FEEDSTOCK RECYCLING OF WASTE POLYMERS BY THERMAL CRACKING IN MOLTEN METAL – THERMODYNAMIC ANALYSIS OF THE PROCESS

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Abstract

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. Feedstock recycling of scrap polymers by thermal and chemical methods are well known and environmentally accepted. The paper presented results of thermodynamic analysis of the process conversion of polyolefins to fuel like mixture of hydrocarbons by thermal cracking in a new type of the tubular reactor with molten metal. Evaluation of the efficiency of the process was based on exergy calculations. The calculated exergy efficiency was equal to 80%. It means that feedstock recycling of the wastes is the better process from the energetic and ecological point of view than other processes, particularly incineration of them.

Keywords: *plastic wastes, thermodynamic analysis, exergy, pyrolysis, thermal cracking*

1. Introduction

Feedstock recycling of scrap polymers by thermal and chemical degradation are well known and environmentally accepted. These methods have overcome a long way from the scientific idea to the industrial application. 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 [1,2]. However, the industrial plants are rare. It means that the proposed solutions were imperfect and their profitability was weak. The unfavorable situation of feedstock recycling of waste polymers was mostly based on the high investments costs, necessity of frequent cleaning of the reactor, costs of catalysts and other economic circumstances e.g. taxes. The paper presents the results of the study of conversion of waste polyolefins to the liquid mixture of hydrocarbons that was performed by thermal cracking in a new type of the tubular reactor with molten metal. The construction of this reactor differs from the known basin reactors that have been patented until now. The final product consists of gaseous stream (8-16 weight % of the input) and liquid (84-92 weight %) stream. The light, “gasoline” fraction of the liquid hydrocarbons mixture (C4-C10) made over 50% of the liquid product. The obtained results indicate that thermal degradation may be in some cases also as good as catalytic cracking and the method makes possible obtaining the high quality liquid product with good yield of it and good selectivity for “gasoline” and “diesel” fractions. Based on the laboratory experiments, a pilot-scale plant was proposed for feedstock recycling of waste polyolefins to fuel like mixture of hydrocarbons or electricity power. The thermodynamic (based on exergy calculations) analysis was also performed for the process to show its energetic efficiency.

2. Methods

The first law of thermodynamics states that for every process, no energy can disappear or be created; the second law notes that the quality of energy decreases. This quality, expressed as “useful energy”, is called exergy. Exergy is the maximum amount of work that can be obtained from a material, taking into account the state of the surroundings [3, 4]. The loss of exergy is linearly related to the entropy generated in the process. Every product is useful, and waste can be seen as potential resources as long as it has exergy content. A number of environmental indicators can be defined for evaluation of energy efficiency of the processes and assessment of the impact of them on the environment. However, it seems that indicators based on thermodynamic considerations based on exergy, can illustrate whether a development is sustainable in the best way. The basic principles of the methodology used to assess the impact of industrial processes on the environment and their energetic efficiencies are discussed in many articles [3, 5]. This type of analysis is used also for the evaluation of the recycling method of wastes. This paper presents a simplified assessment of the feedstock recycling process for waste polyolefins using thermal degradation and conversion to a fuel-like mixture of hydrocarbons.

The description of the laboratory set-up and the results of the laboratory thermal degradation of waste polyethylene and polypropylene can be found in a previous study [6]. The yields of gaseous and liquid products and their composition indicate that the proposed reactor and method of scrap polyolefin degradation meets all demands for profitable technology. Over 90% of waste polyolefins may be converted into a liquid product. The light (i.e., “gasoline”) fraction makes up 50 to 70% of the liquid product. The fraction of light waxes is below 18% for polyethylene (PE) degradation and below

10% for polypropylene (PP) degradation in liquid products, which means that the liquid product is very useful as a raw product for fuel production. No solid product (i.e., coke) was obtained from the laboratory experiments for the degradation of pure plastics. However, impurities that are usually present in genuine waste of polymers may cause cooking, and a small amount of the solid product consisting of mineral impurities and coke may be obtained during the conversion of this type of wastes. The experimental results were used to design pilot-scale experiments and create a mass balance for them

Exergy analysis was performed for the pilot-scale reactor, in which 50 kg/h of genuine polyethylene (PE) wastes would be utilized by thermal degradation. Hot flue gases from gasification of the biomass are the source of the heat demanded to waste plastic degradation. It was assumed that 28 kg/h of sawdust (11.7 kJ/kg) is gasified in the gasifier and combusted to continue this process. Combustion of the recycled gas product is a supplementary source of energy. Water is required for cooling of the liquid product and to the scrubber for purifying flue gases. Electric power is also needed: for the waste and sawdust feeders, fans, water and product pumps, control and acquisition data systems and the lighting system. The experimental reaction rate of the degradation process was between 951 and 9183 kg/(m^3h). The reaction rate in the pilot plant was assumed to be 2877 kg/(m^3h). Assessment and calculation of the exergy efficiency of the process were based on the following assumptions:

1. no mechanical disintegration of the waste was performed, as no additional energy was needed,
2. generally, the total exergy of the stream is the sum of kinetic exergy, potential exergy, nuclear exergy, physical (or termomechanical) exergy and chemical exergy, but only chemical and physical exergy are taken into account,
3. the reference state was T=298.15 K and P=0.101325 MPa,
4. the calculations of physical exergy were based on standard values of enthalpy and entropy,
5. the chemical exergy of the sawdust, the wastes and coke was calculated using the higher heating value of the components,
8. the exergy of electricity was equal to energy power,
9. the exergy of SO_2, NO_x, construction materials, labor and capital was not considered.

3. Results and Discussion

The exergy efficiency of the described process was calculated for two case studies, resulting in 79.9% for the first one, in which the liquid mixture of hydrocarbons (C4-C24) was the required product and 81,9% for the second one, in which the electricity power was generated using total product – mixture of hydrocarbons ((C4-C24) without condensation of them. The true efficiency may not be so high after including the exergy of the construction materials, labor and capital. However, it should be higher than the efficiency of incineration processes for waste plastics, which usually have efficiency levels ranging from 25 to 35%.

4. Conclusions

The method for the thermal decomposition of PE or PP in a molten metal bed is a promising process as compared with catalytic cracking in vessel reactors using a stirrer or tubular flow reactors. In the proposed method, no catalyst and no stirring are needed. Over 90% of scrap polyolefins may be converted into a liquid product.

The exergy efficiency of the process is high, which means that thermal cracking is a more valuable technology than the incineration of waste plastics. In this context, gasification of this type of waste may be the only process that is more environmentally friendly

The well-known technologies for utilizing waste plastics, particularly incineration, produce high levels of entropy and require a great deal of attention. At present, there are numerous better options to use and recycle waste and waste energy. Depending on local conditions, each specific situation requires the selection of the best technology that takes into account several implications, such as ecological, social, economical, legal and technical consequences. The best way to assess and compare different technologies for waste utilization may be performed through thermodynamic (that is, exergy) analysis because many of these implications can be taken into account. The application of exergy analysis to account for the amount of raw materials and waste used to produce energy is effective in screening alternative technologies for sustainable development. This allows us to identify targets for direct or indirect waste recycling with respect to a single industrial process and for the waste management system at the national level.

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