Temperature Effects on the Extraction of Rubber and Melon Seed Oils

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Oils were extracted from the seeds of rubber [*Hevea brasiliensis* (Kunth) Muell. Arg.] and melon (*Colocynthis vulgaris* Schrad) using different solvents at varying temperatures. The objective was to determine temperature coefficients (n) for enhanced oil removal and the enthalpy changes accompanying the extraction process.

Values of n, obtained from the slopes of the plots of the natural logarithm of equilibrium oil yield vs T/10, were on the order of 1.10, showing that oil yield increased by a factor of about 1.10 for every 10° rise in temperature. Also, n values were used to predict oil yields at other temperatures by knowing the oil yield at a given temperature.

Enthalpy changes (ΔH) in the extraction of both oils were determined using the Arrhenius equation. The ΔH values obtained were in the range of 4–13.5 kJ mol^{-1}, indicating the physical nature of oil extraction by a solvent.

Solvent power is temperature dependent, with solubility of the solute being generally enhanced with increased temperature. Solvent extraction of oils as a dissolution process has been shown to be temperature dependent (1). However, to our knowledge no effort has been made to quantify this dependence for the oils used in this work. Of interest is the determination of the temperature coefficient for the expected increase in oil yield with temperature. Also, the energy (enthalpy) changes in the oil extraction process are parameters that are of fundamental importance. This work aims at providing this information for the seed oils of rubber [*Hevea brasiliensis* (Kunth) Muell. Arg.] and melon (*Colocynthis vulgaris* Schrad).

MATERIALS AND METHODS

Rubber and melon seeds. The rubber seeds were obtained from the Nigerian Rubber Board (Benin, Nigeria). The melon seeds were purchased from a local market. The moisture-free oil contents of the rubber and melon seeds were 27.6% ± 1.4% and 31.8% ± 2.51%, respectively. For solvent extraction, both seeds were shelled, dried in an oven at 60°C to constant weight and then ground with a kitchen grinder to a mesh size of 120, which is smaller than the standard U.S. mesh size.

Solvents. The following analytical grade solvents were used as purchased for the extractions: petroleum benzene (100–140°C), cyclohexane, carbon tetrachloride, chloroform, dichloromethane, ethyl acetate, tetrahydrofuran, 2-propanol and acetone.

Equipment. The extraction equipment consisted of a glass cylindrical jar (diameter, 8 cm; and height, 25 cm) with a flat bottom and a quickfit neck for attaching a reflux condenser, a temperature-controlled water bath, a mini thimble and a thermometer.

Extraction procedure. Ground seed (60.0 g) was put in a weighed mini thimble. The thimble was placed in the cylindrical glass jar containing 300.00 mL of extracting solvent. The jar and its contents was submerged in a temperature-controlled water bath. The following temperatures were used: 27, 35, 45, 55, 65, 75 and 85°C.

The time of extraction was kept constant at 5 hr—this time period was found sufficient to achieve equilibrium oil extraction. At the end of the extraction period, the thimble was removed, and the solution in the tube was transferred to a weighed flask. The thimble was replaced in the jar to drain by raising it inside the stoppered jar by means of a small hollow cylindrical piece of glass (4 cm high). The drained solution was added to the rest of the oil solution. The extract was then stripped of its solvent and the oil yield determined.

RESULTS AND DISCUSSION

Values of percent oil yield for the different solvents at varying temperatures are given in Tables 1 and 2 for rubber and melon seed, respectively. Each oil yield was the mean of three replicates. A few general observations are evident from the oil yield data in the two tables. Oil yield increased with increased temperature, reaching its maximum value at the boiling point of the solvent. This trend is due to the increased ease of penetration of the meal matrix by the energized solvent molecules. The low boiling solvents, such as CH_2Cl_2 and acetone, gave oil yields that were comparable to those of high boiling solvents, such as petroleum benzene (100–140°C) and 2-propanol. This is of industrial importance where energy costs in both the extraction and solvent recovery process must be considered. Also, the use of low boiling solvents minimize the degradation of the oil extract, particularly at the oil recovery stage. However, solvent losses are generally higher when low boiling solvents are used.

Temperature (extraction) coefficient and its application. A quantitative analysis of temperature effect on oil yield was carried out using a vant Hoff type of expression (2):

$$Y_T = Y_0 n^{T/10} \qquad [1]$$

where Y_T is the percent oil yield at temperature T°C; Y_0 is the percent oil yield at zero temperature; and n is a constant designated temperature (extraction) coefficient.

Using equation [1], plots of ln Y_T vs T/10 were carried out and were found to be linear. The least square method was used to curve fit the points. Values of n obtained from the slopes of the curves are given in Table 3, which also contains theoretical oil yields Y_0 at 0°C.

In both rubber and melon seed oils, the n value for the hydrocarbon solvents was 1.05, while its value for the chlorinated solvents shows some significant variation from about 1.02 (CCl_4) to 1.14 (CH_2Cl_2) for the case of rubber seed. For the other solvents in both oils the n value has a magnitude of about 1.05, with the exception of acetone, which has an n value of about 1.10. The n value for each oil/solvent system represents the factor by which the oil yield increases for every 10° rise in temperature. The recorded n values show that there is no doubling effect in oil yield with rise in temperature. The n values of

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TABLE 1

Oil Yield (Rubber Seed) at Varying Extraction Temperature (°C)

Solvent	Boiling Point (°C)	Oil Yield (%)						
		27	35	45	55	65	75	85
Petroleum benzene	100–140	35.92	37.84	41.24	43.42	45.20	46.40	47.25
Cyclohexane	80.73	31.75	33.39	37.33	39.25	41.69	43.00	44.58
CCl_4	76.80	34.59	40.92	44.09	46.04	47.96	49.42	—
$CHCl_3$	61.20	35.15	41.00	42.67	46.75	—	—	—
CH_2Cl_2	39.80	36.17	46.58	49.96	—	—	—	—
Ethyl acetate	77.11	35.38	38.15	39.88	41.50	44.13	45.88	—
Tetrahydrofuran	66.00	37.25	39.39	40.99	41.71	45.25	—	—
2-Propanol	82.26	34.82	35.42	38.75	40.09	42.07	43.00	43.58
Acetone	56.29	35.00	35.92	40.39	44.25	—	—	—

TABLE 2

Percent Oil Yield (Melon Seed) at Varying Extraction Temperature (°C)

Solvent	Boiling Point (°C)	Oil Yield (%)						
		27	35	45	55	65	75	85
Petroleum benzene	100–140	35.09	36.09	36.55	39.92	41.75	44.48	45.96
Cyclohexane	80.73	33.75	35.92	37.17	39.29	40.67	43.67	45.17
CCl_4	76.80	35.88	36.34	38.75	43.25	45.92	46.84	—
$CHCl_3$	61.20	38.11	38.64	41.84	45.96	—	—	—
CH_2Cl_2	39.80	36.46	42.35	45.30	—	—	—	—
Ethyl acetate	77.11	35.20	37.07	39.25	41.21	45.46	46.58	—
Tetrahydrofuran	66.00	36.13	36.42	38.50	42.07	42.63	—	—
2-Propanol	82.26	34.26	35.74	38.38	40.47	41.08	45.00	47.75
Acetone	56.29	34.34	36.75	40.59	45.64	—	—	—

TABLE 3

Values of n (Temperature Coefficient), Y_0 (Oil Yield at 0°C), E (Percent Difference in Observed and Calculated Oil Yield at or Near Boiling Point, T°C) and ΔH (Enthalpy Changes) for Rubber and Melon Seed Oil Extraction

Solvent	Rubber				Melon			
	$n \times 10^2$	Y_0 (%)	E (T°C)	ΔH (kJ)	$n \times 10^2$	Y_0 (%)	E (T°C)	ΔH (kJ)
Petroleum benzene	105 ± 0.60	32.14 ± 0.33	0.88 (85)	4.41 ± 0.29	105 ± 0.21	30.37 ± 0.12	1.33 (85)	4.36 ± 0.17
Cyclohexane	105 ± 0.80	29.28 ± 0.45	5.5 (80.7)	5.32 ± 0.31	105 ± 0.15	29.84 ± 0.08	2.90 (80.7)	4.59 ± 0.15
CCl_4	102 ± 0.10	32.01 ± 0.06	4.43 (75)	5.91 ± 0.31	107 ± 0.83	29.65 ± 0.42	1.30 (75)	5.57 ± 0.51
$CHCl_3$	110 ± 3.8	28.27 ± 1.54	3.19 (55)	7.57 ± 1.61	110 ± 0.71	28.63 ± 0.29	4.98 (55)	6.97 ± 0.51
CH_2Cl_2	114 ± 3.2	28.23 ± 1.14	6.34 (39.8)	13.48 ± 2.06	112 ± 4.19	27.44 ± 1.49	6.11 (39.8)	12.86 ± 3.97
Ethyl acetate	105 ± 0.05	31.32 ± 0.25	2.53 (75)	4.56 ± 0.27	105 ± 0.65	31.17 ± 0.33	4.79 (75)	5.16 ± 0.35
Tetrahydrofuran	105 ± 0.08	33.12 ± 0.03	2.00 (65)	3.88 ± 0.69	105 ± 1.65	31.41 ± 0.75	2.04 (65)	4.06 ± 0.44
2-Propanol	104 ± 0.40	31.53 ± 0.22	0.76 (82.3)	4.47 ± 0.13	106 ± 0.44	29.13 ± 0.24	5.00 (82.3)	5.21 ± 0.18
Acetone	109 ± 1.59	26.85 ± 0.11	0.68 (55)	7.16 ± 1.68	111 ± 1.25	26.00 ± 0.51	0.79 (55)	8.21 ± 1.06

the chlorinated solvents (CCl_4, $CHCl_3$ and CH_2Cl_2) show an increasing order with decreasing molecular size, i.e., $CH_2Cl_2 > CHCl_3 > CCl_4$. This appears to be a size effect in a homologous series since the smaller-sized solvent molecules are expected to penetrate the cell walls of the seed more easily than the larger molecules.

The temperature coefficients in Table 3 have been used to calculate oil yields at any given temperature using the modified form of equation [1], as shown in equation [2]:

$$Y_T = Y_s n^{(T-T_s)/10} \qquad [2]$$

where Y_T is the oil yield at the required temperature T; Y_s is the oil yield at known temperature T_s; and n is the temperature coefficient. Thus, if the oil yield is known at room temperature, for example, the oil yield at any other temperature can be predicted using equation [2]. Such calculations of oil yield were carried out for rubber and melon seed oils at or near the boiling temperatures of the solvents involved. There is good agreement between the observed and the calculated oil yields as revealed by the small percent differences between them (columns 4 and 8 of Table 3). Thus, the experimentally determined n values appear useful in this regard.

Enthalpy of extraction of rubber and melon seed oils. The enthalpy changes in the extraction of rubber and melon seed oils were determined using the expression:

$$\ln Y_T = -\Delta H/R.T + \Delta S/R + \ln Y \qquad [3]$$

where Y_T is the equilibrium oil yield at temperature T; ΔS is the entropy change; R is the universal gas constant; and Y is the equilibrium unextracted oil. Equation [3] was obtained by applying Gibb's free energy expressions: $\Delta G = \Delta H - T.\Delta S$ and $\Delta G = -RT \ln K$, to our extraction system under equilibrium condition and replacing K with Y_T/Y.

Plots of $\ln Y_T$ vs $1/T$ were carried out using the oil yield values in Tables 1 and 2. Enthalpy changes (ΔH) in the extraction of the two oils were obtained from the slopes of these plots and are given in columns 5 and 9 of Table 3.

The ΔH values lie within the range of 4–13.5 kJ mol^{-1}, indicating the physical nature of the oil extraction process. Also, the chlorinated solvents seem to exhibit some trend in their enthalpy changes, with CH_2Cl_2 showing the highest value and CCl_4 the least. This trend shows that it is the entropy change that makes CH_2Cl_2 the most effective solvent of the three in oil extraction.

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[Received August 21, 1989; accepted February 25, 1990]