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Prediction of the self-accelerating decomposition temperature of organic peroxides based on support vector machine

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Abstract

Organic peroxides are self-reactive substances that are susceptible to decomposition and redox reactions under external energy, causing catastrophic accidents such as fires and explosions. Self-accelerating decomposition temperature (SADT) is one of the most important parameters for describing the thermal hazard of organic peroxides in process industries. This study presented a quantitative structure-property relationship (QSPR) model to predict the SADT of 71 organic peroxides through their molecular structures. All molecular descriptors are calculated by DRAGON 6.0 software. Genetic algorithm (GA), along with multiple linear regression (MLR) was employed to select the optimal subset of descriptors. Two different models are developed by employing multiple linear regression (MLR) and support vector machine (SVM), respectively. Both models are considered to be valid and able to predict the SADT of organic peroxides through rigorous model validations. The average absolute error of the MLR model for the training set and test set is 7.976 ℃ and 8.585 ℃, while that for the SVM model is 5.676 ℃ and 8.172 ℃, respectively. The predicted results showed that the SVM model has an obvious superiority in prediction performance when comparing to the MLR one. This study could provide a new method for predicting the SADT of organic peroxides for engineering.

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Keywords: organic peroxide, thermal hazard, SADT, SVM;

Nomenclature

n_{Ext}	number of all samples in the test set
x_i	molecular descriptors
$y_{i,obs}$	observed value of i-th sample of training set
$y_{i,cvpre}$	predicted value of i-th sample obtained by interactive verification
$y_{j,obs}$	observed of the j-th sample in the test set
$y_{j,pre}$	predicted values of the j-th sample in the test set
$\bar{y}_{obs}$	average of all observed values
y_{pred}	predicted value
y_{obs}	observed value
A_i	corresponding regression constants

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AAE	average absolute error
Q^2_{Ext}	squared correlation coefficient for external validation
Q^2_{LOO}	leave-one-out (LOO) cross-validation coefficient
R^2	coefficient of determination
RMSE	root-mean-square error and
SADT	self-accelerating decomposition temperature (℃)
Y	the predicted property

1. Introduction

Organic peroxides are self-reactive compounds containing the peroxides functional group (−O−O−), which are inherently unstable and can be easy to break and form free radicals of the form RO when organic peroxides are heated over a certain temperature [1,2]. Organic peroxides have widely served as a polymerization initiator, catalyst, crosslinking or hardening agent. However, many serious accidents such as thermal runaway explosions have happened frequently in the actual industrial process due to their self-reactive nature, resulting in a large number of casualties and property damage globally [3]. It is significant to study the thermal hazard parameters, such as self-accelerating decomposition temperature (SADT), for organic peroxided for safety and effective management.

Self-accelerating decomposition temperature (SADT) is one of most important parameters for characterizing the thermal risk of organic peroxides. According to the United Nations (UN) definition, self-accelerating decomposition temperature is defined as the lowest ambient temperature at which self-accelerating decomposition may occur in organic peroxides or self-reactive substances in the packaging for transportation purposes [4, 5]. SADT determines whether the materials should be temperature controlled to avoid the occurrence of thermal hazards in the storage and transport. Generally, experimental methods such as calorimetric tests, the United States SADT test, the adiabatic storage test, the isothermal storage test and the heat accumulation storage test, are applied to measure SADT values [6-8]. Unfortunately, the values determined by these experimental methods require plenty of time, as well as a lot of manpower, material and financial resources. In addition, the variety and quantity of organic peroxides are large, the recommended test procedures can be dangerous due to ambiguity reaction mechanism. Thus, it is absolutely necessary to develop a convenient and reliable method to predict the SADT of organic peroxides.

Quantitative structure-property relationship (QSPR), that can predict desired properties of organic peroxides by relating the properties of chemical substance to the molecular structure of the materials, has been widely employed. It reveals the relationship between molecular structure and desired properties at the molecular level. This approach is superior to other methods in that it only requires molecular structure information without any other experimental properties. Common methods for developing QSPR are multiple linear regression method (MLR), partial least squares method (PLS) and support vector machine method (SVM). To the best of our knowledge, among these three methods, MLR method is linear and greatly popular due to its simplest algorithm, while SVM method is nonlinear and complicated so that it is not widely used in QSPR. Yong Pan et al. [9] used molecular descriptors that were calculated with Dragon software to construct predicted models by the MLR method to predict SADT values of 41 organic peroxides. Vinca Prana et al. [10] also used MLR method to develop predicted model for the decomposition heat (-ΔHd) and the onset temperature (T_0) of 38 organic peroxides. Yuan Lu et al. [11] used Partial least-squares method (PLS) and multiple linear regression method (MLR) to predict the detected onset temperature (T_0) and heat of decomposition (-ΔHd) of 16 organic peroxides. Therefore, it can be seen that most of the existing models were only built with linear regression methods rather than nonlinear relationship. Furthermore, although there have been some researches on QSPR work for predicting the thermal hazards, most of which were for predicting the properties of heat of decomposition (-ΔHd) and the detected onset temperature (To). Moreover, sample dataset adopted in the literatures was small so that there were some errors and low accuracy.

In this study, the quantitative relationship between molecular structures and experimental SADT values of 71 organic peroxides were explored by two QSPR methods. In both models, QSPR methodology was combined with molecular descriptors obtained by DRAGON 6.0. These descriptors have definite physical and chemical meanings, which have significant contribution to the targeted properties. The prediction models were developed by employing multiple linear regression method (MLR) and nonlinear regression method (SVM) which were compared with each other.