



A critical evaluation on chemical exergy and its correlation with high heating value for single and multi-component typical plastic wastes

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ABSTRACT

Chemical exergy of plastic waste is very critical for the optimization design of its thermochemical conversion system. The chemical exergy of six kinds of typical plastic wastes was calculated. The linear relationship between chemical exergy and high heating value for the samples was identified. The universal set of simulated multi-component plastic wastes was divided into five subsets based on the number of the components. The sample set was generated from five subsets by using the systematic sampling. Based on the sample set, the above linear relationship was validated for evaluating the chemical exergy of multi-component plastic wastes. The developed model had a good ability on predicting the chemical exergy of multi-component plastic wastes with a low error of less than 5%. This model required only the input of high heating value, which can be directly examined for the multi-component plastic wastes with unknown components. This study could provide a simple and effective tool for the evaluation of chemical exergy of multi-component plastic wastes.

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1. Introduction

Plastic products are playing an important role in the production activities and daily life of human beings due to their diversity, low density, and durability and resistant to corrosion [1]. All kinds of plastics have been widely used in many fields, such as construction, medicine, engineering, automation, aerospace, electronics product, packaging, food industry, and so on [2]. Large-scale application of plastic products must produce a large number of plastic wastes, which can bring a serious challenge for plastic waste management. The inadequate disposal of the plastic wastes may cause serious environmental problems and can lead to the loss of valuable resources [3]. Plastic waste treatment methods include landfill,

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recycling, incineration, thermochemical treatment [4]. The direct landfill of the plastic wastes is a simple and rough treatment way, which occupies a huge space and causes the damage of soil environment [5]. Incineration may produce greenhouse gases and some toxic pollutants such as polychlorinated dibenzo para dioxins and polychlorinated dibenzo furans [6]. Recycling technique is an alternative method for managing plastic waste, which can weaken the environment contamination [5]. Thermochemical treatment technology is considered as a promising recycling technology, in which the pyrolysis oil or syngas produced can be used as chemical raw materials in many chemical processes including Fischer-Tropsch synthesis, methane synthesis, and hydrogen production. In addition, thermochemical reaction occurring in an oxygen-free or oxygen-deficient atmosphere can hinder the generation of toxic substances. Assessing the energy utilization of thermochemical reactors is a very important task for its high-efficiency performance.

The assessment standards of energy utilization performance should include energy and exergy efficiency. Compared to the conventional energy analysis, exergy analysis including the quantity and quality of energy is a comprehensive index for assessing the chemical reactors due to its ability to identify irreversible

processes [7,8]. In addition, some extended exergy analyses including the exergoeconomic and exergoenvironmental analyses are used to evaluate sustainability aspects of chemical processes [7,9].

The assessment on the exergy efficiency of chemical processes is carried on based on the values of physical exergy and chemical exergy of the feedstock [10]. The chemical exergy of organic matter is a key part in its total exergy due to the fracture and reorganization of many chemical bounds. Some work about the assessment of chemical exergy of organic matters including biomass and coal has been carried out. Huang et al. [10] evaluated the chemical exergy of agricultural biomass, and developed a neural network prediction model based on its elemental compositions. Bilgen and Kaygusuz [11] calculated the chemical exergy of coal-based fuels, and pointed out that the elemental composition has a significant effect on the chemical exergy of the fuel, and that higher water content or ash content can result in smaller chemical exergy. Bilgen et al. [12] calculated the chemical exergy of liquid products from catalyzed pyrolysis of biomass, and noticed that the high oxygen content in the liquid product leads to the low chemical exergy. Song et al. [13] assessed the chemical exergy of liquid and solid fuels, and noted that the chemical exergy of inorganic materials is far less than that of organic materials. Gharagheizi et al. [14] established a simple functional group contribution model to predict the chemical exergy of organic matter, and concluded that the model is sensitive to hydrocarbon, nitrogen, oxygen, and sulfur compounds. Zhang et al. [15] addressed the chemical exergy of lignocellulosic biomass, and identified the relationship between ash exergy and ash content, and the relationship between chemical exergy and high heating value or low heating value. Gharagheizi and Mehrpooya [16] developed a quantitative structure-property model to predict the standard chemical exergy based on the molecular descriptors. The model is feasible for regular organic substances, but it is useless for high molecular polymer. The above developed calculation models have been used in the exergy optimization of some chemical processes [17–19], but they are actually unsuitable for plastic waste due to the difference between their chemical structures. Usually, the calculation model of chemical exergy for other matters is directly used in the exergy analysis on the thermochemical conversion of plastic waste. The inappropriate application may affect strongly the evaluation accuracy of exergy efficiency.

The purposes of the present work are to seek out reliable chemical exergy of typical plastic wastes, and to develop a robust model for predicting the chemical exergy of multi-component plastic wastes. Standard chemical exergy of plastic wastes was calculated based on the thermodynamic theory. The relationship between chemical exergy and heating value of the samples was further identified, which was also extended to determine the chemical exergy of multi-component plastic wastes.

2. Materials and methods

2.1. Plastic samples

Typical plastic wastes consist of polystyrene (PS), high density polyethylene (HDPE), low density polyethylene (LDPE), polypropylene (PP), polyethylene terephthalate (PET), and polyvinyl chloride (PVC), whose molecular structures are shown in Fig. 1.

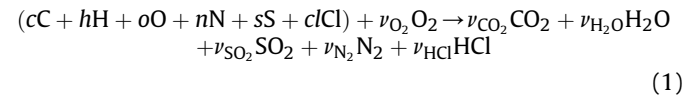
Proximate analyses, ultimate analyses, and HHVs of six typical plastic wastes are listed in Table 1.

From Table 1, the volatile matter contents of PS, HDPE, LDPE and PP exceed 99%, while PET and PVC consist of volatile matter and fixed carbon. For the elemental analysis, PS, HDPE, LDPE and PP are mainly composed of carbon and hydrogen. The PET is composed of carbon, hydrogen and oxygen. The PVC is composed of carbon,

hydrogen and chlorine. The heating values for some samples are absent, but the heating value for each plastic waste is relatively stable. Therefore, their average value is treated as a valid value.

2.2. Standard chemical exergy

Chemical exergy of a sample is equal to the maximum amount of work obtained as it is close to chemical equilibrium with reference substances. According to the definition of chemical exergy, the standard molar chemical exergy of the sample is approximately equal to the standard molar Gibbs free energy of formation. Reference substances of C, H, O, N, S and Cl elements in plastic samples are carbon dioxide (CO₂), water (H₂O), sulfur dioxide (SO₂), nitrogen (N₂) and hydrogen sulfide (HCl). Conversion of the sample into reference substances can be expressed as:



where c , h , o , n , s and cl refer to the molar number of C, H, O, N, S and Cl in per kg sample (dry ash free basis). The molar numbers of all the products are calculated by:

$$\nu_{CO_2} = c \quad (2-a)$$

$$\nu_{H_2O} = \frac{1}{2}(h - cl) \quad (2-b)$$

$$\nu_{SO_2} = s \quad (2-c)$$

$$\nu_{N_2} = \frac{1}{2}n \quad (2-d)$$

$$\nu_{HCl} = cl \quad (2-e)$$

$$\nu_{O_2} = c + \frac{1}{4}(h - cl) + s - \frac{1}{2}o \quad (2-f)$$

The standard molar chemical exergy of the sample can be expressed as [10]:

$$\bar{e}_F^{ch} = -\Delta G + \nu_{CO_2}\bar{e}_{CO_2}^{ch} + \nu_{H_2O}\bar{e}_{H_2O(l)}^{ch} + \nu_{N_2}\bar{e}_{N_2}^{ch} + \nu_{SO_2}\bar{e}_{SO_2}^{ch} + \nu_{HCl}\bar{e}_{HCl}^{ch} - \nu_{O_2}\bar{e}_{O_2}^{ch} \quad (3)$$

where \bar{e}^{ch} is the standard molar chemical exergy (kJ mol⁻¹), ΔG the molar Gibbs free energy of formation (kJ mol⁻¹), which can be given as:

$$-\Delta G = \Delta H - T_0\Delta S \quad (4)$$

where ΔH is the enthalpy change (kJ mol⁻¹), ΔS the entropy change (kJ K⁻¹mol⁻¹), T_0 the reference temperature (K).

In addition, the enthalpy of the sample can be approximately equal to the high heating value at the standard state. Therefore, Eq. (3) can be replaced with [10]:

$$e_F^{ch} = HHV - T_0 \left[S_F + \nu_{O_2}S_{O_2} - \nu_{CO_2}S_{CO_2} - \nu_{H_2O}S_{H_2O(l)} \right] - \nu_{N_2}S_{N_2} - \nu_{SO_2}S_{SO_2} - \nu_{HCl}S_{HCl} + \nu_{CO_2}e_{CO_2}^{ch} + \nu_{H_2O}e_{H_2O(l)}^{ch} + \nu_{N_2}e_{N_2}^{ch} + \nu_{SO_2}e_{SO_2}^{ch} + \nu_{HCl}e_{HCl}^{ch} - \nu_{O_2}e_{O_2}^{ch} \quad (5)$$

where S_i is the standard entropy of pure substance (kJ K⁻¹kg⁻¹), S_F the standard entropy of the plastic sample (kJ K⁻¹kg⁻¹). The HHV

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