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Low–Temperature and Semi–Batch Production of Liquid Fuel Comparable to Commercial Grade Diesel by Portland Cement – Catalyzed Pyrolysis of Waste Polypropylene

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Abstract: The increased demand and consumption of virgin plastics have led in parallel to growing waste plastics disposed in landfills causing serious hazards towards the environment. In the present study, a Portland cement (PC) was used for the first time as very cheap and commercially available catalyst for the low– temperature pyrolysis of waste polypropylene (WPP) to diesel range pyrolytic oil, utilizing a single – stage semi–batch reactor designed well at appropriate pyrolyzer / catalytic reformer ratio. 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 physic–chemical properties of fuels. The PC–catalyzed pyrolysis resulted in remarkably increased liquid and gaseous products, and reduced char yield. Moreover, it significantly prevented the wax production. The results obtained in this work prove that the liquid fuel produced by the PC– catalyzed pyrolysis has nearly similar hydrocarbon composition and functional properties of the commercial grade diesel.

Keywords: Catalytic Pyrolysis, Liquid Fuels, Waste Plastics, WPP, PC, CG–MS

1. Introduction

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

However, 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], and difficult decomposition of crossed chain polymers, *e.g.*, high– density, and low– density polyethylene (HDPE and LDPE) with polypropylene (PP) [11]. The catalytic pyrolysis has been developed to overcome such problems. Moreover, the use of catalyst can reduce the pyrolysis temperature, and also enhance the quality of the pyrolytic products in terms of desired range of carbon atom number and high energy efficiency [12–14].

Because of their simple design and easy operation, batch / semi–batch reactors have been used widely for the catalytic pyrolysis of plastics. But the *in situ* catalytic pyrolysis, in which the catalysts and plastic feedstock are in direct contact with each other in a single– stage batch reactor, has many drawbacks, such as low reaction rates, fast catalyst deactivation [14], and sophisticated catalyst recovery [15]. Such problems can however be resolved via *ex situ* catalytic pyrolysis by designing semi–batch reactors with a combination of sequential pyrolysis and catalytic reforming stages [16–21].

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 m^3, so that pyrolyzer to catalytic reforming portion was maintained at the ratio of 3:1 (Figure 1). The analytical results of the liquid fuels produced by the PC– catalyzed pyrolysis of WPP were presented and discussed in comparison with those obtained from the uncatalyzed one.

2. Experimental

A high–quality Portland cement (PC catalyst) was purchased from the local market supplied by the National Cement Company (NCC) – Hayel Saeed Anam & Co Ltd. (HAS), Lahij – Yemen. Finely ground powder of the PC catalyst was activated by pre–heating at 500°C in a muffle furnace for 5 hrs.

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.

The catalytic pyrolysis experiments were carried out in a single– stage semi–batch reactor made of stainless steel as shown in Figure 1 by packing the as– dried WPP pieces into the pyrolyzer upto the two thirds of its capacity. The activated PC catalyst (9% with respect to the total WPP added) was then introduced to cover the bottom of catalytic reformer. 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 aforementioned steps were repeated without adding the catalyst in case of uncatalyzed pyrolysis experiments. 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}.

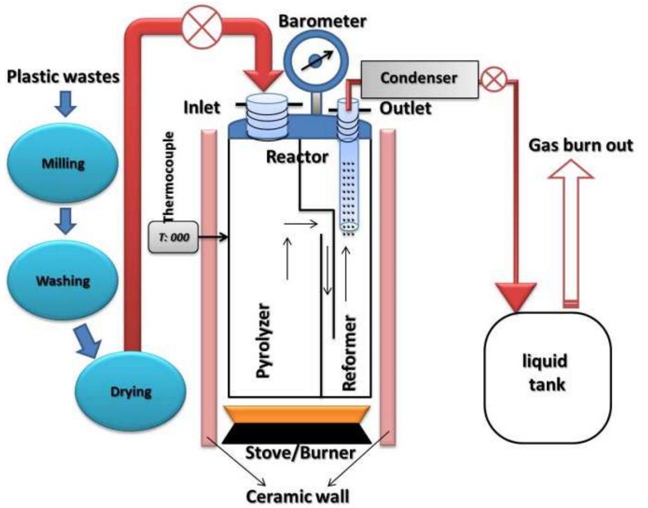

Figure 1. *Schematic of process and semi-batch reactor used for the catalytic pyrolysis.*

The chemical composition of pyrolyzed liquid fuels 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 µL liquid sample was injected by a split mode into a HP–PONA capillary column (50 m × 0.25 mm i.d., 0.50 µL 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 interface 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 fuels. IR spectra were 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.

3. Results and Discussion

TG and Derivative TG curves of WPP (Figure 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 [22]. 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 Figure 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.

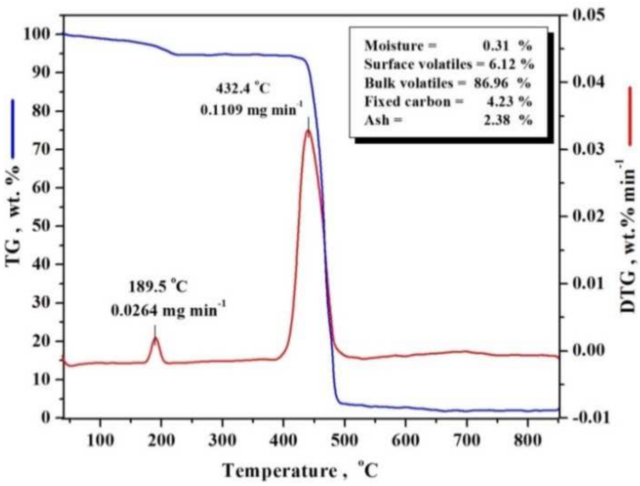

***Figure 2.** TG and DTG curves of WPP.*

The effect of the presence of PC– catalyst on the distribution of the product yields for WPP pyrolysis at 280°C can be seen in Figure 3. As expected, the PC– catalyzed pyrolysis resulted in remarkably increased liquid and gaseous products coupled with the reduction of char yield as compared to the uncatalyzed pyrolysis. Interestingly, the PC– catalysis prevents the production of wax, constituting 22.61% for the uncatalyzed pyrolysis of WPP at the same temperature. These results are well agreed with what have been reported for the catalytic pyrolysis of some waste plastics [11, 23–25].

The GC–MS results of liquid fuels produced by the catalytic and non–catalytic pyrolysis of WPP are illustrated in Figure 4, and Tables 1 and 2. It is clearly observed that the number of chromatographic peaks in the GC–MS chromatogram of the liquid fuel obtained from the PC–catalyzed pyrolysis (Figure 4 (a)) is slightly greater than that of the uncatalyzed one (Figure 4 (b)). The last two hydrocarbons eluted at retention time (RT) of 46.14, and 48.02 min for the liquid fuel produced by the PC– catalyzed pyrolysis are hyptacosane ($C_{27}H_{56}$), and 2,5,10,15–tetramethylheptadecane ($C_{21}H_{44}$) (Table 1), while tertacosane ($C_{24}H_{50}$) is the last hydrocarbon produced by the uncatalyzed pyrolysis eluted at RT=44.76 min (Table 2). This is clearly evident that the wax produced by the non–catalytic pyrolysis of WPP contains hyrocarbons with carbon number, and molecular weight greater 27, and 380, respectively.

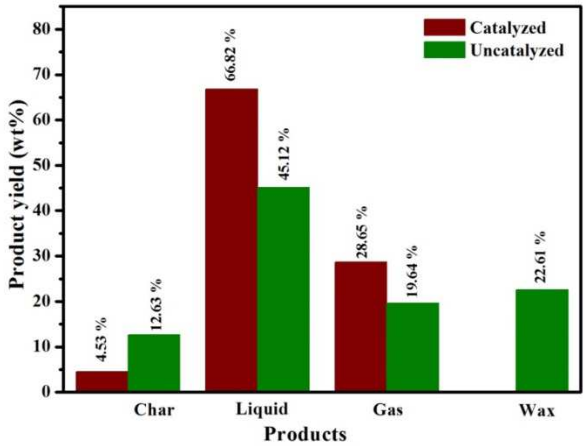

***Figure 3.** Distribution of product yields of PC- catalyzed and uncatalyzed pyrolysis of WPP.*

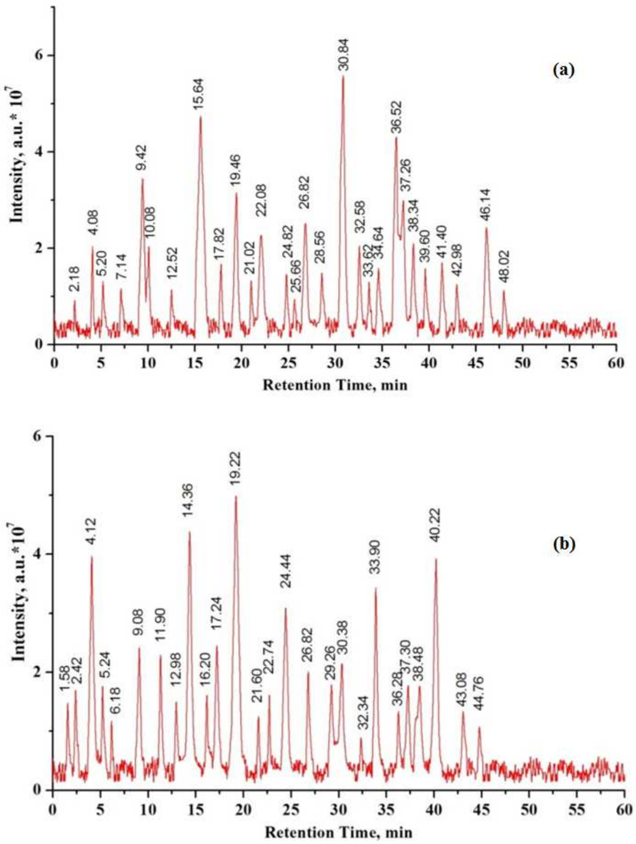

***Figure 4.** GC-MS chromatograms of liquid fuels produced by (a) PC-catalyzed and (b) uncatalyzed pyrolysis of WPP.*

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, 26, 27]. The IR spectra of liquid fuels obtained from the PC–catalyzed and uncatalyzed pyrolysis of WPP (Figure 5) seem somehow identical, revealing the presence of similar functional groups in both two investigated fuels. 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–CH_3 and –CH_2–, 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 fuels under investigation as assigned by their IR spectra without a doubt arises from the pyrolyzed enols (Tables 1 and 2), which undergo a reversible tautomerization to carbonyl compounds [28]. The scissor vibrations of –CH_2– and antisymmetric deformation of —CH_3 can be seen in the range of 1480 – 1400 cm^{-1}. The short band at ~ 1230 cm–is assigned to the C≡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 ~ 950, 880 and 815 cm^{-1} are a clear evidence for the presence of (*cis*) –CH=CH– and conjugated polyenes.

Table 1. *List of GC-MS identified compounds present in the liquid fuel obtained from PC- catalyzed pyrolysis of WPP.*

Peak #	RT (min)	Peak area%	Trace Mass (*m/z*)	Name	Formula	MW	Prob%	NIST Lib #
1	2.18	0.77	81	Cyclohexene, 4-methyl-	C_7H_{12}	96	14.3	125422
2	4.08	3.09	91	1,3,5-Cycloheptatriene	C_7H_8	92	18.1	230230
3	5.20	1.09	55	2-Octene, (*E*)-	C_8H_{16}	112	23.6	107269
4	7.14	1.32	81	Bicyclo [4.1.0] heptane, 3-methyl-	C_8H_{14}	110	11.5	46298
5	9.42	6.20	67	Cyclopentane, (1-methylethylidene)-	C_8H_{14}	110	14.9	61656
6	10.08	3.34	83	Cyclohexane, ethyl-	C_8H_{16}	112	39.8	113476
7	12.52	1.31	43	Cyclohexanol, 2,4-dimethyl	$C_8H_{16}O$	128	10.6	114589
8	15.64	12.25	55	1-Undecene	$C_{11}H_{22}$	154	7.7	34717
9	17.82	1.32	57	Decane	$C_{10}H_{22}$	142	41.4	291484
10	19.46	5.98	56	3-Undecene, (*Z*)-	$C_{11}H_{22}$	154	7.5	142598
11	21.02	1.08	55	1,11-Dodecadiene	$C_{12}H_{22}$	166	8.1	6213
12	22.08	3.32	41	1-Tridecene	$C_{13}H_{26}$	182	12.7	107768
13	24.82	1.16	55	1-Hexadecyne	$C_{16}H_{30}$	222	7.7	233098
14	25.66	0.81	55	4-Tetradecene, (*E*)-	$C_{14}H_{28}$	196	9.3	142625
15	26.82	4.04	55	*E*-2-Hexadecacen-1-ol	$C_{16}H_{32}O$	240	10.6	131101
16	28.56	1.39	55	1-Hexadecene	$C_{16}H_{32}$	224	6.4	118882
17	30.84	16.23	57	Octadecane	$C_{18}H_{36}$	254	18.9	57273
18	32.58	3.08	97	*E*-2-Octadecadecen-1-ol	$C_{18}H_{36}O$	268	7.6	131102
19	33.62	1.08	55	9-Nonadecene	$C_{19}H_{38}$	266	10.2	113627
20	34.64	1.29	55	1-Nonadecene	$C_{19}H_{38}$	266	8.8	113626
21	36.52	11.41	57	Eicosane	$C_{20}H_{42}$	282	17.6	290513
22	37.26	5.68	55	10-Heneicosene	$C_{21}H_{42}$	294	9.4	113073
23	38.34	3.56	57	Heneicosane	$C_{21}H_{44}$	296	33.7	107569
24	39.60	1.24	57	1-Docosene	$C_{22}H_{44}$	308	8.7	113878
25	41.40	1.71	57	1-Tricosene	$C_{23}H_{47}$	323	5.3	133854
26	42.98	1.07	55	*E*-2-Docosene	$C_{22}H_{44}$	308	6.7	113879
27	46.14	3.85	55	Heptacosane	$C_{27}H_{56}$	380	7.4	150574
28	48.02	1.29	55	Heptadecane, 2,6,10,15-tetramethyl-	$C_{21}H_{44}$	296	10.4	14103

Table 2. *List of GC-MS identified compounds present in the liquid fuel obtained from the uncatalyzed 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_7H_{12}	96	11.7	38642
2	2.42	1.61	81	Cyclohexene, 4-methyl-	C_7H_{12}	96	17.4	125422
3	4.12	9.75	91	1,3,5-Cycloheptatriene	C_7H_8	92	22.2	230230
4	5.24	1.93	55	2-Octene, (*E*)-	C_8H_{16}	112	16.9	107269
5	6.18	1.02	67	Cyclopentene, 1-propyl-	C_8H_{14}	110	8.9	142659
6	9.08	3.56	43	4,4-Dimethyl-cyclohex-2-en-1-ol	$C_8H_{14}O$	126	21.4	143725
7	11.30	3.34	91	Bicyclo [2.1.1] hexan-2-ol, 2-ethenyl-	$C_8H_{12}O$	124	10.2	221372
8	12.98	1.32	43	Cyclohexanol, 2,4-dimethyl	$C_8H_{16}O$	128	11.3	114589
9	14.36	11.05	55	*cis*-2-Nonene	C_9H_{18}	126	10.1	113508
10	16.20	1.35	105	Cyclopentanol, 1-(1-methylene-2-propenyl)	$C_9H_{14}O$	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

Peak #	RT (min)	Peak area%	Trace Mass (*m/z*)	Name	Formula	MW	Prob%	NIST Lib #
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 (twice)	$C_{21}H_{44}$	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

Based on the GC–MS results of the liquid fuels produced by PC– catalyzed and uncatalyzed 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 Figures 6, 7, and 8, respectively. It is clear that the PC– catalysis leads to increased open– chain structures (Figure 6), and a remarkable lowering of unsaturated compounds (Figure 7) in the produced liquid. The interesting point to be emphasized here is that more than 50% of hydrocarbons produced by the catalytic pyrolysis have a carbon range of C_{18}– C_{24}, followed by a kerosene (C_{11}–C_{17}) as much as 30.03% (Figure 8). This indicates that, to a great extent, the liquid fuel pyrolyzed by the PC– catalysis approaches the composition of conventional diesel [29–31]. These results suggest that the PC–catalyzed pyrolysis of WPP follows the free– radical mechanism proposed by Sekine and Fujimoto for the pyrolysis of PP catalyzed with the Fe–activated carbon [32].

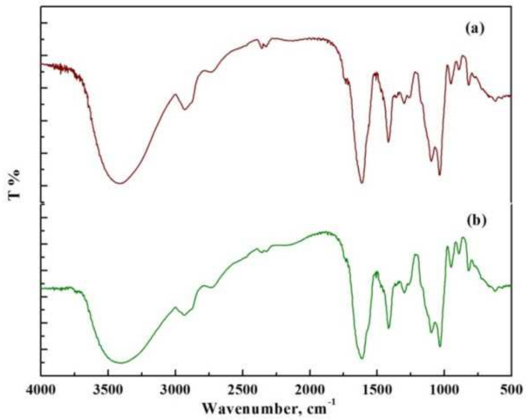

Figure 5. IR spectra of liquid fuels produced by (a) PC- catalyzed and (b) uncatalyzed pyrolysis of WPP.

Values of characteristic parameters of liquid fuels obtained from the catalytic and non– catalytic pyrolysis of WPP are summarized in Table 3. It can be observed that the properties measured for the produced liquid fuel of the PC– catalyzed pyrolysis are significantly better than those of the uncatalyzed one. This expectedly matches well with the GC–MS results revealed earlier. Interestingly, These parameters measured for both two liquids fall within the acceptable ranges reported for the conventional diesel [9, 21, 33]. Therefore, the results obtained in the present study prove that the low– temperature pyrolysis of WPP catalyzed with a low–cost Portland cement can potentially be used for producing high– yield liquid fuels comparable to the commercial grade diesel.

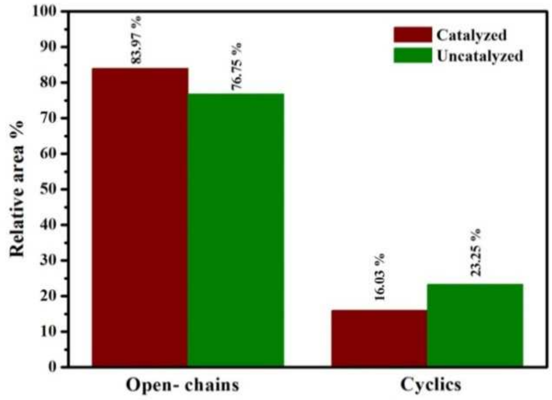

Figure 6. Distribution of open- chain and cyclic compounds of liquid fuels produced by catalytic and uncatalyzed pyrolysis of WPP.

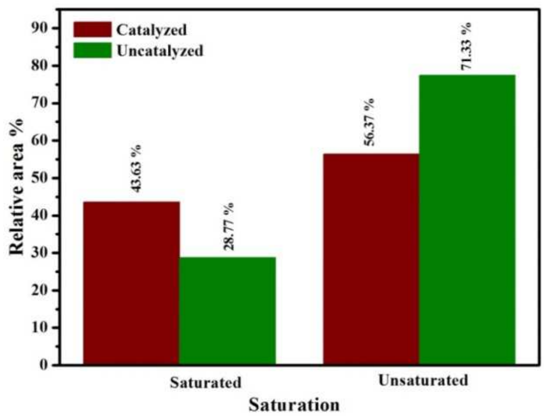

Figure 7. Distribution of saturated and unsaturated compounds of liquid fuels produced by catalytic and uncatalyzed pyrolysis of WPP.

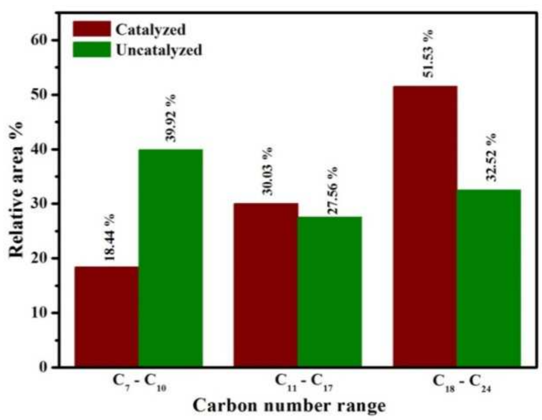

Figure 8. Distribution of carbon number ranges for compounds of liquid fuels produced by catalytic and uncatalyzed pyrolysis of WPP.

Table 3. *Properties of liquid fuels produced by PC- catalyzed and uncatalyzed pyrolysis of WPP.*

Properties	Unit	Catalytic pyrolysis	No catalyst	Test method
High heating value	MJ/kg	44.79	46.80	ASTM D 240
Flash point	°C	29	32	ASTM D 93
Fire point	°C	37	38	-
Cetane index	-	44	47	ASTM D 976
Carbon residue	wt%	0.092	0.111	ASTM D 189
Moisture content	wt%	0.086	0.110	ASTM D 95
Density @ 20°C	kg/m^3	802.7	854.3	ASTM D1298
Kinematic viscosity @ 40°C	cSt	2.18	2.36	ASTM D 445

4. Conclusion

The use of very cheap and commercially available Portland cement along with the simple semi–batch reactor designed well at appropriate ratio of pyrolyzer and catalytic reformer 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 PC–catalyzed pyrolysis were found to be similar to what have been reported for the commercial grade diesel.

It can be concluded that the use of the produced liquid fuel as 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 catalytic pyrolysis of waste plastics. Moreover, this will contribute to address the problems related to the environmental protection from the accumulation of such waste plastics.

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