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Recovering of Carbon from Plastic Waste in Overheated Vapor Environment and its Structure/property investigation

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Abstract **-** The novel two stage method of recovering nanoscale carbon in overheated vapor environment from plastic (PET) waste that includes low-temperature pyrolysis of waste at the initial stage and following high temperature (up to 900 ^{0}C) thermal/chemical treatment in vapor environment was developed. The investigation showed that application of low temperature pyrolysis before second stage treatment in control environment (CO2 & Argon) allows essentially to reduce loses of char before second stage processing and increases output of nanoscale carbon after high temperature treatment in overheated water vapor environment. The vapor treatment at low temperatures (up to 700^{0}C) activates the pyrolysis process and increases the primary reactions of hydrocarbon decomposition. Accordingly, the release of gases increases and the main part of which during the pyrolysis process is extracted as a liquid fraction - pyrolytic oil and reminder amorphous coal containing different organic/inorganic impurities. After increasing of the temperature above 700^{0}C with simultaneously feeding of vapor, the overheated water vapor increases the rates of side reactions and full decomposition pyrolytic reminders takes place. As a result, the loosening of the formed carbon aggregates occurs and formation of the highly dispersed, nanoscale carbons with essentially increased surface area there takes place. As investigation showed (including SEM observation) the characteristics of obtained nanoscale carbon changes in wide range depending from processing conditions (vapor temperature, vapor feeding rate, processing period etc.) and may reach to 1000 m^2/g (BET surface area) and 98.7% (purity) respectively.

Keywords**:** Carbon; nanoscale; Plastic Waste; Recovering; Pyrolysis, Structure; Surface

1. Introduction

Plastic waste materials generated in different sectors of the economy are growing rapidly and are either recycled, combusted (waste incineration) or disposed of [1]. The main portion of plastic waste are polyethylene and polypropylene [2].

The increase of world population and subsequent living standards have caused a rapid increase in municipal solid waste generation of to up to 1.3 billion tons per annum [3]. Plastic waste is the third largest contributor of municipal solid waste [4]. Currently, the volume of plastic production is growing by 5-6% on average every year. The widespread use of polymers is due to its properties: durability, versatility, economy, ease of use and low cost of production. Over the past 60 years, consumer plastic consumption has increased approximately 20-fold. Globally, annual consumption of bottled water alone has reached 500 billion units per/year. The most plastic waste is not biodegradable, is not subject to decay and corrosion, practically does not break down over time, and when burned, extremely toxic substances are released that cannot be removed from the body. Therefore, the recycling of plastic waste is a very urgent problem nowadays. In addition, the problem of plastic waste recycling becomes relevant not only from the point of view of environmental protection, but also due to the fact that in the conditions of shortage of polymer raw materials, plastic waste becomes a powerful raw material and energy resource.

The interest in thermomechanical conversion of plastic wastes, particularly pyrolysis has increased considerably over the last few years primarily since China stopped accepting post-consumer plastic waste in 2018, after having taken up to 45% of the world plastic waste for recycling, landfilling and incineration [5-8]. The perspective of one of the most convenient and promising methods of plastic recycling - pyrolysis is correct, both in terms of environmental safety (does

not pollute the environment with combustion gases) and obtaining useful products. The peculiarity of the process is the lack of oxygen for all combustion components. The production of pyrolysis products is influenced by various factors. Temperature is the dominant factor affecting the distribution of gas, liquid and solid phase pyrolysis products and its physical and chemical properties. Additional important factors include: heating rate, particle size, feedstock composition, pyrolysis time, atmospheric pressure, and catalyst presence [11-16].

Today existing methods of pyrolysis (slow, fast or flash pyrolysis), cannot provide high-quality, highly dispersed carbon black (CB) and activated carbon. The methods are based on short vapor residence time in the hot zone and mainly focused towards of obtaining gas and liquid (oil & wax) reminder products [17,18]. It is obtained mainly from petroleum products, which is connected with great economic and ecological problems: a large amount of released CO_2, intensively reduced reserves of oils and etc. Therefore, it is very important to find alternative methods of obtaining and production of activated carbon with improved properties, which will eliminate environmental problems and reduces product cost too.

In presented paper an ecologically safe and economically profitable method of obtaining highly dispersed, activated carbon from polymer waste are considered. The offered 2 stage method with low-temperature pyrolysis of the waste at the first stage and second – high temperature thermo-chemical treatment in overheated water vapor environment contributes to a nanostructured, activated carbon free from negative organic and inorganic impurities.

In contrast to existing results in current investigation all attention was focused forward to obtain high quality nanoscale carbon with significant output and high purity. To achieve this result and to improve heat/mass transfer during the pyrolysis process in experiments were applied continues vapor feeding method for whole high temperature pyrolysis processing and as a result increasing the vapor residence time in the hot zone (in reactor).

2. Materials and Methods

To achieve good heat/mass transfer during the pyrolysis process the shredded and crushed plastic waste (plastic bottles- polyethylene terephthalate - PET), which is a polymer complex ether with chemical formula (C10H8O4) was used in experiments. A high volatile matter content along with a high carbon and hydrogen content makes PET an excellent candidate for the pyrolysis process, leading to a high conversion to the solid carbon and liquid/gas product. The proximate and ultimate data of PET according to [19] are presented in table 1 & 2.

Table 1: Ultimate analysis of PET plastic waste.

Plastic type	Carbon	Hydrogen	Oxygen	Nitrogen	Sulfur
PET	77	13	5	0.20	N/A

Table 2: Proximate analysis of PET plastic waste.

Plastic type	Moisture Content	Fixed Carbon	Volatile Matters	Ash Content	HHV (MJ/kg
PET	0.5	7.8	91.8	0.1	30.2

At first stage the bottles are washed with water to remove contents and inorganic mineral components (dust, soil, sand, etc.). After washing, the bottles are cut, air-dried and melted in a metal pot (heated to 300-330°C). For quick solidification the molten mass was poured into water. After cooling to room temperature and crushing the obtained pieces were put in a drying box at 120-140°C.

The physical and chemical characteristics of the obtained nanostructured, activated carbon: dispersion, specific surface area, porosity, purity and yield are limited by international standards: ASTM B822-20 (for dispersion), ASTM E1131-20 (for yield and purity reminder carbon) and ASTM D6556 to determine specific surface area and porosity.

The plastic waste after drying is loaded into a modified reactor working in water vapor environment developed by TIMMS for recycling plastic waste (Fig. 1).

The prepared sample is heated to 350-550°C (heating rate 200/min) for 35-40 minutes. At 450°C, the pyrolysis process begins, which continues up to a temperature of 550-580°C. At this time, the primary reactions of decomposition of the polymer chain are taking place. Accordingly, gases and volatile products are released. In the relatively cold part of the reactor, condensation of volatile products of pyrolysis takes place, and the separated gas leaves the reactor through a gas pipe. A dry residue of -14.2% remains in the reactor, which contains various types of organic and inorganic pyrolytic residues. After the end of pyrolysis, instead of argon, we supply 700-800 ml of water to the reaction zone (speed is 4 ml/min) and increase the temperature to 700-900°C. Activation with water vapor lasts 3-3.5 hours.

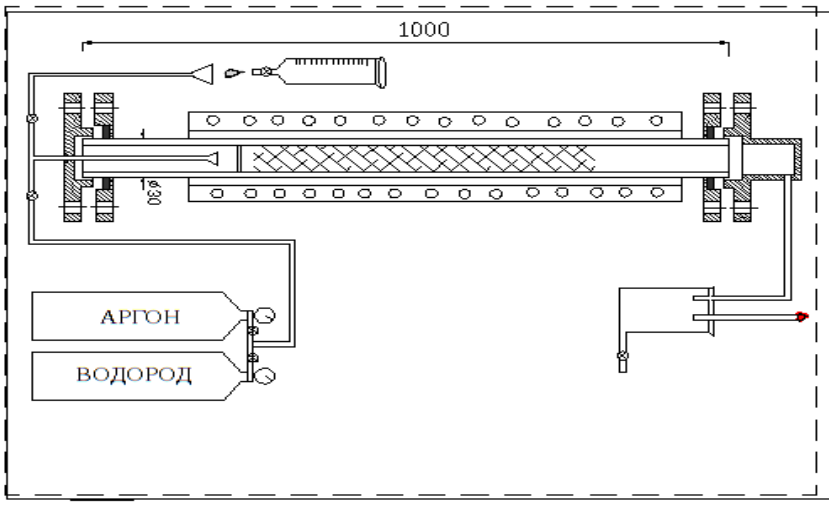


Fig. 1: A horizontal cylindrical reactor for recycling plastic waste working in water vapor environment.

3. Results & Discussion

The preliminary experiments showed that direct feeding of vapor to reactor to high temperature plastic scrap at 800-950^{0}C leads to intensive decomposition of plastics and its oxidation to CO2 resulting only in extraction of oil and gas. No significant reminders of solid residues there were not observed after processing. In order to prevent mentioned and to maintain solid residues of carbon the experiments were performed in 2 stages as it's described above, that gave possibility to maintain the solid residue of carbon and investigate its structure/property relationship. The purity, structure/properties and yield of the obtained reminder carbon depends on value of the temperature and duration of processing.

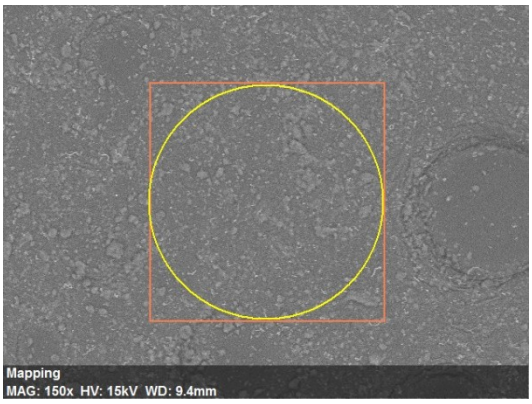
Figure 2 and 3 represents the structures (including TEM investigation) and results of spectral analysis of obtained carbon after 277 min processing at 850^{0}C.

As it's seen from SEM and TEM investigations (Fig. 2 & 3) reminder solid yield contains mainly carbon in amount 98.2 at% (Fig. 2a & 2c) Additionally in reminder may be observed another minor inclusion of Si, Fe, Al, Ca, S, that may be considered as a technological additives and impurities from CB (Fig. 2b & 2d) appeared in plastics after processing. The observation of TEM pictures (Fig. 3) allows to fix that the sizes of reminder carbon particles are below of 50nm.

In order to optimize the process and to determine the optimal heating rate of the reactor the method of thermogravimetric analysis was applied. Thermogravimetric analysis of the initial raw material (pre-prepared plastic waste) was carried out for different heating rates at 100/min and 200/min. It was established that the temperature of destruction of plastic waste does not depend on the heating rate and in all cases, it is equal to 450°C in. The duration of the process and the yield of dry residue changes according to the change of the heating rate. when heating rate is 100/min, the pyrolysis process lasts for 60–65 min, while when at 200/min, the pyrolysis process is completed within 30–35 min and an increasing in the yield of dry residue is observed too. Based on mentioned the heating rate of 200/min was selected in further experiments, which is economically beneficial (reduces process duration and energy consumption) too.

Spectrum: Point

Element	AN	Series	norm. C [wt.%]	Atom. C [at.%]
Carbon	6	K-series	95.54	98.20
Silicon	14	K-series	2.91	1.28



a) b)

Fig. 2: The stracture (SEM investigation) of reminder carbon after 2 stage (277 min) pyrolysis processing at 850^{0}C with continues feeding of steam during the all processing (Amount of water 2L). 1st Zone at 650^{0}C - 40 min (no water, heating period 19 min). 2nd Zone processing in Reactor at 850^{0}C with water vapor – 210 min. The heating up to 850ºC - 8 min; Starting plastic scrap 1900 gr. Reminder: Carbon 350 gr (18.5%). Oil – 1.5L.

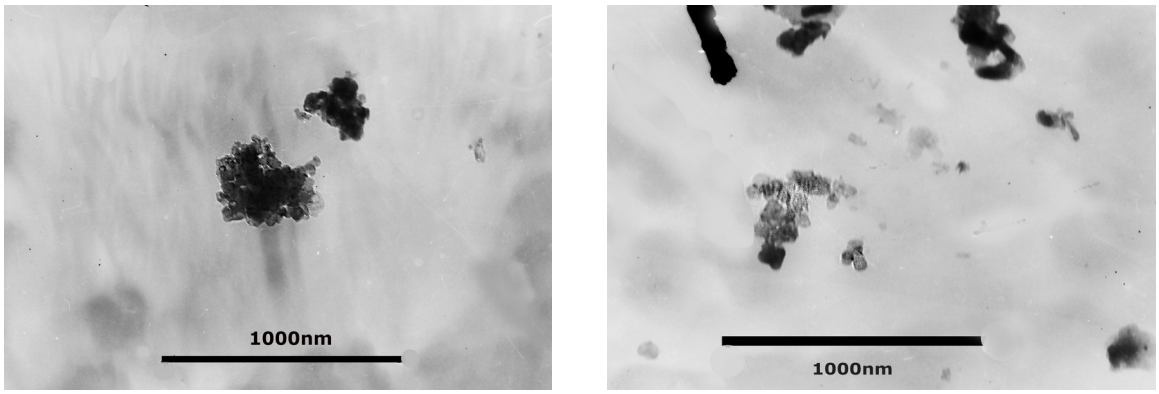
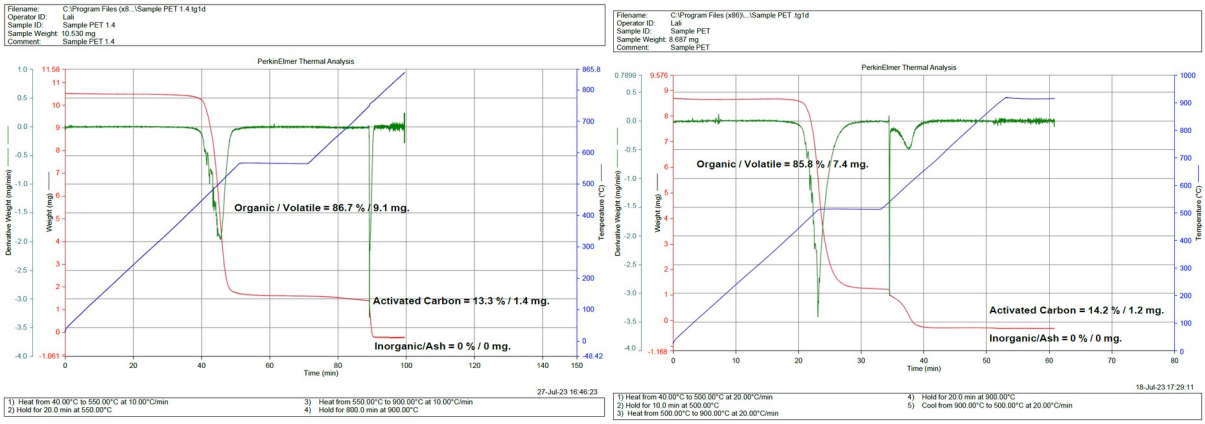


Fig. 3: The fine stracture (TEM investigation) of reminder carbon after 2 stage (277 min) pyrolysis processing at 850^{0}C with continues feeding of steam during the all processing (Amount of water 2L). As it's seen from TEM pictures the obtained reminder conglomerated carbon is nanoscale. Within the may be observed different dimension nano nano particles(grains) even less then 40-50 nm.

The overheated water vapor at 700-800^{0}C starts the activation of the received dry residue (coal). Increases the rates of side reactions (polymerization, polycondensation, cyclization) and completely destroys pyrolysis residues. At 800-900^{0}C, the obtained carbon products are oxidized to gasification. This results in the formation of free carbon atoms in the gas, which begin to solidify in the vapor area to form highly dispersed, activated carbon "aggregates" that are jet milled/processed into high-quality, nanostructured carbon (activated carbon).

The figure 4 represents the results of Thermogravimetric Analysis (TGA) of plastic waste for different rates of heating.



a) b)

Fig. 4: The TGA analysis of plastic waste for different rate of heating. a) Heating rate 10^0/min, the yield of pyrolysis carbon (PC) = 13.3%; b) Heating rate 20^0/min, the yield of pyrolysis carbon (PC) = 14.2%.

As it was established with increasing of period of pyrolysis at 900^0C from 180 to 210 min, the surface characteristics and porosity changes too from 826 m^2/g & 627 m^2/g to 920 m^2/g & 603 m^2/g correspondently. So, the period of treatment has positive role for surface improvement and increases it, when, the reduction of porosity in reminder carbon was observed.

The figure 5 represents the results of measuring the specific surface area and porosity of the obtained AC depending on processing condition.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Gemini VII 5.03 Gemini VII Version 5.03 Serial # 1029 Unit 1 Page 1 of 9
Sample: 2022 11 02 Plastic =Gemini
Operator: Maguli
File: C:\Gemini VII\data\2022 11 02 Plastic =Gemini.SMP
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Completed: 2022-12-14 3:40:13 PM
Report time: 2022-12-14 3:40:13 PM
Sample mass: 0.4110 g
Free space type: Measured
Evac. rate: 30.0 mmHg/min
Analysis adsorptive: N2
Equilibration time: 5 s
Sat. pressure: 720.240 mmHg
Free space diff.: 1.0427 cm³
Sample density: 1.000 g/cm³
Gemini model: 2390 p
Comments: 2022 11 02 Plastic =Gemini
Summary Report
Surface Area
BET Surface Area: 825.8902 m²/g
t-Plot Micropore Area: 627.2290 m²/g
t-Plot external surface area: 198.6612 m²/g
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Gemini VII 5.03 Gemini VII Version 5.03 Serial # 1029 Unit 1 Page 1 of 9
Sample: 2022 11 29 Plastic =Gemini
Operator: Maguli
File: C:\Gemini VII\data\Archili#1.SMP
Started: 2022-12-06 2:30:26 PM
Completed: 2022-12-06 5:26:04 PM
Report time: 2022-12-06 5:26:04 PM
Sample mass: 0.5453 g
Free space type: Measured
Evac. rate: 30.0 mmHg/min
Analysis adsorptive: N2
Equilibration time: 5 s
Sat. pressure: 727.752 mmHg
Free space diff.: 1.3328 cm³
Sample density: 1.000 g/cm³
Gemini model: 2390 p
Comments: 2022 11 29 Plastic =Gemini
Summary Report
Surface Area
BET Surface Area: 916.6815 m²/g
t-Plot Micropore Area: 602.6816 m²/g
t-Plot external surface area: 313.9999 m²/g

a) b)

Fig. 5: The data of measuring the specific surface area and porosity of the obtained carbon after the high temperature (900^0C) pyrolysis of plastics in overheated vapor environment depending on processing condition. a) Processing time 180 min, water feeding rate 4 ml/min; b) Processing time 210 min, water feeding rate 4 ml/min.

It was determined and confirmed that the received activated carbon (AC) is ash-free from organic and inorganic pyrolytic residues and the content of amorphous carbon in residue is up to 98.5% (Fig. 6).

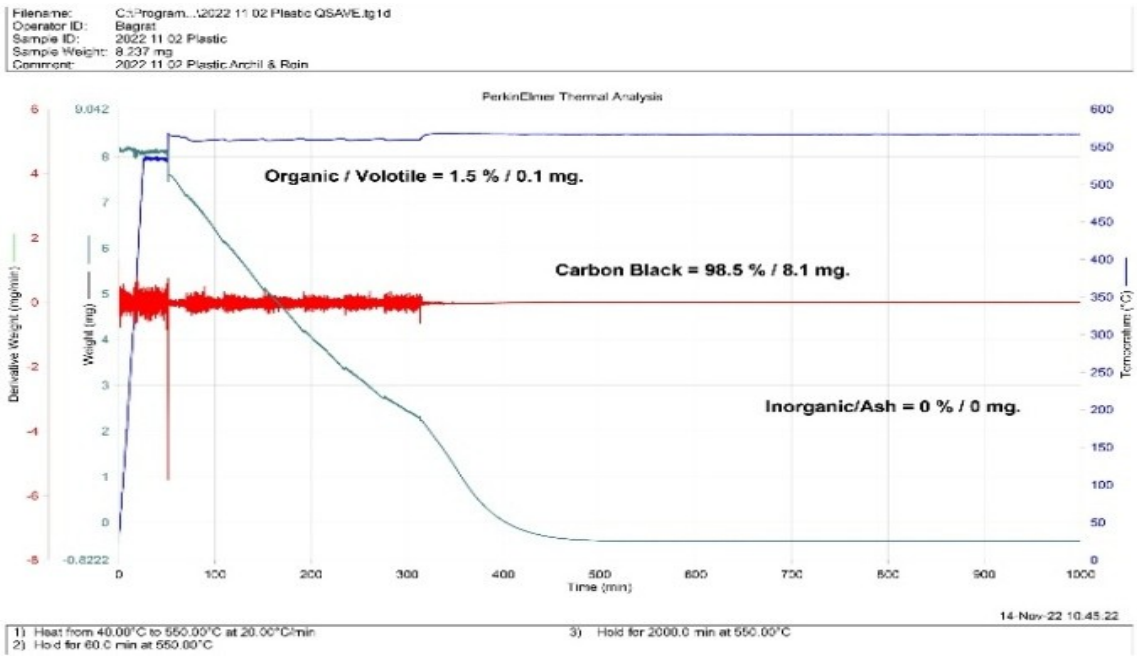

Fig. 6: Results of measuring the purity (organic and inorganic pyrolytic residues - 0%) and yield (98.5%) of the obtained AC.

4. Concluding remarks

The economically profitable and safe 2 stage combined method of thermal treatment of polymer waste was developed. The developed method provides for low-temperature pyrolysis of waste at the initial stage and then at second stage - thermo-chemical treatment high-temperatures, in overheated water vapor environment. The method helps to obtain nanostructured, activated carbon free of unwanted organic and inorganic impurities.

A modified reactor working in water vapor environment was developed and manufactured. Mandatory operating parameters were defined for process optimization: destruction temperature (450°C) and heating rate (200/min). Under these conditions, the pyrolysis process is completed in 30-35 minutes and an increase in the yield of dry residue is observed. which indicates that the process is economically profitable.

The mass fractions of the products released as a result of pyrolysis were determined:

1. Pyrolytic carbon – 22.4%;
2. Volatile solids (white sublimated mass, that mainly consists of benzoic and terephthalate acids) - 16.7%;
3. Gas (main products CO2, CO, H2O steam) – 60.9%.

It was established that pyrolytic carbon with overheated water vapor activation increases both: the purity and yield of the resulting activated carbon. Thus, presented combined method of high temperature pyrolysis in overheated steam environment provides to obtain an impurity-free, nanostructured, activated carbon where the content of amorphous carbon is 98.5% (Fig. 4); Specific surface area - 825 - 920 m^2/g and micropore area - 603 - 627 m^2/g (Fig. 5).

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