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Vapor Pressures and Saturated Liquid Densities of Catalytic Cracking Petroleum Products

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Vapor pressures and saturated liquid densities for four low-boiling fractions from a fluid catalytic cracking (FCC) process have been measured in a range of temperatures from the normal boiling point up to 593 K using an apparatus with a constant-volume *PVT* cell. The new experimental data add to the existing information on thermophysical properties of petroleum products at saturation conditions. Equations for the prediction of vapor pressures at saturation and liquid saturated densities both for straight-run and deep-refining petroleum products are reported.

Introduction

Methods for calculating vapor pressures and orthobaric densities of individual hydrocarbons are rather well developed.[1,2] However, valid predictive procedures for undefined-composition hydrocarbon mixtures and especially petroleum fractions are limited. This is explained by the limited character or full absence of experimental data on these properties at the saturation curve, especially for deep petroleum refining products. Therefore, an experimental investigation of vapor pressures at saturation (P_s) and liquid saturated densities (ρ_s) for fractions of the fluid catalytic cracking (FCC) process has been undertaken at temperatures above the normal boiling point.

Experimental Section

Apparatus and Procedure. A saturation curve was determined as a curve corresponding to points of experimental isotherm breaks for the transition from a liquid-phase to a two-phase region. Experimental $P-\rho-T$ measurements were carried out by means of a constant-volume *PVT* cell apparatus over the range of temperature from 293 K to 593 K and pressures up to 30 MPa both in the liquid phase and in the liquid−vapor two-phase region. A stainless steel cylindrical piezometer was equipped with an electromagnetic mixer located inside the measuring *PVT* cell for the purpose of rapid establishment of thermodynamic equilibrium during the measurements in the two-phase region. An extraction of liquid during the process of measurements on isotherms was carried out from a part on the bottom of the cell to prevent wasting the light components of the petroleum fraction that would cause a corresponding change in sample composition during the measurements. The correctness of this approach was confirmed by a special experiment on the sample composition made by chromatography as described by Shevchenko and Kharchenko.[3]

Temperature T was measured with a platinum resistance thermometer with an uncertainty of $\sigma(T) = 0.05$ K at pressure P by a dead-weight piston pressure gauge with an uncertainty of $\sigma(P) = 0.003$ MPa. The mass of extracted liquid was measured with an analytical balance with an accuracy of ±0.0001 g. The average uncertainty in the experimental density data in the liquid and two-phase

Table 1. Physicochemical Properties of Some FCC Petroleum Products

substance	$\rho_{277}{}^{293}$	$n_D{}^{293}$	MW	MVBP/K[a]
FR 353−383 K CC	0.7492	1.4189	90.5	368.55
FR 383−413 K CC	0.7906	1.4418	109.7	399.55
FR 413−443 K CC	0.8243	1.4613	123.0	432.15
FR 443−473 K CC	0.8475	1.4751	139.0	453.15

[a] Mid-volume boiling point.

Table 2. Cinematic Viscosity of Petroleum Products at 20 °C

petroleum product	ν_{20}/cSt
FR 353−383 K of catalytical cracking	0.542
FR 383−413 K of catalytical cracking	0.741
FR 413−443 K of catalytical cracking	0.893
FR 443−473 K of catalytical cracking	1.053
FR 323−343 K of Malgobec oil	0.600
FR 383−393 K of Malgobec oil	0.750
FR 378−413 K of Mangishlac oil	0.793
Grozny gas condensate	0.559
FR 453−513 K of Mangyshlac oil	1.960
FR 335−413 K of Samotlor oil	0.720
FR 413−453 K of Mangyshlac oil	1.140
FR 335−413 K of Mangyshlac oil	0.741
FR 393−403 K of Malgobec oil	0.920
FR 433−443 K of Malgobec oil	1.230

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Table 3. Experimental Values of the Saturated Liquid Density versus Saturation Pressure and Temperature

petroleum product	T/K	P_s/bar	ρ_{sat}/kg·m^{-3}	T/K	P_s/bar	ρ_{sat}/kg·m^{-3}	literature source
FR 383−413 K of catalytic cracking	445.15	2.62	646.8	522.66	10.33	541.7	this study
	481.52	5.18	602.8	540.46	13.62	511.7	
	504.96	7.8	571.1	558.25	17.95	458.3	
FR 413−443 K of catalytic cracking	443.15	1.27	689.8	526.36	5.63	597.8	this study
	479.02	2.48	650	556.12	9.08	533.4	
	500.59	3.63	628.2	579.74	13.07	464	
FR 443−473 K of catalytic cracking	472.3	1.39	692	556.57	5.96	598.2	this study
	502.63	2.39	659.2	575.15	7.93	571.3	
	525.93	3.62	632.7	593.15	10.45	543.1	
FR 353−383 K of catalytic cracking	393.62	3.08	619.3	459.28	10.96	537	this study
	416.75	4.85	591.3	498.48	17.86	471	
	434.78	6.7	588.9	522.75	24.6	409.3	
FR 383−393 K of Mangyshlac oil	423.15	2.4	616.1	543.15	18.06	447	5
	453.15	4.39	584.5	553.15	20.74	421.9	
	483.15	7.43	548.5	563.15	23.63	388.8	
	513.15	11.72	506.6	568.15	25.18	363.5	
FR 378−413 K of Mangyshlac oil	388.15	0.957	663.6	553.15	19.66	445.4	5
	423.15	2.32	630.1	573.15	25.44	377.4	
	453.15	4.18	598.4	578.15	27.01	347.5	
	503.15	9.68	536.5	581.65	28.16	314.9	
FR 453−513 K of Mangyshlac oil	483.15	1.76	645.7	573.15	6.82	548.8	5
	513.15	2.72	616.4	589.15	8.93	528.8	
	543.15	4.36	582.3				
FR 323−343 of Malgobec oil	353	2.18	631	473	19.75	464.6	9
	413	7.37	561.8				
FR 393−403 K of Malgobec oil	413	1.91	643.2	473	5.88	578.2	9
FR 335−413 K of Mangyshlac oil	353	1.38	679.9	473	9.37	551.1	6
	413	3.4	621.9				
FR 335−413 K of Samotlor oil	473	9.48	548.5				8
Grozny gas condensate	353	1.79	636.6	443	11.85	535.5	9
	383	3.71	607.7	473	18.96	485.2	
	413	6.92	575.2	503	28.67	420.5	

regions is estimated to be 0.05%, and at saturation conditions, it is 0.1%. A detailed description of the apparatus and experimental procedure used for vapor pressure and liquid saturated density investigations is given by Shevchenko and Kharchenko.[3]

Materials. Four light-boiling fractions from the FCC process, each with an individual boiling range of 30 K, were selected as objects of investigation. The total boiling range was from (353 to 473) K. The fraction of FCC products was denoted as follows: FR 353−383 K CC (fraction of FCC process with a boiling range from (353 to 383) K). Basic physicochemical properties, such as relative density $\rho_{277}{}^{293}$, midvolume boiling point (MVBP), refractive index ($n_D{}^{293}$), and molecular weight (MW), were determined by conventional methods and presented in Table 1. For the characterization of all petroleum products used for generalization in this study, we have measured the coefficient of cinematic viscosity ν at 20 °C by capillary viscometry to within ±1.0%. The ν data are presented in Table 2. A special procedure was used to remove the dissolved air from investigated samples by freezing in liquid nitrogen and subsequent vacuum pumping. The thermal stability of the samples during the measurements was constantly monitored by means of checking the reproducibility of basic physicochemical properties.

Results and Discussion

The experimental data of the saturated liquid density at saturated pressure and temperature for fractions of catalytic cracking reported here are presented in Table 3. This Table also includes experimental data for fractions of Mangyshlac, Malgobec, and Samotlor oils and Grozny gas condensate from different investigators.[5,6,8,9]

Saturated Liquid Density. To develop a calculation scheme suitable for predicting the density of both straight-run and deep-refining petroleum products, we used data from refs 4−9. This work employed light-boiling fractions of Samotlor oil, Mangyshlac oil, West-Siberian oil, Troitsko-Anastasyevskaya oil, and Grozny gas condensate. The combined experimental data were generalized using a corresponding states principle. Because the critical density of petroleum fractions is calculated with a rather great uncertainty, it is reasonable to use the reduced density as a parameter of reduction. The value of the saturated liquid density $\rho_s^{\tau=0.7}$ at reduced temperature $\tau = 0.7$, determined

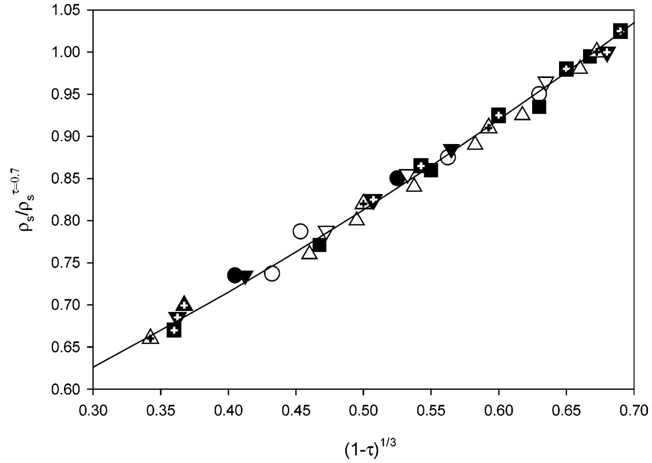

Figure 1. Reduced density $\rho_s/\rho_s^{\tau=0.7}$ as a function of the quantity $(1 - \tau)^{1/3}$, where τ is the reduced temperature: ●, FR 353−383 K FCC; ○, FR 383−413 K FCC; ■, FR 413−443 K FCC; △, FR 443−473 K FCC; ▼, FR 323−343 K Malg. Oil; ▽, FR 383−393 Malg. Oil; ▲ with +, FR 378−413 K Malg. Oil; △ with +, FR 353−453 K West-Sib. Oil; ▼ with +, FR 353−453 K Tr.-An. Oil; ■ with +, Grozny gas condensate.

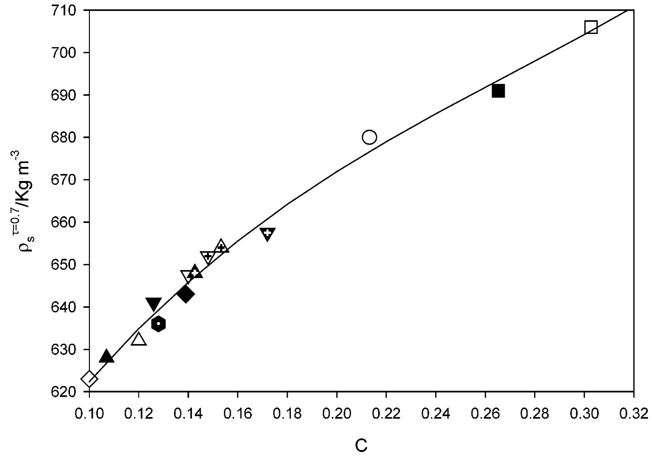

Figure 2. Density $\rho_s^{\tau=0.7}$ as a function of correlation parameter C: ⬢ with center dot, FR 353−383 K FCC; △ with +, FR 453−513 K Mang. Oil; ▼ with +, FR 353−453 K Tr.-An. Oil; ○, FR 383−413 K FCC; ■, FR 413−443 K FCC; □, FR 443−473 K FCC; ▽ with +, FR 378−413 K Mang. Oil; ▽, FR 335−413 K Samotl. Oil; ▲, FR 323−343 K Mang. Oil; △, FR 393−403 K Mang. Oil; ▼, FR 383−393 K Mang. Oil; ♦, FR 335−413 K Mang. Oil; ▲ with +, FR 413−453 K Mang. Oil; ◊, Grozny gas condensate.

from experimental data, was chosen as this parameter. Reduced temperature τ was determined from $\tau = T/T_{pc}$, where T_{pc} is the pseudocritical temperature of the petroleum product that was calculated according to an expression quoted by Riazi and Daubert.[10]

Figure 1 presents the reduced density $\rho_s/\rho_s^{\tau=0.7}$ versus the quantity $(1 - \tau)^{1/3}$.

This dependence was approximated by an equation of the form

$$\frac{\rho_S}{\rho_S^{\tau=0.7}} = \sum_{i=0}^{2} a_i (1 - \tau)^{i/3} \tag{1}$$

in which the parameters were found as follows: $a_0 = 0.409622$; $a_1 = 0.592019$; and $a_2 = 0.430023$.

It was found that saturated liquid density $\rho_s^{\tau=0.7}$ at a reduced temperature $\tau = 0.7$ is a function of the correlation parameter C. This parameter may be used for the characterization of individual petroleum products and is given by

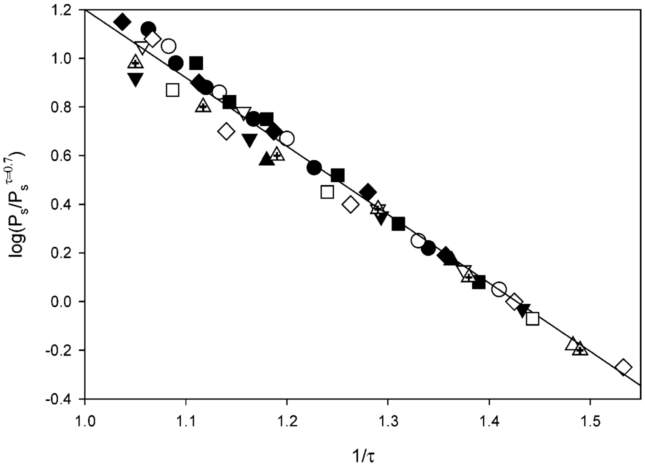

Figure 3. log($P_s/P_s^{\tau=0.7}$) plotted as a function of reciprocal reduced temperature $^1/_\tau$: ●, FR 383−413 K FCC; ○, FR 413−443 K FCC; ■, FR 443−474 K FCC; □, FR 323−343 K Malg. Oil; ▲, FR 335−413 K Mang. Oil; △, FR 413−453 K Mang. Oil; ▼, FR 353−453 K Tr.-An. Oil; ▽, FR 378−413 K Mang. Oil; ♦, FR 383−393 K Mang. Oil; ◊, FR 353−453 K West-Sib. Oil; △ with +, Grozny gas condensate.

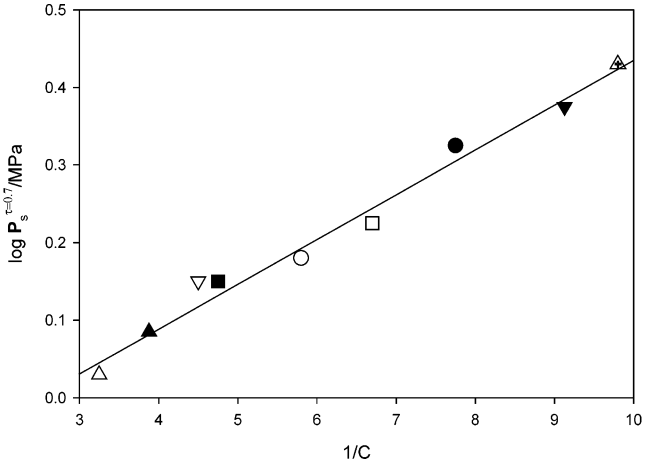

Figure 4. log $P_s^{\tau=0.7}$ as function of the reciprocal correlation parameter $^1/_C$: ●, FR 353−383 K FCC; ■, FR 383−413 K FCC; ▲, FR 413−443 K FCC; △, FR 443−473 K FCC; ▼, FR 323−343 K Malg. Oil; ▽, FR 393−433 K Malg. Oil; ○, FR 433−443 K Malg. Oil; □, FR 373−413 K Mang. Oil; △ with +, Grozny gas condensate.

$$C = \left(\frac{\rho_{293}^{pp}}{\rho_{293}^{pen}}\right) - \left(\frac{\tau_B^{pp}}{\tau_B^{pen}}\right) \tag{2}$$

The notation we use is as follows: ρ_{293}^{pp} is the liquid density of the petroleum product at $T = 293$ K and $P = 101\,325$ Pa; ρ_{293}^{pen} is the liquid density of pentane at $T = 293$ K and $P = 101\,325$ Pa; and $\tau_B^{pp} = T_B/T_{pc}$ is the reduced normal boiling point of the petroleum product. Temperature T_B corresponds to the midvolume boiling point (MVBP). Temperature τ_B^{pen} is the reduced normal boiling point of pentane.

The relationship of $\rho_s^{\tau=0.7}$ versus parameter C is plotted in Figure 2 and is expressed by eq 3.

$$\rho_s^{\tau=0.7} = \sum_{i=0}^{3} b_i C^i \tag{3}$$

where $b_0 = 576.330$, $b_1 = 354.553$, $b_2 = 1307.602$, and $b_3 = -3512.286$.

Equations 1, 2, and 3 form a predictive procedure for the calculation of the saturated liquid density. The required input information is limited to the values of reduced density $\rho_{277}{}^{293}$ and the midvolume boiling point, applicable in the range of reduced temperature (τ) of 0.6 to 0.95 for both straight-run petroleum fractions and FCC products. An average uncertainty of saturated liquid density predictions according to eqs 1, 2, and 3 is estimated to be 0.45%.

Saturated Vapor Pressure. To generalize the experimental data of the saturated vapor pressure, we used an approach similar to that described in section 4.1. In Figure 3, we plotted the generalized dependence of the reduced saturated vapor pressure $\log(P_s/P_s^{\tau=0.7})$ versus the reciprocal reduced temperature $^1/_\tau$.

The relationship between $\log(P_s/P_s^{\tau=0.7})$and $^1/_\tau$ was fitted with a linear function given by

$$\log\left(\frac{P_s}{P_s^\tau} = 0.7\right) = 4.0125 - \frac{2.8114}{\tau} \tag{4}$$

It was found that the value of the saturated vapor pressure $P_s^{\tau=0.7}$ at reduced temperature $\tau = 0.7$ is a function of the correlation parameter C (Figure 4).

Analytically, this relationship is represented by an equation of the form

$$\log P_s^{\tau=0.7} = \frac{0.057742}{C} - 0.1427 \tag{5}$$

Equations 4 and 5 together with eq 2 may be used for vapor pressure predictions on the liquid side of the saturation curve for both straight-run petroleum fractions and FCC products. The range of reduced temperatures (τ) that are suitable is 0.65 to 0.90. The average uncertainty of P_s calculations according to eqs 2, 4, and 5 was found to be 7.8%.

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