Rheological and Thermal Properties of Soybean Oils with Modified FA Compositions

Tong Wang[a,*] and Jenni L. Briggs[b]

Departments of [a]Food Science and Human Nutrition and [b]Agricultural and Biosystems Engineering,
Iowa State University, Ames, Iowa 50011

ABSTRACT: Rheological and thermal properties of five soybean oils with modified FA compositions were studied. Viscosity decreased with increasing temperature at different rates for the different oils. Oil with a high-oleic acid content had higher viscosity and a greater rate of change than did oils with typical FA compositions, oil with low-saturated FA or low-linolenic acid content, or oil from lipoxygenase-free soybeans. The melting and crystallization behaviors of the oils were examined using DSC. The high-oleic acid oil and the oil with low-saturated FA content had different DSC profiles compared with the other oils. Specific heat capacities of oils were estimated using a mathematical model; the high-oleic acid oil had a higher specific heat value, and the low-saturated FA oil had a lower value than did the other oils.

Paper no. J10103 in *JAOCS 79*, 831–836 (August 2002).

KEY WORDS: Heat capacity, melting temperature, oil quality, soybean oil, viscosity.

Physical properties of vegetable oils (i.e., viscosity, melting and crystallization behaviors, and specific heat capacity) are important engineering parameters. They are essential for designing processing equipment, such as that used for heat transfer, piping, deodorization, crystallization, and so on. Changing the FA compositions of oils to improve food or industrial applications may alter these properties (1). Such physical property changes need to be quantified to predict processing variations or to modify processing equipment for more efficient operation.

Modifying the FA compositions of soybean oils has been an important goal of plant breeding and molecular genetics research. Soybean oils with improved nutritional and functional properties have been and still are being developed by elevating or reducing the percentage of particular FA. During refining of soybean oils with modified FA compositions, we observed differences in viscosity and heat transfer among different types of oils. Therefore, this research was conducted to determine viscosity, melting characteristics, and specific heat of four soybean oils with modified compositions, and these were compared with a commodity soybean oil.

EXPERIMENTAL PROCEDURES

Soybean oils. Four types of soybean oils with modified FA compositions—high-oleic acid oil (HO), low-saturated FA oil (LS), low-linolenic acid oil (LLL), oil from lipoxygenase-free soybeans (LOX), and one commodity seed oil (CS)—were processed by conventional solvent extraction and then fully refined by degumming, neutralization, bleaching, and deodorization, as described by Wang and Johnson (2). The FA compositions were determined according to the method described by Wang *et al.* (3); these results are presented in Table 1. Effective carbon number (ECN) was determined by multiplying the number of carbon atoms in the FA chain by its percentage of composition, and the products were summed. The influence of double bonds was approximated by subtracting 1 for each double bond from the actual carbon atoms to compensate for the reduction in viscosity (1). The ECN values are presented in Table 1, along with FA compositions.

Rheological properties. Viscosity, also referred to as dynamic or absolute viscosity, was measured using a Haake RS-150 rheometer (Paramus, NJ) equipped with a 35-mm cone and plate sensor. The shear rate range used was 10–100 s^{-1}. Triplicate measurements were performed at 10, 20, 40, 60, and 90°C. Precision of the repeated measurement, as expressed as a coefficient of variation, was 1.39%. The influence of temperature on viscosity (μ) for Newtonian fluids can be expressed in an Arrhenius type of equation (4) involving absolute temperature (T), the universal gas constant (R), and the energy of activation for viscosity (E_a):

$$\mu = A\, e^{E_a/RT} \quad [1]$$

E_a and the equation constant (A) were determined using linear regression from experimental data. Higher E_a values indicated a more rapid change in viscosity with temperature.

Crystallization and melting profiles. A Seiko Exstar 6000 DSC (Seiko Instruments, Inc., Chiba, Japan), with Seiko measurement software (v. 5.8) and Seiko analysis software (v. 5.5), was used to measure the thermal transition of the oils. Samples of about 10 mg were weighed into aluminum pans to the nearest 0.1 mg. Both crystallization and melting profiles of the sample were measured based on a modified AOCS method (Cj 1-94) (5) and the method of Tan and Che Man (6). All samples were subjected to the following temperature program: heating to 60°C and holding for 5 min; cooling at

---

*To whom correspondence should be addressed at Department of Food Science and Human Nutrition, 2312 Food Sciences Bldg., Iowa State University, Ames, IA 50011. E-mail: tongwang@iastate.edu

TABLE 1
FA Compositions (mol%) of Modified Soybean Oils and Their Calculated Effective Carbon Numbers (ECN)[a]

	16:0	18:0	18:1	18:2	18:3	ECN[b]
CS	10.82	4.89	25.21	51.61	7.47	16.275
LOX	10.15	4.60	33.14	45.42	6.68	16.357
HO	6.72	3.80	79.22	7.15	3.12	16.837
LS	4.61	3.82	22.43	62.02	7.12	16.230
LLL	10.74	4.55	25.03	56.60	3.07	16.311

[a] CS, commodity soybean oil; LOX, lipoxygenase-free soybean oil; HO, high-oleic acid soybean oil; LS, low-saturated FA soybean oil; and LLL, low-linolenic acid soybean oil.
[b] See Reference 1.

5°C/min to –60°C and holding for 5 min; and heating to 60°C at 5°C/min. Duplicate samples of each oil were analyzed. The crystallization and melting characteristics of each sample can be described by the resulting thermal profile. In this study, the onset and completion temperatures, the temperature of the major phase transition peak, and the heat of fusion were determined.

Specific heats. A mathematical model established by Morad *et al.* (7) was applied to estimate the specific heat capacities of the five oils. A Rowlinson–Bondi equation was used to estimate liquid specific heat capacity (C_p) for pure FA. The liquid specific heat capacities of the oils were estimated by using mixture properties corresponding to the FA compositions and a correction factor, which accounted for the TAG form. The Rowlinson–Bondi equation is as follows:

$$(C_p - C_p^0)/R = 1.45 + 0.45\,(1 - T_r)^{-1} + 0.25\,\omega[17.11 + 25.2\,(1 - T_r)^{1/3}\,T_r^{-1} + 1.742\,(1 - T_r)^{-1}] \qquad [2]$$

where C_p^0 is the ideal gas specific heat capacity, T_r is the reduced temperature, and ω is the acentric factor, a parameter widely used as a measure of the complexity of a molecule with respect to both geometry and polarity. C_p^0 was calculated using the method of Rihany and Doraiswamy (8):

$$C_p^0 = \Sigma\, a + T\, \Sigma\, b + T^2\, \Sigma\, c + T^3\, \Sigma\, d \qquad [3]$$

The constants *a, b, c*, and *d* for various chemical groups were used to calculate the ideal gas capacity for pure FA (Table 2). The reduced temperature was calculated as $T_r = T/T_c$ (critical temperature). The values for T_c and ω of the five FA of soybean oil are listed in Table 3.

The terms in Equation 2 must take into account the mixture properties when the equation is applied to oils, because vegetable oil can be viewed as a substance consisting of a mixture of different FA. Therefore, any parameter in the equation for an oil can be replaced by the sum of the products of FA molar percentages and the corresponding parameter for FA. For example,

$$C_p^0\,(\text{mix}) = \Sigma\, x_i\, C_{p\,i}^0 \qquad [4]$$

A correction factor was used to correct for the difference between calculated and experimental values, as derived from the research of Morad *et al.* (7). For M.W. >850, as in our sample,

$$\text{correction factor } (F) = -0.2836 - 0.0005\,(\text{M.W.} - 850) \qquad [5]$$

$$C_p\,(\text{estimated for oil}) = C_p\,(\text{calculated for mixed FA}) + F \qquad [6]$$

Statistical analysis. The general linear model of the SAS program (9) was used for ANOVA. A factorial design was used to examine the viscosity as affected by temperature and type of oil. LSD were calculated ($P = 0.05$) to compare treatment means.

RESULTS AND DISCUSSION

Rheological properties. The viscosities of the five oils measured at various temperatures (10, 20, 40, 60, and 90°C) are shown in Figure 1. Viscosity clearly decreased with temperature, but the degree of reduction was dependent on oil composition (the interaction between oil type and temperature was significant, $P < 0.001$). HO oil had significantly higher viscosity than the others at lower temperature, but at greater than 60°C, its viscosity became similar to the other oils. The

TABLE 2
Constants Used to Calculate the Ideal Specific Gas Heat Capacities (C_p^0) for FA[a]

Group	*a*	$b \times 10^2$	$c \times 10^4$	$d \times 10^6$
$–CH_3$	0.6087	2.1433	–0.0852	0.001135
$>CH_2$	0.3945	2.1363	–0.1197	0.002596
–COO–(ester)	2.7350	1.0751	0.0667	–0.009230
–CH=CH–	–3.1210	3.8060	–0.2359	0.005504

[a] $C_p^0 = \Sigma a + T\,\Sigma\, b + T^2\,\Sigma\, c + T^3\,\Sigma\, d$ (Ref. 7).

TABLE 3
Primary Properties of FA Used in Specific Heat Capacity Calculations[a]

FA		T_c (K)[b]	ω[c]
Palmitic	16:0	799.88	1.109
Stearic	18:0	819.00	1.237
Oleic	18:1	819.14	1.185
Linoleic	18:2	819.82	1.129
Linolenic	18:3	820.23	1.072

[a] Cited from Reference 6.
[b] Critical temperature.
[c] Acentric factor.

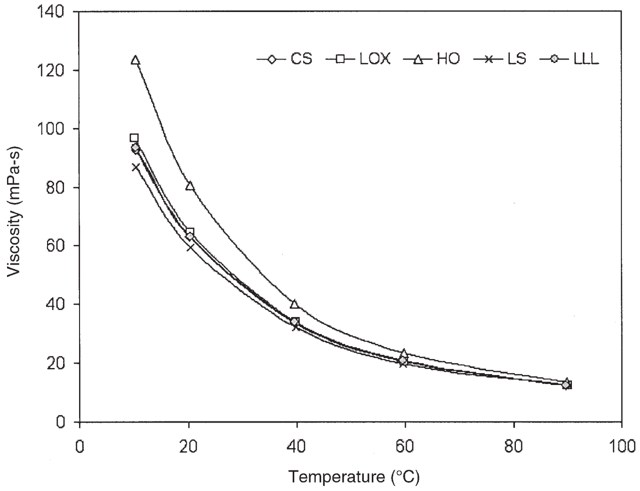

FIG. 1. Dynamic viscosity as a function of temperature for soybean oils with various FA compositions. CS, commodity soybean oil; LOX, lipoxygenase-free soybean oil; HO, high-oleic acid soybean oil, LS, low-saturated FA soybean oil; and LLL, low-linolenic acid soybean oil.

LSD at 5% was 0.894; this can be used to compare the differences among various oils. LS oil had the lowest viscosity. The value for LLL was not significantly different from those of LOX and CS, although LOX had significantly higher viscosity than did CS.

Thermodynamic parameters derived from the viscosity equation (Eq. 1) are shown in Table 4. The value for E_a of HO oil was significantly higher than those of the other oils, which indicates more rapid reduction in viscosity with increases in temperature, as demonstrated in Figure 1. This result suggests that when handling oils with modified FA compositions at low temperature, the differences in viscosities should be considered in processing design.

The differences in viscosities of various oils are due to the FA composition and the molecular conformation of the TAG molecules. When a *cis* double bond is present in a long-chain fatty acyl molecule, a bend or kink of the chain occurs. This bending prevents strong interaction or alignment among molecules; therefore, the intermolecular friction is reduced. ECN was calculated based on the total number of carbons as well as the number of double bonds in the acyl chain. ECN can possibly be used as a structural parameter and can be correlated with viscosity (1) and E_a. Significant correlations exist between ECN of the soybean oils and their viscosities and E_a, as shown in Figure 2. Therefore, the longer the chain of the fatty acyl groups, the more viscous the oil and the greater the E_a.

Geller and Goodrum (1) observed a second-order relationship between viscosities of saturated homogeneous TAG and their chain lengths. When this model was used to estimate viscosities of vegetable oils using their calculated ECN, 5% error was observed. Although this model is fairly accurate in predicting viscosities of vegetable oils, a model established with vegetable oils of mixed fatty acyl chains and with a wide range of FA compositions may better predict viscosity. In our work, the five soybean oils showed a good linear relationship between ECN and viscosity. More oils with a wide range of compositions should be analyzed to model the composition–viscosity relationship accurately.

Geller and Goodrum also reported (1) that the viscosity of oil was shear dependent below a shear rate of 7 s^{-1}, indicating non-Newtonian flow or pseudoplastic behavior at a very low shear rate. But when the rate was >7 s^{-1}, oil behaved as a Newtonian fluid. At the shear rate used for this experiment, the oils behaved as Newtonian fluids, as shown by the linear relationship between shear rate and shear stress. The non-Newtonian behavior at a very low shear rate may be due to instrument inertia as reported by Krieger (10). This instrument inertia often contributes to time-dependent viscosities found with Newtonian samples under certain conditions.

Crystallization and melting of oils. The crystallization and melting curves determined by DSC are presented in Figure 3. Melting curve parameters—onset, completion, peak temperatures, and heat of fusion—are presented in Table 5.

Thermal behaviors during the cooling and heating phases were very different. The heat released (exotherm) during cooling was much smaller than the heat absorbed (endotherm) during heating for all samples except the HO oil, which had similar thermal responses for the two phases. Two exothermic peaks were observed during cooling, with the high-melting peak being slightly larger and more defined than the low-melting one. The onset and completion temperatures from the melting curves were much better defined than those of the crystallization curves. Therefore, these parameters from melting are more useful in the comparison of oils than are those from crystallization. Tan and Che Man (11) reported that the crystallization curves were more reproducible and simpler than the melting curves. This was attributed to the fact that crystallization was influenced only by the chemical composition of the sample and not by the initial crystalline stage,

TABLE 4
Thermodynamic Parameters Derived from Equation 1 for Various Oils[a]

	E_a/R	E_a (cal/mol)	A (mPa-s)	R^2
CS	2617.8	5199.2	8.0E-03	0.9907
LOX	2677.3	5317.4	7.0E-03	0.9907
HO	2893.3	5746.4	4.0E-03	0.9914
LS	2554.1	5072.7	1.0E-02	0.9904
LLL	2615.0	5193.7	9.0E-03	0.9918

[a] R, universal gas constant = 1.9861 cal/mol K; E_a, energy of activation; A, equation constant; R^2, regression coefficient of Equation 1. For other abbreviations see Table 1.

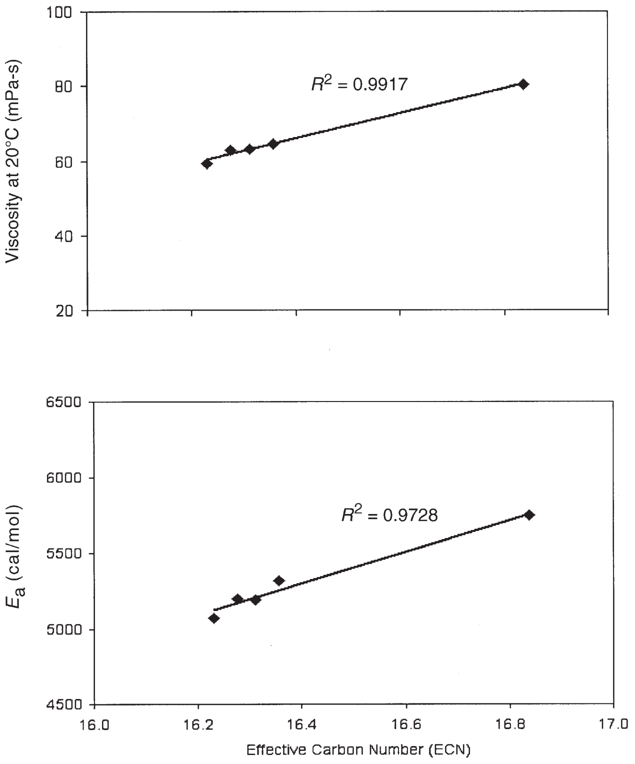

FIG. 2. Effect of ECN on viscosity and energy of activation (E_a).

because all samples started from the liquid state. It is possible that the crystalline forms of our samples were different despite undergoing the same heating and cooling treatments; therefore, the melting curves may represent melting of different crystal forms. Nevertheless, melting curves allow us to examine the complex issue of polymorphism, and the melting profiles reflect the natural crystallization behavior. Polymorphism is a property of natural oils and fats that is recognized as being composition-dependent (12).

The endothermic curves of CS, LLL, and LOX oils were very similar. The multiple peaks are due to polymorphism of mixed lipids (12). Most vegetable oils are polymorphic and can exist in at least three crystalline forms, designated as α, β′, and β. When oil samples were cooled rapidly in the DSC pans, they may have solidified in the lower-melting α or β′ forms. During the gradual temperature increase, the less stable forms may have melted first and recrystallized into higher-melting forms to give the melting profiles (Fig. 3). The LS oil had a unique melting profile compared with the three mentioned above. It had very well-defined double peaks, with a significant heat release from the low-melting to high-melting transition, giving an exothermic peak. The low-melting crystalline form may have had high energy content that was released before crystallizing into the higher melting crystalline form. HO oil had a single exothermic and endothermic peak, possibly due to its more homogeneous composition. Interestingly, HO oil

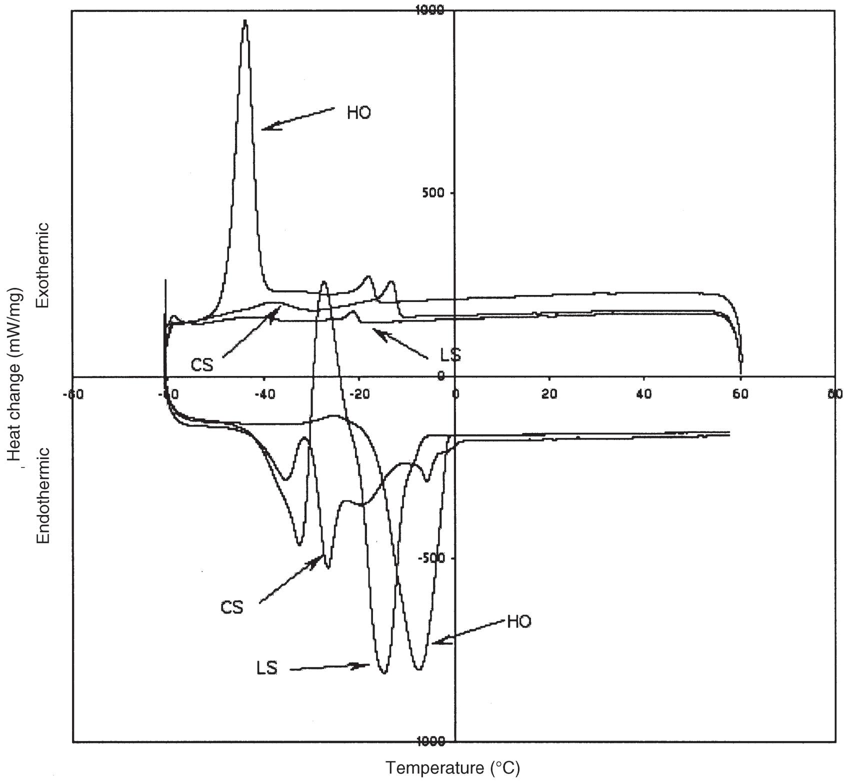

FIG. 3. DSC crystallization and melting curves of soybean oils with modified FA compositions. For abbreviations see Figure 1.

TABLE 5
DSC Thermal Transition of the Melting Curves[a]

	Onset (°C)	Completion (°C)	Peak (°C)	Heat of fusion (J/g)
CS	-42.7^{B}	2.6^{A}	-26.8^{D}	$58.0^{B,C}$
LOX	-42.3^{B}	2.2^{A}	-27.0^{D}	$62.1^{B,C}$
HO	-17.6^{A}	-0.5^{B}	-7.4^{A}	74.7^{A}
LS	-42.3^{B}	-5.7^{C}	-15.0^{B}	59.9^{C}
LLL	-41.8^{B}	3.1^{A}	-25.8^{C}	65.3^{B}
$LSD_{0.05}$	1.06	1.25	0.31	5.60

[a] The same capital letter in each column indicates no statistical difference at $P < .05\%$. See Table 1 for abbreviations.

had the highest melting temperature among the oils tested, but its crystallization temperature was the lowest, as indicated by the major peak.

Comparison of the various temperatures listed in Table 5 shows that all samples had similar onset temperatures except the HO oil. Their completion temperatures were similar except for HO and LS, which had significantly lower temperatures than the others. The peak temperatures were quite different among all samples except for the CS and LOX oils. These values were determined as the temperature of the highest peak, and they may not always represent the true peak temperature. A correlation analysis was also performed to determine any relationship between various DSC temperatures and ECN of the five oils. No well-defined relationship was observed.

For heat of fusion, there were statistically significant differences among the oils. The HO oil had the highest value, and the LS oil had the lowest value. A relationship between heat of fusion and energy of activation of viscosity was also established (Fig. 4). This positive correlation suggested that both of the parameters may relate to the molecular structure in a similar manner. When the TAG molecules are more saturated, the molecular (hydrophobic) interaction is stronger. Thus, higher energy is needed to disrupt the molecular association to cause melting or relative molecular movement. There was relatively more scatter of the data compared to other regressions, although the reason is unknown.

Specific heat capacity. The calculated C_p values for the oil samples at temperatures between 25 and 300°C (298–573 K) are shown in Figure 5. The HO oil had a higher value, and the LS oil had a lower value than for the other three oils. All oils had the same rate of heat capacity change with temperature, which was 0.0024 J/g °C. The intercepts of the linear relationship were 1.8583 and 1.7992 for HO and LS oils, which were the highest and lowest values among all oils tested. The constants were 1.8146, 1.8178, and 1.8210 for CS, LLL, and LOX oils, respectively. The effect of temperature on C_p of fats and oils in the temperature range of 15 to 60°C was also suggested by Formo (13) to be

$$C_p = 1.9330 + 0.0026\,T \qquad [7]$$

which was very similar to that calculated using the model of Morad *et al.* (7). The accuracy of Morad's estimation method was also evaluated by the authors. The estimated C_p values for pure TAG and vegetable oils were compared with the ones

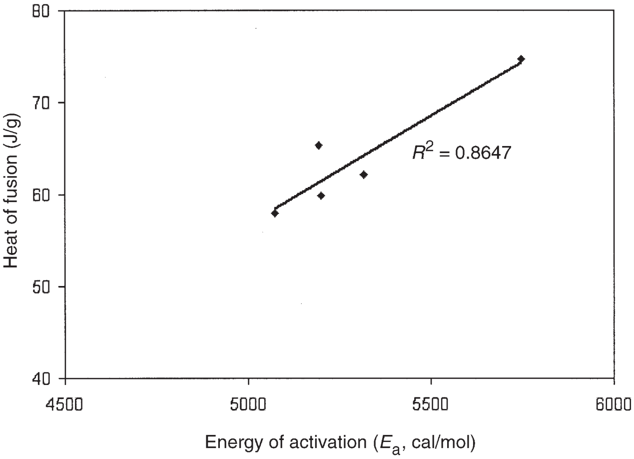

FIG. 4. Relationship of heat of fusion derived from DSC analysis and E_a derived from viscosity determination.

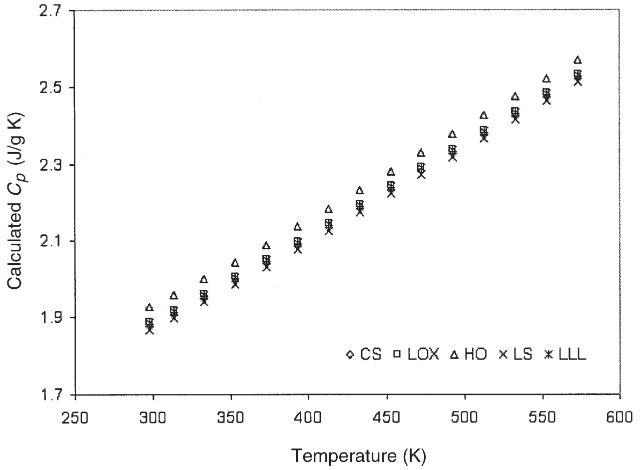

FIG. 5. Calculated specific heat (C_p) values as a function of temperature for soybean oils with various FA compositions. For abbreviations see Figure 1.

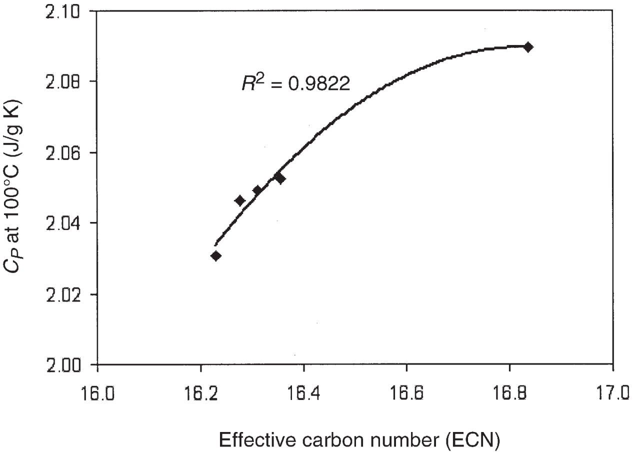

FIG. 6. Relationship between C_P and ECN of soybean oils. For abbreviations see Figures 2 and 5.

obtained from the experiments, and the error was found to be ±5%.

The effect of FA composition on C_p of fats and oils was also generalized (13) such that increases in chain length and degree of saturation increased the C_p. Our results show that this relationship is curvilinear over the composition range tested (Fig. 6). More oils with a wider range of FA compositions need to be tested to validate this relationship.

The C_p of these oils were also determined by DSC, using conditions similar to those described by Morad *et al.* (14,15). The reproducibility of the analysis was not satisfactory and the data are not shown.

ACKNOWLEDGMENTS

Journal Paper No. J-19562 of the Iowa Agriculture and Home Economics Experiment Station, Ames, Iowa. Project No. 0178, supported by the Hatch Act and State of Iowa funds.

REFERENCES

1. Geller, D.P., and J.W. Goodrum, Rheology of Vegetable Analogs and Triglycerides, *J. Am. Oil Chem. Soc. 77*:111–114 (2000).
2. Wang, T., and L.A. Johnson, Refining Normal and Genetically Enhanced Soybean Oils Obtained by Various Extraction Methods, *Ibid. 78*:809–815 (2001).
3. Wang, T., E.G. Hammond, and W.R. Fehr, Phospholipid Fatty Acid Composition and Stereospecific Distribution of Soybeans with a Wide Range of Fatty Acid Compositions, *Ibid. 74*:1587–1594 (1997).
4. Steffe, J.F., Introduction to Rheology, in *Rheological Methods in Food Process Engineering*, Freeman Press, East Lansing, 1996, pp. 1–93.
5. *Official Methods and Recommended Practices of the American Oil Chemists' Society*, 4th edn., edited by D. Firestone, AOCS Press, Champaign, 1994, Method Cj 1–94.
6. Tan, C.P., and Y.B. Che Man, Differential Scanning Calorimetric Analysis of Edible Oils: Comparison of Thermal Properties and Chemical Composition, *J. Am. Oil Chem. Soc. 77*:143–155 (2000).
7. Morad, N.A.M., A.A. Mustafa Kamal, F. Panau, and T.W. Yew, Lipid Specific Heat Capacity Estimation for Fatty Acids, Triacylglycerols, and Vegetable Oils Based on Their Fatty Acid Composition, *Ibid. 77*:1001–1005 (2000).
8. Rihani, D.N., and L.K. Doraiswamy, Estimation of Heat Capacity of Organic Compounds from Group Contributions, *Ind. Eng. Chem. Fundam. 4*:17–21 (1965).
9. SAS, *SAS User's Guide: Statistics*, SAS Institute, Inc., Cary, NC, 1984.
10. Krieger, I.M., The Role of Instrument Inertia in Controlled-Stress Rheometers, *J. Rheol. 34*:471–483 (1990).
11. Tan, C.P., and Y.B. Che Man, Quantitative Differential Scanning Calorimetric Analysis for Determining Total Polar Compounds in Heated Oils, *J. Am. Oil Chem. Soc. 76*:1047–1057 (1999).
12. Roos, Y.H., Food Components and Polymers, in *Phase Transitions in Foods*, Academic Press, New York, 1995, pp. 142–149.
13. Formo, M.W., Physical Properties of Fats and Fatty Acids, in *Bailey's Industrial Oil and Fat Products*, 4th edn., edited by D. Swern, John Wiley & Sons, New York, 1979, Vol. 1, pp. 177–232.
14. Morad, N.A., M. Idrees, and A.A. Hasan, Improved Conditions for Measurement of the Specific Heat Capacities of Pure Triglycerides by Differential Scanning Calorimetry, *J. Therm. Anal. 44*: 823–835 (1995).
15. Morad, N.A., M. Idrees, and A.A. Hasan, Specific Heat Capacities of Pure Triglycerides by Heat-Flux Differential Scanning Calorimetry, *Ibid. 44*:1449–1461 (1995).

[Received September 26, 2001; accepted May 27, 2002]