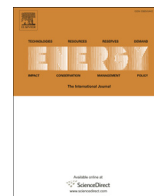




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A group contribution method for determination of the standard molar chemical exergy of organic compounds

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ABSTRACT

Exergy analysis can be used to achieve the optimal conditions at which a system or a process can precede; as close as possible to the environmental conditions (with minimum loss of energy). In order to do such an analysis, the chemical exergy of each compound should be available. Since there are a limited number of organic compounds for which the chemical exergy values have been reported in the literature, it would be of great interest to have a reliable method for the estimation of this parameter. In this communication, a group contribution method is proposed for the prediction of the chemical exergy of pure organic compounds at the standard condition of 1 atm and 298.15 K for pressure and temperature respectively. In order to develop and validate the model, and also to evaluate its predictive capability, a dataset of 133 pure organic compounds composed of carbon, hydrogen, nitrogen, oxygen, and sulfur was used. The model proposed has a low average absolute relative deviation of 1.6% from literature data and indicates the reliability of the method. It can be used as a predictive tool for the estimation of the standard chemical exergy of pure organic compounds.

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1. Introduction

In many engineering systems, all the substances involved may be in stable equilibrium with each other; however, they may not be in mutual equilibrium with their surroundings. This lack of a mutual stable equilibrium may result in the production of shaft work. The second law of thermodynamics (SLT) provides information about the spontaneous direction in which a process proceeds. Thus, it can be used to evaluate how close a system is to stable equilibrium with its surrounding when all the system's species are in equilibrium with each other. In other words, thermodynamic analysis methods based on the SLT are much more comprehensive than the analysis methods that are just based on the first law of thermodynamics, due to the fact that they consider the equilibrium

state of a system both internally (between substances involved) and externally (between system and its surroundings).

One of the SLT-based analysis techniques that has attracted the attention of many researchers in various fields is the method of exergy analysis. Exergy is a very useful method for the evaluation of the thermodynamic and energy performance of various chemical processes such as study of auto-cascade Rankine cycles [1], evaluation of polygeneration energy systems [2], environmental impact assessment of turboprop engines [3], investigation of steam methane pre-reforming systems [4], analysis of refrigeration shaft power in industrial clusters [5], analysis of thermosolar and heat pumps [6], utilizing of the criteria for decision making in energy systems [7], improving the performance of natural gas fired combined cycle power plants by coupling Kalina cycles [8], assessment of silicon production processes [9], modifying pulp and paper mills [10], analysis of oil and gas processing platforms [11], analysis of coal systems [12], and bottoming rankine cycle for engine exhaust heat recovery [13]. In chemical processes, the components of process streams are changed as a result of different unit operations which occur in different unit operations such as distillation towers, reactors, etc. The application of exergy analysis in these systems is

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however in general limited due to the lack of chemical exergy data for components of interest.

Chemical exergy (CE) refers to the maximum work obtainable from a system at the temperature and pressure of the reference environment [14]. It is also defined as the minimum work required to synthesize a pure compound at the reference state of the environment from its constituents at the same state. In other words, chemical exergy has two parts; one that is related to the reaction needed to produce species that are not in their stable forms in the reference state, and another that is related to translating the species from the system state to the reference state. Therefore, the reference state should be introduced in terms of temperature and pressure so that the chemical exergy can be calculated. Generally, the reference environment is considered as 298.15 K and 1 atm in terms of temperature and pressure, respectively.

Naturally, there are several compounds that are in their most stable states at the reference environment conditions (e.g. CO₂, O₂, N₂, H₂O, noble gases). Therefore, one is not able to obtain more useful work from these kinds of compounds. Thus, their chemical exergy is equivalent to 0 kJ mol⁻¹ [15,16].

From a thermodynamic point of view, the standard molar chemical exergy (SMCE) of a compound can be calculated from the appropriate Gibbs energy of formation and the values of the chemical exergy of its constituent chemical elements. Taking into account the reversible reaction for chemical formation of a compound, the SMCE may be written as follows:

$$\varepsilon^{\circ} = \Delta G_f^{\circ} + \sum n_j \varepsilon_j^{\circ} \quad (1)$$

where ΔG_f° , n_j , and ε_j° represent the standard Gibbs free energy of formation; the number of atoms of the constituent element j ; and the SMCE of the constituent element j , respectively.

Several models have, to date, been proposed for the estimation of chemical exergy. Probably the first attempt to correlate the chemical exergy is Rant's work [17] in which a constant ratio of chemical exergy to calorific value for solid, and then for liquid fuels was proposed. Szargut and Styrylska [18] showed that Rant's correlation constant depends on the composition of fuels and they developed a new correlation taking this fact into account.

In another model developed by Shieh and Fan [19] a simple correlation for the estimation of the chemical exergy of materials was introduced that had complicated chemical structures. While developing their model, they assumed that the entropy of a fuel is equal to the entropies of its constituent elements. This assumption is far from the reality in many cases and therefore their correlation is not entirely correct.

A modification of Shieh and Fan's model [19] proposed by Stepanov [20] used the entropy model proposed by Ikumi et al. [21]. Using the same idea, Bilgen and Kaygusuz [22] implemented the entropy correlation proposed by Eisermann et al. [23] to modify Shieh and Fan's model [19]. The final models proposed by Stepanov [20] and Bilgen and Kaygusuz [22] are very complicated to use and have a limited applicability domain because both the models have been proposed for coal or coal liquids.

Song et al. [24] developed a model for the estimation of entropy of major constituents of biomass and then extended Shieh and Fan's model [19] for major components of biomass. According to Szargut and Styrylska's investigations [18], the model proposed by Song et al. [24] demonstrated a high level of accuracy for the estimation of biomass, however, its applicability domain was very narrow and limited to a few substances, as in the case of Stepanov's [20] and Bilgen and Kaygusuz's [22] models.

Using a database of pure organic compounds, Gharagheizi and Mehrpooaya [25] developed a quantitative structure-standard molar chemical exergy relationship. Their model was simple and has just

three parameters; viz. molecular weight, sum of atomic polarizabilities (scaled on carbon atoms), and number of atoms in any compound. Although their model was simple, the secondary parameter of the model needed computation using a computer program and could not be simply calculated.

Recently, Song et al. [26] developed a model for liquid and solid fuels on a dry basis. They considered the specific exergy of a dry fuel in two separate parts; one for organic matter and the other for inorganic matter. They subsequently developed a model for the estimation of entropy of organic matter for solid and liquid fuels. Implementing the ash analysis data, they also developed a model for the estimation of chemical exergy of inorganic compounds. They showed that the chemical exergy of both ash and inorganic compounds can be neglected when compared with the chemical exergy of dry solid and liquid fuels.

In this study, a new group contribution model is developed for the estimation of the standard molar chemical exergy of pure organic compounds. In this approach the chemical structure of a compound is decomposed into several chemical substructures which have either a positive or negative contribution to the chemical exergy of compounds. This method is simple and can be used to predict the standard chemical exergy of organic compounds.

In the proceeding sections, a dataset of SMCE of pure organic compounds is initially collected. Then, their chemical structures are investigated to find all the extractable chemical substructures (functional groups). In the next step, a mathematical algorithm is used to relate the number of occurrences of an efficient subset of the chemical substructures to the SMCE of pure organic compounds.

2. Data preparation

In order to develop a reliable model for the estimation of the standard chemical exergy of pure organic compounds, a reliable collection of data is required. The dataset used in this study is that of Kotas [15]. The dataset comprises standard molar chemical exergy values for 133 pure organic compounds. The data values range from 303,580 kJ mole⁻¹ (for formic acid) to 13,254,570 kJ mole⁻¹ (for tetraphenylmethane). The organic compounds within the database are composed of elemental carbon, hydrogen, nitrogen, oxygen, and sulfur. The minimum and maximum number of carbon, and hydrogen atoms of the compounds are for methane (1 carbon atom) and tetraphenylmethane (25 carbon atoms), formaldehyde (2 hydrogen atoms) and octadecane (38 hydrogen atoms), respectively. In the dataset, there are 22 nitrogen, 63 oxygen, and 18 sulfur-containing compounds. The maximum occurrence of nitrogen, oxygen, and sulfur atoms is related to melamine (6 nitrogen atoms), β -maltose (11 oxygen atoms), and cystine (2 sulfur atoms), respectively. Therefore, the dataset covers a fairly wide range of organic compounds.

In order to develop a predictive model, it is required to divide the dataset into three parts: the first part for developing the model (called the "training set"), the second for evaluating the internal validity of the model (called the "validation set"), and the last for assessing the predictive capability of the obtained model (called the "test set"). To undertake this task, the simplest way is to split the dataset randomly. This may cause some inappropriate assignments of data to each sub-data set. To prevent this problem, several methods have been proposed. One of the most widely used methods is the K-means clustering technique [27,28]. This method partitions a dataset into n sub-datasets in which each data point belongs to the subset with the nearest mean. This can help to resolve the problem of inappropriate allocation of data to datasets.

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