

## **MEASUREMENT AND CALCULATION OF HEAT CAPACITY OF HEAVY DISTILLATION CUTS UNDER PRESSURE UP TO 40 MPa**

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### **Abstract**

Isobaric heat capacities of natural mixtures were determined up to 40 MPa with a modified C-80 Setaram calorimeter equipped with cells designed for high pressures. The systems investigated were heavy distillation cuts with respective boiling points of 150, 200, 250 and 300°C. These experimental data were used as discriminatory values to test thermodynamic models and more precisely to choose among the great number of equations of state and mixing rules proposed in the literature, the most appropriate for the characterization of the heavy components.

**Keywords:** equations of state, heat capacity, heavy component, hydrocarbon, mixture, pressure

### **Introduction**

In a number of deep oil reservoirs, petroleum fluids are stored under high-pressure and high-temperature. In these conditions, the heavy fraction  $C_{11}^+$ , which includes all the substances with 11 or more carbon atoms, may become significant. The behaviour of such fluid in reservoir is then strongly influenced by the heavy fraction. In order to identify the influence of heavy cuts on the behaviour of crude oils, experimental data of distillation cuts with high boiling points are required. The properties often studied for this purpose are vapour pressures and densities. However, calorimetric data are also useful throughout the conditions of exploitation from bottomhole to separator where crude oil is subjected to thermal gradients or thermodiffusion phenomena.

For this reason, measurements of heat capacity were carried out on four narrow distillation cuts, which stem from the distillation of a same crude oil, with respective boiling points around 150, 200, 250 and 300°C. Measurements were performed at pressures from 0.1 to 40 MPa within the temperature range from 293.15 to 373.15 K by means of a C80 Setaram calorimeter with cells specially designed for high-pressures.

The heat capacity data acquired on these heavy cuts, complemented with density measurements made at the same conditions of temperature and pressure with an Anton Paar DMA 60 densimeter equipped with a high pressure cell DMA 512P, were

used to test the capability of various equations of state, often used in petroleum engineering, to predict calorimetric properties of these kind of liquid mixtures under pressure.

## Experimental technique

The experimental apparatus which has been described in detail in a previous publication [1] consists mainly of a Setaram C-80 Calvet type calorimeter in which the standard cells were replaced by 40 MPa pressure resistant cells. These are made up of a cylindrical hastelloy chamber on top of which a capillary tube, itself containing a second coaxial tube, is accommodated in order to allow the filling of the cells. Measurements of the heat capacity of the liquid volume contained in the cell were carried out along linear temperature steps of 10 K increments at fixed pressures. The temperature and pressure dependence of the volume of the cell, which is needed to convert the measurements by mass unit was determined by calibration using hexane [2] as a reference fluid. The pressure was regulated by means of a buffer volume of gas (fifty times higher than to the cell inner volume) which was monitored by a Sefram recorder. The pressure was measured by an HBM P3M gauge which was frequently checked *vs.* a dead mass tester (Bundenberg Brand) to an accuracy of better than 0.2%. Different tests performed with *n*-decane have shown that the accuracy of the heat capacity [3, 4] measurements is about 0.2% over the whole experimental *P-T* conditions.

The densities required to express the heat capacity by mass unit were measured under pressure in an Anton Paar DMA 60 densimeter equipped with a high pressure cell DMA 512P. The method consists in determining the period of oscillation of a U-shaped tube containing the fluid. The density of the liquid is related to the square of the measured period by a linear function with two constants which are obtained by the calibration method developed by Lagourette *et al.* [5] using water as reference liquid with the density data of Kell and Walley [6].

## Results and discussion

The four systems studied were obtained by the separation of the same crude oil into narrow cuts by distillation. The compositions of each cut were analysed by gas chromatography. Description of the composition of each cut is restricted to a succinct representation by lumping components with the same number of carbon atoms into four classes of compounds (normal paraffins, isoparaffins, naphthenes and aromatics). The lower-boiling cut studied (C150) has a boiling temperature range from 150 to 175°C. Its carbon number ranges from 8 to 11 and the molecular mass is 133.4 g mol<sup>-1</sup>. It contains (Table 1) approximately 50% of paraffins (normal and iso) 25% of naphthenes and 25% of aromatics. The second cut considered (C200) comes from a distillation plateau between 195 and 210°C. Its carbon number distribution is around C11. The other cuts involved in this study (C250 and C300) have boiling temperature range from 230 to 270°C and from 300 to 325°C, respectively. Their carbon number range from 12 to 16 for the cut C250 and from 15 to 19 for the last one.

**Table 1** Composition of the several cuts

Carbon number	Mass% of				
	total	<i>n</i> -paraffins	<i>iso</i> -paraffins	naphthenes	aromatics
C150 $M_w=133.4 \text{ g mol}^{-1}$					
5	0.01	0.01	0.00	0.00	0.00
6	0.01	0.01	0.00	0.00	0.00
7	0.04	0.01	0.00	0.01	0.02
8	2.74	0.32	0.13	0.55	1.73
9	39.69	10.47	4.85	9.87	14.50
10	52.75	12.12	25.51	9.66	5.46
11	4.77	0.23	3.02	1.52	0.00
Total	100.00	23.17	33.52	21.60	21.71
C200 $M_w=143.7 \text{ g mol}^{-1}$					
9	0.14	0.02	0.00	0.00	0.13
10	16.95	0.33	0.01	7.08	9.53
11	49.60	17.51	5.95	15.27	10.87
12	32.09	5.46	19.26	6.55	0.82
13	1.21	0.00	1.21	0.00	0.00
Total	100.00	23.32	26.43	28.90	21.35
C250 $M_w=187.6 \text{ g mol}^{-1}$					
11	2.31	0.00	2.04	0.19	0.08
12	10.55	0.52	0.06	2.05	7.92
13	33.86	7.30	4.47	8.93	13.15
14	31.37	9.48	10.84	5.61	5.45
15	17.51	5.06	9.89	2.56	0.00
16	4.40	0.15	4.24	0.00	0.00
Total	100.00	22.51	31.54	19.34	26.60
C300 $M_w=243.1 \text{ g mol}^{-1}$					
14	0.01	0.00	0.00		0.01
15	13.61	0.05	0.00		13.56
16	3.49	0.24	0.22		3.03
17	18.05	3.28	4.87		9.90
18	48.06	11.37	32.92		3.77
19	9.63	4.30	5.02		0.31
20	7.16	1.88	5.19		0.00
Total	100.00	21.11	48.23		30.57

Measurements were performed at regular temperature intervals between 293 and 373 K at fixed pressures from 0.1 to 40 MPa in steps of 5 and 10 MPa for density and heat capacity, respectively. In order to determine densities at the middle of the temperature increment used during heat capacity measurements, volumetric data were fitted with a modified Tait equation with an absolute average deviation better than  $6.89 \cdot 10^{-5}$ :

$$\rho(T,P) = \frac{\rho_o}{\left[ 1 + (A_o + A_1T + A_2T^2) \ln \frac{P + (B_o + B_1T + B_2T^2)}{P_o + (B_o + B_1T + B_2T^2)} \right]} \quad (1)$$

where

$$\rho_o = \rho_{01} + \rho_{02}T + \rho_{03}T^2 + \rho_{04}T^3 \quad (2)$$

All the coefficients are listed in Table 2. In Eqs (1) and (2)  $T$  is in K, and  $P$  is in MPa, and  $P_o=0.1$  MPa.

The heat capacity data obtained are given in Table 3 and some are plotted in Figs 1 and 2. These sets of curves show smooth nearly linear variations corresponding to positive temperature coefficients  $(\partial C_p/\partial T)_P$  and negative pressure coefficients  $(\partial C_p/\partial P)_T$  which means that in this range of pressure the higher the density is, the lower the heat capacity is. This can be observed in Fig. 3 in which heat capacity is represented as a function of density.

Measurements made on different cuts which come from separation of the same crude oil enable to plot heat capacity and density against boiling point or more easily against the molecular mass of cuts (Figs 4 and 5). These figures show a regular variation of these properties with molecular mass. Heat capacity decreases with increasing boiling point while density exhibits an inverse trends. However at the higher pressures, this behaviour tends to reverse and the curve passes through a minimum.

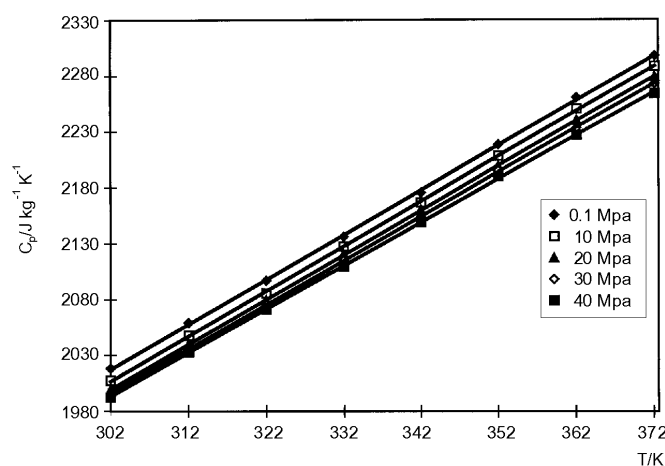
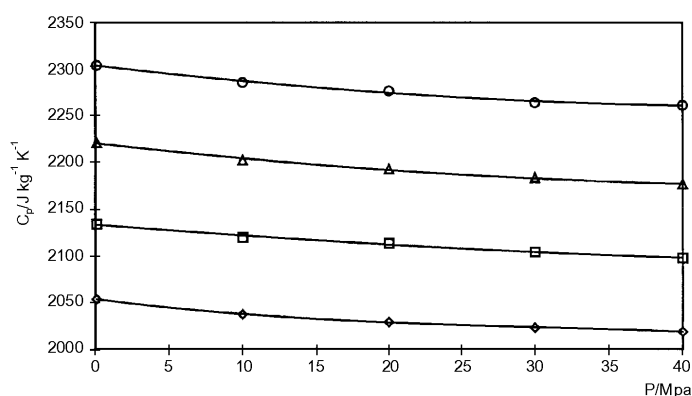


Fig. 1 C250 heat capacity ( $J kg^{-1} K^{-1}$ ) vs. temperature



**Fig. 2** C150 heat capacity ( $\text{J kg}^{-1} \text{K}^{-1}$ ) vs. pressure. ○ – 362 K, △ – 342 K, □ – 322 K, ◇ – 302 K

*PVT* equations of state are usually used in petroleum engineering to calculate thermophysical properties when pressure has to be taken into account. However, most equations of state have been developed to represent only phase equilibria and volumetric properties. The use of existing equations of state to calculate other derived properties such as heat capacity involves then extrapolation. In order to test the validity of this extrapolation in the case of heavy cuts, a comparative study has been performed between the predictive abilities of various models and the heat capacities measured in the present work. For this test three cubic equations of state were selected: the Peng-Robinson equation in its original version [7] and in the version cor-

**Table 2** TAIT equation coefficients

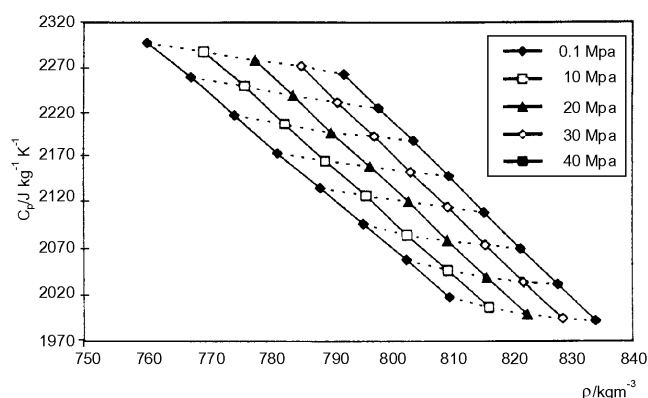
Parameters	$X_{\text{cut}}$			
	C150	C200	C250	C300
$\rho_{01}$	1.088906E+03	1.138321E+03	1.164564E+03	1.1546957E+03
$\rho_{02}$	-1.700397E+00	-1.9414723E+00	-1.977403E+00	-1.6841527E+00
$\rho_{03}$	3.065575E-03	3.722594E-03	3.845801E-03	3.0068530E-03
$\rho_{04}$	-3.4143000E-06	-3.86670E-06	-3.896E-06	-2.985800E-06
$A_0$	-1.1936725E-01	-1.7932614E-01	-1.4020725E-01	-1.1346606E-01
$A_1$	1.56010E-04	4.9859 E-04	2.7732E-04	1.4840E-04
$A_2$	-1.860E-07	-6.6600E-07	-3.480E-07	-1.760E-07
$B_0$	3.006486E+02	4.7189297E+02	4.4285120E+02	4.2709738E+02
$B_1$	-1.43957202E+00	-1.8110721E+00	-1.56609199E+00	-1.4271669E+00
$B_2$	1.37159E-03	1.86441E-03	1.477480E-03	-1.276840E-03
AAD%	1.676E-03	6.839E-03	5.67E-03	2.34E-03
MD%	2.17E-02	1.81E-02	1.65E-02	1.53E-02

AAD: absolute average deviation; MD: maximum deviation

rected by volume translation [8] and the Soave equation [9]. The non cubic modification of the Peng-Robinson equation of state proposed by Jullian *et al.* [10] was also selected. Finally, two modified Benedict-Webb-Rubin [11] equations of state were tested: the version proposed by Nishiumi and Saïto (NS) [12], in which all parameters are correlated with the acentric factor, and Lee-Kesler (LK) correlation [13] which represents an application of the corresponding states principle with two references and three parameters ( $T_c$ ,  $P_c$ ,  $\omega$ ). We have tested not only the original form [13] but also the procedures with a new series of coefficients developed by Muñoz and Ricardo [14] with *n*-methane and *n*-octane as reference substances in the first form and *n*-methane and *n*-decane in the second form.

**Table 3** Heat capacity results  $C_p$  ( $\text{J kg}^{-1} \text{K}^{-1}$ )

$T/\text{K}$	302.83	312.76	322.69	332.62	342.55	352.48	362.41	372.33
$P/\text{MPa}$	C150							
0.1	2053.40	2092.25	2134.12	2176.10	2220.40	2261.73	2303.80	
10	2037.06	2076.73	2120.38	2161.93	2201.86	2241.47	2284.96	2329.76
20	2028.94	2068.65	2113.77	2153.36	2192.41	2230.73	2275.93	2317.75
30	2023.06	2061.81	2104.41	2145.36	2183.00	2221.45	2263.13	2304.90
40	2018.90	2055.93	2098.40	2138.18	2176.61	2217.20	2260.33	2305.31
	C200							
0.1	2033.46	2077.45	2116.78	2154.17	2198.70	2245.58	2285.29	
10	2023.93	2066.30	2107.03	2145.76	2183.52	2225.11	2269.04	2312.93
20	2013.81	2056.76	2099.35	2136.28	2176.96	2214.67	2258.44	2292.85
30	2009.00	2051.50	2094.00	2130.00	2170.00	2209.50	2251.00	
40	2005.49	2047.99	2088.95	2124.64	2164.57	2205.41	2244.31	2287.82
	C250							
0.1	2018.42	2058.62	2096.71	2135.86	2175.25	2218.22	2260.33	2298.00
10	2007.70	2047.41	2085.39	2127.13	2166.61	2208.33	2250.30	2288.31
20	1999.44	2039.69	2079.01	2120.56	2160.46	2199.00	2240.27	2279.18
30	1995.00	2034.83	2074.78	2115.23	2153.59	2194.96	2233.00	2272.92
40	1992.52	2032.52	2070.74	2109.33	2149.35	2189.95	2226.46	2264.06
	C300							
0.1	1999.42	2039.44	2079.41	2119.17	2160.87	2199.88	2242.03	2285.32
10	1995.70	2034.13	2074.98	2112.53	2154.28	2195.60	2236.24	2278.70
20	1992.85	2032.26	2072.73	2108.99	2151.63	2192.26	2232.84	2274.48
30	1990.32	2030.54	2070.83	2106.88	2149.54	2190.13	2229.47	2269.20
40	1988.00	2026.00	2067.00	2104.00	2146.00	2186.00	2226.50	2266.00



**Fig. 3** C250 heat capacity ( $\text{J kg}^{-1} \text{K}^{-1}$ ) vs. density

As petroleum cuts involve many components, mixing rules were necessary for using different equations of state. Besides usual mixing (internal rules) which combines equation parameters, a number of mixing rules (external mixing rules) based on critical properties were also tested. These rules were proposed respectively by Hankinson and Thomson [15], Lee and Kesler [13], Pedersen *et al.* [16], Plocker *et al.* [17], Spencer and Danner [18], Teja [19], Joffe [20].

Equations of state enable the calculation of heat capacity by reference to the ideal gas state by the following relation:

$$C_p(P,T) = C_p^0(T) + \int_0^V T \left( \frac{\partial^2 P}{\partial T^2} \right) dV - T \frac{(\partial P / \partial T)_V^2}{(\partial P / \partial V)_T} - R$$

However, as the residual ( $C_p - C_p^0$ ), which is the part given by equations of state, represents only 25% of the heat capacity, it is worth doing a test on the residual property rather than on the heat capacity itself. For this reason experimental data were translated by subtracting ideal gas heat capacity which were calculated by group contribution [21].

The absolute average deviations obtained with various equations of state using different mixing rules are reported in Table 4. The first observation that is applicable to all equations of state and models shows the fact that the more the boiling point (or the molecular mass) is, the less accurate the prediction is.

Whatever mixing rule is used, the values are very homogeneous for all equations of state and for all cuts investigated. The Peng-Robinson and Soave equations of state are not accurate in their descriptions of the residual heat capacity, apart from the C300 (in this case, the reliable  $\Delta C_p$  evaluation seems due to an error compensation).

Calculation of the  $\Delta C_p$  implies a double differentiation of the attractive term vs. temperature, while this term was determined through the adjustment of data available on vapour pressure of pure components having smaller molecular mass.

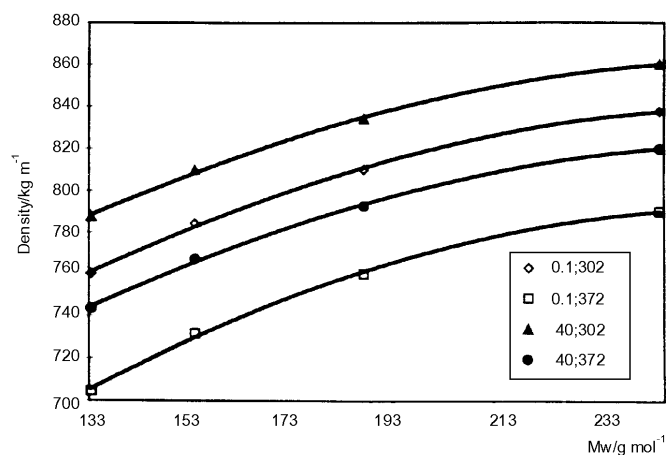


Fig. 4 Density vs. molecular mass for several ( $P$ ,  $T$ ) experimental values

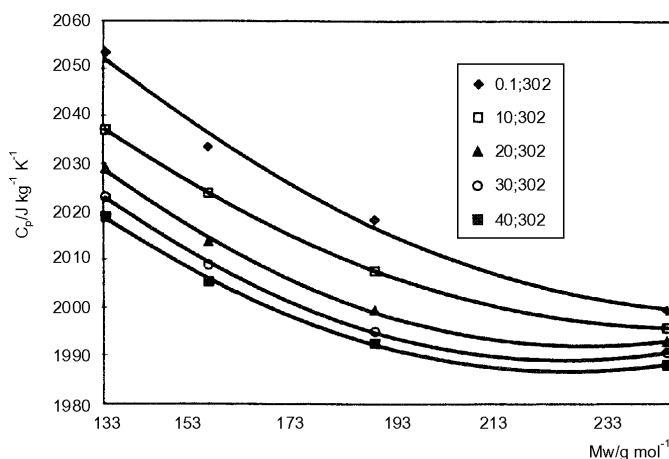


Fig. 5 Heat capacity vs. molecular mass for several ( $P$ ,  $T$ ) experimental values

Peneloux-proposed volume translation induces a noticeable improvement in the residual heat capacity restitution certainly due to a better evaluation of volume. Contrary to the other equations, the residual heat capacity is better restituted for heavy cuts by the SBRJ equation. As a matter of fact, a number of these equations' parameters were fitted on vapour pressures of components having high molecular mass, thus improving the restitution for these substances. This was already stressed by Boutrouille *et al.* [22] for normal paraffins at atmospheric pressure.

Furthermore, the analysis of Table 4 shows that the predictions of the viriel (LK, NS) derived equations of state are closer to the experimental values than the calculated values obtained with other equations. It also appears that calculated values deviate more from experimental values as the boiling temperature increases, in other words while we depart further from the reference samples (C1 and C8 in the case of



**Table 4** Absolute average deviation on the residual heat capacity (%) predicted by equations of state and mixing rules

Equation of state	Mixing rules									
	Internals	Pedersen	Spencer	Hankinson	Teja	Lee-Kesler	Plocker	Joffe		
	C150									
Soave	46.40	46.44	46.44	46.49	46.48	46.44	47.00	46.54		
Peng-Robinson	27.43	27.44	27.46	27.44	27.45	27.43	27.55	27.46		
PR-RP	21.68	21.68	21.70	21.67	21.69	21.69	21.80			
SBRJ		17.21	17.22	17.15	17.17	17.22	16.47			
Lee-Kesler 2		15.81	15.79	15.85	15.81	15.82	15.88	15.82		
Lee-Kesler 0		2.70	2.69	2.70	2.68	2.71	2.47	2.66		
Lee-Kesler 1		1.67	1.67	1.66	1.66	1.67	1.55	1.05		
Nishiumi-Sado		4.18	4.55	3.8	3.80	4.89	41.83	10.60		
	C200									
Soave	45.72	45.82	45.84	45.91	45.87	45.82	46.29	45.99		
Peng-Robinson	31.30	31.35	31.39	31.31	31.39	31.36	31.45	31.42		
PR-RP	26.40	26.50	26.53	26.47	26.54	26.51	26.61	26.56		
SBRJ		23.28	23.34	23.32	23.38	23.29	23.38	23.55		
Lee-Kesler 2		7.36	7.39	7.26	7.37	7.37	7.20	7.33		
Lee-Kesler 0		9.89	9.93	9.79	9.91	9.90	9.73	9.86		
Lee-Kesler 1		6.62	6.61	6.65	6.62	6.62	6.68	6.63		
Nishiumi-Sado		6.97	6.97	4.73	4.73	5.53	36.28	22.58		

Table 4 Continued

Equation of state	Mixing rules									
	Internals	Pedersen	Spencer	Hankinson	Teja	Lee-Kesler	Plocker	Joffe		
	C250									
Soave	41.50	42.00	41.93	41.50	42.00	41.93	42.37	42.11		
Peng-Robinson	30.01	30.07	30.10	30.05	30.06	30.07	30.24	30.16		
PR-RP	26.32	26.37	26.40	26.35	26.36	26.37	26.53	26.45		
SBRJ		11.98	11.99	11.95	11.96	11.99	11.58	11.92		
Lee-Kesler 2		10.91	10.96	10.79	10.81	10.93	10.58	10.80		
Lee-Kesler 0		13.67	13.73	13.55	13.57	13.68	13.36	13.57		
Lee-Kesler 1		7.02	7.03	6.96	6.97	7.02	6.78	6.93		
Nishiumi-Sado		27.94	19.46	9.59	9.59	30.48	28.12	8.89		
	C300									
Soave		4.70	4.70	4.70	4.80	4.70	4.70	4.70		
Peng-Robinson		4.41	4.40	4.40	4.20	4.40	4.00	4.20		
PR-RP		13.66	13.62	13.57	13.43	13.66	13.10	13.31		
SBRJ		6.94	7.01	6.84	7.13	7.01	7.07	7.10		
Lee-Kesler 2		13.10	13.18	12.89	13.21	13.20	12.81	13.04		
Lee-Kesler 0		12.90	13.06	12.52	13.11	13.11	12.38	12.79		
Lee-Kesler 1		20.05	19.99	20.15	20.12	19.97	20.56	20.25		
Nishiumi-Sado		20.50	280.50	250.32	250.32	249.32	195.5	166.25		

the Lee-Kesler 0 procedure). The set of coefficients originated by Muñoz (C1 and C8 as reference samples, noted Lee-Kesler 1) provided with results which are close to the Lee-Kesler, whereas Lee-Kesler 2 (C1 and C10 as reference samples) proposed by Muñoz also logically implies an improvement on the values of the C250 cut and, above all of the C200 cut.

Finally, the results given by the Nishiumi-Saito model are very satisfactory for the C150 and C200 cuts but give totally irrelevant values for the C300. The main feature of our study is well illustrated with this model: our results show that the Nishiumi-Saito equation of state fails to calculate the residual heat capacity in the case of high molecular mass. However, the excellent results obtained for the C150 and C200 cuts show that adjustment of the equations of state parameters on heavy components data will certainly enable to obtain reliable values.

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