

INTER OFFICE MEMO



TO Mr. R. Chartier

AT Assonet

DATE 28 February 1973

FROM V. C. Pitts

AT New Haven

COPY TO W. Boswell

SUBJECT

POLYVINYL CHLORIDE - Current Awareness

PROJECT 8625-004

NHTIS 73-11 - Supplement I

(see also NHTIS 72-3, and 71-30)

38 Polyvinyl - Chloride current awareness

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Attached is our most recent collection of patents and articles on polyvinyl chloride.

As in the past, we will obtain copies of abstracted articles or full copies of those in which only the first page has been included as you request them.

Prepared by

Virginia C. Pitts
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Attachments

SOURCES:

F&S Index of Corporations & Industries, December 5, 1972
Trends in End-Use Markets for Plastics, December 1972
Modern Plastics, November-December 1972
Plastics World, October 1972
Kunststoffe-German Plastics, September-October 1972
Plastics & Rubber Weekly, October-December 29, 1972
Modern Packaging, December 1972
Europlastics, November 1972

OLI 7540

By J.L. Throne* and R.G. Griskey†

Heating values and thermochemical properties of plastics

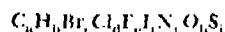
No extensive tabulation of heating values or heats of combustion exists for plastics. This report was prepared at the suggestion of Modern Plastics to fill this important need. It gives thermochemical data for most common plastics and the methods used to compute these data. Heating values for common fillers, additives, monomers, and crosslinking agents also are included. Heating values for several common plastics exceed the heating values of some conventional fuels.

A technical feature

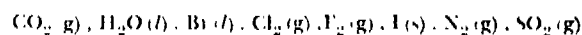
Gordon M. Kline, technical editor

The critical theme of our times is environmental impact (1-3)¹. Nowhere is this more evident than for plastics. The durability and effectiveness of plastics seem to be a drawback because of the difficulty in disposing of them. This, however, is not necessarily correct because plastics are materials with high heating values. In fact, they are not only comparable to most fuels, but in some cases exceed the heating values of commercial fuels. For example, polyethylene, which represents 50% of all disposable plastics, has a heating value greater than that of fuel oil, coal, or wood.

Heats of formation for nearly all common plastics are given in the Encyclopedia of Polymer Science and Technology (4). These data form the basis for the calculation of the heats of combustion, heating values, stoichiometric air requirements, and theoretical flame temperatures given in this report. From a standard text on thermochemistry (5), we find that if we *completely burn* a compound of the following form:



to the following final products:



where (g) = gas, (l) = liquid, and (s) = solid, we can calculate the heat of combustion from:

$$\Delta H_r = -\Delta H_f - 91.05 a - 31.16 b - 70.96 i$$

(in Kcal./g. mole)

Here the heat of combustion is determined by the heat of formation (as shown in Table I), and the heats of formation (6) of CO_2 , H_2O , and SO_2 , respectively. All other components are converted to their elemental state. Most of the heats of combustion in Table I are negative, indicating

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1—Numbers in parentheses designate references at end of article.

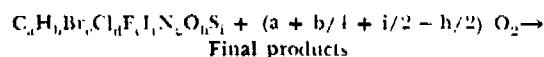
that energy is given off when these plastics are burned. Note that we are assuming here that sufficient air is available for *complete* oxidation of the plastic. In practice, the presence of CO , HCl , HF , NO_2 , and the like in flue gases indicates that incomplete combustion is taking place. More vigorous stirring of the combusting waste, higher incinerator operating temperatures, and adequate air supply are some of the methods that have been recommended to insure complete combustion (3). In Table I we have tabulated the standard heats of combustion, calculated assuming complete combustion to their final products. Note that heat of combustion is based on the molecular weight of the mer or repeat unit of the polymer.

To obtain the heating value, we converted the heat of combustion to B.t.u./lb. as follows:

$$\text{Heating value, B.t.u./lb.} = -\Delta H_r \times (1800/MW)$$

where MW is the molecular weight of the repeat unit. The values obtained here correlate well with calculations made by others (5).

The total number of moles of oxygen (O_2) required from the combustion air for stoichiometric combustion was obtained from the stoichiometric equation:



Note that if a polymer has oxygen in its repeat unit, we assume that this oxygen is available to aid in combustion. Thus the oxygen demand from the combustion air is proportionately reduced. Thus, the stoichiometric oxygen requirement of polyvinyl alcohol (C_2H_4O) is smaller than that for polyethylene (C_2H_4).

The total amount of *combustion air* required for the stoichiometric combustion is calculated from the total number of moles of O_2 :

$$\begin{aligned} \text{Stoichiometric ft.}^3 \text{ combustion air/lb. resin} &= \\ &= (\text{Moles } O_2/\text{mole repeat unit}) \times 392 \\ &= (0.21 \text{ moles } O_2/\text{mole air}) \times MW \text{ repeat unit} \end{aligned}$$

This value assumes *dry* air at 760 Torr and 25° C.

The theoretical flame temperature, as presented in Table I, is the temperature attained when the plastic is burned in a stoichiometric amount of combustion air without gain or loss of heat. In this calculation, we have assumed mean heat capacities for the combustion products, and used the following equation:

$$(T - 25) = (-\Delta H_r + (b/2) 10.5) / \{ 13.2a + 10.6 (b/2) + [(79/21) (a + b/4 + i/2 - h/2 + g/2) 8.1 + 12.6 (c/2) + 9.0 (d/2) + 8.3 (e/2) + 10.7 f + 8.1 (g/2) + 13.0 i] \}$$

The third (bracketed) term in the denominator is the total number of moles of nitrogen present in the flue gas. The second term in the numerator represents the amount of heat required to convert $H_2O(l)$ into $H_2O(g)$ at 25° C. The mean heat capacity values were obtained from stan-

Table I: Thermochemical properties of common plastics and fillers

Composition of sub-unit	Sub-unit MW	ΔH_f° (25° C.), Kcal./g. mole ^a	ΔH_c° (25° C.), Kcal./g. mole ^b	Heating value, B.t.u./lb.	Stoichiometric burning			Common name
					Moles O ₂ per mole compound	Cu. ft. air/lb., 760 Torr, 25° C.	Theoretical flame temp., °C./°F.	
C ₂ H ₄	28.05	-12.25	-312.5	20,050	3	200	2120/3850	High density polyethylene
C ₃ H ₆	28.05	-12.79	-312.0	20,020	3	200	2120/3850	Low density polyethylene
C _{2.31} H _{4.22}	32.04	-14.30	-360.8	20,270	3.46	202	2120/3850	Ethylene/propylene (69/31) random copolymer
C ₃ H ₆	42.08	-18.84	-468.3	20,030	4.5	200	2120/3850	Polypropylene, isotactic or syndiot.
C ₃ H ₆	42.08	-19.27	-467.8	20,010	4.5	200	2120/3850	Polypropylene, atactic
C ₄ H ₈	56.11	-24.13	-625.4	20,060	6	198	2120/3850	Poly-1-butene, isotactic
C ₄ H ₈	56.11	-21.24	-628.2	20,150	6	198	2130/3870	Polyisobutylene
C ₅ H ₁₀	70.13	-31.07	-780.8	20,040	7.5	198	2120/3850	Poly-1-pentene, isotactic
C ₅ H ₁₀	70.13	-31.64	-780.2	20,030	7.5	198	2120/3850	Poly-3-methyl-1-butene, isotactic
C ₆ H ₁₂	84.16	-38.54	-935.7	20,010	9	198	2120/3850	Poly-4-methyl-1-pentene, isotactic
C ₆ H ₆	54.09	+3.13	-584.3	19,440	5.5	189	2220/4020	Poly-1, 4-butadiene, atactic
C _{4.18} H _{6.00}	56.34	+3.0 ^c	-604.2	19,300	5.70	189	2220/4020	Butadiene/styrene (8.58%) copoly
C _{4.60} H _{6.29}	61.59	+3.0 ^c	-650.5	19,010	6.17	187	2220/4020	Butadiene/styrene (25.5%) copoly (GRS rubber)
	53.70	+3.0 ^c	-512.6	17,180	4.84	168	2190/3970	Butadiene/acrylonitrile (37%) copolymer
	68.12	-6.0	-737.5	19,490	7	190	2190/3970	Natural rubber (no sulfur)
C ₆ H ₆	104.2	+7.09	-1033	17,850	10	179	2210/4010	Polystyrene, isotactic
C ₆ H ₆	104.2	+8.27	-1034	17,870	10	179	2210/4010	Polystyrene, atactic-crystal
C ₆ H ₁₀	118.2	+7.88	-1196	18,220	11.5	181	2210/4010	Poly- α -methylstyrene
C ₁₂ H ₈	152.2	+27.13	-1429	16,900	14.0	183	2230/4040	Polyacenaphthalene
C ₂ H ₂ F	46.05	-55.8	-238.8	9,180	2.75	112	1710/3100	Polyvinyl fluoride
C ₂ H ₂ F ₂	64.04	-116.1	-140.3	3,940	2.5	73	1090/2000	Polyvinylidene fluoride
C ₂ F ₄	100.0	-196.1	+8.01	-144	2	37		Polytetrafluoroethylene
C ₂ F ₂ Cl	116.5	-156.9	-31.2	482	2	32	320/615	Polychlorotrifluoroethylene
C ₂ H ₂ Cl	62.50	-22.6	-268.0	7,720	2.75	82	1960/3550	Polyvinyl chloride
C ₂ H ₂ Cl ₂	96.95	-24.0	-232.4	4,315	2.5	48	1840/3340	Polyvinylidene chloride
C ₂ H ₂ O	56.06	-48.2	-370.6	11,900	3.5	117	2110/3830	Ethylene/carbon monoxide (1:1) copolymer
C ₃ O ₂	68.03	-57.57	-224.06	5,940	2	55	2260/3910	Polycarbon suboxide
CH ₂ O	30.03	-40.83	-121.4	7,280	1	62	2050/3750	Polyoxymethylene
C ₂ H ₄ O	44.05	-44.13	-280.6	11,470	2.5	106	2120/3850	Polyethylene oxide
C ₃ H ₆ O	58.08	-54.41	-432.7	13,410	4	129	2100/3810	Polypropylene oxide, 27% isotactic
C ₃ H ₆ O	58.08	-54.78	-432.3	13,400	4	129	2100/3810	Polypropylene oxide, 100% atactic
C ₃ H ₆ O	58.08	-49.5	-437.6	13,560	4	129	2130/3860	Polyoxytrimethylene
C ₂ H ₄ O	72.11	-56.8	-592.7	14,790	5.5	142	2120/3850	Polytetrahydrofuran
C ₂ H ₄ O	44.05	-61.53	-263.2	10,760	2.5	106	1980/3600	Polyvinyl alcohol
C ₃ H ₆ O ₂	72.06	-85.5	-333.3	8,330	3	78	2075/3770	Poly- β -propiolactone
C ₃ H ₆ O ₂	100.1	-105.8	-637.7	11,470	6	112	2070/3760	Polymethyl methacrylate
C ₆ H ₆ O	120.2	-31.88	-993.8	14,880	9.5	148	2200/3990	Polyphenylene oxide
C ₁₆ H ₁₂ O ₂	254.3	-103.26	-1880	13,310	18	132	2190/3980	Polycarbonate
C ₃ H ₆ OCl ₂	155.0	-82.8	-660.7	7,673	6.5	78	1990/3610	Chlorinated polyether
HCN	27.03	+14.0	-150.3	10,010	1.25	86	2410/4370	Polyhydrocyanic acid
C ₂ H ₂ O ₂ N	73.05	-19.98	-278.7	6,870	1.75	45	2670/4830	Polynitroethylene
C ₃ H ₂ N	53.06	+15.85	-408.6	13,860	3.75	132	1860/3380	Polyacrylonitrile
S	32.06	+3.56	-74.5	4,180	1	58	1740/3160	Polysulfur
C ₃ H ₆ SO ₂	106.1	-95.4	-462.70	7,850	4.5	79	1970/3570	Polypropylene sulfone
C ₄ H ₈ SO ₂	120.2	-101.5	-618.9	9,290	6	93	2000/3640	Poly-1-butene sulfone
C ₆ H ₁₂ SO ₂	148.2	-113.7	-913.5	11,310	9	114	2040/3710	Poly-1-hexene sulfone
C ₆ H ₆ O ₂ (7)	224.3	-120.0 ^c	-1496	12,000	17	142	1860/3380	Phenol-formaldehyde (1:1)
C ₂ H ₄ N ₂ O (7)	84.09	-60.0 ^c	-358.8	7,680	3.5	78	1950/3540	Urea-formaldehyde (1:2)
C ₆ H ₆ N ₆ (7)	162.2	-20.0 ^c	-749.3	8,310	7.5	120	1990/3610	Melamine-formaldehyde (1:3)
C ₆ H ₆ N ₆ NO ₂ (7)	130.3	-100.0 ^c	-743.1	10,180	7.02	101	2100/3810	Polyurethanes, ester-based
C _{2.77} H _{4.23} O _{1.63} (8)	101.6	-33.0 ^c	-723.2	12,810	6.52	120	2250/3910	Unsaturated polyesters (maleic anhydride-based; 1:1 styrene)
C _{11.43} H _{20.37} O _{2.63} N _{0.3} (7)	212.1	-110.0 ^c	-1700.0	14,430	15.53	137	2220/4030	Bisphenol A epoxy (3000 MW; 10% diethylenetriamine)
				7,590 (9)	—	70		Paper
				8,520 (9)	—	80		Woodflour
C ₆ H ₆	104.2	+24.91	-1050.6	18,160	10	180		Styrene

standard tables (5). The temperature is given in °C.; conversion to °F. is straightforward.

In addition to the conventional plastics, we also present data on fillers, additives, monomers, and crosslinking agents. These data were obtained in the same fashion as the data for the plastics. Note that for some fillers, such as calcium carbonate, we must supply energy to decompose these materials into gaseous products. Flame-retardant additives such as aluminum hydroxide ($\text{Al}_2(\text{OH})_6$) decompose endothermically to alumina (Al_2O_3) and water. This water must then be heated to combustion temperature, thus requiring additional thermal energy. As a result, the heating values for such materials are negative. For other materials, such as glass fiber and talc, the heating values are zero. This means that plastics filled with these materials have a much lower fuel value per pound than the equivalent unfilled plastic.

In Table II we compare the heating values of some representative plastics with heating values of other materials. As has been stated by others (3), addition of many types of

plastics (in the form of packaging or coatings) to conventional domestic waste paper or sewage sludge actually increases its fuel value, thus making it "more burnable." We hasten to add that we are not comparing the rates of combustion or the ignition temperatures of these materials, only the amount of energy ultimately available to the incinerator operator for possible use to produce steam and electricity.

Rates of combustion and ignition temperatures of these materials must be determined experimentally. The data that are presented here can be used by engineers in the design of special incinerators such as hospital incinerators and to objectively evaluate incineration as a viable interim method of solid waste disposal of plastics.

References

- 1) Modern Plastics 48, 44 (July); 76 (Oct.); 18 (Dec. 1971).
- 2) R.B. Engdahl, "Solid Waste Processing," U.S. Department of Health, Education and Welfare, Report SW-

Table I, cont'd.

Composition of sub-unit	Sub-unit MW	ΔH_f° (25° C.), Kcal./g. mole ^a	ΔH_c° (25° C.), Kcal./g. mole ^b	Heating value, B.t.u./lb.	Stoichiometric burning			Common name
					Moles O_2 per mole compound	Cu. ft. air/lb., 760 Torr, 25° C.	Theoretical flame temp., °C./°F.	
C_6H_{12}	82.15	-9.15	-896.8	19,650	8.5	193		Cyclohexane
$\text{C}_2\text{F}_3\text{Cl}$	116.5	-134.6	-53.50	827	2	32		Chlorotrifluoroethylene
$\text{C}_2\text{H}_3\text{Br}$	107.0	+18.7	-309.3	5,200	2.75	48		Vinyl bromide
CH_2O	30.03	-28.2	-134.2	8,040	1	62		Formaldehyde
$\text{C}_2\text{H}_4\text{O}$	44.05	-46.2	-278.5	12,510	2.5	106		Acetaldehyde
$\text{C}_4\text{H}_6\text{O}_2$	86.09	-103.6	-477.6	9,985	4.5	98		Methacrylic acid
$\text{C}_3\text{H}_6\text{O}_2$	100.1	-92.7	-650.8	11,700	6	112		Methyl methacrylate
$\text{C}_3\text{H}_4\text{O}_2$	72.06	-80.54	-338.3	8,450	3	78		Acrylic acid
$\text{C}_3\text{H}_6\text{O}$	56.08	-51.72	-435.4	13,970	4	133		Acetone
$\text{C}_2\text{H}_6\text{O}_2$	62.07	-93.1	-300.0	8,700	2.5	75		Ethylene glycol
$\text{C}_4\text{H}_8\text{O}_2$	86.09	-75.2	-505.9	10,580	4.5	98		Vinyl acetate
$\text{C}_4\text{H}_6\text{O}_3$	98.06	-112.4	-332.1	6,100	3.5	67		Maleic anhydride
$\text{C}_3\text{H}_8\text{O}_3$	92.10	-159.8	-395.6	7,730	3.5	71		Glycerol
COCl_2	98.92	-53.3	-40.75	742	0.5	10		Phosgene
$\text{C}_2\text{H}_5\text{N}$	43.07	+30.12	-397.1	16,600	4.25	58		Ethylenimine
$\text{C}_6\text{H}_{10}\text{O}_5$	167.2		-1011	7,520 (9)	—	48		Cellulose
			0	0	—	0		Sand
			0	0	—	0		Quartz
			0	0	—	0		Diatomaceous earth (dry)
			0	0	—	0		Kaolin (clay)
			0	0	—	0		Mica
$\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$	277.2		+34.4	-234 (5)	—	0		Asbestos
CaSiO_3	116.2		+21.3	-331 (5)	—	0		Calcium metasilicate
CaCO_3	100.1		+42.5	-736 (5)	—	—		Calcium carbonate
BaSO_4	233.4		+145.8	1,210 (5)	—	—		Barium sulfate
CaSO_4	136.2		+119.6	-1,800 (5)	—	—		Calcium sulfate
MoS_2	160.1		+216.4	3,040 (5)	—	15		Molybdenum sulfide
C	12.01		-94.05	14,110 (5)	—	156		Carbon, graphite
			0	0	—	0		Talc
			0	0	—	0		Glass, fiber
$\text{Al}_2(\text{OH})_6$	156.0		+41.6	-500	—	—		Aluminum hydrate
CON_2H_4	60.06	-58.7	-188.2	5,640	3.5	109		Urea
$\text{C}_6\text{H}_6\text{N}_6$	126.2	15.35	-520.3	11,450	10.5	156		Melamine

^a ΔH_f° = heat of formation, from reference 4

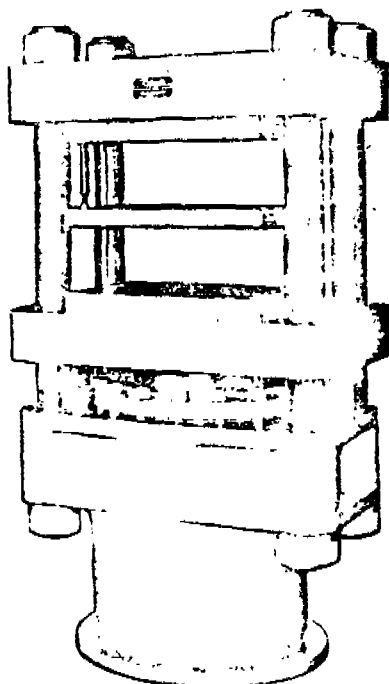
^b ΔH_c° = heat of combustion

c-Value estimated by authors

d-Will not support combustion

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3) C.E. Chastain, "Plastics are ecologically preferred materials," SPE Antec Preprints /8, Part I, 202-205 (1972).

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Table II: Comparison of heating values and theoretical flame temperatures of plastics, fuels, and other materials

Material	Heating value, B.t.u./lb.	Theoretical flame temp., °C./°F.
Methane	23,590 ^a (5)	2012/3654
Butane	21,000 ^a (5)	2084/3783
Ethylene	21,400 ^a (5)	2250/4082
Propylene	20,750 ^a (5)	2180/3956
City gas (MW=20)	10,300 ^a (5)	
Natural gas (MW=20)	22,700 ^a (5)	
No. 1 fuel oil	19,800 (9)	
No. 6 fuel oil	18,300 (9)	
Bituminous coal (med. volatile, W. Va.)	15,178 (9)	
Lignite (Texas)	11,084 (9)	
Peat (Minn.)	9,057 (9)	
Wood	8,835 (9)	
Peat	3,586 ^b (9)	
Oil shale	6,300 (9)	
Straw	6,700 ^b (9)	
Sewage sludge	7,500 ^b (9)	
Paper	7,590 (9)	
Polyethylene	20,050	2120/3850
Butadiene/styrene copolymer (GRS rubber)	19,010	2220/4020
Polystyrene	17,870	2210/4010
Polyvinyl chloride	7,720	1960/3550
Polycarbonate	13,310	2190/3980
Phenol-formaldehyde resin	12,000	1860/3380
Unsaturated polyesters	12,810	2260/3910
Epoxies	14,430	2220/4030
Glass-reinforced polyester (70% resin)	8,970	
Synthetic marble (30% polyester, 70% calcium carbonate)	3,000	
Melamine laminate (50% melamine-formaldehyde resin, 50% paper)	7,950	
Chipboard (90% woodflour, 10% urea-formaldehyde resin)	8,715	

^a—At 760 Torr, 60° F.
^b—As received.

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