Catalytic pyrolysis of high-density polyethylene for the production of carbon nanomaterials: effect of pyrolysis temperature

Salma Belbessai, El-Hadi Benyoussef, and Nicolas Abatzoglou

***Abstract*−** **A two-stage reaction process is followed to convert high-density polyethylene (HDPE) into carbon nanofilaments (CNFs) and hydrogen-rich gas. The experiments are performed in a continuous mode in a two-stage quartz reactor: thermal pyrolysis of HDPE followed by the catalytic decomposition of the pyrolysis gases over a nickel catalyst prepared from mining residues. To examine the effect of the pyrolysis temperature on the yield and quality of the final products, two steps were followed. First, non-catalytic pyrolysis experiments were run at different temperatures (600, 650, and 700 °C), and the products were examined. Second, pyrolysis–catalysis experiments were performed at the same pyrolysis temperatures and a fixed catalytic temperature (600 °C) to examine the CNF and hydrogen yields. The results showed that the production of carbon nanomaterials (CNMs) and H_2 is optimal at 650 °C, with yields of 70.8 and 38.0 wt%, respectively. Scanning electron microscopy (SEM) revealed the presence of carbon filaments with different diameters and lengths at the three different temperatures. Moreover, thermogravimetric analysis (TGA) confirmed that the produced carbon is filamentous, with the presence of amorphous carbon at 700 °C.**

Keywords **− Carbon nanomaterial, pyrolysis, catalysis, high-density polyethylene, hydrogen.**

NOMENCLATURE

CNF	Carbon nanofilament
CNM	Carbon nanomaterial
CNT	Carbon nanotube
HDPE	High-density polyethylene
MWCNT	Multi-walled carbon nanotube
PET	Polyethylene terephthalate
SEM	Scanning electron microscopy
SLPM	Standard Liter Per Minute
TGA	Thermogravimetric analysis
UGSO	UpGraded slug oxides

I. INTRODUCTION

The continuous demand for plastic across the world has led to the accumulation of plastic waste. Of the different ways to treat plastic waste, the mechanical recycling of mixed plastics is very limited as it deals with pure single-polymer streams. Polyethylene terephthalate (PET) is the only plastic that can be mechanically recycled in closed-loop circulation [1]. In addition, the incineration of plastic waste is a practice that has several drawbacks; burning waste polymers releases greenhouse gases and hazardous chemicals into the environment [2]. On the other hand, thermal cracking, such as pyrolysis, is a promising alternative since it is more robust toward mixed and contaminated plastics. During pyrolysis, the waste polymers are thermally degraded, in the absence of oxygen, into liquids, gases, and solid residues.

One of the applications of pyrolysis is the production of carbon nanomaterials (CNMs), such as carbon nanotubes (CNTs) and carbon nanofilaments (CNFs). These materials are high-value products and can be used in several applications, acting as composite fillers, for example [3]. They can be synthesized in one- or two-step processes: in the former, pyrolysis and catalytic cracking occur in the same reactor, while in the latter, they take place in two separate reactors [4]. The second configuration is favoured as it avoids catalyst poisoning [5].

Both the pyrolysis and catalysis temperatures have an impact on CNM production. Liu et al. [6] investigated the effect of temperature during the conversion of polypropylene (PP) into multi-walled carbon nanotubes (MWCNTs), finding that the composition of the pyrolysis gas changed with the temperature. The concentrations of H_2, CH_4, and C_2H_4 increased with the temperature, and the concentrations of the C3 and C4 alkenes reached a maximum at 650 °C. The MWCNT yield followed the same trend of propylene and butylene. From 550 to 650 °C, the MWCNT yield increased because the overall amount of gas increased; however, when the temperature exceeded 650 °C, the alkenes decreased, leading to a decrease in the MWCNT yield. This is expected as unsaturated compounds produce more CNTs than methane. The effect of catalytic temperatures on the quality and quantity of CNMs has been widely studied in the reported literature; however, studies on the effect of the pyrolysis temperature are lacking.

This work aims to investigate the effect of the pyrolysis temperature on the yield of CNFs produced during the pyrolysis–catalysis of used high-density polyethylene (HDPE). The pyrolysis products formed at different temperatures were examined and compared. Thereafter, the same experiments were conducted in the presence of a catalyst in a two-stage reactor to compare the yields of the produced CNMs; the catalyst, Ni-UpGraded Slug Oxides (Ni-UGSO), is prepared

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from mining residues and has been proven to be efficient in CNF production [7].

II. MATERIALS AND METHODS

Used HDPE, with particle sizes varying from 3 mm to 1 cm, was obtained from KWI Solutions Polymers Inc. The plastic was used without further treatment. UGSO was provided by Rio Tinto Iron & Titanium, and the nickel nitrates were purchased from Sigma-Aldrich.

Ni-UGSO was prepared by incipient wetness impregnation. UGSO particles with sizes below 53 µm were mixed with nickel nitrates and droplets of water, with the Ni loading at 10 wt%. The mixture was dried for 3 h at 105 °C and subsequently calcined for 16 h at 900 °C. Finally, the particles were crushed and sieved to recover those smaller than 53 µm in size.

The pyrolysis and pyrolysis–catalysis experiments were performed in a two-stage fixed-bed quartz reactor. In the pyrolysis experiments, quartz wool was placed in the middle of the reactor to receive the waste plastic fed by a two-stage feeder at a rate of $0.33\ g\cdot min^{-1}$. The temperature in both stages was the same, and N_2 flowed through the reactor at a rate of 0.03 SLPM to clear out the pyrolysis gases. In the pyrolysis–catalysis experiments, the degradation of HDPE occurred in the first stage, followed by catalytic cracking in the second stage. For each experiment, 5 g of catalyst was dispersed in quartz wool positioned in the catalytic zone. Another piece of quartz wool was placed in the middle of the setup in the first stage for the pyrolysis reaction. In these experiments, the catalyst was activated with H_2 at a flow rate of 0.10 SLPM for 3 h at 600 °C. The duration of each reaction was 2 h, and condensable liquids were recovered in a cold trap immersed in an ice bath. The gas exiting this condenser passed through a charcoal column to retain all possible liquid hydrocarbons. Samples of the gas were taken every 10 minutes for gas chromatography (GC) analysis using a SCION 456-GC equipped with FID and TCD detectors.

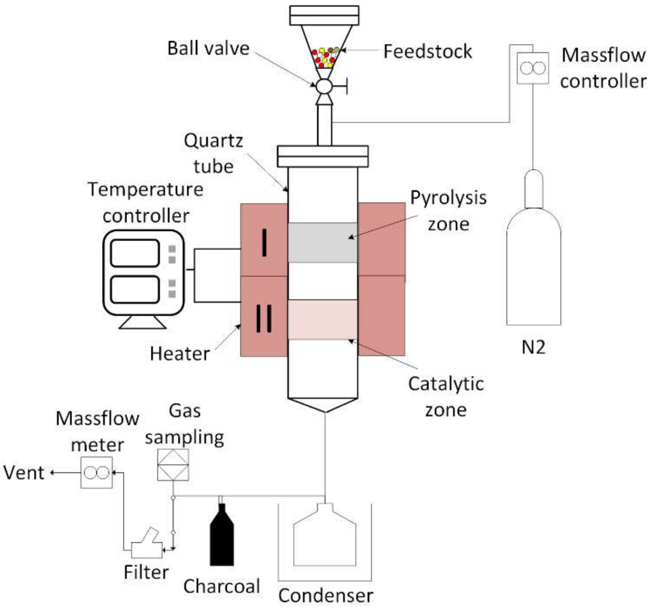

Fig. 1: Schematic diagram of the experimental setup

To examine the morphologies of the CNMs, scanning electron microscopy (SEM) micrographs were obtained using the Hitachi S-4700 field emission gun.

Thermogravimetric analysis (TGA) was used to quantify the amount of carbon deposited on the catalytic surface and detect the presence of amorphous carbon. The analysis was performed using a Setaram Setsys 24 analyzer under a stream of 20% O_2 and 80% Ar from room temperature to 1000 °C at a heating rate of $10\ °C\ min^{-1}$.

III. MATHS

The accumulated solids on the quartz wool and catalytic bed (catalyst on quartz wool) were weighed to estimate the yield of solid products, Y_{solid}, as given by Equation 1:

$$Y_{solid}(wt\%) = \frac{m_{solid}}{m_{plastic}} \times 100 \tag{1}$$

The cold trap and the adsorbent were also weighed to determine the yield of the liquids and wax, $Y_{liquids}$, as given by Equation 2:

$$Y_{liquids}(wt\%) = \frac{m_{liquids+wax}}{m_{plastic}} \times 100 \tag{2}$$

The gas yield, Y_{gas}, was determined according to Equation 3:

$$Y_{gas}(wt\%) = 100 - Y_{liquids} - Y_{solid} \tag{3}$$

The yield of filamentous carbon was determined as in Equation 4:

$$Y_{filamentous\ carbon}\,(wt\%) = \frac{m_{filamentous\ carbon}}{m_{carbon\ contained\ in\ the\ plastic}} \times 100 \tag{4}$$

The yield of hydrogen was determined as in Equation 5:

$$Y_{hydrogen}(wt\%) = \frac{m_{hydrogen} \times 2}{m_{hydrogen\ contained\ in\ the\ plastic}} \times 100 \tag{5}$$

IV. RESULTS AND DISCUSSION

A. *Effect of temperature on pyrolysis products*

Table I shows the product distribution for the pyrolysis experiments at different temperatures. As the pyrolysis temperature increases from 600 to 700 °C, the amount of pyrolysis gas increases significantly from 37.0 to 79.0 wt%, the liquid yield decreases significantly from 62.3 to 20.0 wt%, and the solid yield changes slightly. These results are similar to those obtained during the pyrolysis of polyethylene (PE) in a fixed-bed reactor [8]. The gaseous stream is mainly composed of H_2, CH_4, C_2H_4, and C_2H_6. Both H_2 and CH_4 have optimum yields – 25.8 and 51.3 vol%, respectively – at 650 °C, while C_2H_4 and C_2H_6 follow the opposite trend, with minimum yields at 650 °C. As the temperature increases from 600 to 650 °C, the production of light components increases, while increasing the temperature further to 700 °C leads to further cracking of the HDPE and the generation of more gaseous products.

Table. I

PRODUCT DISTRIBUTION AND GAS COMPOSITION FROM PYROLYSIS OF HDPE AT DIFFERENT TEMPERATURES

Temperature (°C)	600	650	700
Solid yield (wt%)	0.7	3.2	1.0
Gas yield (wt%)	37.0	58.3	79.0
Liquid yield (wt%)	62.3	38.5	20.0
Gas composition (vol%)			
H_2	11.2	25.8	16.77
CH_4	39.9	51.3	45.8
C_2H_4	36.7	19.2	30.9
C_2H_6	12.1	3.5	6.4

Fig. 2 shows the mass yields of the main products from the pyrolysis of HDPE at different temperatures. The liquid fraction mainly contains unsaturated C_7–C_9 and saturated C_{12} hydrocarbons. These components decrease with the temperature, which is expected as the liquid yield decreases from 62.3 to 20.0 wt%. The mass yield of C_2H_4 decreases from 39.5 to 20.6 wt% as the temperature increases from 600 to 650 °C, and it increases to 37.3 wt% as the temperature reaches 700 °C. The mass yields and volumetric compositions (Table I) of CH_4 and C_2H_4 follow the same trends.

HDPE decomposes following the random chain scission mechanism [9]. The process involves several steps, including initiation, propagation and/or free radical transfer, and termination. The monomer is produced during the propagation reactions, while hydrogen abstraction occurs in the free radical transfer reactions, resulting in the formation of one saturated and one unsaturated end and a new free radical [10]. When intramolecular hydrogen transfer is favoured, the process leads to an increase in the production of olefins, while intermolecular transfer increases the paraffins [11]. From Fig. 1, one can note that at 600 °C, the production of olefins is favoured, which decreases when the temperature is increased to 650 °C. This indicates that at 600 °C, intramolecular hydrogen transfer is dominant.

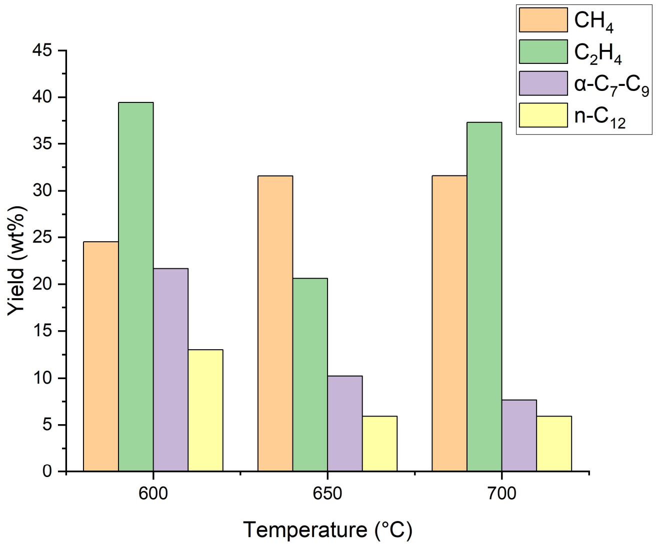

Fig. 2: Mass yields of the main products from the pyrolysis of HDPE at different temperatures.

B. *Pyrolysis–catalysis of used HDPE*

Table II presents the results of the pyrolysis–catalysis of used HDPE using Ni-UGSO at different temperatures. The total yield of filamentous carbon varies between 40 and 71 wt%, with the maximum production at 650 °C. The yields of filamentous carbon and H_2 at this temperature are 70.8 and 38.0 wt%, respectively. Consequently, the rate of production of the former at this temperature is at its optimum (2.4 $g_C \cdot g_{cat}^{-1} \cdot h^{-1}$). Additionally, the amount of liquid residue is the lowest at 650 °C, with a yield of 9.5 wt%, whereas the gas yield at this temperature is similar to that at 700 °C. This indicates that the filamentous carbon is produced from the catalytic decomposition of mostly liquid hydrocarbons, such as α-C_7-C_9 and n-C_{12}. The gaseous stream is mainly composed of H_2.

One would expect greater production of filamentous carbon at 600 °C because of the large presence of unsaturated hydrocarbons, as explained in Section IV.A. However, the results reveal that the optimum production occurs at 650 °C. The growth of CNMs depends on several parameters, such as the pyrolysis and catalytic temperatures, metal particle size, and type of feedstock. All these factors influence the process interdependently [5].

Table. II

CNM AND H_2 YIELDS FROM PYROLYSIS–CATALYSIS OF HDPE USING NI-UGSO AT 600, 650, AND 700 °C AND A FIXED CATALYSIS TEMPERATURE (600 °C)

Temperature (°C)	600	650	700
Solid yield (wt%)	37.3	59.6	46.5
Gas yield (wt%)	43.5	30.9	33.9
Liquid yield (wt%)	19.2	9.5	19.6
Filamentous carbon production rate ($g_C \cdot g_{cat}^{-1} \cdot h^{-1}$)	1.5	2.4	1.8
Total filamentous carbon yield (wt%)	44.1	70.8	55.1
Total H_2 yield (wt%)	27.2	38.0	32.5
Gas composition (vol%)			
H_2	57.2	73.5	65.5
CH_4	39.2	22.4	24.1
C_2H_4	9.1	5.5	4.3
C_2H_6	2.8	1.8	5.7

SEM images of Ni-UGSO after the reaction at the different pyrolysis temperatures are shown in Fig. 3. The produced carbon is crystalline and in the form of filaments of different diameters and lengths. At 600 °C, more filaments with larger diameters are present. Crystals of the catalyst are also visible, indicating that the form of CNF does not considerably affect the access of the reactants to the surface of the catalyst. The metal particles are located at the top of the nanofilament.

Fig. 4 shows the derivative plots of the TGA of the spent Ni-UGSO at the different pyrolysis temperatures. At 600 and 650 °C, the weight loss occurs at 615 °C, and only one peak is present in each plot. On the other hand, the plot at 700 °C presents two peaks, one at 590 and the other at 650 °C. The higher the crystallinity of the carbon, the higher the oxidation temperature [4]. This indicates that the carbon produced at 600 and 650 °C is mostly crystalline, while that produced at 700 °C is a mixture of filamentous and amorphous carbon.

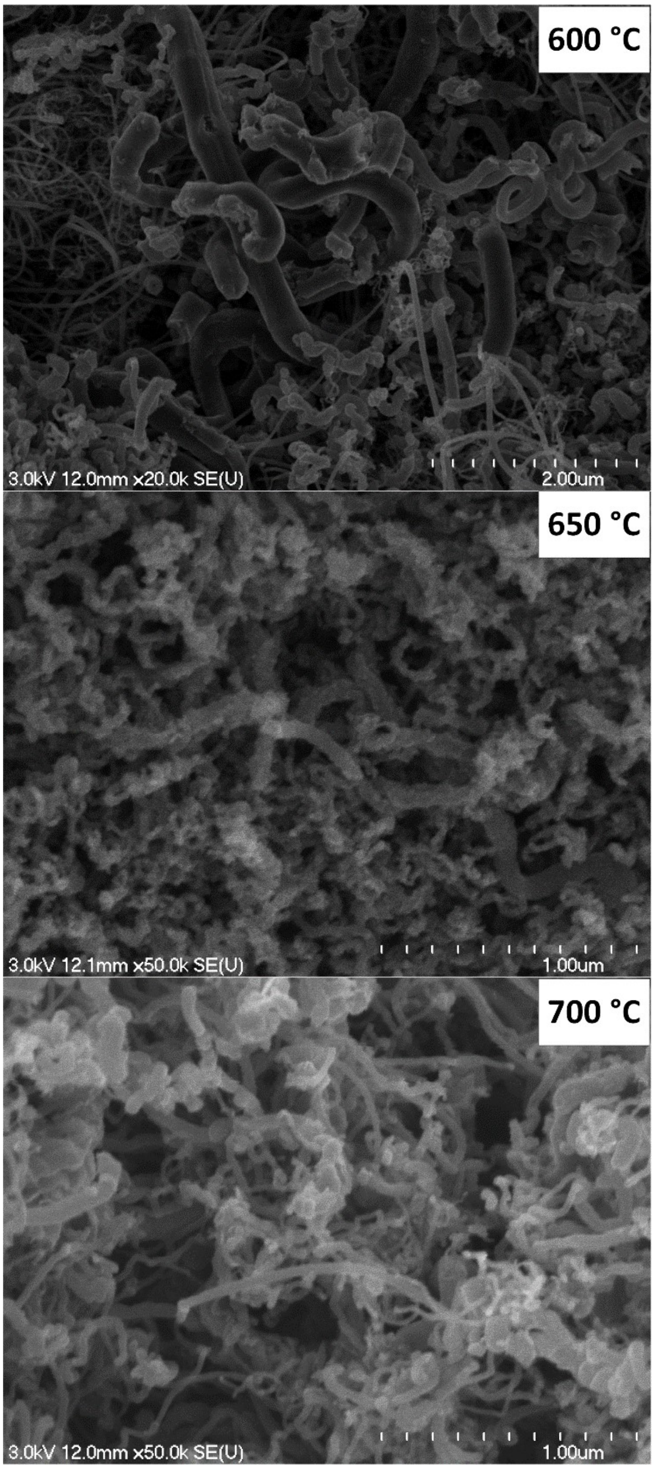

Fig. 3: SEM images of the carbon produced at different pyrolysis temperatures.

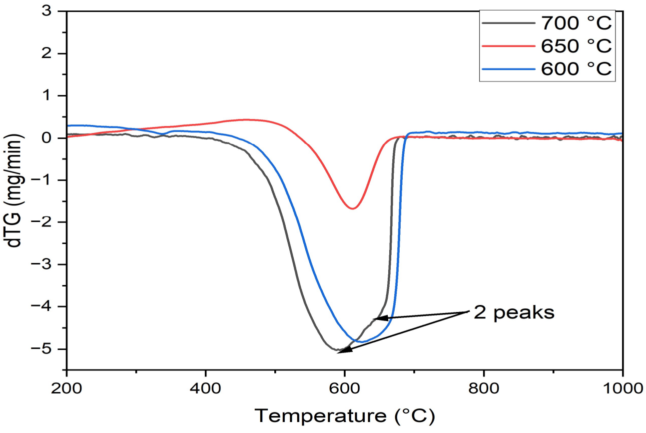

Fig. 4: Derivative plots of the TGA of spent Ni-UGSO at different temperatures.

V. CONCLUSION

The pyrolysis temperature affects the quantity and composition of the pyrolysis products and the yield of CNMs. The optimum production of CNMs and H_2, with yields of 70.8 and 38.0 wt%, respectively, occurs at 650 °C. The liquid yield is the lowest at this temperature, which indicates that the long-chain hydrocarbons are further cracked in the presence of Ni-UGSO to form filamentous carbon.

TGA revealed that the carbon produced at 600 and 650 °C is mostly filamentous, while there is an indication of the presence of amorphous carbon at 700 °C. This indicates that the pyrolysis temperature also affects the quality of the carbon produced.

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