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Please cite this article as U. S. Vural, A. Yinanc, and H. C. Sevindir, *J. Serb. Chem. Soc.* (2024) <https://doi.org/10.2298/JSC230828035V>

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J. Serb. Chem. Soc. **00(0)** 1-17 (2024)
JSCS-12559

Two-stage thermocatalytic conversion of waste XLPE to diesel-like fuel

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(Received 28 September 2023; revised 8 October 2023; accepted 21 March 2024)

Abstract: Cross-linked polyethylenes (XLPE) are not preferred in industrial pyrolysis applications and mechanical recovery methods due to great thermochemical resistance to heat and deformation. Studies on pyrolysis of XLPE up to 600°C to obtain fuel have generally yielded high levels of wax and have not been of interest to the energy sector. In this study, two-stage pyrolysis of XLPE was carried out catalytically and without catalyst (thermal, *T-pyr*) under 500°C with heating rates of 5°C.min⁻¹ and 10°C.min⁻¹. In the pyrolysis experiments, three different catalytic studies were performed by adding (MCM-41 + HZSM-5) catalyst mixture to the polymer phase only (*PPC-pyr*), by filling (Cu(I)-MAS + HZSM-5) catalyst mixture to the gas outlet column only (*GPC-Pyr*) and adding catalyst mixtures in both polymer phase and gas phase (*MPC-pyr*). The highest diesel-like fuel (wt. 91.40 %) was obtained in multiphase catalytic pyrolysis experiments at 460°C with a heating rate of 5°C.min⁻¹. The calorific value, kinematic viscosity, density, flash point and cetane number of the fuel were found as 45.97 MJ.kg⁻¹, 2.72 cSt, 832.5 kg.m⁻³, 57 °C and 59 °C, respectively. The results of the two-stage catalytic cracking and the heating rate profile will be a guide for industrial pyrolysis applications. The simple feasibility for industrial applications showed that it would be a very profitable investment.

Keywords: cross-linked polyethylene; thermal cracking; heterogeneous catalysis; zeolite.

INTRODUCTION

Cross-linked polyethylenes are cross-linked thermoset polymers made from low-density (LDPE) or high-density polyethylene (HDPE), commonly known as XPE or XLPE. Cross-linked polyethylenes are synthesized by three different cross-linking methods: peroxides, silane, and high-energy irradiation.^{1,2} Polymers

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<https://doi.org/10.2298/JSC230828035V>

obtained by peroxide crosslinking reaction are classified as *PE-Xa* (or *P-XLPE*), by silane linkage as *PE-Xb* (or *Si-XLPE*), and by high irradiation linkage as *PE-Xc* (or *I-XLPE*), and crosslinking degree is 75 %, 65 % and 60 %, respectively.^{3,4} Cross-linked polyethylene are used in the wire and pipe industries, in healthcare prosthetics, primarily in cable, as they have excellent power insulation, good heat resistance, dimensional stability and resistance to environmental stress cracking due to cross-links.⁵ A feasible and successful method has not yet been developed for the recovery of defective products that do not comply with the reaction conditions during the production of cross-linked polyethylene.⁵ Scrap cross-linked polyethylene cables consist of cables that are replaced during periodic maintenance of electrical distribution lines or cables that cannot be used as a result of faulty production. Since *XLPE* is a thermosetting polymer, it hardens irreversibly⁶. For this reason, it makes it impossible to recover by melting it to be reshaped and used again. Mechanical recovery is also not possible, as it inhibits flow at high temperatures.⁶ While producing *HDPE* in subcritical and supercritical methanol and water is somewhat promising, the cleavage of the main chain and the selectivity of removal of crosslinks still remains to be studied.⁶ Although recently, experiments on thermo plasticization by selective degradation of the cross-linked structure using supercritical fluids have been successfully carried out, it has not yet been put into practice on an industrial scale.⁶⁻⁷

Wang *et al.*⁸ succeeded in producing fuel by hydrogenating polyethylene with a tungstated zirconia catalyst at low temperatures of 250 °C. Although the method was carried out under mild conditions than thermal and catalytic pyrolysis experiments, thermal or catalytic pyrolysis methods are still seen as more convenient processes since they are high-cost processes in terms of industrial application. Recycling of *XLPE* by thermal decomposition methods is a more satisfactory method as it will provide alternative contributions to energy production.⁶

Catalysts play an important role in the pyrolysis of hydrocarbons and olefins.⁹ The catalyst lowers the pyrolysis temperature by reducing the activation energy required to break the carbon bonds, thus shortening the pyrolysis time.⁹ In addition, the catalyst is effective in the selectivity of pyrolytic products according to their molecular weight distribution. During the catalytic pyrolysis process, carbocationic decomposition of volatile molecules, isomerization, oligomerization, cyclization and aromatization reactions occur.⁹ Homogeneous catalysts such as AlCl_3 , heterogeneous catalysts such as zeolite solid acid catalyst and *FCC* are used in the pyrolysis of polymers.⁹ Heterogeneous catalysts are more preferred over homogeneous catalysts because of the difficulty in separating the catalyst from the products after pyrolysis. The most commonly used solid acid catalysts in polymer pyrolysis are heterogeneous catalysts such as *ZSM-5*, *HZSM-5*, *Y*-zeolite and *MCM-41*.^{9,10,11} The acid content, pore structure and shape of

zeolites plays an important role in diffusion and cracking of molecules into the acid region of the catalyst during pyrolysis. As the diffusion rate of molecules into the pores of the catalyst increases, the retention time and cracking rate decrease and more liquid product is obtained. Increasing the residence time of molecules in the pores of the catalyst increases secondary reactions and therefore gas formation.^{9,10,11} ZSM-5 with a micro pore diameter of 0.55 nm and HZSM-5 with a medium pore diameter of 0.9 nm catalyze the conversion of hydrocarbons and olefins into low molecular weight components.^{10,11} The catalytic activity of ZSM-5 with smaller pore diameter is higher than HZSM-5. In the pyrolysis of plastics, small molecules such as gasoline are formed with ZSM-5, while larger molecules such as diesel oil or jet fuel are formed with HZSM-5.^{10,11} Due to the high catalytic activity of ZSM-5, more gas is produced in the pyrolysis of plastics than other zeolites. Eze *et al.*¹² investigated the pyrolysis of different plastics with various catalysts and catalyst mixtures. They observed that the highest degradation rate was obtained with zeolite catalysts, and the highest liquid yield was obtained in 1:1 ratio MCM-41 and ZSM-5 catalyst mixtures. They stated that since pyrolytic liquids contain high amounts of aromatic compounds, pyrolytic liquids are a product similar to gasoline. Eze *et al.*¹² also obtained 76 %, 77 %, 58 %, and 63 % liquid product from the pyrolysis of LDPE, LLDPE, HDPE, and XLPE, respectively at 430 °C with silica-alumina catalyst. They stated that the reason for obtaining a lower rate of liquid product from HDPE and XLPE was due to wax formation. Santos *et al.*¹³ stated that HDPE cracked 48.3 % with ZSM-5, 88.4 % with HZSM-5 at 450 °C, and <16.3 % without catalyst. Ratnasari *et al.*¹⁴ investigated the effect of MCM-41 and ZSM-5 catalysts on the thermal degradation of HDPE using a two-stage pyrolysis method. Approximately 65 % pyrolytic oil was obtained with MCM-41 alone, the amount of non-condensable gas increased with ZSM-5 alone. They stated that the thermal cracking rate of ZSM-5 is much faster than MCM-41 because ZSM-5 has a higher Si:Al ratio and acidic character than MCM-41.

During cracking, the surface activity of the catalyst decreases rapidly as the catalyst surface is covered with carbonaceous residues formed by secondary reactions. When transition metals such as Zn, Cu or alkali metals are immobilized on the catalyst surface, secondary reactions that cause coke formation are reduced. As the acidity and surface activity of the metal-loaded catalyst increases, wax formation decreases and the formation of gasoline and kerosene-like molecules increases.^{10,11,15} One of the most important features of metal-loaded zeolites is that they reduce the sulfur value of the fuel. Mesoporous Molecular Sieves (MCM-41), MESOPOROUS ALUMINOSILICATE (MAS) and Y-type zeolite (NaY) were used for the desulphurization of hydrotreated naphtha.¹⁶⁻¹⁸ Amorphous inner walls leading to poor stability and weak acidity reduce the catalytic powers of mesoporous molecular sieves. To improve the stability and acidity of the mesoporous

molecules, the amorphous matrix is modified with aluminum and silica and partially converted into the nano-sized zeolite phase. The desulfurization activity of *MAS*, *MCM-41* and *NaY* in hydrotreated diesel sample containing 207 ppm and 315 ppm sulfur was compared. *MAS* showed a higher activity than *MCM-41* and *NaY*, and sulfur values were found to decrease to 53 ppm and 109 ppm, respectively.^{16,17} Although the pore diameter (3.51 nm) and surface area (940 m².g⁻¹) of *MAS* were lower than *MCM-41*, *MAS* showed higher activity against sulfur because it was more acidic than *MCM-41*. Li *et al.* reduced sulfur value of diesel from 315 ppm to 54 ppm with Cu-*MAS*.¹⁷

In this study, thermochemical transformation of *XLPE* was carried out without catalyst, using mesoporous *MCM-41* heterogeneous catalyst in the polymer phase, Cu-*MAS* catalyst in the gas phase and catalysts in both phases, with a heating rate of 5°C and 10°C. Since it is aimed to produce diesel equivalent fuel, microporous catalysts (*ZSM-5* and *HZSM-5*) with high acidic and catalytic activity were not preferred. To obtain products in the boiling point range of diesel, mesoporous *MCM-41* polymer phase, which has a larger pore diameter and lower catalytic activity and acidity than microporous catalysts, was used. To reduce coking and desulfurization, Cu-*MAS*, which has higher catalytic activity, was used as a catalyst in the gas phase. In multiphase catalytic cracking experiments performed with low heating rate, the highest amount of fuel and the least amount of gas and wax were obtained.

EXPERIMENTAL

The cross-linked polyethylene was obtained from a local power cable manufacturer's copper recovery department in shreds <10 mm. The composition of waste plastic is given in Table I. Cetyltrimethylammonium bromide (*CTMAB*, 98 %), sodium aluminate (NaAlO₂) were obtained from Sigma-Aldrich, Aluminum Sulfate (Al₂(SO₄)₃.18H₂O), sodium silicate solution (8 % Na₂O, 27 % SiO₂), K₂CO₃, H₂SO₄ (97 %), NaOH, Cu(NO₃)₂, γ-Al₂O₃ (particle size 63 μm -200 μm, pore size 9 nm), and silica gel (Particle size: 63-200 μm, pore size: 60 Å, pore volume: 0.7 cm³.g⁻¹ - 0.85 cm³.g⁻¹, surface area: ≥ 480 m².g⁻¹) was obtained from Merck company.

Table I. Waste *XLPE* composition

Ultimate Analysis, wt. %		Proximate Analysis, wt. %	
C	85.94	Volatiles	98.43
H	13.21	Fixed Carbon	0.16
N	0.07	Ash	0.54
S	0.24	Moistures	0.87
		Croslinked degree	84.00

Thermal cracking experiments were carried out in a two-stage fixed bed reactor. The first reactor is 50 cm long, 30 cm high, made of 4 mm 316Ti stainless steel and is designed to melt the polymer. The empty volume of the reactor is 35 liters. During the melting of the polymer, a 80 cm length and 14 cm diameter column was connected to the reactor for volumetric expansion

and removal of gases. The reactor is heated with a 7.5 kW electrical resistance. The second fixed bed reactor with a diameter of 20 cm, a length of 30 cm and an empty volume of 10 L (Fig. 1), was used in the pyrolysis experiments. The amount of polymer melt fed into the cracking reactor is controlled by the overflow pipe connecting the two reactors. A column with a diameter of 14 cm and a length of 160 cm, consisting of 3 sections, was connected to the steam outlet of the reactor. The first section, the upper part of the column, is the reflux part. The gas phase catalytic reactions were carried out with the catalyst in pellet form, which was charged to the second section of the column. The column also acts as a reflux column to separate waxes and liquids from the gas phase that escape the gas phase as a result of sudden expansions. In the last section of the column, gases are discharged from the reactor and polymer melt is fed into the reactor from the first reactor. The reactor is heated with a 7.5 kW electrical resistance. The column is connected on a single pass condenser column with a length of 1.5 m, a diameter of 16 cm and a 1/2-inch tube bundle. Two collection vessels are connected to the condenser outlet to separate the light and heavy distillate phases. The uncondensed gases were burned after desulfurization by passing through sodium hydroxide solution.

The temperature values measured by the *pt100* sensors placed inside the reactors and on the column, the heating rate was realized with a computer-controlled *K-type* thermocouple. The pyrolysis process was carried out at atmospheric pressure using inert N_2 carrier gas (a flow rate of $200\text{ cm}^3\text{ min}^{-1}$). *LECO*, *CHNS-932* elemental analyzer was used for C, H, N, and S analysis in fuel. Viscosities were measured according to the *ASTM D445* method by the Ostwald viscometer at $40\text{ }^\circ\text{C}$. The calorific value of the pyrolysis oil samples was measured using a *U-Therm YX-ZR* model Semi-Automatic Calorimeter. Densities of pyrolytic oils were measured with *Anton Paar DMA 38N* densimeter according to the *ASTM D7777* method. The flash point of the pyrolytic oil samples was determined using the *PMA 500* model *Pensky-Martens* device according to the *ASTM D93* method. In order to find the amounts of diesel and gasoline-like fractions, distillation of pyrolytic oils was carried out according to *ASTM D-93*. *Sunflow* brand, 1440 rpm, $5\text{ L}\cdot\text{min}^{-1}$, *SF-025* model, 0.2 kw, 220 V hot oil transfer pump was used for the transfer of the polymer melt. The cetane number was calculated according to the *ASTM D'4737-03* method.

Determination of Crosslinking Degree of Waste XLPE

Polyvinyl Chloride (*PVC*) and metallic impurities in the sample are separated in water by density difference and dried at room temperature. Crosslinking degree of *XLPE* sample was determined by gel content according to *ASTM 10147:2004*. To determine the gel content of *XLPE*, approximately 0.30 grams of sample was placed in a xylene weighing flask and extracted by heating at $110\text{ }^\circ\text{C}$ for 8 hours. It was then dried under vacuum at $150\text{ }^\circ\text{C}$ for 30 minutes. The gel content of the *XLPE* was determined by weighing the weight of the remaining cross-linked fraction. Cross-linking degree was determined as 84 %.

Mesoporous MCM-41 Synthesis

MCM-41 was synthesized according to the method in the literature.^{16,19} 72 g of *CTMAB* was dissolved in 1000 cm^3 distilled water under stirring 265 g of sodium silicate and was then introduced into the mixture. H_2SO_4 was added dropwise to give a solution with a pH of 11. The mixture was allowed to heat in an oven at $100\text{ }^\circ\text{C}$ for 24 h. The precipitate was filtered, washed, and dried at $55\text{ }^\circ\text{C}$ under a vacuum, before calcination. Then, the dried precipitate was calcined under airflow at $550\text{ }^\circ\text{C}$ for 6 h.

Mesoporous Aluminosilicate (MAS) Synthesis

MAS was synthesized by a two-step method.^{16,17} Nanoclustered zeolite *Y* seeds were prepared by reacting NaOH (0.088 mol) and NaAlO₂ (0.10 mol) in H₂O (8.5 mol) with silicate anions (0.90 mol) in the form of a sodium silicate solution containing 27 % SiO₂ and 14 % NaOH under vigorous stirring at 100 °C overnight. The addition of cetyltrimethylammonium bromide (0.20 mol), sulfuric acid (0.52 mol) and water (127 mol) to the seeds solution, followed by an additional stirring period of 20 h at 100 °C afforded a hexagonal alumina-silicate mesostructure, which we denote as MAS. The synthesized MAS was calcinated under a nitrogen atmosphere at 550 °C for 1 h, and then in the air at the same temperature for 6 h.

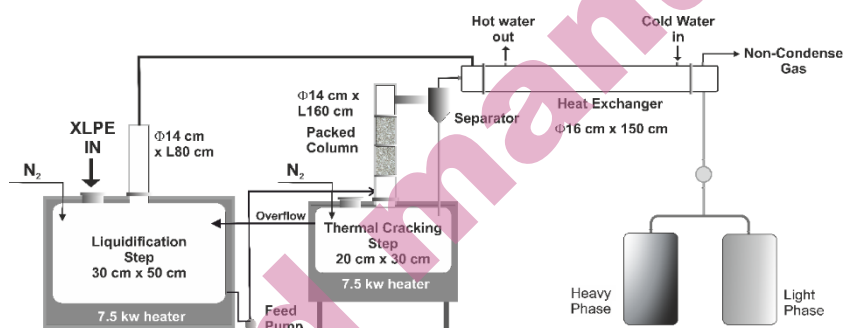


Fig 1. Apparatus to experimental set-up

Cu(I)-MAS Synthesis

Ion exchange was performed by mixing MAS with 0.5 M Cu(NO₃)₂ solution for 24 h.^{16,17} Then, the filtered adsorbent was dried at 100 °C for 24 h. Finally, Cu⁺² ions were reduced to Cu⁺ by calcining in nitrogen atmosphere at 450 °C for 3 h.

Pellet Synthesis

Pellets were synthesized by the literature method.¹⁶ 20 % by weight < 2 mm of γ -Al₂O₃ was added onto the synthesized zeolites. Deionized water was carefully added until the mixture became mushy. The mixture, which came to the consistency of dough, was cut in the dimensions of 3 mm x 10 mm by passing through a laboratory-type extruder. Wet pellets were kept at room temperature overnight and then dried in an oven at 120 °C for 4 hours. Dried pellets were calcined at 550 °C for 6 h.

Two-Stage Thermal and Catalytic Cracking of XLPE

12 kg of XLPE was added to the reactor, and melting of polymer was carried out in an inert nitrogen atmosphere. In the first stage reactor, the heating rate was kept low (2 °C) to prevent sudden volumetric expansion and heated until all of the polymer was liquefied. In the second step, 12 kg melted polymer was added to the second reactor (cracking reactor). The thermal cracking process was completed by keeping the heating rate at 5 °C.min⁻¹ and 10 °C.min⁻¹. The experiments were repeated by adding 120 g of catalyst to the molten polymer alone, adding catalyst to the column only, and adding catalyst to both the polymer and the column. MCM-41 as polymer phase catalyst was added to the liquefied polymer in the second stage, and Cu(I)-MAS was added as gas phase catalyst to the catalytic column connected to the steam outlet.

Pretreatment and Setting of Sludge

Before the distillation process, impurities such as polymeric substances, asphaltenes and water must be separated from the pyrolytic oil. Thus, coking is minimized during the distillation process. A flocculent/coagulant containing wt. 0.2 % polyacrylamide and wt. 0.5 % sodium silicate was added to pyrolytic oil and mixed with an air compressor at 60 °C for 2 h, then left for 6 hours to settling of the precipitate. Thus, the residue and water were separated from the pyrolytic oil.

Distillation

To purify the pyrolytic liquids obtained from the pyrolysis of *XLPE*, the pyrolytic liquids were first catalytic distilled, then treated with active silica gel and filtered. 600 cm³ of the supernatant was placed in a catalyst-filled packed column-mounted distillation kettle. Ceramic wool was placed at the bottom of second column section and Cu(1)-*MAS* in pellet form was filled on the column. The distillates were collected in the collection vessels between 55 °C and 360 °C. The non-condensed gases were burned in the burner after desulphurization by passing from the 4 M NaOH solution. Distillates up to 180 °C were deposited in the light distillate vessel, and those between 180-360 °C were collected in the heavy distillate vessel.

Desulfurization and decolourization Process

100 mL of distilled pyrolytic oil and 12 mL of formic acid was added to a 250 mL three-necked flask and mixed with a magnetic stirrer in a thermostatic water bath at 50 °C for 30 minutes. Then, 7 ml (30 %) H₂O₂ was added to the mixture and the solution was stirred for additional 180 minutes. Air was passed through the balloon during mixing. The mixture was transferred to a separatory funnel, after 45 minutes the oxidized pyrolytic oil and oxidant phase were separated. The sulphur containing components were extracted by mixing the oxidized pyrolytic oil with a 1:1 ratio of 50 % aqueous methanol solution.

Purification Step

To decolorize and remove impurities in the distilled and desulfurized pyrolytic oil, 1 % silica gel was added to the solution and stirred at 60 °C and 80 rpm for 45 minutes, then filtered. The process steps are given in Fig. 2 until a diesel equivalent product is obtained from *XLPE*.

Calculations

After the pyrolysis and distillation experiments, the liquid product volume and density were measured, and the liquid product amount was calculated by weight. The residue remaining in the reactor was weighed to measure the amount of non-pyrolysis *XLPE* (char). The amount of uncondensed gas was measured by subtracting the amount of liquid and solid phase from the amount of *XLPE* added to the reactor. The pyrolytic liquid was settled for 8 h and the wax formed was separated from the liquid product by separatory funnel. The amount of wax in solid form at room temperature was weighed and its ratio in the pyrolytic liquid product was determined.

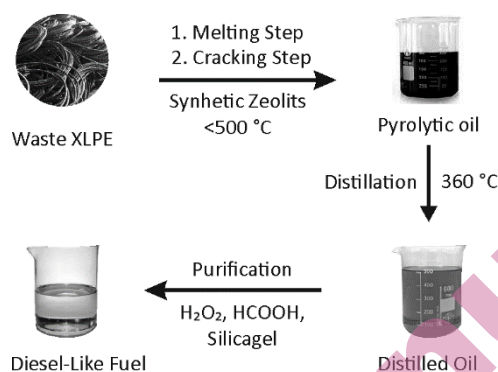
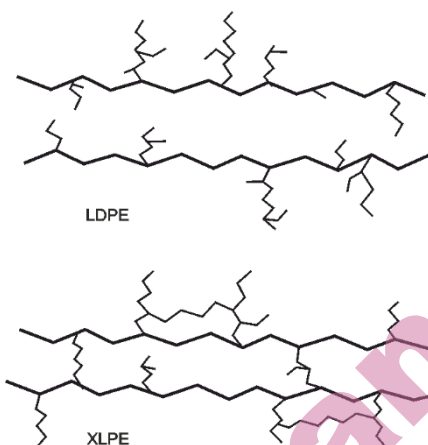
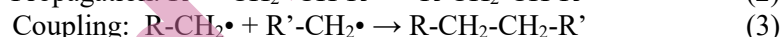
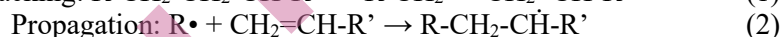


Fig 2. The conversion of waste *XLPE* cables to diesel-like fuel

RESULTS AND DISCUSSIONS

The biggest difference between polyethylene and *XLPE* is that polyethylene melts above its melting point temperature, while *XLPE* softens by acting like rubber. Crosslinking reduces melt index and elongation at break, improves creep resistance, impact strength, environmental stress crack resistance (*ESCR*) and resistance to slow crack growth. The density and tensile strength of polyethylene are not affected by crosslinking. The crosslinking of polyethylene takes place in four stages: initiation, propagation, branching and termination.⁴ Cross-linking changes the physical properties of the polymer such as density, flexibility, hardness, and viscosity. Crosslinking occurs between carbon atoms or other chain branches in adjacent chain molecules or between chains branches joined to the same polymer chain (Fig. 3).²⁰

According to Chen *et al.*²¹ three types of radical chain reactions occur between volatile compounds during pyrolysis: initiation, propagation and termination. These radical reaction mechanisms are (1) cracking of molecules to form alkanes and alkenes by the Rice-Kossiakoff mechanism (2) adding alkenes to radicals to increase carbon chain growth and radical scattering, and (3) adding radicals to each other to form larger molecules (Eq. 1, Eq. 2 and Eq. 3). Radical scattering and interrelationships are more dominant at low temperatures, leading to an increase in carbon chain length and thus a decrease in non-condensable gas yield. These results show that the reactions between the volatile components occurring during the pyrolysis of hydrocarbons are not stable in the cracking process. The reactions between the volatile components are dependent on the pressure, heating rate and temperature, as well as the varying residence time. Since cracking is more dominant at high temperatures, the carbon chain of the molecules will shorten, so the oil yield decreases and the amount of non-condensed gas increases.

Fig 3. The view of polyethylene and crosslinked polyethylene²⁰

The two stage pyrolysis processes of *XLPE* obtained from scrap cables were carried out catalyst-free thermal pyrolysis (*T-Pyr*), polymer phase catalytic pyrolysis (*PPC-Pyr*), gas-phase catalytic pyrolysis (*GPC-Pyr*), multi-phase catalytic pyrolysis (*MPC-Pyr*) at different heating rates. *MCM-41* was chosen to obtain higher liquid products in the polymer phase with boiling points in the range of diesel fuel. *MCM-41* has a larger pore diameter than other synthetic zeolites, which is weaker than microporous catalysts, also reduces the amount of non-condensable gas.^{10,11} Its only disadvantage is that the catalyst efficiency decreases due to rapid clogging of the catalyst pores. Since the catalyst will be added again in each experiment, the disadvantage of catalyst poisoning will be eliminated. Strongly acidic and microporous catalysts such as *ZSM-5* and *HZSM-5* were not preferred in this study because they increased the amount of non-condensable gas and gasoline was obtained as the main product. In the gas phase, *Cu(I)-MAS* was used as a catalyst. *Cu(I)-MAS* in the gas phase, it ensures the re-cracking of large molecules formed as a result of secondary reactions, thus reducing the amount of wax and sulfur amount in the liquid product.^{17,18}

As seen in Table II, 83.84 % and 91.40 % diesel equivalent fuel was obtained in gas phase and multi-phase catalytic pyrolysis of *XLPE* with a heating rate of 5 °C, respectively. These values appear to be close to the 83.15 % gasoline value obtained from the two-stage catalytic pyrolysis of *HDPE* by Ratnasari *et al.*¹⁴ The amount of fuel obtained from single-stage catalytic pyrolysis of *XLPE* (63 %) by

Eze *et al.*¹² is much lower than that obtained in our study. Single-stage pyrolysis is insufficient to completely crack high-density plastics such as *HDPE* and *XLPE*.

Mo *et al.*²² investigated the pyrolysis characteristics of cross-linked polyethylene cables by thermogravimetric method. As seen in Fig. 4, in the study carried out from room temperature to 800 °C, at $P=40$ °C, 20 mL.min⁻¹ in air, 98.83 % weight loss is observed between 400 °C-500 °C, which is the pyrolysis stage of the polymer. The peak of the DTG curve showing the endothermic reaction is 484.96 °C, and it merges with the DSC curves. In our study, in two-stage multi-phase catalytic pyrolysis experiments, the pyrolysis temperature was found to be 448 °C at 5 °C heating rate and 441 °C at 10 °C heating rate. The pyrolysis temperature at both heating rates is lower than the temperature found by Mo *et al.*²² It is clear from these results that the two-stage catalytic pyrolysis method of *XLPE* has reduced the pyrolysis temperature, so that less energy will be consumed to complete pyrolysis in industrial processes.

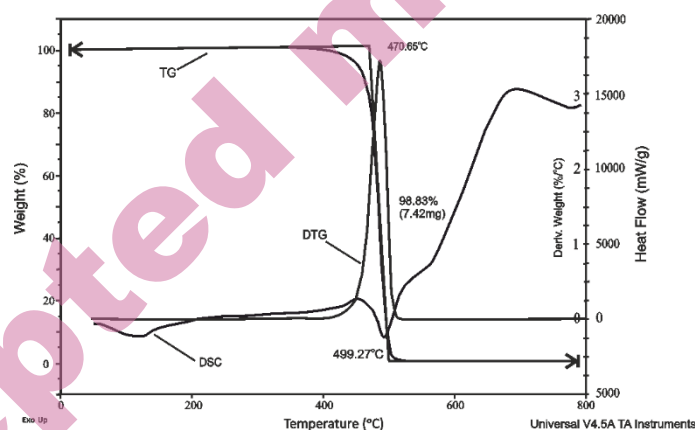


Fig 4. TGA-DSC curve on *XLPE* cable material²²

Due to the low heat conductivity of the polymer in the first stage of pyrolysis, no significant increase was observed in the pyrolysis temperature in the first 45 min, the temperature rose slowly between the 45th and 60th min, and the temperature increase suddenly accelerated after the 60th min. From these results, it was understood that the melting of the polymer started at the 45th min, completed at the 60th min, and thermal degradation started after the 60th min. The conversion of the polymer via time at 5 °C.min⁻¹ is shown in Fig. 5. As can be seen from Fig. 5, the liquid product yield is low in the first 60 min. The thermal degradation started to accelerate after 60 min as the heat given to the system up to the liquefaction temperature was spent on loosening the crosslinks and phase change in the polymer. The pyrolysis process was completed in the 105th minute.

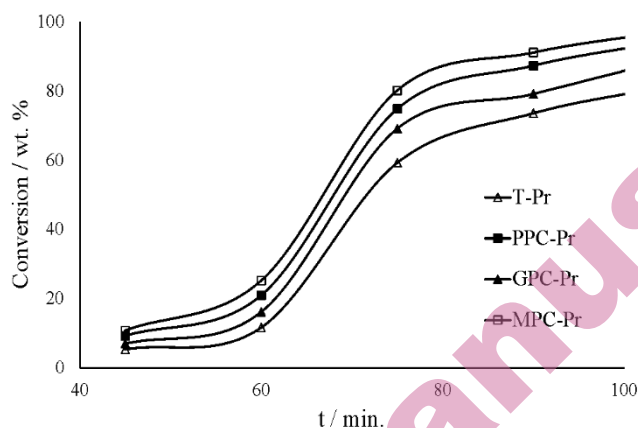


Fig 5. Conversion % of *XLPE* to liquid products at a $5\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ heating rate

Table II. The experimental results of *XLPE* pyrolysis at $5\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ and $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$

Pyrolysis Method	Liquid, wt. %	Gas, wt. %	Residue ^a , wt. %	Wax ^b , wt. %	Liquefaction temp. / $^{\circ}\text{C}$	Pyrolysis temp. / $^{\circ}\text{C}$
Heating Rate, $5\text{ }^{\circ}\text{C}/\text{min}$						
<i>T-Pyr</i>	46.59	5.52	9.26	38.63	237	482
<i>SPC-Pyr</i>	72.83	4.78	6.18	16.21	218	467
<i>GPC-Pyr</i>	83.84	4.11	5.42	6.63	-	458
<i>MPC-Pyr</i>	91.40	3.21	3.56	1.83	-	448
Heating Rate, $10\text{ }^{\circ}\text{C}/\text{min}$						
<i>T-Pyr</i>	27.83	7.23	8.43	56.51	216	473
<i>SPC-Pyr</i>	44.60	6.42	7.12	41.86	207	461
<i>GPC-Pyr</i>	59.17	5.76	6.73	28.34	-	452
<i>MPC-Pyr</i>	72.07	5.11	5.56	17.26	-	441

^aRemaining char in the reactor, ^bThe waxes were separated by settling the pyrolytic liquid for 8 h. *T-Pyr*: Thermal pyrolysis, *PPC-Pyr*: Polymer phase catalytic pyrolysis, *GPC-Pyr*: Gas phase catalytic pyrolysis, *MPC-Pyr*: Multiphase catalytic pyrolysis.

In Table II, the highest amount of liquid product was determined as 91.40 % in multi-phase catalytic experiments. At the same time, the amounts of uncondensed gas and residue remaining in the reactor are lowest in the multi-phase catalytic pyrolysis experiment. At high heating rate, the amount of liquid decreases, and the amount of uncondensed gas and residue is found to be slightly higher. At high heating rate, the rate of cracking and the speed of cracked gas molecules increased, thus the catalytic interaction decreased. By increasing coking at high heating rate, the amount of residue remaining in the reactor increased slightly. These results show that the retention time decreases depending on the heating rate, thus the evaporation rate increases, and the secondary reactions decrease. Therefore, the amount of uncondensed gas increased, and larger molecules were obtained in the form of wax without cracking.

Table II shows that the liquefaction temperature and pyrolysis temperature in the pyrolysis experiments of *XLPE* decreased depending on the increase in the heating rate. With the increase in heating rate, the intermolecular cross-links loosened faster and the polymer passed into liquid form before the bonds started to break. This was observed during pyrolysis as the temperature remained constant throughout liquefaction and started to rise with the start of cracking. In the Table II, it is also seen that the liquefaction and pyrolysis temperatures in catalyst-free pyrolysis experiments are higher than in catalytic pyrolysis. It is clearly seen that the catalyst reduces the activation energy required to break intermolecular bonds. The temperature of gas phase catalytic pyrolysis is lower than that of polymer phase catalytic pyrolysis. The catalytic interaction in the gas phase is faster than in the solid phase, and the catalyst minimizes secondary reactions. In both polymer phase and gas phase catalytic experiments, the pyrolysis temperature and liquefaction temperature are the lowest. Using catalysts in both phases accelerates the faster degradation of the polymer.

As a result of thermal cracking of *PE* plastic types, molecules that have not completed the full cracking reaction form waxes with a boiling point higher than 500 °C. In order to obtain high amounts of fuel in the pyrolysis of plastics, it is desired that the amount of wax is at a minimum level. Al-Salem *et al.*²³ obtained 32 % and 64.5 % wax in the pyrolysis of *HDPE* and *LDPE* at 500 °C, respectively. Arabiourrutia *et al.*²⁴ obtained wax in the range of 70 %-80 % from the pyrolysis of *HDPE*, *LDPE* and *PP* at 450-600 °C. They found that the amount of wax decreased due to the decrease in secondary reactions at high heating rate and pyrolysis temperature. As can be seen from Table II, the liquid yield was increased, and the amount of wax was reduced because of the correct catalyst determination strategy in the gas phase and polymer phase. The catalyst used in the polymer phase increased the cracking rate, on the one hand, large molecules continued to be cracked in the gas phase, and on the other hand, the amount of uncondensed gas decreased due to catalytic radical reactions. The packed column also acts as a molecular sieve and thus prevents the escape of non-condensed gases, while large molecules such as waxes continue to break down into smaller molecules in the gas phase. Parameters such as retention time of cracked molecules, pyrolysis temperature and heating rate affect the amount of fuel, gas and wax. While no wax is observed in the catalytic pyrolysis of plastics at high heating rates, the amount of gas increases and the amount of fuel decreases. As the retention time of cracked gases increases at low pyrolysis temperatures, coking and wax formation increases. For this reason, thermal and catalytic pyrolysis experiments were carried out under mild conditions, below 500 °C. It is aimed to increase fuel efficiency rather than completely preventing wax formation. As seen in Table II, the lowest amount of wax and the highest amount of fuel were obtained in multiphase catalytic cracking

experiments at a heating rate of 5 °C. In thermal cracking experiments, the highest wax and lowest fuel amount were obtained.

In Table III, the carbon, hydrogen and nitrogen content of the fuel were found to be close to diesel fuel. The reason why the carbon content of the fuel obtained by multi-phase catalytic cracking is slightly higher than the others may be due to the higher amount of cracked low molecular weight hydrocarbons. The ash content of fuels is in the negligible range.

As seen in Table III, the sulfur value of the fuel obtained from multi-phase catalytic cracking experiments was reduced from 0.24 ppm to 0.052 ppm. The desulfurization efficiency was calculated as 78.4 %. In catalytic pyrolysis experiments of *XLPE*, the sulfur removal efficiency was found to be less than the hydrotreated diesel sample, since factors such as steric hindrance of large molecules, coking and wax reduce the catalytic activity of Cu(I)-*MAS*. As seen in Table III, the desulfurization efficiency is listed as *MPC-pyr* > *GPC-pyr* > *PPC-pyr* > *T-pyr*. Cu(I)-*MAS* showed higher catalytic activity than *MCM-41* in sulfur removal. Pyrolytic oil samples were distilled and treated with formic acid-hydrogen peroxide and finally silica gel to remove impurities, thus a light transparent lemon-yellow colored diesel quality fuel was obtained.

As can be seen in Table III, the density values obtained in the vapour phase catalytic experiments were found to be closer to diesel fuel due to the higher degradation of the polymer in the multiphase catalytic cracking process. The density value of the fuel obtained from thermal pyrolysis and polymer phase catalytic pyrolysis experiments is lower than that obtained in the gas phase and multi-phase. The reason for this may be repolymerisation or isomerization reactions that occur by catalyzing secondary reactions in the gas phase. The density value of the fuel formed by multi-phase catalytic cracking is the lowest, as expected. Some of the small molecules formed as a result of cracking in the polymer phase cracked again in the gas phase, reducing the density values of the fuel. The density of liquid from the gas-phase catalytic pyrolysis was found to be equivalent to diesel fuel in Table III.

Table III. Physicochemical properties of liquid products according to pyrolysis method with 5 °C.min⁻¹ of heating rate.

Properties	<i>T-Pyr</i>	<i>PPC-Pyr</i>	<i>GPC-Pyr</i>	<i>MPC-Pyr</i>	<i>DF</i>
C	84.56	84.60	84.89	85.38	86.43
H	13.72	14.76	13.98	13.78	13.99
N	0.56	0.62	0.58	0.61	0.13
S	0.17	0.11	0.059	0.052	Nd
Ashes, wt. %	0.02	0.04	0.03	0.02	Nd
<i>GCV</i> , MJ / kg	44.56	46.12	45.34	45.97	44.79
Density, kg/m ³	811.24	810.16	832.54	796.67	830.00
ν , cSt at 40 °C	2.69	2.32	2.72	2.17	2.43
Flash point, °C	56	53	57	52	56
Yield, wt. %	53.92	70.12	86.48	89.56	
Cetane Number	55	54	59	53	57
Distillation Temperature / °C					
IBP	168	164	174	147	165
10 % recovery	201	197	221	187	209
50 % recovery	247	244	287	234	281
90 % recovery	344	342	352	339	344
FBP	366	364	370	358	368

ν : Kinematic Viscosity, *GCV*: Gross calorific value

The gross calorific value (*GCV*) of the fuels obtained from catalytic and thermal pyrolysis of *XLPE* compared with diesel fuel (*DF*) was found to be close to each other (Table III). The calorific value of the fuel obtained from polymer phase catalytic pyrolysis was found to be slightly higher than the others (46.12 MJ/kg). This may be because more olefinic molecules are formed by catalytic reactions in the polymer phase. The diesel product used in the comparison was obtained from local companies, and there may be differences between the calorific values of diesel products of different companies. In general, it has been observed that the calorific values of the fuel obtained from the catalytic pyrolysis of *XLPE* are at the same level as the diesel supplied from the market.

The kinematic viscosity values are between 2.17 and 2.72 cSt and correspond to the kinematic viscosity value of diesel fuel (2.43 cSt). It is understood that the ratio of olefin and aromatic compounds in pyrolytic fuels is higher than in paraffinic compounds. Thus, it has been observed that the high wax ratio seen in the single-stage pyrolysis experiments is eliminated by the cascade pyrolysis method in Table III.

As can be seen in Table III, the flashpoint of the fuels obtained from polymer phase catalytic pyrolysis is lower (52 °C). The flashpoint of the fuel obtained as a result of catalytic pyrolysis in the gas phase is 57 °C, slightly higher than the flashpoint of diesel fuel at 56 °C. From this, it was understood that the paraffinic structure of the molecules formed because of thermal decomposition in the gas phase is higher than that of diesel fuel. In a way, this shows that the fuel obtained

as a result of gas-phase catalytic pyrolysis is comparable to diesel fuel. The cetane number was found to be 57 in the gas phase catalytic pyrolysis process (Table III). This value is close to the cetane number (56) of the diesel fuel used in the comparisons. The number of paraffinic molecules in fuels can be explained as more regular burning of the fuel.

The cetane number of the fuel was found at the desired value due to the paraffinic molecules formed because of the pyrolysis of *XLPE* in Table III. Since the best cetane number and other physical properties are obtained from the gas phase catalytic pyrolysis, the fuel obtained from the gas phase catalytic pyrolysis of *XLPE* can be used as a diesel equivalent fuel by adding fuel additives without the need to blend with other fuels, or it can be directly blended with diesel in any ratio, can reduce consumption costs. It was observed that the distillation data (10 %, 50 % and 90 % recovery values) obtained from gas phase catalytic pyrolysis were compatible with diesel fuel. The distillation range of the fuel obtained in the gas phase coincides with that of diesel.

CONCLUSIONS

Scrap *XLPE* is the most economical potential raw material source in obtaining fuel by pyrolysis method as free waste. In industrial applications, the pyrolysis of *XLPE* is not preferred because it produces a high amount of wax. Also, wax causes major problems as it clogs the process lines. In this study, the formation of wax was minimized by the two-stage heating method and the diesel equivalent pyrolytic fuel was obtained at the maximum ratio. To obtain the highest fuel efficiency in the catalytic or thermal pyrolysis process, it has been determined that the polymer should be melted at a low heating rate up to 207 °C-214 °C, and then the pyrolysis should be completed by increasing the heating rate not exceeding 10 °C.min⁻¹. In addition, the successful applicability of the column-filled distillation method has been observed for the purification of the obtained pyrolytic fuels. The thermal catalysis, polymer phase catalysis and gas phase catalysis methods were compared, and it was understood that the most suitable method in terms of fuel properties was the multi-phase catalytic pyrolysis method. The most widely known thermal cracking catalyst, synthetic zeolites, was used in the experiments to determine the difference between thermal cracking and catalytic cracking.

The main purpose of the study is to reveal a decisive method in industrial applications by decreasing the wax ratio with the gradual heating rate and increasing the fuel efficiency. The type and amount of catalyst, reactor types, the pyrolysis of *XLPE* with scrap tires, waste mineral oil, or waste vegetable oil, and changes in the chemical structure of the products in these application differences are planned as the subject of further studies. Waste *XLPE* is still collected in nature as garbage or directly incinerated. Recovery of waste *XLPE* polymers as an energy source rather than mechanical recovery is a work that should be considered in

waste management plans. It will take its place in the recycling sector as an alternative method for the disposal of such wastes with high energy value in a way that will minimize environmental problems.

Acknowledgments: We thank Corlu Vocational High School for technical support and assistance in this research.

ИЗВОД

ДВОФАЗНА ТЕРМОКАТАЛИТИЧКА КОНВЕРЗИЈА ОТПАДНОГ XLPE У ГОРИВО СЛИЧНО ДИЗЕЛУ

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Умрежени полиетилен (XLPE) нису пожељни у индустријским апликацијама пиролизе и методама механичког рециклирања због велике термохемијске отпорности на топлоту и деформације. Студије о пиролизи XLPE до 600 °C за добијање горива генерално су дале велику количину воска и нису биле од интереса за енергетски сектор. У овој студији, двостепена пиролиза XLPE изведена је у присуству катализатора и без катализатора (термално, T-pyr) на 500 °C, са брзинама загревања од 5 °C min⁻¹ и 10 °C min⁻¹. Изведене су три различите каталитичке студије додавањем смеше катализатора (MCM-41 + HZSM-5) само у полимерну фазу (PPC-pyr), пуњењем излазне колоне гаса смешом катализатора (Cu(I)-MAS + HZSM-5) (GPC-Pyr) и додавањем смеше катализатора у полимерну и гасну фазу (MPC-pyr). Највећа количина дизел горива (91,40 %) добијена је у експериментима вишефазне каталитичке пиролизе на 460 °C са брзином загревања од 5 °C min⁻¹. Утврђено је да калоријска вредност, кинематичка вискозност, густина, тачка паљења и цетански број горива износе 45,97 MJ kg⁻¹, 2,72 cSt, 832,5 kg m⁻³, 57 °C и 59 °C, респективно. Резултати двостепеног каталитичког крекинга и профил брзине загревања биће водич за индустријску примену пиролизе. Једноставна изводљивост указује да би то била веома исплатива инвестиција за индустријску примену.

(Примљено 28. августа 2023; ревидирано 8. октобра 2023; прихваћено 21. марта 2024.)

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