Correlating Chemical Structure and Physical Properties of Vegetable Oil Esters

Jorge de A. Rodrigues, Jr., Fabianne de P. Cardoso, Elizabeth R. Lachter, Luciana R.M. Estevão, Edson Lima, and Regina S.V. Nascimento*

Instituto de Química–Departamento de Química Orgânica, Universidade Federal do Rio de Janeiro (UFRJ), Cidade Universitária, Rio de Janeiro, Rio de Janeiro, CEP 21941-590, Brazil

ABSTRACT: The influence of FA ester chemical structures on the rheology and crystallization temperature of those compounds was evaluated using methyl, *n*-butyl, *n*-octyl, and 2-ethyl-1-hexyl FA esters with different chain lengths and different degrees of unsaturation. The rheological properties were analyzed in a high-precision rheometer at various temperatures, and the crystallization temperatures were determined by DSC. Esters produced from the esterification of pure FA and from the transesterification of vegetable oils (i.e., soybean, corn, linseed, and babassu coconut oils) were evaluated. The length of the FA chain was shown to have a marked influence on the viscosity and crystallization temperature of the systems, whereas branching affected only the crystallization temperature to a significant extent. The viscosity and crystallization temperature of the systems were also influenced by the degree of unsaturation. One double bond was shown to increase viscosity, whereas two or three double bonds caused a decrease in the viscosity of the systems. Unsaturation lowered the crystallization temperature in all cases, regardless of the number of double bonds. From all the oils studied, methyl esters from babassu coconut oil presented the lowest crystallization temperatures.

Paper no. J11173 in *JAOCS 83*, 353–357 (April 2006).

KEY WORDS: Biodiesel, crystallization temperature, DSC, vegetable oils, viscosity.

Vegetable oil esters have been widely used in the chemical industry. Their current use for biodiesel—a useful renewable energy source—is a likely substitute for diesel oil in future years because of the imminent exhaustion of petroleum reserves worldwide (1). Many studies have aimed to obtain biodiesel with properties (e.g., flash point, cetane number, viscosity, cloud point, pour point, and crystallization temperature) suitable for utilization in diesel engines (2–5).

The viscosity of a fluid plays a major role in its pumping and flow within an engine. According to Ma and Hanna (6), the desirable viscosity for diesel oil at 37.8°C ranges from 1.9 to 4.1 cSt. At this temperature, soybean oil exceeds the optimal range, giving values as high as 32.6 cSt. For biodiesel, transesterification is an efficient method of reducing the high viscosity of vegetable oils while also improving other desirable prop-

erties (6). Methanol is one of the preferred alcohols used to transesterify vegetable oils and produce biodiesel. Generally, methyl esters have a Newtonian behavior within typical working temperatures. However, preliminary results from our laboratory have shown that methyl esters from soybean oil present a pseudoplastic behavior when temperatures reach values below 5°C, presenting high viscosity under low shear rates and low viscosity under high shear rates. Similar results were also obtained by Srivastava and Prasad (5) with methyl esters from soybean and mustard seed oils, confirming our data. This high viscosity at lower temperatures could be a result of micro-crystal formation and would cause serious problems in fuel lines and in engine filters.

Therefore, the crystallization temperature is an important factor to be considered. DSC is an efficient method for investigating crystallization temperatures, as it is more accurate than the classical pour point or cloud point measurements frequently used for this purpose (2). Lee *et al.* (4) and Nascimento *et al.* (7) have studied the effects of chemical structure on the crystallization temperature by using a series of branched alcohol esters. They observed that branching in the carbon chain reduces the crystallization temperature of the esters studied. Unsaturation also influences the crystallization temperature, since the spatial configuration of the molecule can interfere with crystal packing efficiency. Thus, molecules presenting a spatial arrangement that disrupts their packing ability will have lower crystallization temperatures. It has been reported in the literature that more than one unsaturation in the carbon chain lowers both the crystallization temperature and the viscosity by hindering molecular packing (8). Friedheim and Conn (9) showed that double bonds positioned near the ends of the carbon chain enable a more efficient packing than those found near the middle of the molecule.

In principle, a large variety of vegetable oils such as soybean, babassu coconut, corn, linseed, and castor oil could be used for the production of biodiesel, and depending on the vegetable oil and alcohol chosen, the ester mixture produced will present very different properties. Hence, to help select the esters that best fulfill the desired properties, a systematic study of the influence of each of the structural factors in FA esters, particularly the crystallization and viscosity properties, becomes necessary. This study aims at evaluating the effect of the chemical structure of FA esters on their viscosity and crystallization temperature. Both pure esters and ester mixtures obtained from

the transesterification of different vegetable oils were used in the study of factors such as M.W., unsaturation, and chain branching.

EXPERIMENTAL PROCEDURES

Esterification of FA. Pure esters were obtained by esterification reactions using various FA and alcohols. Lauric (12:0), palmitic (16:0), stearic (18:0), and oleic (18:1) acids were used, each one being submitted to esterification reactions with methanol, *n*-butanol, *n*-octanol, and 2-ethyl-1-hexanol. An excess of alcohol was used, and the FA-to-alcohol molar ratio was kept constant at 1:10. In all cases, 1% (molar percentage relative to the FA) of *p*-toluenesulfonic acid was added as catalyst.

All the reactions, except those using methanol, were carried out in reflux equipment under magnetic stirring at 80°C. Reactions involving methanol were kept at a reflux temperature of approximately 65°C. The systems were kept under these conditions for 24 h, and the products obtained were purified by acid–base extraction using hexane and a solution of sodium carbonate at 10 wt%. Reactions using methanol produced an alcohol-free organic phase, contrary to the reactions using the other alcohols. The excess of *n*-butanol was removed in a rotatory evaporator, whereas the excess of *n*-octanol and 2-ethyl-hexanol was removed by steam distillation. The products obtained were analyzed by FTIR using a Nicolet 740 FTIR instrument to monitor the axial carbonyl deformation in the ester samples, which is typically found between 1744 and 1739 cm^{-1}.

Transesterification of vegetable oils. Methanol was used for the transesterification of soybean, linseed, babassu coconut, and corn oils. Potassium carbonate (3% molar percentage relative to the oil) was used as catalyst. An excess of methanol was used in a 1:10 oil-to-methanol molar ratio. The reactions were kept under reflux (approximately 65°C) for 2 h. The products were purified by solvent extraction using hexane and a saturated NaCl solution. Proton NMR (^{1}H NMR), performed in a Brucker Advance DPX-200 instrument, was used to characterize the products. The singlet at 3.6 ppm, corresponding to the –OCH$_3$ groups in esters, was used to evaluate the degree of purification attained by the process, since the multiplet at 4.2–4.4 ppm, corresponding to the methylene groups of glycerol in TG, disappeared, indicating pure products.

Ester/ethyl acetate binary mixtures. Binary mixtures were prepared by varying the concentration of the fatty esters in ethyl acetate. The mixtures were used to determine the effect of the ester chemical structure and ester concentration on the viscosity of the final solutions. *n*-Octyl stearate and *n*-octyl oleate were used to prepare mixtures containing 0, 0.2, 0.8, and 1.0 molar fractions of the esters in the acetate solution.

Rheology. The rheology of the systems was studied using an RS-150 Haake rheometer. Viscosity data were obtained in a steady shear mode, while controlling the shear rate. The analyses were carried out using shear rates varying from 10 to 1500 s^{-1} in step mode, with a DG41 sensor and coaxial cylinders for low-viscosity fluids ($\eta < 1000$ mPa·s). The esters synthesized from the pure FA were methyl linoleate (18.2) and methyl linolenate (18.3) (acids supplied by Sigma, St. Louis, MO) and were evaluated in the 0 to 100°C temperature range, whereas for the vegetable oil methyl esters, temperatures of 0 to 30°C were used.

Crystallization temperature. The crystallization temperatures (T_{CO}) of the esters produced were determined by DSC in a Perkin-Elmer Model DSC7 instrument, where 1.5-mg samples were submitted to heating and cooling in the 50 to −30°C temperature range at 10°C/min under nitrogen flow. The T_{CO} was taken to be the onset temperature in the cooling process. However, Cebula and Smith (10) have observed that crystallization temperatures vary with the cooling rate, owing to nucleation effects.

RESULTS AND DISCUSSION

Rheology. The viscosity vs. shear rate curves obtained for the esters revealed a Newtonian behavior in all the temperatures studied. However, the viscosity of the systems was temperature dependent. By analyzing the rheological behavior of the pure esters, the effects of the molecular structure (such as the length of the carbon chain, unsaturation, and branching) and ester concentration on the viscosity of the systems could be evaluated.

Effect of the carbon chain length. The effect of the FA and alcohol chain lengths on viscosity is illustrated in Figure 1.

A tendency toward a viscosity increase with increasing length of the hydrocarbon segment was observed for either the
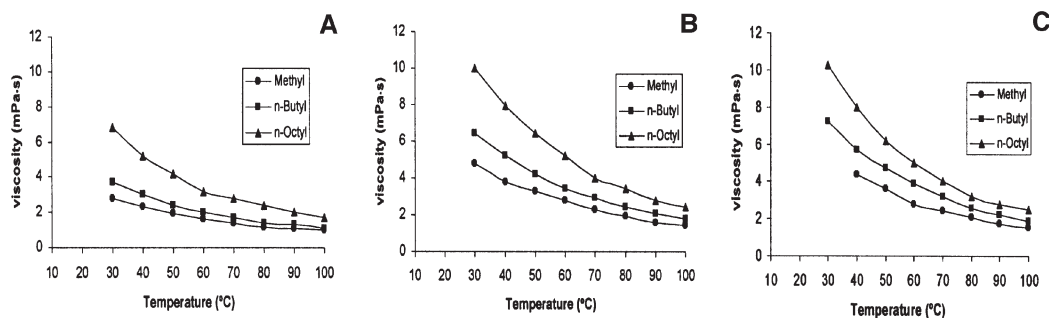

FIG. 1. Influence of the alcohol hydrocarbon chain on the viscosity of esters derived from (A) lauric acid, (B) palmitic acid, and (C) stearic acid.
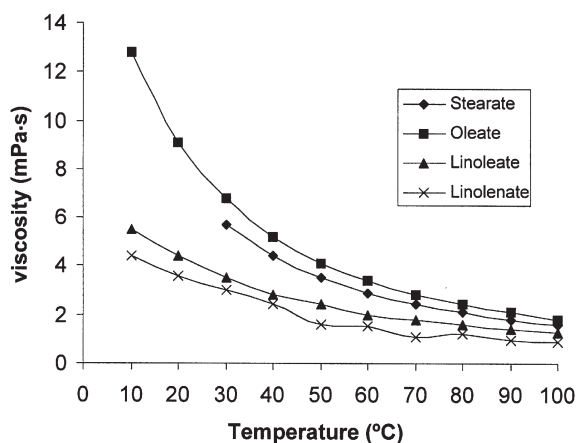
FIG. 2. Viscosity–temperature dependence of methyl esters with different degrees of unsaturation.

FIG. 3. Influence of the concentration of octyl esters on viscosity, measured at 40°C.

alcohol or FA chain segment. The phenomenon became more evident at lower temperatures, where the stearic and palmitic acids esters showed significantly higher viscosities than did the lauric acid esters. The palmitate and stearate esters might begin to form crystallites at lower temperatures, contributing to a viscosity increase. As the lengths of the acid and alcohol segments in the ester molecules increased, so did the degree of random intermolecular interactions, and consequently the viscosity. The effect became more evident at lower temperatures, where the molecular movement was even more restricted.

Effect of unsaturation in the hydrocarbon chain. Figure 2 shows the viscosity as a function of temperature for four fatty methyl esters with the same carbon chain lengths but with different degrees of unsaturation.

By comparing the viscosities of methyl stearate and methyl oleate, we observed that the presence of one double bond did increase the viscosity. In contrast, two or three double bonds (methyl linoleate and methyl linolenate, respectively) reduced the viscosity, as compared with the results for methyl stearate.

The presence of one carbon–carbon double bond in the structure of oleates gave rise to stronger intermolecular inter-
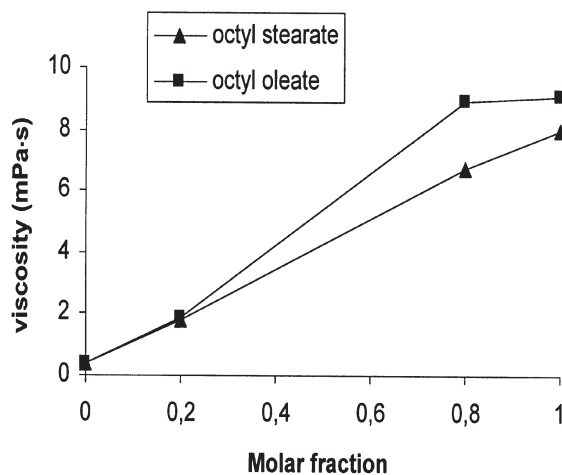
actions between the π electrons of the double bonds. This kind of interaction may have occurred because the spatial geometry of the *cis* configuration of the one double bond of the oleate still allowed a close packing between the molecules. Obviously, strong orbital interactions could not be found between the stearate molecules, where only weaker van der Waals interactions were possible. On the other hand, the interactions between the π orbitals in linoleates and linolenates were reduced because of the spatial geometry of these molecules, where the alternate double bonds, all in *cis*-conformation, led to a configuration like a coil, hindering the approach of the sp^2 atoms from the double bonds of neighboring molecules. These effects should account for the differences in viscosity observed for these systems.

Effect of ester concentration. To verify whether the interactions between π electrons of the double bond of the oleate molecules were responsible for the higher viscosity as compared with the ones presented by stearate, the effect of the concentration of saturated and unsaturated esters on the viscosity of the ester so-
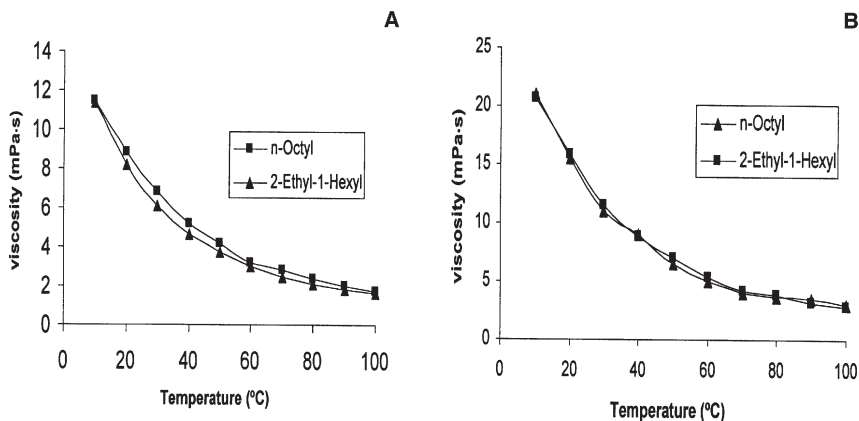

FIG. 4. Effect of branching on the viscosity of (A) *n*-octyl and 2-ethyl-1-hexyl laureates and (B) *n*-octyl and 2-ethyl-1-hexyl oleates.
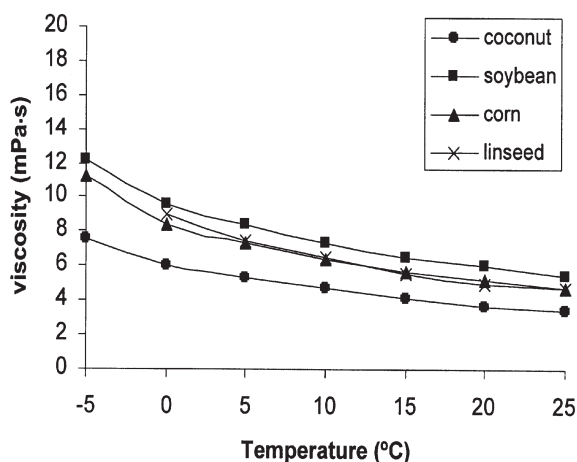
FIG. 5. Viscosity of vegetable oil methyl esters as a function of temperature.

lutions was evaluated. *n*-Octyl stearic and oleic acid esters were mixed with ethyl acetate in various proportions and submitted to rheological analysis. Figure 3 shows that in diluted solutions (molar fraction of 0.2), the saturated and unsaturated esters had similar viscosities, whereas in concentrated solutions (molar fraction of 0.8), the oleate had higher viscosities.

In dilute solutions, interactions occurred mainly between solute–solvent or solvent–solvent molecules, resulting in very weak interactions, since the viscosities observed were very low. In this case, solute–solute interactions did not play a major role in determining the final viscosity of the solutions. An opposite phenomenon occurred in concentrated solutions, where solute–solute interactions became significant. Hence, at lower concentrations, stearate and oleate had very similar viscosities, since solvent effects exceeded all others. Even if the ethyl acetate molecules were able to interact with the double bond of the *n*-octyl oleate, this effect would not have been as significant as the π–π interactions between oleate molecules in a concentrated solution. Therefore, double bond solute–solute interactions in oleates became significant only at higher concentrations.

Branching effects. Branching can alter viscosity, although to a lesser extent than unsaturation. In preliminary essays, when comparing esters derived from the same carboxylic acid and chain isomer alcohols (*n*-octanol and 2-ethyl-1-hexanol) that contained the same number of carbon atoms, little variation in the viscosity of the systems was observed, as confirmed by Figure 4. Lauric acid esters were the only ones slightly affected by branching, possibly because of their shorter hydrocarbon chains. Branching reduces the interactions between carbon chains by hindering the approach of neighboring molecules, as verified by Lee *et al.* (4). This effect probably reduced the viscosity of the systems in the same way it reduced their crystallization temperatures. These effects were more significant in shorter carbon chains than in longer ones, where molecular intertwining was more pronounced.

Vegetable oil methyl esters. We evaluated the rheological properties of mixtures of methyl esters obtained from the trans-esterification of different vegetable oils, i.e., soybean, linseed, babassu coconut, and corn oil. The typical compositions of these oils can be found elsewhere (11).

The effect of temperature on the viscosity of the esters is shown in Figure 5. As expected, the viscosity of the esters decreased with a temperature increase. It is worthwhile to note that the lowest viscosities were obtained with the babassu coconut methyl esters. These results are in agreement with those just discussed during the analyses of individual esters. Babassu coconut oil is composed mainly of lauric acid esters, whereas in the other oils, esters from 18-carbon-atom acids are predominant.

All the other methyl esters showed similar viscosities, as they all have a considerable percentage of 18-carbon-atom FA and varying unsaturated compositions.

Crystallization temperature. The onset crystallization temperature (T_{CO}) is the highest temperature at which the substance still remains in the liquid state. Crystallization temperatures differ when obtained from the melting or crystallization thermogram. The T_{CO} values presented herein were determined by the initial temperature of the crystallization peak in the DSC thermograms.

Effect of the carbon chain length and branching. The crystallization temperatures of nine linear and branched saturated esters were determined. The esters analyzed were produced from the reaction of different FA and alcohols. The results are shown in Table 1.

Among the esters produced from linear-chain alcohols, no relationship could be identified between alcohol chain length and crystallization temperature. Butyl esters showed the lowest crystallization temperatures, regardless of the acid used for esterification, indicating that nucleation for these esters seems to have been hindered to a greater extent than for the methyl or *n*-octyl esters. Crystallization phenomena involve a high level of organization to promote nucleation. Linear esters pack efficiently into crystals, and because van der Waals attractions are large, they have relatively high crystallization temperatures. Branching interferes with the crystal packing, hence decreasing the T_{CO}, as clearly confirmed by comparing the *n*-octyl- and 2-ethyl-1-hexanol-derived esters.

It is interesting to note that although little difference in viscosity was detected between branched and linear esters, the crystallization temperature of these compounds was strongly influenced by branching. Crystallization is highly dependent on molecular ordering and is thus affected by chain branching (7).

Effect of unsaturation in the hydrocarbon chain. Methyl esters from 18-carbon-atom acids and with different degrees of unsaturation were analyzed with regard to T_{CO}. The results obtained are shown in Table 2. One can observe that the presence of unsaturation in the hydrocarbon chain caused a marked decrease in the crystallization temperature of the esters.

Both viscosity and crystallization temperature are physical properties that depend on the interactions between molecules. However, crystallization requires not only interaction, but also good molecular packing to reach the adequate entropy level. The results presented here showed that one double bond in the FA increased the viscosity of the ester because of increased in-

TABLE 1
Crystallization Temperatures (°C) of the Esters of FA and Alcohols

Alcohol	Acids			
	Lauric	Palmitic	Stearic	Oleic
Methanol	−4.0	23.2	31.6	−19.8
n-Butanol	−22.4	11.4	13.5	ND[a]
n-Octanol	−0.6	17.3	16.9	−13.0
2-Ethyl-1-hexanol	<−30	−6.0	ND[a]	<−30

[a]Not determined.

TABLE 2
Influence of Unsaturation on the Crystallization Temperature (T_{CO}) of Methyl Esters

Ester	T_{CO} (°C)	No. of double bonds
Methyl stearate	23.2	0
Methyl oleate	−19.8	1
Methyl linoleate	<−30.0	2
Methyl linolenate	<−30.0	3

termolecular interaction. However, even though this type of interaction exists in unsaturated systems, the molecular packing to form crystals is not as effective as in a saturated system, hence giving a lower T_{CO}. This effect can also account for the fact that two or three double bonds lower the crystallization temperature to below −30°C.

Vegetable oil methyl esters. The T_{CO} of the methyl esters derived from soybean, corn, babassu coconut, and linseed oils were measured and the results are as follows (°C): soybean, −6.1; corn, −8.0; babassu coconut, −10.8; linseed, −15.1.

The esters that showed the lowest crystallization temperatures were those obtained from linseed and babassu coconut oils. Those oils contain high levels of linolenic acid (triunsaturated) and lauric acid (C_{12}) esters, respectively. As discussed, the presence of unsaturation affects the interaction among the chains, and also shorter FA chains result in weaker random interactions among the molecules. These factors could then be responsible for the low crystallization temperatures observed.

The results obtained contribute to a better understanding of the structure–physical property relationships in FA esters. These relationships are of particular importance when choosing vegetable oils that will give the desired biodiesel quality. By having accurate knowledge of the influence of the molecular structure on the properties determined, the composition of the oils and the alcohol used can both be selected to give the optimal performance.

ACKNOWLEDGMENTS

REFERENCES

1. Schuchardt, U., R. Sercheli, and R.M. Vargas, Transesterification of Vegetable Oils: A Review, *J. Braz. Chem. Soc.* 9:199–210 (1998).
2. Dunn, R.O., Thermal Analysis of Alternative Diesel Fuels from Vegetable Oils, *J. Am. Oil. Chem. Soc.* 76:109–115 (1999).
3. Geller, D.P., and J.W. Goodrum, Rheology of Vegetable Oil Analogs and Triglycerides, *J. Am. Oil. Chem. Soc.* 77:111–114 (2000).
4. Lee, I., L.A. Johnson, and E.G. Hammond, Use of Branched-Chain Esters to Reduce the Crystallization Temperature of Biodiesel, *J. Am. Oil. Chem. Soc.* 72:1155–1160 (1995).
5. Srivastava, A., and R. Prasad, Rheological Behaviour of Fatty Acid Methyl Esters, *Indian J. Chem. Technol.* 8:473–481 (2001).
6. Ma, F., and M.A. Hanna, Biodiesel Production: A Review, *Bioresour. Technol.* 70:1–15 (1999).
7. Nascimento, R.S.V., V.L.P. Soares, S. Albinante, and L.R. Barreto, Effect of Ester-Additives on the Crystallization Temperature of Methyl Hexadecanoate, *J. Therm. Anal. Cal.* 79:249–254 (2005).
8. Lowitz, D., and J. Spencer, Temperature–Pressure Effects on the Viscosity of Several Higher Hydrocarbons, *J. Chem. Phys.* 30:73–83 (1959).
9. Friedheim, J.E., and Conn, H.L., Second-Generation Synthetic Drilling Fluids, *J. Pet. Technol.* 49:724–728 (1997).
10. Cebula, D.J., and K.W. Smith, Differential Scanning Calorimetry of Confectionery Fats–Pure Triglycerides—Effects of Cooling and Heating Rate Variation, *J. Am. Oil. Chem. Soc.* 68:591–595 (1991).
11. Weast, R.C. (ed.), *Handbook of Chemistry and Physics*, 49th edn., CRC Press, Cleveland, OH, 1969, Section D, pp. 190–191.