

EXPERIMENTAL INVESTIGATION ON THE THERMO-CATALYTIC PYROLYSIS OF POLYPROPYLENE PLASTIC WASTE FOR PRODUCTION OF FUEL

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Abstract: Fuel obtained from waste plastics by pyrolysis method is a prospective way to decline the dependence on non-renewable resources and to meet environmental concern. The present work is focused on the thermo-catalytic pyrolysis of waste polypropylene plastic to produce fuel in a lab scale batch reactor. The plastics were pyrolyzed at 350 – 450 °C, with catalyst (Alumina and Zinc oxide) and without catalyst, to obtain liquid fuel and to observe the effect of critical factors such as temperature, reaction time, and catalyst. The maximum liquid fuel yield was found 60 wt. % at 450 °C in the absence of catalyst and 58 wt. % at 450 °C in the presence of catalyst. The physical properties and the quality of fuel obtained by both thermal and catalytic pyrolysis were measured and found to be very close to ideal values of commercial fuel oil.

Keywords: Pyrolysis, Fuel, Waste plastics, Physical properties, and Catalyst.

1. INTRODUCTION

In recent years, Industrial development and population growth have led to an escalation in the global demand for energy. Without the saving of fossil energy, the present rate of economic growth is unsustainable. According to International Energy Outlook 2016, the world consumption of liquid and petroleum product goes from 90 million barrel per day in 2012 to 100 million barrel per day in 2040 [1]. Effects of fossil fuel emissions on the environment and concerns about energy security proliferated the use of nonfossil renewable energy sources. The quality of human lives has improved due to the invention of plastics. But the environmental problem arises as plastic waste are not presently biodegradable. The predominant source of post-consumer plastic waste is local sourced including household, markets, small commercial establishments, hotels, and hospitals. According to the World Bank, plastic waste accounted for 8-12% of total MSW generated and it is estimated that plastic waste generation will increase to 9-13% of total MSW in 2025 [2]. In Bangladesh, total 3, 36,000 tons/year plastic wastes are available for recycling. Among them Unsoiled (30%) 1, 34,400 tons/year and Soiled (30%) 2, 01,600 tons/year. From Soiled and unsoiled, 2, 33,202 tons/year plastics are available for recycle (the percentage of recycled about 69%).

Rest of them is thrown into the landfill [3]. With improved recycling, Bangladesh can save US\$ 801 million every year [4]. Plastic waste management follows the ensuing order to mitigate the environmental impact: waste minimization, reuse, recycling, energy recovery, and landfilling [5]. Recycling processes are categorized into four types, namely primary recycling (in-plant recycling), secondary recycling (mechanical recycling), tertiary recycling (chemical recycling or thermolysis), as well as quaternary recycling (energy recovery) [6]. However, each of these methods has its limitations and can be adopted for different purposes to a certain extent. Among them, chemical recycling or thermolysis (pyrolysis) can provide a solution to the energy crisis [7]. Pyrolysis is a thermal cracking reaction of the large molecular weight polymer carbon chains under an oxygen-free environment and produces small molecular weight molecules [8]. However, there are certain limitations in the conventional thermal pyrolysis, where the whole process is temperature-dependent [9]. The quality of liquid oil produced from thermal pyrolysis is low, and it may contain impurities like residues, chlorine, and sulfur [10]. To resolve these issues, catalytic pyrolysis of plastic waste has emerged with the use of a catalyst. A range of catalysts have been utilized, including Red Mud, ZSM-5 [11], FCC [12], HZSM-5 [13], Y-Zeolite [14], Fe₂O₃

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[15], Al₂O₃, Ca(OH)₂ [16], Natural zeolite [17] and Silica-Alumina [18] in catalytic pyrolysis to improve the quality of liquid fuel.

The materials to be tested in this study is PP which account for 23% of the total plastics demand in the world. It is a crystalline thermoplastic and one of the major and versatile members of the polyolefin family. Like plastic, it is used to make things like dishwasher-safe food containers, and as a fiber, it is used to make indoor-outdoor carpeting. Also, polypropylene is used in several markets, for instance, in medical bags, computer components, automotive industry, pipes, food packaging, and general containers, etc. The aim of the present work is to investigate the pyrolysis of waste polypropylene plastic in the presence and absence of Alumina and Zinc Oxide mixture as a catalyst in a designed batch reactor. The effect of Alumina and Zinc Oxide as a catalyst on the yield and quality of liquid fuel is also observed and compared with that of obtained from thermal pyrolysis. The study also includes the measurement of liquid fuel properties gained in the optimum conditions to know its suitability as a conventional fuel substitute.

2. EXPERIMENTAL SECTION

2.1 Materials

The plastic used in this study was waste polypropylene collected from the local plastic granulating shop in Sylhet. The melt flow index of the polypropylene plastic was measured, which was 17.677 g / 10 min when the applied load was 2.16 Kg and was preheated at 230°C for 5 minutes. The plastics were washed and shredded to increase the surface area in contact with the catalyst during pyrolysis. Alumina (Al₂O₃) (M.W. 101.96 g/mol, pH value 6.8-7.8) and Zinc Oxide (ZnO) mixture were used as the catalyst.

FTIR: FTIR spectra were recorded on an IR-Affinity-1S infrared spectrophotometer using KBr pellets with the resolution of 4 cm⁻¹, in the range of 400-4000 cm⁻¹ to determine the functional group in the post-consumer plastic sample. Fig. 1 indicates the FTIR of waste pp plastic taken for the experiment.

Data of peaks and the representative functional groups are shown in Table 1.

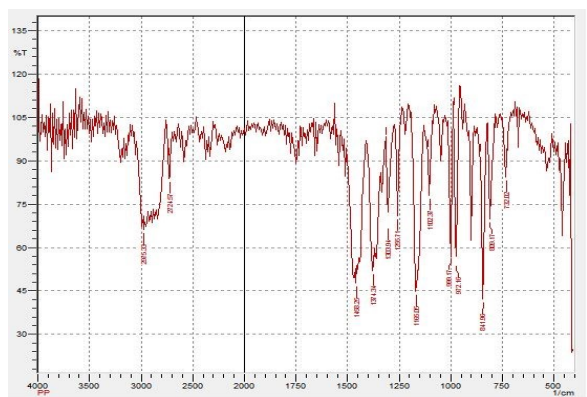


Fig. 1 FTIR of waste PP sample.

Table 1 FTIR functional group composition of Plastic

No.	Peak	Compound group
1	2975.33	Sp ³ CH stretching
2	2724.57	CH stretching
3	1458.25	CH ₂ bending
4	1374.34	CH ₃ bending
5	1303.94	CH bending
6	1255.71	C-C skeletal
7	1165.05	C-C stretching
8	1102.37	C=C stretching
9	999.17	=CH ₂ , alkene
10	972.16	=CH ₂ , alkene
11	841.96	=CH ₂ , alkene
12	809.17	=CH ₂ , alkene
13	732.02	Long chain bands

TGA: To know the thermal degradation property of the waste polypropylene sample, TGA was carried out using the thermogravimetric analyzer. TGA determines the changes in weight with the changes in temperature. The result of TGA is shown in Fig. 2. It reveals that the degradation of PP sample started at 237.35 °C, and continued degrading until it reached 392.56 °C where loss of weight was almost 97%.

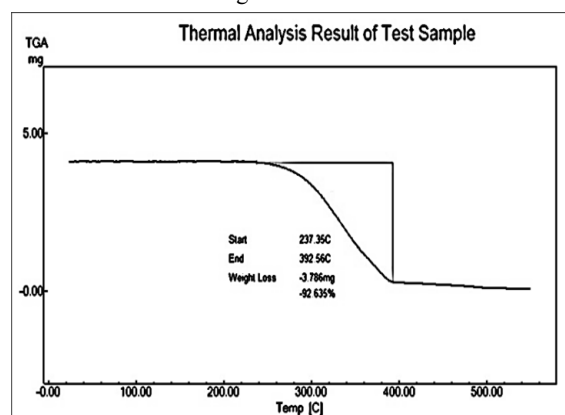


Fig. 2 TGA of PP plastic sample.

2.2 Experimental Setup

The pyrolysis setup used in this experiment is a designed batch reactor shown in Fig. 3. It consists of a reactor made of stainless steel sealed at one end and an outlet tube at another end for obtaining the products of the reaction. The stainless steel tube is heated externally by an electric furnace. A thermocouple fixed inside the reactor to measure the temperature and the temperature is controlled by an external PID controller. Stainless steel is fitted around the reactor pipe (as shown in Fig. 3) which works as a condenser. It is used to condense the fuel vapor by cooling water, circulated by a centrifugal pump. The full reactor is surrounded by a concrete chamber in order to minimize heat loss. One discharge path is used for collecting liquid.

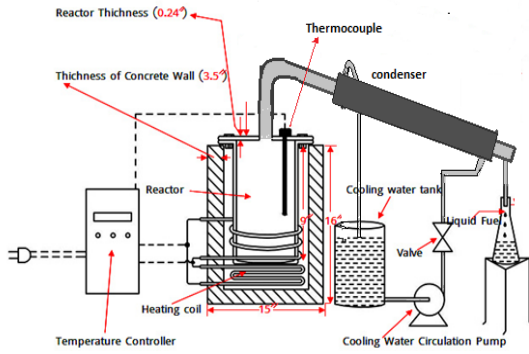


Fig. 3 Experimental setup.

2.3 Experimental Procedure

After the waste plastics being collected, these were washed to remove the impurities. Then it was dried to remove remaining water droplets. Finally, they were cut into pieces for ease of feeding the raw materials and for good heat transfer. 100 gram of solid waste plastic was weighed and then fed to the reactor. It was tightly sealed to protect the gas from leaking. The heater was then started and the reaction continued until the last drop of liquid fuel was being found in the measuring cylinder. The solid waste plastic was melted and then cracked at different temperatures in the reactor during the pyrolysis process. The gas produced is allowed to pass through the SS pipe. The gas from the pipe is directly condensed by the continuous circulation of the cooling water pump. The temperature and time were noted down when the first distillate has been seen in the measuring cylinder. The volume of fuel oil produced was also recorded with time and temperature. Every experiment was initiated with 100 gm. raw materials and heated at a temperature range of 350 °C to 450 °C.

At first, four experiments were done without using any catalyst at four different temperatures (350 °C, 400 °C, 420 °C, and 450 °C) and then, these tests were repeated using Alumina and Zinc oxide as a catalyst. The experiments were started with 100 gram of waste plastics. The percentage of catalyst used in the experiment is 4% with plastic to catalyst ratio of 2:1. The goal of this experiments was to determine the conversion rate and to determine the effect of catalyst [Alumina (Al_2O_3) and Zinc Oxide (ZnO)] by comparing the percentage of liquid, percentage of conversion, and quality of fuel obtained by catalytic pyrolysis with that of thermal pyrolysis.

3. RESULTS AND DISCUSSION

3.1 Effect of Temperature

Effect of temperature on liquid yield and conversion is given in Fig. 4 and Fig. 5. From Fig. 4 we clearly observed the effect of temperature during thermal pyrolysis. The percentage of liquid increased from 17 wt. % at 350 °C to 60 wt. % at 450 °C. The percentage of conversion also raised from 18 wt. % to 63 wt. %. So, the higher the temperature the more cracking will occur and hence gives a higher conversion and liquid yield. Again, during catalytic pyrolysis, the percentage of liquid yield

and conversion also increased with temperature as shown in Fig. 5.

It shows that as the temperature raised from 350 to 420 °C, the Conversion and liquid percentage increased which was greater than the thermal pyrolysis shown in Fig. 4, but at 450 °C the percentage was found lower than the thermal pyrolysis, which might occur due to catalyst deactivation at this temperature. At 350 °C, the percentage of liquid yield increased from 17 wt. % to 20 wt. % when we used the catalyst. Similarly, for temperatures 400 and 420 °C, Alumina and Zinc Oxide mixture as a catalyst improves the yield and conversion percentage which proves the significant effect of the catalyst.

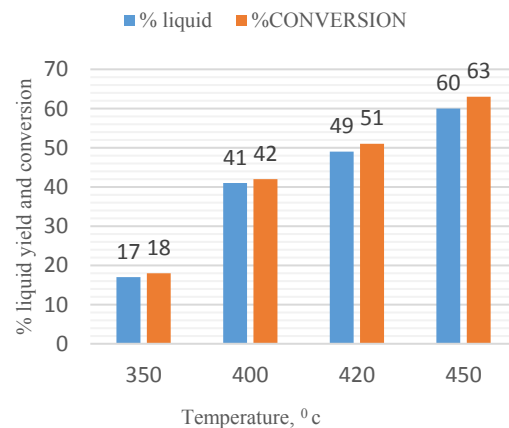


Fig. 4 Effect of temperature during thermal pyrolysis.

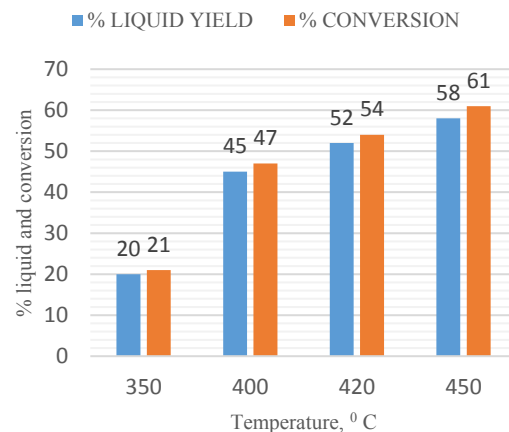


Fig. 5 Effect of temperature during catalytic pyrolysis.

3.2 Effect of Catalyst

Fig. 6 shows the effect of Alumina and ZnO catalyst at 400 °C. It is evident from the figure that the catalyst rapidly increased the percentage of liquid yield as soon as the reaction time started.

In between 21 to 70 minutes, the curve steadily increased along with the thermal pyrolysis curve. After that, the curve again rose sharply than thermal pyrolysis curve. This behavior proves the significant effect of the catalyst on the pyrolysis process of pp plastic to produce fuel.

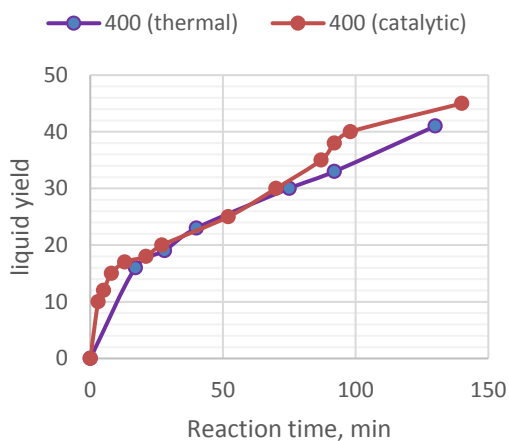


Fig. 6 Effect of catalyst at 400 °C.

3.3 Effect of Reaction Time

Effect of reaction time on liquid fuel yield was shown in Fig. 7 and 8, both for thermal and catalytic pyrolysis at four different temperatures (350 °C, 400 °C, 420 °C, and 450 °C). These figures show that as the reaction time increased more cracking occurred, and hence, more percentage of conversion of plastic occurred. The rate of liquid obtained in thermal pyrolysis (as shown in Fig. 7) raised from zero to almost 60 % as the reaction time increased from zero to 150 minutes, and for catalytic pyrolysis (as shown in Fig. 8), it increased from zero to almost 58 % as the reaction time raised from zero to 150 minutes. From the graphs, it is also seen that the cracking occurred rapidly at the very beginning but as the time proceeded the rate of cracking occurred slowly. Comparing the fuel obtained by thermal and catalytic pyrolysis, it was found that the liquid drop rate, at first 15 minutes, was higher in the catalytic process than thermal pyrolysis process. After that, the liquid fuel dropped slowly. A large amount of residue remained after pyrolysis of polypropylene plastic. This may be due to the presence of contaminants in waste plastics.

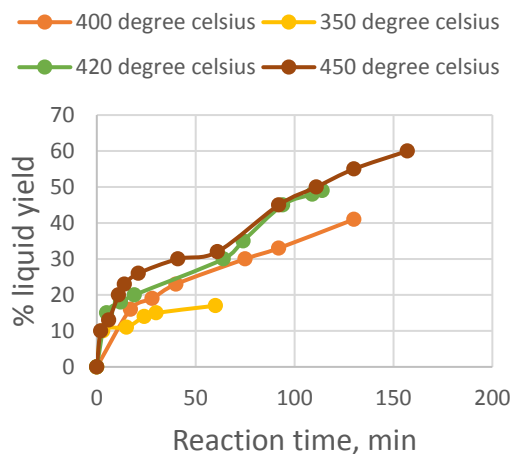


Fig. 7 Effect of reaction time during thermal pyrolysis.

It is also observed in Fig. 7 that at 350 °C, 400 °C, 420 °C, 450 °C, reaction time was 60 min, 111 min, 130 min, and 157

min respectively. After this, no drops of fuel were found. This means, as the temperature and reaction time increased, more cracking of pp plastic occurred which in the result produced more fuel after getting condensed. Similarly, Figure 8 showed a similar behavior between reaction time and liquid percentage yield. Again, we observed from the experiments that the conversion rate increased and reaction time decreased with increasing temperature.

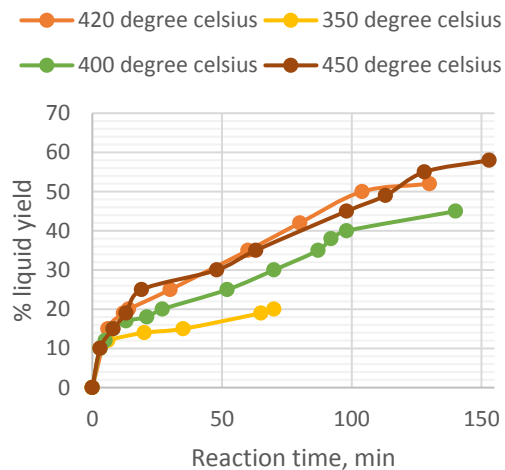


Fig. 8 Effect of reaction time during catalytic pyrolysis.

3.4 Physical Analysis

The liquid fuel obtained by both thermal and catalytic pyrolysis was analyzed by the standard method to know their physical properties. The measured properties and their comparison with the conventional fuel are shown in Table 2.

Distillation curves provide a depth of information about the petroleum fuel or crude oil. In many cases, the boiling point distribution is representative of the composition of the petroleum fraction. From the distillation result by ASTM D 86, the boiling range of the oil, obtained by thermal pyrolysis, was found 61-330 °C whereas, for oil found from catalytic pyrolysis this range is 72-311°C. This result suggests the presence of different oil components, for example, gasoline, kerosene, and diesel in the oil.

Flashpoint of the produced fuel oil was found 24 °C and 25 °C which is low enough for greater safety in handling and storage. This result also closed to the flash point of diesel oil.

Cetane number is a measure of ignitability. The more the cetane number, the greater the chance of complete combustion and the cleaner the exhaust. The cetane number of our produced fuel is 58.36 and 54.05 which is higher than the minimum value of Diesel. So, the produced fuel oil from pp plastic has better ignitability with complete combustion.

Fuel consumption, engine temperature, and load on the engine increase with Viscosity. Again, if the viscosity of the oil is too high, excessive friction may take place. The viscosity of the produced oil was measured 3.31 cSt and 1.25 cSt which is within the range of conventional diesel oil.

The density is an important property of fuel. Too low or too

high density of the fuel is not desirable. It may cause damage to the engine. The density of the produced fuel oil is within the range of density of gasoline and close to diesel density, which is suitable.

Low-temperature installations of oil are determined by pourpoint. It is the temperature at which the paraffin in the fuel has crystallized and becomes resistant to flow. Pour point of the

produced fuel were found -16°C and -28°C , which determines the least limit of flow, and it is close to the pour point of diesel. Hence, the values of physical properties measured for produced oil are very close to the traditional fuel. So, the fuel oil produced by thermo catalytic pyrolysis is convenient to use as an alternative fuel.

Table 2 Physical properties of produced fuel and comparison with traditional fuel

SL.NO	Test Name	Method	Fuel oil by Thermal Pyrolysis	Fuel oil by Catalytic Pyrolysis	Compared Value [19], [20]
1	Distillation, IBP ^o C	ASTM D86	61	72	Boiling point range: 180-360 ^o C (Diesel), 150-273 ^o C (Kerosene), 35-200 ^o C (Gasoline)
	10%		119	133	
	20%		150	150	
	30%		174	166	
	40%		195	183	
	50%		212	200	
	60%		234	218	
	70%		253	236	
	80%		273	257	
	90%		305	286	
	95%		325	306	
	EBP ^o C		330	311	
	Recovery, %vol		95.5	97.00	
	Residue, %vol		4.5	3.00	
Loss, %vol	0.00	0.00			
2	Density @ 15 ^o C, Kg/L	ASTM D 4052	0.77835	0.77720	0.72-0.78 (Gasoline) 0.8-0.89 (Diesel)
3	ASTM Color, ASTM color unit	ASTMD 1500	ASTM color < 2	ASTM color < 2	0.5-1.5 (Gasoline) 2.5-3 (Diesel)
4	RVP @ 37.8 ^o C, psi	ASTM D 323	2.5	1.3	Min. 0.2 (Diesel) 8-15 (Gasoline)
5	Copper strip corrosion (3 hours @ 50 ^o C	ASTM D 130	1a	1a	1 (Gasoline), 3 (Diesel)
6	TAN, mg KOH/g	ASTM D 664	0.406	0.473	0.35-1.5 (Diesel)
7	Pour point, ^o C	ASTM D 97	-16	-28	-34 (Diesel)
8	Flash point, ^o C	ASTM D 93	24	25	Max. 32 (Diesel)
9	Viscosity, cSt	ASTM D 445	3.31	1.25	1.3-5.5 (Diesel)
10	Cetane index	ASTM D 976	58.36	54.05	>45 (Diesel)
11	Water content, ppm	ASTM D 6304	437	238	200 (Diesel)

4. CONCLUSIONS

The thermal and catalytic pyrolysis of waste polypropylene plastic was done in this study experimentally to produce liquid fuel at four different temperatures, namely, 350 ^oC, 400 ^oC, 420 ^oC, and 450 ^oC. The catalytic effect, as well as effect of other key factors such as temperature and reaction time, were also observed. The highest yield of liquid fuel was found 60 wt. % for thermal pyrolysis and 58 wt. % during catalytic pyrolysis at 450 ^oC. Though the percentage fuel yield for catalytic pyrolysis was lower at 450 ^oC than thermal pyrolysis, this yield was higher at other temperatures for catalytic pyrolysis. The physical

properties of produced fuel were also analyzed and compared with the traditional fuel which showed that the quality of fuel increased when the catalyst was used. So, we can conclude that both thermal and catalytic pyrolysis of waste polypropylene leads to the production of fuel which is a valuable resource recovery. It is also found that Alumina and Zinc Oxide mixture as a catalyst has a significant effect on improving the quality and yield of fuel. However, further studies are required to utilize this fuel as transportation or furnace oil.

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