

Studying and Evaluating Sustainable Materials for Converting Plastic Waste to Fuel

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Abstract

Gasification is one of the most important solutions for plastic waste management. We researched the conversion of plastic waste to fuel using sustainable material (Nano Clay) modified with Nano transition metals (TiO₂, MnO, and ZnO). This was processed in a fix bed reactor design. After studying the reaction mechanism of the gasification process, we evaluated the optimize (reactor temperature, reaction time and feeding ratio of the modified catalyst) on the gasification process with its application for the modified catalyst on the degradation of polyethylene high density (PEHD), other waste plastic to fuel (CH₄, H₂, and other light component gasses). This method can be used as an important resource for renewable energy (like generating electricity and clean fuel), rather than waste for landfills and the incineration process which is the main source of CO₂ emissions.

Key words: modified catalyst, gas yield, polyethylene high density, waste plastic, gasification, TiO₂, MnO, ZnO and CH₄

1. Introduction

Many plastic productions started in 1950 and this caused almost 8 billion metric tons of waste mainly in disposable material. Scientists are trying to find a better solution for this humongous waste for landfills and an alternative resource for fossil fuels to change to an environmentally friendly renewable fuel like biodiesel (Semwal, Arora, & Tuli, 2011). Plastic (polymeric) materials are known for their universal use and rapid growth in various markets. Given the low density, strength, ease of design, process ability, durability, low weight and low cost of plastic, it became very popular in different sectors such as packaging, automotive, industrial applications, piping, construction, thermal and acoustic insulation (Rebeiz, K. S., Craft, 1995). The increase in manufacturing and use of polymeric materials are the causes of enormous plastic waste [Rafatet al (2008), & Buclet, N, Brandt 2010]. Plastic recycling is a method that can solve this problem compared to throwing the plastic waste in landfills or incineration. The specified benefits of gas over solid fuel and the gasification process is that they transfer the heating value of the solid fuel to a gaseous energy carrier (Van Swaaij, 1981).

For example, gases are easy to transport and clean. They efficiently combust with less excess air and they emit a lower level of some pollutants Comolli, et al (1997). Catalysis has become essential for the chemical industry. It makes use of natural resources while reducing the pollution during the chemical process. Also, catalysis has become a foundation of large-scale production in the chemical and petroleum industry (Yadav, Nair (1993), Vermeiren, et al (2009), Chen et al (2015) and Sharifzadeh, et al (2015). However, there are still problems that require constant solutions Wolczanski, Chirik, (2015) & Tanaka (2010). With the development of nanotechnology, catalysis has introduced both advantages and disadvantages. For example, metal nanomaterial as a heterogeneous catalyst Dutta et al (2015) has very high catalyst activity and selectivity for specific reactions. Nano catalysts used for catalytic chemical reactions mainly contain the oxidation reaction, the reduction reaction Yasukawa et al, (2015), the coupling reaction Zhang, Shen (2015) & Zhang, et al, (2015) and the electrochemical reaction (Zhou

et al (2003), Tripkovic et al, (2002), Choi et al (2006), Shen et al (2015) and Xiao, et al (2015). Nano catalysts have been proven successful in many industries such as adsorbents, catalysts or catalyst supports, and ion exchangers. Clay-modified catalysts will be explored, according to different modification methods: such as thermal, acid and cation exchange, and pillared clays. In addition, the synthetic catalysts from clays zeolites and alumina were also explored.

The first hydrocracking process evolved over 8 decades ago. It was based on acid-modified clays Centi, G. & Perathoner, S. (2008) but zeolites and aluminosilicates were announced later. Clays are still used in some cases such as in treating some heavy fractions. Clays with different acidities can be acquired by thermal treatment before preparing the catalyst. The temperature of the thermal treatment of clay determines the type and concentration of the hydroxyl groups (Herrero et al, (1990) and this thereby determines its acidity. Montmorillonites or acid-modified montmorillonites have been used for numerous reactions (Mishra et al (2010), Turgutbasoglu et al, (2005) and Hettinger (1991) Transition metal-based catalysts, particularly supported Ni catalysts, have been greatly used for biomass gasification due to their high activity in tar cracking and improving the quality of the produced gas (Baker & Mudge 1987).

The cracking of plastic polymerics into their component monomer or other low molecular weight hydrocarbons has become an essential process for getting rich light hydrocarbon and aromatic olefin components. Also, a large amount of plastic waste is expanded quickly every year (Worldwatch Institute, 2016). Pyrolysis and/or gasification of plastic waste such as PEHD and its waste serve as a pertinent tool for restoring energy and plastic waste disposal simultaneously Al-Salem et al. (2009). Compared with other proposition feedstock like biomass and coal, PEHD has a higher heating value and it is much cleaner in terms of fuel quality. This causes less fuel pre-processing costs. Pyrolysis or gasification of PEHD results in a product stream rich in hydrogen and minimal CO or CO₂ content compared to cellulose-based wastes (biomass) (Vassilev et al., 2010 & (Liu et al., 2014a) that yield relatively higher carbon monoxide and lower hydrogen product compositions. This is mainly because of the presence of oxygen in the cellulose-based feedstock.

2. Material and Methods

2.1 Materials

2.1 Polyethylene High Density (PEHD) Sample

Feedstock used for the process was PEHD B1054, a high density polyethylene specially developed for large blow molding and jerry cans. The material offers high stiffness, good process ability and it is an excellent combination of stiffness/ESCR. Saudi Basic Industries Corporation, SABIC. All chemicals used for nano-oxide metals were purchased from Lobe chime (India) and they were used without purification. Also, the raw material plastic waste (PVC, PEHD, PELD, EP, STYRENE, resin) was collected from Beni suef university Camp.

2.2 Catalyst

The structure of montmorillonite is a 2-to-1 layered smectite clay mineral with a platy. Each layer has 2 tetrahedral sheets containing an octahedral sheet between individual platelets. The thicknesses are just one nanometer, but surface dimensions range between 300 to more than 600 nanometers. Hundreds or thousands of these layers were stacked together with Vander Waals forces to form clay particles (Murray, 2007)

The modified catalyst used in our study is bentonite modified with three transition metal oxides (TiO₂/MnO₂/, ZnO) in Nano size. Catalysts were prepared in Nano scales by sol-gal and co-precipitation methods. Their characterizations are outlined in our previous work (Belova et al, (2008), V. Subramanian et al (2005), iyadh, (2015), M.Galamboš et al, (2010).

2.3 Methods

2.3.1 Gasification System.

The gasification of plastic polymer (PEHD) and other different plastic waste was carried out using a fixed-bed reactor (SS 318, 0.98 mm ID). The height of the reactor was 40 cm with a capacity volume of 40 cm³. It was heated by an electrical furnace. The reactor had three main parts that were connected together during preparation for the experiment. The feeding waste plastic and catalyst were added through the lower part, and the upper and lower part were joined together with a union fitting connection as shown in Fig-1. In a typical experiment of gasified 1g of sample (with and without catalyst), then loaded together inside, adjustable other parameters (temperature at 750°C and reaction time is one hour) for the reactor process. This design is installed in the Faculty of Post Graduated for Advanced Science, Renewable energy Department, Beni suef University in Egypt (Aly M. Radwan, (2015)

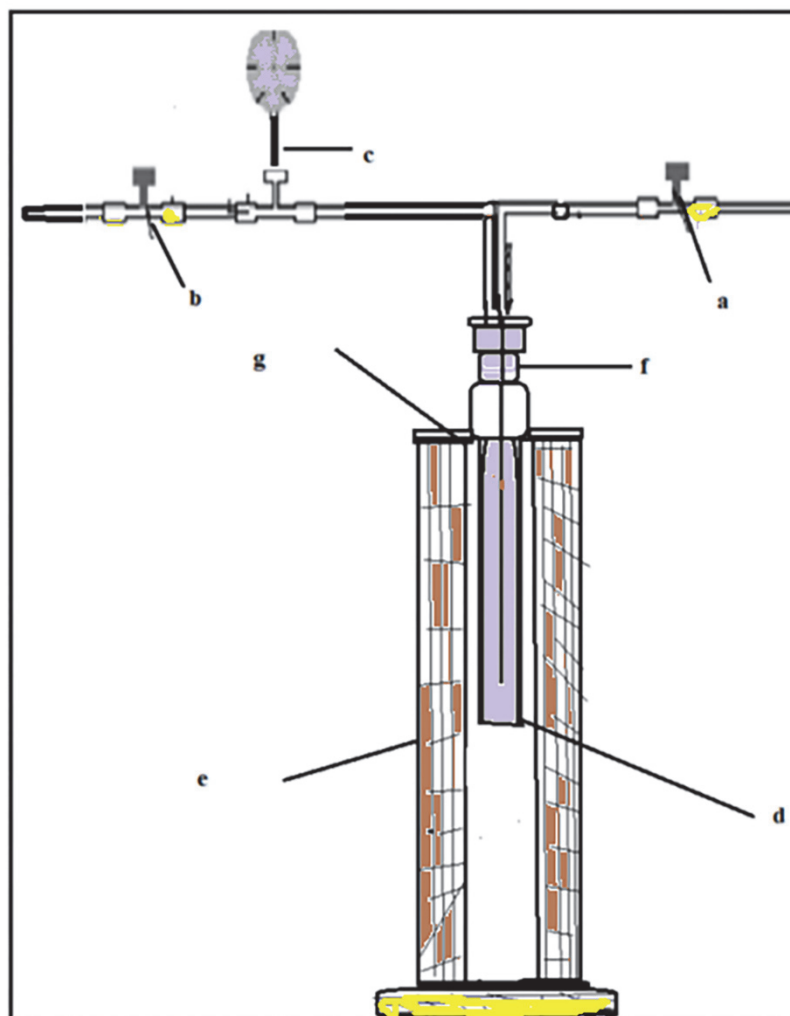


Figure (1). Schematic of the gasification system with (a) inlet valve, (b) outlet valve, (c) pressure gauge, (d) gasified reactor, (e) furnace, (f) union connection and (g) thermocouple k-type

2.3.2 Gasification PROCEDURE

The loaded reactor was placed inside the furnace at the selected reaction temperature and heated for the required 10 to 15 minutes to reach isothermal heating. The electrical furnace was 65cm long, 8 cm ID and 22 cm OD. It was completely insulated with glass wool material and it was used to maintain the reaction temperature for the gasification of plastic waste. A controller for temperature with a thermocouple (type K) was connected to the outer surface of the reactor for recording and controlling the temperature of the reactor. within complete reaction, we removed the reactor from the furnace and it was cooled with an electrical fan. It took 15 minutes for the reactor to cool down to room temperature. Afterwards, we collected producer gases and injective inside GC for the gas yield analysis and other remaining solids (char) were also collected to conduct other tests.

3. Results

3.1 Study of Reaction Mechanism of the Gasification Reaction.

The reaction mechanism of the modified catalyst with clay and poly ethylene high density or other plastic is illustrated in fig 2. The chemical structure of bentonite clay is sodium montmorillonites which has the chemical composition $\text{Na}_{0.2}\text{Ca}_{0.1}\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2(\text{H}_2\text{O})_{10}$. Smectite minerals are composed of two silica tetrahedral sheets with a central octahedral sheet. They are designated as a 2:1-layer mineral. It is easily dissolved in water. Water molecules and cations occupy the space between the 2:1 layers by making coordination complexes (DeStefanis, 2006).

Various modifications of clays such as thermal-, acid-, alter the structure properties and produce catalysts with high acidity, surface area, porosity and thermal stability (Ding Z et al, (2001), Williams (2006) & Murray (1999).

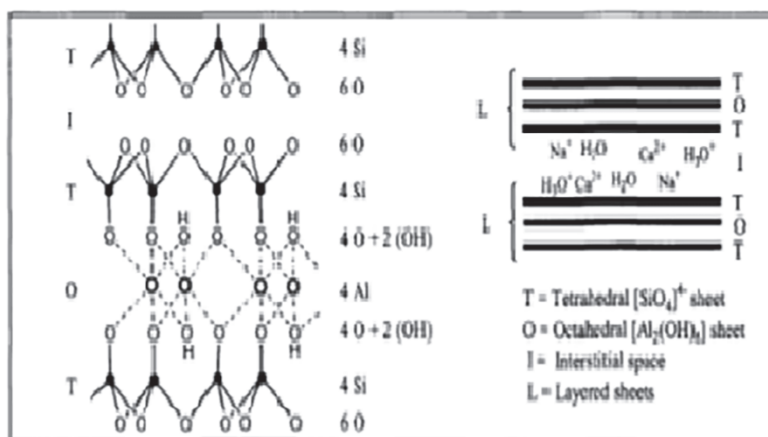


Figure (2). Structure of sodium montmorillonite

3.1.1 Metals of Transition Elements Have Different Oxidation States Which Make It Easy to Chelate with Some Sites of Clay Containing OH as a Ligand

The impregnation process explains how transition metals chelate with aluminum and silica elements such as vanadia, chromia, zirconia and alumina. Pillared clays are modified and the ions on the clays are exchanged with specific chemicals such as Al-hydroxide which goes into an interlayer position Gilman, Jeffery et al, (199). Particle size, surface area, and aspect ratio are highly important characteristics desired in Nano clays. The length and breadth of the particles can range from 1.5 nm to a few tenths of a micron. The third dimension of a particle has been described in literature as thickness, width, or diameter. However, diameter seems more appropriate. The diameter of a particle is exceptionally smaller relative to its length (1 nm).

Therefore, an extremely high average aspect ratio (length to diameter ratio) of 200 to 500 is possible. A small amount of Nano bentonite exhibits a high surface area; i.e., a Nano clay product is known with a surface area in excess of 750 m²/g, (Clay Minerals—Sci-Tech (2007). The surface area for newer metals oxide TiO₂, MnO and ZnO play an important role in catalyzing polymers (plastic) with a surface area of 287.1, 253 and 15.45 m²/g i.e. TiO₂>MnO>ZnO of the same order for the ease of catalysis.

The Lewis acidity of the metal ions correlates with the charge-to-size (z/r) ratio. The higher z/r, the stronger the Lewis acidity of the cation. This results in more polarization power of the metal centre and more of a catalyst effect. The z/r for Ti, Mn and Zn are 287.1, 253 and 15.45 m²/g, respectively Kuo-Tseng et al (2012). However, despite a much higher Z/r ratio for Zr⁴⁺ and HF⁴⁺ (5.56 and 5.63) respectively, the corresponding complex exhibited poor catalytic activity.

The second factor that has a great effect on the reaction mechanism is the electronic configuration for electrons in the d- orbital for transition element metals and the p-orbital Oxygen atom in side Bentonite sheets.

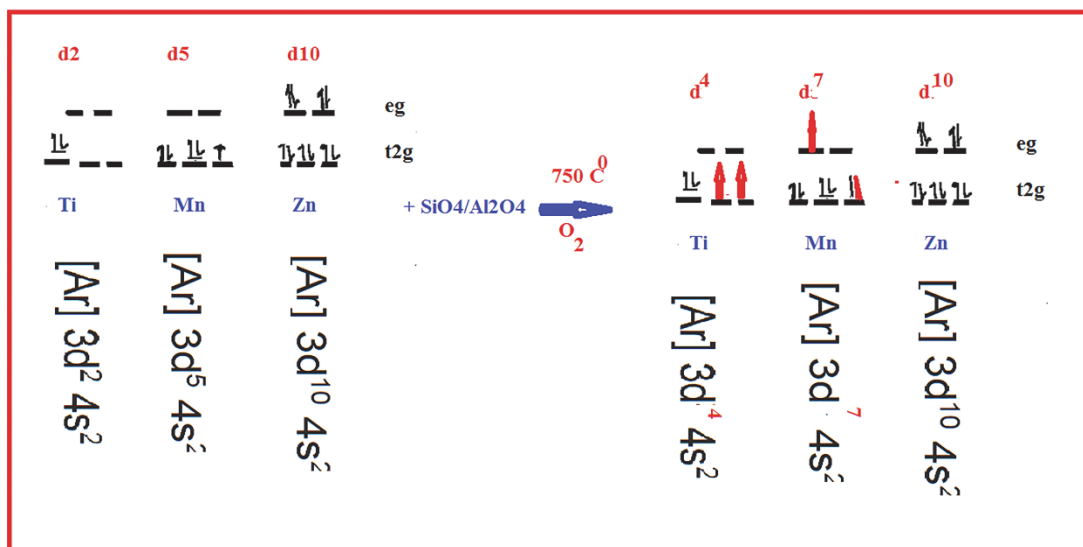


Figure (3). Schematic of reaction mechanism for the electronic distribution in the d-orbital of the outer shell

The electronic state for transition metals (Ti, Mn and Zn) is illustrated by figure (3). According electronic configuration of three transition elements in **t_{2g}** (lower energy state) and **eg** (excited state), in case titanium atom there are four empty orbitals in the d shell. So, it is easy to fill 2 of them with 4 electrons according to the hunds rule so it shearing or chelating with free electron of O atom. The charge transfer in which an electron is momentarily transferred from O in the OH group of Bn to the 3d-orbital of the metal (the momentarily changes O²⁻ to O⁻ and reduces the oxidation stat of the metal Ti or Mn from 4⁺ to 3⁺) can promote through the d-orbital of unequal energy that is freely in case of Ti to Mn and does not occur in the case of Zn. On the other hand, this free transition affects the ease of catalization of the Nano composite through PEHD as seen in in fig -4. The structure of the clay particles is perceived in layers. Each layer is composed of two types of structural sheets: octahedral and tetrahedral. The tetrahedral sheet is composed of silicon-oxygen tetrahedra linked to neighboring tetrahedral sharing three corners. This results in a hexagonal network (Y. Rao & Blanton (2008)).

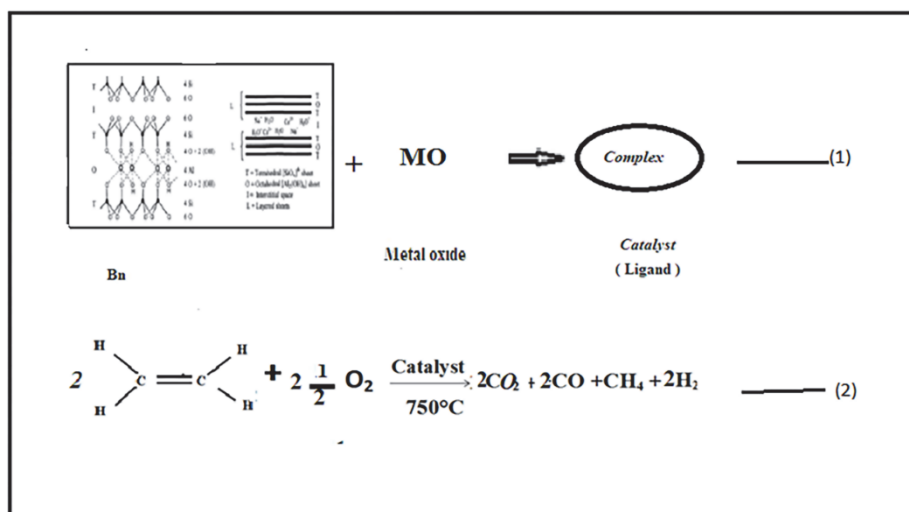


Figure (4). Schematic illustrating the complex formation

The remaining fourth corner of each tetrahedron forms a part of the adjacent octahedral sheet. The octahedral sheet is usually composed of aluminum or magnesium in six-fold coordination with oxygen from the tetrahedral sheet and the hydroxyl. The two sheets together form a layer, and several layers may be joined in a clay crystallite by interlayer cations, Vander Waals force, electrostatic force or hydrogen bonding.

3.2 Studying Optimized Parameters for Gasification Processes.

3.2.1 Studying Temperature with Reaction Time on the Gasification Process for PEHD.

There are many parameters that affect the gasification process such as pressure, temperature and reactions times. They have a great impact on the quality and quantity of product distribution, and they affect the degradation of polymer (plastic). By increasing the temperature, the polymer is converted from plastic to a glassy state, rubbery state, liquid state, and a decomposed state. The reaction mechanism of polymerization passes four stages during the plastic degradation process: initiation, propagation, hydrogen transfer, and termination reactions. Through the initiation reaction process, there are three types of cracking or reforming processes: random, end chain, and chain strip cracking (Bockhorn et al., 1999; Faravelli et al., 1999, 2003; Kruse et al., 2001, 2002, 2003, 2005; Levine and Broadbelt, 2008, 2009; Marongiu et al., 2003, 2007; Poutsma, 2003, 2005, 2009; Westerhout et al., 1997a,b) They are determined by the side functional group on the plastic molecular carbon backbone. Then, there are propagation reactions, especially β -scission, (Vinu and Broadbelt, 2012b) which is the cracking of large molecular weight. The second factor which is also important for degrading plastic is reaction time. This means the economic value for the industrial sector. The reaction time is inversely proportional to the temperature and pressure. It gradually increases with increasing temperature and then it's constant. This means the polymers are completely converted. This is shown in fig -5 which illustrates the typical relation of temperature and pressure against the reaction time during the degradation of polyethylene high density (PEHD) in the gasification process. By increasing the temperature, the degradation of the polymer increases with increasing pressure until it is fixed at 750°C. This is at almost one hour and there is no change in other parameters. This means there is complete conversion and the gasification process is done. The cracking of plastic polymer waste is a very complex process, which consists of many reactions and products. By increasing the temperature, we demonstrated the cracking of plastic. From our experiments, we reached optimal conditions for the gasification process of degrading poly ethylene high density to fuel at 750 °C and a one hour reaction time. We also got a high ratio of gases with reduced liquid which contaminated with tar. This has a negative impact and plugs the pipe and precipitate on the inner surface of the reactor. in addition to char (solid waste is easy recycle or reused management) the results from the gasification of plastic can be used in other industrial fields rather than emission carbon di oxide which result direct combustible or incineration process.

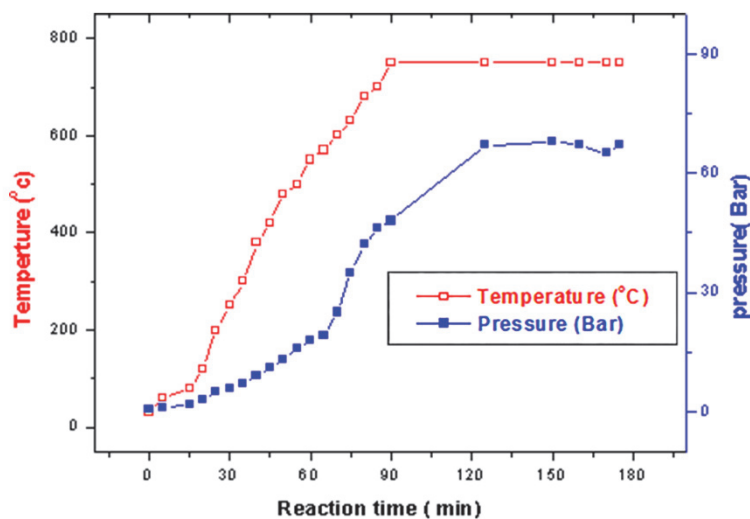


Figure (5). Profile of temperature and pressure against time for the gasification reaction

3.2.2 Effect of Temperature on Gasification Process

One important factor in the gasification process is temperature and also, that determine the relative yields of the products (Bridgwater, 2012). By studying the effect of temperature from 400°C to 900°C for 1hour on the degradation of poly ethylene high density, we get the product distribution of gas yield and char. This is seen in fig-6. As long as the gasification temperature increases from 450°C to 750°C, the gas yield increases from 0.58 m³/kg to 0.98 m³/kg. It then decreases at 750°C to 0.9 m³/kg. While char is recorded as a high value at 550°C, it slowly decreases to 38.2 and that demonstrates a complete conversion of plastic to gas at this range of heat.

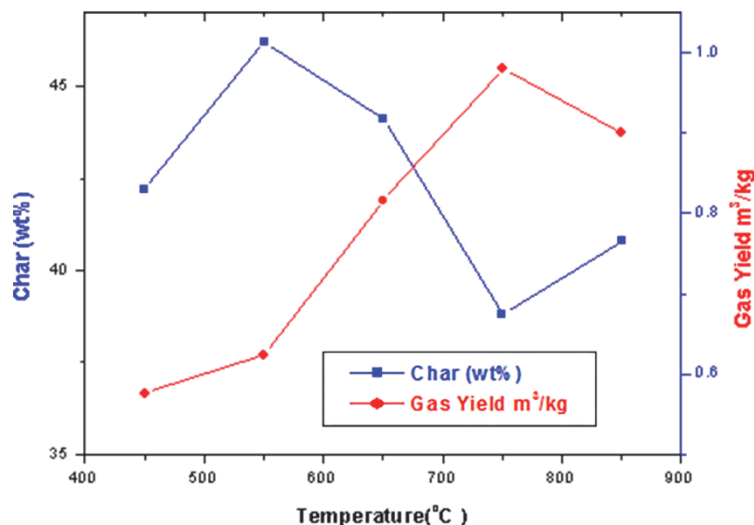


Figure (6). Effect of temperature on the gasification of polyethylene (PEHD; Reaction time: 60min

3.2.3 Evaluating the Feeding Ratio of Modified Catalysts (Composite Catalyst) on the Gasification of PEHD.

In this study, we tried to get the best feeding ratio of the catalyst (MnO, ZnO, TiO₂ -Bn) at 750°C for one hour. So we conducted our experiments with different ratios of the composite catalyst and plastic sample (PEHD) (0:1, 0.008:1, 0.02:1, 0.04:1 and 0.06:1) in a gasified fixed reactor. Results are shown in fig-7. So, the best ratio for the composite catalyst is 0.04:1 which is clear in quantity of gas yield and char%. This means there is complete cracking conversion of PEHD to fuel. The gas yield value slightly increased from 0.26 m³/kg at 6% used catalyst to 0.94 m³/kg at 4%. Also, the char ratio changed with a different feeding ratio of catalysts. We got less amount of char (18.2) with a catalyst ratio of 6% of its weight in the gasification process, and a high amount of char (55.3) with 2% catalyst. it was the least amount %t 6 of weighting the same catalyst. This means PEHD was not completely converted during the gasification process. From the data analysis, we found that the best ratio of the feeding catalyst in the process is 4%. Since it gave a high ratio of gas yield and an acceptable amount of char ,this proves there is good catalytical cracking for PEHD related to Le Chateliers' principle. Higher temperatures favor the reactants in exothermic reactions and the products in endothermic reactions. The main reactions are endothermic.

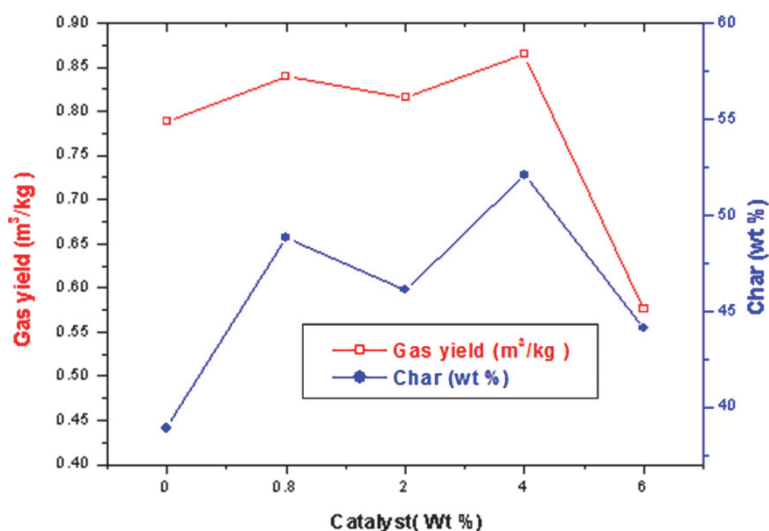


Figure (7). Studying the optimized feeding ratio for modified catalysts on the gasification of PEHD at 750 °C for 1 hour

3.3 Study and Evaluation Modified Catalysts at Optimize Conditions on Plastic Gasification Process.

3.3.1 Gasification Process of Virgin Polyethylene High Density (PEHD)

Applying modified catalysts on PEHD gave good results as shown in fig-8. There were optimized conditions (temperature was 750°C, reaction time was 1 hour and loading composite catalyst was 4%). Through the experiment, we noticed that char conversion for TiO₂-Bn is lower than other modified catalysts but more than PEHD and bentonite alone. On the other hand, compared to ZnO -Bn, there was a high ratio of carbon char conversion (68.6%) and gas yield (94). This proves that the electron movement in the d- orbital may create oxidation states number the MnO₂ and ZnO with Bentonite. In conclusion, the best ratio of gas yield (1.02) is given by modified bentonite with three metal oxides (TiO₂, MnO and ZnO), adding to the carbo char conversion (67%). This means there is good coordination bonding between the free electron in configuration d Orbital and the ion exchange in Bentonite sheets. This affects the activation energy of the reaction.

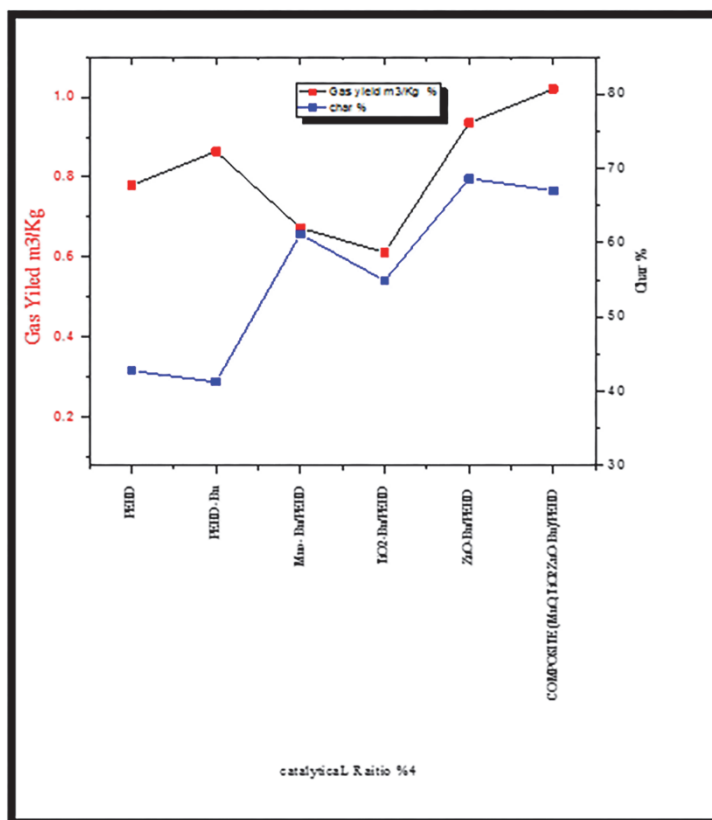


Figure (8). Effect of modified catalysts on gasification of PEHD at 750 °C for 1 hour

3.3.2 Gasification Process on Waste Polyethylene High Density

Figure (9) explains the gas yield and char components resulting from the degradation of polyethylene high density waste. from results, also, we noticed composite catalyst gave better results than the others at the same reaction conditions. Meanwhile, noticed the ZnO/Bn> MnO/Bn> TiO₂ /Bn for gas yield

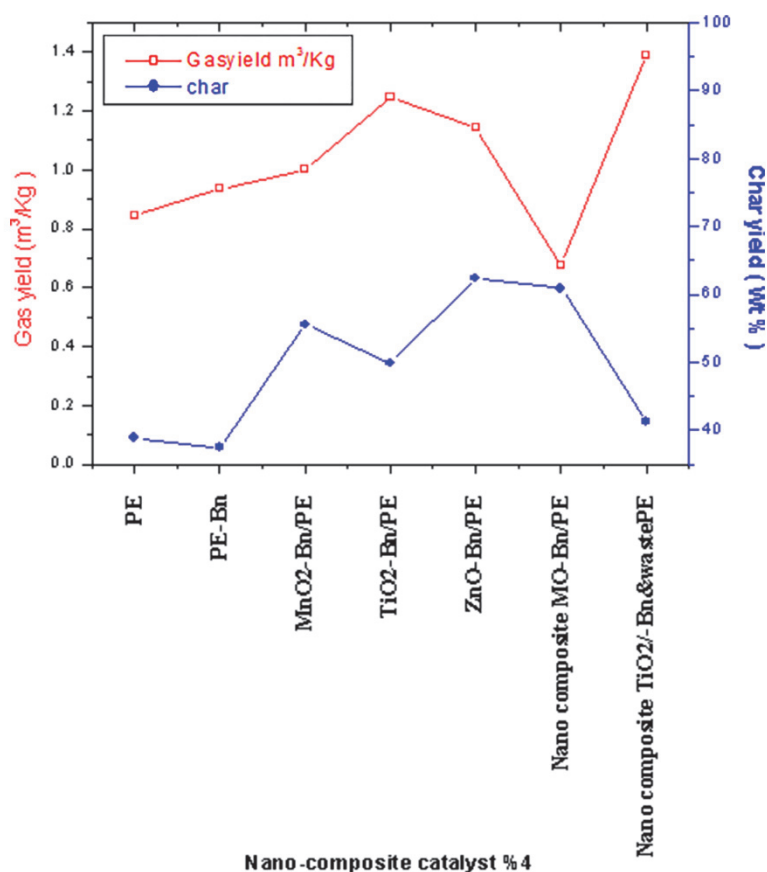


Figure (9). Gasification of Waste PEHD at optimize reaction conditions

3.3.3 Gasification of Different Types Plastic Waste

when, we applied the same optimize condition (reaction time for one hour, loading catalyst is %4 and temperature is constant at 750 °C) on degradation of different sorts of plastic waste like (PELD, PP, PVC, PS,) we get less quantities of (gas yield and char) comparing to virgin PEHD.that is shown in figure (10), might be due to contamination of different plastic, or there wasn't complete conversion for plastic at those parameters (temperature, reaction time and loading catalyst).

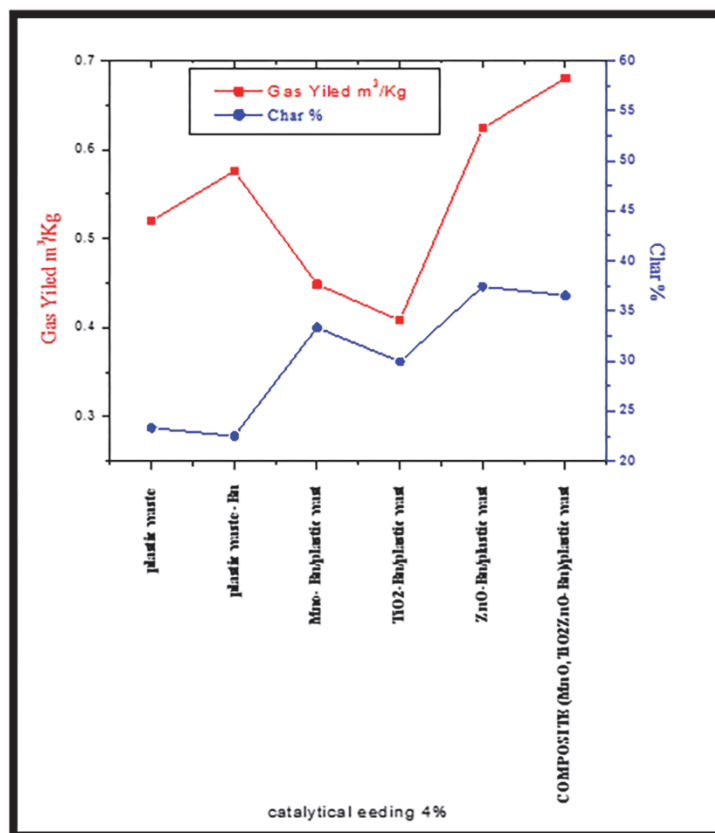


Figure (10). Gasification of Different sorts plastic Waste at optimize reaction conditions.

3.4 Characterization of Gas Yield Distribution, Products of Gasification PEHD and Waste

3.4.1 GC Analysis for PEHD Gas Yield Distribution Products

Char and gas samples resulting from the degradation of plastic waste at different conditions during the gasification process were analyzed by a variety of characterization techniques at the Central Analytical Laboratories of National Research Centre in Egypt. One technique used was elemental analysis (CHNSO elemental, Vario EL III). Gaseous products were analyzed using a Gas Chromatograph (VARIAN model CP-3800) at the Egyptian Petroleum Research Institute (EPRI) in Egypt.

On the other hand, analyzing the gases resulting from the degradation of plastic using GC, many components were detected such as aromatic, light olefin, methane gas, CO, CO₂, and H₂ as shown in table (1). Thus, modified catalysts play an important role not only in gas yield quantity but also in the quality of product. The creaking process (catalytic process) occurred with different catalysts. This demonstrated positive results reforming with different quantities of gas product. The main product in the gasification process is **Methane** that can be used as a source of energy.

Table (1) Major product distributions for the gasification process of PEHD and its waste at 4%. at different modified catalytic at 750 °C and a reaction time of 1hour.

(Mol. %)	Without catalyst	With catalyst 0.4 wt%					
		Bn	Bn/TiO ₂	Bn/MnO	Bn/ZnO	Composite TiO ₂ ,MnO ₂ ,ZnO/Bn & PEHD	TiO ₂ ,MnO ₂ ,ZnO/Bn &waste PEHD
Methane	83.41	83.29	85	88.91	89.7	96.34	89.55
Hydrogen	0.88	2.61	4.87	1.53	0.63	2.93	0.001
Benzene	0.95	0.85	0.04	0.23	0.27	.004	0.23
Carbon Dioxide	2.37	3.5	4.92	2.70	2.89	0.22	0.16
Nitrogen	3.2	3.12	0.58	0.44	0.83	0.17	3.6
Ethane	4.56	1.75	0.59	4.21	4.03	0.08	4.5
Carbon Monoxide	3.4	3.89	3.47	0.96	0.42	0.20	1.18

The best methane ratio is 96.34 by **TiO₂, MnO, ZnO/Bn & PEHD** compared to 83.4 **Bn without**. We obtained an excess amount of Hydrogen (4.87) as given by the **Bn/TiO₂** catalyst in fig-10. that is can be used in fuel cell in future studies, prove that ,the activity of TiO₂/Bn which can make a coordination bond with the ligand and result in many products through the gasification process, such as Benzene, CO and char.

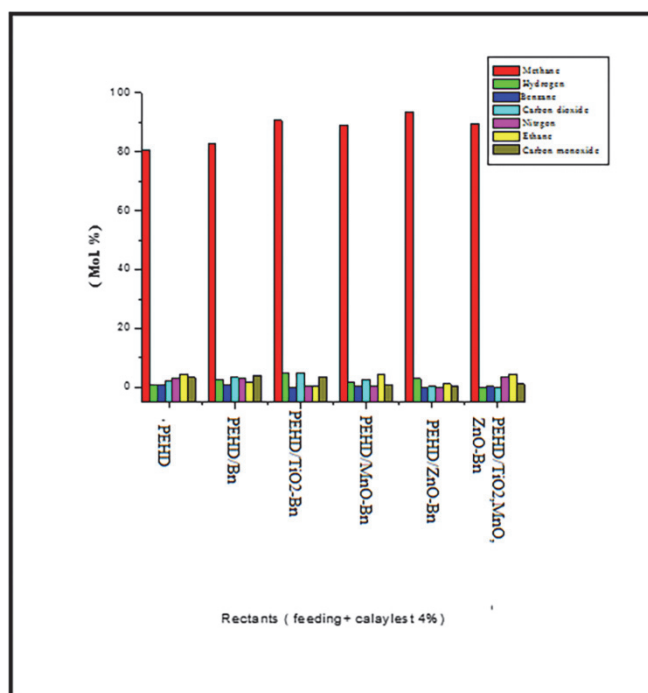


Figure (10). Product distribution of gasification of PEHD using different modified catalysts at 750 °C for 1 hour

3.4.2 GC Analysis Gas Yield Distribution Products Resulting from for Gasification of Different Plastic Waste (PW) when analyzing the sample results for the gasification of degradation of different plastic waste (PW), we got good results but they are less than in the virgin PEHD and its waste. This is explained in table -2. There is a high ratio of methane gas from plastic waste according to Bn(TiO₂) >Bn(ZnO)> Bn(metals oxides) >Bn(MnO)> Bn.

Table (2) Major product distribution for the gasification process of plastic waste (PW) at 4% at different modified catalytic at 750 °C and a reaction time for 1hour.

(Mol. %)	WP	With catalyst 0.4 wt%					
		Bn-WP	Bn-TiO ₂ / WP	Bn/MnO/ WP	Bn/ZnO/ WP	CompositeTiO ₂ ,Mn O,ZnO/Bn & WP	Composite TiO ₂ ,MnO ₂ ,ZnO/Bn & Waste plastic
Methane	80.41	82.94	90.6	88.91	89.7	93.63	89.55
Hydrogen	0.79	2.61	1.24	1.53	0.66	2.88	0.001
Benzene	0.95	0.88	0.06	0.23	0.34	0.05	0.23
Carbon Dioxide	3.15	3.6	3.88	2.70	2.90	0.22	0.16
Nitrogen	3.6	3.4	3.06	0.44	0.86	0.17	3.6
Ethane	4.5	1.82	0.55	4.21	4.06	1.08	4.5
Carbon Monoxide	3.4	3.89	3.47	1.01	0.82	0.22	1.18

Also, comparing other components of gases (H₂, Benzene), we found a great ratio with the modified catalyst. In addition, there was less amount of CO and CO₂ which shows that there was complete conversion of plastic to gas (Levine and Broadbelt (2009) and Kannan et al. (2014).Figure (10): Product distribution of gasification of PEHD using different modified catalysts at 750 °C for 1 hour.

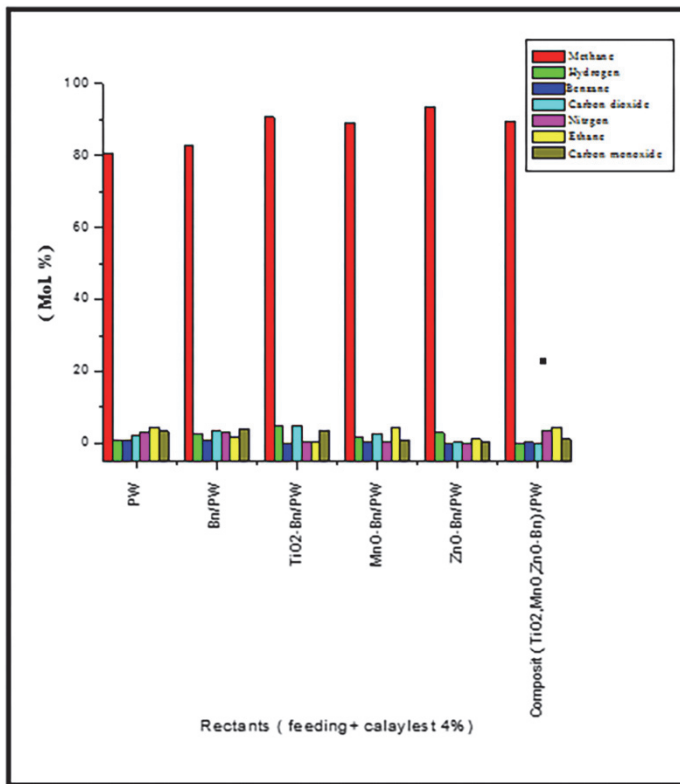


Figure (11). Product distribution of the gasification of waste plastic (PW) using different modified catalysts at 750 °C for 1 hour

3.5 Characterization of the Char Resulting of Gasified PEHD.

3.5.1 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) was used to illustrate the surface morphologies of the prepared samples. The surface morphologies of the char product in Fig-12 showed irregular and sharp-edged properties (W. D. KELLER et al 1986). The char exhibited porous and textural structure characteristics. The char consisted of small, relatively uniform particles and each particle was smooth and compressed. The surface morphologies of the char contained modified Bentonite composite as shown in Fig-12. A significant difference in morphology can be seen for the char. The char’s surface was smooth and compact. No obvious pore structure were found in the char’s surface, which might be attributed to the agglomeration and melting during the gasification of plastic. which manifest by EDAX analysis.

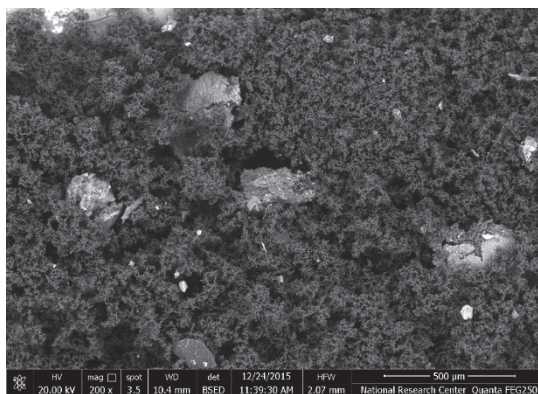


Figure (12). SEM image of the char sample gasification of polyethylene high density at 750 °C for 1 hr.

3.5.2 Energy-Dispersive X-Ray Spectroscopy (EDX)

(EDX) confirmed the results of SEM. by analysis char sample which resulted from the gasification process. After analyzing the sample, it was clear that it has the same chemical composition of modified bentonite seen in fig-13. This proves that the new modified catalyst has good and maybe more stability in high temperatures like 750 °C.

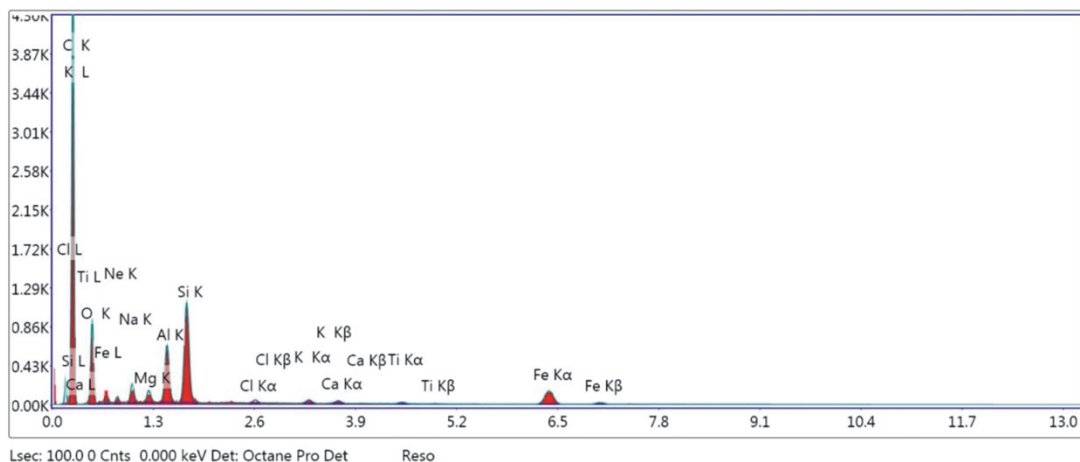


Figure (13). EDAX of catalytically pyrolysis HDPE Char with modified composite bentonite

3.5.3 Elemental Analysis

Proximate and ultimate analysis of virgin HDPE. The proximate and ultimate analysis of the virgin PEHD sample before and after the gasification process (char sample) is shown in Table (3). First, in the sample before gasification, the volatile matter is 100% in the proximate analysis. Due to the negligible percentage of ash in the virgin HDPE sample, its degradation occurs with minimal residue formation. The oxygen is 2.51% in the ultimate analysis of virgin HDPE. The nitrogen and oxygen in the virgin PEHD sample may not be due to the fillers but because of different components added during the fabrication of PEHD. Also, we can refer to Table (3) which illustrates the comparison between the proximate and ultimate PEHD **after** the gasification process. The ratio element H, C, N and S composition compounds were completely changed. Due to many factors, one of them is modified composite during of gasification process. On the other hand, this demonstrates conversion of PEHD due to the large quantity of C% transformed during the gasification process. Furthermore, H% changed from 14.1% to 3.45% which confirmed the complete conversion process for PEHD during the gasification process.

Table (3). Proximate and ultimate analysis of PEHD before and after the gasification process

Proximate analysis (wt%)		Elemental composition (wt% on dry ash free)				
Volatile matter	ash		C	H	N	S
96.83	3.17	Before gasification	85.7	14.1	0.0	0.0
		After gasification	63.05	3.45	1.058	Nil

4. Discussion.

Through our experiment, we noticed many important points which open the door for researchers in the future. Metal transition is variable oxidation states that means make coordination compounds (complexes) and organometallic compounds is easier than other elements in addition to increase the surface area of reaction and decrease activation energy of reaction. Further, we used three different metal oxides (TiO_2 , MnO and ZnO) which ARE subdivided into groups - D (different electronic configurations for each element) and explain how made chelating complex with clay (geo-polymer).

In addition, reactor design and setting up for pyrolysis and gasification process in add to choose the ideal parameters (reaction time, temperature and catalyst ratio). Optimized parameters gave good results for converting plastic waste and plastic PEHD to fuel. Also, we approached many scientific points like the reaction mechanism poly ethylene high density on gasification process with studying the effect of Nano transition metals oxides in modification clay through better results than using Bentonite without any additives.

Nano clay composites gave a gas yield (CH_4) and other light components is higher than other using modified catalysts. On the other hand, catalysts like MnO_2/Bn gave a higher amount of Hydrogen than other catalysts. Also, there were excellent results with TiO_2/Bn and different types of plastic (PEHD and Waste). One important thing is that ideal parameters for that reaction are the temperature at 750°C and reaction time not more than one hour. This helps to get a higher yield of light olefins, methane, Hydrogen and aromatic compounds. Furthermore, the catalyst also affects single-ring aromatic compounds by increasing their yield when this variable is increased. Also, the heating rate had a lower effect on the activation energy in our conditions. The heating rate does not significantly affect the char production although the char content tended to be less with a high heating rate. The gas yield ratio with the virgin PEHD is higher than other waste plastic. Although the reaction conditions are the same, may be return to some additive or contamination which has a great effect on the reaction mechanism of new composite catalysts. The results from different plastic waste is lower than virgin PEHD.

All in all, energy recovery from waste (renewable source) is enough to use in energy generation. beside to gasification or pyrolysis process is a good way to get rid of massive solid waste which takes hundred years to decay. The landfill process also has a negative impact in underground water in future and incineration is the main reason for carbon dioxide emission and climate change.

Using new modified materials is one of the most sustainable resources for converting plastic waste to fuel (source of renewable energy). In addition, it reduces the cost of production in the petroleum refining industry. The discussion includes different types of clay and clay-modified catalysts. The mechanism and results will open new opportunities for applying geopolymers in different fields.

Applying modified catalysts on a high temperature has many advantages. First, the thermal and catalytical cracking of polymers occur in high temperatures. It's also easier for condensed gas to flow in the pipeline, better than tar or asphalt (the result at a low temperature) which plugs the pipeline. This is a big problem in the production process. Also, we take into consideration the reaction time which verses proportion with temperature (increase activation energy of reaction). On the other hand, the modified catalyst carried out at a high temperature or 750°C is the ideal temperature for a reaction with a time of 1 hour for the complete conversion of plastic to gas. This means it has stability and strong coordination bonds in composition.

Getting a good product distribution from plastic waste (low-value energy) with a modified catalyst to a high energy value like Methane is a high ratio. Hydrogen and other hydrocarbon compounds.

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