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Measurement of Vapor Pressure of a Series of Edible Oils

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The vapor pressure of a series of edible oils (soybean oil, rape seed oil, cotton-seed oil, safflower oil, rice wax and sesami oil) were measured in a temperature range of 250 °C to 330°C by using an assembly of U-tube mercury manometer and vacuum pump.

It was tried to apply the Riedel's type equation (Riedel, 1945a, b) to the measured results to obtain relationship between the vapor pressure and the temperature.

The results obtained could be summarized, as follows :

1) The vapor pressure increased with increasing temperature. Soybean oil, rape seed oil, cotton-seed oil and rice was showed sigmoid curves which had a inflection point at about 290°C. In the case of Sesami oil the curve had the constant value in a range from 280°C to 300°C. Only in safflower oil the curve showed simple exponential type.

2) Generally, vapor pressure estimates using the integral of the Clausius-Clapeyron's equation assuming constant evaporation heat. But for these sigmoid type curves it is clear that such equation could 'not express the curves. Thus the Riedel's type equation with 4 parameters was introduced, the data of each oil were fitted to the equation by the leasts squares method as follows :

$$\ln P_{vp} = A + B \cdot T^{-1} + C \cdot \ln T + D \cdot T^{6} \qquad (3)$$

The results agreed well with the experimental results and their standard deviations were in the range of 0.3026～0.9043kPa.

The latent heat of evaporation could be estimated from eq. (3).

Further, the other thermal characteristics were measured.

INTRODUCTION

To design a "fryer" which has isolated frying chamber from the surrounding atmosphere, or to make use an existing "fryer" as a isolatded frying equipment, needs to know the pressures of air, steam, and the vapor pressure of edible oil inside the fryer, separately.

The objectives of this study were to find the saturated vapor pressure characteristics of selected edible oils, and hence to develop a mathematical relationship to get these vapor pressure values by simple calculation, without measuring.

MATERIALS AND METHODS

Materials

In this study, representative samples of six edible oils (soybean oil, rape seed oil, cotton-seed oil, safflower oil, rice wax and sesami oil) were used. The chemical characteristics and the fatty acids of refined oils are shown in Table 1. The values of any properties of materials were closely allied to typical values in literature (Abe,

Table 1. Chemical characteristics and components of fatty acid for each oil Samples.

	Samples					
	Soybean oil	Rape seed oil	Cotton seed oil	Safflower oil	Rice wax	Sesami oil
Chemical characteristics (-)						
Acid value	0.06	0.04	0.06	0.05	0.08	1.88
Saponification value	189.3	186.5	191.0	190.8	185.4	190.0
Iodine value	133.0	116.9	116.1	144.2	109.9	113.3
Components of fatty acid (%)						
$C_{14:0}$ Myristic acid	0.1	0.1	0.8	0.1	0.3	
$C_{16:0}$ Palmitic acid	10.7	3.8	20.6	6.9	16.3	9.2
$C_{16:1}$ Palmitoleic..acid	0.2	0.2	0.7	0.1	0.3	0.2
$C_{18:0}$ Stearic acid	3.8	1.7	2.5	2.4	1.8	5.2
$C_{18:1}$ Oleic acid	22.6	59.5	17.6	14.3	40.0	38.0
$C_{18:2}$ Linoleic acid	53.8	21.0	55.2	73.4	37.6	45.4
$C_{18:3}$ Linoleic acid	7.3	9.8	0.4	1.2	1.8	0.7
$C_{20:0}$ Arachidic acid	0.4	0.6	0.5	0.4	0.7	0.7
$C_{20:1}$ Icosenoic acid	0.3	1.7	0.3	0.4	0.8	0.3
$C_{22:0}$ Behenic acid	0.7	0.3	0.2	0.3	0.2	0.2
$C_{22:1}$ Erucic acid		0.7				
Others	0.1	0.6	1.2	0.5	0.2	0.1
Molar mass (kg/Mol)	287.87	281.79	275.65	279.49	277.71	279.57

1988).

Desolved gasses in the oil samples were removed by a vacuum pump (Satoh industrial Co., vacuum degree is 1.33×10^{-4} kPa. Exhaustion capacity is 20 l/min) in advance of measurements, to get the saturated vapor pressure values accurately.

Methodology

Apparatus used to measure the vapor pressure of oil samples is shown in Fig. 1. This system is an assembly of U-tube mercury manometer (sensitivity is 0.5mmHg), vacuum pump, isoteniscop (Gotoh, 1965), reflux condenser, L.P. gas burner, stirrer, adjustor and recorder. Each of them were joined with rubber tubes which can stand against high vacuum, and the joined parts were sealed up by silicone grease to prevent any leaks. But only the joint between the neck of the flask which contains the sample. (A ; volume is about 25ml) and the isoteniscope (B,C ; volum is about 10ml) was joined with a ground-grass connecttion, to prevent any interferences due to the vapor pressure of silicone grease, if it is sealed with silicone grease. In this system, gas leak could not be found by an U-tube mercury manometer (inner diameter is 6.0mm).

The flask which contains the sample was heated over the gas burner, and at the same time reduced the inside pressure by the vacuum pump. Then the evaporated vapor of the sample (20 ml) were condensed in the reflux condenser and then collected in to the isoteniscope. At this time, the inside of the flask which is totally isolated from the surrounding atmosphere, was totaly filled with the saturated vapor of the oil.

Silicone grease bath was used to heat the sample (silicone can withstand up to 330 ℃). While doing the test, silicone grease was stirred to get heating uniformity. In this study, it was assumed that the temperature of silicone grease and the temperature of

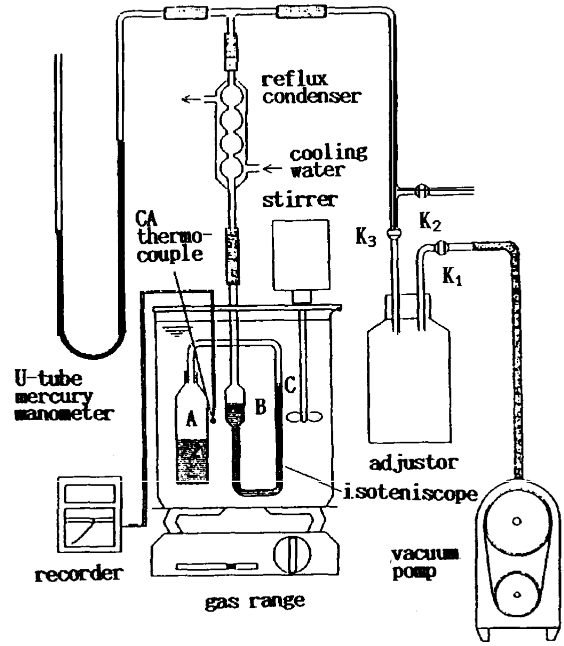

Fig. 1. Schematic diagram of experimental apparatus.

saturated vapor of silicone grease are equal. CA thermocouples (0.3mm) and recorder (Yokokawa Denki Co. Model 4156, sensitivity 0.1 c/div) were used to detect and record the temperature of silicone grease bath.

RESULTS AND DISCUSSION

Results

Figs. 2-7 show the relationship between measured saturated vapor pressure and temperature, in a temperature range of 250°C to 330°C. According to the figures the vapor pressure increases unevenly with the increasing temperature. But the value of saturated vapor pressure at each point on the graph is similar to the saturated vapor pressure of the respective fatty acid in the edible oil (ed. by Nippon Kagakukai, 1975).

Soybean oil (in Fig. 2), rape seed oil (in Fig. 3), cotton-seed oil (in Fig. 4) and rice wax (in Fig. 5) showed sigmoid curves and an inflection point of 290°C.

In the case of sesami oil the curve has constant value of saturated vapor pressure in a temperature range of 280°C to 300°C (in Fig. 6).

Only in safflower oil, the curve showed simple exponential type (in Fig. 7).

Edible oils are not pure substances but a mixture of some triglycerids. Although considering entropy, enthalpy, free energy, and volume of phase equilibrium of edible oil, its vapor pressure is estimated from the Clausius-Clapeyron's equation (1).

$$\frac{d\ln P_{vp}}{d(1/T)} = \frac{AH}{RAZ}, \qquad (1)$$

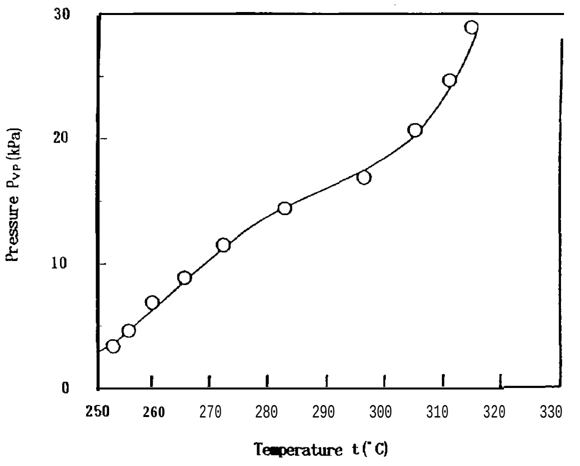

Fig. 2. Vapor pressure plotted against temperature for soybean oil.

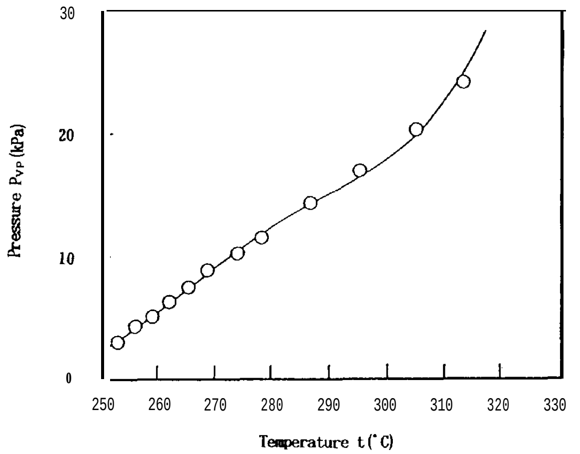

Fig. 3. Vapor pressure plotted against temperature for rape seed oil.

where as:

AH,: the latent heat of evaporation
P_{vp} : saturated vapor pressure in kPa
R : ideal gas constant (=8.31434 kJ/(K·Mol))
T : the absorbed temperature in K
ΔZ_V: compressibility factor

$$\Delta Z_V = \frac{P\Delta V}{RT} \qquad (2)$$

where A V $(=V_v - V_l)$ is the volume change per mol transferred from liquid phase to vapor phase in equilibrium.

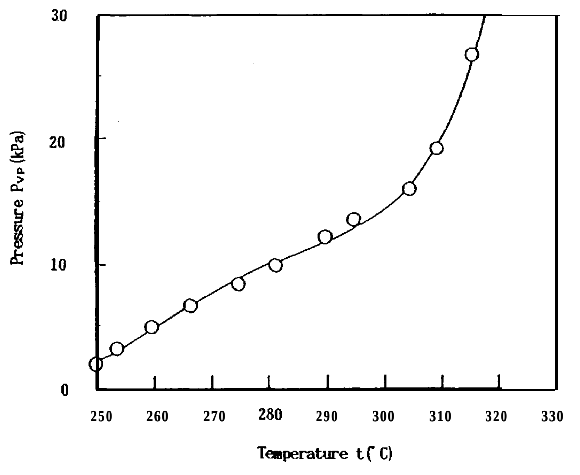

Fig. 4. Vapor pressure plotted against temperature for cotton-seed oil.

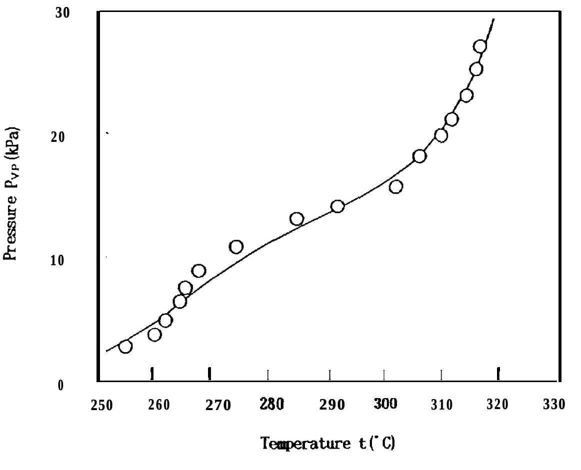

Fig. 5. Vapor pressure plotted against for temperature rice wax.

Although generally, the thermodynamic expression of phase equilibrium for a pure substance is given by the integral of the Clausius-Clapeyron's equation assuming the evaporation heat is constant, it is clear that such equation could not express these sigmoid type vapor pressure characteristic curves of edible oils (Robert, 1985).

The integrated the eq. (1) assuming that the evaporation heat is a simple equation of temperature (Uchida, 1965). Furthermore, adding the Riedel's team (Riedel, 1954a,b) to its results, thus the following equation is led,

$$\ln P_{vp} = A + B \cdot T^{-1} + C \cdot \ln T + D \cdot T^{6} \qquad (3)$$

in which A, B, C and D are introduced by the leasts squares method.

The solid curves in Figs. 2-7 were estimated from the Riedel's type equation (3) with 4 parameters. The results agreed well with the measured results and their

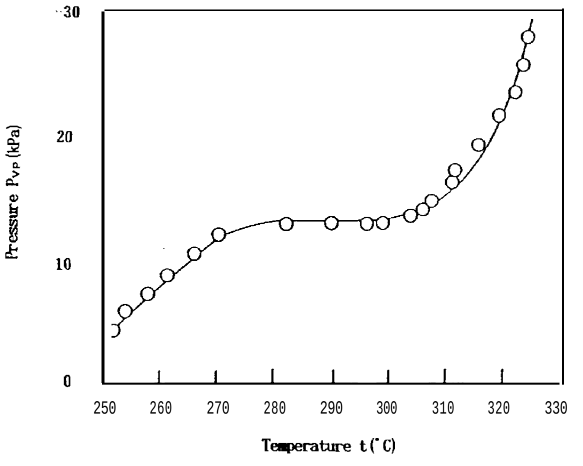

Fig. 6. Vapor pressure plotted against temperature for sesami oil.

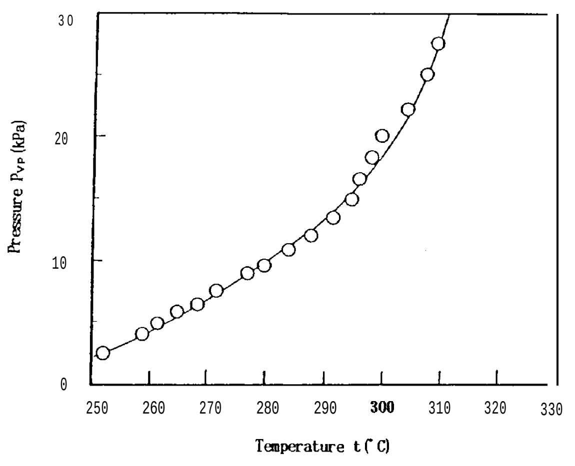

Fig. 7. Vapor pressure plotted against temperature for safflower oil.

standard deviations (σ) were in the range of 0.3026～0.9043kPa. It is useful for frying siumulation (Murata et al., 1991) and for designing vacuum fryer.

Table 2 shows the each constants (A, B, C, D) of eq. (3) and standard deviations of those from the calculated value of each edible oil. Parameters A and D are positive quantities on the other hand B and C are negative. The larger the absolute values of C and D, the stronger the inflection of sigmoid type curves.

Table 3 shows the calculated values of vapor pressure using eq. (3) for every 5°C increment within the temperature range of 250°C to 330°C.

Table 4 shows the boiling points at 101.3kPa (t_b) and the inflection points (t_{inf}) of each sigmoid type curve. Those points were calculated by using Newton-Raphson method. The calculated boiling points were about 330°C and the inflection points were about 290°C.

Table 2. Parameters in eq. (3) and standard deviation for each oil.

Samples	Parameters A	B	C	D	Standard deviation σ (kPa)
Soybean oil	2.302×10^{4}	-1.5564×10^{6}	-3.2111 X 10”	2.3744×10^{-15}	9.043×10^{-1}
Rape seed oil	2.4797×10^{4}	-1.6673×10^{6}	-3.4607×10^{3}	2.6604×10^{-15}	3.898×10^{-1}
Cotton-seed oil	1.9249×10^{4}	-1.3049×10^{6}	-2.6828×10^{3}	1.9609×10^{-15}	3.026×10^{-1}
Safflower oil	1.4982×10^{4}	-1.0100×10^{6}	-2.0901×10^{3}	1.6410×10^{-15}	5.612×10^{-1}
Rice wax	2.1893×10^{4}	-1.4828×10^{6}	-3.0517 x 103	2.2349×10^{-15}	7.850×10^{-1}
Sesami oil	2.6439×10^{4}	-1.7796×10^{6}	-3.6890×10^{3}	2.7598×10^{-15}	6.944×10^{-1}

Table 3. Calculated values of vapor pressure.

Tempcrature (°C)	Pressure (kPa) Samples: Soybean oil	Rape seed oil	Cotton seed oil	Safflower oil	Rice wax	Sesami oil
250	2.637	2.143	2.376	2.127	1.956	3.676
255	4.264	3.380	3.749	3.087	3.210	5.687
260	6.228	4.822	5.415	4.221	4.770	7.863
265	8.335	4.323	7.252	5.490	6.509	9.881
270	10.373	7.738	9.112	6.857	8.267	11.475
275	12.174	8.978	10.871	8.304	9.905	12.518
280	13.665	10.028	12.458	9.842	11.347	13.036
285	14.874	10.946	13.875	11.520	12.593	13.167
290	15.916	11.852	15.159	13.441	13.714	13.104
295	16.972	12.919	16.529	15.772	14.846	13.051
300	18.277	14.387	18.082	18.783	16.181	13.211
305	20.145	16.606	20.107	22.903	17.980	13.800
310	23.028	20.159	22.978	28.850	20.626	15.106
315	27.660	26.110	27.284	37.875	24.734	17.590
320	35.373	36.603	34.031	52.276	31.387	22.120
325	48.792	56.335	45.071	76.528	42.687	30.498
330	73.544	96.565	64.077	119.868	62.970	46.794

Table 4. The boiling points, t_b, at 101.3kPa and the inflection points, t_{inf}.

Sample	t_b (°C)	t_{inf} (°C)
Soybean oil	333.25	289.79
Rape seed oil	330.40	285.55
Cotton-seed oil	335.26	289.30
Safflower oil	328.22	
Rice wax	334.94	289.80
Sesami oil	336.74	289.74

Caluculation of the latent heat of evporation

The quantity of Riedel's term is not compared with that of other terms in eq. (3). Thus it is possible to ignore that term, and ΔZ_v can be regarded as a constant. Furthermore, the molar volume of the vapor phase (V_v) is much greater than that of liquid phase (V_l). Hence it is possible to neglect V_l and to regard the oil vapor as ideal gas. Then obtained.

$$\Delta Z_v \fallingdotseq 1 \qquad (4)$$

Substituted eq. (3) and simplified the relation (4) into eq. (1) and rearranged

$$\begin{aligned} \text{AH}, &= R\ (-B+C\cdot T+6D\cdot T^7) && (\text{KJ/Mol}) \\ &= (R/M)(-B+C\cdot T+6D\cdot T^7) && (\text{KJ/Kg}) \\ &= e+f\cdot T+g\cdot T^7 && (\text{KJ/Kg}) \qquad (5) \end{aligned}$$

in which e, f and g are constants, moler mass, M, shows in Table 1.

Table 5 shows the constants (e, f, g) in eq. (5). Hence the latent heat of evaporation can be estimated from eq. (5) and that of safflower oil is 360.21kJ/kg at 300°C, for example.

Table 5. Parameters in eq. (5).

Sample	Parameters e	f	g
Soybean oil	4.6404×10^4	-9.5739×10^1	4.2476×10^{-16}
Rape seed oil	4.9194×10^4	-1.0211×10^2	4.7097×10^{-16}
Cotton-seed oil	3.9359×10^4	-8.0919×10^1	3.5487×10^{-16}
Safflower oil	3.0046×10^4	-6.2177×10^1	2.9290×10^{-16}
Rice wax	4.4393×10^4	-9.1364×10^1	4.0146×10^{-16}
Sesami oil	5.2924×10^4	-1.0971×10^2	4.9245×10^{-16}

The other thermal charactristics

(1) **density**

The density of a series of edible oils was measured in a temperature range of 0°C to 200°C by using a picnometer and an oil bath. The experimental data of each oil were fitted to the equation by the least squares method as follows :

$$\rho_t = \rho_o (1-\alpha\cdot t) \qquad (6)$$

where as :

t : temperature in °C

α: coefficient of thermal expansion in $°C^{-1}$

ρ: density in g/cm^3

0 : denotes the values at 0 °C

Table 6 shows the parameters (α and ρ_0) in eq. (6), it's standard errors and the density at 25°C.

The results agreed well with the experimental results.

(2) **Evaporating rate**

The evaporating rate was measured and analyzed under surrounding nitororen gas

Table 6. Parameters in eq. (6) and its standard errors.

	α (/°C)	ρ_0 (g/cm^3)	SE. (g/cm^3)	ρ_{25} (g/cm^3)
Soybean oil	-6.11×10^{-4}	0.9319	1.96×10^{-3}	0.9169
Rape seed oil	-6.81×10^{-4}	0.9287	8.36×10^{-4}	0.9129
Cotton-seed oil	-6.32×10^{-4}	0.9285	1.71×10^{-3}	0.9138
Safflower oil	-6.39×10^{-4}	0.9317	1.58×10^{-3}	0.9168
Rice wax	-6.27×10^{-4}	0.9308	1.43×10^{-3}	0.9152
Sesami oil	-7.03×10^{-4}	0.9322	5.78×10^{-4}	0.9158

Table ‘7. Evaporating rate.

Sample			
Rape seed oil			
Temp. (°C)	N (kg·h^{-1}·m^{-2})	Temp. (°C)	N (kg·h^{-1}·m^{-2})
249	2.3148×10^{-3}	250	1.8939×10^{-3}
260	3.5774×10^{-3}	260	2.7778×10^{-3}
270	7.8704×10^{-3}	270	3.0724×10^{-3}
279	9.3434×10^{-3}	279	6.3131×10^{-3}
290	1.2500×10^{-2}	289	1.1742×10^{-2}

Sample			
Cotton-seed oil		Safflower oil	
Temp. (°C)	N (kg·h^{-1}·m^{-2})	Temp. (°C)	N (kg·h^{-1}·m^{-2})
250	2.0623×10^{-3}	250	1.6835×10^{-3}
260	3.0303×10^{-3}	261	2.2727×10^{-3}
270	4.6296×10^{-3}	270	3.7879×10^{-3}
280	8.5859×10^{-3}	280	6.3131×10^{-3}
290	1.3721×10^{-2}	290	1.2205×10^{-2}

Sample	
Rice wax	
Temp. (°C)	N (kg·h^{-1}·m^{-2})
250	3.1987×10^{-3}
260	5.1768×10^{-3}
270	8.3754×10^{-3}
280	1.2626×10^{-2}
290	1.7929×10^{-2}

by using TGA (Thermo Gravimetric Analyzer). Except for sesami oil, the evaporating rate curves showed exponential type with increasing temperature. The experimental data was showed in Table 7.

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