Comprehensive thermodynamic study of alkyl-cyclohexanes as Liquid Organic Hydrogen Carriers motifs

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List of symbols

$\Delta_l^g H_m^o$	standard molar enthalpy of vaporization, kJ·mol⁻¹
$\Delta_l^g S_m^o$	standard molar entropy of vaporization, kJ·mol⁻¹
$C_{p,m}^o$	standard molar heat capacity, J·K⁻¹·mol⁻¹
$\Delta_l^g C_{p,m}^o$	differences of the molar heat capacities at constant pressure, J·K⁻¹·mol⁻¹
p_i	vapor pressure of a compound i, Pa
p_{ref}	reference vapor pressure, Pa
$\Delta_f H_m^o(g)$	standard molar enthalpy of formation in the gas phase, kJ·mol⁻¹
$\Delta_f H_m^o(liq)$	standard molar enthalpy of formation in the liquid phase, kJ·mol⁻¹
$\Delta_r H_m^o(liq)$	standard molar reaction enthalpy in the liquid phase, kJ·mol⁻¹
$\Delta_r H_m^o/H_2$	standard molar reaction enthalpy related to 1 mole H₂,released, kJ·mol⁻¹
J_x	Kovats index
T_b	normal boiling temperature, K
$\Delta_l^g H_m^o(J_x)$	enthalpy of vaporisation derived from correlation with J_x, kJ·mol⁻¹
$\Delta_l^g H_m^o(T_b)$	enthalpy of vaporisation derived from correlation with T_b, kJ·mol⁻¹

Table S1. Group-additivity values for calculation of enthalpies of vaporisation, $\Delta_l^g H_m^o$, and enthalpies of formation, $\Delta_f H_m^o(g)$, at 298.15 K (in kJ mol⁻¹).

	$\Delta_l^g H_m^o$	$\Delta_f H_m^o(g)$
CH₃-(C)	5.65 [a]	-42.05 [b]
-(cyclohexane)	29.75 [c]	-112.7 [d]
-CH₂-(cyclohexane)	34.95 [e]	-129.7 [f]
-(diMe-cyclohexane)-	31.4 [g]	-121.5 [h]

[a] From Ref. [1]; [b] From Ref. [2]; [c] Derived as the difference in enthalpy of vaporisation of methylcyclohexane and CH₃-(C). Experimental data are given in the main text.; [d] Derived as the difference in enthalpy of formation of ethyl-cyclohexane and CH₃-(C). Experimental data are given in the main text.; [e] Derived as the difference in enthalpy of vaporisation of ethyl-cyclohexane and CH₃-(C). Experimental data are given in the main text.; [f] Derived as the difference in enthalpy of formation of methyl-cyclohexane and CH₃-(C). Experimental data are given in the main text.; [g] Derived as the difference in enthalpy of vaporisation of 1,2,3-tri-methyl-cyclohexane and two CH₃-(C). Experimental data are given in the main text.; [h] Derived as the difference in enthalpy of formation of 1,2,3-tri-methyl-cyclohexane and two CH₃-(C). Experimental data are given in the main text.

Table S2. Specific "transfer" contributions, $\Delta_f H_m^o(g)(H{\rightarrow}R)$ derived from gas-phase enthalpies of formation of alkyl-substituted cyclohexanes, as well as $\Delta_l^g H_m^o(H{\rightarrow}R)$ derived from vaporization enthalpies of alkyl-substituted cyclohexanes, (at 298.15 K in kJ·mol⁻¹)[a]

R-cyclohexyl	$\Delta_f H_m^o(g)$	$\Delta_f H_m^o(g)(H{\rightarrow}R)$ [b]	$\Delta_l^g H_m^o$ [3]	$\Delta_l^g H_m^o(H{\rightarrow}R)$ [c]
methyl-	-154.7±1.0 [4]	-31.3±1.3	35.4±0.2	2.3±0.3
ethyl-	-171.7±1.6 [4]	-48.3±1.8	40.6±0.2	7.5±0.3
iso-propyl-	-194.9±2.0 [d]	-70.6±2.2	44.0±0.2	10.9±0.3
tert-butyl-	-222.6±2.0 [d]	-99.2±2.2	47.0±0.2	13.9±0.3

Table S3. Correlation of vaporisation enthalpies, $\Delta_l^g H_m^o$(298.15 K), of alkyl-cyclohexanes with their Kovats indices (J_x)

.compound	J_x [a]	$\Delta_l^g H_m^o$(exp)	$\Delta_l^g H_m^o(J_x)$ [b]	Δ [c]
		kJ·mol^{-1}	kJ·mol^{-1}	kJ·mol^{-1}
cyclohexane	690	33.1±0.2 [3]	32.6	0.5
Me-cyclohexane	739	35.4±0.2 [3]	34.9	0.5
trans-1,2-di-Me-cyclohexane	817	38.4±0.2 [3]	38.7	-0.3
cis-1,2-di-Me-cyclohexane	850	39.7±0.2 [3]	40.3	-0.6
trans-1,3-di-Me-cyclohexane	823	39.2±0.2 [3]	39.0	0.2
cis-1,3-di-Me-cyclohexane	798		37.8	
trans-1,4-di-Me-cyclohexane	796	38.0±0.2 [3]	37.7	0.3
cis-1,4-di-Me-cyclohexane	820	39.1±0.2 [3]	38.9	0.2
trans-2-Me-Et-cyclohexane	930		44.2	
cis-2-Me-Et-cyclohexane	939		44.6	
trans-3-Me-Et-cyclohexane	926		44.0	
cis-3-Me-Et-cyclohexane	909	44.7±0.9 [Table S5]	43.2	1.5
trans-4-Me-Et-cyclohexane	914		43.4	
cis-4-Me-Et-cyclohexane	930		44.2	
Et-cyclohexane	842	40.6±0.2 [3]	39.9	0.7
1,2-di-Et-cyclohexane	1040		49.5	
1,3-di-Et-cyclohexane	1017		48.4	
1,4-di-Et-cyclohexane	1060		50.5	
i-Bu-cyclohexane	1005	47.6±0.2 [3]	47.8	-0.2
n-Pr-cyclohexane	944	45.1±0.2 [3]	44.9	0.2
1,3,5-tri-Me-cyclohexane	870	43.5±1.5 [Table S5]	41.3	2.2
1,2,3-tri-Me-cyclohexane	890		42.3	
1,2,4,5-tetra-Me-cyclohexane	1036		49.3	
penta-Me-cyclohexane	1072		51.1	
hexa-Me-cyclohexane	1192		56.9	
n-Bu-cyclohexane	1061	49.4±0.2 [3]	50.6	-1.2
n-Pe-cyclohexane	1137	53.9±0.2 [3]	54.2	-0.3
n-Hex-cyclohexane	1236	59.0±0.5 [5]	59.0	0.0
n-Hep-cyclohexane	1346	63.7±0.5 [5]	64.4	-0.7
n-Oct-cyclohexane	1449	69.8±1.0 [6]	69.4	0.4
n-Dec-cyclohexane	1638	78.8±0.8 [5]	78.5	0.3
n-Dodec-cyclohexane	1822	88.9±0.8 [5]	87.5	1.4
n-tetra-Dec-cyclohexane	2079	99.4±1.0 [6]	99.9	-0.5
iPr-cyclohexane	934	44.0±0.2 [3]	44.4	-0.4
trans-3-Me-iPr-cyclohexane	1009		48.0	
cis-3-Me-iPr-cyclohexane	1037		49.4	
trans-4-Me-iPr-cyclohexane	1017	46.8±1.5 [Table S5]	48.4	-1.6
t-Bu-cyclohexane	1005	47.0±0.2 [3]	47.8	-0.8

Compound			
trans-4-Me-tBu-cyclohexane	1081		51.5	
cis-4-Me-tBu-cyclohexane	1093		52.1	
1,3-di-tBu-cyclohexane	1351	63.3±2.6 [Table S5]	64.6	-1.3

[a] Kovats indices (J_x) are on the non-polar columns [7–9].; [b] Calculated using equation: $\Delta_l^g H_m^o$(298.15 K) /(kJ·mol^{-1}) = 0.0485×J_x – 0.9 with (R^2 = 0.998). Uncertainties are estimated to account ± 1.5 kJ·mol^{-1}.; [c] Difference between column 3 and 4 in this table.

Table S4. Correlation of vaporisation enthalpies, $\Delta_l^g H_m^o$(298.15 K), of alkyl-cyclohexanes with their normal boiling temperatures (T_b)

.	T_b [a]	$\Delta_l^g H_m^o$(exp)	$\Delta_l^g H_m^o(T_b)$ [b]	Δ [c]
Compound	K	kJ·mol^{-1}	kJ·mol^{-1}	kJ·mol^{-1}
Me-cyclohexane	374.0	35.4±0.2 [3]	34.5	0.9
trans-1,2-di-Me-cyclohexane	396.7	38.4±0.2 [3]	38.8	-0.4
cis-1,2-di-Me-cyclohexane	403.0	39.7±0.2 [3]	40.1	-0.4
trans-1,3-di-Me-cyclohexane	397.6	39.2±0.2 [3]	39.0	0.2
cis-1,3-di-Me-cyclohexane	393.3		38.2	
trans-1,4-di-Me-cyclohexane	392.6	38.0±0.2 [3]	38.1	-0.1
cis-1,4-di-Me-cyclohexane	397.5	39.1±0.2 [3]	39.0	0.1
trans-2-Me-Et-cyclohexane	424.8		44.3	
cis-2-Me-Et-cyclohexane	428.1		44.9	
trans-3-Me-Et-cyclohexane	421.7		43.7	
cis-3-Me-Et-cyclohexane	420.7	44.7±0.9 [Table S5]	43.5	1.2
trans-4-Me-Et-cyclohexane	422.2		43.8	
cis-4-Me-Et-cyclohexane	425.8		44.5	
Et-cyclohexane	405.0	40.6±0.2 [3]	40.4	0.2
1,2-di-Et-cyclohexane	449.8		49.1	
1,3-di-Et-cyclohexane	445.7		48.3	
1,4-di-Et-cyclohexane	458.7		50.8	
i-Bu-cyclohexane	444.4	47.6±0.2 [3]	48.0	-0.4
n-Pr-cyclohexane	429.8	45.1±0.2 [3]	45.2	-0.1
1,3,5-tri-Me-cyclohexane	413.7	43.5±1.5 [Table S5]	42.1	1.4
1,2,4,5-tetra-Me-cyclohexane	446.2		48.4	
n-Bu-cyclohexane	454.1	49.4±0.2 [3]	49.9	-0.5
n-Pe-cyclohexane	477.0	53.9±0.2 [3]	54.3	-0.4
n-Hex-cyclohexane	497.9	59.0±0.5 [5]	58.3	0.7
n-Hep-cyclohexane	518.6	63.7±0.5 [5]	62.3	-1.4
iPr-cyclohexane	428.2	44.0±0.2 [3]	44.9	-0.9
trans-2-Me-iPr-cyclohexane	444.0		48.0	
cis-2-Me-iPr-cyclohexane	444.0		48.0	
trans-3-Me-iPr-cyclohexane	4410.		47.4	
cis-3-Me-iPr-cyclohexane	442.0		47.6	
trans-4-Me-iPr-cyclohexane	443.8	46.8±1.5 [Table S5]	47.9	-1.1
cis-4-Me-iPr-cyclohexane	445.9		48.3	
1,2-di-iPr-cyclohexane	480.0		54.9	
1,3-di-iPr-cyclohexane	480.0		54.9	
1,4-di-iPr-cyclohexane	479.8		54.9	
1,3,5-tri-iPr-cyclohexane	528.9		64.3	
1,2,4-tri-iPr-cyclohexane	528.7		64.3	

1,2,3-tri-iPr-cyclohexane	523.5		63.3	
1,2,4,5-tetra-iPr-cyclohexane	573.0		72.8	
t-Bu-cyclohexane	444.7	47.0±0.2 [3]	48.1	-1.1
2-Me-tBu-cyclohexane	457.0		50.5	
3-Me-t-Bu-cyclohexane	457.0		50.5	
trans-4-Me-tBu-cyclohexane	459.7		51.0	
cis-4-Me-tBu-cyclohexane	462.0		51.4	
3,5-dimethyl-4-tBu-cyclohexane	472.6		53.5	
1,2-di-tBu-cyclohexane	508.7		60.4	
1,3-di-tBu-cyclohexane	518.0	63.3±2.6 [Table S5]	62.2	1.1
trans-1,4-di-tBu-cyclohexane	513.0		61.3	
cis-1,4-di-tBu-cyclohexane	516.0		61.8	
3,5-di-tBu-4-Me-cyclohexane	529.6		64.5	
1,3,5-tri-tBu-cyclohexane	568.0		71.9	
dicyclohexyl-methane	526.0	64.5±3.5 [Table S5]	63.8	

[a] Normal boiling temperatures, T_b, [10,11].; [b] Calculated using equation: $\Delta_l^g H_m^o$(298.15 K) /(kJ·mol^{-1}) = 0.1927×T_b - 37.6 with (R^2 = 0.989). Uncertainties are estimated to account ± 1.5 kJ·mol^{-1}.; [c] Difference between column 3 and 4 in this table.

Table S5. Compilation of enthalpies of vaporisation $\Delta_l^g H_m^o$ for alkyl-cyclohexanes derived in this work from the data available in the literature.

Compound	M[a]	T- range	$\Delta_l^g H_m^o(T_{av})$	$\Delta_l^g H_m^o$(298.15 K)[b]	Ref.
		K	kJ·mol^{-1}	kJ·mol^{-1}	
1,3,5-tri-Me-cyclohexane	n/a	318-410	38.2±0.2	43.5±1.5	[12]
3-Me-ethyl-cyclohexane	E	348.3-367.6	40.3±0.1	44.7±0.9	[13]
4-Me-iso-propyl-cyclohexane	n/a	282-443	41.6±0.2	46.8±1.5	[12]
1,3-di-tert-butyl-cyclohexane	BP	343.2-508.9	50.2±0.2	63.3±2.6	Table S6
dicyclohexyl-methane	BP	396-525.8	49.0±1.6	64.5±3.5	Table S6

[a] Methods: n/a = not available; E = Ebulliometry; BP = derived from boiling points at different temperatures available in the literature (see Table S6).; [b] Vapor pressures available in the literature were treated using heat capacity differences from Table S9 to evaluate the enthalpy of vaporisation at 298.15 K. Uncertainty of the vaporisation enthalpy $U(\Delta_l^g H_m^o)$ is the expanded uncertainty (0.95 level of confidence).

Table S6. Vapor pressures, p_i, at different temperatures compiled from the literature [10], standard molar vaporisation enthalpies, $\Delta_l^g H_m^o$, and standard molar vaporisation entropies, $\Delta_l^g S_m^o$

$T/$	$p_i/$	$\Delta_l^g H_m^o(T)/$ [a]	$\Delta_l^g S_m^o(T)/$
K	Pa	kJ·mol^{-1}	J·K^{-1}·mol^{-1}
1,3-di-tert-butyl-cyclohexane: $\Delta_l^g H_m^o$(298.15 K) = (63.3±2.6) kJ·mol^{-1}			
$\ln(p/p_{ref}) = \frac{343.5}{R} - \frac{196108.8}{RT} - \frac{110.0}{R}\ln\frac{T}{298.15}$; p_{ref} = 1 Pa			
508.9	101325	40.1	79.0
395.2	4200	52.6	106.9
343.2	320	58.4	122.3
dicyclohexyl-methane: $\Delta_l^g H_m^o$(298.15 K) = (64.5±3.5) kJ·mol^{-1}			
$\ln(p/p_{ref}) = \frac{329.0}{R} - \frac{93339.8}{RT} - \frac{96.9}{R}\ln\frac{T}{298.15}$; p_{ref} = 1 Pa			
396.0	2400	55.0	107.8
414.0	6399	53.2	105.7
518.0	100658	43.1	83.3

518.0	97992	43.1		83.1
518.0	100658	43.1		83.3
521.0	99992	42.9		82.3
521.0	100658	42.9		82.3
521.0	97992	42.9		82.1
521.0	100658	42.9		82.3
523.0	101725	42.7		81.7
523.0	99992	42.7		81.6
525.0	101725	42.5		81.0
525.8	101325	42.4		80.7

[a] Uncertainties of the vaporisation enthalpies are expressed as the expanded uncertainty (0.95 level of confidence, k = 2). They include uncertainties from the fitting equation and uncertainties from temperature adjustment to T = 298.15 K. Uncertainties in the temperature adjustment of vaporisation enthalpies to the reference temperature T = 298.15 K are estimated to account with 20% to the total adjustment.

Table S7. Correlation of vaporisation enthalpies, $\Delta_l^g H_m^o$(298.15 K), of alkyl-cyclohexanes with the number of carbon atoms

Compound	$\Delta_l^g H_m^o$(exp)	$\Delta_l^g H_m^o$ (calc) [a]	Δ (exp-calc)	$\Delta_l^g H_m^o$ (calc) [b]	Δ (exp-calc)
Me-cyclohexane	35.4±0.2 [3]	35.8	-0.4	34.9	0.5
trans-1,2-di-Me-cyclohexane	38.4±0.2 [3]	40.5	-2.1	38.4	0.0
cis-1,2-di-Me-cyclohexane	39.7±0.2 [3]	40.5	-0.8	38.4	1.3
trans-1,3-di-Me-cyclohexane	39.2±0.2 [3]	40.5	-1.3	38.4	0.8
cis-1,3-di-Me-cyclohexane	38.0±1.1 [c]	40.5	-2.5	38.4	-0.4
trans-1,4-di-Me-cyclohexane	38.0±0.2 [3]	40.5	-2.5	38.4	-0.4
cis-1,4-di-Me-cyclohexane	39.1±0.2 [3]	40.5	-1.4	38.4	0.7
trans-2-Me-Et-cyclohexane	44.3±1.1 [c]	45.2	-0.9	43.6	0.7
cis-2-Me-Et-cyclohexane	44.8±1.1 [c]	45.2	-0.4	43.6	1.2
trans-3-Me-Et-cyclohexane	43.9±1.1 [c]	45.2	-1.3	43.6	0.3
cis-3-Me-Et-cyclohexane	44.7±0.9 [Table S5]	45.2	-0.5	43.6	1.1
trans-4-Me-Et-cyclohexane	43.6±1.1 [c]	45.2	-1.6	43.6	0.0
cis-4-Me-Et-cyclohexane	44.4±1.1 [c]	45.2	-0.8	43.6	0.8
Et-cyclohexane	40.6±0.2 [3]	40.5	0.1	40.1	0.5
1,2-di-Et-cyclohexane	49.3±1.1 [c]	49.9	-0.6	48.8	0.5
1,3-di-Et-cyclohexane	48.4±1.1 [c]	49.9	-1.5	48.8	-0.4
1,4-di-Et-cyclohexane	50.7±1.1 [c]	49.9	0.8	48.8	1.9
i-Bu-cyclohexane	47.6±0.2 [3]	49.9	-2.3	48.8	-1.2
n-Pr-cyclohexane	45.1±0.2 [3]	45.2	-0.1	45.3	-0.2
1,3,5-tri-Me-cyclohexane	43.5±1.5 [Table S5]	45.2	-1.7	41.9	1.6
n-Bu-cyclohexane	49.4±0.2 [3]	49.9	-0.5	50.6	-1.2
n-Pe-cyclohexane	53.9±0.2 [3]	54.6	-0.7	55.8	-1.9
n-Hex-cyclohexane	59.0±0.5 [5]	59.3	-0.3	61.0	-2.0
n-Oct-cyclohexane	69.8±1.0 [6]	68.7	1.1	71.5	-1.7
iPr-cyclohexane	44.0±0.2 [3]	45.2	-1.2	43.6	0.4
trans-2-Me-iPr-cyclohexane	48.0±1.5 [c]	49.9	-1.9	47.1	0.9
cis-2-Me-iPr-cyclohexane	48.0±1.5 [c]	49.9	-1.9	47.1	0.9
trans-3-Me-iPr-cyclohexane	47.7±1.1 [c]	49.9	-2.2	47.1	0.6
cis-3-Me-iPr-cyclohexane	48.5±1.1 [c]	49.9	-1.4	47.1	1.4
trans-4-Me-iPr-cyclohexane	46.8±1.5 [Table S5]	49.9	*-3.1*	47.1	-0.3

cis-4-Me-iPr-cyclohexane	48.3±1.5 [c]	49.9	-1.6	47.1	1.2
1,2-di-iPr-cyclohexane	54.9±1.5 [c]	59.3	*-4.4*	55.8	-0.9
1,3-di-iPr-cyclohexane	54.9±1.5 [c]	59.3	*-4.4*	55.8	-0.9
1,4-di-iPr-cyclohexane	54.9±1.5 [c]	59.3	*-4.4*	55.8	-0.9
1,3,5-tri-iPr-cyclohexane	64.3±1.5 [c]	73.4	*-9.1*	68.0	-3.7
t-Bu-cyclohexane	47.0±0.2 [3]	46.5	0.5	46.2	0.8
2-Me-tBu-cyclohexane	50.5±1.5 [c]	51.2	-0.7	49.7	0.8
3-Me-t-Bu-cyclohexane	50.5±1.5 [c]	51.2	-0.7	49.7	0.8
trans-4-Me-tBu-cyclohexane	51.3±1.1 [c]	51.2	0.1	49.7	1.6
cis-4-Me-tBu-cyclohexane	51.8±1.1 [c]	51.2	0.6	49.7	2.1
1,2-di-tBu-cyclohexane	60.4±1.5 [c]	61.9	-1.5	61.0	-0.6
1,3-di-tBu-cyclohexane	63.3±2.6 [Table S5]	61.9	1.4	61.0	2.3
trans-1,4-di-tBu-cyclohexane	61.3±1.5 [c]	61.9	-0.6	61.0	0.3
cis-1,4-di-tBu-cyclohexane	61.8±1.5 [c]	61.9	-0.1	61.0	0.8
1,3,5-tri-tBu-cyclohexane	71.9±1.5 [c]	77.3	*-5.4*	75.8	*-3.9*
di-cyclohexyl-methane	64.5±3.5 [Table S5]	64.0		63.7	
mean absolute deviation			1.6		1.1

[a] Calculated using equation $\Delta_l^g H_m^o(298.15\,K) = 4.69(nC - nC4) + 1.3nC4 + 3.0$ from [14].; [b] Calculated using equation $\Delta_l^g H_m^o(298.15\,K) = 5.65nC1 + 5.23nC2 + 3.08nC3 + 0.02nC4$; [c] Taken from Table 6.

Table S8. Correlation of the liquid-phase enthalpies of formation of alkyl-benzenes with the chain length (at T = 298.15 K in kJ·mol⁻¹).

alkyl-benzene	N_C [a]	$\Delta_f H_m^o(liq)_{exp}$ [4]	$\Delta_f H_m^o(liq)_{calc}$ [b]	Δ [c]
n-propyl-benzene	3	-38.3±0.8	-37.9	-0.4
n-butyl-benzene	4	-63.2±1.1	-63.6	0.4
n-pentyl-benzene	5	-89.5±4.2	-89.4	-0.1
n-hexyl-benzene	6		-115.2	
n-heptyl-benzene	7		-140.9	
n-octyl-benzene	8		-166.7	
n-decyl-benzene	10	-218.3±2.3	-218.2	-0.1
n-dodecyl-benzene	12		-269.7	

[a] Number of C-atoms in the alkyl chain.; [b] Calculated using equation: $\Delta_f H_m^o(liq, 298.15\,K) /(kJ·mol^{-1})$ = -25.76×N_C + 39.4 with (R^2 = 0.9999) derived from data in this table. Uncertainties are estimated to account ± 1.5 kJ·mol⁻¹.; [c] Difference between column 3 and 4 in this table.
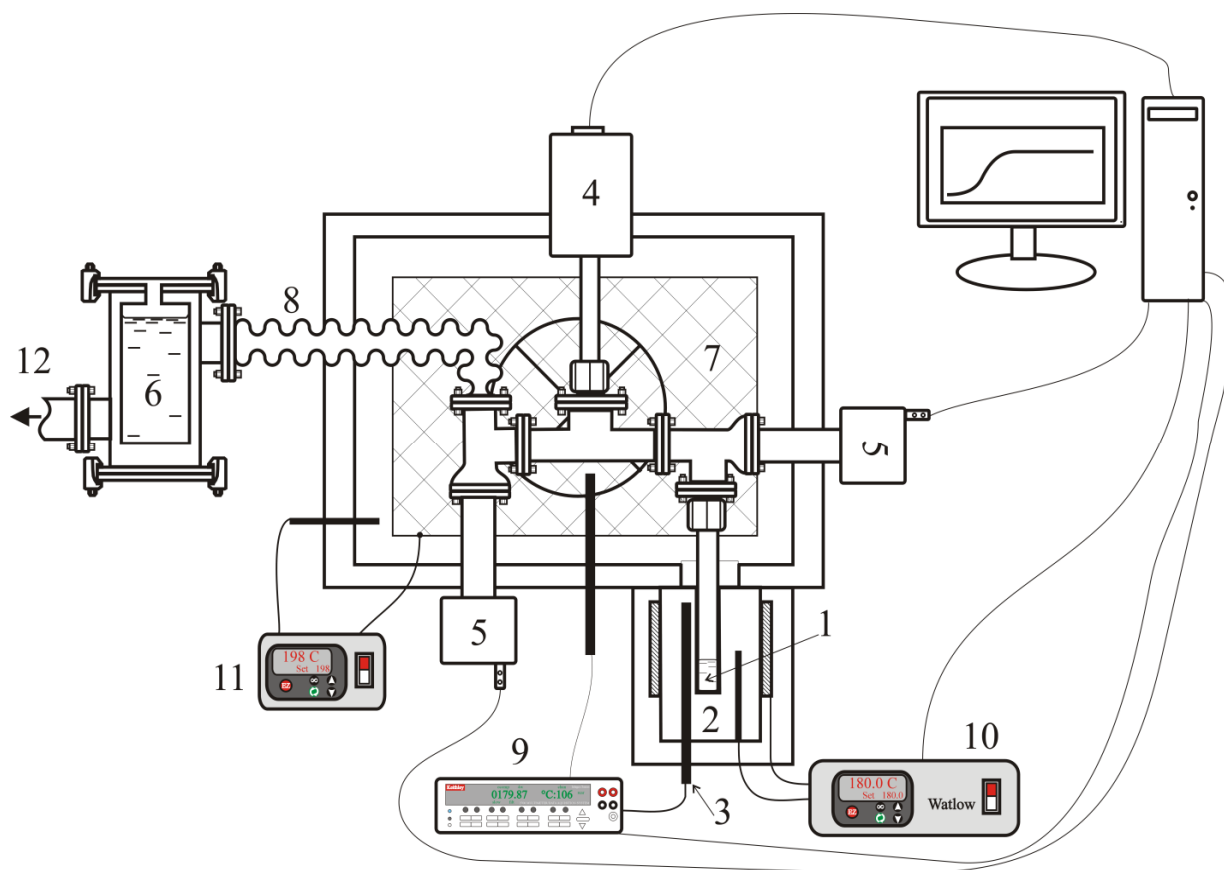
Table S9. Compilation of data on molar heat capacities $C_{p,m}^o(liq)$ and heat capacity differences $\Delta_l^g C_{p,m}^o$ at T = 298.15 K (in J·K⁻¹·mol⁻¹)

Compounds	$C_{p,m}^o(liq)$ [a]	$-\Delta_l^g C_{p,m}^o$ [b]
1,3,5-tri-Me-cyclohexane	244.2	74.1
3-Me-ethyl-cyclohexane	246.5	74.7
4-Me-iso-propyl-cyclohexane	271.9	81.3
1,3-di-tert-butyl-cyclohexane	382.2	110.0
dicyclohexyl-methane	332.1	96.9
cyclohexane	156.9 [15]	51.4
perhydro-dibenzyltoluene (Marlotherm SH®)	450.0 [16]	127.6
methyl oleate [c]	585.4 [17]	108.5 [17]

Static method

The scheme of the experimental devise is shown in Fig. S1.

1- cell with the sample

2- aluminum thermostating block

3- class A4 wire Pt100

4- pressure gauge MKS Baratron

5- all-metal angle valves VAT series 571

6- liquid nitrogen cold trap

7- forced air convection oven

8- bellows connection to the vacuum system

9- Keithley 2100 DMM

10- Watlow PM6C1CA temperature controller

11- rough temperature controller for the air oven

12- HS-2 diffusion pump

Figure S1. The scheme of the static device for vapor pressure measurements of the low volatile compounds.

Validation of the static device [20]

We measured the vapor pressure of the reference materials benzoic acid and naphthalene in order to check the reliability and uncertainty of the experimental apparatus and the data treatment procedure.

Benzoic acid has been recommended as a suitable reference compound for low vapor pressure measurements in the range (0.1 to 10) Pa over the solid sample [21,22]. In this work vapor pressures of benzoic acid were determined over the temperature range

(298 to 339) K and corresponding vapor pressures (0.1 to 8.8) Pa. We avoided the investigation of benzoic acid at higher temperatures because of a possible corrosive reaction of the gaseous benzoic acid with the material of the vacuum system and the pressure gauges.

Naphthalene is also used as a reference compound for testing devices in the vapor pressure range below 1000 Pa [21,23]. Vapor pressures (10 to 142) Pa over the crystalline naphthalene were determined in the temperature range (297 to 327) K. The extended studies of the reference compounds have revealed that our static apparatus has been able to provide reliable vapor pressures. To fit the temperature dependence of experimentally determined vapor pressures we used the well-established Clarke and Glew equation [24]:

$$R ln(p_{sat}/p^o) = -\frac{\Delta_l^g G_m^o(\theta)}{\theta} + \Delta_l^g H_m^o(\theta)\left(\frac{1}{\theta} + \frac{1}{T}\right) + \Delta_l^g C_{p,m}^o(\theta)\left(\frac{\theta}{T} - 1 + \ln\left(\frac{T}{\theta}\right)\right) \text{(S1)}.$$

In Eq. S1 p_{sat} is the vapor pressure of the samples, Pa; $p^o = 10^5$ Pa is the standard pressure; θ is the reference temperature, K; $\Delta_l^g G_m^o(\theta)$ is the change of the Gibbs energy during vaporisation (sublimation) of the sample at reference temperature, J·mol^{-1}; $\Delta_l^g H_m^o(\theta)$ is the enthalpy change during vaporisation (sublimation) of the sample at the reference temperature θ, J·mol^{-1}; $\Delta_l^g C_{p,m}^o(\theta)$ is the heat capacity difference between gaseous and condensed phases, J·K^{-1}·mol^{-1}; T is the temperature of the experimental data, K.

Available vapor pressures of benzoic acid were collected and discussed by Sabbah *et al.* [21] and also very recently by Ribeiro da Silva *et al.* [25].The data by Malaspina *et al.* [26], as well as by Davies and Jones [27] were excluded from approximation due to high systematic deviation (> 10 %) from the most reliable experimental data. Our experimental vapor pressures of benzoic acid agree well (within 3 %) with the reliable literature data. Such a good agreement of our experimental data is an evidence of the high reliability of our new apparatus for vapor pressure measurements in the range (0.1 to 10) Pa. Experimental enthalpies of sublimation for benzoic acid were also recently reviewed [21,25]. Sabbah *et al.* [21] recommended the enthalpy of sublimation $\Delta_{cr}^g H_m^o$ (298.15 K) = (89.7 ± 1.0) kJ·mol^{-1}. Later, the average value $\Delta_{cr}^g H_m^o$(298.15 K) = (90.2 ± 1.9) kJ·mol^{-1}, was re-evaluated by Ribeiro da Silva *et al.* [28] from the data published in 22 original papers. In this work, the value $\Delta_{cr}^g H_m^o$ (298.15 K) = (89.8 ± 0.1) kJ·mol^{-1} was derived from the vapor pressure temperature dependence and this value is in excellent agreement with both recommendations.

Naphthalene is one of the most often studied reference compounds in the literature [29,30]. This compound is easy to get in a very pure quality and it has relatively high vapor pressure ~ 10 Pa at 298.15 K. Just recently, Růžička *et al.* [31] compiled and recommended a set of vapor pressures, used in this work for comparison. Our experimental pressures agree with the recommended values within 2 %. The sublimation enthalpy $\Delta_{cr}^g H_m^o$(298.15 K) = (72.70 ± 0.1) kJ·mol^{-1} derived with this device is in excellent agreement with those recommended by Růžička *et al.*[31], $\Delta_{cr}^g H_m^o$(298.15 K) = 72.44 kJ·mol^{-1}, and with the direct calorimetric value $\Delta_{cr}^g H_m^o$(298.15 K) = (72.6 ± 0.6) kJ·mol^{-1} selected by the International Confederation for Thermal Analysis and Calorimetry (ICTAC)[21].

Table S10. The results of the absolute vapor pressure determination for biodiesel samples, measured using the static method.[a.]

$T/$ K[b]	$p_i/$ Pa	$u(p_i)/$ Pa[c]	$\Delta_l^g H_m^o(T)/$ [d] kJ·mol^{-1}	$\Delta_l^g S_m^o(T)/$ J·K^{-1}·mol^{-1}
(Raps-Methyl-Ester) *RME*: $\Delta_l^g H_m^o$(298.15 K) = (99.8±3.5) kJ·mol^{-1}				
$\ln(p/p_{ref}) = \frac{391.0}{R} - \frac{132177.7}{RT} - \frac{108.5}{R}\ln\frac{T}{298.15}$; p_{ref} = 1 Pa				
412.8	79.8	2.45	87.4	152.4
417.8	107.3	2.49	86.8	151.0
422.7	139.3	-0.62	86.3	149.5
427.7	180.1	-6.19	85.8	148.0

432.6	235.2	-9.40	85.2	146.7
437.6	308.0	-12.40	84.7	145.5
442.5	406.3	-7.98	84.2	144.4
447.5	580.0	45.51	83.6	144.1

(Soy-Methyl-Ester) *SME*: $\Delta_l^g H_m^o$(298.15 K) = (85.1±4.3) kJ·mol^{-1}

$$\ln(p/p_{ref}) = \frac{357.7}{R} - \frac{117471.9}{RT} - \frac{108.5}{R}\ln\frac{T}{298.15} \; ; p_{ref} = 1 \text{ Pa}$$

404.1	62.0	1.93	73.63	120.8
409.0	79.0	0.97	73.10	119.3
413.9	96.7	-3.85	72.56	117.6
418.8	122.7	-5.87	72.03	116.3
423.6	167.0	4.61	71.51	115.6
428.6	200.9	-4.71	70.97	113.9
423.7	163.5	0.33	71.50	115.4
428.6	205.8	0.19	70.97	114.1
433.5	266.2	8.90	70.44	113.2

biodiesel reference sample JRC: $\Delta_l^g H_m^o$(298.15 K) = (71.4±3.0) kJ·mol^{-1}

$$\ln(p/p_{ref}) = \frac{327.4}{R} - \frac{103702.2}{RT} - \frac{108.5}{R}\ln\frac{T}{298.15} \; ; p_{ref} = 1 \text{ Pa}$$

403.2	92.3	1.92	59.96	90.6
408.2	111.3	-0.83	59.42	89.0
413.1	136.2	-2.15	58.88	87.7
418.1	167.9	-1.62	58.34	86.4
423.1	206.0	-0.44	57.80	85.2
428.1	250.7	1.01	57.26	84.0
433.0	302.9	2.95	56.72	82.8

[a] Reference samples from Joint Research Center of Institute for Reference Materials and Measurements (https://www.conffidence.eu/) measured for the EU Project "Metrology of biofuels" ENG-09 REG01 project.; [b] Saturation temperature measured with the standard uncertainty ($u(T)$ = 0.01 K).; [c] Standard uncertainties were calculated with $u(p/\text{Pa}) = 0.025 + 0.025(p/\text{Pa})$.; [d] Uncertainty of the vaporisation enthalpy $U(\Delta_l^g H_m^o)$ is the expanded uncertainty (0.95 level of confidence). Uncertainties include uncertainties from the fitting equation and uncertainties from adjustment of vaporisation enthalpies to the reference temperature T = 298.15 K. Uncertainties in the temperature adjustment of vaporisation enthalpies to the reference temperature T= 298.15 K are estimated to account with 20% to the total adjustment.

The experimental vapor pressures p_i measured in this work were fitted with the following equation [32]:

$$R \times \ln(p_i / p_{ref}) = a + \frac{b}{T} + \Delta_\text{l}^\text{g} C_\text{p,m}^\text{o} \times ln\left(\frac{T}{T_0}\right) \text{(S2)},$$

where $R = 8.31446$ J·K^{-1}·mol^{-1} is the molar gas constant, the reference pressure $p_{ref} = 1$ Pa, a and b are adjustable parameters, the arbitrary temperature T_0 applied in Eq. (S2) was chosen to be $T_0 = 298.15$ K and $\Delta_\text{l}^\text{g} C_\text{p,m}^\text{o}$ is the difference of the molar heat capacities of the gas and the liquid phases respectively (see Table S9). Experimental vapor pressures measured in this work, have been used to obtain the enthalpies of vaporisation using the following equation:

$$\Delta_\text{l}^\text{g} H_m^\text{o}(T) = -b + \Delta_\text{l}^\text{g} C_{p,m}^\text{o} \times T \qquad \text{(S3)}$$

Experimental vapor pressures temperature dependences were also used to derive the vaporisation entropies at temperatures T by using the following equation:

$$\Delta_\text{l}^\text{g} S_m^\text{o}(T) = \Delta_\text{l}^\text{g} H_m^\text{o}/T + R \times \ln(p_i/p^\text{o}) \qquad \text{(S4)}$$

with $p^\text{o} = 0.1$ MPa. Coefficients a and b of Eq. (S2), $\Delta_\text{l}^\text{g} H_m^\text{o}(T)$ and $\Delta_\text{l}^\text{g} S_m^\text{o}(T)$ values are given in Table S10. The combined uncertainties of the vaporization enthalpies include uncertainties from the fitting equation and uncertainties from adjustment of vaporisation enthalpies to the reference temperature $T=298.15$ K.

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