

Thermal Pyrolysis of Waste Polypropylene to Liquid and Gas Fuel Using Single – Stage Semi–Batch Reactor

Niyazi Al–Areqi¹, Elyas Alaghbari¹, Ahlam Al–Alas¹, Hussein Mufadha²

Abstract— Plastics have become indispensable materials of utmost importance in our life. The increased demand and consumption of virgin plastics have led in parallel to growing waste plastics disposed in landfills causing a serious danger towards the environment due to their slow degradation and subsequent contaminants generation. In the present study, a single – stage semi–batch reactor designed well at appropriate pyrolyzer / catalytic reformer ratio was used for the first time for the low– temperature thermal pyrolysis of waste polypropylene (WPP) to diesel range pyrolytic oil. The thermal decomposition of WPP was studied using a thermogravimetric analysis (TGA). The liquid fuels produced by both catalytic and non– catalytic pyrolysis of WPP at 280 °C were investigated by means of gas chromatography – mass spectrometry (GC–MS), Infrared (IR) spectroscopy, and physico–chemical properties of fuels. It can be concluded that the use of the liquid fuel produced by thermal pyrolysis using the well- designed single – stage semi–batch reactor as either a substitute of , or blended with the conventional diesel, besides other products (gas and char) having a variety of promising applications, would essentially enhance the economic viability of the pyrolysis of waste plastics.

Index Terms— Thermal pyrolysis, Liquid fuel, Waste plastics, WPP, PC, CG–MS

1 INTRODUCTION

THE increased demand and consumption of virgin plastics have led in parallel to growing waste plastics disposed in landfills causing a serious danger towards the environment due to their slow degradation and subsequent contaminants generation. In other hand, the incineration of waste plastics emits severe air pollutants which also lead to environmental hazards [1–3]. Therefore. Many methods for recovering and recycling waste plastics have been developed. Among these with a view of the environmental protection and reduction of non–generation resources, a pyrolysis (thermal conversion of waste plastic to oils/fuels) have attracted a crucible interest worldwide [4–6]. This method can be done because the plastic raw materials derived from petroleum derivatives so that it can be returned to hydrocarbons as a basic fuel. This method is included in the recycle but the recycling process that is done is not only converting plastic waste directly into the plastic again, but also converting plastic waste into another form of fuel..

There are four types of mechanisms of plastics pyrolysis, *viz.* end–chain scission, random–chain scission, chain stripping and cross–linking [7,8].

Although, the conventional thermal pyrolysis suffers from certain limitations, such as high temperatures required [9], very broad product range with low yield % of produced liquid and gas fuels [10], Such problems can be resolved by carrying out the thermal pyrolysis in well- designed reactors.

Because of their simple design and easy operation, batch / semi–batch reactors have been used widely for thermal and catalytic pyrolysis of plastics. Among these, a single– stage batch reactor is feasible and well- handled [11–16].

The war and conflicts going on in Yemen since the past five years have led to increasing prices of fuels by nearly ten orders of magnitude, *e.g.*, the diesel fuel, as well as the uncontrollable accumulation of garbage and waste plastics within the main streets of cities, particularly Taiz city which is still being blockaded till now. This has given us a motivation to conduct our research project on the catalytic pyrolysis of waste plastics for achieving that two–fold objective. In the present work, a Portland cement (PC) was used for the first time as very cheap and available catalyst for producing diesel range pyrolytic oil by the catalytic pyrolysis of waste polypropylene (WPP) as one of the most abundant waste plastics in Yemen, and has a large number of hydrocarbon groups, which are linearly chained. A single– stage semi– batch reactor made of stainless steel was designed in a cylindrical geometry with the overall capacity of 0.20 m³, so that pyrolyzer to catalytic reforming portion was maintained at the ratio of 3:1(Fig. 1). The analytical results of the liquid fuel produced by the thermal pyrolysis of WPP were presented and discussed here in details.

2 MATERIALS & METHODS

Samples of WPP were collected from garbage sites and landfills located in several regions of Taiz city, Yemen. The WPP samples were milled into small pieces of 1.5 –2 cm size and thoroughly mixed. The resultant WPP pieces were washed using liquid detergent and water to remove any dirt or oils, and then dried under sun light.

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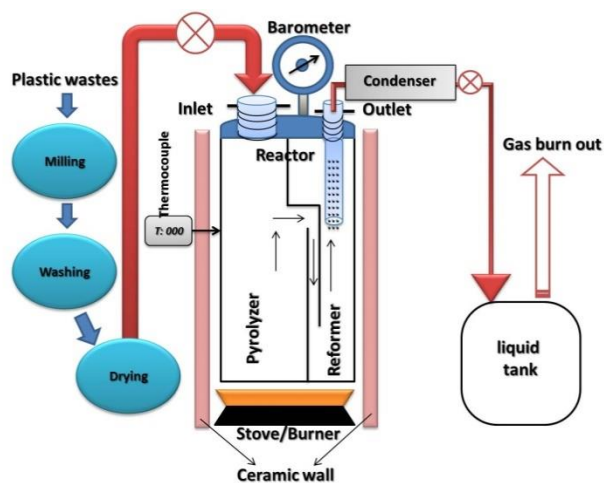


Fig. 1. Schematic of process and semi-batch reactor used for the catalytic pyrolysis.

The thermal pyrolysis experiments were carried out in a single-stage semi-batch reactor made of stainless steel as shown in Fig. 1 by packing the as-dried WPP pieces into the pyrolyzer up to the two thirds of its capacity, while the catalytic reformer remains empty. The nitrogen gas was pumped into the tightly closed reactor for 15 min to displace the resident air prior to the pyrolysis. The reactor was thereafter heated gradually at a constant heating rate of 15 °C min⁻¹. The pyrolytic liquid products were allowed to condensate out into a stainless steel container at fixed outlet temperature and pressure 280 °C and 2.5 bar, respectively maintained over whole the pyrolysis process. The gas products were burned out in air at the vent of the container to avoid the emission of hydrocarbon gases into the atmospheric environment. The yield % of each pyrolytic product (*i.e.*, char, liquid, gas, and wax) was calculated after the completion of production based on the standard mass balance.

The thermal decomposition of WPP was investigated by means of simultaneous thermogravimetric– differential thermal (TG–DT) analysis using a Perkin Elmer thermal analyzer. A 15– mg dried WPP powder sample was applied against α -alumina as a reference material. The instrument was run with 10 °C min⁻¹ heating rate and flowing a nitrogen gas from ambient temperature of 40 °C to 600 °C, and then air flowing upto 850 °C at a constant flow rate of 100 mL min⁻¹.

The chemical composition of pyrolyzed liquid fuel was investigated by the gas chromatography coupled with mass spectrometry (GC–MS) using a Shimadzu–QP–2010 Ultra instrument with a flame ionization (FI) detector. An 1.0 μ L liquid sample was injected by a split mode into a HP–PONA capillary column (50 m \times 0.25 mm i.d., 0.50 μ L thick). Helium of high purity was used as a carrier gas with a purge flow rate of 5 mL min⁻¹. The oven temperature was first set at 40 °C for 1 min, and it was thereafter increased upto 150 °C with a heating rate of 2 °C min⁻¹. The temperature of the ion source and inter-

face were maintained at 200, and 250 °C, respectively. The chromatographic peaks were identified by means of the NIST mass spectral data library.

A Shimadzu IR spectrometer was also used to identify the functional groups of compounds present in the produced liquid fuel. IR spectrum was scanned within the frequency range of 4000 – 400 cm⁻¹ with a spectral resolution of 4 cm⁻¹.

The high heating value, flash point, kinematic viscosity, and some other properties of liquid fuels were measured according to standard ASTM methods, considering three replications each.

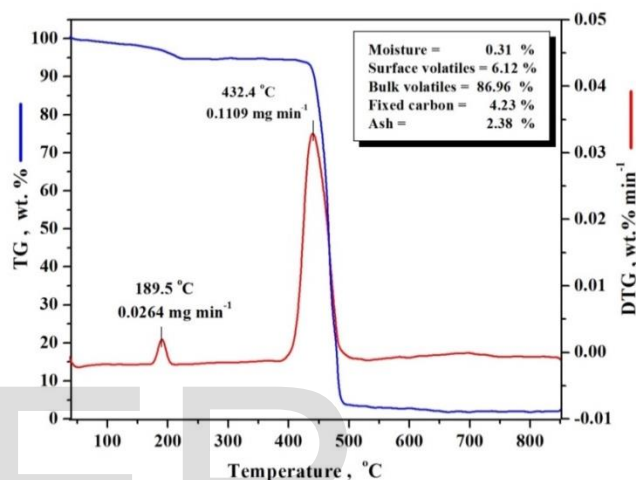


Fig. 2. TG and DTG curves of WPP.

3 RESULTS & DISCUSSION

TG and Derivative TG curves of WPP (Fig. 2) show a clear two-step thermal degradation in the nitrogen atmosphere, *i.e.* in the temperature range of 40 – 600 °C, where the instrument was run under nitrogen flowing. The very low weight loss of the first step as 189.5 °C may be attributed to the elimination of short, defective PP chains, which weakly bound to the surfaces of WPP particles. While the second high loss occurring at 432.4 °C is evidently the characteristic feature of the thermal history of the single step degradation of virgin PP [17]. Thus, the weight loss % of the first and second step were referred to the surface and bulk volatiles, respectively. The proximate analysis of WPP degradation is illustrated in the inset of Fig. 2. The moisture content was calculated from the weight loss % between ambient temperature and 150 °C. The ash content was equal to a constant weight % remaining after heating the sample at temperatures greater than 600 °C under air flowing. The fixed carbon was then computed using the mass % balance equation. It is interesting to note that the ash content and total volatiles play an important role in the production of liquid fuels by pyrolysis of waste plastics. The higher the ash content, the higher the production of gases and char, and the increase of volatile materials enhances the liquid yields.

TABLE 1
LIST OF GC-MS IDENTIFIED COMPOUNDS PRESENT IN THE LIQUID FUEL OBTAINED FROM THERMAL PYROLYSIS OF WPP

Peak #	RT (min)	Peak area %	Trace Mass (m/z)	Name	Formula	MW	Prob%	NIST Lib #
1	1.58	1.30	81	Cyclopentene, 4,4-dimethyl-	C ₇ H ₁₂	96	11.7	38642
2	2.42	1.61	81	Cyclohexene, 4-methyl-	C ₇ H ₁₂	96	17.4	125422
3	4.12	9.75	91	1,3,5-Cycloheptatriene	C ₇ H ₈	92	22.2	230230
4	5.24	1.93	55	2-Octene, (E)-	C ₈ H ₁₆	112	16.9	107269
5	6.18	1.02	67	Cyclopentene, 1-propyl-	C ₈ H ₁₄	110	8.9	142659
6	9.08	3.56	43	4,4-Dimethyl-cyclohex-2-en-1-ol	C ₈ H ₁₄ O	126	21.4	143725
7	11.30	3.34	91	Bicyclo[2.1.1]hexan-2-ol, 2-ethenyl-	C ₈ H ₁₂ O	124	10.2	221372
8	12.98	1.32	43	Cyclohexanol, 2,4-dimethyl	C ₈ H ₁₆ O	128	11.3	114589
9	14.36	11.05	55	cis-2-Nonene	C ₉ H ₁₈	126	10.1	113508
10	16.20	1.35	105	Cyclopentanol, 1-(1-methylene-2-propenyl)	C ₉ H ₁₄ O	138	8.9	152742
11	17.24	3.69	57	Decane	C ₁₀ H ₂₂	142	37.8	291484
12	19.22	14.75	56	3-Undecene, (Z)-	C ₁₁ H ₂₂	153	6.8	142598
13	21.60	1.07	55	1,11-Dodecadiene	C ₁₂ H ₂₂	166	6.4	6213
14	22.74	1.43	41	1-Tridecene	C ₁₃ H ₂₆	182	10.4	107768
15	24.44	8.67	55	1-Hexadecyne	C ₁₆ H ₃₀	222	6.2	233098
16	26.82	3.23	55	E-2-Hexadecacen-1-ol	C ₁₆ H ₃₂ O	240	8.8	131101
17	29.26	1.41	57	Hexadecane	C ₁₆ H ₃₄	226	38.7	107738
18	30.38	3.53	57	Octadecane	C ₁₈ H ₃₆	254	22.6	57273
19	32.34	0.92	97	E-2-Octadecadecen-1-ol	C ₁₈ H ₃₆ O	268	5.8	131102
20	33.90	7.90	55	9-Nonadecene	C ₁₉ H ₃₈	266	12.4	113627
21	36.28	1.26	57	Eicosane	C ₂₀ H ₄₂	282	15.6	290513
22	37.30	1.86	55	10-Heneicosene	C ₂₁ H ₄₂	294	8.2	113073
23	38.48	1.37	57	Heneicosane (c.t.)	C ₂₁ H ₄₄	296	40.5	107569
24	40.22	10.21	57	Heneicosane	C ₂₁ H ₄₄	296	19.4	107569
25	43.08	1.34	55	3-tricosene	C ₂₃ H ₄₆	322	7.2	113487
26	44.76	1.09	57	Tetracosane	C ₂₄ H ₅₀	338	15.7	248196

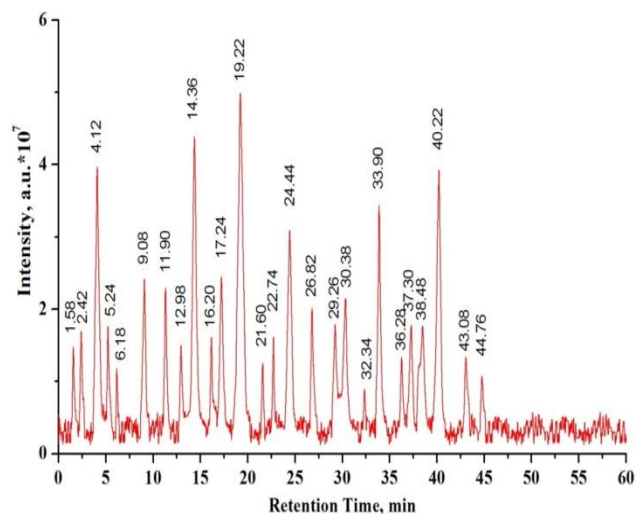


Fig. 4. GC-MS chromatograms of liquid fuels produced by thermal pyrolysis of WPP

The distribution of the product yields for WPP thermal pyrolysis at 280 °C can be seen in Fig. 3. As expected, the thermal

pyrolysis resulted in remarkably increased liquid and gaseous products coupled with the reduction of char yield along with the production of wax, constituting 22.61%.

The GC-MS results of liquid fuel produced by the non-catalytic pyrolysis of WPP is illustrated in Fig. 4, and Tables 1. The last hydrocarbon produced by the thermal pyrolysis eluted at RT=44.76 min is tetracosane (C₂₄H₅₀) (Table 1). This is clearly evident that the wax produced by the non-catalytic pyrolysis of WPP contains hydrocarbons with carbon number, and molecular weight greater 27, and 380, respectively.

The IR spectroscopy can also be used as a powerful characterization technique for identifying the chemical functional groups present in the pyrolyzed liquid fuels [4,18,19]. The IR spectrum of liquid fuel obtained from the thermal pyrolysis of WPP is shown in Fig. 5. The broad band in the region 3500 – 3200 cm⁻¹ accounts for the O–H stretching of alcohols and water residue. The two joint peaks at ~ 2920 and 2870 cm⁻¹ are assigned to stretching vibrations of C–CH₃ and –CH₂–, respectively. The strong wide band in the region 1700 – 1610 cm⁻¹ can be ascribed to the presence of C=O groups, while the shoulder apparent at ~ 1560 cm⁻¹ is due to the aliphatic C=C stretching vibrations. Although the GC-MS analysis showed on any carbonyl compound, the presence of C=O group in the

liquid fuel under investigation as assigned by their IR spectrum without a doubt arises from the pyrolyzed enols (Tables 1), which undergo a reversible tautomerization to carbonyl compounds [20]. The scissor vibrations of $-CH_2-$ and anti-symmetric deformation of $-CH_3$ can be seen in the range of $1480 - 1400\text{ cm}^{-1}$. The short band at $\sim 1230\text{ cm}^{-1}$ is assigned to the $C\equiv C$ stretching vibrations and the two peaks at ~ 1100 and 1030 cm^{-1} may be attributed to the different alcoholic and carbonyl $C-O$ stretching vibrations. However, the three peaks at $\sim 950, 880$ and 815 cm^{-1} are a clear evidence for the presence of (*cis*) $-CH=CH-$ and conjugated polyenes.

Based on the GC-MS results of the liquid fuel produced by thermal pyrolysis of WPP, the distribution of pyrolyzed compounds in terms of their chromatographic peak area % as a function of cyclization, carbon number range, and saturation can be viewed in Figs. 6, 7, and 8, respectively. It is clear that the thermal pyrolysis leads to increased open-chain structures (Fig. 6), and a remarkable increase of unsaturated compounds (Fig. 7) in the produced liquid.

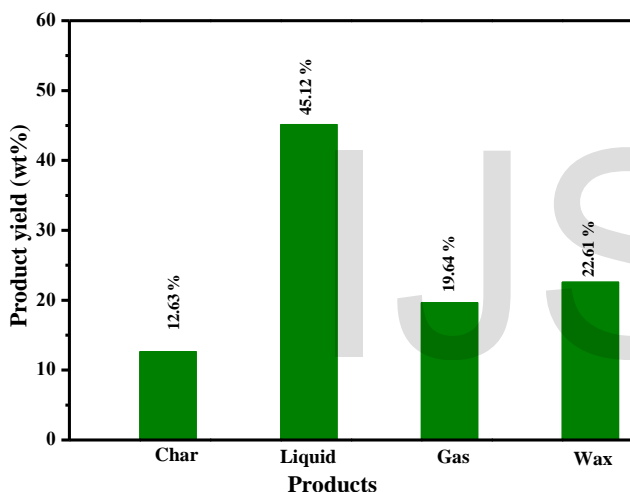


Fig. 3. Distribution of product yields of thermal pyrolysis of WPP.

The interesting point to be emphasized here is that more than 39.92 % of hydrocarbons produced by the thermal pyrolysis have a carbon range of $C_7 - C_{10}$, followed by ($C_{18} - C_{24}$) and then ($C_{11} - C_{17}$) as much as 32.52, and 27.56 %, respectively (Fig. 8). This indicates that, to a great extent, the liquid fuel pyrolyzed thermally approaches the composition of conventional diesel [21-23].

Values of characteristic parameters of liquid fuel obtained from the thermal pyrolysis of WPP are summarized in Table 2. It can be observed that the properties measured for the produced liquid fuel significantly match well with the GC-MS results revealed earlier. Interestingly, These parameters measured for the investigated liquid fall within the acceptable ranges reported for the conventional diesel [9,16,24]. Therefore, the results obtained in the present study prove that the low-temperature thermal pyrolysis of WPP using such well-designed single-stage, semi-batch reactor can potentially be used for producing high-yield liquid fuels comparable to the

commercial grade diesel.

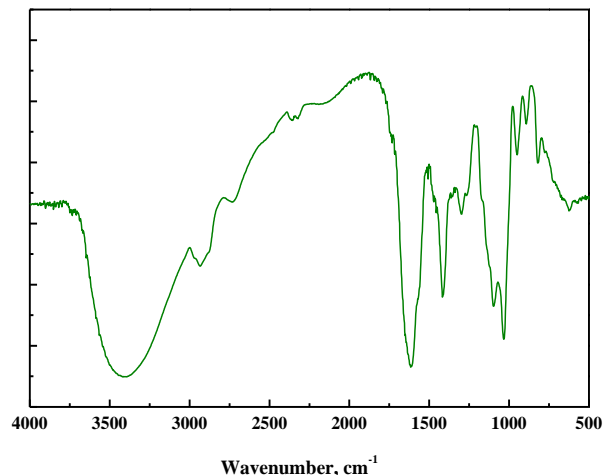


Fig. 5. IR spectrum of liquid fuel produced by thermal pyrolysis of WPP.

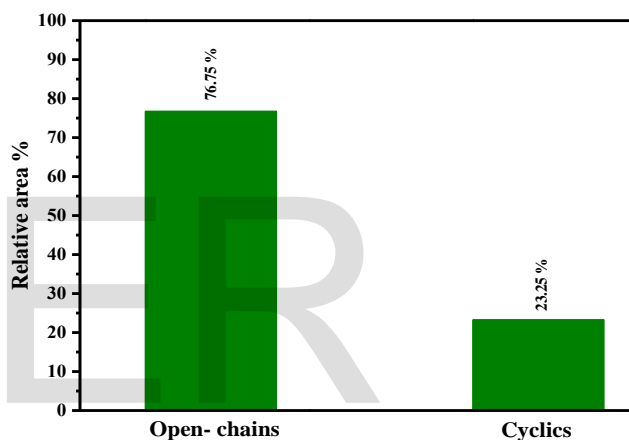


Fig. 6. Distribution of open-chain and cyclic compounds of liquid fuel produced by thermal pyrolysis of WPP.

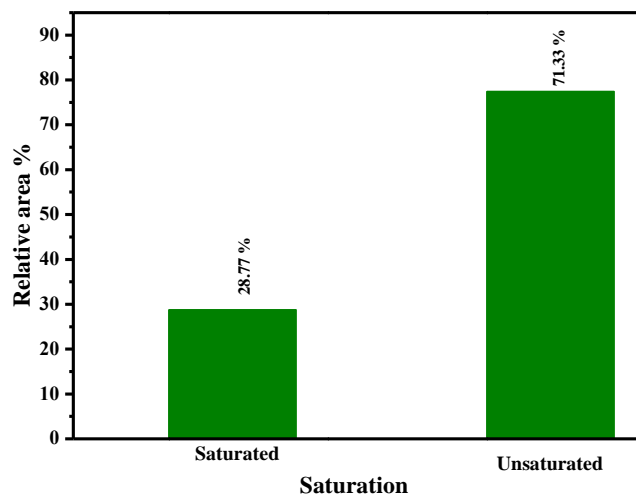


Fig. 7. Distribution of saturated and unsaturated compounds of liquid fuel produced by thermal pyrolysis of WPP.

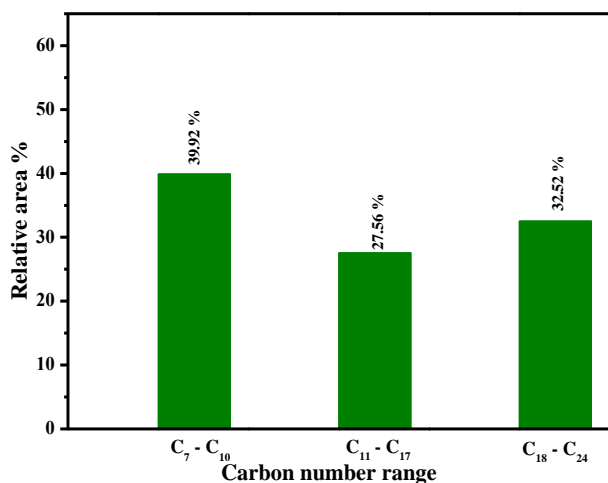


Fig. 8. Distribution of carbon number ranges for compounds of liquid fuel produced by thermal pyrolysis of WPP.

TABLE 2

PROPERTIES OF LIQUID FUELS PRODUCED BY THERMAL PYROLYSIS OF WPP.

Properties	Unit	Thermal pyrolysis	Test method
High heating value	MJ/kg	46.80	ASTM D 240
Flash point	°C	32	ASTM D 93
Fire point	°C	38	-
Cetane index	-	47	ASTM D 976
Carbon residue	wt %	0.111	ASTM D 189
Moisture content	wt %	0.110	ASTM D 95
Density @ 20 °C	kg/m ³	854.3	ASTM D1298
Kinematic viscosity @ 40 °C	cSt	2.36	ASTM D 445

4 CONCLUSION

The use of single-stage, semi-batch reactor designed well at appropriate ratio feasibly allowed the low-temperature production of high-yield liquid fuel from the WPP pyrolysis. The hydrocarbon composition and functional properties of the liquid fuel produced by the thermal pyrolysis were found to be similar to what have been reported for the commercial grade diesel, and hence it can be used as a substitute of, or blended with the conventional diesel, besides other products (gas and char) having a variety of promising applications. This would essentially enhance the economic viability of the thermal pyrolysis of waste plastics.

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