Ester-additives as inhibitors of the gelification of soybean oil methyl esters in biodiesel

Vera L. P. Soares · Regina S. V. Nascimento · Sandra R. Albinante

Abstract Biodiesel from soybean oil transesterified with methanol (TSO) becomes viscous and gelifies at low storage temperatures which makes it difficult to pump. To inhibit this behaviour bulky esters were added to reduce the crystallization temperature of TSO and to modify the rate of conversion of crystallized mass. This rate was found to follow a JMAK kinetic model. The Avrami's parameter n was constant for TSO, while two n values were found for TSO-additive solutions, meaning that the additives first slowed down the rate of nucleation and, later on as enough nuclei had been formed, crystal growth rate dominated and the previous crystallization rate was recovered.

Keywords Soybean oil methyl ester · Biodiesel · Crystallization kinetics · DSC · Cyclohexyl ester · Pentaerythrityl ester

Introduction

Due to its good fuel properties and biodegradability [1] soybean oil transesterified with methanol (TSO) is currently used as biodiesel in order to substitute diesel oil. However, after long period of storage at temperatures below 0 °C TSO becomes viscous and tends to gelify and solidify. This leads to handling difficulties and to increased operational costs. The main components of TSO are 10–15% of methyl hexadecanoate (methyl palmitate), 3% of methyl octadecanoate (methyl stearate) and about 85% of methyl esters of unsaturated fatty acids of 18 carbon atoms [2]. As methyl hexadecanoate and octadecanoate solidify at 30 and 45 °C, respectively, it is probable that at low temperatures these components would preferentially come out of solution. One possibility to increase the fluidity of trasesterified soybean oil at low temperatures (−5 °C) is the gradual cooling of the oil followed by filtration of the precipitated solids [3]. Another solution employed to inhibit crystallization of solutions is the addition of substances able to prevent the agglomeration and the consequent crystallization of solution components. Cristallization inhibition by mixture of additives having branched or cyclic chains has been demonstrated by several authors [4–6]. For example, Lang et al. [5] reported a reduction in the crystallization temperature of biodiesel by as much as 4 °C by the addition of a mixture of fatty esters of branched chain alcohols. Another class of ester-additives to modify the properties of TSO due to its bulkness is the use of polyhydroxylated alcohols [7]. However, the evaluation of the effect of each individual ester on the pour point or on the temperature of crystallization of soybean oil transesterified with methanol (TSO) is not discussed in these works, which makes difficult to evaluate the influence of structural features such as chain size and unsaturation. The effect of the acid chain size of esters on the crystallization temperature of methyl hexadecanoate (palmitate) has been demonstrated by the present authors in [8]. Esters derived from linear or branched chain acids having 8–16 carbon atoms and branched or cyclic alcohols were capable to reduce crystallization temperatures of melted methyl hexadecanoate by as much as 12 °C as measured by differential scanning calorimetry (DSC). The best results were achieved with cyclohexyl hexadecanoate and 2-ethyl-hexyl hexadecanoate. DSC is a

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very useful technique to measure the thermal behaviour of modified vegetable oils [9, 10].

In order to be effective in inhibiting crystallization the added substance must have special features such as (a) a structural similarity with the target substances in order to favour the required interaction with it, and (b) bulky groups that would prevent the formation of an organized structure, keeping the target substances in the liquid state. The nucleation of crystals that precedes crystallization is dependent on the formation and growth of aggregates or clusters of molecules. These aggregates must overcome a critical size in order to keep a steady growth and become a crystal of detectable dimensions [11, 12]. At the stage of crystal growth, molecules of solute adsorb on the crystal surface and the process depends on the diffusion of material from the liquid phase to the solid phase which is being formed. Any of these stages can control crystal growth. The added substance must be capable to interfere with one of these stages: either avoiding or delaying the growing of aggregates to a critical size or reducing crystal growth rate [13].

In the present work several esters derived from branched chain, cyclic monohydroxylated alcohols or polyhydroxylated alcohols were added to methyl transesterifed soybean oil (TSO) to investigate their effect on the TSO crystallization behaviour monitored by DSC. Kinetic studies were conducted in order to detect differences in crystallization mechanisms due to differences in additive structures.

Experimental

Materials

The reagents and respective suppliers used in this work were: nonanoic (pelargonic) acid: Aldrich, USA, (cis) octadec-9-enoic (oleic) acid: Aldrich, USA, tetra-(hydroxymethyl)-methane (pentaerythritol): Aldrich, USA, 2-ethyl-2-(hydroxymethyl)-1,3-propanediol (trimethylolpropane): Aldrich, USA, dodecanoic (lauric) acid: Vetec S.A., Brazil, hexadecanoic (palmitic) acid: Vetec S.A., Brazil, methanol and catalyst p-toluyl-sulfonic acid: Vetec S.A., Brazil, and 3-ethyl-butano: Isofar, Brazil.

The alcohols and acids had 98% purity as indicated by their suppliers. Cyclohexanol and 3-ethyl-butanol were distilled before being used. The methyl-transesterified soybean oil (TSO) was supplied by Miracema-Nuodex S.A., Brazil. The purity of all reagents was checked by infrared spectrometry and chromatography as described below.

Preparation of esters

The esters of monohydroxylated alcohols listed in Table 1 were prepared for this work as described in [8]. Product

Table 1 Purity of esters from monohydroxylated alcohols by GC-MS and respective codes

Esters of monoalcohols	Codes	MM (g/mol)	Purity (%)
(3-ethyl)butyl nonanoate	C9ISA	228	95,5
(3-ethyl)butyl dodecanoate	C12ISA	270	95,5
Cyclohexyl nonanoate	C9Cyclo	240	97,8
Cyclohexyl dodecanoate	C12Cyclo	282	98,5

purity was monitored by gas chromatography with a mass detector (Agilent Thecnologies model GC6850/MS 597). The employed conditions were: a 30 m column of methylsiloxane, $d_i = 0.33$ mm, stationary phase film $= 0.25$ μm; and a heating program from 50 °C up to 250 °C at 10 °C/min.

For the preparation of polyhydroxylated alcohol esters the reagents were mixed in stoichiometric proportion of functional groups, considering the alcohol functionality of 3 or 4, followed by the addition of catalyst p-toluyl-sulfonic acid (2% mass/mass in relation to acid mass) and 100 mL of toluene. The solutions were refluxed for 4 h and a Dean-Stark apparatus was adapted for the azeotropic distillation of water. The reaction was monitored by size exclusion chromatography (SEC) in a Waters equipment provided with a refractive index detector using three polystyrene columns in series having porosities 50, 100 and 500 Å. The products were washed with water to eliminate the catalyst and any unreacted alcohol, then, washed with a 10% aqueous solution of sodium carbonate to eliminate unreacted acid and, finally, dried with anhydrous magnesium sulfate. Toluene was distilled at reduced pressure. The esters were characterized by FTIR spectrometry using a Nicolet Magna 750, by ^{1}H and ^{13}C NMR spectrometry in a Brucker, model Avance 200, at 200 MHz and 50 MHz frequencies, respectively, in CDCl$_3$ solutions. These esters are listed in Table 2.

Induction time measured visually

In order to visualize the formation of solids or gel from TSO at sub-ambient temperatures, flasks with samples of soybean oils and soybean oil solutions with ester-additives were introduced in a water-salt bath kept at -3 ± 0.5 °C. These measurements were conducted in duplicate.

DSC Measurements

Solutions containing 100 g of methyl-transesterified soybean oil (TSO) and 0.02, 0.04, or 0.08 moles of the additives were prepared for both dynamic and isothermal modes of DSC analysis. These molar proportions corresponded approximately to 5, 10 and 20% mass/mass solutions, respectively, of ester-additives derived from

Table 2 Esters from poyhydroxylated alcohols and their purity by SEC

Esters of poyhydroxylated alcohols	Codes	MM (g/mol)[a]	Purity (%) Mono:di:tri
Nonanoate of 2-ethyl-2-(hydroxymethyl)-1,3 propanediol	C9TMP	568	34:65.7:0.3
Laurate of 2-ethyl-2-(hydroxymethyl)-1,3 propanediol	C12TMP	694	5.4:23.3:71.3
Nonanoate of tetra-(hydroxymethyl) methaned	C9PER	696	9.7:41.3:49

[a] Average MM from SEC data

monohydroxylated alcohol (see Table 1) and to 13, 26 and 54% mass/mass of the higher mass additives derived from polyhydroxylated alcohols (see Table 2). The instrument (PerkinElmer, model DSC-7) was calibrated at sub-ambient temperatures with organic compounds (cyclohexane, m.p. 6.5 °C and dodecane, m.p.−9.6 °C).

The dynamic DSC analyses were conducted in duplicate with 1.5–2.0 mg of sample. The crystallization temperatures (T_c) were determined under N_2 atmosphere, after a first run from 0 °C to 30 °C at a heating rate of 10 K min^{-1}, followed by cooling down to −20 °C at the same rate. Deviations of T_c measurements at onset varied from 0.05 up to 0.6 °C. The induction times for crystallization were determined isothermally at −3, −4, −4.5, −5 and −6 °C. These temperatures were reached after a first run from 0 °C to 30 °C at a heating rate of 10 K min^{-1} followed by cooling at 10 K min^{-1} from 30 °C down to the chosen temperature. The experiments were conducted in duplicate or triplicate with sample masses varying between 9.0 and 10.0 mg prepared with 0.02% mol/mass TSO solutions of the additives C12ISA, C12cyclo, or C9PER. The induction time deviations were around 5% for low induction times values (about 10 min) and 10% for high induction times (about 130 min).

The kinetic treatment of DSC curves was applied for TSO and TSO solutions with the additives C12ISA and C9PER. The fraction of crystallized mass $\alpha(t)$ was calculated taking $\alpha(t) = \Delta H(t)/\Delta H(\text{total})$. The enthalpy data were obtained by dividing the curve of thermal processing into equal slices and integrating the ΔH values for each subsequent time. The graphs of α versus time gave S-shaped curves shown in Fig. 5. In order to determine the $(f(\alpha))$ function that best describes the S-shaped curve the α versus $d\alpha/dt$ plot drawn with the experimental data was compared with the curves plotted with equations from several kinetic models considering that $d\alpha/dt = k(T)f(\alpha)$ where: α = fraction crystallized; t = processing time; $f(\alpha)$ = function to be determined and k = a temperature dependent rate constant.

Results and discussion

The effect of additives on TSO crystallization was initially verified by observing with the naked eye the behaviour

of TSO and its solutions in a water-salt bath kept at −3.5 ± 0.5 °C. Visually the TSO became viscous after 30 min and gelified soon after. At these same conditions the TSO solutions with additives started to become viscous only after 90 min keeping certain fluidity without gelifying.

Effect of additives on TSO crystallization temperature

The crystallization of TSO occurs in a wide temperature range showing two main peaks partially overlapped as shown in Fig. 1. The onset of crystallization was found to occur at −6.1 ± 0.6 °C. The reduction of TSO crystallization temperature caused by the addidtives is also illustrated in this figure. In general all additives were able to reduce the crystallization temperature (T_c) of TSO depending on the type of additive and its concentration as shown in Table 3. These additives do not differ greatly in their capacity to reduce T_c of TSO if one considers their molar concentration. However, if mass concentrations are considered, the esters from polyhydroxylated alcohols are less effective in a mass/mass basis as they have a higher molecular mass. A small effect of chain length on T_c's was registered, as previously for the system containing ester-additives in melted methyl hexadecanoate [8].
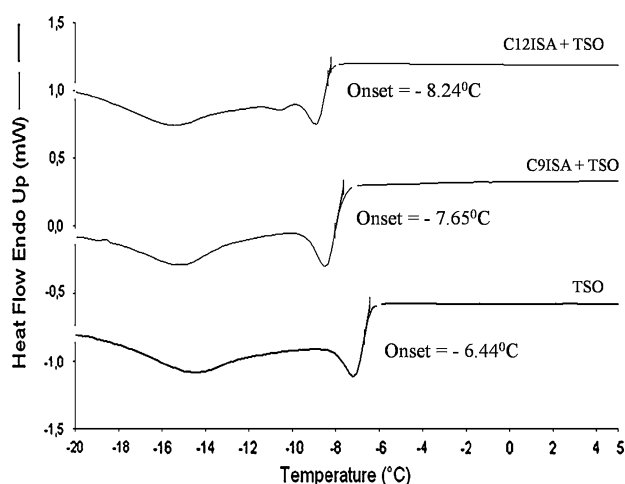

Fig. 1 DSC curves of TSO and TSO-0.02% additives showing T_c's at onset

Table 3 Onset crystallization temperature for TSO with additives at different concentrations from DSC curves

Additive	Additives code	Crystallization temperature of TSO with additives (°C)		
		Additive concentration (mol/100 g TSO)		
		0.02	0.04	0.08
Cyclo-hexyl nonanoate	C9Cyclo	−7.10 ± 0.02	−7.9 ± 0.2	−9.5 ± 0.6
Cyclo-hexyl dodecanoate	C12Cyclo	−7.3 ± 0.2	−8.10 ± 0.02	−8.80 ± 0.02
3-methyl-butyl nonanoate	C9ISA	−7.6 ± 0.1	−8.2 ± 0.2	−10.0 ± 0.6
3-methyl-butyl dodecanoate	C12ISA	−8.2 ± 0.1	−8.80 ± 0.01	−10.3 ± 0.2
(trimethylol)propanyl nonanoate	C9TMP	−6.7 ± 0.4	−8.1 ± 0.3	−10.6 ± 0.1
(trimethylol)propanyl dodecanoate	C12TMP	−6.8 ± 0.5	−8.10 ± 0.02	−11.8 ± 0.1
Pentaerythrityl nonanoate	C9PER	−6.7 ± 0.3	−8.80 ± 0.02	−10.60 ± 0.05
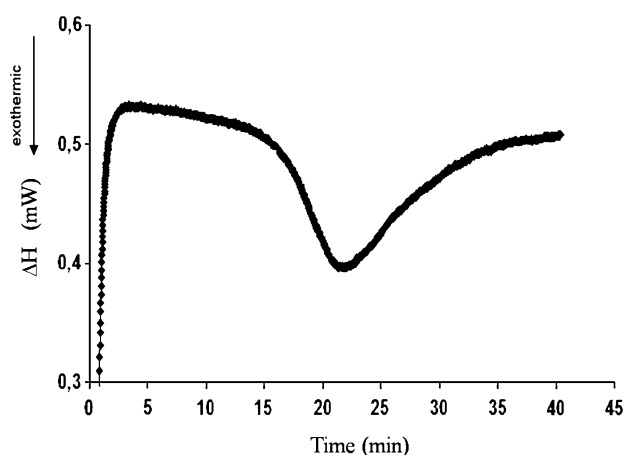
Fig. 2 DSC curve for TSO at −4.5 °C
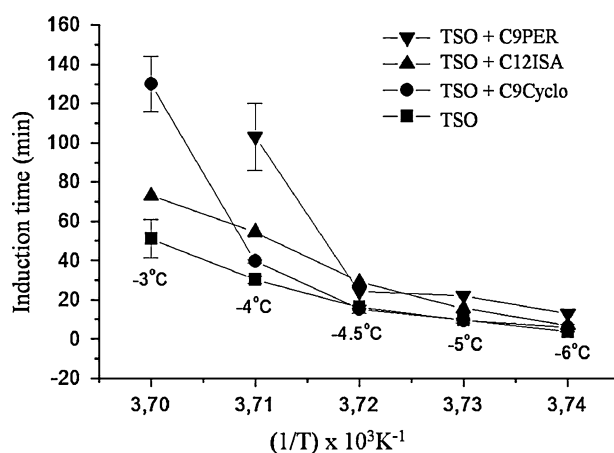
Fig. 3 Effect of temperature on induction times for crystallization of TSO with 0.02% of additives

Effect of additives on TSO induction times

The induction times for crystallization were determined from DSC curves in experiments conducted isothermally (Fig. 2) and plotted versus inverse of temperature (Fig. 3). As expected, smaller induction times occurred at lower temperatures. It took 50 min for TSO without additives to solidify at −3 °C and a very few minutes at −6 °C. The induction times obtained for TSO followed a linear behaviour with temperature in this range. The addition of C12ISA (or C9ISA) increased the induction times while keeping a certain linearity with temperature, but moving this line upward. The other two additives, one derived from a cyclic alcohol (C9cyclo) and the other from a poly-hydroxylated alcohol (C9PER), modified this linear behaviour and more than doubled TSO crystallization induction times at −4.0 and −3.0 °C.

Kinetic studies

There are several well established methods to describe overall crystallization kinetics. The Avrami theory is

widely used for this description together with the ones developed by Jonhson, Mehl and Kolmorov that are sometimes called JMAK equations [13]. These kinetic models describe how the extension of the phase transformation of a given material occurs as a function of time and temperature. Their equation is based on the suppositions of isothermal condition of crystallization, aleatory homogeneous or heterogeneous nucleation and that the new phase growth rate is temperature dependent.

Avrami admitted that a number of tiny nuclei (aggregates of subcritical size) are already present in the phase to be transformed and that these aggregates must grow to a critical size to start a steady growth. By simplifying his statistical treatment presented in the calculation of transformed matter, he came to the generalized expression:

$$\alpha = 1 - \exp(-kt^n) \tag{1}$$

where α is the volume fraction transformed (crystallized mass); k is dependent on a shape factor, on nucleation probability, on nucleation *and* growth rates and on the dimensionality of crystal growth while n reflects the

Fig. 4 Rate of formation of crystallized mass α isothermally for **a** TSO, **b** TSO + C12ISA
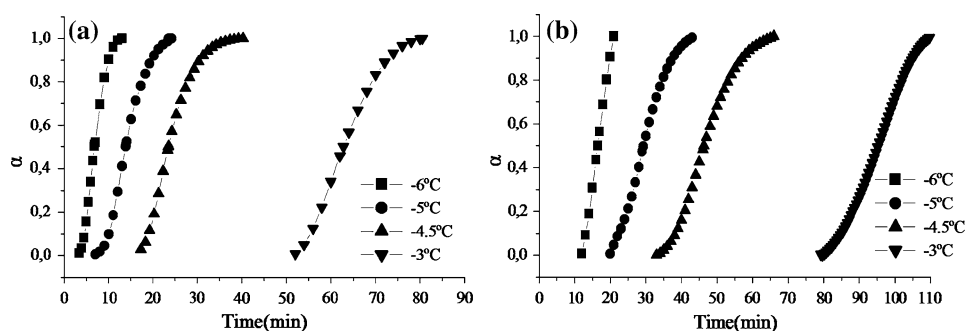
mechanism of nucleation and growth and the crystal morphology [11, 12].

The equation for the overall rate of crystallization results from differentiating Eq. 1 in relation to time:

$$d\alpha/dt = kn(1 - \alpha)[-\ln(1 - \alpha)]^{(n-1)/n}, \qquad (2)$$

also known as a JMAK equation. Avrami parameters k and n can be determined from the slope of the $\ln[-\ln(1 - \alpha(t))]$ versus $\ln(t)$ plot that corresponds to linearization of Eq. 1.

The fraction α of crystallized material calculated from enthalpy data was plotted versus time giving the S-shaped curves that are shown in Fig. 4. These S-shaped α–t curves, as temperature decreased, became very steep, almost becoming a straight line. This suggests that at the chosen conditions the number of aggregates of critical size were large and crystal growth was dominating.

The experimental graph of dα/dt versus α gave a good agreement with the curve plotted employing Eq. 2, as shown in Fig. 5.

The values obtained for parameter n (Fig. 6) based on TSO crystallization curves with no additives did not vary with temperature and stayed around 1.6. The interpretation of this value is not straightforward because by the equations in Avrami's model this value not only corresponds to
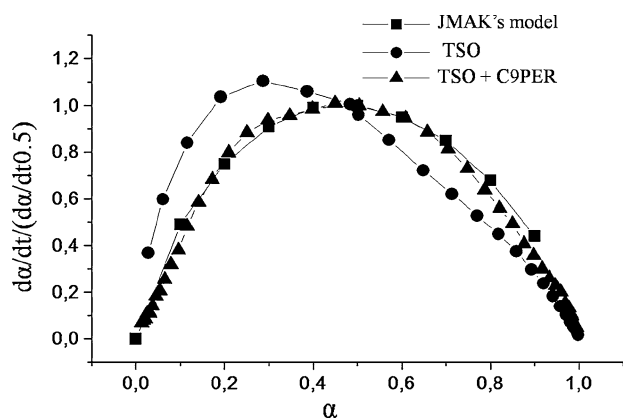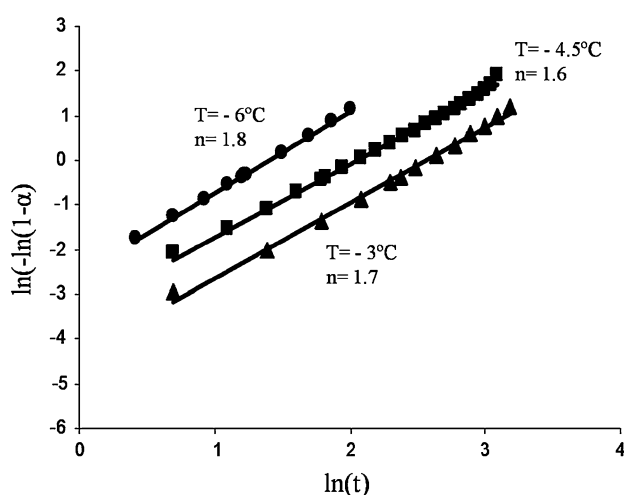

Fig. 6 Determination of parameter n from TSO data at different temperatures

a linear crystal growth with a constant nucleation but also to a bidimensional growth under instantaneous nucleation. The importance of discussing this parameter lies in the modification observed when esters were added.

The linearized curves drawn from the crystallization data of TSO solutions (Fig. 7) at −3 and down to −5 °C presented two segments, while at −6 °C only one segment was observed. This resulted in two n-values for each of the −3 to −5 curves and a single n-value for the −6 curve. The first n ranged from 0.6 to 0.9, while the second value was higher. The lower n value was interpreted as due to the effect of additives on the first steps of the crystallization mechanism. Additives could have slowed down the rate of formation of aggregates (nuclei) of critical size, affecting the overall rate of crystallization. Later on, as enough aggregates of critical size had been formed, crystal growth rate dominated and the previous crystallization rate was observed ($n > 1$). At the temperature of maximum nucleation rate (−6 °C) only one line resulted ($n = 1.3$) showing that at this temperature the additive had a less effect in overall crystallization rate.

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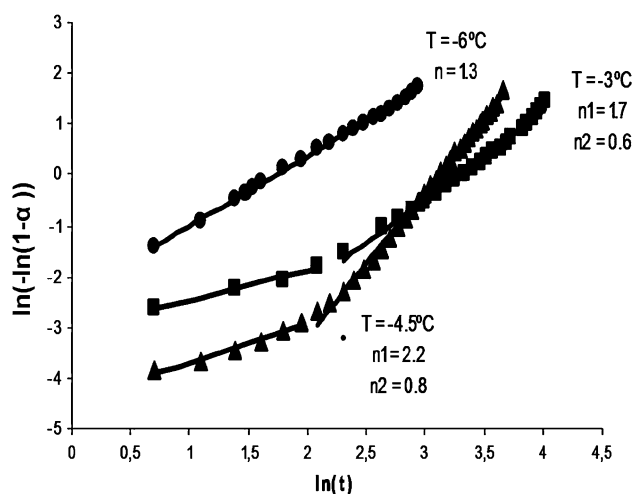

Fig. 5 Rate of mass conversion of TSO with and without additive (at −4.5 °C) compared to the theoretical curve given by the JMAK equation

Fig. 7 Determination of parameter n from TSO-C9PER data at different temperatures

presented two segments, while at −6 °C only one segment was observed. This resulted in two *n*-values for each of the −3 to −5 curves and a single n-value for the −6 curve. The first *n* ranged from 0.6 to 0.9, while the second value was higher. The lower *n* value was interpreted as due to the effect of additives on the first steps of the crystallization mechanism. Additives could have slowed down the rate of formation of aggregates (nuclei) of critical size, affecting the overall rate of crystallization. Later on, as enough aggregates of critical size had been formed, crystal growth rate dominated and the previous crystallization rate was observed (*n* > 1). At the temperature of maximum nucleation rate (−6 °C) only one line resulted (*n* = 1.3) showing that at this temperature the additive had a smaller effect in overall crystallization rate.

The shape of the α–t curve of TSO containing pentaeritrityl nonanoate (C9PER) was visibly much less steep at higher temperature (−3 °C). This could indicate that, in this case, not only the nucleation rate was being affected but also the crystal growth rate. It has been shown that this additive increases TSO viscosity [14] at higher temperatures, suggesting that this is another important variable to be considered in crystallization inhibition.

Conclusions

All ester-additives investigated lowered the crystallization temperature of TSO, the reduction achieved depended on additive concentration. In the conditions studied, it was possible to double the induction time for the crystallization of soybean–biodiesel at −3 °C.

The kinetic of mass crystallization in methyl transesterified soybean followed the JMAK model. The Avrami′s parameter *n* indicated a constant overall crystallization rate for TSO without additives, at the range of temperatures investigated. The additives modified this behaviour by interfering with first stage of the crystallization process— the formation of aggregates of critical size. This influence was limited to the temperatures below that of maximum nucleation rate.

The larger effect of additive C9PER on induction time at a higher temperature may be related to its capability to increase medium viscosity [14] and must be studied further.

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