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Thermal conversion of waste polyolefins to the mixture of hydrocarbons in the reactor with molten metal bed

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ABSTRACT

Energy crisis and environmental degradation by polymer wastes have been imperative to find and propose technologies for recovery of raw materials and energy from non-conventional sources like organic wastes, plastic wastes, scrap tires, etc. A variety of methods and processes connected with global or national policies have been proposed worldwide. A new type of a tubular reactor with the molten metal bed is proposed for conversion of waste plastics to fuel like mixture of hydrocarbons. The results of the thermal degradation of polyolefins in the laboratory scale set-up based on this reactor are presented in the paper. The melting and cracking processes were carried out in a single apparatus at the temperature 390–420 °C. The problems with: disintegration of wastes, heat transfer from the wall to the particles of polymers, cooking at the walls of reactor, and mixing of the molten volume of wastes were significantly reduced. The final product consisted of gaseous stream (8–16 wt% of the input) and liquid (84–92 wt%) stream. No solid products were produced. The light, "gasoline" fraction of the liquid hydrocarbons mixture (C_4–C_{10}) made over 50% of the liquid product. It may by used for fuel production or electricity generation.

1. Introduction

Waste plastics contribute to great environmental and social problems due to the loss of natural resources, environmental pollution, depletion of landfill space on the one hand and demands of environmentally-oriented society on the other hand.

Production of plastics in the world amounted to about 230–250 million tones in 2005 (only in the EU to about 45–50 million tones) [1,2]. Similar data may be given for other developed countries, the USA, Japan and China. In Japan, the consumption of plastics amounted to more than 10 million tones/per year in 2004 [3] and in China rose from 23 (in 2000) to 31.2 million metric tons in 2003, with an average annual growth rate of 11.8% [4]. In Poland, plastics consumption (without chemical fibers) exceeded 1.67 million tons in 2007 and over 75% of them were polyolefins [5]. The consumption of plastics per capita differs very much in the world even in developed countries; in Europe the consumption of plastics was about 24–150 kg/person in the years 2003–2005 while 10 years earlier the average consumption in the EU had been about 50–60 kg/person [2,6]; in Poland it was about 45 kg/person in 2007 [5]. The amount of post-consumer plastics was estimated for 22–25 million tones only in EU, in 2005 [2,6]. They represent only 7–9% of total wastes in terms of mass but 30% in terms of volume (in household wastes). Their amount has been increasing 6–7% year by year and will be increasing due to low consumption of plastics in developing countries [1,7,8]. The main part (over 70% by mass) of household waste plastics stream are polyolefins (LDPE, HDPE, LLDPE, PP), and polystyrene (PS).

At present, it is almost impossible to dispose of waste plastics by landfill due to the law, high costs, and higher ecological consciousness of people. However, there are also some technological and economic constrains that limit the full and efficient recycling of plastic wastes into useful products, e.g. contaminated waste plastics can be only partly recycled into new products and reuse of packaging containers is limited by the collection systems.

Mechanical recycling that probably is the best way of reclaiming plastics refers to the processes which involve sorting, shredding or melting and re-granulation. It may be applied only for the same type and clean plastics.

Up to the present moment, energy recovery by incineration has seemed to be the second attractive option for waste plastics utilization that takes advantage of the high energy content of plastics and reducing the garbage volumes by over 90%. However, sometimes, it was questioned due to the lack of raw materials recovery, the low thermodynamic efficiency, the possible emission of toxic gaseous compounds and necessity of purification of flue gases that is difficult and expensive. Even though, current technologies would conform the emission requirements, incineration arouses almost always public resistance and objections [2,9,10].

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Feedstock recycling by thermal and chemical methods of conversion of scrap polymers, as gasification, liquefaction, liquefaction with hydrogenation, hydrolysis, pyrolysis, and thermo-catalytic degradation, are well known and environmentally accepted. They reduce the impact of waste plastics on the environment and may be a cheap source of energy and useful raw materials. These methods have overcome a long way from the scientific idea to the industrial technologies. Numerous scientific papers presented different problems that have been investigating. They concern selectivity, productivity, kinetics of the degradation processes, selection of the catalyst, methods of degradation, types of the rectors, etc. Generally, the processes are based often on thermal and catalytic cracking or pyrolysis in batch, semi-batch, vessel and tubular reactors. The yields of liquid, gaseous and solid products obtained via pyrolysis/cracking of plastic wastes depend on many parameters such as composition of the wastes mixture, temperature, type of catalyst, residence time in the reactor, type of the reactor and type of the process (multistage or single stage, in gas or liquid phase with a solvent), and heating rate. Typical pyrolysis may have some disadvantages. One of them and probably most important one is cooking that may occur at the walls of the reactors. It decreases the yield of the liquid product, makes heat transfer difficult, and cause necessity of frequent cleaning of the reactor. Therefore stirring is demanded due to continuous removing of the molten polymer layer from the wall of the reactor. The catalytic process has also disadvantages. Though, catalysts may decrease the temperature of the process, change the selectivity and the composition of the products, they give more gas product, the catalysts are quickly deactivated and recovering and regeneration of them is not easy. It may increase the costs of the process. Many researchers and inventors propose fluidized-bed reactors due to their advantages – difficulties with the mixing of the wastes, removing of the coke, regeneration of the catalyst, and heat transfer resistance may be solved and/or reduced in an easy way. However, the fluidized-bed reactors may be profitable probably only in large industrial-scale plants due to the investment costs.

The investigated heterogeneous catalysts are based often on zeolites [1–3,10,11]. Sometimes (but rare), other chemical compounds and even spent industrial catalysts are also proposed for industrial processes [12–14]. Homogeneous catalysts are mostly based on classic Lewis acids, e.g. aluminum trichloride [1,2].

Laboratory investigations of utilization of post-consumer polymers have been also performed for: vacuum pyrolysis, microwave pyrolysis, decomposition in supercritical water or oxidation in thermal plasma. New solution in construction of the reactors is a "free fall" reactor for running flash pyrolysis [1,2,9,10,15].

At least, 30 commercial technologies were available for thermal degradation of post-consumer plastics, based on pyrolysis or catalytic cracking, to fuel like liquid mixture of hydrocarbons as basic product [1,2,9–16]. They were usually carried out at temperature 350–430 °C. However, the industrial plants are rare or have been running for a very short time. It means that proposed reactors and technologies were imperfect and their profitability was weak. The unfavorable situation of feedstock recycling of waste polymers is mostly based on the high investments costs of recycling, necessity of frequent cleaning of the reactor, costs of catalysts and other economic circumstances, e.g. taxes. During the period 2004–2006, over 30 small industrial plants were built in Poland and waste plastics were liquefied with the yield of 70–80% (for the liquid product). The processes were based on three different technologies that exploited thermal or thermo-catalytic cracking. All of them were closed due to decreased profitability during 2007. Therefore, searching for new technologies and reactors is strongly recommended. The new technologies (and reactors) should have following features:

- Low operating costs and investments costs are needed because the plastics, waste plastics, the products of degradation are not expensive and running of the conversion process has to be profitable for investors.
- The process should be carried out without catalysts due to difficulties and cost of their recovering.
- The yield of liquid product should have been high as it is usually more valuable than gaseous product.
- Frequency of cleaning of the reactor has to be low.
- The heat transfer resistance between particles of wastes and heating medium should be minimized.
- Cooking process should be minimized or even eliminated.
- The plant in the industrial scale should have modular construction. It allows for greater flexibility and enables construction of small or large plants with almost the same profitability. In some local and economical conditions, small plants may be more profitable and in other larger industrial plants will be more efficient (e.g. if it be constructed in the area of oil refinery plant).

There are also technologies carried out in molten metals or molten inorganic salts. Waste plastics may be:

- gasified in the temperature – about 1300 °C to hydrogen/synthesis gas as via *Hydromax® Technology* proposed by *Alchemix Corporation* [9,17],
- decomposed to simple inorganic compounds, by *Molten salt oxidation* (MSO) [18],
- converted to the mixture of monomers or mixture of simple hydrocarbons via process based on thermal degradation of wastes in molten metal or on the surface of it [9,19].

The process carried out in molten metal (called sometimes "*Clementi Process*") is performed beneath 600 °C and used metals are: tin, lead and bismuth or the alloys of them. Gaseous product consists of light hydrocarbons (C_1–C_6) and liquid product is the mixture of C_4–C_{24} hydrocarbons. Several reactors, based on this method, were patented [e.g. 20–22]. Up until now, the reactors have been constructed as basin reactors with low height of the molten metal layer. Scrap polymers are put on the surface of it or into the bed and then transported horizontally in the molten metal along the reactor to the output. During transporting, wastes are melted and thermally decomposed to the mixture of hydrocarbons.

A new type of the tubular reactor [23] with the molten metal bed is proposed for conversion of waste plastics to the valuable product – the (fuel like) mixture of hydrocarbons. The results of the preliminary investigations of thermal degradation of polyethylene and polypropylene in this type of the reactor are presented in the paper.

2. Experimental

2.1. Materials

Thirteen kilograms of the alloy consisted of tin and lead were used to create molten metal bed. The properties of the alloy are presented in Table 1.

Table 1
The composition of the alloy used in the process.

Fraction of tin (wt%)	59–61
Fraction of lead (wt%)	38–40
Fraction of impurities (wt%)	1
Specific gravity (g/cm^3)	8.5
Melting temperature (°C)	183–185