

# Organic Fuels: Composition and Formation Enthalpy Part I — Wood Derivatives, Related Carbohydrates, Exudates, and Rosin

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## ABSTRACT

*The utilization of free energy minimization computer programs in areas of combustion research is likely to increase in the future. These programs require the specification of the reactant chemical formulas and their respective formation enthalpies as part of the input data set. Frequently, for common compounds, the values required are readily available in handbooks. Complex organic compounds or poorly characterized mixtures may not have the required data available in a directly usable form. This article evaluates a variety of organic fuels used in pyrotechnics from the perspective of establishing useful chemical formulas and formation enthalpies. Along the way, it is the author's intention to simplify the methods used, to illustrate how many disparate sources of information may be drawn upon to achieve the estimation of the required values, and to demonstrate that each of the methods used is itself relatively easy to perform or calculate.*

**Keywords:** chemical composition, enthalpy of formation, higher heating value (HHV), Benson group, free energy minimization, ultimate analysis, trace elements, wood, monosaccharide, disaccharide, oligosaccharide, polysaccharide, sugar, lactose, sucrose, cellulose, hydroxyethyl cellulose, carboxymethyl cellulose, cellulose nitrate, lignin, starch, gum, gum arabic, gum tragacanth, guar gum, rosin

## Introduction

Considerable varieties of organic fuels are available for and are used in pyrotechnic formulations. Choosing the right fuel for the intended application is made all the more difficult if the data required to make an informed decision is incomplete or unavailable. The primary focus of this article is to present chemical formulas and formation enthalpy estimates for common organic fuels that will be useful to the pyrotechnist and energetics chemist.

The author believes that, in the future, the use of free energy minimization software will find wider acceptance as an important tool for use in the combustion products analysis of pyrotechnic formulations. These programs allow the investigator to simulate, study, and optimize the combustion properties of a pyrotechnic formulation prior to actually handling the potential ingredients. This will certainly expedite the formulation development cycle and improve the end product.

These programs require, in part, that the chemical composition and formation enthalpies of the ingredients—the *reactants*—be specified as part of the input data set. The compositions of these fuels range from simple, pure compounds to complex mixtures that are poorly characterized. Many of the fuels have variable compositions. This may be due in part to the source location, climate, collection time of year, or species. In some cases, the chemical compositions are readily available in handbooks. The formation enthalpies, on the other hand, are rarely available, but may be estimated using a variety of methods.

The reference values listed in the following tables are expressed as either *higher heating value* (HHV), *formation enthalpy* ( $\Delta_f H^\circ$ ), or *combustion enthalpy* ( $\Delta_c H^\circ$ ). Units of kilojoule (kJ) or megajoule (MJ) per kilogram (kg) or mole are used for both. Formation enthalpies are for the solid phase unless otherwise indicated. *Molecular weights* (MW) are in gram-moles. The method used for estimating the  $\Delta_f H^\circ$  is denoted by superscripted letter(s) following the value:

H	HHV
C	Combustion enthalpy
B	Benson group additivity
PB	Partial Benson group additivity
D	Simple difference method
F	Flame temperature and formulation

Each of these methods is described in "Six Methods for Estimating the Formation Enthalpy of Organic Compounds".<sup>[1]</sup> For convenience, the chemical formulas are generally represented using a common basis such that comparisons may be readily made between the different fuels. The author arbitrarily chose a C<sub>6</sub> formula basis because many fuels are derived from simple C<sub>6</sub>-based molecules. Chemistry Abstract Service Registry Numbers (CAS numbers) are provided when available.

It is assumed that the reader has some familiarity with basic chemistry. Most of the detailed and often confusing nomenclature used in carbohydrate chemistry will be oversimplified or avoided altogether, perhaps to the distress of the chemistry purist. This nomenclature is generally not relevant to the purpose of this article.

This article covers organic fuels based on wood, its direct derivatives, related carbohydrates, exudates, and rosin.

Part II of this series of articles covers acaroid resin, shellac, destructive distillation of wood: charcoal and pitch; gilsonite; waxes; and a sampling of pure fuels and synthetic polymers.

Wood is the source for many fuels used in pyrotechnics; thus it is the logical starting point.

## Wood and Its Derivatives: Wood

*Wood*, by itself, is generally not used in pyrotechnic formulations. Occasional references, such as Shimizu,<sup>[2]</sup> use finely divided sawdust as a fuel. *Hardwoods* are generally characterized as deciduous trees such as oaks, and *softwoods* are coniferous trees such as pines.<sup>[3]</sup> A sampling of common tree species is listed in Table 1.

The energy value of wood depends in part on the tree species and the wood material, such as the bark, heartwood, sapwood, etc. These values cannot be defined precisely for a given species, tree or even part of the tree. This is due, in part, to variations in location, climate, season, and soil conditions.<sup>[4]</sup> Accumulated data from various labs over many years has yielded average values. Representative ultimate elemental compositions and heating values appear in Table 1.

The three primary polymers that make up the bulk of wood are *cellulose*, *lignin*, and *hemicellulose*. A general compositional analysis reveals the following:<sup>[5]</sup>

	Cellulose	Lignin	Hemi-cellulose
Hardwoods	43%	22%	35%
Softwoods	43%	29%	28%

Note: Values are on a dry, extractive free basis.

Wood has a roughly uniform composition with a C<sub>6</sub>-based chemical formula of: C<sub>6</sub>H<sub>8.7</sub>O<sub>3.921</sub>N<sub>0.012</sub>S<sub>0.001</sub>, and a corresponding  $\Delta_f H^\circ$  of -738.8 kJ/mole<sup>H</sup>.

Ash composition is a function of the trace elements present in wood (see Table 2) and is composed primarily of calcium and potassium oxides. Bark has approximately 10–20 times the ash content of wood and is slightly different in trace element composition. This may be due, in part, to extraneous mineral matter being inadvertently picked up during handling.<sup>[7]</sup>

**Table 1. Ultimate Elemental Compositions and Heating Values of Selected Woods.**

	Elemental Analysis (% weight, dry basis)						HHV (MJ/kg)	$\Delta_f H^\circ_{298}$ (MJ/kg <sup>H</sup> )	Ref.
	C	H	O	N	S	Ash			
<b>Hardwoods</b>									
Beech	51.64	6.26	41.45	0.0	0.0	0.65	20.38	-5.427	5
Hickory	49.67	6.49	43.11	0.0	0.0	0.73	20.17	-5.316	5
Oak, Black	48.97	6.04	43.48	0.15	0.02	1.40	18.65	-5.957	6
Maple, Big Leaf	49.89	6.09	43.27	0.14	0.03	0.60	18.86	-6.120	6
Poplar	48.45	5.85	43.69	0.47	0.01	1.33	19.38	-4.788	6
Walnut, Black	49.80	5.82	43.25	0.22	0.01	0.78	19.83	-4.737	6
Willow, Hybrid	48.32	6.09	44.70	0.14	0.08	0.73	19.30	-5.171	6
Average	49.53	6.09	43.28	0.16	0.02	0.89	19.51	-5.359	
<b>Softwoods</b>									
Fir, Douglas	50.64	6.18	43.00	0.06	0.02	0.10	20.37	-4.981	5
Fir, White	49.00	5.98	44.75	0.05	0.01	0.25	19.95	-4.582	5
Hemlock, Western	50.4	5.8	41.4	0.1	0.1	2.2	20.05	-4.706	4
Pine, Ponderosa	49.25	5.99	44.36	0.06	0.03	0.29	20.02	-4.610	5
Redwood	50.64	5.98	42.88	0.05	0.03	0.36	20.72	-4.350	5
Average	49.99	5.99	43.28	0.06	0.04	0.64	20.22	-4.646	
<b>Overall Average:</b>	49.72	6.05	43.28	0.12	0.03	0.79	19.77	-5.062	

Note: Reference 6 included trace amounts of chlorine in the elemental analysis percentages.

**Table 2. Trace Element Analysis for Selected Woods.**

	Trace Elements (ppm)									
	Ca	K	Mg	P	Mn	Na	Cu	Zn	Fe	Cl
<b>Hardwoods</b>										
Aspen, Quaking <sup>[a]</sup>	950	1050	270	100	35	5	7	17	12	—
Maple, Red <sup>[a]</sup>	750	600	120	30	70	5	5	29	11	18
Oak <sup>[b]</sup>	400	900	170	20	10	33	73	38	30	15
Sweetgum <sup>[c]</sup>	600	350	355	205	70	85	—	21	—	—
<b>Softwoods</b>										
Fir, Balsam <sup>[a]</sup>	850	650	270	—	110	18	17	11	13	—
Hemlock, Eastern <sup>[a]</sup>	950	350	110	120	135	6	5	2	6	—
Pine, Eastern White <sup>[a]</sup>	250	200	70	—	25	9	5	11	10	19
Spruce, Red <sup>[a]</sup>	750	150	70	50	125	8	4	8	14	0.3
<b>Average</b>	688	531	179	88	73	21	17	17	14	13

All values based on moisture-free wood. Data from reference 4. Items designated “—” not used in average.

[a] Average of atomic spectroscopic and neutron activation methods.

[b] Average of White and Southern Red Oak.

[c] Average of Bottomland and Upland Sweetgum.

The trace elements present in wood might adversely affect, for example, the purity of a flame's color. It requires very little sodium to produce the generally undesirable, characteristic yellow 589 nm emission doublet. See Ta-

ble 2. Many of these trace elements find their way into wood derivatives, such as charcoal, or exudates, such as gums.

## Carbohydrates

### Monosaccharides

Wood-based *polymers* all start with *monomers*. The fundamental monomer building blocks are *monosaccharides*. Many have the general formula  $C_6H_{12}O_6$ .<sup>[8]</sup> They are also known as *simple sugars*, or just *sugars*.<sup>[8]</sup> The general formulas of monosaccharides are classified according to the number of carbon atoms they contain. Those that are of importance in this article are *pentoses*,  $C_5H_{10}O_5$  and *hexoses*,  $C_6H_{12}O_6$ .<sup>[9,10]</sup> These monosaccharides can form either linear molecules or stable ring structures. The *furanose* ring form is five sided (see D-ribose Figure 1), and *pyranose* is six sided (see D-arabinose Figure 1). On both, one ring position is occupied by an oxygen atom. The ring forms are of the most concern in this article. Figure 1 illustrates a few representative monosaccharides. Table 3 lists a few common monosaccharides and their abbreviated names.

A variety of different molecular representations may be encountered in chemical literature. The author took the liberty of displaying a few common styles in Figure 1:  $\alpha$ -D-xylose is shown using both *Fischer* and *Haworth* projections (sometimes referred to as *Haworth hexagonal*).<sup>[11]</sup> D-sucrose in Figure 2 uses a *Haworth conformational* style, which better illustrates the *chair* conformation of the ring structures. Solid wedge bonds project toward the viewer from the plane of the paper, and hashed wedge bonds project away from the viewer. Typical of most rendering schemes, hydrogens have been removed for clarity.

From these illustrations and the data presented in Table 3, it is evident that the chemical formulas and their corresponding *molecular weights* (*MW*) are the same for many of the compounds, but the position of the *hydroxyl* (*OH*) group may be above or below the equator of a ring sugar. This leads to, for the  $C_6H_{12}O_6$  hexoses as an example, 16 different *stereoisomers*. Each has a different name and properties.

The proper nomenclature to sort this out gets involved.

For combustion purposes the chemical compositions are identical, and the  $\Delta_f H^\circ$  is essentially constant for the various stereoisomers—the variations in  $\Delta_f H^\circ$  are generally less than 1%. (See Table 3.) For these reasons, this article will dispense with most of the exact carbohydrate nomenclature. Focus is instead directed toward formulating practical estimates of the formation enthalpies and chemical formulas. Average  $\Delta_f H^\circ$  values based on the references may be used when specific values are unknown.

### Oligosaccharides

*Oligosaccharides* are polymers composed of from 2 to 10 monosaccharides.<sup>[8]</sup> This quantity is an arbitrary number, but fortunately, nature produces very few carbohydrates between 5 and 15 sugar residues.<sup>[9]</sup> If the oligosaccharide is composed of two monosaccharides, then it is sometimes referred to as a *disaccharide*.<sup>[16]</sup> The individual monosaccharides are linked together with a *glycoside bond*.<sup>[17]</sup> (This is also known as an *oxygen bond*.<sup>[18]</sup> It may also be a *glucoside* bond depending on the specific monosaccharides involved, etc.<sup>[16]</sup> In this article *glycoside* will be used for uniformity.) This bond is formed between the hydroxyl group on the anomeric<sup>[9]</sup> (hemi-acetal)<sup>[17]</sup> carbon atom of one monosaccharide and any hydroxyl group on the other monosaccharide. Water ( $H_2O$ ) is eliminated in the process. Figure 2 illustrates the glycoside bond, elimination of water, and two familiar disaccharides that form as a result: *lactose* (“milk sugar”) and *sucrose* (“cane sugar”). Note that sucrose is composed of a pyranose and a furanose sugar.

In a fashion similar to that of the monosaccharides, there are *many* possible oligosaccharides. Note that the chemical compositions are identical ( $C_{12}H_{22}O_{11}$ ) for the oligosaccharides listed in Table 3, and the variations in  $\Delta_f H^\circ$  are within 1% of their average.

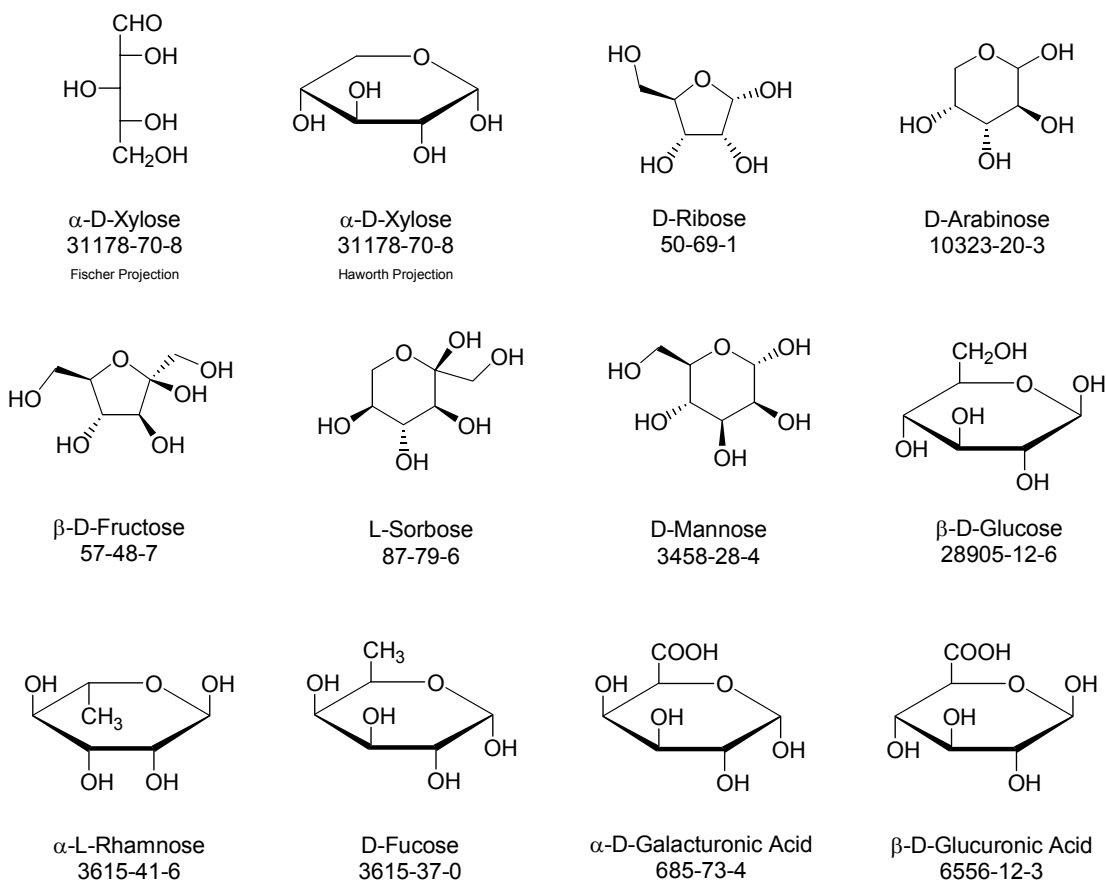


Figure 1. Some representative monosaccharides.

When a disaccharide forms, the resulting  $\Delta_f H^\circ$  is not equal to the sum of that of the constituent monosaccharides. This is due, in part, to the rearrangement of the atoms that participate in the glycoside bond and the elimination of water. If the  $\Delta_f H^\circ$  of the monosaccharides (reactants) are added, and this sum is then sub-

tracted from the  $\Delta_f H^\circ$  of the disaccharide (product), the difference represents the change in enthalpy (*heat of reaction*<sup>[8,10]</sup>  $\Delta_r H^\circ$ ) for glycoside bond formation and water elimination. Using the averages from Table 3, see calculation at bottom of next page.

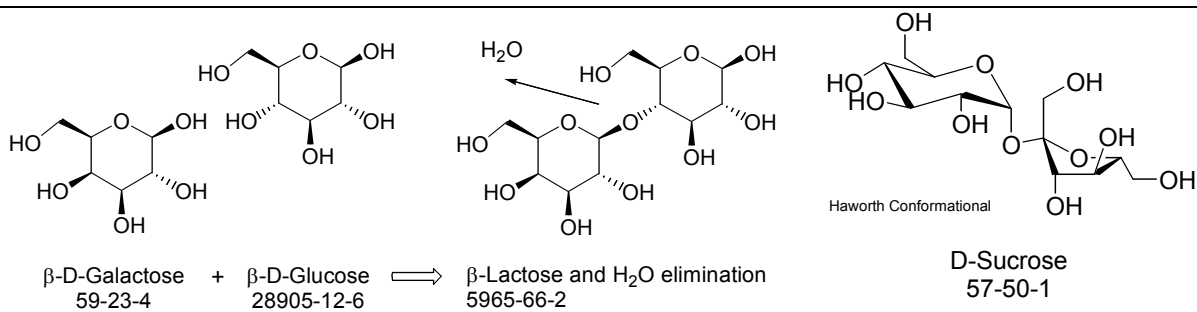


Figure 2. Glycoside bond formed by elimination of water from two monosaccharides; and two familiar disaccharides:  $\beta$ -lactose and D-sucrose.

**Table 3. Chemical Formulas, Abbreviations, and Formation Enthalpies for Some Common Mono- and Oligosaccharides.**

Name	Abbr. <sup>[9]</sup>	CAS No.	References	$\Delta_f H^\circ$ kJ/mole <sup>[a]</sup>
$\alpha$ -D-xylose	Xyl	31178-70-8	12, 13	-1053.6
D-ribose	Rib	50-69-1	12 – 15	-1053.4
D-arabinose	Ara	10323-20-3	12 – 15	-1056.6
<b>C<sub>5</sub>H<sub>10</sub>O<sub>5</sub></b>	<b>MW 150.13</b>		<b>Average:</b>	<b>-1054.7</b>
L-rhamnose	Rha	3615-41-6	12, 15	-1073.2
D-fucose	Fuc	3615-37-0	12, 15	-1099.1
<b>C<sub>6</sub>H<sub>12</sub>O<sub>5</sub></b>	<b>MW 164.16</b>		<b>Average:</b>	<b>-1086.2</b>
$\alpha$ -D-glucose	Glc	26655-34-5	12 – 15	-1273.8
$\beta$ -D-glucose	Glc	28905-12-6	13, 14	-1267.5
$\beta$ -D-fructose	Fru	57-48-7	12 – 15	-1266.4
$\alpha$ -D-galactose	Gal	3646-73-9	12 – 15	-1286.0
L-sorbose	—	87-79-6	12, 13	-1271.1
D-mannose	Man	3458-28-4	12, 13, 15	-1263.1
<b>C<sub>6</sub>H<sub>12</sub>O<sub>6</sub></b>	<b>MW 180.16</b>		<b>Average:</b>	<b>-1271.4</b>
D-sucrose	—	57-50-1	12 – 15	-2223.2
$\beta$ -lactose	—	5965-66-2	12 – 15	-2236.2
Cellobiose	—	528-50-7	13, 15	-2221.5
Maltose	—	69-79-4	13, 15	-2215.1
<b>C<sub>12</sub>H<sub>22</sub>O<sub>11</sub></b>	<b>MW 342.30</b>		<b>Average:</b>	<b>-2226.1</b>

[a] All values based on averages of the references.

Each of the two monosaccharides participates in *half* of this bond, so the average respective  $\Delta_f H^\circ$  *per monosaccharide* is approximately 158.35 kJ/mole<sup>D</sup>. This value will be used in subsequent estimates. The change in MW by elimination of *each* H<sub>2</sub>O molecule is -18.02.

### Polysaccharides

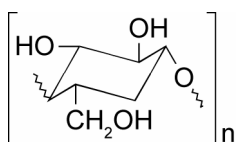
*Polysaccharides* are polymers where the number of sugar residues is greater than 10.<sup>[17]</sup> As with oligosaccharides, the glycoside bond links the monosaccharides together. There are usually two, but sometimes more, glycosidic bonds between the monosaccharides.

One disaccharide	= 1 C <sub>12</sub> H <sub>22</sub> O <sub>11</sub>	= -2226.1	kJ/mole
Two monosaccharides	= 2 C <sub>6</sub> H <sub>12</sub> O <sub>6</sub> = 2 × -1271.4	= -2542.8	kJ/2 moles
Glycoside bond formation (average) and H <sub>2</sub> O elimination		= $\frac{-2542.8}{2}$	316.7 <sup>D</sup> kJ/mole

## Cellulose

*Cellulose* (9004-34-6) is the main constituent of plant cell walls and is perhaps the most abundant naturally occurring polymer.<sup>[19]</sup> See Figure 3. Cellulose is found in its purest natural form in seed hairs, of which cotton is notable. The generally accepted empirical formula for cellulose (C<sub>6</sub>H<sub>10</sub>O<sub>5</sub>)<sub>n</sub> agrees closely with the elemental analysis for purified cotton cellulose:<sup>[20]</sup>

	Cotton	C <sub>6</sub> H <sub>10</sub> O <sub>5</sub>
Carbon	44.35	44.45
Hydrogen	6.14	6.22
Oxygen	49.51	49.34



Cellulose  
9004-34-6

Figure 3. Cellulose.

The *degree of polymerization (DP)*, or “n” in the empirical cellulose formula, denotes the number of repeating monomer units in an *average* polymer. For cotton, the *DP* is between 6200 and 6700, for pine it is 3300, and for wood pulp it ranges from 500 to 2000.<sup>[19]</sup> The “squiggly lines” in Figure 3 represent the glycoside bonds that connect adjacent monomers. Polymers of this nature are often referred to as *macromolecules* due to their enormous sizes.<sup>[8]</sup>

Cellulose is constructed from glycosidic bonds between adjacent monosaccharides. Each monomer participates in *two* glycoside bonds, with the exception of the monomer “caps” at each end of the chain that participate in only one bond. Considering the *DP* of cellulose, it is reasonable to ignore the “caps” only having a single glycoside bond and to base the cellulose  $\Delta_f H^\circ$  estimate on two bonds for all monomers as illustrated in Figure 3 (an infinitely long chain).

One monosaccharide	= C <sub>6</sub> H <sub>12</sub> O <sub>6</sub>	= -1271.4	kJ/mole
Two glycoside bonds and elimination of H <sub>2</sub> O	= 2 × 158.35	= + 316.7	kJ/2 moles
Cellulose(C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> ) <sub>n</sub>		= -954.7 <sup>D</sup>	kJ/mole

The calculation at the bottom of this page agrees well with the  $\Delta_f H^\circ$  of -979.0 kJ/mole<sup>C</sup> for filter paper cellulose. (See Table 5 near the end of this article.)

Cellulose (paper) may be used, for example, as tubing for pyrotechnic devices, as liners for composite propellant rocket motor grains, or directly as a fuel in hybrid rocket motors.

## Lignin

*Lignin* (9005-53-2) is a polymer of amorphous structure<sup>[8]</sup> with an approximate formula of C<sub>10</sub>H<sub>11</sub>O<sub>2</sub>.<sup>[21]</sup> It consists of a complex array of bonds between hydroxy- and methoxy-substituted phenylpropane units. The three primary precursors (see Figure 4) are:

*p-coumaryl alcohol* (3690-05-9, C<sub>9</sub>H<sub>10</sub>O<sub>2</sub>), *coniferyl alcohol* (458-35-5, C<sub>10</sub>H<sub>12</sub>O<sub>3</sub>), and *sinapyl alcohol* (537-33-7, C<sub>11</sub>H<sub>14</sub>O<sub>4</sub>)<sup>[18]</sup>

The  $\Delta_f H^\circ$  of -1153.3 kJ/mole<sup>C</sup> will be considered representative. Lignin is not directly utilized in pyrotechnic formulations or rocketry.

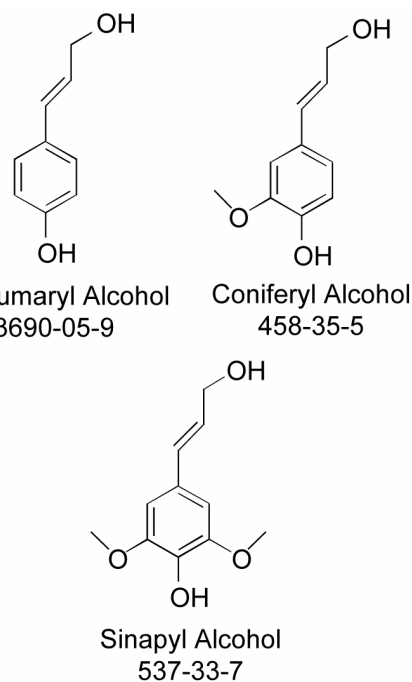


Figure 4. Primary precursors of lignin.

## Hemicellulose

The hemicelluloses are polymers related to cellulose and have a *DP* of 150 or less.<sup>[8]</sup> Hemicellulose is generally easily hydrolyzed and is a branched and amorphous structure<sup>[22]</sup> that is rather ill-defined.<sup>[10]</sup> Whereas cellulose is a *homopolysaccharide* based on repeating glucose monomers,<sup>[8]</sup> hemicellulose is a *heteropolysaccharide* incorporating other sugars. Softwoods generally have higher concentrations of mannose and galactose, and hardwoods generally have more xylose.<sup>[23]</sup>

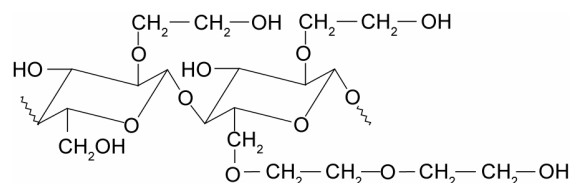
## Cellulose Derivatives

Cellulose may be modified into other useful compounds, each with different properties and applications. Most of the modifications involve substituting different functional groups or short polymers for one or more of the hydroxyl groups. The *degree of substitution*, or *DS*, denotes the *average* number of hydroxyl groups that have been substituted per monomer. The *molar substitution*, or *MS*, denotes the *average* number of units substituted per monosaccharide, and this number can be any value equal to or greater than the *DS* depending on the length of these side chains.

### Hydroxyethyl Cellulose

*Hydroxyethyl cellulose* (9004-62-0), (See Figure 5) sometimes called *Cellosize*<sup>[8]</sup> or *HEC*,<sup>[24]</sup> is a cellulose ether where some of the hydroxyl (OH) groups have been replaced by hydroxyethyl groups (using *ethylene oxide*, 75-21-8, C<sub>2</sub>H<sub>4</sub>O). The *DS* is variable and ranges from 0.2–0.5 for paper sizing to 1.5 for adhesives.<sup>[17]</sup> A *DS* of 0.8–1.5 is usually encountered.<sup>[19,22]</sup>

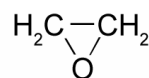
The maximum possible *DS* is 3.0 as there are only three hydroxyls per monosaccharide available for substitution. Typically, the *MS* ranges from 1.4–2.0.<sup>[19]</sup> Figure 5 is a simple case where there are 3 substitutions on two monosaccharides, hence the *DS* is 1.5 (3.0 OH substitutions ÷ 2.0 sugar units). There are a total of 4 ethylene oxide units, so the *MS* is 2.0 (4.0 C<sub>2</sub>H<sub>4</sub>O units ÷ 2.0 sugar units).



Hydroxyethyl Cellulose  
9004-62-0

Figure 5. *Hydroxyethyl cellulose.*

Each ethylene oxide (see Figure 6) unit adds C<sub>2</sub>H<sub>4</sub>O and a  $\Delta_f H^\circ$  of  $-185.0$  kJ/mole<sup>B</sup> to the cellulose molecule. In the example illustration, the *MS* of 2.0 per sugar residue adds  $2.0 \times -185.0 = -370.0$  kJ/mole and  $2.0 \times C_2H_4O = C_4H_8O_2$  to the cellulose formula of C<sub>6</sub>H<sub>10</sub>O<sub>5</sub> and a  $\Delta_f H^\circ$  of  $-954.7$  kJ/mole; thus giving this particular (and perhaps typical) hydroxyethyl cellulose molecule a formula of (C<sub>10</sub>H<sub>18</sub>O<sub>7</sub>)<sub>n</sub> and a  $\Delta_f H^\circ$  of  $-1324.7$  kJ/mole<sup>PB</sup>. In C<sub>6</sub> units this would be C<sub>6</sub>H<sub>10.8</sub>O<sub>4.2</sub> and a  $\Delta_f H^\circ$  of  $-794.8$ <sup>PB</sup>.

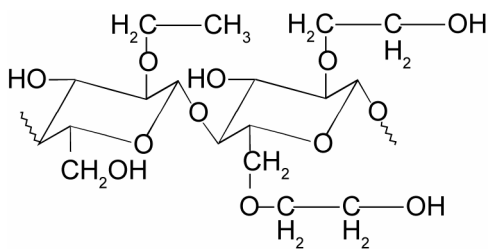


Ethylene Oxide  
75-21-8

Figure 6. *Ethylene oxide.*

A similar polymer is *ethyl hydroxyethyl ether cellulose* (9004-58-4),<sup>[25]</sup> and it is illustrated<sup>[24]</sup> in Figure 7. Both ethyl and hydroxyethyl groups substitute for hydroxyl groups. *DS* equals 1.5, ethyl *MS* equals 0.5, and hydroxyethyl *MS* equals 1.0. As in hydroxyethyl cellulose, each ethylene oxide substituted adds C<sub>2</sub>H<sub>4</sub>O and a  $\Delta_f H^\circ$  of  $-185.0$  kJ/mole. The ethyl group adds C<sub>2</sub>H<sub>4</sub> and a corresponding  $\Delta_f H^\circ$  of  $-79.74$  kJ/mole<sup>B</sup>. Performing the arithmetic gives a formula of (C<sub>6</sub>H<sub>9</sub>O<sub>6</sub>)<sub>n</sub> and a  $\Delta_f H^\circ$  of  $-1179.6$  kJ/mole<sup>PB</sup>.





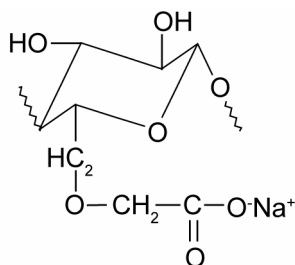
Ethyl Hydroxyethyl Cellulose  
9004-58-4

Figure 7. Ethyl hydroxyethyl ether cellulose.

The commercial product is a white fibrous material that contains 1–2% ash that is probably a sodium salt.<sup>[22]</sup> Principle uses are a binder, thickening agent, in gel lacquers, and in paper sizing.<sup>[17,19]</sup>

### Carboxymethyl Cellulose

Carboxymethyl cellulose, or CMC, has some of the hydroxyls substituted with carboxymethyl groups.<sup>[17]</sup> Sodium carboxymethyl cellulose (9004-32-4) is illustrated<sup>[19]</sup> in Figure 8. It has a *DS* that typically ranges from 0.5–0.85,<sup>[19]</sup> and has a sodium cation in place of the hydroxyl's hydrogen. The illustration's chemical formula is  $C_8H_{11}NaO_7$ . The MW ranges from 21,000–500,000.<sup>[8]</sup>



Sodium Carboxymethyl Cellulose  
9004-32-4

Figure 8. Sodium carboxymethyl cellulose.

The author could not find  $\Delta_f H^\circ$ ,  $\Delta_c H^\circ$ , or HHV data for sodium carboxymethyl cellulose, and the required sodium Benson Group values are unavailable for the solid phase.<sup>[26]</sup> The author derived a required group value and arrived

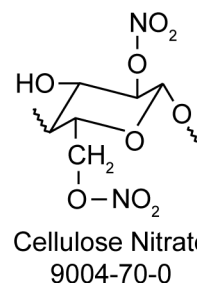
at a tentative  $\Delta_f H^\circ$  estimate, for the example illustration, of  $-1564 \text{ kJ/mole}^{\text{PB}}$ . [Derivation: Crystalline sodium acetate (127-09-3,  $C_2H_3NaO_2$ ) has a  $\Delta_f H^\circ$  of  $-708.8 \text{ kJ/mole}$ .<sup>[27]</sup> It is composed of three Benson Groups:<sup>[28]</sup> (C)-(H)<sub>3</sub>(CO) with a  $\Delta_f H^\circ$  of  $-46.74 \text{ kJ/mole}$ ; (CO)-(C)(O) with a  $\Delta_f H^\circ$  of  $-153.60 \text{ kJ/mole}$ ; and the unknown group O-(Na)(CO). Difference yields an estimated  $\Delta_f H^\circ$  of  $-508.46 \text{ kJ/mole}_{\text{solid}}^{\text{B}}$  for the O-(Na)(CO) group.]

It is used for paper sizing,<sup>[8]</sup> as a binder, and as a thickening agent in pyrotechnics.<sup>[29]</sup>

### Cellulose Nitrate

Cellulose nitrate (9004-70-0) has some of its hydroxyls substituted with nitro groups.<sup>[19]</sup> (See Figure 9.) Frequently the literature uses percent nitrogen instead of *DS*. Typical ranges<sup>[19]</sup> of these parameters are:

Nitrogen (%)	DS	DP	Application
10.7–12.3	1.9–2.4	70–850	plastics & lacquers
12.3–13.5	2.4–2.8	3000–5000	explosives & propellants



Cellulose Nitrate  
9004-70-0

Figure 9. Cellulose nitrate.

Each nitro group adds  $\text{NO}_2$ , eliminates an H and a  $\Delta_f H^\circ$  of  $75.66 \text{ kJ/mole}^{\text{B}}$ . For the sample illustration, the *DS* equals 2.0 and the resulting formula is  $C_6H_8N_2O_9$  with a  $\Delta_f H^\circ$  of  $-803.4 \text{ kJ/mole}^{\text{PB}}$ . For a *DS* of 2.5, the resulting formula would be  $C_6H_{7.5}N_{2.5}O_{10}$  with a  $\Delta_f H^\circ$  of  $-765.6 \text{ kJ/mole}^{\text{PB}}$ .

## Starch

*Starch* (9005-84-9, *soluble*), sometimes called *dextrin*<sup>[29]</sup> or *starch gum*<sup>[8]</sup> when partially hydrolyzed, occurs naturally as small granules whose size and shape are characteristic of the plant from which it is obtained. It consists of both *amylose* (9005-82-7) (C<sub>6</sub>H<sub>10</sub>O<sub>5</sub>)<sub>n</sub>, which is water soluble, and *amylopectin* (9037-22-3), approximate formula (C<sub>6</sub>H<sub>10</sub>O<sub>5</sub>)<sub>n</sub>, a branched polysaccharide that is water insoluble.<sup>[16]</sup> The amount of amylose in starch ranges from less than 2% in waxy maize to 80% in amylo maize, but the majority of starches contain between 15 and 35% amylose.<sup>[9]</sup> Twenty percent amylose will be considered representative. Amylose (see Figure 10) is very similar in structure to cellulose and has a *DP* of between 1000 and 4000. In this article its  $\Delta_f H^\circ$  will be considered the same as cellulose (-954.7 kJ/mole<sup>D</sup>), which compares favorably with a reference value of -955.6 kJ/mole<sup>C</sup>. See Table 5.

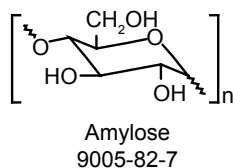


Figure 10. Amylose.

Amylopectin (see Figure 11) has a branched structure slightly more complex than that of amylose. Note the arrow pointing to the oxygen atom. The monomer drawn below this oxygen has three, rather than two, glycoside bonds. Approximately 5% of the monomers in amylopectin have three glycoside bonds rather than two. The length of each amylopectin chain is approximately 20 units.<sup>[16,19]</sup> This yields an approximate chemical formula of (C<sub>6</sub>H<sub>9.96</sub>O<sub>4.96</sub>)<sub>n</sub>.

The  $\Delta_f H^\circ$  may be estimated from this *ideal* structure as in the example at the bottom of this page. Starch (dextrin), the most commonly used binder in pyrotechnic formulations,<sup>[29]</sup> is used as an adhesive, in textile sizing, and as a thickener in foods.<sup>[10]</sup>

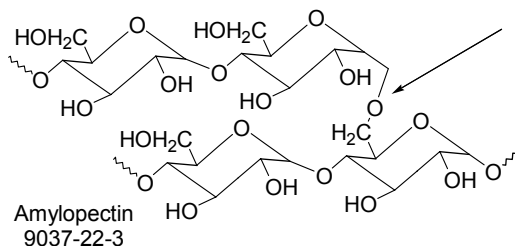


Figure 11. Amylopectin.

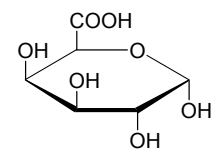
## Gums and Resins: Gums

*Gums* are polysaccharides or their derivatives that hydrate in hot or cold water to form viscous solutions. The source of gums may be microbial, algal, seed endosperm, or plant exudates.<sup>[30]</sup> Two plant exudates and one seed gum will be considered in this article, though the methods used apply to all gums. Gums typically consist of from two to five different monosaccharides that are linked by glycosidic bonds in a branched manner.<sup>[31]</sup>

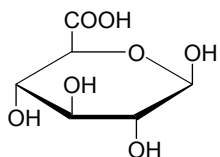
In addition to the monosaccharides that have already been encountered in this article, two additional ones are frequently present in gums:  $\alpha$ -D-galacturonic acid and  $\beta$ -D-glucuronic acid. See Figure 12. Note that, for combustion purposes, these two molecules (C<sub>6</sub>H<sub>10</sub>O<sub>7</sub>) are fundamentally the same. The  $\Delta_f H^\circ$  value of -1468.8 kJ/mole<sup>PB</sup> will be used for both.

Carbohydrate literature generally simplifies the graphical representation of gum polymers for reasons of brevity and clarity. Abbreviations

Amylose	= 20% of -954.7 [(C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> ) <sub>n</sub> , bonds included]	= -190.94 kJ/mole
Amylopectin	= 80% of -1271.4 [C <sub>6</sub> H <sub>12</sub> O <sub>6</sub> monomer]	= + -1017.12 kJ/mole
	95% 2 glycoside bonds	
Plus	5% 3 glycoside bonds	
=	(2 × 0.95) + (3 × 0.05) = 2.05 bonds	
=	80% of bonds: 0.80 × 2.05 × 158.35	= + 259.69 kJ/mole
Starch (C <sub>6</sub> H <sub>9.96</sub> O <sub>4.96</sub> )	$\Delta_f H^\circ$	= -948.4 <sup>D</sup> kJ/mole



$\alpha$ -D-Galacturonic Acid  
685-73-4



$\beta$ -D-Glucuronic Acid  
6556-12-3

Figure 12. Two monosaccharides frequently present in gums.

for the constituent monomers are used and numbers indicate which ring positions are taking place in the various glycoside bonds. This article will dispense with the numbering system. The monosaccharide abbreviations (see Table 3) have either a “p” for pyranose or an “f” for furanose appended, and in the case of an acid, an “A” appended after that; thus, the furanose form of arabinose is **Araf**, and the pyranose form of  $\beta$ -D-glucuronic acid is **GlcA**.

### Gum Arabic

*Gum arabic* (9000-01-5) is an exudate collected from the various species of the thorny, shrub-like tree *Acacia*, including *A. arabica*, *A. senegal*, *A. vereck*,<sup>[32]</sup> and *A. seyal*.<sup>[30]</sup> When a plant is wounded it often produces a sticky sap-like substance that covers the incision. This fluid dries to a translucent and glassy mass on exposure to air. It is then collected, sorted, possibly cleaned, then crushed to a powder. Commercial grades are most likely mixtures of varying composition and stored under varying conditions.<sup>[33]</sup>

Gum arabic is also known by dozens of other names including *Acacia*,<sup>[29]</sup> *Abyssinia*, black wattle (from *A. mollissima*, *Willd*<sup>[34]</sup>), Ba-

bool, Jeddah, Senegal, Sudan, sunt, Turic, and white gum just to name a few.<sup>[32]</sup>

The generally accepted structure for this gum is illustrated in Figure 13.<sup>[31–34]</sup> A recent report<sup>[35]</sup> indicates that the branching structure—as determined by a variety of analytical methods—may be slightly more complicated than that used here. The molecular weight has a broad distribution. It has been variously reported as a low of 200,000,<sup>[34]</sup> approximately 240,000–250,000,<sup>[32,36]</sup> 580,000,<sup>[31,37]</sup> and a high of 1,160,000;<sup>[30]</sup> 250,000 is considered representative.

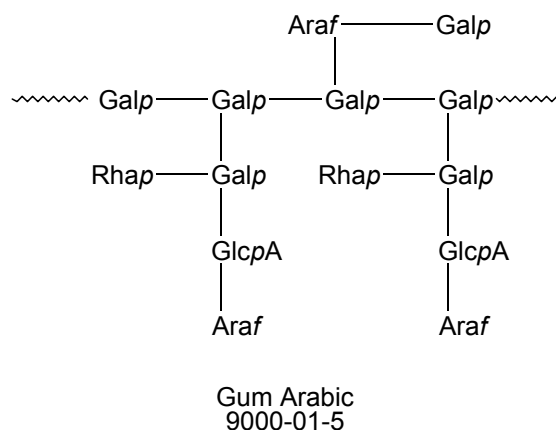


Figure 13. *Gum Arabic*, ideal polysaccharide structure.

Gum arabic is acidic due to the high concentration of glucuronic acids. These acids usually form salts where sodium, calcium, and potassium represent the majority of the cations involved.<sup>[32,34,36,38]</sup> Trace amounts of iron and magnesium are present.<sup>[32]</sup> Industrial grades of gum arabic contain from 1–3% ash<sup>[32,38]</sup> that is mainly sand or dirt,<sup>[34,39]</sup> and may contain up to 10% bark.<sup>[39]</sup> Discoloration is generally caused by bark tannins.<sup>[32]</sup> Foreign matter may be removed by washing-precipitation-filtering cycles using ethanol and water.<sup>[32,34]</sup>

The following example estimates the chemical formula and the  $\Delta_f H^\circ$  based on the specific monosaccharide average values from Table 3 and the ideal polysaccharide illustrated in Figure 13 and detailed at the top of the next page.

Qty.	Sugar	$\Delta_f H^\circ$ (kJ/mole)		Total (kJ/mole)	Formula	C	H	O
3	Araf	-1056.6	=	-3169.8	$C_5H_{10}O_5$	15	30	15
7	Galp	-1286.0	=	-9002.0	$C_6H_{12}O_6$	42	84	42
2	Rhap	-1073.2	=	-2146.4	$C_6H_{12}O_5$	12	24	10
2	Glc pA	-1468.8	=	-2937.6	$C_6H_{12}O_7$	12	20	14
14			=	-17255.8		81	158	81
26	Bonds	158.35	=	4117.1	$\frac{1}{2} H_2O^{[a]}$	—	-26	-13
	Gum Arabic			-13138.7 <sup>D</sup>	$C_{81}H_{132}O_{68}$	81	132	68

[a] There are 26 “participants” in the bonds, each eliminating *half* a water molecule (13 total water molecules eliminated).

Gum Arabic ( $C_{81}H_{132}O_{68}$ )<sub>n</sub> has a  $\Delta_f H^\circ$  of -13138.7 kJ/mole<sup>D</sup>. Based on a molecular weight of 250,000, “n” is approximately 114. In  $C_6$  units this is  $C_6H_{9.778}O_{5.037}$  with a  $\Delta_f H^\circ$  of -973.2 kJ/mole<sup>D</sup>. Recalculating using the *representative averages* that appear in Table 3 gives a  $\Delta_f H^\circ$  of -967.2<sup>D</sup>, less than a 1% difference. The  $C_6$ -based formula and the corresponding  $\Delta_f H^\circ$  also agree closely with that of starch ( $C_6H_{9.96}O_{4.96}$ ) with a  $\Delta_f H^\circ$  of -948.4 kJ/mole<sup>D</sup>. Accounting for the sodium, calcium, and potassium cations present in a commercial food grade gum (1.643% ash), its corresponding caloric value,<sup>[38]</sup> and the carbon, hydrogen, and oxygen—based on the ideal polysaccharide—results in a  $C_6$ -based formula of:

$C_6H_{9.778}O_{5.037}Na_{0.035}Ca_{0.036}K_{0.010}$  with a  $\Delta_f H^\circ$  of -1353.0 kJ/mole<sup>C,D</sup>.

Gum Arabic is used as a binder in pyrotechnics,<sup>[29]</sup> probably more so in the past than today (see *Starch* above). It is also used as an adhesive in foods,<sup>[10]</sup> pharmaceuticals, and cosmetics, and in coatings and inks.<sup>[32]</sup>

### Gum Tragacanth

*Gum tragacanth* (9000-65-1) is an exudate from several species of tree of the genus *Astragalus*.<sup>[30]</sup> The MW is approximately 840,000.<sup>[25]</sup> Solutions of this gum have an extremely high viscosity,<sup>[30,39]</sup> heat stability, a long shelf life,<sup>[36]</sup>

and are acid resistant.<sup>[39]</sup> Gum tragacanth impurities (dirt) are typically 1% maximum,<sup>[39]</sup> and ash content is 3%.<sup>[34]</sup>

Based on the structure<sup>[9,37]</sup> in Figure 14, a chemical formula of  $(C_{51}H_{76}O_{46})_n$ , and a  $\Delta_f H^\circ$  of -8570.8 kJ/mole<sup>D</sup>, and “n” equals 448 may be estimated. In  $C_6$  units this is equivalent to  $C_6H_{8.941}O_{5.412}$  and a  $\Delta_f H^\circ$  of -1008.3 kJ/mole<sup>D</sup>. At the time of this writing, no data was readily available to the author regarding the caloric value or concentrations of cations present.

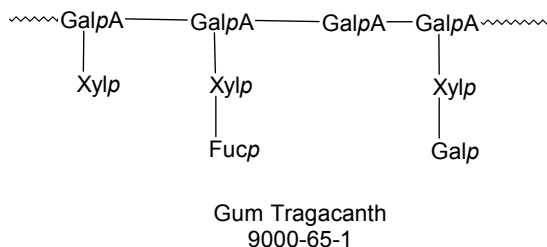


Figure 14. *Gum Tragacanth*.

Gum tragacanth has also found occasional use as an adhesive in fireworks.<sup>[40]</sup> At one time it was used in matchhead compositions in conjunction with gum arabic but has been replaced due to its high cost.<sup>[39]</sup> Other uses include food applications, pharmaceutical emulsions, cosmetics, and adhesives.<sup>[25,30]</sup>

## Guar Gum

Guar gum (9000-30-0) is representative of seed gums. It is derived from the endosperm of the guar plant (*Cyanopsis tetragonoloba*).<sup>[8,36]</sup> The endosperm comprises approximately 40% of the seed, which is then milled to the final product guar flour.<sup>[30]</sup>

Guar gum has an ash content ranging from 0.3<sup>[38]</sup> to 1.07%,<sup>[41]</sup> 0.67% nitrogen and 0.06% phosphorous.<sup>[41]</sup> The MW is approximately 220,000.<sup>[30,36]</sup> Guar gum is one of the few natural alternating copolymers.<sup>[9]</sup>

Based on this ideal structure,<sup>[9]</sup> (see Figure 15) a formula of  $(C_{36}H_{60}O_{30})_n$ , a  $\Delta_f H^\circ$  of  $-5724.2 \text{ kJ/mole}^D$ , and “n” equals 244 may be estimated. In  $C_6$  units this becomes  $C_6H_{10}O_5$  and a  $\Delta_f H^\circ$  of  $-954.0 \text{ kJ/mole}^D$ . Accounting for the sodium, calcium, and potassium cations present in a commercial food grade gum (0.308% ash), its corresponding caloric value,<sup>[38]</sup> the aforementioned nitrogen and phosphorous, and the carbon, hydrogen, and oxygen—based on the ideal polysaccharide—results in a  $C_6$ -based formula of  $C_6H_{10}O_5N_{0.077}P_{0.003}Na_{0.002}Ca_{0.003}K_{0.009}$  and a  $\Delta_f H^\circ$  of  $-1320.1 \text{ kJ/mole}^{C,D}$ .

Guar gum is the most extensively used gum in food and industrial applications: a paper sizing

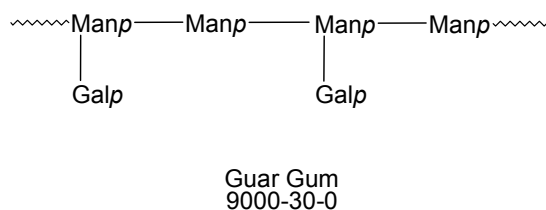


Figure 15. Guar gum.

agent, food stabilizer, gelling agent for slurry explosives, and flocculent in mineral processing to name just a few.<sup>[30]</sup>

## Rosin

Rosin (8050-09-7), also known as *colophony*,<sup>[22,40]</sup> is a natural resin that is obtained from pine trees, chiefly *Pinus palustris* (long-leaf) and *P. caribaea* (Caribbean),<sup>[8,22]</sup> but also *P. taeda* (loblolly) and *P. elliotii* (slash).<sup>[42,43]</sup> The bulk of rosin comes from the distillation of tall oil<sup>[44]</sup> (*tall oil rosin*), though smaller commercial quantities are also extracted from stumps<sup>[17,22]</sup> (*wood rosin*) and from the distillation of turpentine<sup>[8,22]</sup> (*gum rosin*). (Note: *Tall Oil* is derived from the Swedish word “*talloolja*”, which translates to “*pine oil*”.<sup>[42]</sup>)

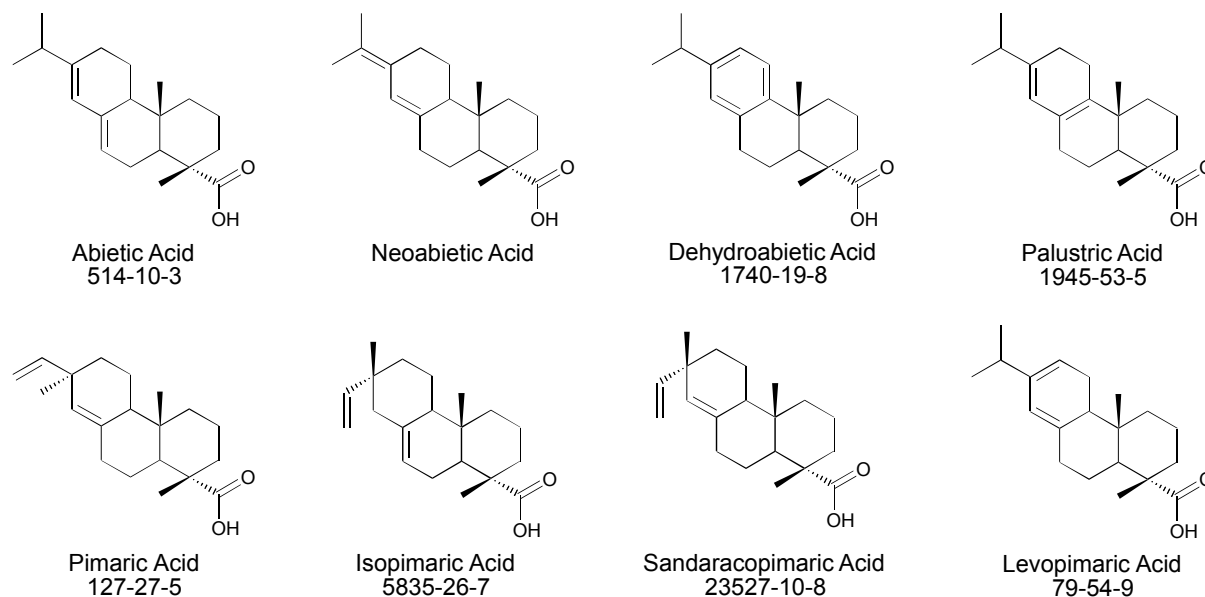


Figure 17. Principle acids found in rosin.

**Table 4. Principle Acids Found in Rosin, Their Compositions and  $\Delta_f H^\circ$ .**

Acid <sup>[a]</sup>									
	Abietic	Neo-abietic	Dehydro-abietic	Palustric	Pimaric	Isopimaric	Sandaracopimaric	Other <sup>[b]</sup>	
CAS	514-10-3	N/A	1440-19-8	1945-53-5	127-27-5	5835-26-7	23527-10-8		
$\Delta_f H^\circ$ (kJ/mole <sup>B</sup> )	-686.88	-615.5	-631.1	-635.0	-547.1	-590.1	-547.2		
Pinus Species	Percent of Various Acids								$\Delta_f H^\circ$ (kJ/mole <sup>B</sup> )
<i>taeda</i>	69	4.7	8.1	10	5.5	0.9	0.9	0.9	-663.8
<i>elliottii</i>	19	16	7.2	25	5.5	23	1.8	2.5	-624.5
<i>palustris</i>	18	15	8.6	35	4.8	16	1.6	1.0	-628.2

[a] Only the acid fraction of rosin is considered for the  $\Delta_f H^\circ$  estimates. The neutral fraction (approximately 10%) consists of hydrocarbons, terpenes, alcohols,<sup>[22,42]</sup> and C<sub>18</sub>–C<sub>26</sub> fatty acids.<sup>[43]</sup>

[b] Not included in the  $\Delta_f H^\circ$  estimate. May consist, in part, of levopimaric acid (79-54-9, C<sub>20</sub>H<sub>30</sub>O<sub>2</sub>) with a  $\Delta_f H^\circ$  of -683.9 kJ/mole<sup>B</sup>.

The principle ingredients are *abietic acid* (514-10-3, C<sub>20</sub>H<sub>30</sub>O<sub>2</sub>), *pimaric acid* (127-27-5, C<sub>20</sub>H<sub>30</sub>O<sub>2</sub>), and their isomers,<sup>[8]</sup> accounting for approximately 90% of the rosin.<sup>[17,22,42,43]</sup>

Table 4 lists the  $\Delta_f H^\circ$  for the seven principle acids found in rosin (see Figure 17<sup>[42,44]</sup>), the corresponding composition for three species of pine, and their resulting  $\Delta_f H^\circ$ . An average of the three yields a formula of C<sub>20</sub>H<sub>29.84</sub>O<sub>2</sub> and a  $\Delta_f H^\circ$  of -638.8 kJ/mole<sup>B</sup>. The formula is not exactly C<sub>20</sub>H<sub>30</sub>O<sub>2</sub> due to the dehydroabietic acid having a formula of C<sub>20</sub>H<sub>28</sub>O<sub>2</sub>. In C<sub>6</sub> units this becomes C<sub>6</sub>H<sub>8.952</sub>O<sub>0.6</sub>, and  $\Delta_f H^\circ$  is -191.6 kJ/mole<sup>B</sup>. Reference 2 lists an ultimate analysis that converts to a formula of C<sub>20</sub>H<sub>27.72</sub>O<sub>3.04</sub> but unfortunately lists no corresponding  $\Delta_f H^\circ$  value.

Rosin is used in fireworks,<sup>[40]</sup> paper sizing, adhesives, inks, and chewing gums. Chemically modified rosin finds extensive use in modified styrene-butadiene rubber polymers.<sup>[42,43]</sup>

### Conclusion

A variety of disparate sources of data, as illustrated above, may be drawn on to gather, reduce, and estimate useful chemical formulas and formation enthalpies for fuels used in pyrotechnics until such time as exact, laboratory measured values become available. In this process of research and discovery, other potentially

useful information may be found. For example, the trace elements present in many of the fuels might cause undesirable coloration of, say, a star's color purity. This ancillary information assists the energetics chemist in making informed decisions. Hopefully the reader has a greater appreciation for the overall simplicity and variety of methods in which useful estimates may be made. The benefit one gets by estimating and using these values certainly outweighs the costs in getting them.

### Acknowledgments

The author gratefully acknowledges the technical assistance of K. Kosanke, R. Kuzma, and D. Wilson.

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**Table 5. Chemical Formulas (C<sub>6</sub>-Basis) and Formation Enthalpies of Organic Fuels.**

Fuel	CAS	Formula	$\Delta_f H^\circ$ (kJ/mole)	Ref
Hardwood		C <sub>6</sub> H <sub>8.79</sub> O <sub>3.94</sub> N <sub>0.16</sub>	-778.5 <sup>H</sup>	
Softwood		C <sub>6</sub> H <sub>8.57</sub> O <sub>3.90</sub> N <sub>0.06</sub>	-670.6 <sup>H</sup>	
Cellulose	9004-34-6	C <sub>6</sub> H <sub>10</sub> O <sub>5</sub>	-954.7 <sup>D</sup>	
Cellulose (filter paper)			-979.0 <sup>C</sup>	21
Lignin, Douglas Fir	9005-53-2	C <sub>6</sub> H <sub>6.6</sub> O <sub>1.2</sub>	-692.0 <sup>C</sup>	21
Cellulose derivatives				
Hydroxyethyl	9004-62-0	C <sub>6</sub> H <sub>10.8</sub> O <sub>4.2</sub>	-794.8 <sup>BD</sup>	
Ethyl hydroxyethyl	9004-58-4	C <sub>6</sub> H <sub>9</sub> O <sub>6</sub>	-1179.6 <sup>BD</sup>	
Sodium carboxymethyl	9004-32-4	C <sub>6</sub> H <sub>8.25</sub> Na <sub>0.75</sub> O <sub>5.25</sub>	-1173 <sup>BD</sup>	
Nitrate, DS = 2.0	9004-70-0	C <sub>6</sub> H <sub>8</sub> N <sub>2</sub> O <sub>9</sub>	-803.4 <sup>BD</sup>	
Nitrate, DS = 2.5		C <sub>6</sub> H <sub>7.5</sub> N <sub>2.5</sub> O <sub>10</sub>	-765.6 <sup>BD</sup>	
Starch	9005-84-9	C <sub>6</sub> H <sub>10</sub> O <sub>5</sub>	-948.37 <sup>D</sup>	
Starch			-955.62 <sup>C</sup>	15
Starch			-955.37 <sup>C</sup>	45
Gum arabic	9000-01-5	C <sub>6</sub> H <sub>9.778</sub> O <sub>5.037</sub>	-973.2 <sup>D</sup>	
		C <sub>6</sub> H <sub>9.778</sub> O <sub>5.037</sub> Na <sub>0.035</sub> Ca <sub>0.036</sub> K <sub>0.010</sub>	-1353.0 <sup>C,D</sup>	
Gum tragacanth	9000-65-1	C <sub>6</sub> H <sub>8.941</sub> O <sub>5.412</sub>	-1008.3 <sup>D</sup>	
Guar gum	9000-30-0	C <sub>6</sub> H <sub>10</sub> O <sub>5</sub>	-954.0 <sup>D</sup>	
		C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> N <sub>0.077</sub> P <sub>0.003</sub> Na <sub>0.002</sub> Ca <sub>0.003</sub> K <sub>0.009</sub>	-1320.1 <sup>C,D</sup>	
Rosin	8050-09-7	C <sub>6</sub> H <sub>8.952</sub> O <sub>0.6</sub>	-191.6 <sup>B</sup>	

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