신경망을 이용한 물성 예측을 통한 화학공정의 위험성평가

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Thermal hazards assessment from the estimation of physical properties based on Neural networks

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Introduction

When designing the new chemical process, it is vital to assess the risk of reactions in the chemical industries. It is useful to evaluate the heat release of the reactions as the preliminary screening procedures for reactive chemical hazard evaluation. The potential heat energy can be calculated by the physical properties of the materials included in the reactions. But it is not easy to get those data, especially for the new materials or the high molecular substances. Considerable researches have been studied about determining physical property values from a compound's molecular structures. In order to improve the prediction of the physical properties in accuracy and applicability, we extended the database in large numbers, modified the existing group contribution methods and then established new method for predicting the physical properties using neural networks. The results from the new estimation method are found to be more reliable and applicable. It can play an important part in the thermal hazard assessment in terms of the expenses and times.

Theories

1. Estimation of physical properties

Estimating the physical properties theoretically without any experiments can not only reduce the expenses but also minimize the potential to take a risk. Several methods have been studied about theoretical estimations of the physical properties. The method based on the molecular structure and the one based on the computational quantum chemistry are widely known to be reliable.

Although last one, coupled with the statistical thermodynamics, can predict the properties more accurately, it is limited to only the low molecular substances. Even though the software such as GAUSSIAN or GAMESS can be used to predict many kinds of properties, it still can't be applied to many cases, especially the high molecular substances.

Group contribution techniques, based on the assumption that each fragment of a molecule contributes a certain amount to the value of its physical property, are most widely used because it is

relatively easy to use and they comparably have the good abilities to predict. Joback developed the commercial software, CRANIUM, based on Joback's group contribution method. Constantinou proposed the new group contribution method correcting the existing one by adding the second-order groups to the first-order ones. Lee developed the group contribution method using neural network based on same database that Joback used. But the major disadvantage of group contribution methods is that they perform unevenly on predicting. That is, though it has the good performance for specific compounds, it can be too poor to predict properties for other ones. The problem originated in the insufficient database about material properties. For many materials, physical properties were not available for the data which Joback used, especially for the ideal heat capacity. Therefore in order to improve the performance, it is necessary to extend the database. We improved the performance and the reliability using the DIPPR database which has three times larger than those used in Joback's and Lee's method.

And we modified the representative functional groups, found out more important ones by analyzing the correlations between the specific functional groups of the materials and their physical properties and then listed the final distinct groups. These are largely classified to three big groups consisting of 17 Ending groups, 25 Middle groups and 14 ring groups as [Figure 1].

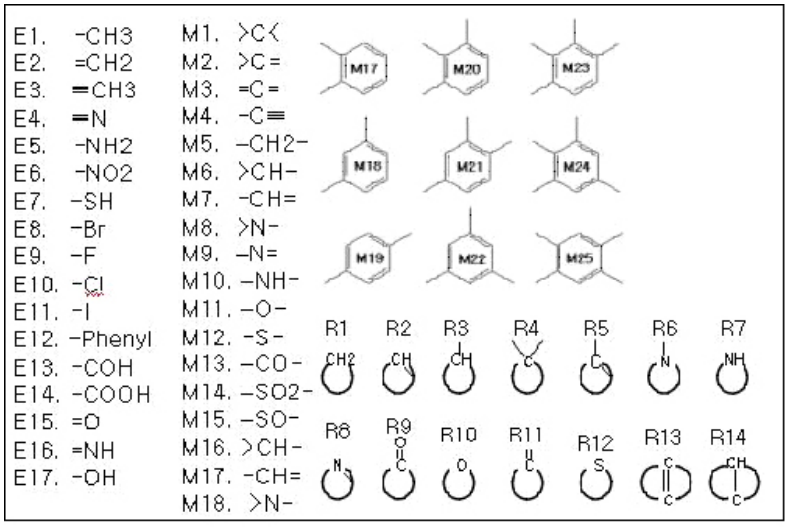

Figure 1 Functional groups used in the new method

2. Neural Networks

Neural networks enable us to develop and implement the new method with easy and accuracy. They produce the weight vector to optimize the model by competing learning. We set the 59 input variables which consisted of 58 functional groups and the molecular weight. We implemented neural networks using SAS program.[Figure 2].

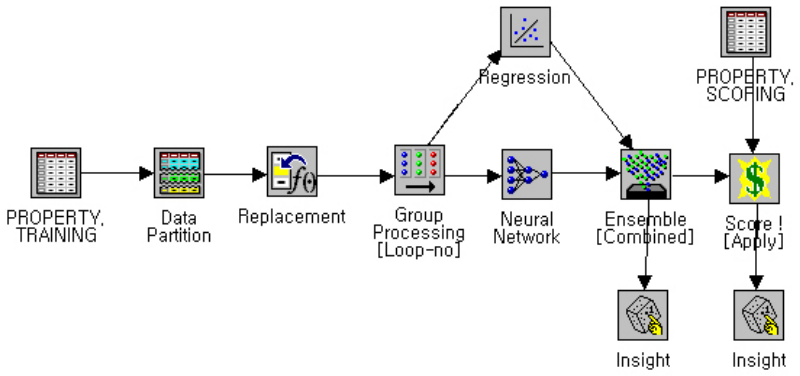

Figure 2 The Diagram of Neural networks used in –SAS

We divided the raw data into two, first are for training and validation and second are for scoring. We used the replacement node especially "mean node" to replace missing values because there were many missing values in the raw data. And we set the 10 hidden units as networks, added the linear regression mode and created a model by averaging the predicted values. Ensemble node can improve the performance for the generalization.

Results and Conclusions

The suggested method was proved to predict the physical properties better than others. The predicted values were found to fit in well in the experimental ones.

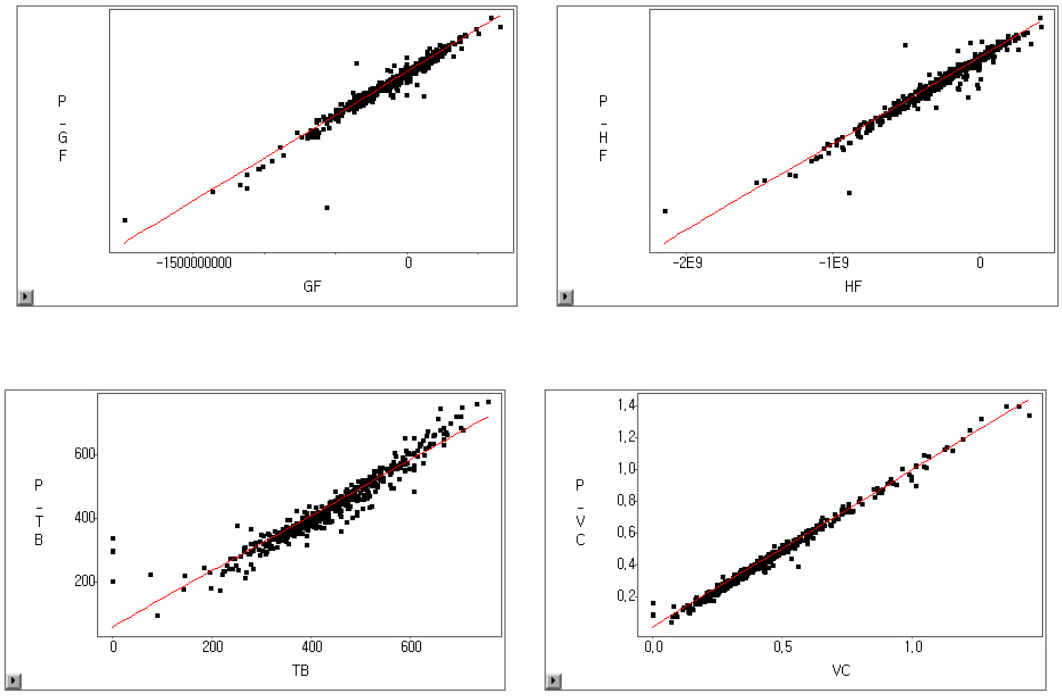

Figure 3 Fitness analyses in the estimation of Gf, Hf, Tb, Vc

Gf : Gibbs energy of formation at 298K(J/Kg/mol)

Hf : Enthalpy of formation at 298K(J/Kg/mol)

Tb : normal boiling point(K)

Vc : critical volume (m^3)

When compared to other methods, it showed the high performance as the following table.

	Average Absolute Percent Error		
	Joback method	Lee's model	New model
Hf(J/Kg/mol)	16.78	5.29	0.91
Gf(J/Kg/mol)	14.39	6.21	0.97
Tb(K)	2.99	1.05	1.24
Tc(K)	4.08	0.99	1.70
Tf(K)	11.07	0.45	1.94
Vc(m^3)	6.16	1.56	0.24

Table 1 Comparison of accuracies in the estimation of physical properties

We can calculate the enthalpy of reactions, ΔH_{rxn}, using the predicted enthalpy of formation and then evaluate the potential heat energy and adiabatic temperature increase as the following equation.

$$\Delta T_{AD} = \frac{\Delta H_{rxn}}{Cp}$$

ΔT_{AD} : The adiabatic temperature increase

ΔH_{rxn} : The enthalpy changes for the reaction

Cp : The specific heat capacity for the mixtures

Therefore we can apply to the risk assessment as the preliminary screening without any experimental test.

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