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Research Paper

A new model based on adiabatic flame temperature for evaluation of the upper flammable limit of alkane-air-CO_2 mixtures

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HIGHLIGHTS

- A new model based on adiabatic flame temperature has been proposed.
- A linear relationship exists between dilution ratio and calculated adiabatic flame temperature.
- The flammable zones of n-butane-CO_2 and isopentane-CO_2 were measured to test effectiveness of the VAFT model.
- The average relative differences are less than 3.51% at upper flammability limit for VAFT model.

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ABSTRACT

For security issue of alkane used in Organic Rankine Cycle, a new model to evaluate the upper flammability limits for mixtures of alkanes, carbon dioxide and air has been proposed in present study. The linear relationship was found at upper flammability limits between molar fraction of diluent in alkane-CO_2 mixture and calculated adiabatic flame temperature. The prediction ability of the variable calculated adiabatic flame temperature model that incorporated the linear relationship above is greatly better than the models that adopted the fixed calculated adiabatic flame temperature at upper flammability limit. The average relative differences between results predicted by the new model and observed values are less than 3.51% for upper flammability limit evaluation. In order to enhance persuasion of the new model, the observed values of n-butane-CO_2 and isopentane-CO_2 mixtures measured in this study were used to confirm the validity of the new model. The predicted results indicated that the new model possesses the capacity of practical application and can adequately provide safe non-flammable ranges for alkanes diluted with carbon dioxide.

1. Introduction

Propane and isobutane show good characters as working medium in medium-high temperature Organic Rankine Cycle [1,2] which is an appropriate technology for waste heat recovery like engine and industry. However, flammability of those is a mainly big limitation for using in its practical application. Among flammability characteristics, flammability for alkanes is an important one which defines the range of fuel concentration for flame propagation to occur. Inerting is the process of adding an inert gas to a combustible mixture to reduce the concentration of oxygen below the limiting oxygen concentration (LOC) for the purpose of lowering the likelihood of explosion [3]. Thus, inerting is frequently involved to reduce the possibility of flammability lest the high temperature flammable working medium leaking from Organic Rankine Cycle explodes in the surrounding environment. Using carbon dioxide as an inert gas, Ref. [4] revealed that mixture of carbon dioxide and alkane had a better performance in cycle efficiency than alkane in Organic Rankine Cycle owing to a large temperature glide for alkane-CO_2 mixture.

The prediction of flammability limits for alkane-CO_2 mixture plays some positive significance in practical application of Organic Rankine Cycle. Theoretical approaches can better interpret the effect of inert gas on flammability limits of fuel and easily estimate the flammable ozone than experimental methods. Thus, different methods have been proposed in quantity to estimate the flammability limits for mixture of fuel and inert gas in literatures such as the modified Le Chatelier equation [5] and the thermal theory methods [6]. However, the modified Le Chatelier equations are highly dependent on the experimental data so that the predicted results may be inaccurate for compounds have not been measured. The

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Nomenclature

Abbreviations

CAFT	Calculated adiabatic flame temperature
FAFT	Fixed calculated adiabatic flame temperature
FIP	Fuel inertization point
VAFT	Variable calculated adiabatic flame temperature
LOC	Limiting oxygen concentration
LFL	Lower flammability limit
UFL	Upper flammability limit
RD	Relative difference

Symbols

U	the molar fraction of alkane in the alkane-air-diluent mixture at UFL
y	the molar fraction of diluent in alkane-diluent mixture
H^0	Enthalpy at the initial temperature
H^{ad}	Enthalpy at the calculated adiabatic flame temperature
ΔHc^*	Reaction heat at upper flammability limit
ΔHc	Heat of the combustion
U_1	Lowest volume fraction does not support flame propagation
U_2	Highest volume fraction supports flame propagates
α	The quantity of combustion product at UFL

thermal theory methods that quantify the heating and quenching potentials of each element of the alkane-CO_2 mixture are generally used to predict the flammability zone of the alkane-CO_2 mixture. From the perspective of thermal theory, the flammability limits are related to a certain critical energy generation rate or with a certain level of reaction temperature [7]. The flame temperature calculated by assuming no heat loss is known as calculated adiabatic flame temperature (CAFT) [8]. A threshold temperature must be chosen properly to estimate flammability limits by using the CAFT method. Vapor mixtures with its CAFT above this threshold are considered flammable, and vapor mixtures with its CAFT below this threshold are considered non-flammable [9]. Vidal [10] applied a FAFT value to estimate LFL of alkane and got a relatively satisfactory result. Chen [11] developed predictive methods for estimating flammability limits of combustible gas diluted with carbon dioxide using FAFT at both LFL and UFL. The results clearly showed that predicted values of LFL with FAFT accorded with the experimental values, while those of UFL had a large error in comparison with those of LFL. Recently Shu [12,13] proposed flame temperature theory-based models using the FAFT as well for evaluation of the flammable zones of alkane-air-CO_2 mixtures. Similar results that large error occurred at UFL could be obtained in that paper. In general, the models adopting the FAFT could exactly predict LFL of alkane-air-CO_2 mixtures; however, the same models failed to precisely estimate UFL of alkane-air-CO_2 mixtures.

At the same time some attempts have been focused on the VAFT. Hu [14] considered that the differences between the predictions and measurements at UFL were mainly due to the assumption of FAFT in his model. Palucis [15] also pointed out that a FAFT value could be related to the lower flammability limit (LFL), but this was not the case for UFL. The adiabatic flame temperature calculated in Refs. [14,15] at UFL varied with the addition of the diluent rather than always kept constant. In other words, threshold temperature used for judging flammability limits varied. Therefore, using the FAFT as threshold temperature inevitably resulted in a major error for predicting UFL of alkane-air-CO_2. This may indicate that the FAFT is no longer fit for predicting UFL. A new procedure for estimation of limiting oxygen concentration (LOC) of fuel-air-nitrogen gaseous mixtures was developed using the VAFT in Razus's paper [16]. The results indicated that the relative difference between predicted values and observed values decrease by more than half comparing with those results obtained by using the FAFT. To the authors' knowledge, there are no models using the VAFT to predict UFL of alkane-air-CO_2 mixtures in published literatures.

In conclusion, the existing prediction models have limited ability on precision of prediction at UFL. It is an important task to establish the high precision model to accurately estimate the UFL of alkane-air-CO_2 mixtures. Thus, this paper mainly investigates that whether a method using a VAFT that can successfully predicts the change of UFL for flammable mixtures including diluents such as CO_2 or N_2 exists or not.

As is described above, FAFT was always applied to predict flammability limits of gaseous mixtures of alkane-diluent-air, which may lead to a larger error at UFL in comparison with that of LFL. Thus, the purpose of the present study is to: 1) investigate the VAFT; 2) propose models based on the VAFT to predict the flammability zones of mixtures composed of alkane, carbon dioxide and air; 3) discuss the practical application possibilities and accuracies of the model.

2. Calculation of VAFT

The threshold or critical flame temperature used in models is an important fact to determine flammability. As shown Fig. 1, if the threshold temperature, namely CAFT, chosen to determine flammability limits of propane increased, the UFL determined in Fig. 1 should be decrease. The significance meaning of VAFT to determine UFL was revealed distinctly in Fig. 1.

Values of CAFT for different pure alkane generally varied from 1000 to 1600 K according to literature [17,18]. 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 alkane-CO_2-air mixture at fixed enthalpy and pressure when values of flammability limits of alkane-carbon dioxide-air mixture are known. Hu [14] also used the CHEMKIN to calculate the adiabatic flame temperature of methane-CO_2-O_2 mixture. In this study, the values of flammability limits at 308 K and 1 atm for mixtures were taken from Refs. [19,20] published by Kondo. Thus, the values of adiabatic flame temperature at different dilution ratios can be calculated by using the CHEMKIN. As presented in Table 1, the present results have very

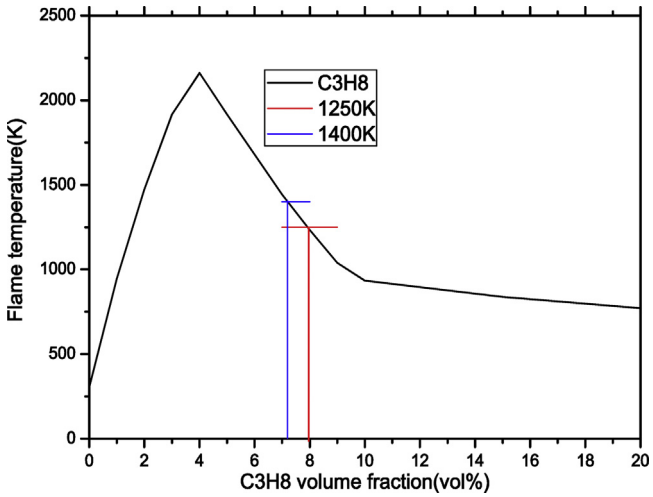

Fig. 1. Comparing the effect of the VAFT on UFL for the mixture of propane-CO_2 at y = 0.6.