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Experimental Investigation on Pyrolysis of Domestic Plastic Wastes for Fuel Grade Hydrocarbons

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Abstract: Plastics usage is rising daily because of increased population, modernization, and industrialization, which produces a lot of plastic garbage. Due to their various chemical structures, long chain polymeric compositions, and thermal/decomposition behavior, it is challenging to recycle these plastic wastes into hydrocarbon fuels. In the current work, domestic plastic waste was pyrolyzed at 473 to 973 K in a fixed bed reactor and compared with the three virgin plastics LDPE (low-density polyethylene), HDPE (high-density polyethylene), and PP (polypropylene), as well as a mixture of the three (virgin mixed plastics). The pyrolysis results showed that maximum liquid hydrocarbons obtained from HDPE, LDPE, PP, mixed plastic, and domestic waste were 64.6 wt.%, 62.2 wt.%, 63.1 wt.%, 68.6 wt.%, and 64.6 wt.% at 773 K, respectively. The composition of liquid fuels was characterized using FTIR and GC-MS, which showed a wide spectrum of hydrocarbons in the C8–C20 range. Furthermore, liquid fuel characteristics such as density, viscosity, fire and flash point, pour point, and calorific value were examined using ASTM standards, and the results were found to be satisfactory. This study provides an innovative method for recycling waste plastics into economical hydrocarbon fuel for use in transportation.

Keywords: domestic plastic waste; pyrolysis; TGA; GC-MS; alternate fuel

1. Introduction

The demand for plastic has increased due to its attractive applications like packaging, utensils, and other industrial uses. According to Central Pollution Control Board, CPCB's latest report, the generation of plastic waste in India for 2018–2019 was around 9.46 million tons per year [1]. As a result, today's biggest concern is how to properly dispose of plastic waste. There are several popular methods used to dispose of plastics, depending on local regulations: landfilling and open dumping, ocean dumping, incineration, and recycling [2,3]. However, these methods result in several economic and environmental concerns. [4–6]. The researcher's focus has been switched in recent years to the recovery of energy from plastic wastes, which not only solves the issue of managing plastic waste but also generates energy as a value-added product. As a result, a simple, effective, and low-cost technique for resolving plastic pollution and converting it into useful energy products is required. A prospective method for meeting the energy needs of the industrial,

transportation, and agricultural sectors as well as solid waste management is the thermochemical conversion of mixed plastic waste (MPW) to fuel. Numerous investigations have been conducted on the pyrolysis of various forms of unmixed plastic materials [7–11]. However, municipal/domestic plastic waste primarily consists of low-density polyethylene (LDPE), high-density polyethylene (HDPE), polyethylene terephthalate (PET), polypropylene (PP), polystyrene (PS), and poly (vinyl chloride) (PVC) [12–16]. Hence, mixed-waste separation and material variability are significant obstacles to the broader use of the technique. Until now, no commercial plants have been available to convert domestic/municipal plastic waste into fuel due to its thermal decomposition behavior, making it challenging to convert usable fuel into a single reactor. The information on plastic waste conversion's technological aspects is scanty and needs to be investigated deeply in order to utilize plastic waste for fuel.

Pyrolysis is one of the important thermochemical conversion technologies for the transformation of plastic waste into valuable products like liquid fuel, gas fuel, and carbon black [17,18]. It is an endothermic response where volatile matter of input plastic waste decomposes to produce condensable vapors, non-condensable gases, and solid pyro-char (fixed carbon and inorganic compounds such as glass, metals, ash, etc.). The inorganic chemicals from pyrolysis are unaltered and can be employed as additives for other polymers, chemical modification or recovery, or road construction [19–21].

Most of the studies have reported on using single-type plastic waste. For instance, Hazrat 2014 performed the pyrolysis of high-density polyolefin in the temperature range 473–853 K and observed that the obtained liquid product contained hydrocarbon of waxes, gums, and coke along with light oils [22]. The batch process of virgin plastic (PE, PP, PS, and PET) to crude liquid fuel was also studied in Parr mini autoclave at 773 K and found yields of 90–95 wt.%, 5–10 wt.% and 1 wt.% of liquids, gases, and solid residue respectively [23]. At the same time, low-temperature pyrolysis of used plastic in a batch reactor with a mixture of LDPE and PP of 3 mm in length had a standard yield of 48.6 wt.% at 548 K of liquid products with the non-catalytic pyrolysis technique [24]. In a different experiment, scientists looked at the catalytic and non-catalytic pyrolysis of PS with LDPE, HDPE, PP, and PET plastics in a batch microreactor at 725 K and 5−6.0 MPa of N2 gas pressure over a 1 h residence period. Each plastic mixture with PS was subjected to three reactions, and it was found that the 1:1 mix ratio produced the highest output of liquid hydrocarbon fuel [25,26]. The outcomes of earlier research were compared to those of other studies, which carried out experiments in a batch autoclave reactor using HDPE plastic as feedstock and recorded a maximum output of 70 wt.% at 753 K in 20 min of residence time [27]. The capacity of a mixture of PP and PE plastics to produce hydrocarbon fuels by thermal cracking in horizontal tubular reactors at various temperatures was also explored by some researchers, and it was determined that yields rely on the makeup of the plastic feed and residence time [28]. These studies showed that pyrolysis is the best technique to convert plastic waste to fuel. However, very few studies are available on the effect of operating temperatures on converting domestic plastic into usable alternate fuels [29]. Hence, this study aims to pyrolyze domestic plastic waste at different temperatures for maximum hydrocarbon yield and to compare it with virgin HDPE, LDPE, PP, and mixed virgin plastic (MVP). The study's main objective was to identify domestic plastic waste's decomposition behavior and temperature, compared to that of virgin plastics and mixed virgin plastic. In addition, reaction products were characterized to see their feasibility as alternative fuels such as gasoline, diesel, or jet fuel.

2. Materials and Methods

2.1. Materials

Virgin low-density polyethylene (LDPE), high-density polyethylene HDPE), polypropylene (PP), and polyethylene terephthalate (PET) were obtained from local vendorAldrich made, Dehradun, Uttarakhand, India. Virgin mixed plastic was made by considering domestic plastic waste (PP 27 wt.%, LDPE 60 wt.%, HDPE 10 wt.%, and PET 3 wt.%) com-

position. Domestic plastic wastes were collected from campus bins. It was observed that domestic plastic waste contains, on average (50–60 wt.% LDPE, 30–35 wt.% PP, 10–12 wt.% HDPE, and 1–3 wt.% PET) which are shredded into small pieces and sieved into a particle size of 3–5 mm as virgin plastic available.

2.2. Characterization of Feedstock

2.2.1. Proximate and Ultimate Analysis

Proximate analysis was performed to assess the combustion properties, including moisture content, volatile matter, fixed carbon, and ash. A bomb calorimeter was used to examine the calorific value. To determine the elemental composition of domestic plastic waste, mixed virgin plastics, and individual virgin plastics (LDPE, HDPE, and PP), as well as hydrocarbon fuels, a CHNS analyzer (varioMICRO CHNS, Elementar Analysensysteme GmbH, Germany) was used. Properties of LDPE, HDPE, PP, mixed virgin plastic (MVP), and domestic plastic waste (DPW) are depicted in Table 1.

Table 1. Characteristic properties of different plastic feedstocks (dry basis).

Properties	Virgin Plastic			Mixed Virgin Plastic	Domestic Plastic Waste
	PP	HDPE	LDPE		
Volatile matter (wt.%)	99.9	97.7	98.78	98.72	93.45
Fixed carbon (wt.%)	0.09	2.12	1.12	1.17	5.34
Ash (wt.%)	0.01	0.18	0.1	0.11	1.21
Bulk Density (kg m^{-3})	0.574	0.584	0.552	0.56	0.862
Conradson Carbon residue	0.2	0.68	0.61	0.51	1.34
Heating value (MJ kg^{-1})	41.1	42.1	45.7	42.04	40.42
Carbon (wt.%)	83.49	85.26	85.85	84.88	84.43
Hydrogen (wt.%)	16.13	14.65	14.15	14.83	12.45
Nitrogen (wt.%)	0.28	0.09	0	0.26	2.71
Sulfur (wt.%)	0.1	0	0	0.03	0.41
H/C ratio	0.19	0.17	0.16	0.17	0.15

It was observed from Table 1 that all plastics feedstock contains high amounts of volatile matter > 97% and less percentages of fixed carbon, which can be inferred to achieve 97% conversion. Plastic feedstock measures higher heating values than diesel, petrol, and natural gas. From the ultimate analysis of plastic, it was observed that virgin polypropylene has a high H/C ratio, whereas domestic plastic waste has 0.15 H/C ratio equivalent to HDPE (Table 1). The lesser the H/C ratio, the lesser will be the heating value of the feedstock. The bulk density of plastic was determined in accordance with ASTM D1895B, and the results revealed that LDPE was the lightest of all the feedstocks selected for the pyrolysis process.

Table 1 shows that domestic plastic wastes have a carbon residue of 5.34 wt.%, compared to mixed virgin plastic's 1.17 wt.% which indicates that the carbon in domestic plastic trash may have a complicated structure. According to ASTM standards, the heating value of liquid hydrocarbon fuels and plastic feedstock was evaluated using a bomb calorimeter.

2.2.2. Thermogravimetric Analysis (TGA)

A thermogravimetric analyzer (SII 6300 EXSTAR, Seiko Instruments Inc., Tokya, Japan) was used to assess the mass loss of plastic feedstock in order to understand how the composition of the feedstock changed with time and temperature. Over a temperature range of 303 K to 1173 K, nitrogen was employed as an inert gas at a flow rate of 150 mL min^{-1}. Differential thermogravimetric analysis was derived and analyzed in further sections. A uniform sample weight of up to 10 mg was used in all TGA analysis.

2.3. Experimental Set Up and Procedure

The experiments were conducted in fixed-bed reactor under inert environment. The primary reactor consisted of a cylindrical quartz column with an internal diameter of 75 mm and a height of 420 mm. The preheating of the feed gas was made possible by the heating zone's proximity to the inlet. The samples used in all of the studies weighed around 50 g. Initially, the reactor was purged with inert gas, i.e., nitrogen, at a flow rate of 500 mL min^{-1}. The ideal heating rate for all tests was 10 °C min^{-1} from room temperature to the desired temperature, and the desired temperature was maintained for 60 min to ensure reaction completion. Three bottle-jacketed water-cooling condenser units, each with a 500 cc capacity, condensed the volatiles released during the pyrolysis process from the plastic waste into liquid form. The bottle condensers were held at a temperature of 6 °C and connected in series. Non-condensable gases leave the system by the available vent, are collected in the bladder, and undergo qualitative analysis thereafter. Each feedstock was pyrolyzed at 473 K to 973 K to optimize the best yield of liquid, solid, and gaseous products. After the completion of the experiment, residue and condensed liquid was measured, and the yields in weight percentage were calculated. Each experiment was repeated twice, and average values are shown in the manuscript. The methodology adopted in this investigation is shown in Figure 1.
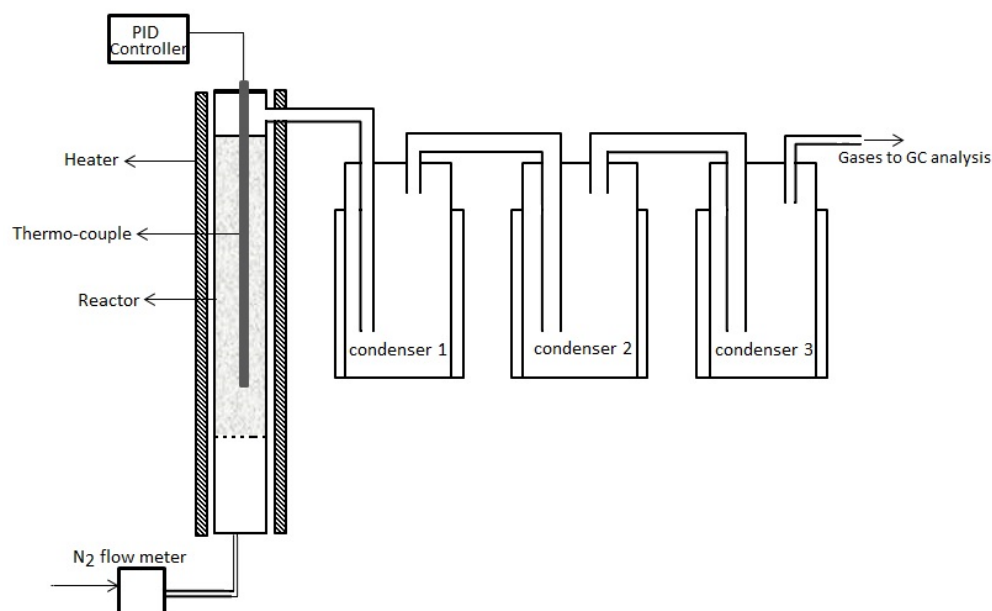

Figure 1. Process pathway for production of hydrocarbon fuels from domestic plastic waste and virgin plastics.

2.4. Product Analysis

The chemical characteristics of solid feedstock and liquid product were analyzed for FTIR to understand the functional group. The usual KBr (potassium bromide) approach was employed to record the IR spectra in the 400–4000 cm^{-1} range at a resolution of 4 cm^{-1} using the Perkin Elmer's FTIR spectrometer. The detailed chemical composition of liquid hydrocarbons was performed using GC-MS and FTIR analysis techniques. Perkin Elmer's GC-MS equipped with DB-5ms capillary column with i.d. 0.25 mm and length of 30 m was used to identify the chemical composition, and unknown compounds were matched with standard NIST 11 libraries. Helium was used as a carrier gas at a flow rate of 1.5 mL min^{-1}, with a split ratio of 50:1, and 70 eV ionization energy was applied to detect the mass. To assure the elution of any potential high boiling compounds, the temperature of the GC oven was initially kept at 348 K for 10 min, increased to 573 K at a heating rate of 10 K min^{-1}, and held for 25 min. GC with a thermal conductivity detector (TCD) and flame ionization detector (FID) was used to collect the non-condensable gases in the balloon and analyze

all immediately. With argon serving as a carrier gas, pyrolytic gases were isothermally separated in a molecular sieve-packed column. The temperature of injector and detector was 393 K and 433 K, respectively. All the physical characteristics were determined as per ASTM standards.

3. Results and Discussion

3.1. Characterization of Plastic Feedstock

3.1.1. Thermogravimetric Analysis (TGA) Analysis of Plastic Waste

TGA is a standard technique that demonstrates the sample's behavior concerning time, temperature, and heating rate and helps to get the optimum temperature range for plastic polymer degradation. The TGA analysis curve of domestic plastic waste and virgin plastics under a non-isothermal (10 K/min) range is represented in Figure 2 and the results revealed that the thermal decomposition of LDPE, HDPE, and PP plastic was almost similar. The decomposition of LDPE started at 573 K with an initial mass of 96.24 wt.% and reached up to mass-loss of 3.4 wt.% at 720 K while the degradation of HDPE started with a mass-loss of 94.20% at 613 K and achieved up to 6.57% at 749 K (Figure 2b). Because HDPE has more branching hydrocarbon bonds than LDPE, which indicates stronger internal molecular forces, its degradation range was marginally larger than LDPE's. As a result, it needed a higher temperature to degrade [4]. On the other side, PP started to degrade at 648 K with an initial mass of 95.2 wt.% and reached a maximum of 2.6 wt.% at 750 K (Figure 2c), indicating single-step degradation. The presence of a single DTG peak also supports the fact that the degradation of all these three plastic feedstocks, i.e., LDPE, HDPE, and PP, takes place in a single step.

The temperature at which the maximum degradation rate takes place is called peak temperature (Tmax). In contrast, the temperature at which maximum degradation began is denoted as onset temperature (To), and the temperature at which degradation ended is termed as end temperature (Te). The values of these temperatures vary for different source materials. Since the rate of degradation changes as reaction time (temperature) increases, the changes in product distribution of both gas and liquid phases are also to be expected. In this study, the peak temperature Tmax for LDPE, HDPE, and PP was 703 K, 700 K, and 721 K, respectively, while the end temperature was 720 K, 730 K, and 740 K, respectively. Total mass loss for LDPE, HDPE, and PP was 92.84 wt.%, 88.63% wt.%, and 90.9 wt.%, corresponding to these temperatures. Therefore, the yield of product distribution varied with these feedstocks. In domestic plastic waste and mixed virgin plastic, Tmax was 740 K and 744 K, respectively, higher than individual plastics. In addition, three peaks were detected in the DTG curve (Figure 2d,e), indicating that the degradation of domestic plastic waste and mixed virgin plastic is a significant multiple-reaction process; therefore, total mass loss occurs in more than two reactions. It may be due to the synergistic effect when all three plastic materials degrade together [30]. However, the onset temperature (To) for domestic plastic waste and mixed virgin plastic was observed to be 614 K and 654 K, while the end temperature (Te) was 749 K and 758 K, and the mass loss was higher for mixed virgin (92.20%) compared to domestic plastic waste (89.93%).

The temperature at which domestic plastic waste decomposed was lower than that of mixed virgin plastics. The primary causes may result from a change in the structural composition of domestic plastic waste while molding completed goods from virgin plastic. Binders, fillers, and coloring chemicals may disintegrate mixed plastic waste more quickly than unprocessed virgin plastics by lowering the temperature. Based on To and Te, it can be predicted that the pyrolytic zone for both domestic plastic waste and mixed virgin plastic lies in the range of 600 to 754 K temperature. These data were found to be similar to other studies carried out by different researchers [8,30,31].
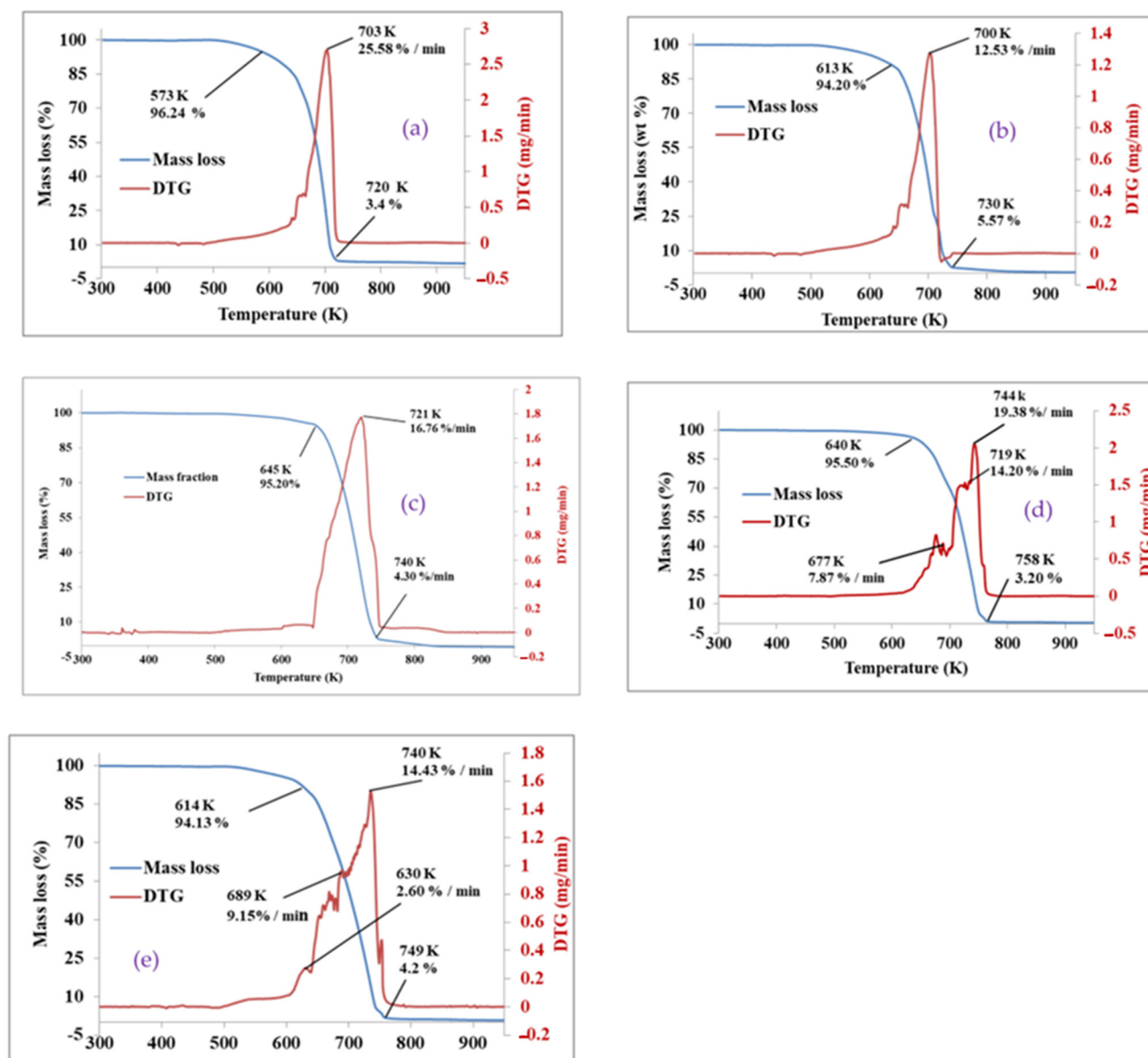
Figure 2. Thermogravimetric (TG) and differential thermogravimetric (DTG) analysis of (**a**) LDPE (**b**) HDPE (**c**) PP (**d**) Mixed virgin plastic (**e**) Domestic plastic waste.

3.1.2. FTIR Analysis of Plastic Feedstock

Figure 3 shows FTIR studies of virgin plastics and domestic plastic waste. Large monomers are combined to produce polymer compounds for use in plastics. Some polymers are supported by oxygen doping, whereas others have olefinic composition. However, domestic plastic waste contains fillers, binders, and additives that FTIR spectra can identify regarding the hydrocarbon composition's stretching frequencies. Figure 3 shows that =C−H, −C−H, and C−C stretching frequencies ranged between 2900 and 3000 cm^{-1}, which indicates the existence of hydrocarbon groups like alkanes, alkenes, and alkynes. Long-chain, closely packed hydrocarbons, and closed, densely packed hydrocarbon molecules are responsible for the behavior. Above 3000 cm^{-1}, wave numbers are slightly skewed. Domestic plastic waste also contains groups that contain oxygen at frequencies between 2600 and 2900 cm^{-1}. The comprehensive summary of the FTIR analysis of domestic plastic waste and mixed virgin plastic are shown in Table 2. Table 2 provides comprehensive details regarding the various functional groups of hydrocarbons and their behavior, strength, and mode of vibration.
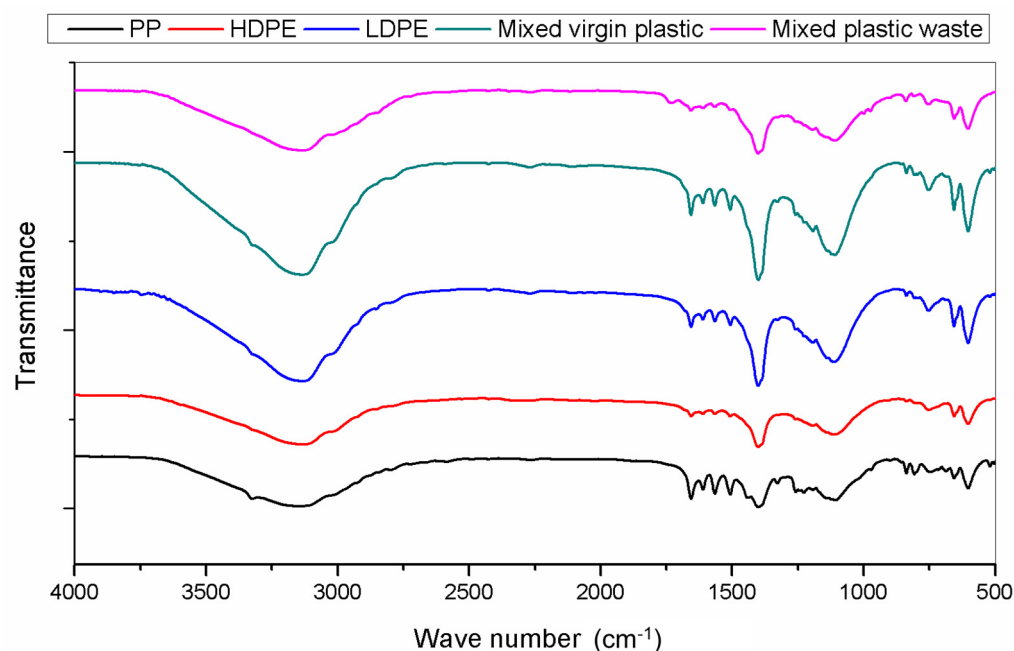
Figure 3. Fourier transformed Infrared spectra of plastic feedstock.

Table 2. Summary of functional group analysis of plastic feedstock.

Wavelength	Remark
3200–3000 cm^{-1}	=C−H stretch, −C−H stretch, CH$_3$, CH$_2$ & CH (strong)
2962 cm^{-1}	−C−H stretch, CH$_3$, CH$_2$ & CH (strong)
1650 cm^{-1}	C=C stretch
1458, 1377 cm^{-1}	−C−H bending, C=C bending.
Below 1000 cm^{-1}	=C−H bending and fingerprint region

3.2. Product Distribution of Pyrolysis Reaction with Domestic Plastic Waste, PP, LDPE, HDPE, and Mixed Virgin Plastic

The product distribution of pyrolysis reaction with domestic plastic waste, PP, LDPE, HDPE, and mixed virgin plastic is depicted in Figures 4 and 5. The temperature range for the pyrolysis of these plastics was 573 K to 973 K with a constant heating rate of 10 K min^{-1}. Liquid hydrocarbon fuel, non-condensable gases (pyrolysis gases), and solid residue (pyro char) were the main products of the reaction. The results showed that the yield of gaseous products was increased with the rising of temperature while liquid product yield increased with a specific temperature, and after that, it was found to be decreased with increasing temperature. As shown in Figure 5a, LDPE's liquid hydrocarbons fuel yield increased from 4.3% (473 K) to 64.6% (773 K) due to the devolatilization reactions being supported by higher temperatures. When the temperature increased beyond 773 K, the liquid product yield was reduced from 64.6% (773 K) to 30.8% (973 K). This may be due to secondary thermal cracking, which results in decomposition of these liquid hydrocarbons into non-condensable hydrocarbons. In addition, higher temperature favors the cracking of the large hydrocarbon molecules into small molecular products [32]. Therefore, the yield of gaseous hydrocarbons was found to be increased with increasing temperature. The poor yield of liquid and gaseous hydrocarbons at lower temperatures was due to incomplete reaction.
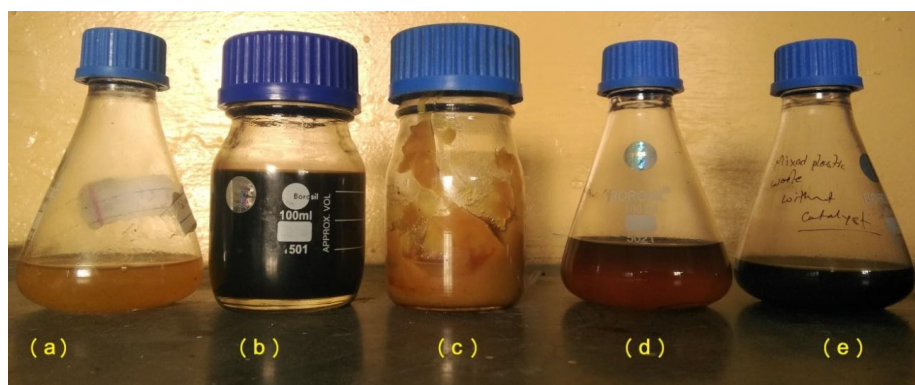
Figure 4. Different alternate fuels produced from (**a**) PP (**b**) LDPE (**c**) HDPE (**d**) Mixed virgin plastic (**e**) Domestic plastic waste (all products shown are produced at optimum temperature condition).

Figure 5b shows the product distribution of HDPE virgin plastic pyrolysis. HDPE liquid hydrocarbons yield was observed maximum (62.2 wt.%) at 773 K. In contrast, gaseous hydrocarbon was maximum (68.6 wt.%) at 973 K. The trend of solid, liquid, and gaseous hydrocarbon yield was almost similar to LDPE pyrolysis products. However, LDPE produced a higher amount of liquid products compared to HDPE and PP. The results of PP pyrolysis are shown in Figure 5c and demonstrated that the maximum value of liquid and gaseous hydrocarbons was 63.1 wt.% and 66.8 wt.% at the temperature of 773 K and 973 K, respectively. At higher temperatures, condensables undergo secondary reactions in which large molecules further break down to smaller molecules, thereby reducing the condensate and increasing the non-condensable gases [33]. Solid residue decreases with increasing temperature and almost produces a fixed amount of 4.2 g to 1.5 g at 773 K onwards. These data were also supported by TGA analysis. The liquid hydrocarbons were lesser than LDPE but higher than HDPE. A similar study was conducted on virgin high-density polyethylene (HDPE) pyrolysis at temperature and pressure ranges of 450–504 °C and 0.1–2 bar in a continuous pilot-scale plant [34]. The findings demonstrated that even at low temperatures and pressures in the examined ranges, the chain-end scission mechanism is the primary mechanism in the HDPE pyrolysis process. The oil produced from the pyrolysis of virgin HDPE at a temperature of 464 °C and sub-atmospheric pressure of 0.1 bar results in the highest linear hydrocarbon concentration (93.2 wt.%). Furthermore, the share of cyclic and branched hydrocarbons was improved up to 17.4 wt.% at higher pressure and temperature compared to 6.8 wt.% at vacuum pressure and lower temperature.

In addition, to see the combined effect of PP LDPE, and HDPE pyrolysis, all these three virgin plastics were mixed into a particular ratio, and results were compared with mixed virgin plastic and domestic plastic waste. It was noted that the mixed virgin plastic composition was almost identical to that of domestic plastic garbage collected from university campuses. The pyrolysis results of mixed virgin plastic and domestic plastic waste are shown in Figure 5d,e. Pyrolysis of mixed virgin plastic was carried out to identify the fuel quality and compare it with the real-time quality of domestic plastic waste. It was observed that liquid hydrocarbon fuel from HDPE virgin plastic was waxy oil while PP and LDPE virgin plastic pyrolysis resulted in a clear liquid. In the case of mixed virgin plastic, liquid hydrocarbons were again completely in liquid form, which may be because waxy oil from HDPE is soluble in other liquid hydrocarbons fuel at room temperature. As illustrated in Figure 4d, the mixed virgin plastic yielded maximum 68.6% liquid product at 723 K temperature, while domestic plastic waste resulted in 64.5%. In addition, the liquid products yield was higher for mixed virgin plastic compared to individual virgin plastic. The reason behind this may be due to the synergetic effect of decomposition of LDPE, HDPE, and PP simultaneously during pyrolysis reaction [35]. On the other hand, gaseous hydrocarbon yield was reached up to 64 wt.% at 973 K.
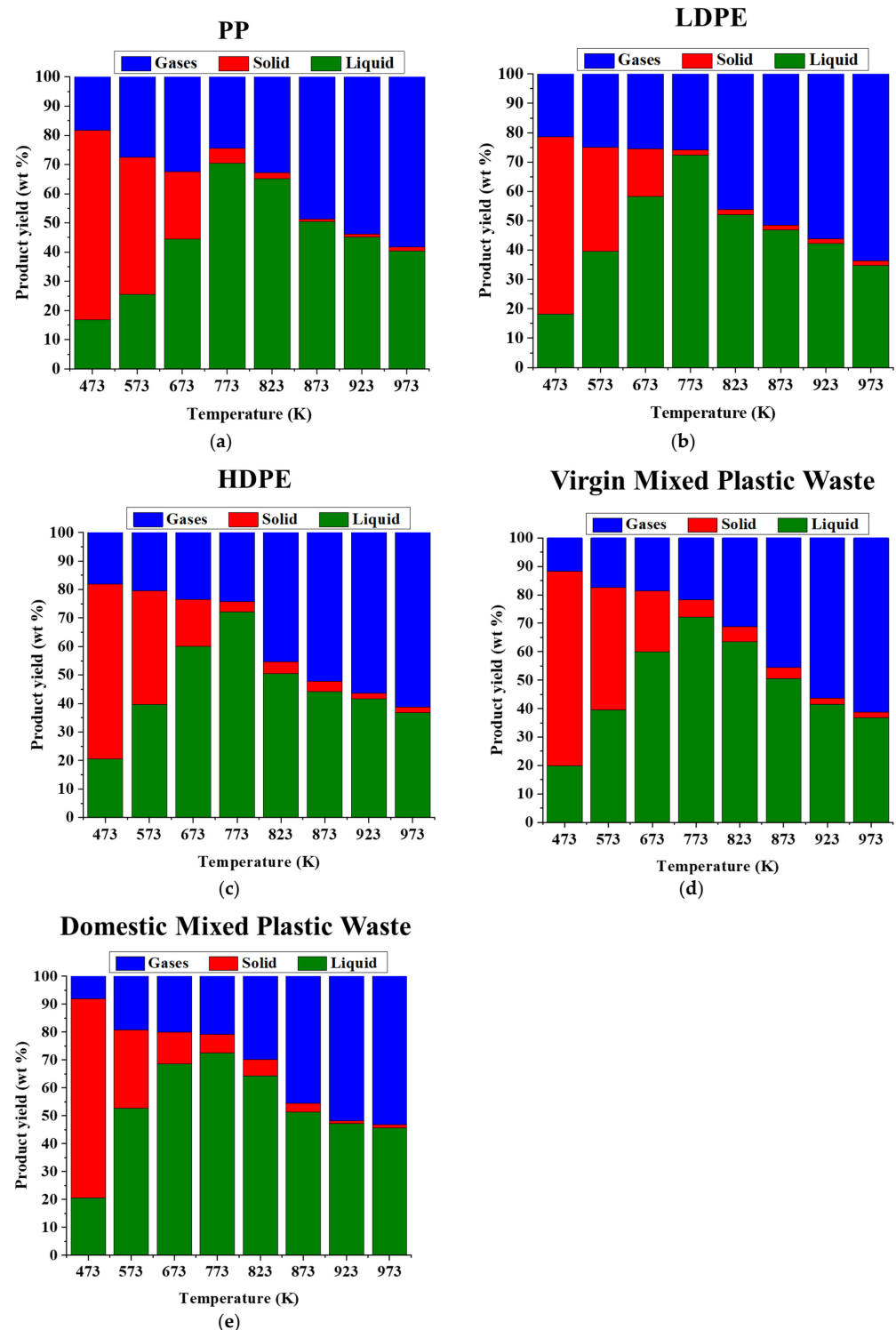
Figure 5. Product yield obtained from pyrolysis of (**a**) PP, (**b**) LDPE, (**c**) HDPE, (**d**) MVP, (**e**) DPW.

Domestic plastic waste behaves quite differently in pyrolysis than mixed virgin plastics because it contains a variety of other polymers in traces (1–5%), as well as coloring agents, additives, and other materials. In the narrow temperature range of 723–773 K, the highest yield of liquid product was reported to be 60.3 wt.% to 64.5 wt.% (Figure 5e). However, the maximum yield of liquid and gaseous products was observed to be lower for domestic plastic waste compared to mixed virgin plastic. This may be due to some polymer binders and coloring agents present in domestic plastic waste [35].

3.3. Analysis of Liquid Products Extracted from Plastic Feedstock by Pyrolysis Process

3.3.1. FTIR of Pyrolysis Liquid Fuels

The FTIR spectra of alternative fuel produced by the pyrolysis of plastic feedstock are shown in Figure 6. Chemical bonds absorb specific wavelengths that describe the fuel's structure and molecular bond strength as it interacts with infrared light in the FTIR spectrometer. The spectra of all feedstocks, i.e., PP, LDPE, HDPE, mixed virgin plastic, and domestic plastic waste, were almost similar.
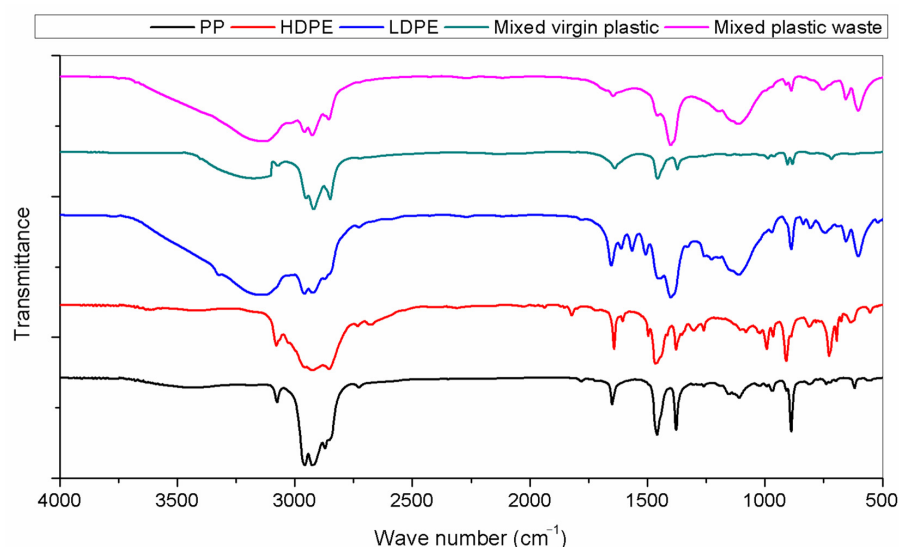

Figure 6. FTIR spectra of liquid hydrocarbon fuel from pyrolysis of LDPE, HDPE, PP, MVP, and DPW.

Figure 6 illustrates the presence of C-H, C=C, and =C−H bonds in the spectra of hydrocarbon fuels. Alkenes were detected at 3138 and 3444 cm^{-1} with a significant peak signal associated with the =C−H stretching vibration. The alkanes in the hydrocarbon fuel have a high −C−H vibrational signature, as indicated by the wavenumber of 2922 cm^{-1}. Alkene was detected by the presence of C=C vibrational bending, C=C bending, and −C−H stretching vibration signals with wavenumbers of 1642, 1466, 1398, and 1376 cm^{-1}. GC−MS analysis was used to determine the precise chemical structural composition because FTIR analysis only gives an impression of the existence of functional groups for the preliminary structure of the chemical composition.

3.3.2. GC-MS Analysis

Utilizing GC-MS, the chemical make-up of liquid hydrocarbons extracted from LDPE, HDPE, PP, mixed virgin plastic, and domestic plastic waste was examined. The findings showed that aliphatic (alkane, alkene, and alkyl compounds) carbon, in the range of C8–C20, made up the majority of the liquid hydrocarbon fuels produced. It was observed from Table 3 that a major constitute of most of virgin plastics and domestic hydrocarbon was 1-Dodecene, 1-Decene, Undecane, Tetradecane and 1-Pentadecene, Pentadecane, 1-Heptadecene, Hexadecane. When individual virgin plastic (LDPE, HDPE, and PP) pyrolyzed, LDPE showed the maximum concentration of 1-Decene (12.43%), Undecane (12.31%), 1-Dodecene (9.13%), Decane (8.58%), 1-Heptadecene (8.56%), and Dodecane (6.65%) while HDPE liquid fuel was with the major constituent of Pentadecane (11.71%), 1-Pentadecene (10.58%), 1-Heptadecene (9.09%), Hexadecane (8.19%), and 1-Dodecene (5.78%). Furthermore, PP liquid fuel was majorly composed of 1-Octadecene (13.46%), 1-Hexadecene (11.61%), 1-Heptadecene (10.06%), Hexadecane (12.46%), and 1-Tetradecene (6.83%). All the virgin plastics liquid hydrocarbons were in the range of C8 to C20 with a major constituent alkene. In the case of mixed virgin plastic, 1-Pentadecene (9.08%), Pentadecane (9.16%), 1-Hexadecene (8.32%), Hexadecane (8.52%), and 1-Decene (6.8%) appeared as significant hydrocarbons.

Table 3. Chemical composition of liquid hydrocarbon fuel obtained from LDPE, HDPE, PP, MVP, and DPW.

Compound	Molecular Formula	LDPE	HDPE	PP	Mixed Virgin	Domestic Plastic Waste (wt.%)
1-Octene	C_8H_{16}	1.78			1.35	0.81
Toluene	$C_{10}H_{20}$	0		4.05	5.26	1.01
Nonane	C_9H_{20}	3.01	2.41		1.08	
1-Nonene	C_9H_{18}	1.06	2.62		3.16	3.52
1-Decene	$C_{10}H_{20}$	12.43	4.14	2.57	6.8	3.84
Decane	$C_{10}H_{22}$	8.58	5.21	2.24	5.42	3.17
cyclodecane	$C_{10}H_{20}$		5.76		3.9	
1-Undecene	$C_{11}H_{22}$		5.47		1.7	6.06
Undecane	$C_{11}H_{24}$	12.31	5.6	3.27	1.2	2.41
1-Dodecene	$C_{12}H_{24}$	9.13	5.78	4.74	4.15	3.61
Dodecane	$C_{12}H_{26}$	6.65	3.65		5.49	12.63
Tridecane	$C_{13}H_{28}$				1.93	5.32
1-Tridecene	$C_{13}H_{26}$	5.32	1.97	5.73	3.58	9.96
1-Tetradecene	$C_{14}H_{28}$	2.02	5.23	6.83		8.31
Tetradecane	$C_{14}H_{30}$	6.55	4.66	5.09	5.83	5.97
1-Pentadecene	$C_{15}H_{30}$	6.12	10.58	3.65	9.08	2.28
Pentadecane	$C_{15}H_{32}$		11.71	6.82	9.16	10.21
1-Hexadecene	$C_{16}H_{32}$	5.08		11.61	8.32	5.24
1-Heptadecene	$C_{17}H_{34}$	8.56	9.09	10.06	5.71	0.17
Hexadecane	$C_{16}H_{34}$	3.61	8.19	12.46	8.52	2.62
Dibutyl adipate	$C_{14}H_{26}O_4$					5.9
Heptadance	$C_{17}H_{36}$	3.66	5.48	4.38	3.01	3.08
1-Octadecene	$C_{18}H_{36}$	0	2.45	13.46	1.31	
1-Nonadecene	$C_{19}H_{38}$	2.06		1.52	2.02	0.94
Eicosane	$C_{20}H_{42}$	2.07		1.52	2.02	2.94

Domestic plastic waste's composition was almost like mixed virgin plastic. However, it showed a slightly different hydrocarbon composition. Dodecane (12.63%), 1-Tridecene (9.96%), Pentadecane (10.21%), 1-Hexadecene (9.24%), Tetradecane (5.97%), and Tridecane (5.32%) were the major hydrocarbons compared to mixed virgin plastics. In thermo-catalytic pyrolysis, random scission of LDPE, HDPE, and PP occurs, resulting in radicals. After that, β-scission of these radicals takes place to produce a monomer which undergoes a stabilization process by transfer of intramolecular or intermolecular hydrogen. Olefins and dienes are made when the secondary radicals undergo a series of β-scission reactions. Paraffine is produced simultaneously as a result of the intermolecular hydrogen transfers. Due to the abundance of the hydrogen atom in the radical chain at elevated temperatures, the probability of successive β-scission with intramolecular hydrogen transfer is highly expected [35]. In addition, Dibutyl adipate, a specific oxygenated compound utilized generally as a plasticizer in the paint industry, was also identified in domestic liquid hydrocarbon fuels. These findings were in line with those obtained using FTIR.

On the other hand, when mixed virgin plastic and domestic plastic waste were pyrolyzed under the same temperature conditions using mineral clay as a catalyst, the results showed that the catalyst favored the formation of alkanes. Due to catalytic reaction, alkanes increased from 43.66% to 58.55% and from 48.35% to 61.5% in the case of mixed virgin plastic and domestic plastic waste, respectively. In addition, a slight increase in aromatics was also observed. Besides, wax formation was also reduced in liquid products, which may be due to the reason that clay is more acidic in nature and, therefore, leads to crack waxes (C13–C28) into lighter hydrocarbon [36].

3.3.3. Analysis of Physic-Chemical Properties of Liquid Fuels

After obtaining the liquid hydrocarbons fuel, various tests were performed for its characteristic properties such as ultimate and proximate analysis, viscosity, density, fire

and flash point, cloud and pour point, and moisture analysis, and are depicted in Table 4. All the techniques were carried out as per the standards mentioned.

Table 4. Characteristics properties of alternate fuel obtained from different plastic.

Parameter	PP	LDPE	HDPE	Mixed Virgin Plastic	Domestic Plastic Waste	Gasoline	Diesel
Appearance	Pale yellow	Pale yellow	Dark brown	Brown	Dark brown	No color	Pale yellow
Moisture (% *v/v*) (ASTM D95)	0	0	0	0	2.4	0.4–0.5	0.1–0.3
API gravity @ 60 °F (ASTM D287)	33.03	27.48	34.21	36.72	39.6	55	38
Density @ 15 °C g/cc (ASTM D4052—16)	0.86	0.89	0.92	0.91	0.86	0.78	0.807
Kinematic viscosity @ 40 °C (cSt) (ASTM D445)	4.09	3.98	5.08	4.53	4.48	1.17	2–4.5
Gross heat of combustion (MJ/kg) (ASTM D240—17)	45.72	45.59	43.63	44.61	43.92	47.64	45.21
Conradson carbon residue (wt.%) (ASTM D189)	0.12	0.19	0.11	0.15	0.15	0.14	0.35
Ash (wt.%) (ASTM D482)	0.013	0	0	0.11	0.013	0.001	0.01
Pour point (°C) (ASTM D97)	−9	−10	35	30	18	−	6
Flash Point (°C) (ASTM D93)	30	48	29	40	35	42	52
Aniline point (°C)	40	45	50	50	60	71	77.5
Diesel index	42.5	38.01	40.23	38.54	35.34	−	40

Liquid hydrocarbons from virgin HDPE plastic were found to be waxy, whereas PP and LDPE produced a clear liquid. Furthermore, the quality of the hydrocarbon fuel made from domestic plastic waste and mixed virgin plastic in this investigation was comparable to that of standard petroleum fuels, with kerosene and unpleasant odor and a dark brown color. This fuel color may be due to coloring and binding agents in the input feed. On the other hand, the produced hydrocarbon fuels were free-flowing and could be utilized directly for heating applications. Table 4 illustrates various properties such as viscosity, density, fire and flash point, cloud and pour point, and calorific value of the liquid hydrocarbon fuels from LDPE, HDPE, PP, mixed virgin plastic, and domestic plastic waste. Density and viscosity are the main fuel properties which highly affect the engine performance and emissions. Higher density and viscosity may affect the atomization process during combustion, resulting in decreased engine performance [37,38]. The density of liquid hydrocarbon fuels derived from LDPE, HDPE, PP, mixed virgin plastic, and domestic plastic waste was 0.89 g/cc, 0.92 g/cc, 0.86 g/cc, 0.91 g/cc, and 0.86 g/cc, respectively, in comparison to gasoline (0.78 g/cc) and diesel (0.807 g/cc). Similarly, the kinematic viscosity of LDPE (3.98 cSt), HDPE (5.08 cSt), PP (4.09 cSt), mixed virgin plastic (4.53 cSt), and domestic plastic waste hydrocarbon fuels (4.48 cSt) was lower than MVP fuel (4.53 cSt); nonetheless, it was in the range of ASTM standards (2–6 cSt). Other properties such as flash point were also found to be lesser for individual virgin plastics (LDPE—30 °C, HDPE—34 °C, PP—29 °C) compared to mixed virgin plastic (40 °C) and domestic plastic waste (35 °C). The values of flash point for diesel and gasoline were observed to be 52 °C and 42 °C, respectively, which is in agreement with other research [4,29]. On the other hand, the calorific value of mixed virgin plastic and domestic waste plastic was 44.61 MJ kg^{-1} and 43.92 MJ/kg, respectively, compared to diesel (45.21 MJ/kg) and gasoline (47.64 MJ kg^{-1}). Moreover, the calorific value of individual virgin plastics, i.e., LDPE (45.72 MJ kg^{-1}), HDPE (45.59 MJ kg^{-1}), and PP (43.63 MJ kg^{-1}), was also in the range of the values obtained for diesel and gasoline. Calorific value is one of the main properties of fuel that highly affects combustion. Similar results for calorific value of LDPE, HDPE, and PP were also obtained by Budsaereechai et al. 2019 [36]. Table 4 shows a comparison of the pour points of the resulting hydrocarbon fuels and commercial fuels. Due to the high volatility of the sample, the pour point of gasoline was not examined in this study. The pour point of pyrolytic liquid fuels derived from mixed virgin plastic and domestic plastic waste was poorer than

that of diesel fuel. The diesel index is a measurement of a diesel fuel's ignition efficiency. It is calculated on the basis of the sample's specific gravity and aniline point. In the present study, the diesel index of plastic hydrocarbon fuels was 42.5 (LDPE), 38.01 (HDPE), 40.23 (PP), 38.54 (mixed virgin plastic), and 35.34 (domestic plastic waste). These values were in good agreement with the standard value of diesel [38]. Based on these fuel properties, it can be observed that liquid hydrocarbon fuels, derived either from virgin plastic or plastic waste, have an excellent potential for use as an alternative fuel.

3.4. Gas Analysis Obtained from Pyrolysis of Plastic Waste

Table 5 summarizes the analysis of the gases produced during the pyrolysis of the plastic feedstock. The findings showed that the gas compositions obtained during the pyrolysis of mixed virgin plastic and household plastic garbage were almost similar. Significant levels of alkane and alkene hydrocarbon gases from C1 to C4 have been found in pyrolytic gases. These gases are produced due to irregular scission of larger hydrocarbon groups at a higher temperature. These gases are also feasible if secondary cracking reactions of condensable gases continue for a longer period of time in the primary reactor. The GC results showed that pyrolytic gases derived from individual virgin plastics have hydrocarbons such as ethene and propene as a major product. In addition, some traces of hydrogen gas are also identified in pyrolytic gases. However, LDPE, HDPE, PP, and mixed virgin plastic showed no CO and CO_2 in pyrolytic gaseous composition. However, small traces of CO and CO_2 were examined in domestic plastic waste, which may be due to impurities, binder, filler, or coloring agent. Butene was also observed in the least amount for all types of plastic pyrolytic gases. Unsaturated hydrocarbons, which are produced by the random scission breakdown of plastic followed by the stabilization of intermediate radicals, were also examined. These hydrocarbons include ethene, propylene, butene, and its derivative [34]. The gross and net calorific values of pyrolytic gases obtained from virgin and domestic plastic wastes were observed in the range of 66.74 MJ m^{-3} to 75.61 MJ m^{-3} which confirm that these pyrolytic gases can be used as fuel gas for heating and engines. The pyrolytic gas compositions obtained from virgin plastics and domestic plastic waste were found to be consistent with other studies carried out by different researchers [30,31,34]. Furthermore, the pyrolytic gases have good potential to utilize in turbines for power generation or to be used directly in boilers as a substitute for coal without any additional pretreatment.

Table 5. Non-condensable gas composition of plastic feedstock (wt.%).

Plastic	LDPE	HDPE	PP	Mixed Virgin Plastic	Domestic Plastic Waste
Hydrogen	0.31	0.46	0.96	1.58	0.45
Carbon dioxide	0	0	0	0	0.82
Carbon monoxide	0	0	0	0	0.44
Methane	7.47	9.28	1.48	6.07	7.6
Ethane	12.1	11.56	14.42	11.69	12.12
Ethene	27.99	26.41	38.65	31.02	27.41
Propane	8.1	8.67	8.87	8.55	8.44
Propene	26.34	26.74	29.9	27.66	26.71
Butane	2.52	1.51	1.67	1.9	1.98
Butene	15.17	15.37	4.05	11.53	14.03
Gross calorific value (MJ nm^{-3})	69.99	69.02	75.61	70.97	69.38
Net calorific value (MJ nm^{-3})	67.49	66.60	71.02	67.84	66.74

4. Conclusions

The pyrolysis of individual and mixed virgin plastic was compared with domestic plastic waste collected from UPES, University. This study has demonstrated the production of various grades of hydrocarbons fuels from individual virgin plastics (LDPE, HDPE, and

PP), mixed virgin plastic, and domestic plastic waste at the temperature range 473 K to 973 K. All types of plastic feedstock showed more similarity with diesel fuel hydrocarbons. Additionally, gas fuel products from pyrolysis of domestic plastic waste and virgin plastic feedstock contain C1–C4 hydrocarbons that have high calorific value compared to other sources (biomass). Hence, catalytic conversions of plastics using inexpensive catalysts provide an innovative and feasible refinery pathway, explicitly targeting jet-fuel-range hydrocarbon fuels.

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