metals like Bornite, Magnetite, and Hematite may be used as a catalyst.

If the desired product is liquid oil, then an increased residence time to a certain limit is needed, which increases the amount of heat duty, consequently making the entire process less economical. However, the process can be made self-sustainable by bringing into use the produced gases through

pyrolysis as a fuel. We may also reduce the residence time by decreasing the pressure of the reactor.

Conclusion

The aim of this review is the observation of different products yield by the pyrolysis of different plastic in municipal waste under different conditions such as variation in pyrolytic temperature, retention time, heating rate, change in composition, and effects of different catalyst on the product. The challenge was to find out a way to maximize the pyrolytic oil yield while lowering the carbonaceous residue. We found out that in terms of pyrolytic temperature the most desirable results were achieved at 430 °C with PS while using Natural Zeolite as a catalyst, producing around 70% PO while 14.2% gases and rest of the carbonaceous residue [7]. While in terms of retention time the most desirable results were achieved at 15min at 430 °C for pyrolysis of HDPE with a yield of around 90% pyrolytic oil and 8.7% gases and rest of carbonaceous residue [6]. In terms of catalyst usage, the most desirable product distribution was obtained by the pyrolysis of HPDE in presence of CuCO_3 as catalyst yielding around 85% Pyrolytic Oil and also with Pyrolysis of PP in presence of red mud and kaolin (5wt%) producing around 90.2% Pyrolytic Oil. If we discuss bentonite, the yield of pyrolytic oil (liquid fuel) has slightly increased its composition that is beneficial for excellent fuel. But the use of catalyst results in an increased flash point, which is not desirable. And the overall efficiency of the catalyst is lower than compared to the other economical catalysts like activated carbon and fly ash.

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