

Article

Experimental Study of Thermal and Catalytic Pyrolysis of Plastic Waste Components

Azubuikwe Francis Anene ^{1,*}, Siw Bodil Fredriksen ², Kai Arne Sætre ²  and Lars-Andre Tokheim ¹

¹ Department of Process, Energy and Environmental Technology, University of South-Eastern Norway, 3918 Porsgrunn, Norway; Lars.A.Tokheim@usn.no

² Norner Research AS, 3962 Stathelle, Norway; siw.fredriksen@norner.no (S.B.F.); kai.sætre@norner.no (K.A.S.)

* Correspondence: francisazu_anene@yahoo.com; Tel.: +47-4063-0211

Received: 10 October 2018; Accepted: 26 October 2018; Published: 31 October 2018



Abstract: Thermal and catalytic pyrolysis of virgin low-density polyethylene (LDPE), high-density polyethylene (HDPE), polypropylene (PP) and mixtures of LDPE/PP were carried out in a 200 mL laboratory scale batch reactor at 460 °C in a nitrogen atmosphere. Thermogravimetric analysis (TGA) was carried out to study the thermal and catalytic degradation of the polymers at a heating rate of 10 °C/min. The amount of PP was varied in the LDPE/PP mixture to explore its effect on the reaction. In thermal degradation (TGA) of LDPE/PP blends, a lower decomposition temperature was observed for LDPE/PP mixtures compared to pure LDPE, indicating interaction between the two polymer types. In the presence of a catalyst (CAT-2), the degradation temperatures for the pure polymers were reduced. The TGA results were validated in a batch reactor using PP and LDPE, respectively. The result from thermal pyrolysis showed that the oil product contained significant amounts of hydrocarbons in the ranges of C₇–C₁₂ (gasoline range) and C₁₃–C₂₀ (diesel range). The catalyst enhanced cracking at lower temperatures and narrowed the hydrocarbon distribution in the oil towards the lower molecular weight range (C₇–C₁₂). The result suggests that the oil produced from catalytic pyrolysis of waste plastics has a potential as an alternative fuel.

Keywords: thermal pyrolysis; catalytic pyrolysis; TGA; plastics; HDPE; LDPE; gasoline; diesel; catalyst

1. Introduction

Plastics are an essential part of the human life and the global economy. The use of plastics has increased immensely over time as it serves as a key component for different sectors such as packaging, construction, transportation, electronics and healthcare. Plastics are used in these sectors due to their durability, versatility [1], resistance to corrosion, low weight, excellent thermal and electrical insulation, and low production cost [2,3]. However, these properties, which describe the usefulness, may also be a challenge when considering the end of life phase of plastics [4].

Plastic wastes are divided into two main types: industrial plastic waste (IPW) and municipal plastic wastes (MPW) [5–7]. These waste types will usually contain polyethylene (PE), polyvinyl chloride (PVC), polystyrene (PS) and polypropylene (PP) [5,8]. About 50–70% of MPW is made up of packaging materials [9].

Polyolefins (PE, PP) are non-biodegradable and remain in the environment for a long time, prompting research related to different management techniques, including: disposal to landfill sites, reuse, recycling and waste to energy (WTE) processes [10,11]. Landfilling was the most used method of waste treatment because of its simplicity and the poor awareness of its environmental

impact. As landfilling causes water pollution, greenhouse gas emissions and local inconvenience [12], alternatives are needed. Thermochemical conversion of plastics to energy and fuel is another option to recover the materials that cannot be material recycled [10]. Examples of this WTE or plastic-to-fuel (PTF) technology are pyrolysis, gasification, plasma arc gasification, and combustion of refuse-derived fuel (RDF) [10,11].

Pyrolysis can be thermal or catalytic [6,13]. The advantages of catalytic pyrolysis are degradation at a lower temperature (lower energy consumption), increased selectivity, faster-cracking reactions, shorter residence time, inhibition of the formation of undesirable products, increased product yield and production of liquid products with a lower boiling point [13,14].

Marcilla et al. [15] studied the catalytic pyrolysis behaviour of mixtures of high-density polyethylene (HDPE) and polypropylene (PP) using thermogravimetric analysis (TGA). They discovered that the maximum thermal degradation temperature of PP was 447 °C, while that of HDPE was 467 °C. The thermal degradation of PP occurred at a lower temperature compared to HDPE, as expected due to the tertiary carbons in the polymer backbone. They further observed that the degradation temperature of HDPE/PP mixture was between the range 447–467 °C.

Williams et al. [16] studied the analysis of products from the pyrolysis and liquefaction of single plastics and waste mixtures, using a batch autoclave reactor at 500 °C. The thermal pyrolysis of PE and PP (virgin polymers) at 500 °C gave a high yield of liquid fraction (oil), and no char was formed. An oil yield of 95 wt % was obtained from PP, while PE produced 93 wt % oil.

Yan et al. [17] studied the thermal cracking of virgin and waste plastics PP and low-density polyethylene (LDPE) in a semi-batch reactor, under atmospheric pressure at 460 °C. The thermal pyrolysis of LDPE and PP at 460 °C gave a high yield of liquid fraction (84 wt %) in both cases. The gas chromatography analysis of the oil yield obtained from the pyrolysis of PP contained 58% gasoline range hydrocarbons, while the oil obtained from pyrolysis of LDPE contained 21 wt % of gasoline range hydrocarbons.

Catalytic pyrolysis is a way to improve the product yield and selectivity and reduce the pyrolysis temperature [13,18]. The lower reaction temperature, which may lower the energy requirement of the process, is due to the lowered activation energy of the pyrolysis reactions. A catalyst may favour the yield of lighter hydrocarbons, gasoline range products and gases [5,10]. The distribution of the products obtained depends on the type of polymer, their sources and their structures [5,19].

Many studies on the catalytic pyrolysis of plastic waste have been carried out. However, virgin polymers are most commonly investigated [13,17], and there is little emphasis on polymer blends [15]. Zeolites appear to be the most used catalysts for pyrolysis. Marcilla et al. [20] studied the HUSY zeolite catalyst and compared it to the HZSM5 zeolite catalyst using HDPE and LDPE in a batch reactor at 550 °C. The gas yield was high when HZSM5 was used with LDPE (71 wt %) and HDPE (73%), while the HUSY catalyst gave a higher liquid yield (62% for LDPE and 41% for HDPE). The results showed that different zeolite catalysts have different selectivity because of different acidity and pore sizes.

Seo et al. [21] investigated the effect of a catalyst (ZSM-5) on the degradation of HDPE at 450 °C in a batch reactor. A liquid yield of 35 wt % and a gas yield of 65 wt % was obtained. Gas chromatography–mass spectrometry (GC–MS) analysis of the liquid product gave a carbon distribution of 99% of C6–C12 (gasoline) and 1% of C13–C23 (diesel). Kaixin et al. [22] investigated the catalytic activity of microporous and mesoporous catalysts in the pyrolysis of waste PE and PP mixture in a batch reactor at 500 °C. Three microporous catalysts (HUN-ZSM-5, C-ZSM-5, and β -zeolite) and three mesoporous catalysts (Al-MCM-41, KFS-16B, Al-SBA-15(wo)) were investigated. They reported that the highest gasoline fraction was produced by HUN-ZSM-5 (96%) followed by β -Zeolite, which produced 85%. The Al-SBA-15 catalyst has an excellent selectivity for diesel (C13–C20) fractions (54%). They concluded that the acidity and textural properties of the catalysts determined the yield and that the catalytic pyrolysis products could be a potential alternative to fossil fuel.

Previous studies have compared the thermal and catalytic degradation of LDPE, PP and their mixtures, but most of these studies were carried out with catalysts that favour gas production and not a high liquid fraction.

The objective of this study was to determine the C₇–C₁₂ fraction in the product from pyrolysis of virgin polyolefins (LDPE, PP, HDPE and blends thereof) via thermal and catalytic pyrolysis using a suitable catalyst (CAT-2). Commercial samples of virgin HDPE, LDPE, PP and mixtures of LDPE/PP were analysed by TGA to characterize the decomposition behaviour and select suitable conditions for the pyrolysis reaction. The pyrolysis experiments were made in a laboratory scale batch reactor, and the effect of the catalyst on the quality and quantity of the pyrolysis products was examined. The liquid fraction produced was analysed using gas chromatography–flame ionisation detector (GC–FID), and the simulated distillation curve was used to determine the hydrocarbon ranges corresponding to gasoline, diesel and heavy hydrocarbon fractions present in the pyrolysis product.

2. Materials and Methods

Three different types of commercially available virgin polymers were used: high-density polyethylene (HDPE), low-density polyethylene (LDPE), and polypropylene (PP). The polymers were obtained as pellets. Selected properties of the polymers are presented in Table 1.

Table 1. Properties of the polymer materials.

Plastic	Type	Density [kg/m ³] <i>—</i> ISO 1183	Melt Flow Rate [g/10 min] <i>—</i> ISO 1133	Melt Temperature [°C] ^a
HDPE	PE copolymer	945	0.3 (190 °C, 2.16 kg)	129
LDPE	PE copolymer	923	0.2 (190 °C, 2.16 kg)	124
PP	PP homopolymer	905	12 (230 °C, 2.16 kg)	220–260

^a Analysed by Differential Scanning Calorimetry (DSC). ISO: International Organisation for Standardisation.

The catalyst (CAT-2) used in this study is a fully characterised zeolite type catalyst supplied by a commercial catalyst supplier (Hulteberg Chemistry & Engineering AB, Sweden). The catalyst composition cannot be disclosed due to a non-disclosure agreement with the supplier. The catalyst was stored in a glove box to prevent absorption of moisture from the atmosphere.

A C₇–C₄₀ Saturated Alkanes Standard obtained from Sigma-Aldrich (St. Louis, MO, USA) was used for the identification of hydrocarbons in the liquid pyrolysis product. Hexane, heptane and rectified spirit were locally available at the Norner laboratory. Hexane was used for the dilution of the standard solution and the liquid product for GC analysis, while heptane and rectified spirit were used for the cleaning of pyrolysis equipment.

2.1. Thermogravimetric Analysis

Prior to the pyrolysis experiment, TGA of the samples was carried out to determine the degradation (decomposition) rate of the polymers and temperature, using a TGA from TA Instruments (Newcastle, DE, USA) (TGA Q500), controlled by a PC. A Mettler Toledo weighing balance (type: NewClassic MF, Switzerland; model: MS204S/01) was used to weigh the samples before loading the TGA sample pan.

TGA analysis was done on pellets as received and on pellets shredded down to 1.5 mm in a Retsch shredder (Type ZM 100, Retsch GmbH & Co. KG, Haan, Germany) in the presence of liquid nitrogen. The sample amount used in each analysis was 20 mg loaded in a 4 mm platinum pan. The TGA furnace was purged for 5 min with nitrogen (N₂ = 99.9999%) to ensure pyrolysis conditions, i.e., by displacing air and oxygen in the furnace and thereby avoiding oxidation of the samples. After purging, the experiment was performed in a nitrogen atmosphere with a flow rate of 60 mL/min under the experimental conditions shown in Table 2.

The catalyst was ground to powder, with a particle size <1.5 mm using a laboratory pestle and mortar. The shredded polymer and catalyst particles were stored in a glove box to prevent

contamination and ensure undeviating samples during the different runs. A catalyst feed ratio (C/F) of 1:10 was used for the TGA and pyrolysis analysis. This corresponds to findings from the literature [17,23,24]. Three dynamic runs for each sample were performed to test for repeatability of the results.

Table 2. Experimental cases (wt %) for the TGA analysis. A heating rate of 10 °C/min was applied in the entire temperature range from 25 to 600 °C.

CAT-2	HDPE	LDPE	PP
NO	100	-	-
NO	-	100	-
NO	-	75	25
NO	-	66	34
NO	-	50	50
NO	-	34	66
NO	-	-	100
YES	100	-	-
YES	-	100	-
YES	-	75	25
YES	-	66	34
YES	-	50	50
YES	-	34	66
YES	-	-	100

2.2. Pyrolysis Experiment and Procedure

The batch pyrolysis experiments were performed in a laboratory scale installation which included a 200 mL stainless steel reactor with a fitted lid. The reactor was fitted with a nitrogen inflow and product outflow pipe. A pressure gauge was installed to measure the pressure of N₂ flowing into the furnace and through the reactor. A muffle furnace (Heraeus Instruments, Type M110, D-6450, Hanau, Germany) was used to heat up the reactor (see Figure 1).

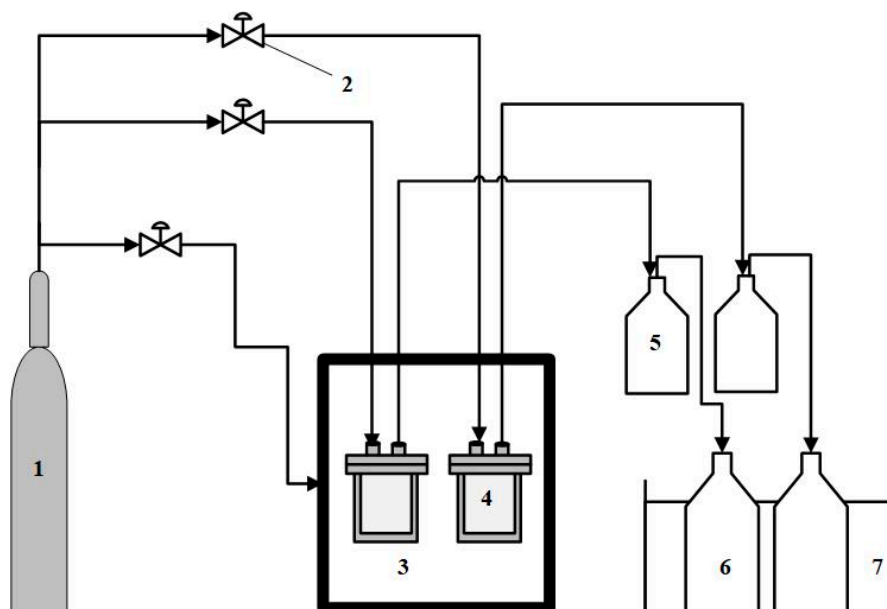


Figure 1. Pyrolysis equipment setup. (1) N₂ cylinder, (2) Diaphragm valve, (3) Muffle furnace, (4) Reactor, (5) Product collection bottles, (6) Collection bottles filled with de-ionized water, (7) Ice bath.

In the thermal pyrolysis experiments, polymer samples of ~10 g (single and mixtures) were pyrolysed under the experimental conditions given in Table 3. The temperature was selected based

on the TGA runs. In addition, 460 °C was chosen as the final pyrolysis temperature after a series of runs with temperatures < 450 °C led to the formation of wax in the product lines. The pre-weighed materials were added to the reactor after premixing using a stirrer. The reactor was assembled in the furnace with a connected nitrogen inlet and products' outlet lines.

Table 3. Experimental cases (wt %) for the pyrolysis experiments. All experiments were carried out at 460 °C and 1 atm.

CAT-2	LDPE	PP
No	-	100
No	34	66
No	66	34
No	100	-
Yes	-	100
Yes	34	66
Yes	66	34
Yes	100	-

Nitrogen (N₂ 99.9999%) was used to purge the reactor for 30 min to secure an inert atmosphere (no air). The reactor was heated slowly to the desired setpoint temperature (Table 3) using the programmable temperature controller (Thermicon P) of the muffle furnace. A hand-held thermometer (ANRITSU digital surface thermometer, HFT-80, Tokyo, Japan) was used to monitor the temperature in the furnace to make sure the temperature indicated by the furnace is approximately the same inside the furnace since N₂ was used to purge the furnace continuously. The sample was left in the reactor at the setpoint temperature until the completion of the reaction (no liquid product recovery).

In the catalytic pyrolysis experiments (Table 3), the catalyst was premixed mechanically with the polymer in a glove box to avoid absorption of moisture from the atmosphere. The condensable products were collected in two collection bottles (as there were two reactors in the muffle furnace), after cooling in another collection bottle filled with distilled water in an ice bath, while the non-condensable product (gas) was vented.

The liquid products from the pyrolysis were analyzed using a gas chromatograph equipped with a flame ionization detector (GC-FID). No residue was generated in the experiments; the only material left in the reactors at the end of the run was the catalyst residue in the catalytic process.

The percentage yield of the pyrolysis liquid collected at the end of the reaction and gas was calculated by the Equations (1)–(3) [2]:

$$Y_{liquid} = \frac{M_2}{M_1} 100\%, \quad (1)$$

$$Y_{residue} = \frac{M_3}{M_1} 100\%, \quad (2)$$

$$Y_{gas} = 100\% - (Y_{liquid} + Y_{residue}). \quad (3)$$

Here:

M_1 : Mass of the sample,

M_2 : Mass of liquid product,

M_3 : Mass of residue.

The mass of the liquid product is the sum of the liquid product and wax collected at the end of the experiments.

2.3. Pyrolysis Product Analysis and Characterisation

A GC-FID instrument (Hewlett Packard, HP 6890 Series GC System, G1530A, Palo Alto, CA, USA) was used to analyse the pyrolysis product (liquid) to determine the hydrocarbons present. The GC-FID was not able to analyse compounds ($<C_7$) because of the standard used. Table 4 shows the characteristics of the method employed. The hydrocarbon contents were identified by comparison of their retention time with that of the calibration sample (standard solution) using a computer with installed GC software (Agilent OpenLab CDS, A.01.09.126).

Table 4. Gas chromatograph specifications applied in determination of the hydrocarbon range distribution range (liquid product), ISO 3924:2016.

GC	HP 6890 Series
Column	DB-1 HT
Column length	15
Column ID (mm)	0.32
Stationary Phase thickness	0.1
Carrier gas	He/H ₂
Total flow rate (mL/min)	68.9
Initial column temperature (°C)	40
Final column temperature (°C)	350
Detector	FID
Injection temperature (°C)	340
Injection volume (μL)	1
Detector temperature (°C)	360
Heating rate (°C/min)	10

3. Results and Discussion

3.1. Thermal and Catalytic Degradation of Polymers and Their Mixtures

The maximum degradation temperatures of pure HDPE, LDPE, PP, as well as mixtures of the LDPE/PP at the experimental conditions given in Table 2, are presented in Figure 2. This is the temperature at which the weight losses of the polymers reach the maximum.

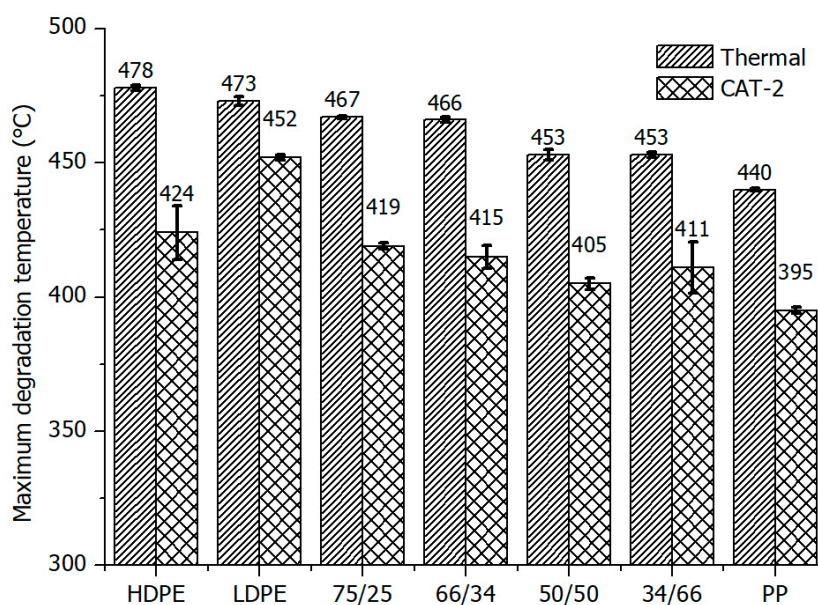


Figure 2. Temperatures of maximum weight losses in thermal and catalytic TGA experiments for pure HDPE, LDPE, PP polymers and LDPE/PP mixtures.

When applying a catalyst, the degradation temperatures of the single polymers and their mixtures decrease. CAT-2 is effective in reducing the maximum degradation temperature of both the single polymers and LDPE/PP mixtures as seen in Figure 2. The effect of the catalyst is more pronounced in HDPE than PP and LDPE, indicating that the catalyst is polymer specific. The effect varied between the LDPE/PP mixtures as follows: 66/34 > 75/25 > 50/50 > 34/66.

Figure 3 shows the weight loss of HDPE, LDPE, PP, and LDPE/PP mixtures. The thermal degradation of PP occurred at a lower temperature than HDPE, LDPE and LDPE/PP mixtures. However, the TG curves (Figure 3a) of all the samples follow the same trend, due to the similar chemical bonds in their molecular structures and degradation mechanism [7]. Figure 3a flattened out in the temperature range 450–510 °C and show complete decomposition of the samples with no char formation.

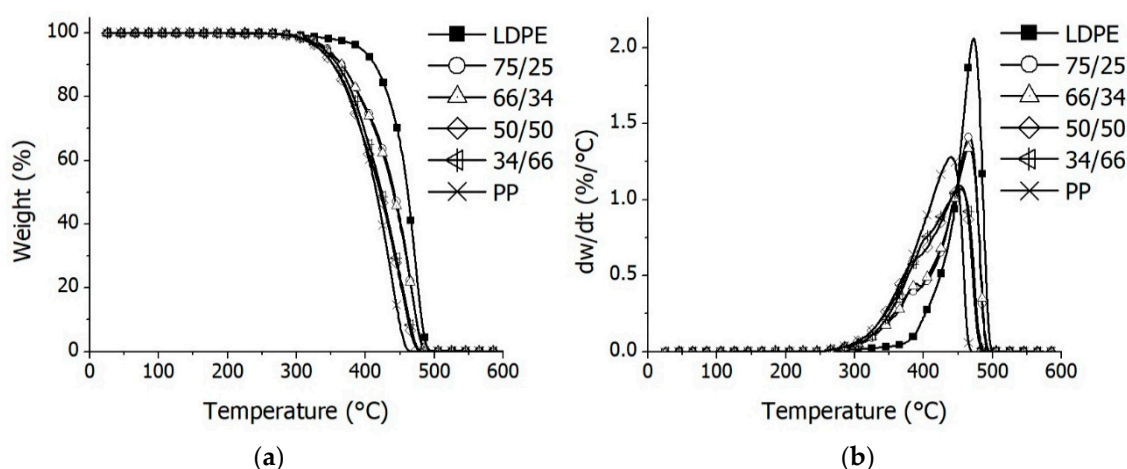


Figure 3. (a) TG curve of LDPE/PP mixtures and pure LDPE and PP; (b) DTG curve of LDPE/PP mixtures and pure LDPE and PP.

Thermal degradation of HDPE occurs within the temperature range 452–489 °C. Furthermore, LDPE degraded within the range 437–486 °C, whereas the degradation of PP occurs within the range 378–456 °C as shown in Figure 3a. The maximum degradation temperatures of the mixtures were observed to be between that of single PP and LDPE. However, the derivative thermogravimetric analysis (DTG) curves have two partially overlapped peaks (Figure 3b), which indicate an interaction between LDPE and PP. This complies with results reported by Kaixin et al. [22].

The mechanism of degradation of LDPE and PP is a radical chain mechanism; the tertiary radical which is present in the polymeric chain of PP, initiated by random chain scission captures the hydrogen from LDPE, thereby enhancing the degradation of LDPE at a lower temperature and amplifying the degradation of the LDPE/PP mixture [22]. It is important to note that no residue was left at the end of the experiments.

3.2. Pyrolysis Yields

Thermal and catalytic cracking of pure polymers (LDPE and PP) and mixtures (LDPE/PP) of polymers was performed in a batch reactor at conditions stated in Table 3. The condensable fraction of the gaseous products from the reactors was condensed and collected as a liquid fraction, while the non-condensable fraction was vented and calculated from Equation (3). The results from the thermal and catalytic pyrolysis yields at 460 °C are presented in Figure 4.

The yield of oil from thermal pyrolysis of pure LDPE was significantly higher (96 wt %) than the oil produced from pure PP (86 wt %). The low liquid yield obtained from the thermal pyrolysis of PP can be attributed to the formation of more gaseous products. This agrees with TGA results, where the maximum degradation temperature of PP is 440 °C. A similar result was obtained by

Sriraam et al. [19] when they carried out the pyrolysis of PP at 450 °C and concluded that 450 °C is too high of a temperature for the pyrolysis of PP.

The presence of PP in the mixture initiates the cracking of LDPE in the mixture at a lower temperature, leading to low liquid production, which corresponds to other reports [22,25,26]. However, an unusual behaviour was observed in the mixture with a higher PP portion, where a higher liquid yield was observed. This is contrary to other reports [27], which state that, when PP is co-pyrolysed with LDPE and the mass fraction of PP is higher than 20 wt %, the yield of liquid product is reduced. This might be explained by the uneven distribution of heat in the furnace.

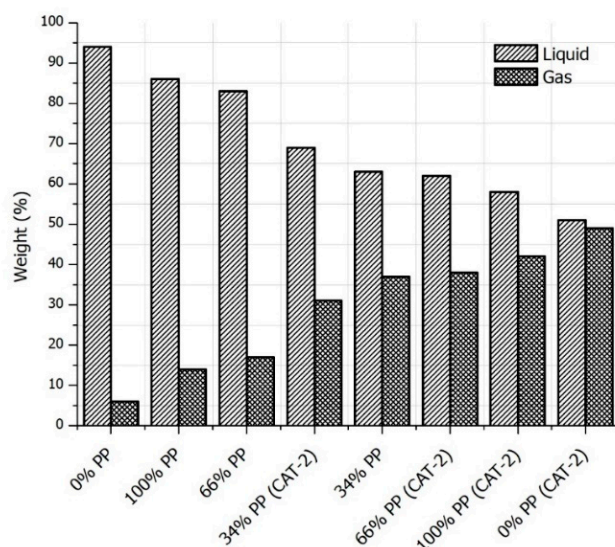


Figure 4. Thermal and catalytic yields of liquid and gaseous productions of LDPE, PP and their mixtures.

In the presence of a catalyst, the yield of liquid fraction from PP was significantly reduced to 58 wt %, while the liquid fraction yield from LDPE reduced to 51 wt %. The mixtures followed the same trend except for the mixture with a lower proportion of PP, whereby the liquid yield increased to 68 wt % compared to the thermal process liquid yield of 62 wt %.

The difference in the thermal and catalytic pyrolysis liquid yields could be attributed to the selectivity of the catalyst, and the homogeneity of the catalyst and the polymers. No residue was formed in these processes, indicating a high conversion of the samples, which validates the TGA analysis results.

From Figure 4, it can be suggested that catalytic pyrolysis is a two-step process. Thermal pyrolysis is the first step in the reaction since the liquid yield is higher in the absence of a catalyst. The second step is catalytic pyrolysis, where the catalyst cracks the liquid products further to lower hydrocarbon products, leading to a lower liquid yield. The role of the catalyst in this work is consistent with other reports [14,22].

3.3. GC-FID Analysis

The hydrocarbon number distribution of the oil products obtained from the thermal and catalytic process is presented in Figure 5.

As shown in Figure 5, the carbon number distribution obtained from analysis of the liquid yield of the polymers and their mixtures from thermal pyrolysis was a mixture of C₇–C₄₀ compounds, in which the diesel fraction compounds (C₁₃–C₂₀) were similar in both the pure polymers and their mixtures. A higher number of heavy hydrocarbons (C₂₁–C₄₀) were present in the oil yield of LDPE compared with that of the yield obtained from the other polymers and their mixtures. A significant percentage of gasoline fraction (C₇–C₁₂) was observed in the product from the mixture with a higher proportion of

PP and from pure PP. The diesel fraction percentage in this study is similar to results obtained in the literature [17] at the same pyrolysis conditions.

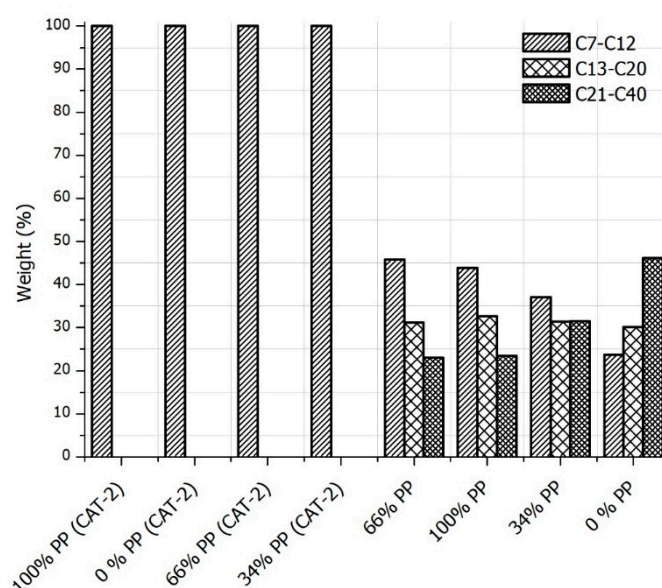


Figure 5. Carbon number distribution of liquid oil products determined by GC-FID.

The use of CAT-2 gave a narrower carbon distribution range that is skewed towards the gasoline range (C_7 – C_{12}) hydrocarbons (Figure 5). The GC-FID analysis agrees with the low yield of liquid products and an increased yield of gaseous products as shown in Figure 4, which confirms the cracking efficiency of CAT-2. CAT-2 proved to have an excellent high selectivity of gasoline range fractions (C_7 – C_{12}). No diesel range fraction (C_{13} – C_{20}) or heavy fractions (C_{21} – C_{40}) were detected in the analysis of the oil yield from the catalytic pyrolysis of the polymers and their mixtures. From the results, it is evident that the quality and the composition of the liquid fraction varied because of the catalyst used.

As seen in Figure 6, the use of CAT-2 gave advantages over thermal processes in terms of the quantity and selectivity of its oil product. CAT-2 has shown a good potential to produce gasoline from plastic wastes since the oil products obtained contains only gasoline (C_7 – C_{12}) range hydrocarbons. Catalytic pyrolysis occurred at a lower temperature than thermal pyrolysis.

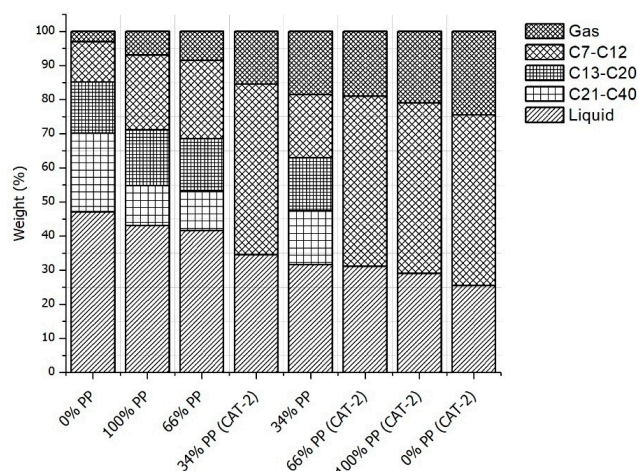


Figure 6. Thermal and catalytic pyrolysis yields of pure polymers and LDPE/PP mixtures.

The hydrocarbon composition of the liquid product obtained from the thermal and catalytic processes is quite similar to that of hydrocarbon fuels. Hence, such a product may be considered an alternative to conventional, non-renewable fuels.

4. Conclusions

In this study, thermogravimetric analysis (TGA) and thermal and catalytic pyrolysis of pure and mixed polymers often occurring in plastic wastes have been carried out.

TGA studies on the degradation of the pure polymers showed that HDPE, LDPE and PP have a very similar thermal behaviour. However, the LDPE/PP mixture presented a slightly different thermal behaviour from pure LDPE and PP, implying an interaction between LDPE and PP. Use of a catalyst lowered the degradation temperature of the polymers, indicating an energy consumption reduction in the pyrolysis process.

In thermal cracking of PP and LDPE in a reactor, total conversion of the polymers to liquid was about 86 wt % for PP and 94 wt % in the case of LDPE. GC-FID results showed that the hydrocarbon distribution of the liquid products were distributed within the C₇–C₄₀ carbon range. The selectivity of the gasoline range hydrocarbons was 24%, whereas the diesel range fraction was 30% and the heavy fraction reached 46% in the oil obtained from LDPE. In comparison, the oil obtained from thermal pyrolysis of PP contained 44% gasoline range hydrocarbons, 33% diesel range hydrocarbons and 23% heavier components. The LDPE/PP mixture with 66 wt % PP gave 46% of gasoline range hydrocarbons, whereas the mixture with 34 wt % of PP gave 37% gasoline range hydrocarbons. Hence, a higher proportion of PP increases the gasoline range fraction. The use of catalyst had a significant influence on the product yield and hydrocarbon properties. It promoted gas production and narrowed the hydrocarbon distribution in the oil product from both pure polymers and mixtures to the gasoline range fractions (C₇–C₁₂).

This study shows that, through pyrolysis, it is possible to convert commodity plastics (PE and PP) to hydrocarbons with carbon numbers in the gasoline and diesel range. This may contribute to solving the plastic waste problem in the society. The use of a suitable catalyst in the pyrolysis process may make it possible to tailor product composition and improve the energy efficiency of the process.

Author Contributions: Conceptualization, S.B.F. and K.A.S.; Methodology, S.B.F. and K.A.S.; validation, A.F.A., L.-A.T., S.B.F. and K.A.S.; Formal Analysis, A.F.A.; Investigation, A.F.A.; Resources, Norner Research AS; Writing—A.F.A.; Writing—Review and Editing, A.F.A., L.-A.T., S.B.F. and K.A.S.; Supervision, L.-A.T. and S.B.F.; Project Administration, A.F.A.

Funding: This research received no external funding.

Acknowledgments: The authors would like to thank the staff and management of Norner Research AS, for providing the catalyst, polymers, equipment and training on the equipment used in this research.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Forum, W.E. *The New Plastics Economy: Rethinking the Future of Plastics*; Ellen MacArthur Foundation: Geneva, Switzerland, 2016.
2. Ahmad, I.; Khan, M.I.; Khan, H.; Ishaq, M.; Tariq, R.; Gul, K.; Ahmad, W. Pyrolysis study of polypropylene and polyethylene into premium oil products. *Int. J. Green Energy* **2015**, *12*, 663–671. [CrossRef]
3. Sharuddin, S.D.A.; Abnisa, F.; Daud, W.M.A.W.; Aroua, M.K. A review on pyrolysis of plastic wastes. *Energy Convers. Manag.* **2016**, *115*, 308–326. [CrossRef]
4. European Commission. Plastic Waste—Strategy and Background. 2017. Available online: http://ec.europa.eu/environment/waste/plastic_waste.htm (accessed on 28 February 2017).
5. Kunwar, B.; Cheng, H.N.; Chandrashekar, S.R.; Sharma, B.K. Plastics to fuel: A review. *Renew. Sustain. Energy Rev.* **2016**, *54*, 421–428. [CrossRef]
6. Kyaw, K.T.; Hmwe, C.S.S. Effect of various catalysts on fuel oil pyrolysis process of mixed plastic wastes. *Int. J. Adv. Eng. Technol.* **2015**, *8*, 794–802.

7. Ayhan, D. Pyrolysis of municipal plastic wastes for recovery of gasoline-range hydrocarbons. *J. Anal. Appl. Pyrolysis* **2004**, *72*, 97–102.
8. Scott, D.S.; Czernik, S.R.; Piskorz, J.; Radlein, D.S.A.G. Fast pyrolysis of plastic wastes. *Energy Fuels* **1990**, *4*, 407–411. [[CrossRef](#)]
9. Panda, A.K. Studies on Process Optimization for Production of Liquid Fuels from Waste Plastics. Ph.D. Thesis, National Institute of Technology, Rourkela, India, 2011.
10. Miandad, R.; Barakat, M.A.; Aburizaiza, A.S.; Rehan, M.; Nizami, A.S. Catalytic pyrolysis of plastic waste: A review. *Process Saf. Environ. Prot.* **2016**, *102*, 822–838. [[CrossRef](#)]
11. Miandad, R.; Barakat, M.A.; Aburizaiza, A.S.; Rehan, M.; Ismail, I.M.I.; Nizami, A.S. Effect of plastic waste types on pyrolysis liquid oil. *Int. Biodeterior. Biodegrad.* **2017**, *119*, 239–252. [[CrossRef](#)]
12. Breyer, S.; Mekhitarian, L.; Rimez, B.; Haut, B. Production of an alternative fuel by the co-pyrolysis of landfill recovered plastic wastes and used lubrication oils. *Waste Manag.* **2017**, *60*, 363–374. [[CrossRef](#)] [[PubMed](#)]
13. Almeida, D.; de Fatima Marques, M. Thermal and catalytic pyrolysis of plastic waste. *Polímeros* **2016**, *26*, 44–51. [[CrossRef](#)]
14. López, A.; de Marco, I.; Caballero, B.M.; Laresgoiti, M.F.; Adrados, A.; Aranzabal, A. Catalytic pyrolysis of plastic wastes with two different types of catalysts: ZSM-5 zeolite and Red Mud. *Appl. Catal. B Environ.* **2011**, *104*, 211–219. [[CrossRef](#)]
15. Marcilla, A.; García-Quesada, J.C.; Sánchez, S.; Ruiz, R. Study of the catalytic pyrolysis behaviour of polyethylene–polypropylene mixtures. *J. Anal. Appl. Pyrolysis* **2005**, *74*, 387–392. [[CrossRef](#)]
16. Williams, P.T.; Slaney, E. Analysis of products from the pyrolysis and liquefaction of single plastics and waste plastic mixtures. *Resour. Conserv. Recycl.* **2007**, *51*, 754–769. [[CrossRef](#)]
17. Yan, G.; Jing, X.; Wen, H.; Xiang, S. Thermal Cracking of Virgin and Waste Plastics of PP and LDPE in a Semibatch Reactor under Atmospheric Pressure. *Energy Fuels* **2015**, *29*, 2289–2298. [[CrossRef](#)]
18. Achilias, D.S.; Roupakias, C.; Megalokonomos, P.; Lappas, A.A.; Antonakou, E.V. Chemical recycling of plastic wastes made from polyethylene (LDPE and HDPE) and polypropylene (PP). *J. Hazard. Mater.* **2007**, *149*, 536–542. [[CrossRef](#)] [[PubMed](#)]
19. Chandrasekaran, S.R.; Kunwar, B.; Moser, B.R.; Rajagopalan, N.; Sharma, B.K. Catalytic Thermal Cracking of Postconsumer Waste Plastics to Fuels. 1. Kinetics and Optimization. *Energy Fuels* **2015**, *29*, 6068–6077. [[CrossRef](#)]
20. Marcilla, A.; Beltrán, M.I.; Navarro, R. Thermal and catalytic pyrolysis of polyethylene over HZSM5 and HUSY zeolites in a batch reactor under dynamic conditions. *Appl. Catal. B Environ.* **2009**, *86*, 78–86. [[CrossRef](#)]
21. Seo, Y.-H.; Lee, K.-H.; Shin, D.-H. Investigation of catalytic degradation of high-density polyethylene by hydrocarbon group type analysis. *J. Anal. Appl. Pyrolysis* **2003**, *70*, 383–398. [[CrossRef](#)]
22. Li, K.; Lee, S.W.; Yuan, G.; Lei, J.; Lin, S.; Weerachanchai, P.; Yang, Y.; Wang, J.-Y. Investigation into the Catalytic Activity of Microporous and Mesoporous Catalysts in the Pyrolysis of Waste Polyethylene and Polypropylene Mixture. *Energies* **2016**, *9*, 431. [[CrossRef](#)]
23. Sundararajan, N.K.; Bhagavathi, A.R. Experimental Investigation on Thermocatalytic Pyrolysis of HDPE Plastic Waste and the Effects of Its Liquid Yield over the Performance, Emission, and Combustion Characteristics of CI Engine. *Energy Fuels* **2016**, *30*, 5379–5390. [[CrossRef](#)]
24. Aboulkas, A.; El Bouadili, A. Thermal degradation behaviors of polyethylene and polypropylene. Part I: Pyrolysis kinetics and mechanisms. *Energy Convers. Manag.* **2010**, *51*, 1363–1369. [[CrossRef](#)]
25. Jing, X.; Yan, G.; Zhao, Y.; Wen, H.; Xu, Z. Study on mild cracking of polyolefins to liquid hydrocarbons in a closed batch reactor for subsequent olefin recovery. *Polym. Degrad. Stab.* **2014**, *109*, 79–91. [[CrossRef](#)]
26. Ciliz, N.K.; Ekinci, E.; Snape, C.E. Pyrolysis of virgin and waste polypropylene and its mixtures with waste polyethylene and polystyrene. *Waste Manag.* **2004**, *24*, 173–181. [[CrossRef](#)] [[PubMed](#)]
27. Jing, X.; Zhao, Y.; Wen, H.; Xu, Z. Interactions between low-density polyethylene (LDPE) and polypropylene (PP) during the mild cracking of polyolefin mixtures in a closed-batch reactor. *Energy Fuels* **2013**, *27*, 5841–5851. [[CrossRef](#)]

