Thermochemical properties of rocket fuels

Rui Xu, Hai Wang and Matthew Billingsley

May 22, 2015

Three RP-2 fuels are considered in this report. They are listed in Table 1. The composition of these fuels may be found in the Appendix.

Table 1. Fuels considered

Name	POSF#	Description	Average Formula	MW (g/mol)
R1	7688	YA2921HW10	$C_{12.0}H_{24.1}$	167.9
R2	5433	WC0721HW01	$C_{12.6}H_{25.6}$	177.0
R3	11778	CA2021HW10	$C_{12.1}H_{24.3}$	169.7

The average molecular formula is calculated from the molecular weight and hydrogen mass fraction.

The standard enthalpy of formation is determined from the lower heating value (LHV), enthalpy of evaporation (H_v) and molecular weight. Unfortunately, the latent enthalpy of evaporation is unavailable and has to be estimated based on literature data. Chickos et al.[1] determined the H_v values for several representative jet and rocket fuels. Figure 1 shows these values as a function of molecular weight of four multicomponent aviation and rocket fuels along with some representative pure hydrocarbon compounds. Clearly, H_v increases almost linearly with molecular weight for each type of hydrocarbon compounds. Aromatic compounds tend to have a larger enthalpy of evaporation than paraffins and cycloparaffins of a comparable molecular weight. The data may be correlated by

$$H_v \text{ (kJ/mol)} = 2.6 + 0.333 \text{ MW (g/mol)} + 10.9\, y_A \quad (1)$$

where y_A is the total mass fraction of the aromatic compounds.

[1] Chickos, J. S., Zhao, H. "Measurement of the vaporization enthalpy of complex mixtures by correlation-gas chromatography. The vaporization enthalpy of RP-1, JP-7, and JP-8 rocket and jet fuels at T= 298.15 K." Energy & fuels 19 (2005) 2064-2073.

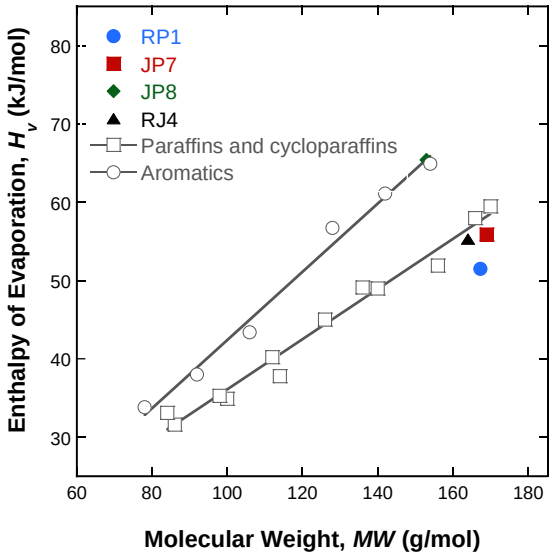

Figure 1. Enthalpy of evaporation versus molecular weight

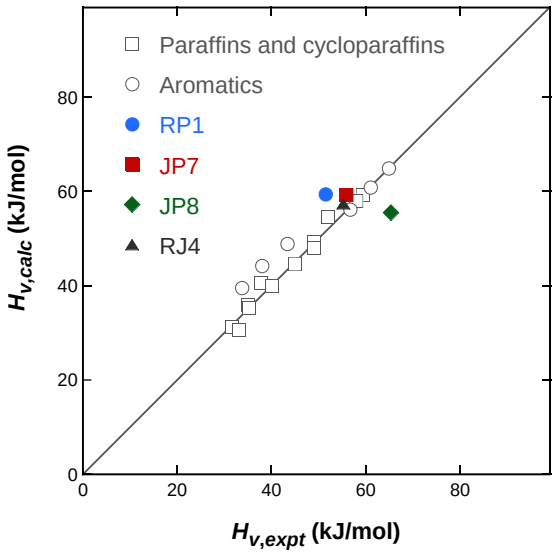

Figure 2. Calculated versus experimental enthalpy of evaporation.

Table 2 summarizes the enthalpy of evaporation estimated from the above equation for fuels listed in Table 1, along with the LHV values, approximate integer molecular formula, and the standard enthalpy of formation. As it can be seen, the H_v values are no larger than 1% of the LHV value. For this reason, the maximum error of 15% in equation (1) leads to a negligible difference in the enthalpy of combustion of vapor-phase fuels.

Table 2. Some key thermochemical properties

Fuel	POSF#	Approximate Integer Formula	Approximate Molecular Weight (g/mol)	LHV (MJ/kg)	H_v[a] (MJ/kg)	$\Delta_f H^o_{298}$ [b] (kcal/mol)	$\Delta_f H^o_{298}$/#C (kcal/mol)
R1	7688	$C_{12}H_{24}$	168.3	43.6	0.35	–54.1	–4.51
R2	5433	$C_{13}H_{27}$	183.4	43.8	0.35	–68.2	–5.25
R3	11778	$C_{12}H_{24}$	168.3	43.5	0.35	–58.1	–4.84

[a] Estimated from eq (1). [b] Derived from LHV, approximate integer formula and H_v.

The specific heat and entropy may be estimated by defining a thermochemical surrogate, as shown in Table 3. For each fuel, a neat reference compound of molecular weight similar to the mean molecular weight of a class of similar compounds (e.g., *n*-alkane) is assigned to that class. Only major compound classes are considered. Attention has been placed on matching the mean molecular weight of the thermodynamic surrogate with that of the real fuel. Table 4 lists the thermochemical property values for the reference compounds considered. The

thermochemical properties of RP-2 fuels are listed in Tables 5 through 7, and the data are presented in the form of NASA polynomials in Table 8.

Table 3. Thermochemical surrogate composition

Name	POSF#	Composition (% mole)	Average Formula
R1	7688	38.91% *iso*- dodecane ($iC_{12}H_{26}$) + 35.87% hexyl-cyclohexane ($MC_{12}H_{24}$) + 25.22% dicyclohexane ($DC_{12}H_{24}$)	$C_{12.0}H_{24.3}$
R2	5433	41.73% *iso*- dodecane ($iC_{12}H_{26}$) + 15.14% *n*-undecane ($nC_{11}H_{24}$) + 22.06% octyl-cyclohexane ($MC_{14}H_{28}$) + 21.07% methyl-dicyclohexane ($DC_{13}H_{24}$)	$C_{12.6}H_{25.8}$
R3	11778	9.25% *iso*- dodecane ($iC_{12}H_{26}$) + 25.63% *iso*-tridecane ($iC_{13}H_{28}$) + 43.30% pentyl-cyclohexane ($MC_{11}H_{22}$) + 21.83% methyl-dicyclohexane ($DC_{13}H_{24}$)	$C_{12.1}$ $H_{24.5}$

Table 4. Thermochemical data of reference species

Species	S^o_{298} (cal/mol-K)	C_p (cal/mol-K)					Reference/ comments
		300 K	500 K	1000 K	1500 K	2000 K	
n-undecane	139.8	61.8	93.1	143.4	162.8	174.7	Burcat & Ruscic[2]
iso-octane	101.1	45.3	70.0	108.7	129.1	142.0	Burcat & Ruscic[2]
iso-dodecane	138.8	67.2	103.0	159.0	185.8	202.7	Group additivity[a]
iso-tridecane	148.2	72.7	111.3	171.6	200.0	217.9	Group additivity[a]
butyl-cyclohexane	105.0	47.0	76.9	122.1	143.3	153.9	JetSurf 2.0[3]
pentyl-cyclohexane	114.4	52.5	85.2	134.6	157.5	169.1	Group additivity[b]
hexyl-cyclohexane	123.8	57.9	93.4	147.2	171.7	184.3	Group additivity[b]
octyl-cyclohexane	142.7	68.9	109.9	172.4	200.1	214.6	Group additivity[b]
dicyclohexane	94.3	48.6	85.5	138.4	166.3	178.6	Group additivity[c]
methyl-dicyclohexane	99.1	53.8	92.7	147.5	179.8	193.0	Group additivity[c]

[a] Drived from iso-octane. [b] Derived from butyl-cyclohexane. [c] Derived from cyclohexane and butyl-cyclohexane.

[2] Burcat, A., Ruscic, B. *Third millenium ideal gas and condensed phase thermochemical database for combustion with updates from active thermochemical tables*. Argonne, IL: Argonne National Laboratory, 2005.

[3] Wang, H., Dames, E., Sirjean, B., Sheen, D. A., Tangko, R., Violi, A. et al. (2010). A high temperature chemical kinetic model of n-alkane (up to n-dodecane), cyclohexane, and methyl-, ethyl-, n-propyl and n-butyl-cyclohexane oxidation, JetSurF version 2.0; September 19, 2010. URL (http://melchior.usc.edu/JetSurF/JetSurF2. 0).

Table 5. Thermochemical properties of POSF7688 (R1)

POSF7688 = 12 C(S) + 12 H2

T (K)	Cp (cal/mol-K)	S (cal/mol-k)	H(T)-H(298) (kcal/mol)	Hf (kcal/mol)	Gf (kcal/mol)
298.	58.806	122.199	0.000	-54.102	26.058
300.	59.207	122.594	0.118	-54.198	26.596
400.	78.266	142.285	7.009	-58.598	54.214
500.	95.177	161.608	15.699	-62.114	82.842
600.	109.824	180.290	25.968	-64.760	112.096
700.	122.266	198.181	37.590	-66.624	141.729
800.	132.739	215.211	50.356	-67.826	171.583
900.	141.656	231.373	64.086	-68.472	201.554
1000.	149.604	246.715	78.654	-68.619	231.569
1100.	156.069	261.282	93.944	-68.321	261.576
1200.	161.892	275.116	109.847	-67.678	291.541
1300.	167.108	288.284	126.302	-66.739	321.440
1400.	171.753	300.842	143.249	-65.550	351.257
1500.	175.865	312.835	160.635	-64.154	380.981
1600.	179.486	324.303	178.406	-62.589	410.606
1700.	182.662	335.281	196.517	-60.891	440.130
1800.	185.440	345.803	214.925	-59.090	469.550
1900.	187.870	355.895	233.593	-57.211	498.868
2000.	190.005	365.587	252.489	-55.276	528.085
2100.	191.901	374.904	271.587	-53.301	557.205
2200.	193.617	383.872	290.864	-51.297	586.230
2300.	195.213	392.514	310.306	-49.270	615.163
2400.	196.755	400.855	329.905	-47.219	644.008
2500.	198.309	408.918	349.657	-45.138	672.766

Table 6. Thermochemical properties of POSF5433 (R2)

POSF5433 = 13 C(S) + 13.5 H2

T (K)	Cp (cal/mol-K)	S (cal/mol-k)	H(T)-H(298) (kcal/mol)	Hf (kcal/mol)	Gf (kcal/mol)
298.	63.518	131.462	0.000	-68.205	23.562
300.	63.934	131.888	0.127	-68.317	24.178
400.	83.578	153.026	7.522	-73.501	55.814
500.	100.853	173.577	16.764	-77.833	88.662
600.	115.738	193.316	27.613	-81.326	122.302
700.	128.390	212.134	39.837	-84.062	156.466
800.	139.144	229.999	53.228	-86.154	190.977
900.	148.515	246.939	67.619	-87.693	225.717
1000.	157.194	263.038	82.907	-88.706	260.599
1100.	163.858	278.339	98.966	-89.251	295.559
1200.	169.856	292.858	115.657	-89.460	330.553
1300.	175.228	306.670	132.916	-89.382	365.553
1400.	180.015	319.834	150.683	-89.065	400.538
1500.	184.260	332.402	168.901	-88.552	435.493
1600.	188.008	344.416	187.518	-87.881	470.408
1700.	191.306	355.915	206.487	-87.085	505.277
1800.	194.203	366.933	225.766	-86.196	540.097
1900.	196.751	377.503	245.316	-85.237	574.865
2000.	199.004	387.654	265.106	-84.228	609.581
2100.	201.017	397.413	285.109	-83.186	644.246
2200.	202.847	406.807	305.304	-82.119	678.861
2300.	204.555	415.862	325.675	-81.034	713.426
2400.	206.201	424.602	346.213	-79.929	747.945
2500.	207.850	433.053	366.915	-78.799	782.416

Table 7. Thermochemical properties of POSF11778 (R3)

POSF11778 = 12 C(S) + 12 H2

T (K)	Cp (cal/mol-K)	S (cal/mol-k)	H(T)-H(298) (kcal/mol)	Hf (kcal/mol)	Gf (kcal/mol)
298.	58.863	121.992	0.000	-58.128	22.094
300.	59.272	122.387	0.118	-58.224	22.632
400.	78.444	142.124	7.025	-62.607	50.269
500.	95.179	161.470	15.726	-66.113	78.912
600.	109.628	180.133	25.984	-68.770	108.180
700.	121.986	197.986	37.581	-70.659	137.831
800.	132.497	214.980	50.320	-71.887	167.707
900.	141.452	231.117	64.029	-72.555	197.701
1000.	149.190	246.430	78.570	-72.729	227.744
1100.	155.823	260.966	93.826	-72.464	257.781
1200.	161.776	274.784	109.712	-71.839	287.779
1300.	167.083	287.947	126.160	-70.906	317.711
1400.	171.784	300.505	143.108	-69.717	347.561
1500.	175.921	312.501	160.498	-68.316	377.319
1600.	179.540	323.973	178.275	-66.746	406.978
1700.	182.691	334.954	196.390	-65.044	436.534
1800.	185.427	345.476	214.799	-63.241	465.987
1900.	187.806	355.566	233.464	-61.367	495.338
2000.	189.887	365.254	252.351	-59.441	524.588
2100.	191.735	374.564	271.433	-57.480	553.742
2200.	193.419	383.523	290.692	-55.494	582.801
2300.	195.009	392.156	310.114	-53.487	611.770
2400.	196.581	400.488	329.693	-51.456	640.650
2500.	198.213	408.546	349.432	-49.389	669.446

Table 8. NASA Polynomials for fuels considered.

POSF7688	S05/15C	12H	24	0	0G	298.000	3000.000	1
0.22292728E+02	0.73076651E-01	-0.20793894E-04	0.12370996E-09	0.58465103E-12				2
-0.39700348E+05	-0.92707802E+02	-0.35378470E+01	0.11644043E+00	0.18290234E-05				3
-0.76465852E-07	0.37018073E-10	-0.31231943E+05	0.47469734E+02					4
POSF5433	S05/15C	13H	27	0	0G	298.000	3000.000	1
0.23592041E+02	0.77888370E-01	-0.24078539E-04	0.12665510E-08	0.43475073E-12				2
-0.47524078E+05	-0.96981651E+02	-0.31802526E+01	0.12693286E+00	-0.12924561E-04				3
-0.69135012E-07	0.37410103E-10	-0.38786742E+05	0.47556671E+02					4
POSF11778	S05/15C	12H	24	0	0G	298.000	3000.000	1
0.20270151E+02	0.75435720E-01	-0.20840080E-04	-0.55227833E-09	0.76199160E-12				2
-0.40776820E+05	-0.81034767E+02	-0.68600278E+01	0.14183873E+00	-0.64431195E-04				3
-0.54145666E-08	0.99425390E-11	-0.32938332E+05	0.61092018E+02					4

The adiabatic flame temperature (T_{ad}) is calculated for the three fuels in air at 1 atm pressure. Figures 3-5 shows the adiabatic flame temperature plotted as a function of the equivalence ratio. Figure 6 collects all curves into one plot. Clearly, the T_{ad} values of all three fuels are similar over the entire range of equivalence ratio, and peak within 2295-2305 K.

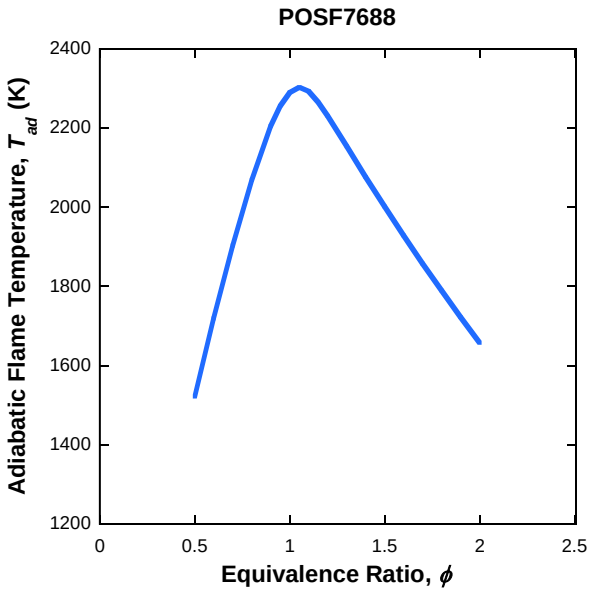

Figure 3. Adiabatic flame temperature of POSF7688 (R1) in air (p = 1 atm, T_0 = 298 K).

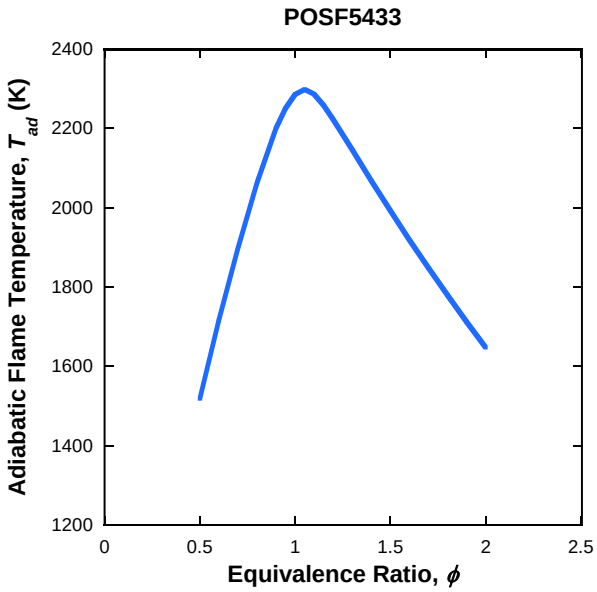

Figure 4. Adiabatic flame temperature of POSF5433 (R2) in air (p = 1 atm, T_0 = 298 K).

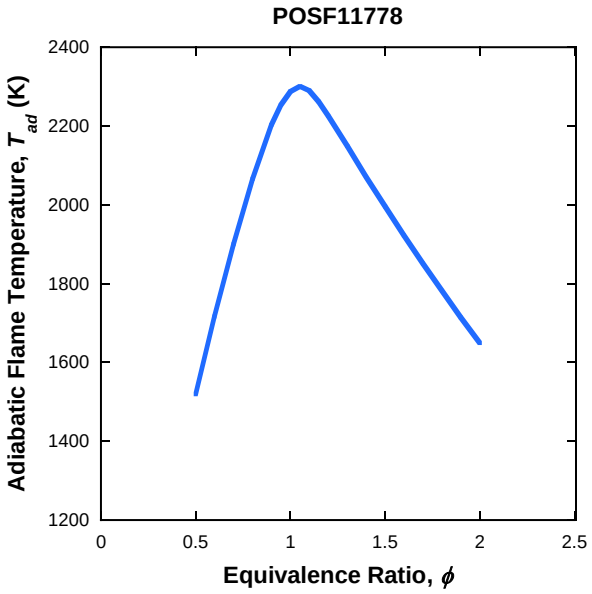

Figure 5. Adiabatic flame temperature of POSF11778 (R3) in air (p = 1 atm, T_0 = 298 K).

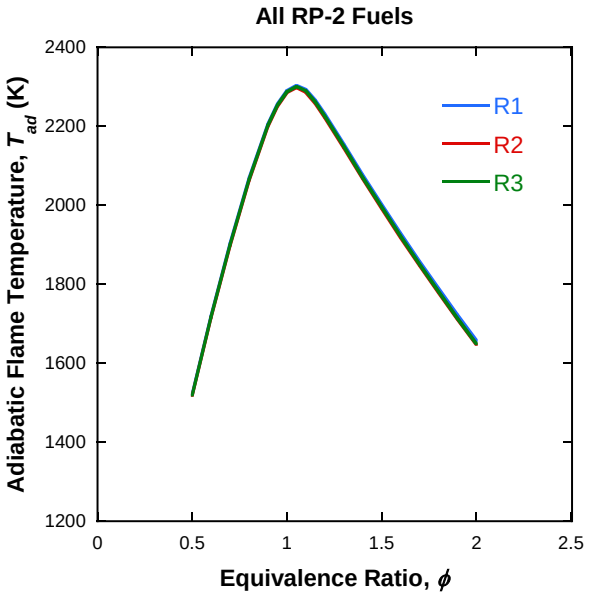

Figure 6. Comparison of adiabatic flame temperatures of selected RP-2 fuels in air (p = 1 atm, T_0 = 298 K).

Appendix

Composition pie charts of selected fuels

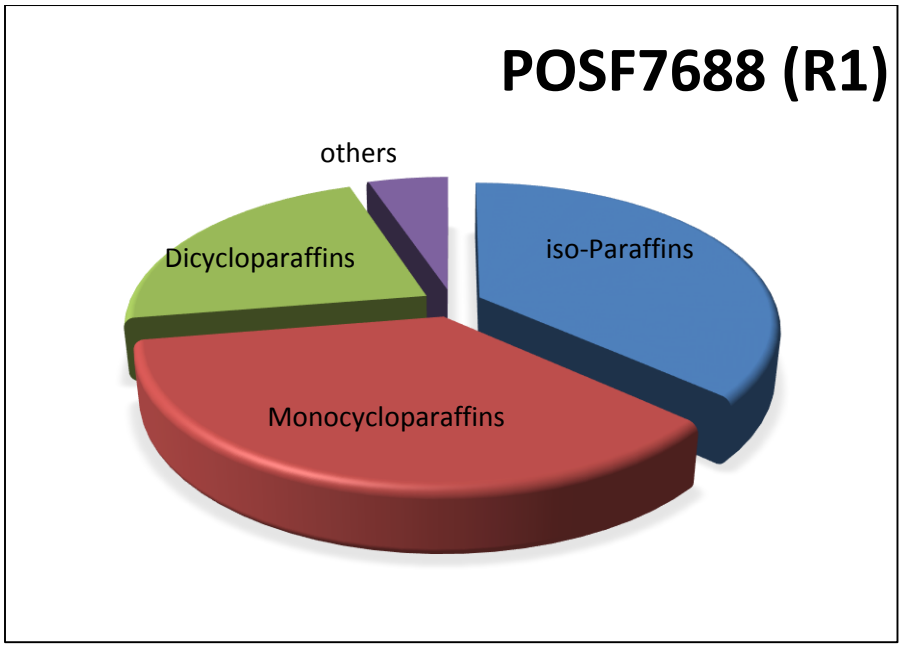

Figure A1. Composition pie chart of POSF7688 (R1)

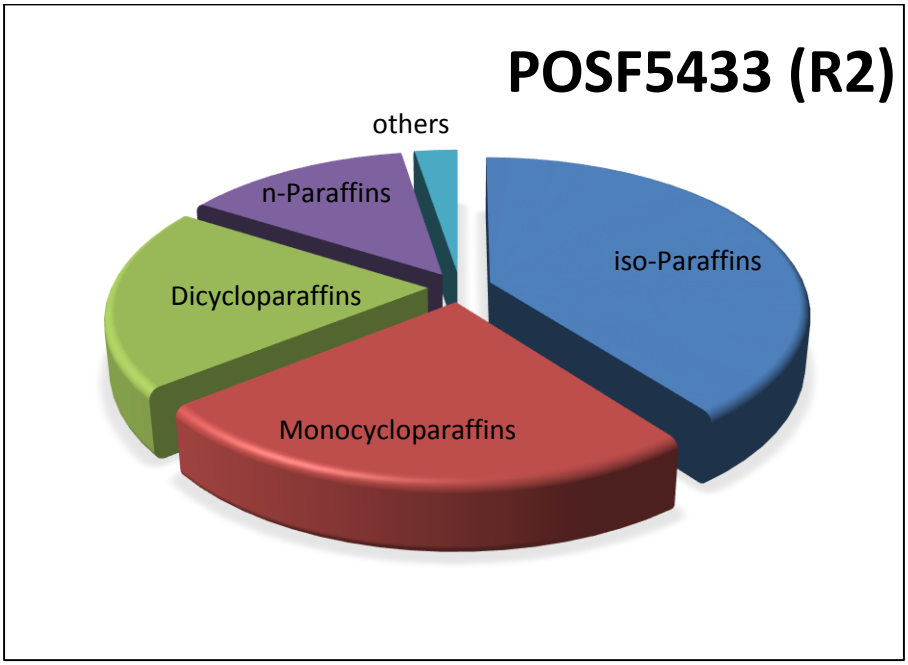

Figure A2. Composition pie chart of POSF5433 (R2)

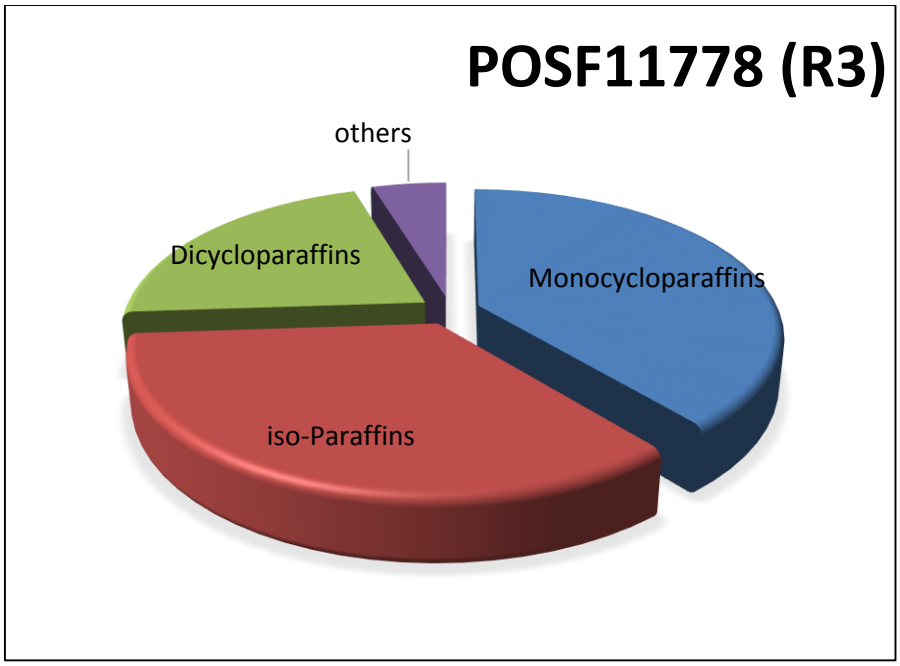

Figure A3. Composition pie chart of POSF11778 (R3)