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Smoke Point Height and Fire Properties of Materials

Archibald Tewarson

Factory Mutual Research
1151 Boston-Providence Turnpike
Norwood, MA 02062

December 1988

Prepared for
U.S. DEPARTMENT OF COMMERCE
National Institute of Standards and Technology
(Formerly National Bureau of Standards)
Center for Fire Research
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U.S. DEPARTMENT OF COMMERCE
C. William Verity, Secretary

NATIONAL INSTITUTE OF STANDARDS AND TECHNOLOGY
Ernest Ambler, Director

Notice

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TECHNICAL REPORT

SMOKE POINT HEIGHT AND FIRE PROPERTIES OF MATERIALS

by
Archibald Tewarson

Prepared for
National Bureau of Standards
Center for Fire Research
National Bureau of Standards
Washington, DC 20234

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May 1988

Approved by

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ABSTRACT

For engineering calculations in the gas phase, correlations have been established between smoke point heights and heat of combustion and yields of CO and particulates. Smoke point heights reported in the literature were modified such that all the data, including those measured by us, were consistent. Based on the data for 165 fuels from the literature and the data measured by us for 16 fuels, relationships have been suggested for the engineering calculations of heat of complete combustion, chemical heat of combustion and its convective and radiative components, and yields of CO and particulates as functions of the molecular weight for fuels with aliphatic and aromatic, saturated and unsaturated bonds between C and H; C, H and O; C, H, N and C, H and S atoms.

The efficiency of combustion decreases with increase in the bond unsaturation and aromatic nature. Substitution of O atoms in the structure increases the efficiency of combustion, whereas substitution of N and S atoms in the structures decreases the efficiency of combustion, S atoms being more efficient than N atoms.

The generalized relationships have been used to assess the decomposition, gasification and combustion processes for polymers.

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I

INTRODUCTION

Fires are hazardous because fire products are responsible for creating thermal (high temperature) and nonthermal (toxic, corrosive and reduced visibility) environments. Fire products are governed by the chemical structures and physical states of fuel vapors, fire ventilation and environmental conditions. For example, for polymers, fuel vapors consist of monomers, oligomers, their mixtures or the decomposition products of the original polymers[1].

A method based on the smoke point height has been investigated in this study to examine the effect of chemical structures on the generation of heat and chemical compounds in the gas phase in fires. Smoke point height is defined as the height of a laminar diffusion flame at which the flame breaks open at its apex and emits a stream of smoke. Smoke point height is related to the smoke forming tendencies and flame radiation characteristics of fuels[2-5]. Smoke point heights have been reported in the literature for a large number of saturated and unsaturated, aliphatic and aromatic gases and liquids with C, H, O, N and S atoms in the structure[2-9].

II
EXPERIMENTS

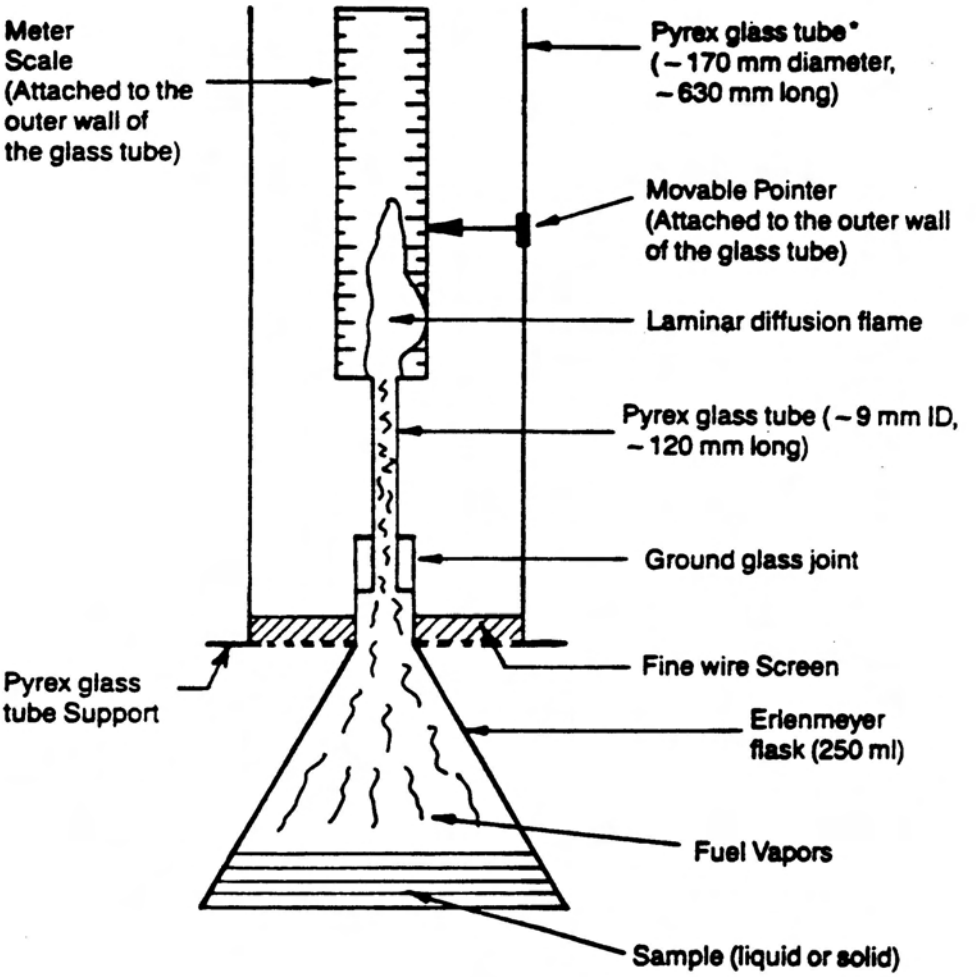
In our study, generation rates of fuel vapors, heat, and chemical compounds and smoke point heights were measured for two gases, nine liquids and five polymers. Details of the experimental apparatus used are described in Reference 10.

2.1 MEASUREMENT OF SMOKE POINT HEIGHT

For the measurement of smoke point heights, diffusion flames inside a 0.60 m long, 0.17 m ID Pyrex glass cylinder were used as shown in Figure 1. The top of the cylinder was covered with a 0.20 m diameter, 0.02 m thick Marinite disc with a 0.05 m hole in the center. The cylinder was placed on a metal ring stand covered with a fine wire screen with a 0.009 m hole in the center for accommodating the tube for fuel vapors. For gases, a 0.15 m long, 0.009 m ID thin stainless steel tube and for liquids and polymers, a 0.12 m long, 0.009 m ID Pyrex glass tube were used. The tubes were located on the axis of the Pyrex glass cylinder, with the tip of the tubes about 0.10 m above the bottom of the cylinder. For the measurement of the smoke point height, a diffusion flame was established at the tip of the stainless or Pyrex glass tube. Smoke point heights were measured visually, using a meter scale with a movable pointer attached to the outside of the cylinder. For each fuel, three measurements were made for the smoke point height and data were averaged.

For the measurement of the smoke point heights of gases, the flame height was varied by varying the fuel flow rate. For liquids and polymers, a 250 ml Pyrex Erlenmeyer flask with a 14/35 ground glass joint attached to the Pyrex glass tube was used. Flame heights were varied by varying the gasification rates of liquids and polymers. For liquids, an electrical heating mantle around the Erlenmeyer flask, and for polymers, a Bunsen burner under the Erlenmeyer flask, were used.

The smoke point heights measured were very similar to the heights reported in the literature for gases. However, the data for identical liquids reported in the literature by various investigators showed significant variations and were different from our measured values. In order to make the literature data compatible with each other as well as with our data, the following procedure was used: 1) for identical liquids, separate



*or double very fine wire mesh cylinder (~190 mm diameter and ~460 mm long)

Figure 1. Smoke Point Apparatus for Liquids and Solids.

relationships were established between the smoke point height data reported by individual investigators and data measured by us; 2) all the data reported by individual investigators were then modified separately using the above relationships; and 3) the modified data for identical liquids were averaged.

2.2 GENERATION RATES OF FUEL VAPORS, HEAT AND CHEMICAL COMPOUNDS

The generation rates of fuel vapors, heat and chemical compounds for turbulent diffusion flames were measured in our flammability apparatus, shown in Figure 2. The fuels were contained in a 0.05 m deep and 0.10 m diameter aluminum dish, or in a 250 ml Erlenmeyer flask and were placed in the apparatus at the location marked "sample" in Figure 2. For varying the generation rate of fuel vapor, two sets of experiments were performed: 1) where external heat flux from four coaxially placed radiant heaters, as shown in Figure 2, was varied; and 2) where power to the heating mantle around the Erlenmeyer flask was varied (used for high vapor pressure liquids). All the experiments were performed under natural air flow conditions for well-ventilated fires. The generation rate of fuel vapor was measured continuously by a load cell assembly as shown in Figure 2.

The fire products were captured in the sampling duct along with air as shown in Figure 2, where the measurements were made for the generation rates of heat and chemical compounds[11]. From the experimental data, the ratio of the generation rate of compound to the generation rate of fuel vapor was calculated, which is defined as the experimental yield, Y_j. The ratio of the experimental yield to the maximum possible theoretical yield was also calculated, which is defined as the generation efficiency, f_j, of the compound. In addition, the ratio of the generation rate of heat to the generation rate of fuel vapor, defined as the heat of combustion, was calculated. The chemical heat of combustion, ΔH_{Chem}, was based on the generation rate of chemical heat, obtained from the generation rates of CO_2 and CO. The convective heat of combustion, ΔH_{Con}, was based on the generation rate of convective heat (total flow rate of fire product-air mixture x gas

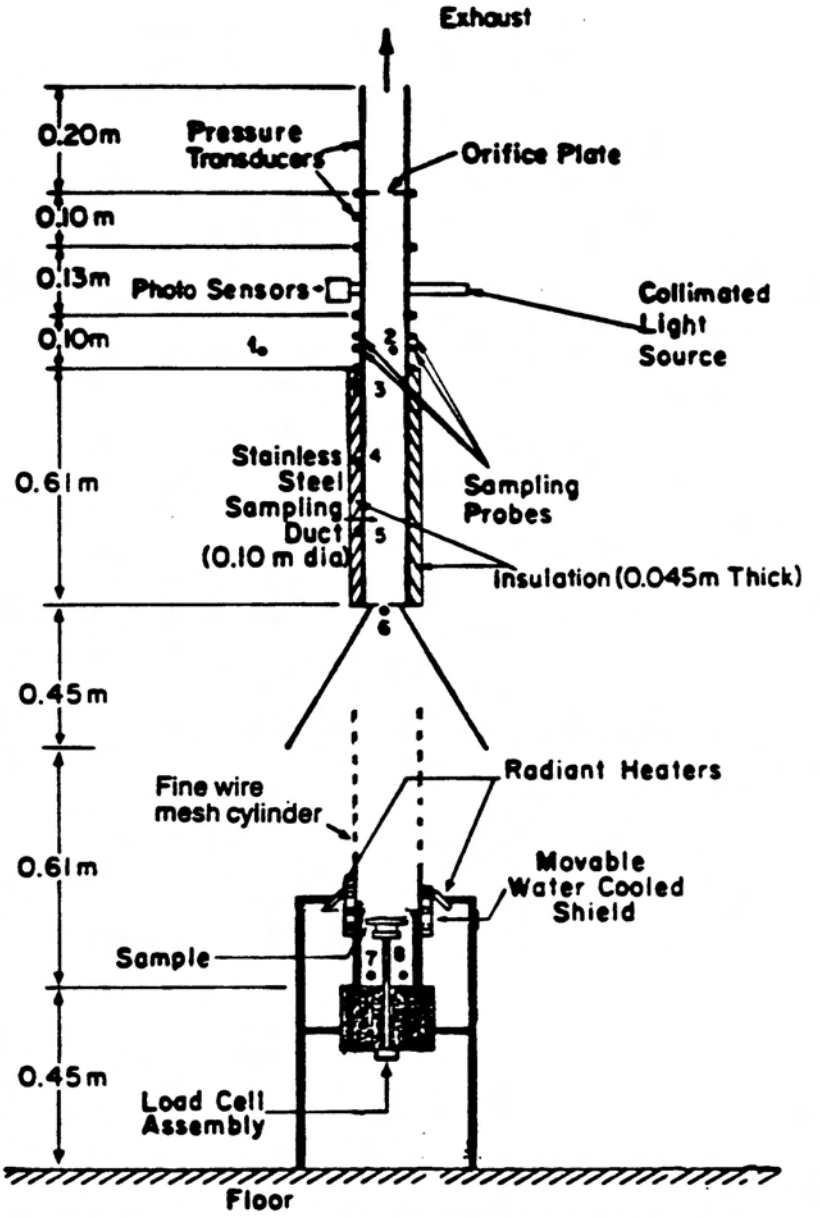


Figure 2. 10 KW - Scale Flammability Apparatus.

temperature above ambient x specific heat of air at the gas temperature). The radiative heat of combustion, ΔH_{Rad}, was calculated from the difference between ΔH_{Chem} and ΔH_{Con}.

The experimental data were also used to calculate the generation efficiency of heat, which is defined as the ratio of the heat of combustion to the net heat of complete combustion, ΔH_T. The data for ΔH_T were either taken from the literature, calculated from the heat of formation of the chemical bonds or measured in an oxygen bomb calorimeter.

III

EXPERIMENTAL RESULTS

Figures 3 and 4 show the experimental data for the generation efficiencies of chemical, convective and radiative heat, CO and particulates as functions of smoke point height (ℓ_s). From the regression analysis for the best fit of the data, relationships and associated coefficients have been derived, which are listed in Table I. The relationship and associated coefficients for x_{Rad} are very similar to those reported by Markstein[5].

In order to calculate the heat of combustion and yield of chemical compounds from the data in Table I, it was necessary that all the literature and measured data for smoke point heights be made consistent. Thus, separate correlations were established between our data and literature data reported by each investigator. Based on these separate correlations, smoke point height data of each investigator were modified and data for common fuels were averaged. As a result of this procedure, it was possible to calculate heat of combustion and yield of chemical compounds from the smoke point heights for 165 fuels with C, H, O, N and S atoms in the structure (saturated and unsaturated, linear, branched and cyclic, aliphatic and aromatic).

From the smoke point heights, coefficients listed in Table I and known values of ΔH_T and k_j, ΔH_i and Y_j values were calculated. The values calculated in this fashion are listed in the Appendix in Tables A1 to A17. Some selected values are listed in Table II along with the directly measured values, where the two sets of values show reasonable agreement.

3.1 RELATIONSHIP BETWEEN HEAT OF COMBUSTION, YIELDS OF CO AND PARTICULATES AND THE MOLECULAR WEIGHT

The values calculated for ΔH_i and Y_j, based on the smoke point heights, are found to be linear functions of the molecular weight,

$$\Delta H_i = A_{i,k} M + B_{i,k} , \qquad (1)$$

$$Y_j = C_{j,k} M + D_{j,k} , \qquad (2)$$

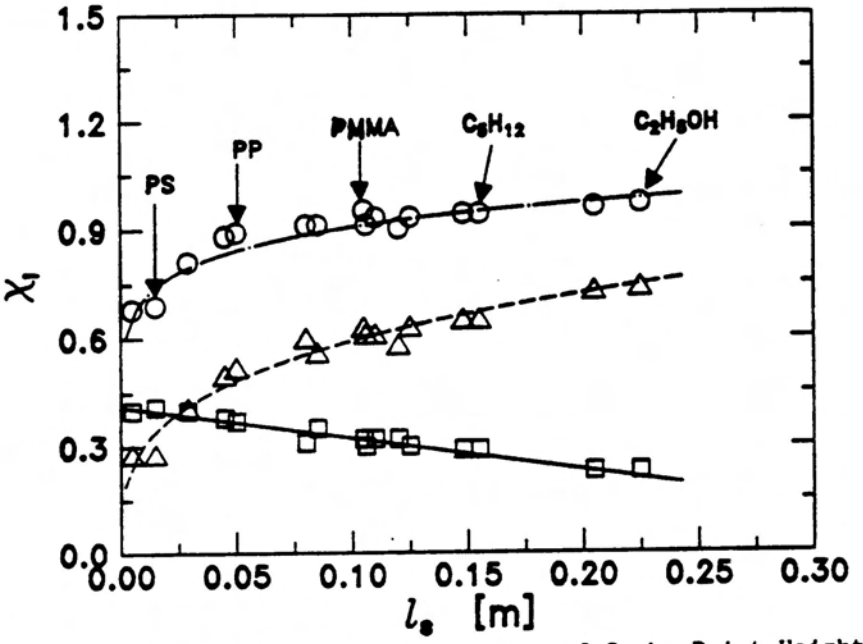


Figure 3. Generation Efficiency as a Function of Smoke Point Height.
○: Chemical; △: Convective; □: Radiative. Only selected fuels are identified.

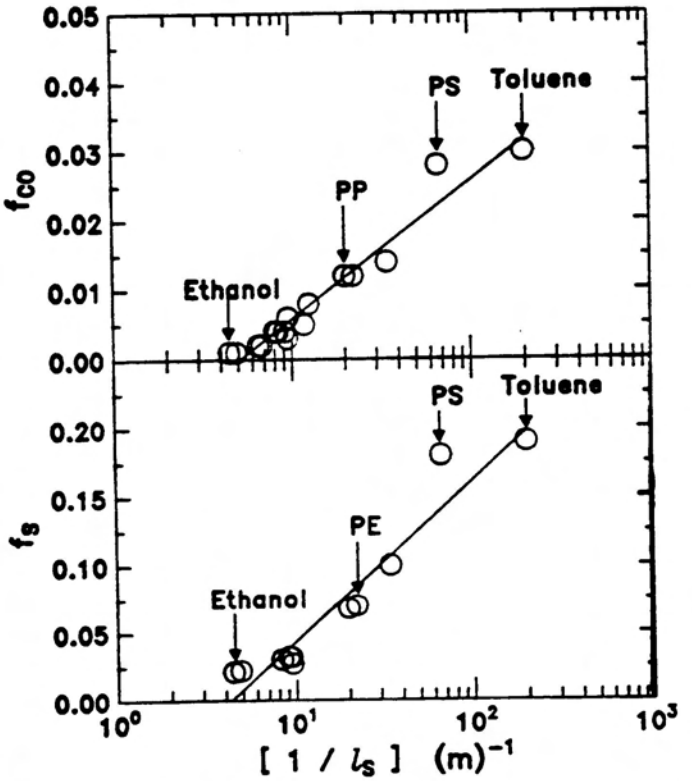


Figure 4. Generation Efficiencies of CO and Particulates as Functions of Smoke Point Height.

TABLE I

Relationships and Coefficients for the Smoke Point Height and Generation Efficiencies of Heat and Chemical Compounds

$a - bt_s$	ct_s^d	$h\ln(1/t_s) - g$
χ_{Rad}	χ_{Chem}	f_{CO}
$a = 0.410$	$c = 1.15$	$h = 8.60 \times 10^{-3}$
$b = 0.852$	$d = 0.104$	$g = 1.28 \times 10^{-2}$
$R^2 = 0.950$	$R^2 = 0.997$	$R^2 = 0.974$
	χ_{Con}	f_S
	$c = 1.13$	$h = 5.03 \times 10^{-2}$
	$d = 0.285$	$g = 6.12 \times 10^{-2}$
	$R^2 = 0.996$	$R^2 = 0.940$
	f_{CO_2}	
	$c = 1.16$	
	$d = 0.108$	
	$R^2 = 0.998$	

R^2: Coefficient of determination. Smoke point height (t_s) in m. Range of validity, $t_s \leq 0.243$ m.

TABLE II

Calculated Versus Measured Yields for CO_2 and Particulates

Fuel	Yield (g/g)[a]					
	CO_2			Particulates		
	Cal.	Meas	Ref.	Cal.	Meas.	Ref.
Ethanol	1.86	1.86	12	0.008	0.010	13
Acetone	2.18	2.14	12	0.014	0.014	13
Propane	2.85	2.85	12	0.025	NR	-
Propanol	2.07	2.11	12	0.012	NR	-
Polymethylmethacrylate	2.07	2.00	12	0.022	0.024	13
Heptane	2.86	2.86	14	0.037	NR	-
Hexane	2.82	2.85	12	0.038	NR	-
Octane	3.09	NR	-	0.039	0.053	13
Polypropylene	2.77	NR	-	0.059	0.046	13
Polyethylene	2.73	2.86	12	0.060	NR	-
Ethylene	2.86	-	-	0.076	0.064	15
Propylene	2.48	2.77	12	0.070	0.091	16
Polystyrene	2.34	NR	-	0.166	0.192	13
Toluene	2.24	2.61	12	0.179	0.155	17

[a]Cal: Calculated (this study); Meas: Measured (listed reference). Ref. 12 - two layer compartment model; Ref. 13: from soot volume fraction in diffusion flames; Ref. 14: 0.008 to 0.92 m^2 pool fires; Ref. 15: Laminar flame, fuel flow rate 5.4 ml/s. 16: 0.91 m diameter burner with a chemical heat release rate of about 1300 kW. Ref. 17: 1.3% toluene-hydrogen fuel mix. NR: Not reported.

where M is the molecular weight in g/mole, ΔH_i is in kJ/mole; Y_j is in g/mole and A, B, C and D are constants within each generic group of fuels. Subscript i represents chemical, convective or radiative; subscript j represents a chemical compound and subscript k represents a generic group. A_i is in kJ/g; B_i is in kJ/mole; C_j is in g/g and D_j is in g/mole. Values of these constants, derived from the regression analysis of the data for 165 fuels from the literature and 16 fuels from our study for well-ventilated fires, are listed in Table III.

Some estimations, based in Eqs. (1) and (2) and constants from Table III, are shown in Table IV, along with the values calculated from the smoke point heights. A comparison of the two sets of values are fairly reasonable.

Kent[18] has examined the relationship between the generation efficiency of particulates and smoke point height and has reported f_s data for 23 hydrocarbons measured in the flame; he finds this data to be about three times the data measured downstream of the flame[15,17]. The ratios of the data reported by Kent[18] and calculated from Eqs. (1) and (2) and Table III, are: 1) alkanes: 2.88 $\pm$ 0.19; 2) alkenes: 2.74 $\pm$ 1.04; 3) alkynes: 2.59 $\pm$ 0.35; 4) cyclic alkanes; 3.03 $\pm$ 0.97; and 5) arenes: 1.94 $\pm$ 0.26. Bard and Pagni's data[13], which are also measured in the flame, agree reasonably well with our data (Table II), as well as various other data for particulate volume fraction measured in the flame. Thus Kent's[18] data are inconsistent.

TAB I

CONSTANTS FOR THE ESTIMATION OF HEAT OF COMBUSTION AND YIELDS OF CO AND PARTICULATES FOR WELL-VENTILATED FIRES

Fuels	Heat of Combustion (kJ/mole)								Yield (g/mole)			
	Complete (Net)		Chemical		Convective		Radiative		CO		Particulates	
	A_T	B_T	A_{Chem}	B_{Chem}	A_{Conv}	B_{Conv}	A_{Rad}	B_{Rad}	C_{CO}	D_{CO}	C_S	D_S
C-H Structure												
Normal Alkanes (C-C-H)	43.6	104	39.3	192	24.8	280	14.5	- 88	0.0135	-0.362	0.0469	-1.02
Branched Alkanes (C-C-H[a])	43.6	101	37.2	268	22.1	364	15.9	-177	0.0226	-0.760	0.0675	-1.81
Cyclic Alkanes (C-C-H[aa])	41.3	209	33.1	430	17.6	457	15.6	- 28	0.0276	-0.700	0.0917	-2.55
Alkenes (C = C-H)	43.3	131	38.4	88	22.2	143	16.3	- 30	0.0245	-0.322	0.0577	0.517
Alkynes (C ≡ C-H)	43.7	107	35.7	27	18.9	- 5	18.9	- 5	0.0339	0.204	0.0934	0.0659
Arenes (d-C-H)[a]	37.4	211	28.5	- 74	11.8	- 59	16.8	- 15	0.0612	0.433	0.165	1.22
Dienes (C=C-C=C-H)	42.8	97	33.3	18	16.5	- 60	18.2	- 18	0.0430	0.280	0.117	0.450
C-H-O Structures												
Esters (Aliphatic) (C-C-H-O)	43.8	-1750	42.3	-1660	25.2	- 863	13.6	-677	0.0186	-1.19	0.0608	-3.67
Esters (Aliphatic-Others) (C-C-H-O)[b]	44.0	-1558	42.1	-1471	30.8	- 974	11.4	-501	0.0159	-1.72	0.0526	-5.01
Normal Alcohols (Aliphatic) (C-C-H-O)	45.4	- 813	40.4	- 682	25.7	- 307	14.7	-378	0.0095	-0.400	0.0371	-1.34
Alcohols (Aliphatic-Others) (C-C-H-O)[c]	44.0	-1558	42.1	-1471	30.8	- 974	11.4	-501	0.0136	-0.186	0.0445	-0.541
Ketones (Aliphatic) (C-C-H-O)	45.0	- 888	42.1	- 825	29.5	- 534	12.6	-290	0.0095	-0.400	0.0371	-1.34
Various (Aromatic) (d-C-H-O)[a]	39.4	- 732	36.5	-1529	22.0	-1379	14.5	-150	0.0470	0.433	0.165	-3.02
C-H-N Structures												
Aliphatic (C-C-H-N)	44.0	- 441	38.9	- 360	23.9	- 188	15.0	-173	0.0176	-0.405	0.0560	-1.22
Aromatic (d-C-H-N)[a]	42.3	- 795	30.8	- 535	13.1	- 127	17.3	-362	0.0763	-3.08	0.204	-7.91
C-H-S Structures												
Aliphatic (C-C-H-S)	39.0	- 706	33.3	- 381	19.5	-189	13.6	-353	0.0248	-1.51	0.0741	-4.02
Aromatic (d-C-H-S)[a]	41.3	- 793	28.3	- 410	11.5	- 59	16.9	-370	0.0897	-4.95	0.237	-12.7

a: d - benzene rings; b: oxalates, malonates, lactates, etc.; c: unsaturated and cyclic.

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TABLE IV

CALCULATED AND ESTIMATED VALUES FOR ΔH_i AND Y_j FOR WELL-VENTILATED FIRES OF SELECTED FUELS[a]

Fuels	Mol. Wt. of Fuel Vapors g/mole	ΔH_i (kJ/g) Complete Comb. Theor.[c]	Complete Comb. Est.	Chemical Cal.	Chemical Est.	Convective Cal.	Convective Est.	Radiative Cal.	Radiative Est.	Y_j (g/g) CO Cal.	CO Est.	Particulates[b] Cal.	Particulates[b] Est.
C-C Structure													
Propane (C_3H_8)	44	46.4	46.0	44.3	43.7	31.6	31.2	12.7	12.5	0.005	0.005	0.025	0.024
Octane (C_8H_{18})	114	44.4	44.5	40.8	41.0	27.1	27.3	13.7	13.7	0.011	0.010	0.039	0.038
Transformer Fluids	300[d]	43.9	43.9	36.9	38.1	24.5	23.3	12.4	15.3	0.019	0.020	0.059	0.061
Ethylene (C_2H_4)	28	47.2	48.0	43.0	41.5	27.8	27.3	15.2	15.2	0.013	0.013	0.045	0.076
Propylene (C_3H_6)	42	45.8	46.4	40.8	40.5	22.9	25.6	17.9	15.6	0.020	0.017	0.103	0.070
Octene (C_8H_{16})	112	44.2	44.5	38.9	39.2	23.9	23.5	15.0	16.0	0.018	0.022	0.057	0.062
Polyethylene	597[d]	43.6	43.5	38.4	38.5	21.8	22.4	16.6	16.2	0.024	0.024	0.060	0.059
Polypropylene	1300[d]	43.4	43.4	38.6	38.5	22.6	22.3	16.0	16.3	0.024	0.024	0.059	0.058
Acetylene (C_2H_2)	26	48.2	47.8	36.6	36.7	17.8	18.7	18.8	18.7	0.045	0.042	0.129	0.096
Dodecyne ($C_{12}H_{22}$)	166	44.4	44.3	35.5	35.9	18.2	18.1	16.9	18.7	0.034	0.035	0.104	0.094
Butadiene (C_4H_6)	54	44.6	44.6	33.0	33.6	15.2	15.4	17.8	17.8	0.048	0.048	0.134	0.125
Styrene (C_8H_8)	104	39.5	39.4	27.1	27.8	10.9	11.2	16.6	16.7	0.067	0.065	0.185	0.171
Naphthalene ($C_{10}H_8$)	128	38.8	39.0	26.4	27.9	10.4	11.3	16.4	16.7	0.072	0.065	0.188	0.175
Triamylbenzene ($C_{21}H_{36}$)	288	38.1	38.1	28.2	28.2	11.8	11.6	16.3	16.7	0.059	0.063	0.166	0.169
Polystyrene	117[d]	39.2	39.2	27.0	27.9	11.0	11.3	16.0	16.7	0.060	0.065	0.166	0.175
C-H-O Structure													
Methanol (CH_4O)	32	20.0	20.0	19.4	19.1	16.6	16.1	2.8	2.9	0.001	0.001	e	e
Ethanol (C_2H_6O)	46	27.8	27.7	27.0	25.6	20.6	19.0	6.4	6.5	0.003	0.004	0.008	0.008
Ethylbutylalcohol ($C_6H_{14}O$)	102	37.8	37.4	34.0	33.7	22.7	22.7	11.3	11.0	0.006	0.007	0.024	0.024
Benzyl Alcohol (C_7H_8O)	108	32.7	32.6	22.8	22.3	9.8	9.2	13.0	13.1	0.050	0.051	0.137	0.137
Acetone (C_3H_6O)	58	28.6	29.0	27.5	27.9	20.9	20.3	6.6	7.6	0.003	0.003	0.014	0.014
Methyl ethyl ketone (C_4H_8O)	72	32.0	32.7	30.6	30.6	23.0	22.1	7.6	8.6	0.004	0.004	0.017	0.018
Phenyl butyl ketone ($C_{11}H_{14}O$)	162	35.0	34.9	26.6	27.1	12.6	13.5	13.7	13.6	0.041	0.050	0.165	0.163
Benzaldehyde (C_7H_6O)	106	32.5	32.5	21.5	22.0	8.1	9.0	13.3	13.1	0.062	0.051	0.140	0.136
Polyoxymethylene	30[b]	15.4	15.4	14.4	14.6	11.2	11.7	3.2	2.9	e	e	e	e
Ethyl Formate ($C_3H_6O_2$)	74	20.4	20.2	20.0	19.9	15.7	13.5	4.3	4.5	0.002	0.003	0.008	0.011
Ethyl laurate ($C_{14}H_{28}O_2$)	228	37.0	37.2	35.2	35.6	24.8	26.5	10.4	9.2	0.007	0.008	0.034	0.031
Polymethylmethacrylate	94[b]	25.2	25.2	24.2	24.6	16.6	16.0	7.6	6.4	0.010	0.006	0.022	0.022
C-H-N Structure													
Diethylamine ($C_4H_{11}N$)	73	38.1	38.0	33.9	34.0	21.0	21.3	13.0	12.6	0.013	0.012	0.042	0.039
Tributylamine ($C_{12}H_{27}N$)	185	41.6	41.6	36.6	37.0	22.5	22.9	14.1	14.1	0.016	0.015	0.050	0.049
Aniline (C_6H_7N)	93	33.7	33.8	24.6	25.0	11.1	11.7	13.5	13.4	0.044	0.043	0.120	0.119
Dimethylquinoline ($C_{11}H_{11}N$)	157	36.7	36.7	27.2	27.1	12.1	12.2	15.0	14.8	0.050	0.054	0.138	0.148
C-H-S Structure													
Hexyl Mercaptan ($C_6H_{14}S$)	118	33.1	33.0	29.1	30.1	17.9	17.9	11.3	10.6	0.012	0.012	0.040	0.040
Decyl Sulfide ($C_{20}H_{42}S$)	314	36.6	36.8	30.0	33.2	16.5	18.9	13.5	12.5	0.026	0.020	0.075	0.061
Cresylmethylsulfide ($C_8H_{10}S$)	154	36.4	36.2	25.7	25.6	10.8	11.1	14.9	14.5	0.060	0.058	0.153	0.155

a: Cal: Calculated based on smoke point height and coefficients from Table I; Est.: Estimated based on Eqs. (1) and (2) and constants from Table III.

b: Assumed to be carbon.

c: Taken from literature or calculated from heats of formation of chemical bonds or measured in an Oxygen Bomb Calorimeter.

d: Suggested generic group and average molecular weight of fuel vapors.

e: <0.001.

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IV
DISCUSSION

For examining the effects in the gas phase of the chemical structures on the generation of heat and chemical compounds and assessment of decomposition, gasification and combustion processes for fuels, Eqs. (1) and (2) and constants from Table III have been used in this study.

4.1 EFFECTS OF CHEMICAL STRUCTURES ON THE GENERATION OF HEAT AND CHEMICAL COMPOUNDS

Figures 5 and 6 show plots for calculated values of Y_{CO} and Y_S as functions of the molecular weight. The slopes in the figures are a measure of the yields in g/g. A higher value of Y_{CO} and Y_S indicates that combustion is less efficient.

The results in Figures 5 and 6 for fuels with C and H atoms in the structure show that with increase in bond unsaturation (changes in the chemical bonds from single to double to triple bonds and benzene rings in the structure) the yields of CO and particulates increase. A comparison between alkynes, dienes and arenes show that the yields of CO and particulates are highest for the arenes followed by dienes and then alkynes.

The results in Figures 5 and 6 for fuels with C, H, O, N and S atoms in the structure show that: 1) yields of CO and particulates are lowest for fuels with C-H-O structures, but increase if a benzene ring or rings are present in the structures; and 2) introduction of N and S atoms instead of O atoms in the structure results in an increase in the yields of CO and particulates. The yields of CO and particulates for fuels with S atoms and aromatic rings in the structures are highest when compared with fuels with similar molecular weight.

The trends found for the variations of Y_{CO} and Y_S with chemical structures are probably related to the thermal stability and nature of chemical bonds. With increase in the thermal stability, resistance to free radical formation is expected to increase. For example, for hydrocarbons, the thermal stability is expected to be as follows: alkanes < alkenes < alkynes < arenes. The pyrolysis data for hydrocarbons[18] show that with increase in the thermal stability, the ratio of the amounts of unsaturated aliphatic and aromatic hydrocarbons to saturated hydrocarbons in the pyrolysis products increase.

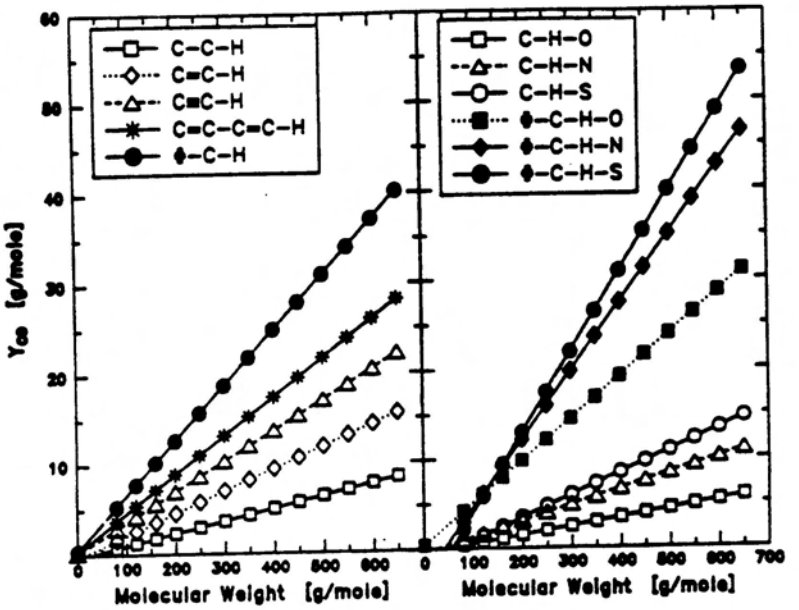

Figure 5. Yield of CO as a Function of Molecular Weight. Symbols are used for identification purposes only.

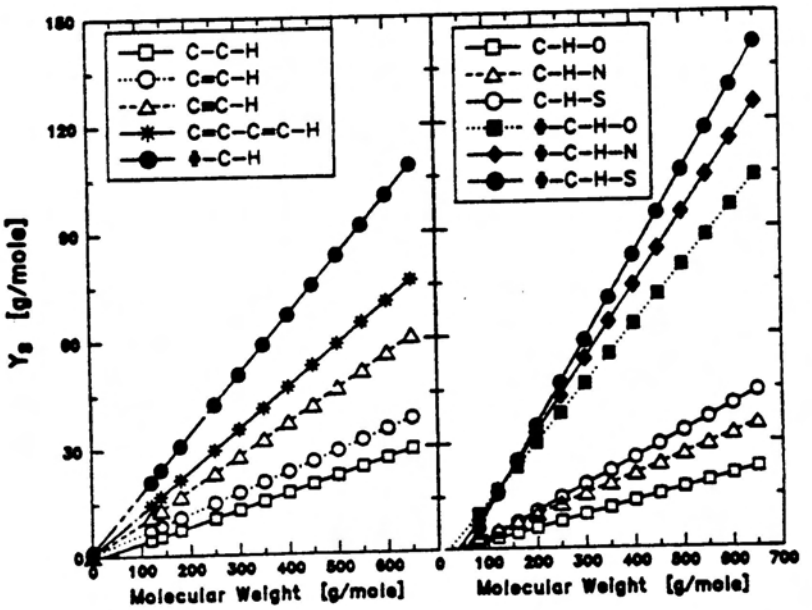

Figure 6. Yield of Particulates as a Function of Molecular Weight. Symbols are used for identification purposes only.

4.2 FIRE BEHAVIOR OF POLYMERS AND HIGH MOLECULAR WEIGHT LIQUIDS

Polymers gasify as monomers, as oligomers or as decomposition products of the original polymer. Since ΔH_T for generic polymers can be measured in an oxygen bomb calorimeter fairly accurately, it is possible to estimate the molecular weight and assess the mode of gasification and combustion efficiency.

Polyethylene (PE), polypropylene (PP), polystyrene (PS), polyoxymethylene (POM) and polymethylmethacrylate (PMMA) gasify as monomers, as oligomers or as mixtures of monomers and oligomers. The average molecular weight of fuel vapors, estimated from ΔH_T are listed in Table IV for these five polymers for which surface temperatures are below 600°C in fires[11]. The estimated values of the molecular weight are found to be reasonably close to the values reported by Madorsky[1] in vacuum pyrolysis. For example, for PE, which gasifies as an oligomer, the average molecular weight of the fuel vapor below 600°C is in the range of 562 to 755 g/mole[1] compared to an estimated value of 597 g/mole. PP which also gasifies as an oligomer, has an estimated molecular weight value of 1300 g/mole. PS gasifies as a mixture of monomer and oligomer and below 600°C, based on the yields and molecular weight of monomer and oligomer, the average molecular weight of fuel vapor is in the range of 150 to 175 g/mole[1] compared with an estimated value of 117 g/mole. POM gasifies as a monomer below 200°C, with a molecular weight of 30 g/mole[1], which is the same as the estimated value. PMMA also gasifies as a monomer with a molecular weight of 100 g/mole[1], compared with an estimated value of 94 g/mole. In addition, the estimated values of ΔH_i and Y_j, based on the average molecular weights of these five polymers show good agreement with the calculated values in Table IV. Thus, the decomposition, gasification and combustion processes for other polymers and fuels can be assessed in a fashion similar to that used for these five polymers. For example, for commercial high molecular weight hydrocarbon transformer fluids, as listed in Table IV, the assessment of gasification and combustion appears to suggest that the fluids gasify as alkanes with an average molecular weight of about 300 g/mole.

The pyrolysis data[1] for PE, PP, PMMA and PS show that the ratio of the amounts of unsaturated aliphatic and aromatic hydrocarbons to saturated aliphatic hydrocarbons is higher for PS than for PE, PP and PMMA, and thus support the trend found for the variations of ΔH_i and Y_j with the chemical structures.

4.3 ASSESSMENT OF DECOMPOSITION, GASIFICATION AND COMBUSTION PROCESSES FOR POLYMERS

Data for ΔH and Y_j have been measured for a variety of polymers[19], which can be used with Eqs. (1) and (2) and constant from Table III to assess the decomposition, gasification and combustion processes. Some selected experimental data for polymers are listed in Table V.

An examination of the data in Table V shows that the assessment is fairly reasonable for polyester, epoxy, nylon, and polystyrene and polyethylene foams, but not for wood, polyurethane foams and polyethylene polymers with chlorine and fluorine atoms, polyvinyl chloride and poly(ethylene-terephthalate), PET.

For halogenated polymers, smoke point heights have not been measured and thus ΔH_i and Y_j cannot be estimated. From the general trend in the experimental data, however, it appears that for fuel vapors, combinations of C-C-X, where X is halogen atom or atoms, C=C-H, C=C-C=C-H and ϕ-C-H structures may be needed. In the pyrolysis of polytetrafluoroethylene (PTFE), in the temperature range of 504 to 538°C, the yield of monomer is 0.966. The data in Table V show that the combustion for PTFE is very inefficient, Y_{CO} is high; however, Y_S is negligibly small, probably due to the reason that PTFE has no H atoms in its structure[21]. For polyethylene with chlorine atoms and poly (vinyl chloride) (PVC), which has 56% by weight of chlorine, the efficiency of combustion decreases and Y_{CO} and Y_S increase with the amount of chlorine. The ratio of the amounts of unsaturated aliphatic and aromatic hydrocarbons to saturated aliphatic hydrocarbons is much higher in the pyrolysis of PVC than PE, suggesting that as the amount of chlorine in PE is increased, the chemical structure of fuel vapor probably changes towards unsaturated and aromatic structure.

PET consists of a combination of an aliphatic and an aromatic structure; connected by O atoms; high yield of CH_2CHO is found in pyrolysis. If fuel vapor is assumed to be represented by C-C-H-O (unsaturated), the estimated values are: M = 89 g/mole; ΔH_T = 26.5 kJ/g; ΔH_T = 25.6 kJ/g; Y_{CO} = 0.012 g/g and Y_S = 0.038 g/g; none of these estimates, except for ΔH_T, are close to the measured values in Table V. If fuel vapor is assumed to be represented by ϕ-C-H-O, then the estimated values are M = 57 g/mole; ΔH_T = 26.5 kJ/g;

TABLE V

EXPERIMENTAL VALUES FOR WH_1 and Y_1 FOR POLYMERS WHICH DECOMPOSE DURING GASIFICATION AND POSSIBLE GENERIC GROUP FOR FUEL VAPORS[a]

Polymer	WH_1 (kJ/g)				Y_j(g/g/)		Possible Average Fuel Vapor Composition
	Comp. Comb.	Chemical	Convective	Radiative	CO	Particulates	
Red Oak	17.7	12.4	7.8	4.6	0.004	0.015	C-C-H-O and d-C-H-O (possible)
Douglas Fir	16.4	13.0	8.1	4.9	0.004	NR	
Pine	17.9	12.4	8.7	3.7	0.005	NR	
Polyester	32.5	20.6	10.8	9.8	0.070	0.091	d-C-H-O; M 106 g/mole
Epoxy	28.8	17.1	8.5	8.6	0.080	0.091	d-C-H-O; M 69 g/mole
Nylon	30.8	27.1	16.3	10.8	0.038	0.075	d-C-H-N; M 69 g/mole
Polyurethane foams[b]	25.6	17.0	7.8	9.2	0.032	0.152	d-C-H-O; d-C-H-N; d-C-H, and C=C-C=C-H (possible)
Polystyrene foams[b]	37.4	25.5	10.7	14.8	0.061	0.194	d-C-H M 120 g/mole
Polyethylene foams[b]	40.9	34.2	19.5	14.7	0.021	0.076	C=C-H; M 600 g/mole
Polyethylene with Chlorine							
25% by weight	31.6	22.6	10.0	12.6	0.042	0.115	C-C-X; C=C-H; C=C-C=C-H and d-C-H (possible)
36% by weight	26.3	10.6	6.4	4.2	0.051	0.139	
48% by weight	20.6	7.2	3.9	3.3	0.049	0.134	
Poly(vinyl-Chloride)	16.4	5.7	3.1	2.6	0.063	0.172	
Polytetra-fluoroethylene	5.3	1.7	0.91	0.80	0.120	0.004	
Poly(ethylene-terephthate)[c]	26.5	19.4	NR	NR	0.057	0.084	C-C-H-O and d-C-H-O (possible)

a: Experimental data taken from Ref. 19; b: Average values for all foams; c: Data measured recently; and are not reported in Ref. 16; NR: Not Reported.

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ΔH_{Chem} = 9.6 kJ/g; Y_{CO} = 0.055 g/g and Y_S = 0.112 g/g; these estimated values, except for ΔH_{Chem}, are closer to the measured values. The estimations thus suggest that the decomposition, gasification and combustion behavior of PET probably can be represented by a structure between C-C-H-O and ϕ-C-H-O; the structure being closer to the latter structure.

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V

CONCLUSIONS

1. Relationships between the smoke point height and generation efficiencies of heat and chemical compounds are useful for examining the fire behavior of fuels in the gas phase.
2. Heat of complete combustion per mole, chemical heat of combustion per mole and its convective and radiative components and yield of CO and particulates are linear functions of the molecular weight of fuel vapors within each generic chemical family. The relationships can be used for engineering calculations and to assess the decomposition, gasification and combustion of fuels in fires.
3. The efficiency of combustion is a strong function of the chemical structures of fuels. Changes in the chemical structures of fuels resulting in the increase in bond unsaturation and aromatic nature are expected to decrease the efficiency of combustion. Introduction of O atoms in the structure is expected to increase the efficiency of combustion, whereas introduction of N and S atoms is expected to decrease the efficiency, the S atoms having more effect than the N atoms.

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NOMENCLATURE

A_i	Constant (kJ/g)
B_i	Constant (kJ/mole)
C_j	Constant (g/g)
D_j	Constant (g/mole)
f_j	Generation efficiency of a compound (-)
ΔH_i	Heat of combustion (kJ/g or kJ/mole)
k_a	Mass air to fuel stoichiometric ratio
k_j	Maximum possible theoretical yield of compound j (g/g)
ℓ_s	Smoke point height (m)
M	Molecular weight of fuel vapor (g/mole)
Y_j	Yield of compound j (g/g or g/mole)
χ_i	Generation efficiency of heat (-)
X	Halogen atom or atoms
ϕ	Benzene ring or rings

Subscripts

T	Net complete combustion
Con	Convective
Chem	Chemical
i	Individual heat components (chemical, convective and radiative)
j	Individual chemical compounds (CO, CO_2, particulates)
Rad	Radiative
S	Particulates

Superscript

$\cdot$	per unit of time (s^{-1})

Polymer Abbreviations

PS	Polystyrene
PP	Polypropylene
PMMA	Polymethylmethacrylate

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APPENDIX

COMBUSTION PROPERTY DATA FOR DIFFUSION FLAMES

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Table A1. Combustion Properties of Normal Alkanes

Fuel	Formula	MW (g/mole)	ka (g/g)	ΔH_T (kJ/g)	ΔH_{Chem} (kJ/g)	ΔH_{Con} (kJ/g)	ΔH_{Rad} (kJ/g)	Y_{co} (g/g)	Y_s (g/g)
Ethane*	C_2H_6	30	16.0	47.1	45.7	34.1	11.6	.001	.013
n-Propane	C_3H_8	44	15.6	46.0	43.7	31.2	12.5	.005	.024
n-Butane	C_4H_{10}	58	15.4	45.4	42.6	29.6	13.0	.007	.029
n-Pentane	C_5H_{12}	72	15.3	45.0	42.0	28.7	13.3	.008	.033
n-Hexane	C_6H_{14}	86	15.2	44.8	41.5	28.1	13.5	.009	.035
n-Heptane	C_7H_{16}	100	15.1	44.6	41.2	27.6	13.6	.010	.037
n-Octane	C_8H_{18}	114	15.1	44.5	41.0	27.3	13.7	.010	.038
n-Nonane	C_9H_{20}	128	15.0	44.4	40.8	27.0	13.8	.011	.039
n-Decane	$C_{10}H_{22}$	142	15.0	44.3	40.7	26.8	13.9	.011	.040
n-Undecane	$C_{11}H_{24}$	156	15.0	44.3	40.5	26.6	13.9	.011	.040
n-Dodecane	$C_{12}H_{26}$	170	14.9	44.2	40.4	26.4	14.0	.011	.041
n-Tridecane	$C_{13}H_{28}$	184	14.9	44.2	40.3	26.3	14.0	.012	.041
n-Tetradecane	$C_{14}H_{30}$	198	14.9	44.1	40.3	26.2	14.1	.012	.042
Hexadecane	$C_{16}H_{34}$	226	14.9	44.1	40.1	26.0	14.1	.012	.042

*Smoke point height at the correlation limit (0.243 m).

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Table A2. Combustion Properties of Branched Alkanes

Hydrocarbon	Formula	MW (g/mole)	ka (g/g)	ΔH_T (kJ/g)	ΔH_{Chem} (kJ/g)	ΔH_{Con} (kJ/g)	ΔH_{Rad} (kJ/g)	Y_{co} (g/g)	Y_s (g/g)
Methylbutane	C_5H_{12}	72	15.3	45.0	40.9	27.2	13.8	.012	.042
Dimethylbutane	C_6H_{14}	86	15.2	44.8	40.3	26.3	14.0	.014	.046
Methylpentane	C_6H_{14}	86	15.2	44.8	40.3	26.3	14.0	.014	.046
Dimethylpentane	C_7H_{16}	100	15.1	44.6	39.9	25.7	14.1	.015	.049
Methylhexane	C_7H_{16}	100	15.1	44.6	39.9	25.7	14.1	.015	.049
Trimethylpentane	C_8H_{18}	114	15.1	44.5	39.6	25.3	14.3	.016	.052
Methylethylpentane	C_8H_{18}	114	15.1	44.5	39.6	25.3	14.3	.016	.052
Ethylhexane	C_8H_{18}	114	15.1	44.5	39.6	25.3	14.3	.016	.052
Dimethylhexane	C_8H_{18}	114	15.1	44.5	39.6	25.3	14.3	.016	.052
Methylheptane	C_8H_{18}	114	15.1	44.5	39.6	25.3	14.3	.016	.052

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Table A3. Combustion Properties of Cyclic Alkanes

Fuel	Formula	MW (g/mole)	ka (g/g)	ΔH_T (kJ/g)	ΔH_{Chem} (kJ/g)	ΔH_{Con} (kJ/g)	ΔH_{Rad} (kJ/g)	Y_{co} (g/g)	Y_s (g/g)
cyclo-Pentane	C_5H_{10}	70	14.7	44.3	39.2	24.1	15.1	.0176	.055
Methylcyclopentane	C_6H_{12}	84	14.7	43.8	38.2	23.0	15.2	.0193	.061
Cyclohexane	C_6H_{12}	84	14.7	43.8	38.2	23.0	15.2	.0193	.061
Methylcyclohexane	C_7H_{14}	98	14.7	43.4	37.5	22.3	15.2	.0205	.066
Ethylcyclohexane	C_8H_{16}	112	14.7	43.2	36.9	21.7	15.3	.0214	.069
Dimethylcyclohexane	C_8H_{16}	112	14.7	43.2	36.9	21.7	15.3	.0214	.069
Cyclooctane	C_8H_{16}	112	14.7	43.2	36.9	21.7	15.3	.0214	.069
Decalin	$C_{10}H_{18}$	138	14.4	42.8	36.2	20.9	15.3	.0225	.073
Bicyclohexyl	$C_{12}H_{22}$	166	14.5	42.6	35.7	20.4	15.3	.0234	.076

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Table A4. Combustion Properties of Alkenes and Polyolefins

Fuel	Formula	MW (g/mole)	ka (g/g)	ΔH_T (kJ/g)	ΔH_{Chem} (kJ/g)	ΔH_{Con} (kJ/g)	ΔH_{Rad} (kJ/g)	Y_{co} (g/g)	Y_s (g/g)
Ethylene	C_2H_4	28	14.7	48.0	41.5	27.3	14.2	.013	.076
Propylene	C_3H_6	42	14.7	46.4	40.5	25.6	14.9	.017	.070
Butylene	C_4H_8	56	14.7	45.6	40.0	24.8	15.2	.019	.067
Pentene	C_5H_{10}	70	14.7	45.2	39.7	24.2	15.4	.020	.065
Hexene	C_6H_{12}	84	14.7	44.9	39.4	23.9	15.5	.021	.064
Heptene	C_7H_{14}	98	14.7	44.6	39.3	23.7	15.6	.021	.063
Octene	C_8H_{16}	112	14.7	44.5	39.2	23.5	15.7	.022	.062
Nonene	C_9H_{18}	126	14.7	44.3	39.1	23.3	15.8	.022	.062
Decene	$C_{10}H_{20}$	140	14.7	44.2	39.0	23.2	15.8	.022	.061
Dodecene	$C_{12}H_{24}$	168	14.7	44.1	38.9	23.1	15.9	.023	.061
Tridecene	$C_{13}H_{26}$	182	14.7	44.0	38.9	23.0	15.9	.023	.061
Tetradecene	$C_{14}H_{28}$	196	14.7	44.0	38.8	22.9	15.9	.023	.060
Hexadecene	$C_{16}H_{32}$	224	14.7	43.9	38.8	22.8	16.0	.023	.060
Octadecene	$C_{18}H_{36}$	252	14.7	43.8	38.7	22.8	16.0	.023	.060
Polyethylene	$(C_2H_4)_n$	601	14.7	43.5	38.5	22.4	16.1	.024	.059
Polypropylene	$(C_3H_6)_n$	720	14.7	43.5	38.5	22.4	16.1	.024	.058

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Table A5. Combustion Properties of Cyclic Alkenes

Fuel	Formula	MW (g/mole)	ka (g/g)	ΔH_T (kJ/g)	ΔH_{Chem} (kJ/g)	ΔH_{Con} (kJ/g)	ΔH_{Rad} (kJ/g)	Y_{co} (g/g)	Y_s (g/g)
Cyclohexene	C_6H_{10}	82	14.2	43.0	35.7	20.2	15.5	.029	.085
Methylcyclohexene	C_7H_{12}	96	14.3	43.1	35.8	19.8	16.0	.029	.085
Pinene	$C_{10}H_{16}$	136	14.1	36.0	33.5	18.9	14.6	.039	.114

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Table A6. Combustion Properties of Alkynes

Fuel	Formula	MW (g/mole)	ka (g/g)	ΔH_T (kJ/g)	ΔH_{Chem} (kJ/g)	ΔH_{Con} (kJ/g)	ΔH_{Rad} (kJ/g)	Y_{co} (g/g)	Y_s (g/g)
Acetylene	C_2H_2	26	13.2	47.8	36.7	18.7	18.0	.042	.096
Heptyne	C_7H_{12}	96	14.3	44.8	36.0	18.8	17.1	.036	.094
Octyne	C_8H_{14}	110	14.4	44.7	35.9	18.9	17.1	.036	.094
Decyne	$C_{10}H_{18}$	138	14.4	44.5	35.9	18.9	17.0	.035	.094
Dodecyne	$C_{12}H_{22}$	166	14.5	44.3	35.9	18.9	17.0	.035	.094

OK3R3.RC

Table A7. Combustion Properties of Dienes

Fuel	Formula	MW (g/mole)	ka (g/g)	ΔH_T (kJ/g)	ΔH_{Chem} (kJ/g)	ΔH_{Con} (kJ/g)	ΔH_{Rad} (kJ/g)	Y_{co} (g/g)	Y_s (g/g)
1-3 Butadiene	C_4H_6	54	14.0	44.6	33.6	15.4	18.2	.048	.125

OK3R3.RC

Table A8. Combustion Properties of Arenes and Polystyrene

Fuel	Formula	MW (g/mole)	ka (g/g)	ΔH_T (kJ/g)	ΔH_{Chem} (kJ/g)	ΔH_{Con} (kJ/g)	ΔH_{Rad} (kJ/g)	Y_{co} (g/g)	Y_s (g/g)
Benzene	C_6H_6	78	13.2	40.1	27.6	11.0	16.5	.067	.181
Toluene	C_7H_8	92	13.4	39.7	27.7	11.2	16.5	.066	.178
Styrene	C_8H_8	104	13.2	39.4	27.8	11.2	16.6	.065	.177
Ethylbenzene	C_8H_{10}	106	13.6	39.4	27.8	11.2	16.6	.065	.177
Xylene	C_8H_{10}	106	13.6	39.4	27.8	11.2	16.6	.065	.177
Indene	C_9H_8	116	13.0	39.2	27.9	11.3	16.6	.065	.176
Propylbenzene	C_9H_{12}	120	13.7	39.2	27.9	11.3	16.6	.065	.175
Trimethylbenzene	C_9H_{12}	120	13.7	39.2	27.9	11.3	16.6	.065	.175
Cumene	C_9H_{12}	120	13.7	39.2	27.9	11.3	16.6	.065	.175
Naphthalene	$C_{10}H_8$	128	12.9	39.0	27.9	11.3	16.6	.065	.175
Tetralin	$C_{10}H_{12}$	132	13.5	39.0	27.9	11.4	16.6	.064	.174
Butylbenzene	$C_{10}H_{14}$	134	13.8	39.0	27.9	11.4	16.6	.064	.174
Diethylbenzene	$C_{10}H_{14}$	134	13.8	39.0	27.9	11.4	16.6	.064	.174
p-Cymene	$C_{10}H_{14}$	134	13.8	39.0	27.9	11.4	16.6	.064	.174
Methylnaphthalene	$C_{11}H_{10}$	142	13.0	38.9	28.0	11.4	16.6	.064	.174
Pentylbenzene	$C_{11}H_{16}$	148	13.9	38.8	28.0	11.4	16.6	.064	.173
Dimethylnaphthalene	$C_{12}H_{12}$	156	13.2	38.8	28.0	11.4	16.6	.064	.173
Cyclohexylbenzene	$C_{12}H_{16}$	160	13.7	38.7	28.0	11.4	16.6	.064	.173
Diisopropylbenzene	$C_{12}H_{18}$	162	14.0	38.7	28.0	11.4	16.6	.064	.173
Triethylbenzene	$C_{12}H_{18}$	162	14.0	38.7	28.0	11.4	16.6	.064	.173
Triamylbenzene	$C_{21}H_{36}$	288	14.3	38.1	28.2	11.6	16.6	.063	.169
Polystyrene	$(C_8H_8)_n$	200	13.2	38.5	28.1	11.5	16.6	.063	.171

OK3R3.RC

Table A9. Combustion Properties of Aliphatic Alochols

Fuel	Formula	MW (g/mole)	ka (g/g)	ΔH_T (kJ/g)	ΔH_{Chem} (kJ/g)	ΔH_{Con} (kJ/g)	ΔH_{Rad} (kJ/g)	Y_{co} (g/g)	Y_s (g/g)
Methyl alcohol*	CH_4O	32	6.4	20.0	19.1	16.1	3.0	.001	.001
Ethyl alcohol	C_2H_6O	46	9.0	27.7	25.6	19.0	6.5	.001	.008
n-Propyl alcohol	C_3H_8O	60	10.3	31.8	29.0	20.6	8.5	.003	.015
Isopropyl alcohol	C_3H_8O	60	10.3	31.8	29.0	20.6	8.5	.003	.015
n-Butyl alcohol	$C_4H_{10}O$	74	11.1	34.4	31.2	21.6	9.6	.004	.019
Isobutyl alcohol	$C_4H_{10}O$	74	11.1	34.4	31.2	21.6	9.6	.004	.019
Sec butyl alcohol	$C_4H_{10}O$	74	11.1	34.4	31.2	21.6	9.6	.004	.019
Ter butyl alcohol	$C_4H_{10}O$	74	11.1	34.4	31.2	21.6	9.6	.004	.019
n-Amyl alcohol	$C_5H_{12}O$	88	11.7	36.2	32.7	22.2	10.4	.005	.022
Isobutyl carbinol	$C_5H_{12}O$	88	11.7	36.2	32.7	22.2	10.4	.005	.022
Sec butyl carbinol	$C_5H_{12}O$	88	11.7	36.2	32.7	22.2	10.4	.005	.022
Methyl propyl carbinol	$C_5H_{12}O$	88	11.7	36.2	32.7	22.2	10.4	.005	.022
Dimethyl ethyl carbinol	$C_5H_{12}O$	88	11.7	36.2	32.7	22.2	10.4	.005	.022
n-Hexyl alcohol	$C_6H_{14}O$	102	12.1	37.4	33.7	22.7	11.0	.006	.024
Dimethylbutyl alcohol	$C_6H_{14}O$	102	12.1	37.4	33.7	22.7	11.0	.006	.024
Ethylbutyl alcohol	$C_6H_{14}O$	102	12.1	37.4	33.7	22.7	11.0	.006	.024
Allyl alcohol	C_3H_6O	58	9.5	31.4	28.6	20.4	8.2	.003	.014
Cyclohexanol	$C_6H_{12}O$	100	11.7	37.3	33.6	22.6	11.0	.005	.024

*Directly measured data. Smoke point height correlations not applicable.

OK3R3.RC

Table A10. Combustion Properties of Aliphatic Esters

Fuel	Formula	MW (g/mole)	ka (g/g)	ΔH_T (kJ/g)	ΔH_{Chem} (kJ/g)	ΔH_{Con} (kJ/g)	ΔH_{Rad} (kJ/g)	Y_{co} (g/g)	Y_s (g/g)
Ethyl formate	$C_3H_6O_2$	74	6.5	20.2	19.9	13.5	6.3	.003	.011
n-Propyl formate	$C_4H_8O_2$	88	7.8	23.9	23.4	15.4	8.0	.005	.019
n-Butyl formate	$C_5H_{10}O_2$	102	8.8	26.6	26.0	16.7	9.3	.007	.025
Methyl acetate*	$C_3H_6O_2$	74	6.5	20.2	19.9	13.5	6.3	.003	.011
Ethyl acetate	$C_4H_8O_2$	88	7.8	23.9	23.4	15.4	8.0	.005	.019
n-Propyl acetate	$C_5H_{10}O_2$	102	8.8	26.6	26.0	16.7	9.3	.007	.025
n-Butyl acetate	$C_6H_{12}O_2$	116	9.5	28.7	28.0	17.8	10.2	.008	.029
Isobutyl acetate	$C_6H_{12}O_2$	116	9.5	28.7	28.0	17.8	10.2	.008	.029
Amyl acetate	$C_7H_{14}O_2$	130	10.0	30.3	29.5	18.6	11.0	.009	.033
Cyclohexyl acetate	$C_8H_{14}O_2$	142	10.2	31.5	30.6	19.1	11.5	.010	.035
Octyl acetate	$C_{10}H_{20}O$	172	11.2	33.6	32.6	20.2	12.5	.012	.039
Ethyl acetoacetate	$C_6H_{10}O_3$	130	7.4	30.3	29.5	18.6	11.0	.009	.033
Methyl propionate	$C_4H_8O_2$	88	7.8	23.9	23.4	15.4	8.0	.005	.019
Ethyl propionate	$C_5H_{10}O_2$	102	8.8	26.6	26.0	16.7	9.3	.007	.025
n-Butyl propionate	$C_7H_{14}O_2$	130	10.0	30.3	29.5	18.6	11.0	.009	.033
Isobutyl propionate	$C_7H_{14}O_2$	130	10.0	30.3	29.5	18.6	11.0	.009	.033
Amyl propionate	$C_8H_{16}O_2$	144	10.5	31.6	30.8	19.2	11.6	.010	.035
Methyl butyrate	$C_5H_{10}O_2$	102	8.8	26.6	26.0	16.7	9.3	.007	.025
Ethyl butyrate	$C_6H_{12}O_2$	116	9.5	28.7	28.0	17.8	10.2	.008	.029
Propyl butyrate	$C_7H_{14}O_2$	130	10.0	30.3	29.5	18.6	11.0	.009	.033
n-Butyl butyrate	$C_8H_{16}O_2$	144	10.5	31.6	30.8	19.2	11.6	.010	.035
Isobutyl butyrate	$C_8H_{16}O_2$	144	10.5	31.6	30.8	19.2	11.6	.010	.035
Ethyl laurate	$C_{14}H_{28}O$	228	12.0	37.2	35.6	26.5	9.1	.008	.031
Ethyl oxalate	$C_4H_6O_4$	102	6.1	28.7	27.7	21.3	6.4	.001	.003
Ethyl malonate	$C_5H_8O_4$	132	7.7	32.2	31.0	23.4	7.5	.003	.015
Ethyl lactate	$C_5H_{10}O_3$	118	7.0	30.8	29.6	22.5	7.1	.001	.010
Butyl lactate	$C_7H_{14}O_3$	146	8.5	33.3	32.0	24.1	7.9	.004	.018
Amyl lactate	$C_8H_{16}O_3$	160	9.0	34.3	32.9	24.7	8.2	.005	.021
Ethyl carbonate	$C_5H_{10}O_3$	118	7.0	30.8	29.6	22.5	7.1	.001	.010

*Smoke point height at the correlation limit (0.243 m).

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Table A11. Combustion Properties of Aliphatic Ketones

Fuel	Formula	MW (g/mole)	ka (g/g)	ΔH_T (kJ/g)	ΔH_{Chem} (kJ/g)	ΔH_{Con} (kJ/g)	ΔH_{Rad} (kJ/g)	Y_{co} (g/g)	Y_s (g/g)
Acetone	C_3H_6O	58	9.5	29.7	27.9	20.3	7.6	.003	.014
Methyl ethyl ketone	C_4H_8O	72	10.5	32.7	30.6	22.1	8.6	.004	.018
Cyclohexanone	$C_6H_{10}O$	98	11.2	35.9	33.7	24.1	9.6	.005	.023
Di-acetone alcohol	$C_6H_{12}O_2$	116	9.5	37.3	35.0	24.9	10.1	.006	.026

OK3R3.RC

Table A12. Combustion Properties of Glycerols-Glycols

Fuel	Formula	MW (g/mole)	ka (g/g)	ΔH_T (kJ/g)	ΔH_{Chem} (kJ/g)	ΔH_{Con} (kJ/g)	ΔH_{Rad} (kJ/g)	Y_{co} (g/g)	Y_s (g/g)
<u>Ethylene Glycol</u>									
Monoethyl Ether	$C_4H_{10}O_2$	90	8.4	26.7	25.8	20.0	5.8	.001	.007
Monoethyl Ether Acetate	$C_6H_{12}O_3$	132	7.8	32.2	31.0	23.2	7.7	.001	.011
Diacetate	$C_6H_{10}O_4$	146	6.1	33.3	32.0	24.2	7.9	.001	.009
<u>Glycerol</u>									
Triacetate	$C_9H_{14}O_6$	218	6.0	36.9	35.4	26.3	9.1	.002	.011

OK3R3.RC

Table A13. Combustion Properties of Aromatic Oxygenated Compounds

Fuel	Formula	MW (g/mole)	ka (g/g)	ΔH_T (kJ/g)	ΔH_{Chem} (kJ/g)	ΔH_{Con} (kJ/g)	ΔH_{Rad} (kJ/g)	Y_{co} (g/g)	Y_s (g/g)
Benzaldehyde	C_7H_6O	106	10.4	32.4	21.2	8.1	13.2	.062	.166
Benzyl alcohol	C_7H_8O	108	10.8	32.6	22.9	9.8	13.1	.050	.137
Cresylic acid	$C_8H_8O_2$	136	9.1	34.0	25.1	11.6	13.5	.039	.107
Ethyl benzoate	$C_9H_{10}O_2$	150	9.6	34.5	27.4	14.1	13.3	.030	.084
Phenylbutyl ketone	$C_{11}H_{14}O$	162	11.9	34.8	26.3	12.6	13.7	.041	.115

OK3R3.RC

Table A14. Combustion Properties of Aliphatic Nitrogen Compounds

Fuel	Formula	MW (g/mole)	ka (g/g)	ΔH_T (kJ/g)	ΔH_{Chem} (kJ/g)	ΔH_{Con} (kJ/g)	ΔH_{Rad} (kJ/g)	Y_{co} (g/g)	Y_s (g/g)
Diethylamine	$C_4H_{11}N$	73	14.6	38.0	34.0	21.3	12.6	.012	.039
n-Butylamine	$C_4H_{11}N$	73	14.6	38.0	34.0	21.3	12.6	.012	.039
sec-Butylamine	$C_4H_{11}N$	73	14.6	38.0	34.0	21.3	12.6	.012	.039
Triethylamine	$C_6H_{15}N$	101	14.6	39.6	35.3	22.0	13.3	.014	.044
Di-n-butylamine	$C_8H_{19}N$	129	14.6	40.6	36.1	22.4	13.7	.014	.047
Tri-n-butylamine	$C_{12}H_{27}N$	185	14.7	41.6	37.0	22.9	14.1	.015	.049

OK3R3.RC

Table A15. Combustion Properties of Aliphatic Sulfur Compounds

Fuel	Formula	MW (g/mole)	ka (g/g)	ΔH_T (kJ/g)	ΔH_{Chem} (kJ/g)	ΔH_{Con} (kJ/g)	ΔH_{Rad} (kJ/g)	Y_{co} (g/g)	Y_s (g/g)
Hexyl Mercaptan	$C_6H_{14}S$	118	12.2	33.0	30.1	17.9	12.2	.012	.040
Heptyl Mercaptan	$C_7H_{16}S$	132	12.5	33.7	30.4	18.1	12.3	.013	.044
Decyl Mercaptan	$C_{10}H_{22}S$	174	13.0	34.9	31.1	18.4	12.7	.016	.051
Dodecyl Mercaptan	$C_{12}H_{26}S$	202	13.3	35.5	31.4	18.6	12.8	.017	.054
Hexyl Sulfide	$C_{12}H_{26}S$	202	13.3	35.5	31.4	18.6	12.8	.017	.054
Heptyl Sulfide	$C_{14}H_{30}S$	230	13.4	35.9	31.6	18.7	13.0	.018	.057
Octyl Sulfide	$C_{16}H_{34}S$	258	13.6	36.3	31.8	18.8	13.1	.019	.059
Decyl Sulfide	$C_{20}H_{42}S$	314	13.8	36.8	32.1	18.9	13.2	.020	.061

OK3R3.RC

Table A16. Combustion Properties of Aromatic Nitrogen Compounds

Fuel	Formula	MW (g/mole)	ka (g/g)	ΔH_T (kJ/g)	ΔH_{Chem} (kJ/g)	ΔH_{Con} (kJ/g)	ΔH_{Rad} (kJ/g)	Y_{co} (g/g)	Y_s (g/g)
Pyridine	C_5H_5N	79	12.6	32.2	24.0	11.5	12.5	.037	.104
Aniline	C_6H_7N	93	12.9	33.8	25.0	11.7	13.3	.043	.119
Picoline	C_6H_7N	93	12.9	33.8	25.0	11.7	13.3	.043	.119
Toluidine	C_7H_9N	107	13.2	34.9	25.8	11.9	13.9	.048	.130
Dimethylaniline	$C_8H_{11}N$	121	13.3	35.7	26.4	12.1	14.3	.051	.139
Quinoline	C_9H_7N	129	12.5	36.1	26.7	12.1	14.5	.052	.143
Quinaldine	$C_{10}H_9N$	143	12.7	36.7	27.1	12.2	14.8	.055	.149
Butylaniline	$C_{10}H_{15}N$	149	13.6	37.0	27.2	12.2	15.0	.056	.151

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Table A17. Combustion Properties of Aromatic Sulfur Compounds

Fuel	Formula	MW (g/mole)	ka (g/g)	ΔH_T (kJ/g)	ΔH_{Chem} (kJ/g)	ΔH_{Con} (kJ/g)	ΔH_{Rad} (kJ/g)	Y_{co} (g/g)	Y_s (g/g)
Thiophene	C_4H_4S	84	9.8	31.9	23.4	10.8	12.6	.031	.086
Methylthiophene	C_5H_6S	98	10.5	33.2	24.1	10.9	13.2	.039	.107
Thiophenol	C_6H_6S	110	10.6	34.1	24.6	11.0	13.6	.045	.122
Thiocresol	C_7H_8S	124	11.1	34.9	25.0	11.0	14.0	.050	.135
Cresolmethyl Sulfide	$C_8H_{11}S$	155	11.6	36.2	25.7	11.1	14.5	.058	.155

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For engineering calculations in the gas phase, correlations have been established between smoke point heights and heat of combustion and yields of CO and particulates. Smoke point heights reported in the literature were modified such that all the data, including those measured by us, were consistent. Based on the data for 165 fuels from the literature and the data measured by us for 16 fuels, relationships have been suggested for the engineering calculations of heat of complete combustion, chemical heat of combustion and its convective and radiative components, and yields of CO and particulates as functions of the molecular weight for fuels with aliphatic and aromatic, saturated and unsaturated bonds between C and H; C, H and O; C, H, N and C, H and S atoms.

The efficiency of combustion decreases with increase in the bond unsaturation and aromatic nature. Substitution of O atoms in the structure increases the efficiency of combustion, whereas substitution of N and S atoms in the structures decreases the efficiency of combustion, S atoms being more efficient than N atoms.

The generalized relationships have been used to assess the decomposition, gasification and combustion processes for polymers.

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