Full Length Article

The thermal theory based equation for correlation between temperature and flammability limits of hydrocarbons

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ABSTRACT

Theoretical equation to evaluate the effect of temperature on the flammability limits of pure hydrocarbons was proposed in present study and compared with other methods available in the literatures. Theoretical equation was based on the thermal theory. Verification of the linear equation has been implemented on the cases of hydrogen, methane, propane, propylene, butylene, pentane and isobutane. The equation in this paper shows an average absolute relative error of 0.43% and 0.93% for lower and upper flammability limits, respectively. The equation possesses better prediction accuracy than other available methods at UFL. The reason for better accuracy is that the simple chemical kinetics about oxygen consumption was used to calculate reaction heat at upper flammability limit. Finally, the temperature range of application of theoretical equation was discussed in detail.

1. Introduction

Studies have shown that hydrocarbons possess the better thermodynamic (a high decomposition temperature) and environmental properties (zero ozone depletion potential) than hydrofluorocarbon in medium-high temperature Organic Rankine Cycle (ORC) system [1,2]. Thus, hydrocarbons are often used for waste heat recovery in engine. However, flammability of such compounds imposes restrictions on their practical application. Thus, it is an important task to investigate flammability characteristics of such compounds for ensuring the safety in practical application. The lower and upper flammability limits are the flammability properties regularly used to evaluate the flammability hazards of gases [3–5]. Many industrial processes such as ORC generally operate at the temperature range of 81–222.5 °C [6,7]. In order to guarantee the safety of operation, it is necessary to get the flammability limits of hydrocarbons at elevated temperature. However, most experimental data for flammability limits was generally measured at 25 °C and few data measured at non-ambient temperature was available for many hydrocarbons. As we all know, the flammable zone of hydrocarbons will broaden if the temperature rises; that is to say, the lower flammability limit (LFL) becomes lower and the upper flammability limit (UFL) becomes higher [8–10]. Thus, safety instructions using the flammability limits at room temperature may result in a severe explosion hazard when temperature rises. Therefore, it is necessary for researchers to investigate the effect of temperature on flammability limits.

Several researchers [8,11–13] have deeply studied the flammability of fuel using different methods, which can be approximately divided into two principal categories: a) the method based on CAFT; and b) the group contribution method based on molecular structure. The latter method requires a large amount of experimental data measured at different temperatures to build the model. Thus, The GC method may be unfit particularly for predicting the temperature dependence of the flammability limits. The latter method is frequently applied to predict flammability limits at ambient temperature. Most forecasting methods based on the calculated adiabatic flame temperature were proposed to account for the temperature dependence of lower flammability limit. This method can determine the LFL of the hydrocarbon when the approximation of the threshold temperature is provided. White [14] deemed that the limit flame temperature remains the same no matter how the initial temperature changes. The modified Burgess-Wheeler law suggested by Zabetakis [15] was a very useful tool in solving the effect of temperature on the LFLs of hydrocarbons:

$$L = L_{25°} - \frac{0.75}{\Delta H_C}(T - 25°) \tag{1}$$

where T is the temperature in °C, $L_{25°}$ is the LFL at 25 °C, and ΔH_C is the heat of combustion in kilocalories per mole. Assuming adiabatic flame temperature was independent of initial temperature, Britton and Frurip [16] considered that the lower flammability limits of the hydrocarbon was linear between the CAFT and initial temperature. Another empirical formula was present by Britton and Frurip:

Nomenclature

AARE	average absolute relative error
CAFT	calculated adiabatic flame temperature
LFL	lower flammability limit
UFL	upper flammability limit
GC	group contribution
n	number of carbon atom in hydrocarbon
m	number of hydrogen atom in hydrocarbon
T_0	initial temperature (known)
T	temperature
L(U)	lower(upper) flammability limit
$L_0(U_0)$	lower(upper) flammability limit at T_0 (known parameter)
$L_T(U_T)$	lower(upper) flammability limit at T
Q	heat of combustion per mole of oxygen
C_P	specific heat at constant pressure
H^T	enthalpy at the temperature of T
H^{ad}	enthalpy at the calculated adiabatic flame temperature
ΔHc^*	reaction heat at upper flammability limit
ΔHc	heat of the combustion

$$L = L_{T°}\frac{T_{ad}-T}{T_{ad}-T_0} \tag{2}$$

where T_{ad} is the CAFT at LFL. Kondo [17] measured the temperature dependence of upper and lower flammability limits of methane, propane, isobutane, ethylene and propylene and used the modified Burgess-Wheeler law to estimate lower flammability limits with respect to different temperatures. Mendiburu [8,18] researched temperature dependence of lower flammability limits of C−H−O and C−H compounds at atmospheric pressure in air. If the variable K in equation proposed by Mendiburu were equal to 1, then the equation proposed by Britton and Frurip would be same as the equation suggested by Mendiburu.

For upper flammability limit, methods to explain temperature dependence is relatively scarce compared with lower flammability limit. Zabetakis [15] also interpreted the effect of temperature using the modified Burgess-Wheeler law:

$$U_T = U_{25°} + \frac{0.75}{\Delta H_C}(T-25°) \tag{3}$$

where ΔH_C is the heat of combustion in kilocalories per mole, $U_{25°}$ is the UFL at temperature 25 °C, and U_T is the estimated UFL at temperature T. The prediction accuracy of the modified Burgess-Wheeler law is poor. Kondo [17] presented the linear equation based on assumption of a constant heat of combustion per mole of oxygen to explain the dependence of UFL on initial temperature:

$$U_T = U_{25°} + \frac{100C_{p,L}}{Q}(T-25°) \tag{4}$$

where Q is heat of combustion per mole of oxygen and $C_{p,L}$ is the heat capacity of unburnt gas at UFL at 25 °C. Kondo proposed the linear equation easily only replacing heat of combustion with constant heat of combustion per mole of oxygen in Eq. (3), however, the prediction accuracy of the method is poor. In order to improve the prediction accuracy, another empirical equation was put forward based on the geometric mean G.

$$U_T = U_{25°}\left\{1 + \frac{100C_{p,L}}{L_{25°}\Delta Hc}(T-25°)\right\} \tag{4a}$$

Mendiburu [19,20] also developed semi-empirical method using chemical equilibrium to estimate the UFL at different initial temperatures for C−H compounds and C−H−O compounds. The prediction accuracy is acceptable; however, the derivation process of the formulas is a bit complex.

For lower flammability limits, most methods to evaluate the temperature dependence are empirical formulas except the equation suggested by Mendiburu [8] and Liaw [4]. The prediction accuracy for those methods is acceptable. This is because using value of $L*\Delta H_C$ can better take the place of value of reaction heat considering complete combustion at LFL. However, for the upper flammability limits, $U*\Delta H_C$ cannot well explain reaction heat due to incomplete combustion. Kondo proposed $U*Q$ rather than $U*\Delta H_C$ to represent reaction heat. The predicted results show that neither the Eq. (3) proposed by Zabetakis nor the Eq. (4) presented by Kondo can accurately represents reaction heat at UFL. The empirical Eq. (4a) proposed by the Kondo can better

predict the temperature dependence of UFL than the Eq. (4). Mendiburu [19,20] tried to use chemical equilibrium to calculate product and reaction heat at UFL and got acceptable accuracy. The above methods indicated that reaction heat at UFL is not equal to $U*\Delta H_C$..

Chemical kinetics of combustion of hydrocarbons play an important part at UFL [21,22] in air. Thus, it is difficult to precisely calculate the reaction heat without involving chemical kinetics or chemical equilibrium in the modeling process.

As described above, there is not an effective and theoretical method to easily estimate reaction heat at UFL. Thus, a simple chemical kinetics about oxygen is introduced to calculate reaction heat. It is a special interest to know whether the UFLs at different initial temperature of low hydrocarbon could be explained well by the equation using simple chemical kinetics.

2. Method

Establishing and validation of the equation contain a procedure consisting of four steps:

(1) Build the equation related to T, U(or L);
(2) Calculate the CAFTs of hydrocarbons with help of the flammability limits at T_0;
(3) Re-formulate equations related to T, U (or L) and getting correlation between U (or L) and T;
(4) Use the developed equations to estimate the lower and upper flammability limits of hydrocarbon-air mixtures at different initial temperatures and validate the reliability of the equations by comparing the estimated values with observed values available in the references;

Values of CAFT for different pure hydrocarbon generally were in the range of 1000–1600 K according to literatures [22,23]. In order to precisely get the values of CAFT, the adiabatic flame temperature was calculated by the CHEMKIN software based on chemical equilibrium and minimization of Gibb's free energy for hydrocarbon-air mixture at fixed enthalpy and pressure when the values of flammability limits of hydrocarbon-air mixture were known. The values of CAFT of hydrocarbons at LFL and UFL are obtained and compared with the values in Refs. [12,23]. As shown in Table 1, A good consistency can be achieved between the present values and those in Refs. [12,23], which demonstrates that the results of the CAFT obtained from CHEMKIN software are valid.

Table 1
Comparison between the present CAFTs and those in Refs. [12,23].

Compounds	UFL[12] (vol%)	CAFT at UFL (K)	Ref.[12] (K)	LFL[23] (vol%)	CAFT at LFL (K)	Ref.[23] (K)
Methane	15	1769.2	1763	5	1482.5	1482
Ethane	12.5	1392.7	1387	3	1535.7	1534
Propylene	11	1440.8	1452	2.4	1624	1621
Propane	10	1249.1	1247	2.1	1530.4	1530