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Performance of Different Catalysts for the In Situ Cracking of the Oil-Waxes Obtained by the Pyrolysis of Polyethylene Film Waste

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Abstract: Currently, society is facing a great environmental problem, due to the large amount of plastic waste generated, most of which is not subjected to any type of treatment. In this work, polyethylene film waste from the non-selectively collected fraction was catalytically pyrolyzed at 500 °C, 20 °C/min for 2 h, in a discontinuous reactor using nitrogen as an inert gas stream. The main objective of this paper is to find catalysts that decrease the viscosity of the liquid fraction, since this property is quite meaningful in thermal pyrolysis. For this purpose, the three products of catalytic pyrolysis, the gaseous fraction, the solid fraction and the liquid fraction, were separated, obtaining the yield values. After that, the aspect of the liquid fraction was studied, differentiating which catalysts produced a larger quantity of waxy fraction and which ones did not. The viscosity of these samples was measured in order to confirm the catalysts that helped to obtain a less waxy fraction. The results showed that the zeolites Y and the zeolites β used in this study favor the obtaining of a compound with a smaller amount of waxes than for example catalysts such as FCC, ZSM-5 or $SnCl_2$.

Keywords: plastic waste; pyrolysis; catalyst; zeolites; viscosity; wax

1. Introduction

Plastics play an important role in the daily life of humans since there is a strong dependence on these materials. This dependence can be justified by the advantages that these materials have over others, due mainly to their lightness and cost. These materials are strategic in sectors such as packaging, construction, motoring, electronics or agriculture, among others [1].

As countries' economies grow the demand for plastic goods increases. In 2018, the global production of plastics was around 360 million tons, of which Europe generated 17%, corresponding to 62 million tons. In addition, in 2018 Europe transformed 51.2 million tons (European converts demand) and Spain was among the six countries that cover 80% of European demand, with 7.6% of the transformation [1].

This high demand for plastics can only lead to a large production of solid plastic waste, which occupies a large part of the municipal solid waste (MSW). In 2018, 29.1 million tons of plastic were collected as post-consumer waste. Of this plastic, 32.5% was recycled, 42.6% was used for energy recovery and 24.9% ended up in landfills. However, in Spain the rate of landfill is relatively large with respect to the rest of the European countries, at 39% [1]. These high values of deposition in landfills and energy recovery, both for developed and underdeveloped countries, give rise to numerous concerns, both health-related and environmental [2].

In the case of Spain, there is a fraction of plastics selectively collected that is managed by the Ecoembes organization and a fraction that is not selectively collected. Special emphasis must be placed on the non-selectively collected fraction, as it contains a large percentage of MSW, since currently in Spain selective separation is not very successful among the population. As an example, in the province of Granada 84.45% of the MSW was organic-rest fraction, while only 15.55% was collected selectively in the year 2015 [3]. The organic-rest fraction is mainly composed of organic matter, plastics, paper-cardboard and glass. A total of 12.6% of this fraction corresponds to the plastic fraction, which is mainly composed of polyethylene film material (43.66%); the second main polymer is polypropylene (10.04%), and the third most abundant plastic is polystyrene (5.69%) [4].

There are two main ways of recycling this plastic waste. Mechanical recycling is a physical treatment based on five stages (collection, sorting, washing, grinding and extrusion) that are used to process and convert plastic waste into new materials [5,6], while chemical recycling consists in polymer degradation to obtain starting monomers or the production of a fuel [7,8]. While mechanical recycling has many advantages, since it is an economic and widely developed process, it has important disadvantages, in terms of the presence of impurities as well as the mixing of polymer typologies. These potential limitations cause the growing interest in chemical recycling, since it can potentially treat heterogeneous plastic waste with impurities [9].

There are many types of chemical recycling, but one of the most used is pyrolysis [10]. There are two main routes, thermal pyrolysis and catalytic pyrolysis. Conventional thermal pyrolysis consists in the degradation of matter in the absence of oxygen in which high temperatures are necessary, in a range of 300 to 550 °C depending on the polymer [11,12]. Catalytic pyrolysis follows the same degradation procedure as thermal pyrolysis, but with the addition of a catalyst, thus decreasing the temperatures and times of pyrolysis. It also presents certain selectivity of products depending on the type of catalyst. Generally, the introduction of a catalyst in this type of process, causes an increase in the yield of the gaseous fraction, a decrease in the liquid fraction and an increase in the amount of char [13–16].

Miandad et al. [13] carried out a review of the catalytic pyrolysis of plastic waste studying how the operating conditions used and the type of catalyst influence the liquid fraction obtained. In this review, catalysts such as ZSM-5, Red Mud, Zeolites Y, natural zeolites, FCC or Al_2O_3 were used. It was determined that the oils from catalytic pyrolysis had very similar characteristics to those of conventional diesel fuel, with a calorific value of 38–45.5 MJ/kg, a density of 0.77–0.84 g/cm^3, a kinematic viscosity of 1.1–2.27 cst, a flash point of 26–48 °C and a boiling temperature of 82–352 °C. Moorthy Rajendran et al. [17] attempted to convert municipal plastic waste into quality fuels from catalytic pyrolysis. This study determined that the typology of the catalyst significantly affects the yield of the fractions as well as their characteristics. To this end, several catalysts such as HUSY, HZSM-5, HMOR, Zeolite Y, silica and FCC were studied. Their results showed that with catalysts the selectivity is improved, in addition to the fact that mild acid catalysts produce more liquid hydrocarbons.

Other researchers such as Susastriawan et al. [18] worked with materials similar to those in this paper. They studied the use of zeolites in the catalytic pyrolysis of polyethylene (low density polyethylene (LDPE), high density polyethylene (HDPE)) waste, and established that the smaller the size of the zeolite and the higher the temperature, the higher the liquid fraction yield. Onwudili et al. [19] worked with a mixture of plastics through catalytic pyrolysis, using catalysts such as FCC, ZSM-5 and zeolites Y. In this work, the yield of the liquid fraction decreased with the addition of the catalyst, and the liquid fraction had properties suitable for use as fuel, although the amount of aromatic compounds present increased. Santos et al. [20] investigated the catalytic pyrolysis of polyethylene (PE) and polypropylene (PP) plastic waste with catalysts such as HZSM-5, USY, NH_4ZSM5. The use of zeolite USY resulted in a higher amount of liquid fraction, whose main components were alkylbenzenes, naphthalenes and olefins.

Kunwar et al. [14] reviewed the catalytic processes of the conversion of plastic waste into fuel. They collected information on catalysts such as ZSM-5, Zeolites Y, Zeolites β and $Ca(OH)_2$, among others, obtaining that yields of the liquid fraction vary from 15 to 93%. Besides that, they established that the use of high acidity and porosity catalysts and the use of hydrogenation would be necessary. Finally, the paper by López et al. [8] dealt with a review of the catalytic pyrolysis of polyolefins, using different catalysts and operating conditions. A wide variety of catalysts have been applied in the recovery of waste polyolefins, the most common being zeolites. According to their results, HZSM-5 proved to be suitable for the production of valuable light olefins. Other larger pore size zeolites such as HY, HUSY or spent FCC catalysts are a better alternative for the production of liquid hydrocarbons. MCM-41, or the less acidic mesoporous SiO_2-Al_2O_3, are also interesting options to produce liquid fuels.

In previous works the thermal pyrolysis of polyethylene film plastic waste of the organic-rest fraction was studied [21], and it was determined that the characteristics of the oil were of quality for its use as a fuel, but this oil was mainly a wax. The problem of the heavy oil-waxes from the pyrolysis is their high viscosity and that they do not have a suitable use [22]. High fuel oil viscosity would cause incomplete combustion and lead to the formation of carbon deposits in the combustion vessel or burner. This parameter also affects the difficulty of ignition and pumping [23]. The addition of a catalyst into the process can result in advantages and better properties of the liquid fraction (lower heavy oil-waxes). Nevertheless, some catalysts can result in an extensive liquid fraction loss in favor of gaseous products due to an over-cracking of the material [24], which is undesirable when liquid fuel production is the preferred output. In this paper, different catalysts are used in order to solve the problem of the presence of a large quantity of heavy oil-waxes, with the aim of obtaining a non-waxy liquid product from the plastic waste of the polyethylene film from the organic-rest fraction without losing extensive liquid fraction. In short, the aim of this paper is to obtain a low viscosity liquid fraction at room temperature (non-waxy fraction), in order to use this material as fuel.

2. Materials and Methods

2.1. Materials

The plastic material used in this study comes from the municipal solid waste collected and treated in the Ecocentral waste recovery and recycling plant in Granada, Spain, and corresponds to the plastic film fraction that had not been selectively collected, known as the organic-rest fraction.

Plastic waste is mechanically pre-treated in the recycling plant in order to separate the different materials and facilitate subsequent recycling and baling. The samples treated in the laboratory come from the bunker corresponding to each type of plastic separated inside the plant [21]. The plastic was polyethylene film and this polyethylene film was converted into pellets to facilitate feeding to the reactor. In addition, these pellets were crushed and sieved to a particle size of less than 2 mm (Figure 1).

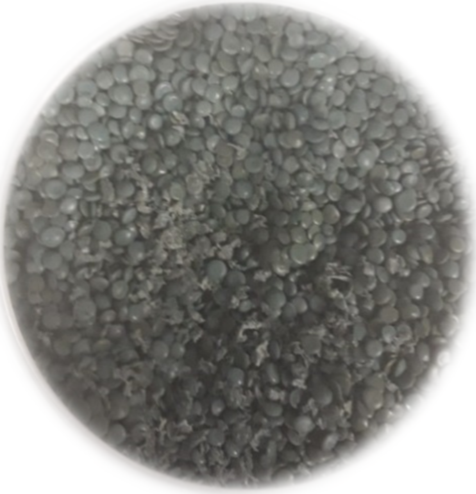

Figure 1. Polyethylene film pellet from the non-selectively collected fraction.

In this work, numerous catalysts were studied; some of them were used in their commercial form, others were subjected to different treatments for their chemical modification and others were impregnated with different metals, such as Ni, Co, Pd or Ru. All catalysts had a particle size between 200–500 µm. These catalysts were summarized in Table 1.

Table 1. Catalysts used in in-situ catalytic pyrolysis.

Catalyst	Nominal Cation Form	Si/Al	Na_2O w. (%)	Surface Area, m^2/g	Pores Volume, cm^3/g	Acidity	References
Zeolite ZSM-5 (CBV3024E)	NH_4	15	0.05	405	Micro. 0.13 Meso. 0.11	B/L 2.32 Total acid sites: 1.10 mmol/g	[25–28]
FCC	-	23.2	-	192	*Micropore Area* 94.2 m^2/g	0.51 meqv. of NH_3/g)	[25,29]
Zeolite Y NaY-Geace (CBV-100)	Na	2.5	13.0	900	Micro. 0.37 Meso. 0.16	Yes	[25,30,31]
Zeolite Y HUSY-5.1 (CBV-600)	H	2.6	0.2	660	Micro. 0.27 Meso. 0.16	B/L 1.51Total acid sites: 0.99 mmol/g	[22,25–27, 31]
Zeolite Y HUSY-5.1-Metal (CBV-600)	H	2.6	-	-	-	Yes	[32]
Zeolite Y ZHA (CBV-600)	H	2.6	-	-	-	Yes	[33]
Zeolite Y HUSY-30 (CBV-720)	H	15	0.03	780	Micro. 0.36 Meso. 0.23	B/L 3.18 Total acid sites: 1.43 mmol/g	[25,34]
Zeolite β HBEA-25 (CPE 814E)	NH_4	12.5	0.05	680	Micro. 0.18 Meso. 0.28	B/L 1.67–0.93 Total acid sites: 1.12 mmol/g	[27,35,36]
Zeolite β HBEA-75 (CPE 811E)	NH_4	37.5	0.05	680	Micro. 0.183 Meso. 0.188	B/L 1.01	[26,37]
Zeolite β HBEA-150 (CPE 814E)	NH_4	75	0.05	680	-	Yes	[38,39]
Zeolite Natural Clinoptilolite		5.67	-	80–100	Micro. 0.0254 Meso. 0.028	Yes	[40,41]
$SiO_2Al_2O_3Co$	-	-	-	-	-	Yes	[41]
SiO_2	-	-	-	-	-	Yes	[42]
Al_2O_3	-		-	265	Micro. 0.019 Meso. 0.438 Macro. 0.017	Total acid sites 0.21 mmol/g	[27,43]
$CaCO_3$	-	-		-	-	No	[44]
Zeolite powder 13X	-	1–1.5	15.93	729	Micro. 0.26 Meso. 0.165 Macro. 0.027	Yes, strong	[45]
Fe_2O_3	-	-	-	4.3	-	No	[46–48]
NH_2SO_3H	-	-	-	-	-	-	[48]
$SnCl_2$	-	-	-	-	-	-	[49]

CBV-600 zeolites treated with HCl. B/L: BrØnsted–Lewis site ratio. Micro.: micropore volume. Meso.: mesopore volume. Macro.: macropore volume.

As mentioned above, most catalysts were not modified in any way. On the other hand, the synthesis of the $SiO_2Al_2O_3Co$ catalyst was carried out following studies already published by Cunping Huang et al. [50]. This catalyst consisted of a support formed by 1% SiO_2 and 99% Al_2O_3, impregnated by incipient wetness with 1% wt of the cobalt metal. ZHA is a commercial zeolite HUSY.5.1 (CBV-600) that was treated with HCl. This same zeolite HUSY.5.1 was impregnated with different metals Ni, Pd and Ru. All catalysts were prepared via the incipient wetness impregnation method [51]. The impregnation of these metals was 1% wt. The incipient wetness impregnation method involve the impregnation of the coals with a solution of salt of the metal to be used, or of an organometallic complex, followed by a drying and reduction stage so that the metallic particles manage to anchor to the surface of the coal.

All the catalysts used in this work were subjected to thermal activation in a Naberthem model L 5/11 muffle furnace. The activation conditions were an air flow rate of 300 mL/min, in a heating rate of 53 °C/min up to 550 °C; it was maintained at this temperature for 5 h.

2.2. Catalysis Test

The polyethylene film samples were subjected to catalytic pyrolysis. The process installation flowchart is presented in Figure 2. A horizontal batch reactor (Naberthem) was used. In each experiment a constant nitrogen stream of 100 mL/min was introduced to ensure the inert atmosphere. An aluminum container with about 20 g of pellet and the corresponding amount of catalyst from each experiment was introduced into the reactor, and this feed stayed as a fixed bed during the course of the experiment. The operation conditions used were a temperature of 500 °C, a heating ramp of 20 °C/min and a residence time of 120 min, residence time being the time in which the pellets and catalyst come into contact inside the reactor. These experimental conditions were chosen according to results reported by a previous work [52]. Before the introduction of the pellet-catalyst sample, this mixture was stirred for 10 min at 300 rpm in order to homogenize the mixture. It should be noted that 10% wt of catalyst was used in most experiments. For some catalysts, different ratios of 5 to 20% wt of catalyst were used, so as to see how this parameter was affected.

Once the pyrolysis process started, the polyethylene waste began to degrade. As the experiment progressed, a stream of gases began to emerge and passed to a condenser, which was an ultrathermostat that allowed these streams to be cooled to a temperature of −4 °C. The volatile products were transferred from the reactor to the condenser with the help of the nitrogen stream. After finishing the condensation process, two phases were separated: the gaseous fraction, which is the non-condensable phase, and the liquid fraction, which is the condensable phase. After completing the total residence time, the aluminum container was removed from the reactor, and here the char and the used catalyst were obtained. All products were recovered, as the transfer lines were completely isolated.

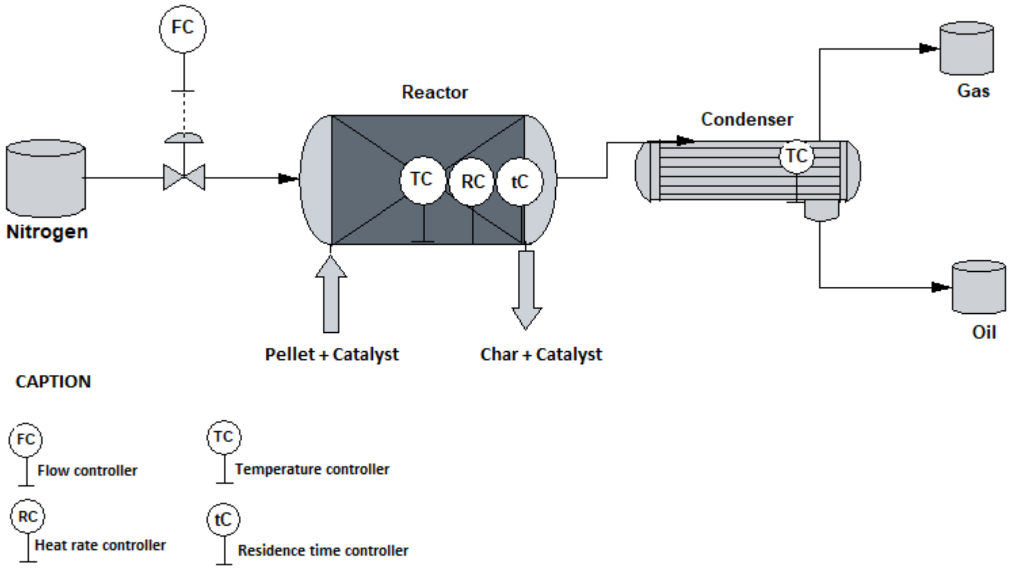

Figure 2. Flowchart of the catalytic pyrolysis process and proportional integral derivative control system (PID).

2.3. Determination of Liquid, Char and Gas Fraction Yields

After the catalytic pyrolysis process, the yield of the liquid fraction and the solid fraction by weight difference and the gaseous fraction by difference of the other two were determined, since the conversion was 100%, according to the following equations:

$$\eta_{oil} = \frac{owf}{pwi} 100 \tag{1}$$

$$\eta_{char} = \frac{cwf}{pwi} 100 \tag{2}$$

$$\eta_{gas} = 100 - \eta_{oil} - \eta_{char} \tag{3}$$

where *owf* is the final weight of oil, *pwi* is the initial weight of polymer and *cwf* is the final weight of char.

2.4. Characterization of Liquid Fraction

Those liquid fractions whose physical aspect at first sight was improved with the catalyst, that is, those liquid fractions that contain less amount of waxes (non-waxy material), were characterized. In order to test the effectiveness of the catalyst in terms of the elimination of waxes, the viscosity property was measured (waxy material is one that has a high viscosity at room temperature).

The oil samples were arranged in a Malvern Kinexus rheometer using a 20 mm diameter flat plate at a constant temperature of 40 °C, so that the dynamic viscosity of the samples could be determined according to ASTM D445. Viscosity was measured at a constant temperature as it is a non-Newtonian fluid and thus its characteristics depend on temperature.

Figure 3 summarizes the research sequence carried out in this paper, specifying what catalysts decreased the viscosity of the liquid fraction obtained by thermal pyrolysis and defining which ones had a higher amount of waxes.

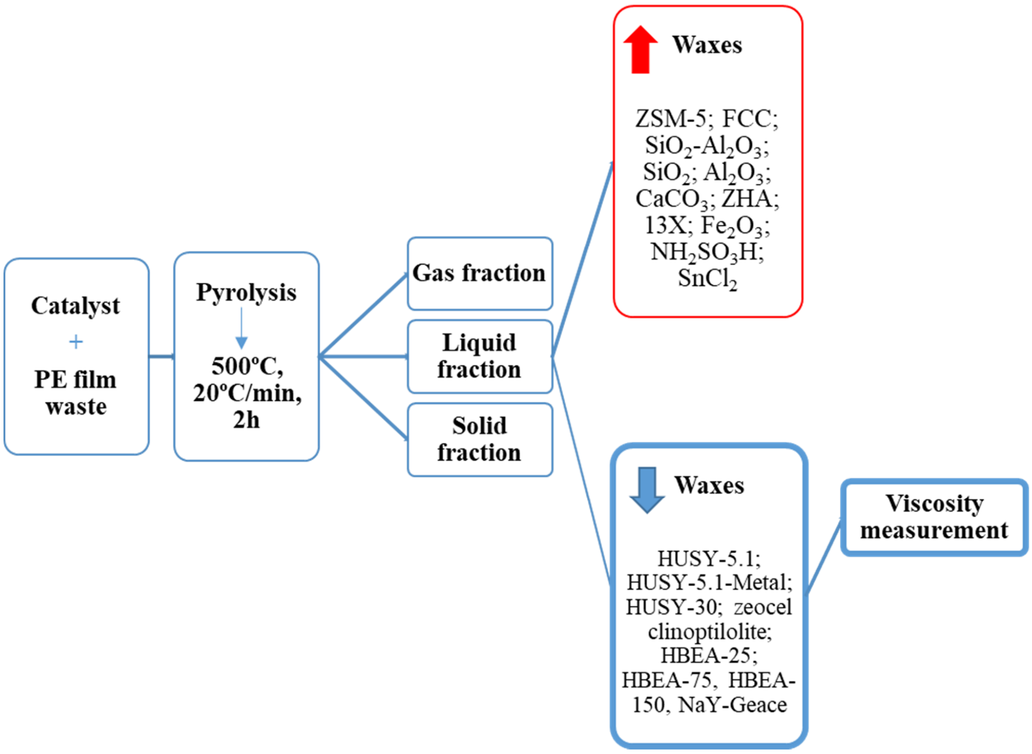

Figure 3. Summary of the investigation sequence.

3. Results and Discussion

3.1. Determination of Liquid, Char and Gas Fraction Yields

Table 2 shows the yields of the products obtained in the catalytic pyrolysis of polyethylene film using different catalysts at 10% wt.

Table 2. Yield of products obtained in catalytic pyrolysis for different catalysts at 10% wt.

Catalyst	**Catalytic Pyrolysis Fractions**		
Catalyst	**Liquid (%)**	**Char (%)**	**Gas (%)**
Without catalyst	72.85	9.28	17.87
ZSM-5	56.12	10.27	39.64
FCC	23.92	14.42	61.65
Zeocel clinoptilolite	54.98	3.32	41.70
HBEA-25	42.96	4.22	52.82
HBEA-75	35.04	4.26	60.69
HBEA-150	44.82	1.78	53.40
NaY-Geace	51.56	1.20	47.24
HUSY-5.1	37.33	5.42	57.25
HUSY-5.1-Ni (1%)	24.98	6.29	68.72
HUSY-5.1-Pd (1%)	17.25	1.14	82.89
HUSY-5.1-Ru (1%)	29.06	3.95	66.99
HUSY-30	39.06	7.87	53.08
ZHA	36.40	7.10	56.50
13X	53.97	6.49	39.54
SiO_2-Al_2O_3-Co	30.81	3.25	65.94
Al_2O_3	56.68	12.05	31.27
SiO_2	57.70	5.77	36.53
$CaCO_3$	63.38	3.30	33.32
$SnCl_2$	67.57	6.92	25.51

It was verified that when introducing the catalyst, the gaseous fraction and the char increased and the liquid fraction decreased compared to the thermal pyrolysis, where in the thermal pyrolysis a 72.85% yield of the liquid fraction was obtained.

Using the ZSM-5 zeolite, a high yield of the liquid fraction of 56.12% was obtained, but this fraction was mainly wax. Authors such as Ates et al. [29] studied catalytic pyrolysis with this catalyst for a mixture of plastic waste and obtained a 45% liquid fraction yield, and López et al. [53] also worked with this waste obtaining a 39.8% oil yield. Other studies such as Gobin and Mandos [54] obtained a 39% of liquid fraction using this catalyst to crack low density polyethylene (LDPE); Manos et al. [55] pyrolyzed high density polyethylene (HDPE), obtaining a 46% yield. Finally, Boxiong et al. [56] and Marcilla et al. [57] investigated the catalytic pyrolysis of polyethylene and other plastic waste, obtaining the entire liquid fraction in the form of waxes, as in this investigation. These average yield values are due to the fact that the ZSM-5 catalyst is an acid catalyst, which causes a higher yield of the gaseous fraction [58], but it also has BET surfaces and a not very high Si/Al ratio, which causes the increase of the liquid fraction [13,59].

In this work, the FCC catalyst in the catalytic pyrolysis of the polyethylene film produced one of the lowest yields of the liquid fraction, 23.92%, the gaseous fraction was the majority fraction with 61.65%, and it even produced one of the highest char yields with 14.42%. Other authors achieved higher yields, but for pyrolysis of plastic waste mixture; for example, Ates et al. [29] got a yield of the liquid fraction of 45% and Olazar et al. [60] studied the catalytic pyrolysis of HDPE, determining that in its entirety the liquid fraction corresponded to wax. This low yield of the liquid fraction obtained with the FCC catalyst may be due to its high Si/Al ratio and its low BET surface [13,59].

Additionally, natural zeolites, such as zeocel clinpoptilolite, were used, obtaining a considerable liquid fraction yield of 54.98% and a low amount of char of 3.32%. In addition, in this case the liquid fraction was not completely waxy. Other researchers used this same catalyst, such as Miskolczi et al. [39], achieving a similar liquid fraction yield of approximately 55%. Authors such as Kim et al. [61] obtained between 55–65% of liquid fraction yield in the catalytic pyrolysis of polyolefin mixtures. Its low Si/Al ratio causes an increase in the liquid fraction, while its low BET surface causes a higher yield of the gaseous fraction, and thus equal values are obtained [59,62].

Zeolites β (HBEA) are some of the most widely used zeolites today. Excellent values were obtained with them, and furthermore the liquid fraction was not a wax. Yields of the liquid fraction of 35.04 to 44.82% were obtained, as well as low char yields of 1.78 to 4.26%. There are numerous studies about the catalytic pyrolysis of plastics with zeolites β, for example Ates et al. [29] determined a 50% liquid yield in the catalytic pyrolysis of mixed plastic waste, or Miskolczi and Ates [63] who produced 34.2% of mixed polyolefins. Finally, researchers like Manos et al. [64] obtained a liquid fraction yield of 48% for the catalytic pyrolysis of HDPE. Zeolites β were mesoporous zeolites with not very strong acidity and a high Si/Al ratio, which resulted in good yield values for the liquid fraction [65].

In this work, Y-zeolites were also used. The use of NaY-Geace zeolite was effective since a high yield of the liquid fraction of 51.56% and low char content of 1.20% were obtained, in addition to the fact that the liquid fraction was not a waxy fraction.

Other Y zeolites studied in this work were the HUSY-5.1 and HUSY-30 zeolites, with which an oil yield of 37.33% and 39.06% was obtained, respectively, being a low waxy liquid fraction. There are numerous studies using these Y-zeolites, such as Ates et al. [29], which determined a liquid fraction of 50% for mixed plastic waste. Others, like Marcilla et al. [57], studied the catalytic pyrolysis of high and low density polyethylene obtaining a yield in the range of 41 to 61.6% for the oil. Miskolczi and Ates [63] researched the catalytic pyrolysis of plastic waste using HUSY-5.1 and produced a 32% liquid fraction, and Manos et al. [64] worked with the catalytic pyrolysis of HDPE with HUSY-5.1 producing a 41% liquid fraction. In addition, Table 2 shows the yield of the products obtained in the catalytic pyrolysis of polyethylene film using 10% wt of the HUSY-5.1 catalyst impregnated with different metals, where the zeolite with metal caused a considerable decrease in the liquid fraction. Authors such as Rizkiana et al. [32] studied co-pyrolysis with these types of catalysts, obtaining better results than with the zeolite Y without metal impregnation. Zeolites Y were micro-mesoporous zeolites, with strong acidity and high surface area, which caused high yields of the gaseous fraction [2,58,65].

With the zeolite Y treated with HCl (ZHA), a liquid yield of 36.40% and a char yield of 7.10% were obtained, not significantly improving the properties of the thermal pyrolysis oil. Authors such as Contreras [66] used this type of catalyst, obtaining a low amount of liquid fraction of approximately 20%. When zeolite Y was activated with HCl it produced more gas than if it was thermally activated due to its high acidity [67].

There are no studies with the use of type X zeolites in the catalytic pyrolysis of plastic waste, in this work almost 54% of liquid yield has been obtained, but it was a waxy material.

Thermal pyrolysis was not improved, with respect to being a less waxy oil, with the use of the SiO_2-Al_2O_3-Co catalyst, since low liquid product yields were obtained, besides the fact that it is a wax. On the one hand Cunping Huang et al. [50] obtained high liquid yields in addition to being completely liquid for polyethylene waste. On the other hand, authors such as Chattopadhyay et al. [41] obtained low liquid product yields with less than 20% of yield, being a waxy material.

The use of catalysts such as Al_2O_3 and SiO_2 did not improve the properties of the oil obtained with respect to the oil obtained in thermal pyrolysis; with respect to being a less waxy oil, high yields of liquid product were obtained, but it was a waxy product. The catalyst $CaCO_3$ is usually used for the treatment of biomass [44]; even so, in this work it was used for the treatment of polyethylene film, obtaining a high yield of liquid product, but being waxy. Al_2O_3, SiO_2 and $CaCO_3$ catalysts produced high yields of the liquid fraction because they are not acidic catalysts and because of their pore volume [2,13].

The use of the $SnCl_2$ catalyst caused a 67.57% liquid fraction, although it is a waxy fraction. This catalyst is usually used in biomass rather than in plastics [39,52,68].

Table 3 shows the performance of catalytic pyrolysis products from polyethylene film using different amounts of the HUSY-5.1 catalyst, in order to see how the amount of catalyst influences the catalytic pyrolysis, since such catalysts showed an un-waxy appearance. As can be seen in Table 3, as the amount of catalyst increases the production of the gaseous fraction increases from 52.55% for 5% wt of catalyst to 59.09% for 20% wt of catalyst; this is because the HUSY catalyst is a mesoporous catalyst, so it promotes the cracking of the gaseous fraction [13]. Therefore, it is not interesting for this study to increase the amount of this catalyst, since it fractionates the gaseous part more. By contrast, Gobin and Manos [54] studied the catalytic pyrolysis of virgin LDPE with the HUSY-5.1 catalyst, and obtained different results to those of this work, because as the amount of catalyst increased, the yield of the liquid fraction increased. This contradictory situation was due to the fact that the material used in this paper was a processed material containing a large amount of impurities.

Table 3. Yields of the products obtained in the catalytic pyrolysis for the HUSY-5.1 catalyst.

Catalyst	Catalytic Pyrolysis Fractions		
Catalyst	**Liquid (%)**	**Char (%)**	**Gas (%)**
5% HUSY-5.1	39.64	7.82	52.55
10% HUSY-5.1	37.33	5.42	57.25
20% HUSY-5.1	34.94	5.97	59.09

A wide variety of catalysts were used in this paper; some, like Fe_2O_3 and NH_2SO_3H, are widely used and cheap, but the use of 10% wt of catalyst does not give adequate results for such research. Therefore, different amounts of catalyst were tested, in order to see if the amount has some influence.

Table 4 shows the yield of catalytic pyrolysis products from the polyethylene film of the organic-residue fraction using different amounts of Fe_2O_3. High yield values of the liquid fraction of 58.57% for 5% wt of catalyst to 64.33% for 20% wt were determined. As the quantity of this catalyst was increased with respect to the weight of the PE waste, the quantity of liquid product increased, but also the quantity of char increased from 6.70% to 21.24%. Microporous–mesoporous catalysts produced a higher gas yield, while macroporous catalysts favored the yield of the liquid fraction; while the HUSY catalyst is a mesoporous catalyst, the Fe_2O_3 catalyst is a macro-mesoporous catalyst [13]. Although by using a macroporous catalyst the yield of the liquid fraction increased, the viscosity of the liquid product was not improved, since the liquid product obtained was a complete wax. Similar results were obtained by Aguirre et al. [46], which determined a liquid product yield of less than 42%, being a wax just like in this work.

Table 4. Yield of products obtained in the catalytic pyrolysis for the Fe_2O_3 catalyst.

Catalyst	Catalytic Pyrolysis Fractions		
Catalyst	**Liquid (%)**	**Char (%)**	**Gas (%)**
5% Fe_2O_3	58.57	6.70	34.73
10% Fe_2O_3	59.78	12.90	27.32
20% Fe_2O_3	64.33	21.24	14.43

Table 5 shows the yield of the products obtained in the catalytic pyrolysis of polyethylene film using the NH_2SO_3H catalyst, which produced a large amount of liquid product in the form of wax, from 55.11% to 63.84%, with high amounts of char from 9.27% to 10.84%. This catalyst has not been used for in situ catalytic pyrolysis, but is usually used for catalytic cracking of oil as a second stage [48].

Table 5. Yield of products obtained in the catalytic pyrolysis for the NH_2SO_3H catalyst.

	Catalytic Pyrolysis Fractions		
Catalyst	**Liquid (%)**	**Char (%)**	**Gas (%)**
5% NH_2SO_3H	60.02	5.87	34.11
10% NH_2SO_3H	55.11	9.27	35.63
20% NH_2SO_3H	63.84	10.84	25.32

In conclusion, different gaseous, liquid or solid fraction yields can be obtained, depending on the type of catalyst used:

- The higher the acidity of the catalyst, the greater the cracking, which causes an increase in the gaseous fraction [2,58].
- The higher the alumina ratio in a catalyst, the higher the yield of the liquid fraction, because it has a larger BET surface and pore volume [62]. In other words, catalysts with a low BET surface area and microporous structures favor the production of gases [59], while macroporous catalysts favor the production of the liquid fraction [13].
- Catalysts such as zeolites have a large internal crystalline structure, which increases the cracking process and therefore increases the yield of the gaseous fraction with the decrease in the yield of the liquid fraction [13].
- When a zeolite is activated in an acidic rather than a thermal way, it causes a higher production of gases, due to its high acidity [67].

In the following section, viscosity measured as a liquid fraction was the most interesting product for this work, and it was meant to be used as a fuel.

3.2. Characterization of Liquid Fraction

According to previous studies [21], the oil obtained from the thermal pyrolysis of the polyethylene film from the organic-rest fraction was a wax, with a high viscosity for low temperatures, while at high temperatures the oil is in a liquid state with low viscosity values. With respect to this product, the viscosity was 1000 cst at 40 °C, 115.36 cst at 50 °C and 67.50 cst at 60 °C. In addition, in this previous study, a gas chromatography with masss spectrometry (GC-MS) was performed and it was determined that the components present in the sample were mostly 1-alkenes and n-alkanes in the range C_7 to C_{28}. Researchers such as Kunwar et al. [14], stated that the oils from the thermal pyrolysis of plastic waste have a high viscosity, hence it is important to reduce this viscosity for the efficient use of these oils.

The introduction of a catalyst into the pyrolysis process is intended, between others objectives, to reduce the viscosity of the oil produced. The viscosity of the liquid product can be modified according to the properties of the catalyst used. Generally, acid catalysts cause an increase in the formation of light hydrocarbons [2]. Authors such as Miskolczi and Ates [60] established that acid zeolites show high activity in the removal of paraffins and olefins and an increase in the concentration of aromatic compounds. Additionally, acid and mesoporous catalysts allow the production of shorter hydrocarbon chains due to the high cracking ability, while microporous and less acidic catalysts favor the production of long hydrocarbon chains [62]. These modifications of the composition of the liquid product finally obtain different viscosities of the oil.

This section reports the viscosity measurements of some oils obtained for different catalysts. Only the values of the oils whose viscosity decreased significantly with respect to the oils obtained without a catalyst are presented (Tables 6 and 7).

In Table 6, the viscosity values at 40 °C are presented for the oils obtained in the catalytic pyrolysis using 10% wt of the catalysts zeocel clinoptilolite, HBEA, HBEA-75, HBEA-150 and NaY-Geace.

In the case of the zeocel clinoptilolite catalyst, a kinematic viscosity of 115.11 cst was acquired. Authors such as Miskolczi et al. [39] determined the viscosity of polyethylene and polystyrene mixture wastes, obtaining a viscosity of 4.4 cst, but this low viscosity is due to the presence of polystyrene [69].

Nonetheless, if the different zeolites β studied are compared (HBEA-25, HBEA-75 and HBEA-150), the HBEA-25 zeolite is the one with the lowest kinematic viscosity, 89.37 cst. Authors such as Elordi et al. [26] studied the composition of the oil obtained from the catalytic pyrolysis of HDPE using HBEA-75, and it was seen that the amount of aromatics increased considerably, leading to a decrease in viscosity. Other authors such as Miskolczi and Ates [63] determined the viscosity of the oil obtained by the catalytic pyrolysis of mixed plastic waste through zeolites β (HBEA) at 40 °C, obtaining a kinematic viscosity value of 113 cst. Zeolites β decreased the viscosity value of the liquid fraction, as they are mesoporous zeolites that favor the production of short hydrocarbon chains [65].

Table 6. Viscosity of the oils obtained in the catalytic pyrolysis with different catalysts.

Catalyst	Dynamic Viscosity (Pa·s)	Kinematic Viscosity (cst)
Zeocel clinoptilolite	0.09	115.11
HBEA-25	0.07	89.37
HBEA-75	0.08	99.62
HBEA-150	0.08	97.89
NaY-Geace	0.08	93.06

Viscosity measured at 40 °C.

As already seen in the previous section, as the amount of HUSY-5.1 catalyst was increased in this process, the amount of gaseous products increased, but it was also necessary to know if this parameter modifies the viscosity (Table 7). It can be seen that as the amount of catalyst was increased, the kinematic viscosity decreased considerably, from 1440.78 cst with the use of 5% wt HUSY-5.1 to 53.21 cst with the use of 20% wt HUSY-5.1. These values are very similar to those obtained by other authors, such as Miskolczi and Ates [63], who studied the catalytic pyrolysis of a mixture of plastic waste with 10% wt of this zeolite at 40 °C, obtaining 119 cst, while in this work 137.28 cst was obtained for those same conditions. In addition, Table 7 shows the viscosities of the different oil samples obtained for 10% wt of catalyst, both in its commercial form and impregnated with different metals, which were slightly lower than the 10% wt zeolite HUSY-5.1 without impregnation, but higher than the 20% wt zeolite HUSY-5.1. Finally, Table 7 also presents the viscosity of the liquid fraction obtained with the 10% wt HUSY-30 catalyst, obtaining a value of 209.38 cst, slightly higher than the 10% wt zeolite HUSY-5.1 with a value of 137.28 cst. Authors such as William et al. [70] studied the catalytic pyrolysis of rubber gloves in the presence of zeolite Y, where the liquid fraction decreased its viscosity considerably by introducing this catalyst in the pyrolysis. The zeolites Y decreased the viscosity value of the liquid fraction, as these have a high acidic and good surface area and pore volume properties.

Table 7. Viscosity of the oils obtained in the catalytic pyrolysis with different proportions of the HUSY-5.1 catalyst.

Catalyst	Dynamic Viscosity (Pa·s)	Kinematic Viscosity (cst)
5% HUSY-5.1	1.17	1440.78
10% HUSY-5.1	0.11	137.28
20% HUSY-5.1	0.04	53.21
10% HUSY-30	0.17	209.38
10% HUSY-5.1Ni (1%)	0.08	96.72
10% HUSY-5.1 Pd (1%)	0.08	97.64
10% HUSY-5.1 Ru (1%)	0.06	75.00

Viscosity measured at 40 °C.

4. Conclusions

The aim of this work was to reduce the viscosity of the liquid fraction obtained in thermal pyrolysis by using catalysts, in order to obtain a less waxy fuel from the polyethylene film waste from the non-selectively collected fraction. For this purpose, numerous catalysts were studied; some of them were used in their commercial form, others were subjected to different treatments for their chemical modification and others were impregnated with different metals.

Catalysts such as ZSM-5, FCC, SiO_2-Al_2O_3-Co, SiO_2, Al_2O_3, $CaCO_3$, 13X, Fe_2O_3, NH_2SO_3 and $SnCl_2$ did not improve the waxy aspect of the liquid fraction of thermal pyrolysis; hence their wax content was high as well as their viscosity value, which was around 1000 cst at a temperature of 40 °C.

Other catalysts, such as HUSY-5.1, HUSY-5.1, HUSY-30, Zeocel clioptilolite, HBEA-25, HBEA-75, HBEA-150 and NaY-Geace, improved the liquid aspect of the liquid fraction, as the wax content decreased and therefore its viscosity compared to thermal pyrolysis as well. In addition, a greater amount of gaseous fraction was produced than in thermal pyrolysis when these catalysts were introduced, due to the extensive cracking they produce. Finally, some viscosity values obtained with the most relevant catalysts (10% wt) should be highlighted. In the case of the Y zeolites (HUSY), a viscosity range of 75 to 137.28 cst was obtained at 40 °C, and for the zeolites β (HBEA) 89.37 to 99.62 cst was obtained at 40 °C.

In future works, it is intended to completely analyze the liquid fraction obtained with the catalysts that reduced its viscosity, in order to know if this product is suitable to be used as a quality fuel. For this purpose, techniques such as FTIR and GC-MS, among others, will be used.

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