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Fast Pyrolysis oil from plastics waste as a Fuel for Gas Turbine Power Plants

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Abstract. Plastic production and usage increase every year due to its low cost, practicality, and flexibility. Despite the advantages of plastics as a raw material, it represents a serious environmental problem when it becomes waste. Most of the plastic is produced from petrol. Its chemical composition provides the opportunity to be transformed into a fuel via a pyrolysis process, with or without a catalyst. The pyrolysis process yields solid, liquid and gas fractions. The liquid fraction has properties similar to those of conventional fuels and can be used in internal combustion engines. However, although fast pyrolysis is cheaper, it produces lower quality products (longer carbon chains) not suitable for these types of engines. In the present paper, main properties of oils from fast pyrolysis are analysed and compared to those of Heavy Fuel Oils (HFO) to demonstrate that they represent a feasible alternative to decrease the impact of plastics in the environment and to obtain an alternative fuel to feed a power plant.

Key words. Waste plastic, HFO, gas turbine, power plants, pyrolysis oil.

1. Introduction

Plastics have many properties that make them suitable for many applications. Properties such as strength, low production costs, lightweight, durability, flexibility, and corrosion resistance have promoted the fast increase of plastics during the last 50 years [1]. However, due to the low degradability, a severe environmental problem arises when plastics become a waste, especially because the majority of the commercialised plastics are single-use plastics. Consequently, the world must face a great challenge in plastic waste management [2]. The most conventional process for plastic waste treatment is landfilling; about 40 % of global plastic waste ends up in landfills [3]. Landfilling is an unsustainable management strategy since it produces by-products that are hazardous to the environment and to human health [4].

According to the report [5], in 2020, the world plastics production was 367 Mt, from which 55 Mt was produced in Europe. Although a stabilisation in plastics production can be observed between 2019 and 2020, this is still a considerable amount of plastic to be treated every year. Several alternative techniques to landfilling can be employed for waste plastic treatment, such as recycling. Plastic recycling can be classified into physical recycling and resource recovery. The last one is attracting increasing attention since it produces valuable products that can be used as fuels. Thermolysis is the primary process for resource recovery, from which pyrolysis is the most widely used [6]. Pyrolysis is also used to upgrade heavy oils due to low operating costs [7].

Pyrolysis is a process in which long-chain polymers are thermally degraded into smaller molecules in the absence of oxygen [8]. The properties of the resulting oil vary if a catalyst is used during the pyrolysis process [9]. A Pyrolysis process yields three fractions: gas, liquid, and char (or solid residue). Since the majority of the plastic is still produced from petroleum, [6] the liquid fraction obtained from a waste plastic pyrolysis has similar properties to those of existing liquid fossil fuels and can be a sustainable alternative in the field of heat engines [9]. The amount of liquid fraction is influenced by the pyrolysis process parameters (temperature, feed rate, and vapour residence time). In a fast pyrolysis process, operating conditions are low temperature, high heating rate, and short residence time of volatiles [11].

It is generally accepted that the target of fast pyrolysis is to maximise the yield of the liquid fraction. It is also accepted that the quality of oil from thermal fast pyrolysis (mainly waxes with carbon number C21+) cannot be considered an alternative for liquid transport fuel unless it is upgraded [10]. Nevertheless, there are applications that don't require fuels of such high quality.

Fuel oil could be obtained as a distilled or residue from petroleum, and it is composed of long hydrocarbons chains (C_9-C_{70}), in particular alkanes, cycloalkanes, and aromatics. Fuel oil is classified into six classes, from 1 to 6. Fuel oil No. 6 is called residual fuel oil (RFO) or heavy fuel oil (HFO). It is the residue of the crude oil after the distillation of gasoline and fuel oils. It is used in industrial burners, and it can fuel thermal power stations or robust engines; some examples are [12],[13]. Due to the high viscosity of HFO, preheating is usually needed for proper pumping. For an HFO typical viscosity of 180 mm^2/s at 50 °C, it is required to heat this fuel to at least 120 °C to reach an adequate viscosity [14].

Gas turbine power plants can operate on different fuels such as natural gas, heavy fuel oil (HFO), or light fuel oil (LFO) as the power plant described by Faisal et al., which consists of ten units with a one-generation unit rating of 126.1 MW under ISO condition [15].

The main advantage of using HFO as a fuel is its lower cost [16] and its high net heating value, which is similar to that of diesel fuel (39.57 MJ/kg for HFO [15], and 42.03 MJ/kg for diesel fuel [17]). However, this fuel needs pre-treatment before combustion and frequent turbine cleaning to avoid lost performance due to fouling [18].

The target of the present study is to determine whether a fast pyrolysis oil (PO) from plastic waste can be used as a substitute for HFO in gas turbine power plants. To reach this target, two POs are produced in a fixed bed reactor, and some of their properties are analysed and compared to those of a regular fuel used in this type of plant. Additionally, it is discussed if it is more appropriate to use a catalyst in the pyrolysis reaction or not since it changes the chemical composition of the PO.

The novelty of the present study is the new application proposed and analysed, that is, to substitute fossil fuels for power generation by a pyrolysis oil from plastic waste. There are few papers dealing with the use of fast pyrolysis oils in gas turbines for power generation, and most of them are focused on biomass fast POs instead of waste plastics fast POs, such as [19],[20]. Since the raw material used in the pyrolysis process [21], as well as the use or not of a catalyst [22], significantly influence the properties of the resulting PO, it is considered interesting to determine if the PO properties, with and without a catalyst, are within the range of the properties of the reference fuel (HFO), so that a realistic alternative can be proposed.

2. Materials and Methods

A. Sample preparation.

In the present paper, two samples are analysed, one produced from catalytic pyrolysis denoted as HDPE+Z, and the other one obtained from thermal pyrolysis denoted as HDPE. In the catalytic pyrolysis process, the mass ratio of plastic/catalyst was 10/1. The catalyst used in the catalytic pyrolysis process was ZAP USY zeolite produced by SILKEM d.o.o. Company. The main properties of this zeolite are presented in Table I.

Table I. - Characteristics of the catalyst used.

SiO_2/Al_2O_3 [mol/mol]	13
BET surface area [m^2/g]	540
Na_2O [wt %]	0.13
Average particle size D50 [µm]	2.25
Pore volume [cm^3/g]	0.1
Pore width [nm]	4.4

Sample preparation begins by weighing 100 g of solid HDPE plastic and subsequently cutting it into smaller pieces of approximately 2 cm^2. Zeolite was mixed with the plastic already prepared before being inserted into the reactor. The experimental tests provide an elemental composition for the solid plastic waste of 0.23% N, 87.23% C, 13.67% H, and 0.03% S, and an HHV of 46.14 MJ/kg.

B. Experimental setup - Pyrolysis process

Fast pyrolysis processes were done using a single batch laboratory scale pyrolysis reactor with a fixed bed. Figure 1 shows the schematic representation of the experimental set-up for producing POs.

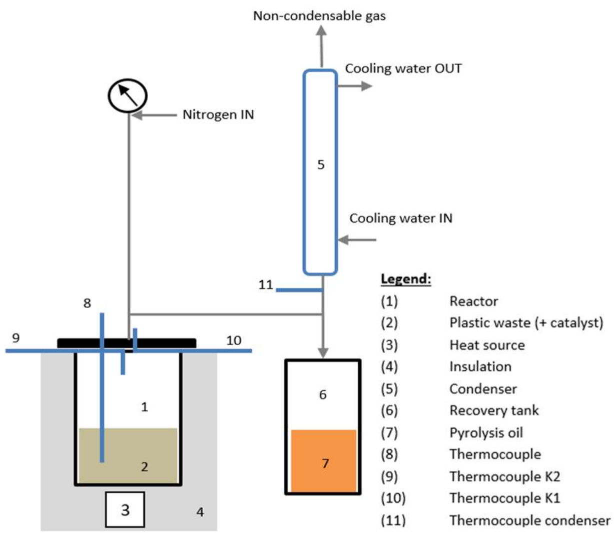

Fig.1. Experimental set-up

The reactor, thermally insulated by a glass wool jacket, is made of stainless steel. The heat source for the pyrolysis process is provided by a 3300 W gas stove. The reactor is sealed and connected to the condenser by a copper pipe. The condenser is a water-cooled countercurrent heat exchanger. Several K-type thermocouples were used to monitor the temperature. Thermocouples K1 and K2 in Figure 1 are used to record the temperature of the vapours that come out at the beginning of the process. The pyrolysis temperature is recorded via the thermocouple (8). Previous to performing each test, a nitrogen flow is passed through the device to ensure an inert atmosphere during the pyrolysis process. The condensated gases (pyrolysis oil) are collected in an oil recovery tank (6). The process is stopped (heat source turned off) when the interval between oil drops is above 10 s. The solid product after the pyrolysis process (char) remains in the reactor (1). The pyrolytic process is monitored via an application made in the LabVIEW program. National Instruments DAQ carrier WLS-9163 and NI-9219 modules are used for temperature data acquisition.

Based on previous studies, the temperature of the thermal fast pyrolysis of HDPE plastic is set at 430°C ± 15°C [23]. On the other hand, the fast-catalytic pyrolysis temperature is slightly lower, 400 ± 15°C, since the use of zeolite reduces the activation energy [24].

C. Equipment for the determination of physico-chemical properties

The carbon number distribution of pyrolytic oils was determined using a Thermo quadrupole Gas Chromatography-Mass Spectrometry (GC-MS) Model DSQ II-Trace Ultra GC analyser. Gas chromatography–mass spectrometry analyses were performed on a Trace GC Ultra gas chromatograph (Thermo Electron SA, Madrid, Spain) coupled to a DSQ II quadrupole mass spectrometer using an electronic ionization source (EI) and a Triplus AutoSampler. The chromatograph was equipped with an DB-5MS capillary column (30 m, 0.25 mm i.d., 0.25 µm film thickness) from Agilent Technologies. Helium (99.999% pure) at a constant flow rate of 1.0 mL/min was used as the carrier gas.

TruSpec Micro analyser, produced by LECO, was used for the determination of PO carbon (C), hydrogen (H), nitrogen (N), and sulphur (S) composition. To control the accuracy of this equipment, it is calibrated every ten measurements by Sulfamethazine.

Density was measured using an Excellence D4 - Mettler Toledo densimeter, which provides fast measurements with automatic temperature control from 0 to 95ºC and an accuracy of up to 0,0001 g/cm^3. In addition, the device has an automatic bubble detection algorithm to avoid sampling errors.

The higher heating (HHV) value of the tested fuels was determined using a 6050 compensated jacket calorimeter designed by Parr company. Samples were tested in the dynamic mode, which uses a sophisticated curve matching technique to compare the temperature rise with a known thermal curve to extrapolate the final temperature rise without waiting for it to develop. This technique significantly reduces the time required by one-half without substantially affecting the precision of the calorimeter. According to the manufacturer, the precision of the 6050 calorimeter can be taken as 0.2 %.

3. Results

Table II includes yields of liquid, gaseous, and char from the thermal pyrolysis process of HDPE waste plastic, as well as from the catalytic pyrolysis of the same type of waste plastic. It is observed that the thermal pyrolysis process (sample HDPE) yields a significantly higher amount of liquid product compared to the catalytic process (sample HDPE+Z). The obtained liquid from the pyrolysis of HDPE was wax, i.e., in a solid phase, at room temperature.

Table II. - HDPE pyrolysis products yield with and without using a catalyst (Zeolite).

	Yield (%wt)		
	Liquid	Gas	Char
HDPE	74.89	15.11	10
HDPE+Z	54.80	35.20	10

Table III collects the elemental composition values from both studied samples and for the reference fuel (HFO), together with density (at 15ºC) and HHV. PO obtained without a catalyst shows a %C similar to the reference fuel, while HDPE+Z has a significantly lower content. Regarding density, both POs show a remarkably lower density and higher HHV than the reference fuel, which enhances the quality of the fuel.

Table III. - Elemental composition and some properties of the reference fuel (HFO) and the POs obtained.

	HFO [15] % by mass		HDPE % by mass		HDPE+Z % by mass	
	%C	85.1	%C	85.5	%C	79.4
	%H	10.9	%H	13.1	%H	12.4
	%S	4.0	%S	0.09	%S	0.11
	%N	0.0	%N	0.22	%N	0.26
Density (kg/m^3)	970		770.4		778.7	
HHV (MJ/kg)	41.83		46.35		45.15	

The GC-MS results from POs obtained, with and without a catalyst, have been analysed and classified into the categories illustrated in Figure 2. The components are grouped according to paraffins, olefins, aromatic hydrocarbons, and non-hydrocarbons (mainly composed of oxygenates).

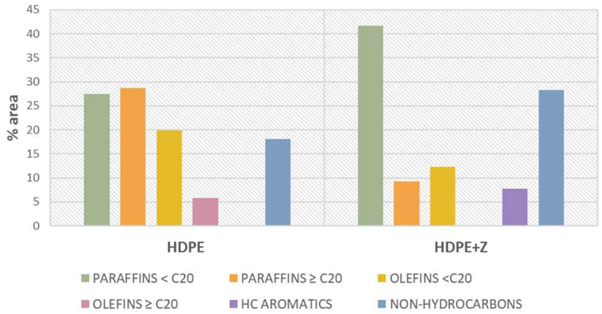

Fig.2. Liquid components distribution from thermal and catalytic pyrolysis of HDPE waste plastic.

Figure 2 shows that the sample obtained by catalytic pyrolysis (HDPE+Z) has more than 40% of paraffins (single bonds) < C20, and the presence of olefins (double and triple bonds) ≥ C20 is not detected. It can be observed that HDPE+Z contains 5% of aromatic hydrocarbons, of which 2.72% are polycyclic aromatic hydrocarbons that are harmful to human health [25].

On the other hand, the sample obtained by thermal pyrolysis (HDPE) has higher contents of heavy carbon chains (paraffins and olefins ≥ C20) and lower content of paraffins < C20. It is also interesting to highlight the absence of aromatics in the sample produced without catalyst and the lower content of non-hydrocarbons compounds.

According to the obtained results, it can be concluded that zeolite facilitates the cracking of carbon chains since there is no presence of double or triple bonds in the long carbon chains (olefins with $C \geq 20$) of the HDPE+Z sample. Furthermore, the percentage of short single-bond carbon chains (paraffins with $C < 20$) is significantly higher (42% for HDPE+Z and 27% for HDPE).

The results obtained also show that the HDPE sample does not contain metallic contaminants harmful to the turbine. Non-hydrocarbons different from oxygenates in this sample account for less than 1%, and they are composed of N_2, F, and Si. However, the HDPE+Z sample has more than 19% of N, Cl, Si, S, and Br compounds.

The absence of metallic contaminants and a significantly lower amount of S are advantages compared to heavy fuels, such as HFO. These fuels require pre-treatment to remove the effects of harmful components in the gas turbine. The metallic contaminants that concern this process are mainly sodium, potassium, calcium, lead, vanadium and magnesium. At elevated temperatures, vanadium, sodium, potassium, and lead are corrosive to turbine blades. These materials, together with the calcium, can be deposited, generating blockages and reducing the gas output. The degree of pre-treatment required, investment in the equipment, and the operating costs depend on the chemical and physical properties of the fuel [26].

4. Conclusions

In this paper, it was proven that a fast pyrolysis oil obtained from waste plastics could be a viable candidate to replace HFO as a fuel in gas turbine power plants. It was observed that the presence or not of a catalyst in the pyrolysis process influences the final properties of the PO obtained. However, both POs show advantages over the use of HFO, such as higher HHV and significantly lower density and percentage of sulphur.

The main conclusions according to the results obtained for both samples analysed are:

Regarding the sample obtained from thermal pyrolysis (HDPE):

- It does not contain aromatic hydrocarbons and, therefore, neither polycyclic aromatics, which are harmful to human health.
- Fast thermal pyrolysis yields a significantly greater amount of liquid product but with poorer quality (higher content of double and triple bonds and carbon chains $C \geq 20$, wax at room temperature). However, the properties of this product are closer to those of HFO.
- It does not contain heavy metals that damage the appropriate turbine operation. Altogether, non-hydrocarbons different from oxygenates account for less than 1%, and they contain N_2, F, and Si.
- Chlorinated components are not found.
- Elemental composition is more similar to HFO compared to the HDPE+Z sample.

Regarding the sample obtained from catalytic pyrolysis (HDPE+Z):

- The presence of heavy metals is detected. Non-hydrocarbons different from oxygenates account for more than 19%, and they contain N, Cl, Si, S, and Br.
- There are 2.72% of polycyclic aromatic hydrocarbons.
- The cracking of carbon chains is better (higher % of olefins and paraffins < C20), which emerges from the use of the catalyst.
- The %C of its elemental composition is significantly less than in HFO.

Based on the properties studied of the two analysed POs, it is recommended to use the PO obtained without a catalyst, that is, through fast thermal pyrolysis.

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