Catalytic thermochemical cracking of polyethylene over nanocomposite bentonite clay

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Abstract. Catalytic thermochemical cracking of polyethylene has been investigated in presence of a series of bentonite clay based nanocomposite with a view toward assessing their suitability in a process for converting plastic waste to fuel. Metal oxides such as manganese oxide (MnO), titanium oxide (TiO₂) and zinc oxide (ZnO) were impregnated with sodium montmorillonite bentonite. The clay catalysts were characterized by x-ray diffraction (XRD), scan electron microscope (SEM), transmission electron microscope (TEM) and energy dispersive x-ray (EDX) spectrometers. The effect of different catalysts on the composition and the yield of gaseous was evaluated. ZnO nanocomposite bentonite clay achieved the highest methane gas formation around 93%. The superior catalytic performance of nanocomposites is probably attributed to their uniform dispersed of oxides particles on montmorillonite support.

1. Introduction
Disposal of plastic wastes are the major issues and challenges associated with the generation of large quantity of plastic waste. Conventional solutions like recycling, landfilling and plasma gasification have inherent challenges which have been listed out in various literature sources [1-8]. Two of the prominent issues are: i) release of toxic emissions such as, carbon monoxide, chlorine, hydrochloric acid, dioxin, furans, benzene, 1,3-butadiene, etc. from its combustion, and ii) leaching of additives like lead, cadmium and di(2-ethylhexyl)phthalate (DEHP) in the ground when this plastic is disposed in
Therefore, there is a strong need in the further Research & Development of advanced waste to energy conversion technologies for effective management of plastic waste.

Earliest references of plastic degradation using thermal conditioning date back to middle of twentieth century. Jellinek [10] performed the thermal degradation of polystyrene and polyethylene in vacuum in the temperature range of 340-400°C. An advanced plastic pyrolysis process had been developed by Western Research Institute [11]. Recently, Kalargaris et al. [12] published a performance analysis of various blends of plastic pyrolysis oil and diesel in a diesel engine and the result was found to be promising. Some of the factors that influence the product distribution in plastic pyrolysis include temperature, type of reactor, pressure, residence time and catalysts [13, 14]. A variety of pyrolysis studies have been conducted on industrial wastes such as tyres and plastics, and several reviews have reported on the characterization of the development of pyrolysis technologies in terms of different aspects, for example, reactor development and product characterization [15-18]; conditions for oil production, oil characteristics and upgrading [19]; the heating rate and other governing variables affecting pyrolysis process and pyrolysis products of tyres and the mechanism investigation or kinetics modeling of the pyrolysis process [19, 20]. The thermo gravimetric analysis (TGA) for polyethylene terephthalate (PET) plastic have shown that the thermal degradation starts at 400°C and no significant change is observed beyond 470°C [21]. Similarly, for high density polyethylene (HDPE) the thermal degradation is reported to start in the range of 378-404°C and it completes at 517–539°C [22]. Poly vinyl chloride (PVC) is found to have a weight loss in two different temperature ranges; i) 260-385°C wherein ~62% weight loss has been reported and ii) 385-520°C wherein ~22% of weight loss occurred [21]. Furthermore, the temperature also affects the product distribution. For maximizing the liquid production, a temperature range of 300-500 °C is recommended. The higher temperatures are found to maximize the char and gas yield [13].

Gasification of plastics was reported first in 1970’s [23]. Borgianni et al. [24] performed gasification of wastes containing PVC using a two-stage reactor with sodium carbonate as an additive for elimination of chlorine gas from the producer gas. Air gasification for polypropylene waste has been demonstrated by Xiao et al. [25] in a fluidized bed reactor and inferred that the equivalence ratio had a major effect on producer gas quality and quantity. They reported a gas yield of 3.9 Nm$^3$/kg, with a tar content of 250 mg/Nm$^3$. One of the greatest challenges encountered in the plastic gasification is to control the syngas quality in terms of tar content and calorific value with changing feed [26].

Catalysts placed in contact with the feedstock inside the pyrolysis unit can not only improve conversion of plastics but also adjust the distribution of volatilized products. Catalysts can also be used downstream of the primary reactor for reformation and upgrading of pyrolysis vapors especially Lewis acid catalysts. Heterogeneous catalysts such as nanocrystalline zeolites, conventional acid solid, mesostructured catalyst, metal supported on carbon and basic oxides have been used for conversion of plastic [27]. The zeolite HZSM-5 has been found to increase the gaseous product yield to 63.5 % during the pyrolysis of HDPE [28]. Aguado et al. [27] had studied the effect of zeolite catalyst in a sequential two step reaction process; i) the plastic was thermally cracked in the batch reactor and ii) the vapors generated were catalytically decomposed in a fixed bed. A considerable rise in gaseous fraction up to the extent of 74.3 wt.% was observed. The effect of catalysts in different contact modes namely liquid phase and vapor phase were performed [29]. The silica-alumina catalyst in liquid phase led to higher liquid yield and the catalyst in gaseous phase assisted the decomposition of higher hydrocarbons thus increasing the gaseous yield fraction.

Clays have been used as acidic catalysts in petroleum cracking and several other organic reactions. To enhance performance, research is now focused on the synthesis of Pillared clays (PILCs), which possess larger two-dimensional pores [30]. Pillaring is achieved by the insertion of voluminous inorganic metal hydroxyl cation between layers of the clay in order to keep them apart. On thermal treatment, the metal hydroxyl cations are transformed into pillars which are responsible for the acidity [30-32]. The surface of the pillars possesses both Lewis and Bronsted acid sites [32-34]. However, the use to catalysts often makes these processes economically unviable. An important research gap can be
found in the development of catalysts which are economical, available in bulk and easy to regenerate [35].

There are large deposits of bentonite clay minerals across the parts of the country. These minerals are not yet exploited for commercial purposes. The unique physicochemical properties of sodium montmorillonite clays are the result of their extremely small crystal size, variation of internal chemical composition, structural characteristics caused by chemical factors, large cation exchange capacity, large chemically active surface area, variation in types of exchangeable ions and surface charge, and interactions with inorganic and organic liquids. Clay minerals have a very strong swelling and adsorption capacity, which is particularly interesting for the impregnation of catalytically active noble metals in the inter-lamellar space of clay. Several methods were reported in the literature [36-40] for the preparation of nanoparticle/clay (especially SiO₂-based clays) composites. The impregnation of preformed nanoparticles into a clay matrix can offer a new and facile procedure for nanometal/clay composite fabrication where the size and morphology of the nanoparticles are better controlled by separate and mostly standard preparation steps.

There are several methods to prepare nano-sized materials. These materials may be used directly or in the form of supported nanoparticles on solids such as oxides, carbon or zeolites. Some usual methods for nano-catalysts preparation are impregnation, precipitation, chemical vapor deposition, and electrochemical deposition. Precipitation and impregnation methods are simple, cheap, and well-studied but it is difficult to control the size of the particles. Chemical vapor deposition is widely used in the electronics industries but it is an expensive method. Electrochemical deposition is an inexpensive method that does not need high temperature and concentration. This method would allow a good control on size and chemical properties of the deposited nanomaterials but usually forms one dimensional nanomaterials [41-43]. In most research, impregnation and precipitation methods have been used as catalysts for biomass conversion. Meanwhile, nanoparticles properties usually adjust by changing synthesis parameters such as pH of the solution, concentration, the reducing agent, and calcination temperature [44].

Various catalysts and adsorbents have been studied for upgrading the quality and debromination of the pyrolysis oil from brominated flame retarded (BFR) plastics [45, 46]. Among them, sodium montemornilite and others modified alumina and clay minerals [47, 48], fluid catalytic cracking (FCC) catalysts [47], metallic oxides [49, 50], and minerals [51] have attracted more concerns. In particular, clay metals oxides-based catalysts such as manganese oxides have shown good performances on the reduction of the amount of bromine in the pyrolysis oil [46, 48]. Meanwhile, clay composites catalysts can be used in the pyrolysis of other types of waste plastics, for example, municipal solid waste (MSW) polyalkene plastics high density polyethylene and polypropylene to improve the quality of the oils [47, 52-56]. The use of different types of clay as catalysts allows a narrower range of hydrocarbons to be produced [56].

2. Experimental

2.1. Samples preparation

Waste plastics were obtained from the cap of used disposable water bottles. These were flushed and cleaned with water, cut and grinded into small portions. High density polyethylene (HDPE B1054) was purchased from Saudi Basic Industries Corporation, SABIC, Saudi Arabia. All chemicals which used for nano-oxide metals were purchased from Loba Cheme (India) and were used without purification. The manganese oxide (MnO) nanoparticles was prepared using co-precipitation method. Two different anions, manganese (II) sulphate and manganese oxalate slats, were used for the preparation. Same quantity of both slats with 0.2M concentration are mixed together with continuous stirring (about 1 hour) at a constant temperature of 60°C. While stirring, NaOH solution was added to the solution till the pH of the mixture becomes 12. So that, brown precipitates were formed then the mixture was filtered and washed with ethanol. Precipitates were dried for overnight at 100°C and then kept in muffle furnace at 500°C for 4 hours [57].
Nanoparticle of titanium oxide (TiO$_2$) powder was prepared by physical grinding. A quantity of 100 g TiO$_2$ powder was put in a grinding machine which having high speed rotator. It was uniformly ground and crushed well for 15 min with utmost precaution to avoid any contamination. At the end, the finely grinded powder was separated to get nano-size powder TiO$_2$ which was packed in plastic pouches and stored in normal room temperature until use [58]. Zinc oxide (ZnO) nanoparticles were prepared using sol-gel method. In a typical procedure 12.6 g of zinc acetate dehydrate was added to 400 ml of double distilled water. The mixture is stirring continuous to dissolve zinc acetate completely. Then the solution was heated to 50°C and 600 ml of absolute alcohol was added slowly with stirring. After this, 6 ml of H$_2$O$_2$ (47%) was dropped to the mixture carefully and mixed it using a magnetic stirrer to get an almost clear solution. This solution was incubated for 24 hours and then was dried at 80°C for several hours to obtain white zinc oxide nanoparticles. Zinc oxide nanoparticles was washed several times with double distilled water to remove the byproducts. After washing, the ZnO nanoparticles were dried at 80°C in hot air oven to obtain a complete conversion of zinc [59].

Bentonite powder was purchased from M-I SWACO, Egypt and its nanoparticles was prepared by physical grinding. TiO$_2$-bentonite, MnO-bentonite, and ZnO-bentonite nano-composites were prepared by simple impregnation method as shown in figure 1. One gram of bentonite nanoparticles was dispersed in 250 ml of water then 0.5 g of each metal oxide was added to prepare the desired composite. The TiO$_2$-bentonite, MnO-bentonite, and ZnO-bentonite nanocomposites were then filtered and washed several times with distilled water. All the samples were left to dry overnight at 100°C and then subjected to physical grinding method to enable size reduction. In brief, a quantity of 100g each composite was put in a grinding machine which having high speed rotator for 10 h. To prepare TiO$_2$-ZnO-MnO-bentonite composite, we took 1 g of each pervious prepared composite (TiO$_2$-Clay, ZnO - clay, and MnO-clay) and grinded with a grinding ball machine, which having high speed rotator for 6 hrs. Then 0.5 g of the solid composite was dissolved in 100 ml of hot deionized water left overnight, then filtrate, washed several times, and dried at oven 100°C for 4 hrs.

Figure 1. Schematic diagram for the impregnated process of metal oxides with Bentonite.

2.2. Characterization
The HDPE samples were studied using thermo gravimetric analyzer (TGA, NETZSCH TG 209F3 Tarsus analyzer). The alumina crucible was cleaned using distilled water and empty crucible was kept in the analyzer for calibration by creating a baseline. After completing the calibration, the grinded portion of HDPE was kept in the crucible which was placed in the sample holder for conducting analysis. The NETZSCH Proetus computer software program was used to record and analyze the
sample, beginning in the range of 25 to 650°C and at 10, 20, and 50°C/min of heating rates, respectively, under a nitrogen atmosphere (flow rate 20 mL/min).

The crystalline structure of the ZnO-Bentonite, MnO-Bentonite and TiO$_2$- Bentonite nanocomposites was detected by X-ray diffraction (XRD). XRD patterns were recorded with a Pan Analytical, which was equipped with CuK$_\alpha$ radiation ($\lambda$ = 0.1542 nm), Ni-filter and general area detector. The diffractograms were recorded in the 2$\theta$ range of 5–80° with step size of 0.02°.

To investigate the nanostructure of the prepared samples, the microstructures were studied using transmission electron microscopy (TEM, JEOL JEM-1230). TEM has been operating at 120 kV and attached to a CCD camera. A copper grid pre-covered with a very thin amorphous carbon film. To investigate the prepared samples, small droplets of the suspended solution for each sample were placed on the carbon-coated grid. Also, scanning electron microscopy (SEM) was performed for the prepared samples using SEM (Oxford instrument INCA/Sight) at 40 kV. The energy dispersive X-ray analysis (EDXA) was used to investigate the pyrolytic char produced by Bentonite.

The waste plastic char samples extracted from the reactor at different conditions during gasification were analyzed by a variety of materials characterization techniques at the Central Analytical Laboratories of National Research Centre, Egypt such as elemental analysis (CHNSO elemental, Vario EL III).

The non-condensable gases from the experiment were analyzed using Gas Chromatography (VARIAN model CP-3800) which has two columns (A and B). Column A used argon as a carrier gas, which measured hydrogen and relatively heavy hydrocarbon gases. In column B, helium was used as the carrier gas to measure nitrogen, oxygen, carbon monoxide, carbon dioxide and methane. The Gas Chromatograph analysis were conducted at the Egyptian Petroleum Research Institute (EPRI), Egypt.

2.3. Pyrolysis system

Pyrolysis of polymer was carried out using a bench scale fixed-bed reactor (SS 316, 0.98 mm ID). The total height of the reactor is 38cm with total volume of 42cm$^3$, externally heated by an electrical furnace. The reactor consists of three main parts, to be connected together during preparation for the experiments. The upper part includes two valves and pressure gauge to monitor the pressure during the experiment as shown in figure 2. The plastic and additives are added through the lower part. The upper and lower parts are collected together through a middle fitting connection. The air in the reactor was purged for at least 5min using the selected pyrolysis agent (100% N$_2$). One gram of pure HDPE or waste plastic with 4% of its weight from different catalysts is loaded for one hour at 750°C. The loaded reactor was placed in the furnace at selected reaction temperature. The electrical furnace (60 x 7 x 20cm$^3$), insulated with glass wool material, is used to supply the heat required to maintain the temperature of reaction for pyrolysis of plastic waste. Furthermore, temperature controller with a thermocouple was placed next to the outer surface of the reactor to record and control the temperature inside the reactor. After a given reaction time, the reactor was taken out of the furnace and cooled with an electrical fan for about 15min to cool down the reactor to room temperature (25°C). The non-condensable gases are flashed from the top of the reactor and measured by displacement of water in the gas sampler collector. Also, char and tar are collected and weighted after the reactor was opened.
Figure 2. Schematic of pyrolysis system where (a) inlet valve, (b) outlet valve, (c) pressure gauge, (d) pyrolytic reactor, (e) furnace, (f) union connection and (g) thermocouple k-type.

3. Results and Discussion

3.1. Physical characterization of catalysts

Figure 3 shows the XRD pattern of the bentonite (clay), MnO, ZnO, TiO$_2$, and their composites. Table 1 lists the peaks ICDD cards for all the samples under study. By comparing the data between XRD pattern in the figure with ICDD data in the table below, which it is clear that, TiO$_2$ and prepared MnO and ZnO and their composites were a good agreement between them. The XRD data for all the oxides state high crystallinity. Average particle size (d) of the particles have been calculated from high intensity peak using the Debye-Scherrer equation (Eq. (1)) as [60]

\[ d = \frac{K\lambda}{B \cos(\theta)} \]  

Where K is the Scherrer constant (0.89), \( \lambda \) is the wave length of X–ray beam used, B is the full width at half maximum (FWHM) of diffraction (in radians) and \( \theta \) is the Bragg’s angle. As clear from figure 3(B), MnO metal nanoparticles synthesized were purely crystalline in nature. Average particle size of MnO nanoparticles was found to be 25-30 nm where the intensity of the main MnO lines sharply increased, in addition to the appearance of new lines at 20 angles: 18°, 38°, 43° and 63°. For ZnO nanoparticles (figure 3C), X-ray diffraction shows that metal oxide is ZnO having hexagonal structure and no peak is detected due to any other material or phase indicating a high degree of purity of the as synthesized sample. The broadening of the X-ray diffraction lines reflects the nanoparticle nature of the sample. Sharpness of the peaks shows good crystal growth of the oxide particles. The calculated average crystallite is 50nm and the surface area of ZnO nanoparticles is 4.3737 m$^2$/g. The intensity of the main TiO$_2$ lines sharply increased, in addition to the appearance of new lines at 20 angles: 21°, 25.5°, 27°, 38°, 57° and 63° as clear in figure 3D. The X-ray pattern reflected that, the TiO$_2$ is very pure and consists in a majority of anatase particles. The indexed peaks can be found on the powder diagrams obtained in figure 3D. The calculated average crystallite is 27 nm and the surface area of TiO$_2$ nanoparticles is 60m$^2$/g.

XRD patterns of MnO-bentonite, ZnO-bentonite and TiO$_2$-bentonite nanocomposites (figure 3(E, F and G) confirmed the preparation of the desired catalysts, where the patterns showed mixed peaks of Bentonite and metal oxides. It is worth mentioning that, in case of TiO$_2$-bentonite and ZnO-bentonite nanocomposites, the peaks of TiO$_2$ and ZnO are predominant in the patterns which may be attributed
to the good distribution of TiO₂ and ZnO on the bentonite-surface. For the ZnO-bentonite, new
diffraction lines with high intensity appeared which are characteristic for the ZnO phase (ASTM 05-
0664). In addition, the lamella line of the Bentonite was shifted to the left (to a higher d-spacing),
which evidenced the penetration of ZnO to inside the bentonite lamella resulting in this expansion.

Figure 3. XRD pattern of the samples under study; (A) bentonite, (B) MnO, 
(C) ZnO, (D) TiO₂, (E) MnO-bentonite, (F) ZnO-bentonite, (G) TiO₂-
bentonite and (H) composite metals oxide clay.
Table 1. Peak positions (2θ degree) of XRD patterns and the ICDD reference code of pure clay and different metal oxides.

| Material       | Peak position (2θ, degree)                      | ICDD Ref. code |
|----------------|-----------------------------------------------|----------------|
| MnO            | 18.18, 37.48, 42.82, 58.81, 6.21, 74.58 and 78.43 | 04-006-0700    |
| ZnO            | 20.57, 26.72, 31.84, 34.51, 36.32, 47.62, 56.67, 62.93, 66.49, 68.02, 69.17 and 77.05 | 01-081-8838    |
| TiO₂           | 25.34, 37.00, 37.85, 38.63, 48.09, 53.96, 55.13, 62.73, 68.79, 70.40 and 75.14 | 03-065-5714    |
| Bentonite      | 6.80, 12.26, 19.80, 20.81, 24.85, 26.64, 35.11, 36.57, 50.16, 54.80, 61.72 and 68.07 | Montmorillonite |

Figure 4. TEM micrograph of (A) pure natural bentonite, (B) MnO-bentonite, (C) ZnO-bentonite, (D) TiO₂-bentonite nanocomposites, and (E) Metals oxides–clay composite.
Figure 4(A-D) shows the TEM micrographs of bentonite, MnO-bentonite ZnO-bentonite and TiO$_2$-bentonite nanocomposites, respectively. It is clear from figure 4A that, the average particle size of natural bentonite exceeded 100 nm with no uniform shape. The MnO- and ZnO nanoparticles are deposited on the bentonite surface (figure 4(B and C)) while the TiO$_2$ nanoparticles uniformly covered the bentonite surface, figure 4D. Due to this uniform coverage the XRD patterns of pure TiO$_2$ and TiO$_2$-bentonite are very close to each other. Since a crystallite can be defined by studying the orientation of the lattice fringes, one can see the average crystallite size in the synthesized TiO$_2$ powder is about 5–10 nm in diameter. As an important functional metal oxide, MnO nanoparticles are one of the most attractive inorganic materials because of its physical and chemical properties and wide applications in catalysis, ion exchange and molecular adsorption. It is clear from figure 4B that, the average size of MnO is about 25-30 nm. There are large numbers of potential applications of MnO nanoparticles such as catalysis application in cracking of polyolefin and petroleum refinery industrial. On the other hand, the size of ZnO-bentonite nanoparticles is about 27-82 nm as shown in figure 3C. They are formed and modified by nano-bentonite which improved the catalytically activity of composite and gave good gas yield when applied on degrading of waste plastic and pure HDPE.

3.2. Thermal Characterization of HDPE
The thermal stability of HDPE sample was studied using thermogravimetric analyzer (TGA). Figure 5 shows the mass-loss behavior as a function of temperature for HDPE sample at different heating rates. HDPE samples at all the heating rates show similar behavior with a single mass loss zone. The zone is approximately centered at (425, 450 and 460) °C for heating rate of 10, 20 and 50°C/min, respectively. For all the three heating rates, the cracking zone of HDPE is in the temperature range of (350-520) °C. Major mass loss in case of heating rate at 10 °C/min started approximately at 350 °C and continued up to 500 ºC with a mass loss of around 93.66%. In case of heating rate at 20 °C/min, major mass loss started approximately at 380ºC and continued up to 500ºC with a mass loss of around 98.80%. Whereas for heating rate of 50°C/min, major mass started approximately at 420 ºC and continued up to 520ºC with mass loss of around of 96.82%, respectively. In all the heating rates, more than 93% of the mass got converted into condensable and non-condensable volatiles. Residue percentage in case of 10°C/min is high as compared to 20 and 50°C/min due to the polymer’s recrystallization properties at lower heating rates.

![TGA](image)

**Figure 5.** Mass loss curves of HDPE at different heating rates (HR).
For a closer analysis of these thermo gravimetric data, derivative curve of mass loss for all the heating rates has been shown in figure 6. The derivative curve gives a clear picture of any major or sudden loss at specific temperatures. In case of heating rate of 50ºC/min, the peak mass loss is at 495ºC with a mass loss rate of 124% mass loss per minute. Whereas for heating rate of 20ºC/min, the peak loss is at 487ºC with a mass loss rate of 57% mass loss per minute.

![Figure 6. Derivative of mass loss for different heating rates.](image-url)

### 3.3. Pyrolytic degradation of waste plastics and pure HDPE

Applying different prepared catalyst at optimum premiers (reaction time, temperature and loading quantity of catalyst) on both pure HDPE and its plastic waste. Table 2 shows the gas yield on the pyrolysis of pure polyethylene high density and its waste (4% of its weight) at 750 ºC for 1 hour after using the prepared catalysis. The Char and condensable fractions from pyrolysis variation were also represented in the table 2. It was found that, nanocomposite catalyst gave the highest gas yield 1.02 m³/kg comparing to other prepared catalysts. In addition, it gives a high gas ratio when it was applied on degradation waste plastic with Char and condensable fractions of 32.12%. So, it is good catalytically in cracking and deforming of polymer process. It is also clear from the table that, ZnO-bentonite is more catalytically activity for producing high gas ratio (0.936 m³/kg) than that in MnO-bentonite (0.673 m³/kg) and TiO₂-bentonite (0.612 m³/kg). This can be connected to the electronic configuration in d-Orbital of ZnO.

| Catalytic Ratio 4%      | Gas Yield (m³/kg) | Char and condensable fractions % |
|-------------------------|-------------------|----------------------------------|
| HDPE                    | 0.65              | 38.88                            |
| Bentonite/HDPE          | 0.72              | 37.5                             |
| MnO-bentonite /HDPE     | 0.673             | 49.9                             |
| TiO₂-bentonite /HDPE    | 0.612             | 55.58                            |
| ZnO-bentonite /HDPE     | 0.936             | 35.7                             |
| Metal oxides –Clay composites /HDPE | 1.02         | 29.87                            |
| Metal oxides –Clay composites /PW- HDPE | 0.98         | 32.12                            |
3.4. Characterization of the pyrolysis gas products

3.4.1. Gas yields analysis. The gas chromatograph analysis of the gas sample obtained by the catalytic pyrolysis of both plastic waste and pure HDPE is summarized in the table 3. It has been observed that the pyrolytic sample contains many components such as aromatic, olefins, alkene, Nature gas, CO, CO$_2$ and Hydrogen. The greatest amount of hydrogen (15.544 %) and the smallest amount of methane (80.621%) are produced when MnO/bentonite is used, which may be due to highly oxidation rate of MnO. This is the important characterization of the transitions metal related to partially empty of d-orbital of Mn that will be easy to make cracking of polymers and release of H$_2$. On the other hand, TiO$_2$ produced lower amount of H$_2$ and larger amount of CH$_4$ which may be returned to the electronic configuration of metal (TiO$_2$ > MnO > ZnO). Presence of free electron in d-orbital of both Ti and Mn while it is filled in Zn. So, MnO is a good catalyst deforming of polymers to get hydrogen which can be used in fuel cell application. On the other hand, composite of nano-Bentonite metal oxide gave high ratio of methane (94.82%) and low ratio of hydrogen with pyrolysis of plastic waste and pure HDPE. This may be due to impregnate the nano-bentonite metal oxide shielding of electrons or chelating with OH group of bentonite. This confirmed the improvement of the cation exchanger in composite and gave good ratio of CH$_4$ which can be used as a source of renewable energy.

Table 3. Comparison of gas products from catalytic pyrolysis of pure and waste HDPE with different catalysts at 750°C for 1 hour and 4% catalytic ratio.

| Catalytic Pyrolysis                  | Components (vol. %) |
|-------------------------------------|---------------------|
|                                     | Methane  | Hydrogen | Carbon Monoxide | Carbon Dioxide | Ethane | Benzene | Nitrogen |
| HDPE                               | 92.531   | 1.144    | 0.128          | 0.130          | 2.911  | 0.170   | 2.986    |
| Bentonite/HDPE                     | 87.722   | 3.811    | 2.899          | 1.537          | 0.751  | 0.159   | 3.121    |
| MnO-bentonite/HDPE                 | 80.621   | 15.544   | 0.856          | 0.180          | 0.374  | 0.017   | 2.408    |
| TiO$_2$-bentonite/HDPE             | 85.480   | 4.885    | 6.500          | 1.923          | 0.590  | 0.035   | 0.586    |
| ZnO-bentonite/HDPE                 | 93.216   | 0.357    | 0.241          | 0.457          | 0.567  | 0.123   | 5.039    |
| Metal oxides – Clay composites /HDPE| 94.819  | 0.013    | 0.103          | 0.746          | 1.671  | 0.053   | 2.052    |
| Metal oxides – Clay composites /PW-HDPE | 93.785  | 0.001    | 0.068          | 0.162          | 3.702  | 0.228   | 2.053    |

3.5. Solid waste (char) characterize

3.5.1. Method of sampling and calculation of char samples. PEHD and PEHD waste char carbon samples extracted from the reactor at different conditions during pyrolysis were been analyzed by a variety of materials characterization techniques at the Central Analytical Laboratories of National Research Centre, Egypt. Elemental analysis was done by CHNSO elemental (Vario EL III). Elemental analysis was useful to evaluate carbon conversion efficiency. Carbon conversion was calculated by Eqs. (2-4):

$$X = \frac{(C_o - C)}{C_o}$$

(2)
\[ \text{Co} = W_o \times M_o \]  
\[ C = W \times M \]  
(3)  
(4)

where \( X \) is the conversion of fractional carbon; \( C_o \) and \( C \) are carbon amount (gm) before and after pyrolysis, respectively; \( W_o \) and \( W \) are carbon percentage before and after pyrolysis, respectively; and \( M_o \) and \( M \) are PEHD plastic weight (gm) before and after pyrolysis, respectively.

3.5.2. Morphology analysis of composites catalyst. The surface morphologies (SEM) of the char presented nano-Bentonite catalyst is shown in figure 7. It is clear from the figure that, exists of flacks on the surface in nano-scales size average 100-120 nm, which is prove that nano-catalyst composite submersed between carbon char. Also, it was found that most of plastic polymers is converted to carbon char and other residual which appears on the surface of char. Figure 8 shows the energy dispersive X-ray analysis (EDXA) spectrum for Bentonite and table 4 listed the char composition. The char contains 65% carbon and other composition such as Silica, Al₂O₃ and Mg are 4.35, 2.6, and 0.6 of their weights, respectively. This data proved that the same chemical compositions of the papered nanocomposite were appeared which carryout under high temperature without desiccation. Also, all plastic waste or pure HDPE was converted to char.

**Figure 7.** SEM image of the char sample pyrolysis at 750 °C for 1 hour.

**Figure 8.** EDXA of catalytically pyrolysis of HDPE char with Bentonite clay.
Table 4. Residual metal element in char sample.

| Element | Weight % | Atomic % | Net Int. | Error % |
|---------|----------|----------|----------|---------|
| C       | 64.96    | 75.65    | 156.17   | 7.73    |
| O       | 20.37    | 17.81    | 39.81    | 11.25   |
| Ne      | 0.53     | 0.36     | 3.92     | 16.19   |
| Na      | 1.61     | 0.98     | 11.86    | 10.55   |
| Mg      | 0.61     | 0.35     | 8.06     | 10.93   |
| Al      | 2.6      | 1.35     | 42.12    | 5.86    |
| Si      | 4.35     | 2.17     | 78.72    | 4.23    |
| Cl      | 0.18     | 0.07     | 2.71     | 20.45   |
| K       | 0.29     | 0.1      | 3.82     | 16.09   |
| Ca      | 0.29     | 0.1      | 3.29     | 18.94   |

4. Conclusion
Throughout previous experiments and results, we conclude that, composites of MnO/Bentonite has unique specific adsorption properties with pw and PEHD. Moreover, Modification of nano-bentonite with metal oxides gives better results than using bentonite or metal oxides alone. Nano-bentonite with metal oxides increases the active sites of composite and also increases the rate of reaction. Useful gases (such as hydrogen and methane), light component paraffin and char were produced from pyrolysis process to degradation plastics. In addition, high amount of syngas was produced which can be utilized for production of ammonia (leading to different nitrogen-based fertilizers) and also, can serve as a hydrogen source. The waste plastic could be used in pyrolysis process (zero waste) better than incineration process because it is become source of green gases emission. Alternative technologies for managing end-of-life plastics exist. MnO/Bentonite nanoparticles is a good catalyst deforming of polymers to produce hydrogen which can be used in fuel cell application.

Acknowledgment
This research was supported by the Scientific Research Developing Unit, Beni-Suef University, and the Academy of Scientific Research and Technology "ASRT" as a joint research grant under the India-Egypt agreement on science and technology cooperation. We thank our colleagues from National Research Center who provided us both of pyrolysis reactor system and experience in their laboratory. Prof. Mohamed Abdel Fatah Hamed and Prof. Ali Radwan that greatly assisted the research.

References
[1] Hillmyer and M. A 2017 J. Sci. 358 868
[2] Haarman A and Gasser M 2016 Managing Hazardous (WEEE Plastic Additives in the Indian Informal Sector) (SRI) p1-68
[3] Vamshi A 2013 Int. J. Eng. Res. 2325 0224
[4] Ruiz-Herrero J L, Nieto D V, López-Gil, A, Arranz, A, Fernández, A, Lorenzana A and Rodríguez-Pérez M Á 2016 Constr. Build. Mater. J. 104 298
[5] Dave P N and Joshi A. K 2010 J. Sci. Ind. Res. 69 177
[6] Bhagat S, Bhardawaj A , Mittal P, Chandak P, Akhtar M and Sharma P 2016 IJOAB J. 7 25
[7] Huysman S, De Schaepmeester J, Ragaert K, Dewulf J and De Meester S 2017 Resour.Conserv. Recy. J. 120 46
[8] Kumar A 2013 Int. J. Soc. Sci. 1 6
[9] Jellinek H and Clark J E 1963 Can. J. Chem. 41 355
[10] Siddiqui M N and Redhwi H H 2009 Fuel Process. Technol. 90 545
[11] Kalargaris I, Tian G and Gu S 2017 Fuel Process. Technol. 161 125
[12] Sharuddin S D, Abnisa F, Daud W M and Aroua M K 2016 Energy Conv. Manag. 115 308
[13] Panda A K, Singh R K and Mishra D K 2010, Renew. Sust. Energ. Rev. 14 233
[14] Sannita E, Aliakbarian B, Casazza A A, Perego P and Busca G 2012 Renew. Sus. Energ. Rev. 16 6455
[15] Fivaga A and Dimitriou I 2018 Energy J. 149 865
[16] Paul T W 2013 Waste Manag. 33 1714
[17] Yang X, Sun L, Xiang J, Hu S and Su S 2013 J. Waste. Manag. 33 462
[18] Quek A and Balasubramanian R 2013 J. Anal. Appl. Pyrolysis 101 1
[19] Al-Salem S M, Lettieri P and Baeyens J 2010 Prog. Energ. Combust. J. 36 103
[20] Çepelioğlu O and Pütün A E 2013 J. Nat. Appl. Sci. 2 694
[21] Chin B L F, Yusup S, Al Shoaibi A, Kannan P, Srinivasakannan C and Sulaiman S A 2014 J. Clean. Prod. 70 303
[22] Hasegawa M, Fukuda J and Kunii D 1979 Energy: a Continuing Bibliography with Indexes (l'Université du Michigan, United States) PP 35-36
[23] Borgianni C, De Filippis P, Pochetti F and Paolucci M 2002 Fuel 81 1827
[24] Xiao R, Jin B, Zhou H, Zhong Z and Zhang M 2007 Energ. Convers. Manage. J. 48 778
[25] Martinez-Lera S and Ranz J P 2017 Fuel. J. 197 518
[26] Aguado J, Serrano D P, San Miguel G, Castro M C, and Madrid S 2007 J. Anal. Appl. Pyrol. 79 415
[27] Seo Y H, Lee K H and Shin D H 2003 J. Anal. Appl. Pyrol. 70 383
[28] Sakata Y, Uddin M A and Muto H A 1999 J. Anal. Appl. Pyrol. 51 135
[29] Fatimah I, Narsito N and Wijaya K 2011 J. Math. Fundam. Sci. 43 123
[30] Binitha N N and Sugunan S 2006 Micropor. Mesopor. Mat. 93 82
[31] Vicente M A, Belver C, Sychev M, Prihod’ko R and Gil A 2009 J. Ind. Eng. Chem. 48 406
[32] Okoye I P and Obi C 2011 Inter. Arch. App. Sci. 2 84
[33] Salerno P, Asenjo M B and Mendioroz S 2001 Thermochim. Acta 379 101
[34] Miandad R, Barakat M A, Aburiazaiza A S, Rehan M and Nizami A S 2016 Process Saf. Environ. Protect. 102 822
[35] Karaborni S, Smit B, Heidug W, Urai J and Van Oort E 1996 J. Sci. 271 1102
[36] Liu C, Lv P, Yuan Z, Yan F and Luo W 2010 Renew. Energy 351 531
[37] Szücs A, Berger F and Dékány I 2000 Colloid. Surface A. 174 387
[38] Pérez A, Centeno M A, Odrozola J A, Molina R, and Moreno S 2008 Catal. Today 133 526
[39] Paek S M, Jang J U, Hwang S J and Choy J H 2006 J. Phys. Chem. Solids 67 1020
[40] Amarasekara A S, Green D and McMillan E 2008 Catal. Commun. 9 286
[41] Aravind P V and de Jong W 2012 Prog. Energ. Combust. 38 373
[42] Wilcoxon J P 2012 Frontiers of Nanoscience (United Kingdom, Elsevier Ltd.) 3 43
[43] Pélisson C H, Vono L L, Hubert C, Denicourt-Nowicki A, Rossi, L. M and Roucoux A 2012 Catal. Today 183 124
[44] Bhaskar T, Matsui T, Uddin M A, Kaneko J, Muto A and Sakata Y 2003 Appl. Catal. A-Gen. 239 229
[45] López A, De Marco I, Caballero B M, Laresgoiti M F and Adrados A 2011 Fuel. Process. Technol. 92 253
[46] López A, De Marco I, Caballero B M, Laresgoiti M F, Adrados A and Aranzabal A 2011 Appl. Catal. A: 104 211
[47] Hall W J and Williams P T 2008 J. Anal. Appl. Pyrolysis. 81 139
[48] Terakado O, Ohhashi R and Hirasawa M 2011 J. Anal. Appl. Pyrolysis 91 303
[49] Terakado O, Ohhashi R and Hirasawa M 2013 J. Anal. Appl. Pyrolysis 103 216
[50] Jung S H, Kim S J and Kim J S 2012 Fuel 95 514
[51] García R, Serrano D P and Otero D 2005 J. Anal. Appl. Pyrolysis 74 379
[52] Miskolczi N, Bartha L and Deák G 2006 Polym. Degrad. Stabil. 91 517
[53] Aguado J, Serrano D P, San Miguel G, Castro M C and Madrid S 2007 J. Anal. Appl. Pyrolysis 747 9415
[54] Marcilla A, del Remedio, Hernández M and García Á N 2007 J. Anal. Appl. Pyrolysis 79 424
[55] Olazar M, Lopez G, Amutio M, Elordi G, Aguado R and Bilbao J 2009 J. Anal. Appl. Pyrolysis 85 359
[56] Cherian E, Rajan A and Baskar G 2016 Int. J. Mod. Sci. Technol. 1 17
[57] Lin J T, Jong S J and Cheng S 1993 Micropor. Mesopor. Mat. 1 287
[58] Alwan R M, Kadhim Q A, Sahan K M, Ali R A, Mahdi R J, Kassim N A and Jassim A N 2015 J. Nanosci. 5 1
[59] Scherrer P 1912 In Kolloidchemie Ein Lehrbuch (Springer, Berlin, Heidelberg) pp.387
[60] Tadokoro H, H. G 1980 Structure of Crystalline Polymers (John Wiley and Sons, Chichester, New York, Brisbane, Toronto) pp 84