Experimental flammability limits and associated theoretical flame temperatures as a tool for predicting the temperature dependence of these limits

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Abstract

The utility and limitations of adiabatic flame temperature calculations and minimum mixture energies in predicting the temperature dependence of flammability limits are explored. The limiting flame temperatures at constant pressure (1 bar) are calculated using a standard widely-used thermodynamic computer program. The computation is based on the calculated limiting flame temperature value at the reference initial temperature and the experimental limit concentration. The values recently determined in large chambers for the lower and upper flammability limits of a variety of simple organic and inorganic gases (methane, ethylene, dimethylether, and carbon monoxide) are used as the basis for the predictions of the limiting flame temperature concept. Such thermodynamic calculations are compared with more traditional ones based on a limiting mixture energy and a constant average heat capacity of the reactant mixture. The advantages and limitations of the methods are discussed in this paper.

1. Introduction

There have been various efforts in the past to predict the flammability limits of fuels based on limiting reactant energy or product flame temperature concepts. The concept of a limit mixture energy (i.e., a lower limit value for the heat of combustion per mole of the fuel–air mixture) was proposed over a century ago with some experimental support (Le Chatelier & Boudouard, 1898). That limit value ranges typically from 10 to 11.5 kcal/mol mixture for common organic fuels. In addition, the relative constancy of the heat produced per mole of oxygen consumed (heat of oxidation) in a fuel–air mixture was demonstrated early in the 20th century (Thornton, 1917), and has been found to be generally true for all types of fuels (NFPA,1980). That heat of oxidation ranges from 96 to 106 kcal/mol O_2, with an average

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close to 100 kcal/mol O_2. The combustion of hydrogen (H_2), carbon monoxide (CO), acetylene (C_2H_2), formaldehyde (H_2CO), ethylene oxide (C_2H_4O), and hydrazine (N_2H_4) are examples of common exceptions to the above energy ranges (Britton, 2002). More recently, reliable and somewhat conservative estimates of both the lowest flammable concentration and limiting oxygen concentration for many fuels have been made using the heat of oxidation, or a combination of the heat of oxidation and the limit heat of combustion of fuel–air mixtures (Britton, 2002; Britton & Frurip, 2003). Despite such success, exceptions to the predicted limits may be found, e.g., hydrogen in air. The problem from a safety perspective is that the predictions may not always be sufficiently conservative for some exceptional fuels. More importantly, the presence of divergent results of flammability measurements creates an uncertainty in delineating the flammable range boundaries, and in attempting to match predicted values with the experimental ones.

Recently, more reliable measurements of the lower flammability (or explosibility) limit (LFL), the upper flammability limit (UFL), and limiting oxygen concentration (LOC – previously known as the minimum oxygen concentration) have become available (Kondo, Takizawa, Takahashi, & Tokuhashi, 2006; Zlochower & Green, 2009). These measurements were made in sufficiently large spheres with spark ignition, so as to minimize wall effects and the influence of overly great ignition energies/limited volume (high ignition energy densities). The larger steel sphere (120-L) used a 7% pressure-rise criterion for explosibility or self-sustained flame propagation (Zlochower & Green, 2009), while the smaller glass sphere (12-L) used a visual flame extent criterion for flame propagation (Kondo et al., 2006, Kondo, Takizawa, Takahashi, Tokuhashi, & Sekiya, 2008). Both chambers featured ignition by high-voltage sparks generated at a 6 mm electrode gap located below the center of the sphere.

The results for the LFL, UFL, and LOC measurements in these chambers were virtually identical. Moreover the results for methane (CH_4) and propane (C_3H_8) agreed within experimental error with those from a very large cylinder (45 cm by 100 cm) with spark ignition near the bottom, and flame propagation to the top (Takahashi, Urano, Tokuhashi, & Kondo, 2003). This agreement lends optimism to the expectation that there are now reliable values for the experimental flammability limits of fuel gases representing saturated hydrocarbons (e.g., methane (CH_4)), unsaturated hydrocarbons (e.g., ethylene ($CH_2{=\!=}CH_2$)), and oxygenated organic and inorganic compounds (e.g., dimethylether (CH_3OCH_3) and CO, respectively). Kondo et al. (2006, 2008) have also reported results on the LFL, UFL, and LOC (with nitrogen (N_2) and carbon dioxide (CO_2) inerting) of some other hydrocarbons, and inorganic and oxygenated organic compounds. They have, furthermore, recently reported results on the effect of initial temperature on the flammability limits of various gaseous fuels (Kondo, Takizawa, Takahashi, & Tokuhashi, 2011).

More recent revisions (e.g., CEA-400) of the popular NASA-LEWIS (Glenn) thermodynamic code (McBride & Gordon, 1999), with its extensive library of thermodynamic properties of product and reactant species, have facilitated the calculation of accurate adiabatic flame temperatures of specified gas mixtures. Among such changes is the incorporation of an accurate dry air model in the thermodynamic library. The combination of reliable data and accurate adiabatic flame temperature calculations motivates the

reexamination of the limit flame temperature concept in this report. This effort was conducted as part of a National Institute for Occupational Safety and Health (NIOSH), Office of Mine Safety and Health Research (OMSHR) research project.

2. Theory: limit flame temperature - mixture combustion energy

The concept of a limit flame temperature as a tool for predicting the LFLs of hydrocarbon fuels and their variation with initial temperature was also proposed early in the 20th century (White, 1925). This concept is rationalized by the fact that the rates of the reactions involved in combustion feature exponential temperature dependence. Key propagation reactions involving hydrogen (H) atoms and hydroxyl (OH) radicals are also common to almost all combustion reactions. At some limit temperature the reaction rates will slow down to the point where self-sustaining exothermic reactions are insufficient to overcome the inherent energy losses to the walls, or the losses due to flame dynamics such as flame stretch (Hertzberg, 1976, 15 pp.). Flame propagation will then cease. Initially, a constant flame temperature was assumed for the family of saturated (alkane) hydrocarbon fuels together with a linear dependence of the LFL with initial temperature. The experimental LFL at the test temperature (normally ambient) and zero (LFL) at the limiting flame temperature then defined the straight line estimate for all temperatures (Zabetakis, 1965). Using 1300 °C (1573 K) as an approximate average flame temperature for the saturated hydrocarbon fuels gives:

$$L_{25} - L_t = L_{25}(t - 25)/(1300 - 25), \text{ or} \quad (1)$$

$$L_t/L_{25} = 1 - 7.84E - 4(t - 25),$$

where L_{25} is the experimental LFL at 25 °C, and L_t is the calculated value at t (°C). Given that the use of 25 °C as the reference temperature is arbitrary, Equation (1) can be equally written as:

$$L_{20} - L_t = L_{20}(t - 20)/(1300 - 20), \text{ or} \quad (1a)$$

$$L_t = L_{20} - L_{20}(7.81E - 4)(t - 20)$$

The virtue of this minor amendment is that 20 °C is an actual temperature used in the determination of experimental limits as a function of mixture temperature (Kondo et al., 2011). Therefore, the experimental values at 20 °C can be used as the basis value for the calculations.

An alternative formulation used by Zabetakis (1965) assumed constant limit mixture combustion energy ($L_{25} \times$ H_c) and a constant average heat capacity ($<C_p>$) of the reactant gases (predominantly, N_2).[1] Equating the mixture combustion energy ($L_t \times$ H_c) at initial

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[1]The brackets $<>$ denote average values.

temperature, t, with that at the standard temperature, t_o (or 25 °C) plus the enthalpy change to take the mixture from t_o to t, gives:

$$L_{25} - L_t = \langle C_p \rangle (t - 25)/Q, \text{ or} \quad (2)$$

$$L_t/L_{25} = 1 - \langle C_p \rangle (t - 25)/(L_{25}Q),$$

where Q is the positive heat released, i.e., – Hc

Equation (2) can be rewritten, as previously indicated, to give:

$$L_t = L_{20} - \langle C_p \rangle (t - 20)/Q \quad (2a)$$

Taking <Cp> as 7.5 cal/mol K and $\langle L_{20} Q \rangle$ as 10,400 cal/mol mixture, gives:

$$L_t = L_{20} - L_{20}(7.21E - 4)(t - 20) \quad (3)$$

Zabetakis (1965) also used an analogous equation for the UFL.

$$U_t/U_{25} = 1 + 7.21E - 4(t - 25) \quad (4)$$

As before, Equation (4) can be rewritten on a 20 °C basis to give:

$$U_t = U_{20} + U_{20}(7.21E - 4)(t - 20) \quad (4a)$$

The above equations presented in Bureau of Mines Bulletin 627 (Zabetakis, 1965) summarize the original findings of White (1925), Egerton (1953), and Zabetakis, Lambiris, and Scott (1959). Britton and Frurip (2003) have summarized and amplified the above findings for the temperature dependence of the LFL. They explicitly included a variable limiting flame temperature (T_f) to give

$$L_T/L_o = 1 - C_L(T - T_o), \text{ or } L_T/L_o = 1 - (T - T_o)/(T_f - T_o), \quad (5)$$

where L_o and T_o refer to the ambient or test temperature (all temperatures are consistently either in °C or K, and $C_L = 1/(T_f - T_o)$.

As before, 20 °C is chosen as the basis temperature to give:

$$L_t = L_{20} - L_{20}C_{20}(t - 20), \text{ where} °C \text{ is used, and} \quad (5a)$$

$$C_{20} = 1/(t_f - 20).$$

Average values for T_f were used given that flame temperatures at the LFL are fuel dependent. Britton and Frurip (2003) used T_f = 1440 K for "typical" hydrocarbons, T_f = 1505 K for other "typical" organic (CHON) fuels, and T_f = 1580 K for chlorinated organic compounds. Hence the single limit flame temperature used previously has been replaced by Britton and Frurip with three such limits for the various types of organic fuels (hydrocarbons, oxygenated organics, and halogenated organic fuels).

Very recently, Kondo et al. (2011) have conducted studies of the temperature dependence of the LFLs and UFLs of a variety of fuels in air using a 12-L glass sphere. Their finding of linear temperature dependence in the temperature range of 50 °C–100 °C was rationalized on the basis of a limit mixture energy using individual values for the average heat capacity and heat of combustion of the various fuels (Kondo et al., 2011). The LFL temperature coefficient was thus taken to be specific to a given fuel. They have also attempted to rationalize the temperature dependence of the UFLs on this basis, using the near constancy of the product of the LFL and UFL values with initial temperature found for most of the fuels they studied. Their derivation of the LFL temperature dependence is similar to that of Equation (2) with the temperature coefficient, $100 < Cp>/Q$, being taken from data on the mixture heat capacities and oxidation heat release per mole of fuel for each fuel. For a basis initial temperature of 25 °C, the equation they use becomes:

$$L_t = L_{25} - M(t - 25), \text{where} M = 10^2 \langle Cp \rangle / Q \quad (6)$$

Again, 20 °C can be used as the basis temperature to give:

$$L_t = L_{20} - M(t - 20) \quad (6a)$$

For UFLs, the corresponding equation is derived on the basis of a temperature invariant LFL × UFL:

$$U_t = U_{25} + U_{25} K_{25}(t - 25), \text{where} \quad (7)$$

$$K_{25} = 10^2 \langle C_p \rangle / (Q L_{25}), \text{and}$$

$$U_t = U_{20} + U_{20} K_{20}(t - 20), \text{where} K_{20} = 10^2 \langle C_p \rangle / L_{20} Q \quad (7a)$$

Having reached this point of specificity in predicting the temperature dependence of the flammability limits of fuels, a similar but more general and rigorous thermodynamic calculation can be considered. The calculation of the dependence of the limit fuel concentrations with initial temperature via the CEA thermodynamic code starts with the calculation of the limit adiabatic flame temperature at constant pressure (1 bar) corresponding to the experimental limiting fuel concentration at a given initial temperature (20 °C). The fuel concentration is varied in increments so that the calculated flame

temperature remains the same at the new initial temperature, t (°C). The process is repeated at other values of t.

3. Results and discussion

Table 1 summarizes experimental data on LFLs and UFLs from the 120-L steel sphere at ambient temperature, and provides the calculated values of the corresponding adiabatic flame temperatures. It also includes such data for hydrogen (H_2) and ammonia (NH_3) since thermodynamic (CEA) calculations extending to relatively high temperatures will be cited in several of the figures. It is noted that there is no constancy in the calculated limiting flame temperatures, neither between the LFL and UFL values for a given fuel, nor for the flame temperatures at the corresponding flammability limits of the species studied in the spheres. Hence, there is little theoretical basis for an invariant limiting flame temperature model. Nonetheless, the utility of this concept lies in the fact that the change in calculated limit fuel concentrations is relatively insensitive to variations in limit flame temperatures (T_f). Thus, it would take a variation of some 300 °C to effect a noticeable change in the experimental limit concentration of methane even at high initial temperatures well beyond the maximum initial temperature (100 °C) reported by Kondo et al. (2011). That is why the original value of 1225 °C chosen by White (1925) or the value 1300 °C chosen by Egerton (1953) gives consistent values for the temperature dependence of the LFL. Moreover, at their experimental LFLs, the adiabatic flame temperatures of the methane family (methane, ethane, propane) and ethylene family (ethylene and propylene) are about 1500 K and 1400 K, respectively. The calculated difference in T_f between methane, propane, and ethylene is, therefore, insufficient to change the effective temperature dependence of their LFL concentrations. This situation is no longer true for the UFL concentrations since there is a more marked variation in their corresponding flame temperatures (1699, 1282, and 1255 K for methane, propane, and ethylene, respectively). Hence, Equations (1a), (3), and (5a) would be expected to reasonably represent the variation of the LFLs of the methane and ethylene families of compounds with initial temperature, t (°C), but would call into question whether the linear Equation (4a) could generally and accurately represent the corresponding variation of the UFLs with initial temperature.

The test of such equations is, of course, a comparison of their predicted values to experimentally determined limit values with temperature. There had been a shortage, however, of such reliable experimental data prior to the recent publication of data by Kondo et al. (2011). With their data in hand, a comparison of the success of the above models in reproducing the temperature dependence data is now possible. That comparison is shown in Table 2. Besides the data based on Equations 1a,3,4a, and 5a, the table lists the experimental values of the Kondo et al. (2011) and their calculated values (Equations (6a) and (7a)), as well as the results of the thermodynamic calculations.

Examination of Table 2 shows little or no difference between the predictions of the above equations for the LFLs in the temperature range (5 °C–100 °C) studied. Significant differences do occur for the UFL of CO at temperatures above 50 °C. Both Equations (4a) And (7a) yield values that are significantly above the experimental ones for this fuel at higher temperatures. A comparison of the values calculated from the above equations with

the thermodynamic values and the experimental ones can, therefore, be conveniently done with reference to just the Kondo Equations (6a) and (7a). The results were graphed and those exhibiting significant differences between the calculations and experiment are shown in Figs. 1–5.

There is no significant difference between the experimental values and the calculated ones for the temperature dependence of the lower flammability limit (LFL) for the hydrocarbon gases (CH_4 and C_2H_4) and CO – at least in the experimental range of 5 °C–100 °C. There is a somewhat significant difference between these values for dimethyl ether, which appears to increase at higher temperatures (Fig. 1). Moreover, the calculated values are not conservative, i.e., the experimental LFL values are lower than the calculated ones. Replication of the work by Kondo and associates and its extension to higher temperatures will do much to clarify the issue. Currently, predictions for the LFL of dimethyl ether (DME) at temperatures outside the experimental range of Kondo et al. must rely on an extrapolation from the empirical linear temperature dependence observed (L_t (DME) = 3.40 − 0.0030t, with "t" in °C).

In contrast, the experimental upper flammability limit (UFL) variation with temperature does show a general deviation from the calculated values. The exception is CO for which there is no significant difference between the experimental values and the thermodynamic calculations (Fig. 2). With CH_4 the difference arises only above 50 °C, with the 2 calculation methods bracketing the experimental values (the thermodynamic values are less conservative – Fig. 3). Extrapolation at temperatures outside the experimental range can be done by averaging the results of the 2 calculation methods, or using the linear equation based on the experimental values (U_t (CH_4) = 15.5 + 0.010t). The same is true for C_2H_4 except that the thermodynamic values are more conservative. Moreover, the experimental UFL variation with temperature appears to be nonlinear and may converge with the thermodynamic calculations at temperatures well above 100 °C (Fig. 4). Again, additional credible experimental values at higher temperatures, i.e., experimental determinations using a sufficiently large chamber are needed to substantiate extrapolations from the current limited database. With DME both calculated values are significantly less conservative (lower) than the experimental ones. The slopes of the calculated temperature dependencies are quite similar and appreciably lower than the slope of the experimental values (Fig. 5). Hence the divergence of the actual value of the UFL of DME at higher temperatures from the calculated ones is expected to increase. As with the LFL, the UFL values for those higher temperatures must currently rely on extrapolation from the linear expression based on the 5 °C–100 °C data (U_t (DME) = 23.2 + 0.0794t).

The thermodynamic method (CEA code) which is based on adjusting the fuel concentrations in air to keep the calculated adiabatic flame temperature constant is perfectly general, and can be used to predict the temperature dependence at arbitrary initial temperatures. Such calculations for temperatures up to 450 °C have been done for a variety of inorganic and organic fuels. The results for CO, H_2, NH_3, and CH_4 are shown in Figs. 6 and 7. All the temperature dependent limits show linear behavior in the thermodynamic calculations. Unfortunately, credible experimental data, i.e., obtained in large chambers using relatively weak ignitors, is lacking, so that a comparison of the calculated and experimental values is

currently unavailable. The significance of higher mixture temperatures lies in the fact that reactions in the chemical industry often occur at such high temperatures. In the absence of experimental data generated in large vessels at temperatures well above 100 °C, it would be prudent to rely more on the thermodynamic calculations for such high temperatures rather than on a large extrapolation from data generated at much lower temperatures using the above Equations (1a)–(7a). Better yet, would be the use of either the thermodynamic prediction or that given by the experimental linear equation – whichever is more conservative.

In summary, there is a definite need for additional experimental determinations of the temperature dependence of flammability limits using sufficiently large chambers and less energetic ignitors to avoid both wall effects and 'ignition overdriving', i.e., to adequately distinguish between ignition and free flame propagation, and to avoid wall interference with the latter process. The need for such additional data is particularly relevant to predictions of the UFL at temperatures well above ambient.

4. Conclusions

The constant limiting flame temperature concept, independent of the nature of the fuel, is seen to be not strictly valid for the general prediction of the limiting concentrations of fuels, since there is considerable variation in such calculated temperatures. Nonetheless, the concept appears useful for the calculation of the dependence of the LFL limit on the initial temperature of many fuels at temperatures not far from ambient. The technique depends on having reliable LFL values at ambient temperatures to use as a basis for calculating limiting flame temperatures. While various calculation schemes based either on a limit flame temperature or a minimum energy of the fuel–air mixture can be used for predicting the LFLs as a function of initial mixture temperature, the thermodynamic method of adjusting fuel concentrations to give a constant flame temperature is more general, and has advantages in predicting the temperature dependence of the UFLs. This method does, however, require an efficient thermodynamic code with an extensive species library of thermodynamic functions over a wide temperature range. The CEA-400 code for PCs, developed at the NASA-LEWIS (Glenn) Research Center, is such a code. Guidance is provided to plant engineers on estimating the flammability limits of a variety of fuels at temperatures well beyond ambient values.

The project supporting this research endeavor has ended, so additional experiments will not be conducted. Therefore, the author can only offer predictions, given the shortage of reliable experimental data on temperature dependence for a large range of temperatures. Hopefully, other researchers will be encouraged to study flammability issues in larger chambers to test these concepts and predictions and to contribute to a reliable database of flammability limits.

I would be remiss not to mention the Japanese group of combustion researchers whose valuable contributions provide the experimental underpinnings of this paper and those of others, as well.

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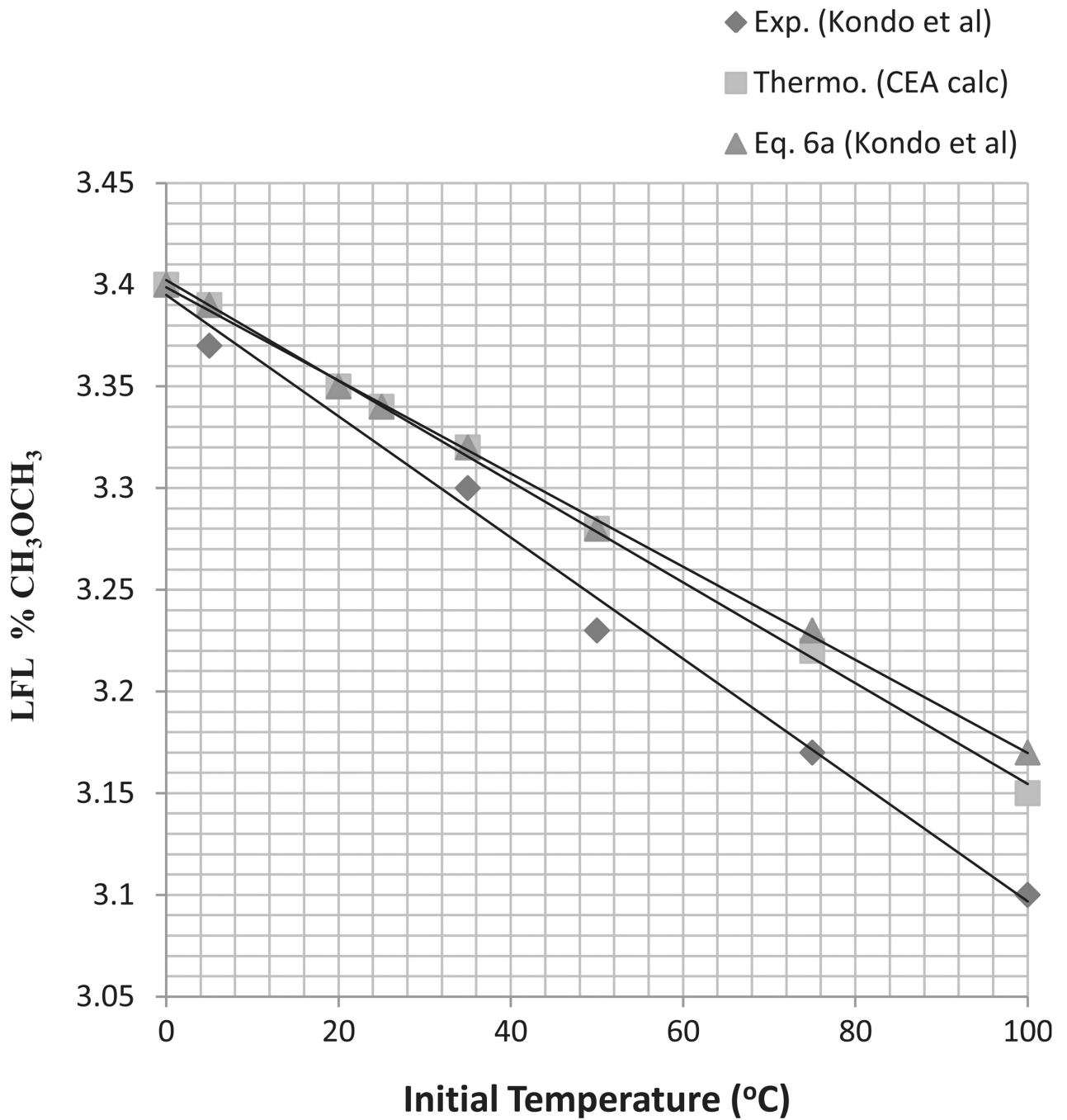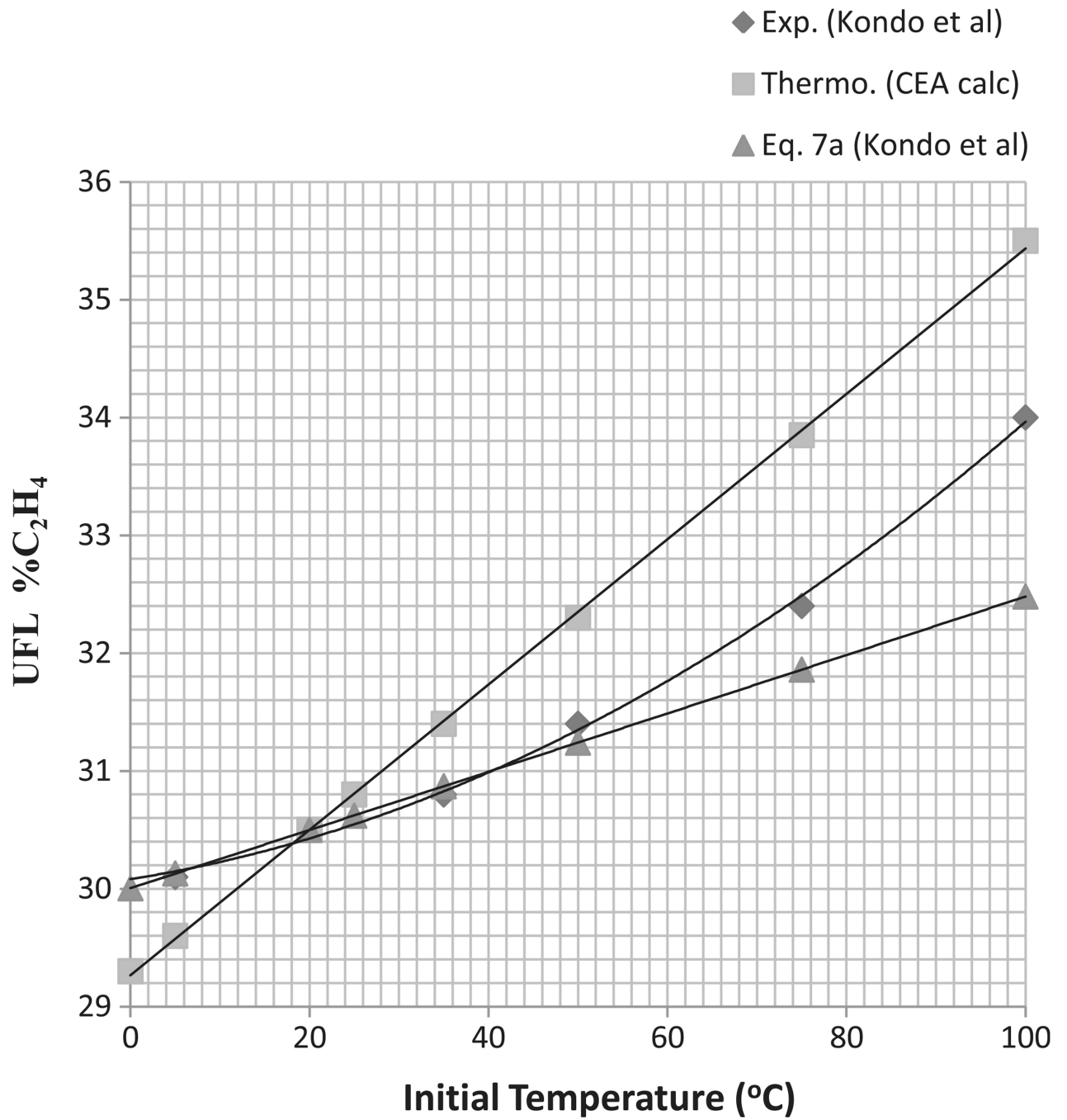
Fig. 1.
The LFL of dimethyl ether (CH_3OCH_3) in air vs. initial mixture temperature:
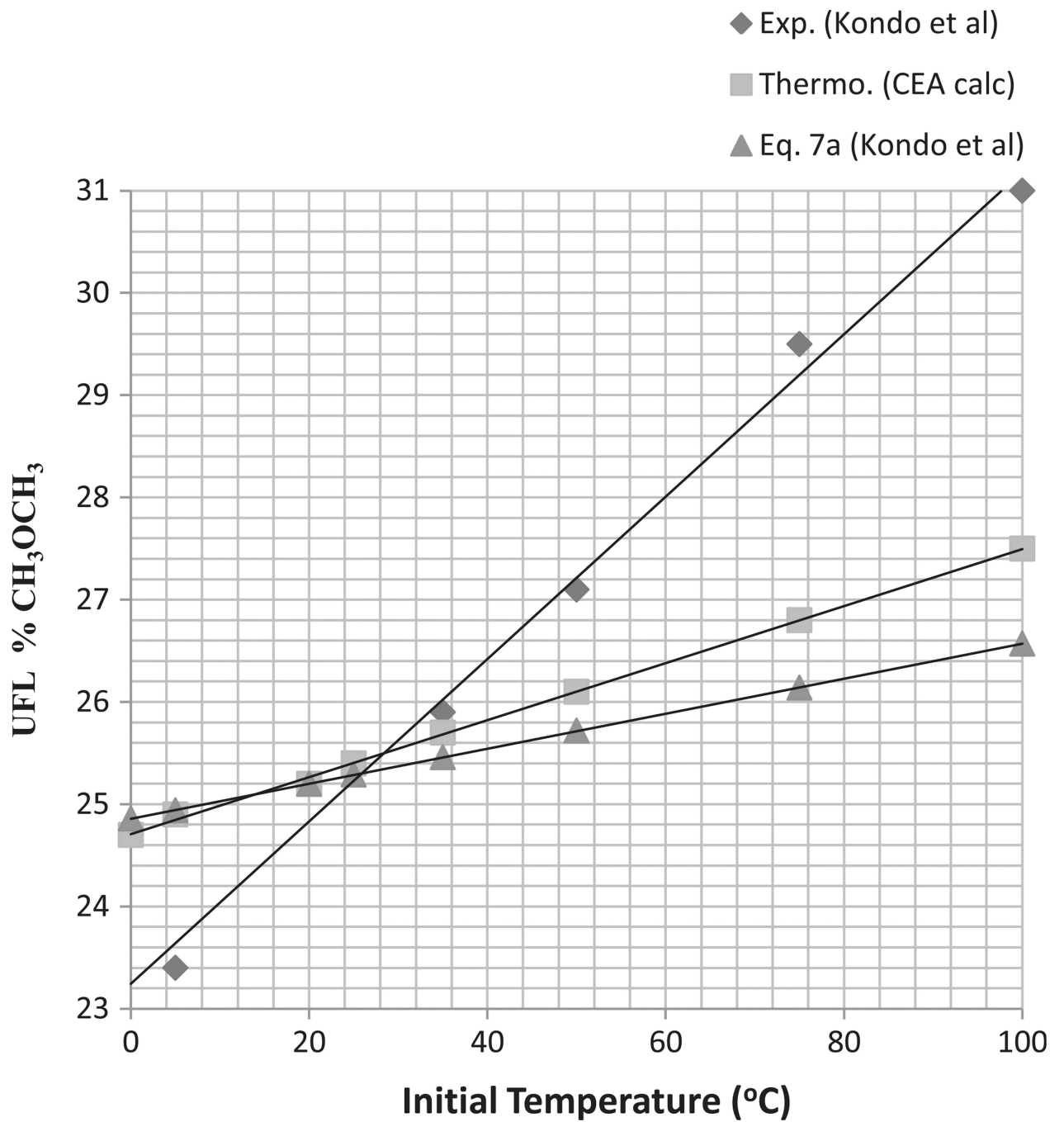thermodynamic (CEA) and Equation (6a) calculations vs. experiment (Kondo et al., 2011).
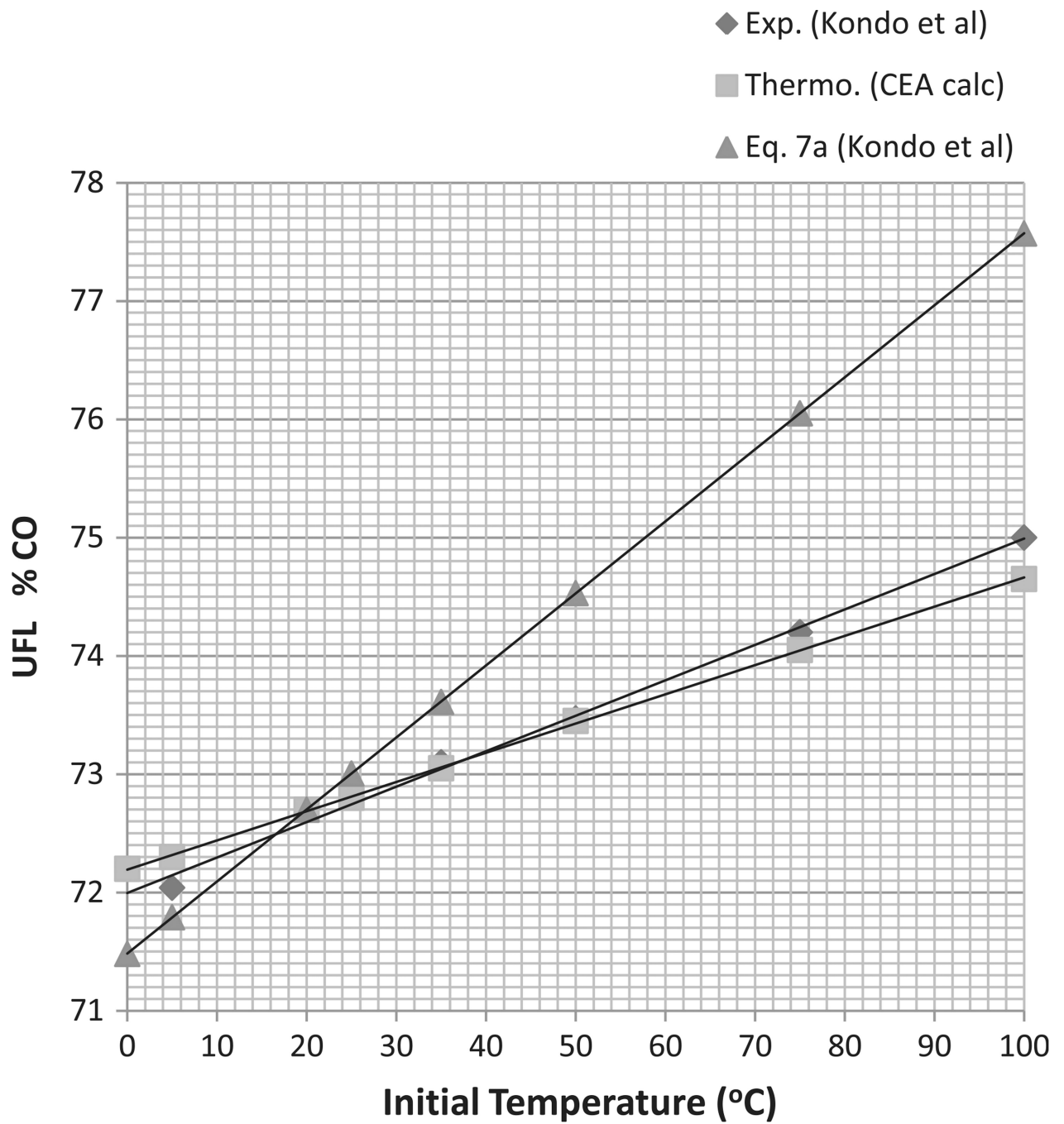
Fig. 2.
The UFL of carbon monoxide (CO) in air vs. initial mixture temperature: thermodynamic (CEA) and Equation (7a) calculations vs. experiment (Kondo et al., 2011).
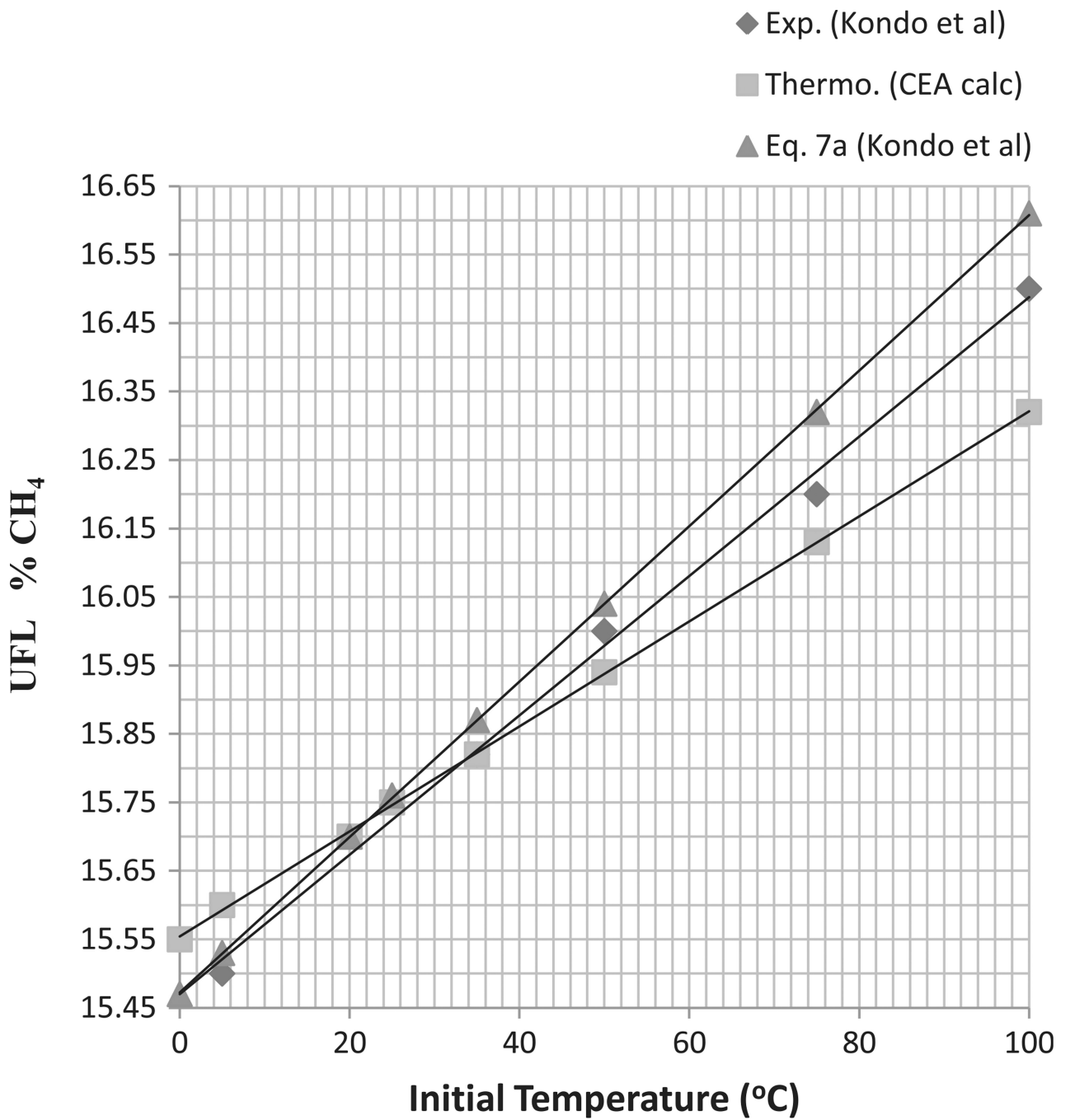
Fig. 3.

The UFL of methane (CH_4) in air vs. initial mixture temperature: thermodynamic (CEA) and Equation (7a) calculations vs. experiment (Kondo et al., 2011).

Fig. 4.
The UFL of ethylene (C_2H_4) in air vs. initial mixture temperature: thermodynamic (CEA) and Equation (7a) calculations vs. experiment (Kondo et al., 2011).
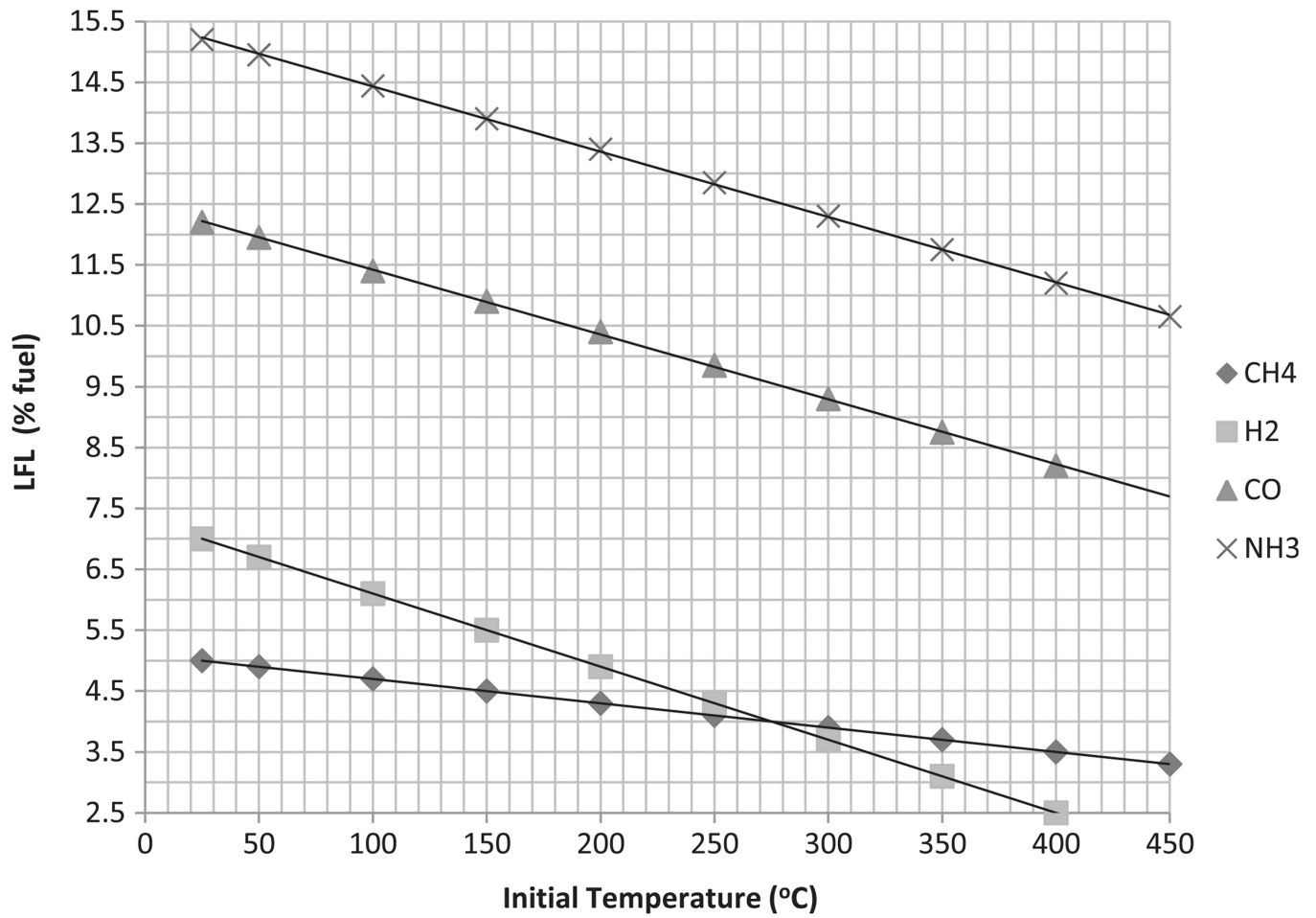
Fig. 5.
The UFL of dimethyl ether in air vs. initial mixture temperature: thermodynamic (CEA) and Equation (7a) calculations vs. experiment (Kondo et al., 2011).

Fig. 6.
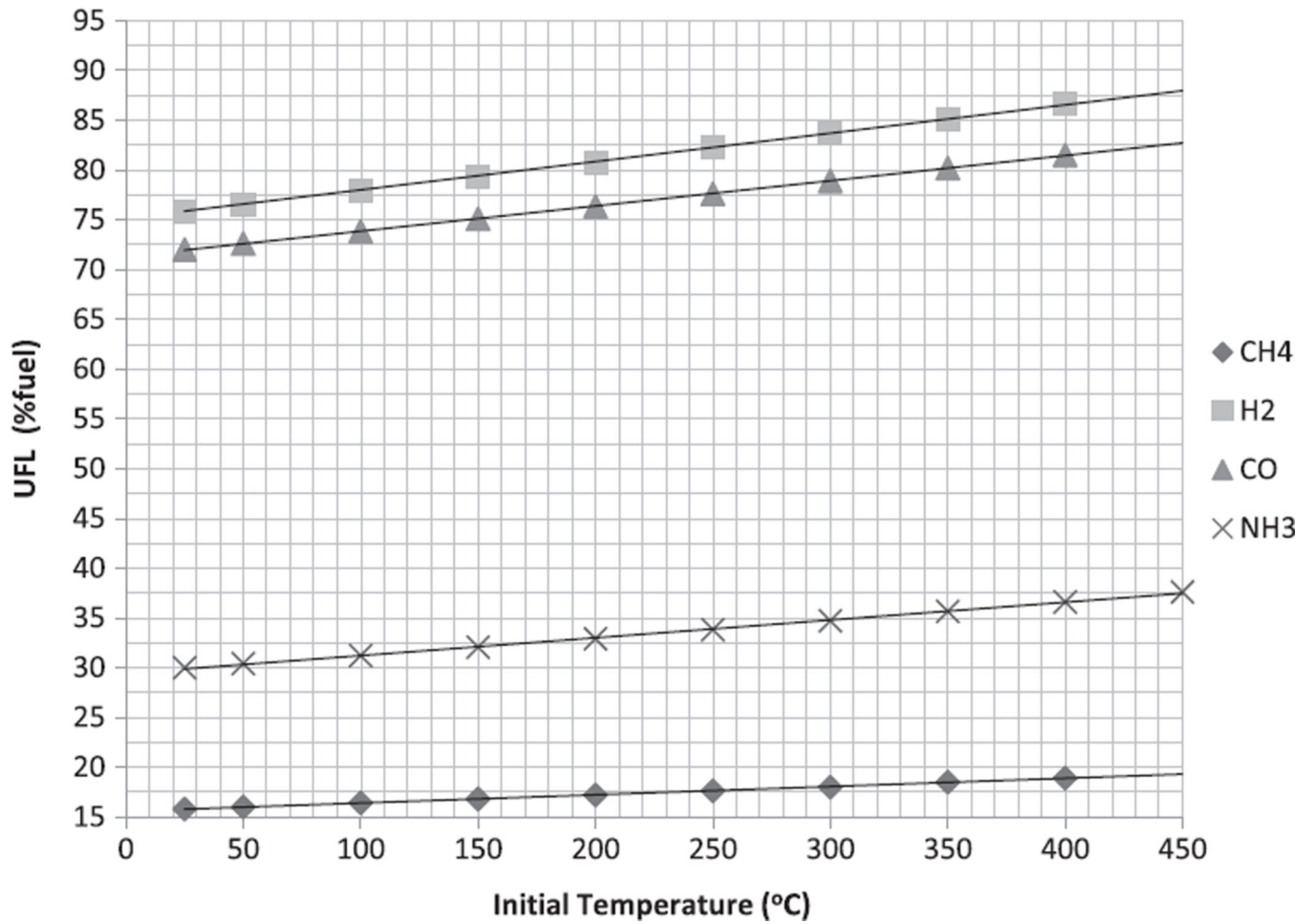The LFL of CH$_4$, CO, H$_2$, and NH$_3$ in air vs. initial mixture temperature: thermodynamic (CEA) calculations.

Fig. 7.
The UFL of CH_4, CO, H_2, and NH_3 in air vs. initial mixture temperature: thermodynamic (CEA) calculations.

Table 1

Experimental flammability limits (120-L sphere) and the theoretical (adiabatic) flame temperatures.

FUEL (F)	Formula (structure)	Lower flammable limit (LFL)		Upper flammable limit (UFL)	
		(mole % F)	Flame T/K	(mole % F)	Flame T/K
Methane	CH_4	5	1484	15.8	1699
Ethylene	$CH_2=CH_2$	2.75	1390	31.4	1255
Dimethyl-ether	CH_3OCH_3	3.4	1568	26.5	977
Carbon-monoxide	$C\equiv O$	12.2	1370	72	1333
Hydrogen	H_2	7	867	75.9	1135
Ammonia	NH_3	15.2^a	1649	30.0^a	1735

[a] Designates data from a 12-L glass sphere by Kondo et al. (2006).

Table 2

Limit concentrations versus initial temperature for four diverse fuels; calculated versus experimental data. The 20 °C data are italicized to indicate that the experimental values are the basis for the calculations.

$T_{initial}$	Lexp.	Thermo.	Lcalc. (1a)	Lcalc. (3)	Lcalc. (5a)	Lcalc. (6a)	Uexp.	Thermo.	Ucalc. (4a)	Ucalc. (7a)
Methane [CH4]										
0		5.03	5.03	5.02	5.04	5.02		15.55	15.47	15.47
5	5.00 ±.10	5.01	5.01	5	5.02	5.01	15.5 ±.10	15.6	15.53	15.53
20	4.95 ±.10	4.95	4.95	4.95	4.95	4.95	15.70 ±.10	15.7	15.7	15.7
25		4.93	4.93	4.93	4.93	4.93		15.75	15.76	15.76
35	4.94 ±.06	4.89	4.89	4.9	4.89	4.9	15.82 ±.10	15.82	15.87	15.87
50	4.88 ±.10	4.835	4.83	4.84	4.82	4.84	16.00 ±.10	15.94	16.04	16.04
75	4.74 ±.10	4.74	4.74	4.75	4.71	4.75	16.20 ±.10	16.13	16.32	16.32
100	4.70 ±.06	4.645	4.64	4.66	4.6	4.66	16.50 ±.10	16.32	16.61	16.61
Ethylene [CH2=CH2]										
0		2.8	2.79	2.79	2.8	2.8		29.3	30.06	30.004
5	2.77 ±.03	2.79	2.78	2.78	2.79	2.78	30.1 ±.8	29.6	30.17	30.13
20	2.75 ±.02	2.75	2.75	2.75	2.75	2.75	30.5 ±1.0	30.5	30.5	30.5
25		2.74	2.74	2.74	2.74	2.74		30.8	30.61	30.62
35	2.72 ±.02	2.72	2.72	2.72	2.71	2.72	30.8 ±.8	31.4	30.83	30.87
50	2.68 ±.02	2.68	2.69	2.69	2.68	2.68	31.4 ±.8	32.3	31.16	31.24
75	2.62 ±.03	2.62	2.63	2.64	2.62	2.63	32.4 ±.8	33.85	31.71	31.86
100	2.57 ±.02	2.57	2.58	2.59	2.56	2.57	34.0 ±.8	35.5	32.26	32.48
Dimethyl ether [CH3OCH3]										
0		3.4	3.4	3.4	3.41	3.4		24.7	24.84	24.86
5	3.37 ±.03	3.39	3.39	3.39	3.39	3.39	23.4 ±.8	24.9	24.93	24.94
20	3.35 ±.05	3.35	3.35	3.35	3.35	3.35	25.2 ±.7	25.2	25.2	25.2
25		3.34	3.34	3.34	3.34	3.34		25.4	25.29	25.29
35	3.30 ±.10	3.32	3.31	3.31	3.31	3.32	25.9 ±.7	25.7	25.47	25.46
50	3.23 ±.02	3.28	3.27	3.28	3.27	3.28	27.1 ±.7	26.1	25.75	25.72
75	3.17 ±.02	3.22	3.21	3.22	3.2	3.23	29.5 ±1.0	26.8	26.2	26.14
100	3.10 ±.03	3.15	3.14	3.16	3.13	3.17	31.0 ±1.0	27.5	26.65	26.57

$T_{initial}$	Lexp.	Thermo.	Lcalc. (1a)	Lcalc. (3)	Lcalc. (5a)	Lcalc. (6a)	Uexp.	Thermo.	Ucalc. (4a)	Ucalc. (7a)
Carbon monoxide [CO]										
0		12.5	12.49	12.48	12.5	12.51		72.2	71.65	71.48
5	12.67 ± .20	12.4	12.45	12.43	12.45	12.45	72.04 ± .15	72.3	71.91	71.79
20	12.3 ± .2	12.3	12.3	12.3	12.3	12.3	72.7 ± .2	72.7	72.7	72.7
25		12.2	12.25	12.26	12.25	12.25		72.8	72.96	73.005
35	12.16 ± .20	12.1	12.16	12.17	12.15	12.15	73.1 ± .1	73.05	73.49	73.61
50	12.0 ± .2	12	12.01	12.05	11.99	11.99	73.47 ± .10	73.45	74.27	74.53
75	11.8 ± .2	11.7	11.77	11.81	11.74	11.73	74.2 ± .2	74.05	75.58	76.05
100	11.5 ± .2	11.4	11.53	11.59	11.48	11.48	75.0 ± .2	74.65	76.89	77.57