CHEMICAL ENGINEERING TRANSACTIONS

VOL. 43, 2015

A publication of AIDIC

The Italian Association of Chemical Engineering
Online at www.aidic.it/cet

Chief Editors: Sauro Pierucci, Jiří J. Klemeš

ISBN 978-88-95608-34-1; **ISSN** 2283-9216

DOI: 10.3303/CET1543080

Characterization of Precipitate Formed Above and Below the Cloud Point of Palm Oil Biodiesel

Liliana Mendoza, Vladimir Plata*, Paola Gauthier-Maradei, Fredy Avellaneda

INTERFASE, Universidad Industrial de Santander, Carrera 27 calle 9, Bucaramanga, Colombia
vladimirplata@gmail.com

Annual biodiesel production has increased due to policies that promote the use of alternative and renewable energy; however, precipitate formation well above the cloud point temperature has limited biodiesel acceptance. Precipitate formation is expected to be accelerated when biodiesel is subjected to low temperatures. However, temperature may affect not only the amount of precipitate but also its physical and chemical nature. Therefore, the nature of precipitate formed above and below the cloud point of palm oil biodiesel (POB) was investigated in this study. POB was incubated at 18 and 4 °C for 16 h and then analyzed to determine the precipitate content and the cold soak filtration time (CSFT) in accordance with the ASTM D7321 and D7501 Standard Tests Methods. Precipitate was isolated and then analyzed using SEM/EDS, FTIR, and DSC. SEM analyses revealed that precipitates isolated from these biodiesels were physically equal. Although differing from each other in their elemental composition, corrugate spherical structures incorporated into a network of snowflake-like structures surrounded by amorphous structures were observed in the precipitates. FTIR spectra suggested that the precipitates were composed of the same compounds, namely FSG and monoglycerides. However, peaks characteristic of FSG were more intense in the spectrum of the precipitate formed at 4 °C. Crystallization and melting profiles obtained by DSC were similar to each other; however, crystallization and melting temperatures and enthalpies of crystallization and fusion were lower for the precipitate formed at 18 °C. Thus, the nature of POB precipitate was not found to be significantly affected by temperature because there were no marked differences in morphology, chemical constitution, and thermal profile between precipitates formed above and below the cloud point.

1. Introduction

Annual biodiesel production has increased due to policies that promote the use of alternative and renewable energy; however, precipitate formation well above the cloud point temperature has limited biodiesel acceptance, especially of palm oil biodiesel (POB) (Plata et al., 2012). Cloud point depends mainly on biodiesel composition. The higher the saturated fatty esters content, the higher the cloud point. POB is characterized by a high percentage of saturates (49.5 wt%, Plata et al., 2015a), thereby causing the cloud point to be around 14 °C (Dunn, 2009).

Precipitate formation has been related to the presence of minor components with different polarity and low solubility in biodiesel such as saturated monoglycerides and free steryl glucosides (FSG) (Tang et al., 2008). Since precipitate has caused plugging of fuel filters in engine fuel delivery systems and formed deposits on engine injectors, the American Society for Testing and Materials (ASTM) developed a cold soak filtration test in an effort to address the fuel filter plugging potential of biodiesel. This test, denominated as the ASTM D7501 Standard Test Method, was intended to determine if biodiesel is sufficiently free of precipitate capable of plugging fuel filters. ASTM D6751 Standard Specification requires that biodiesel have a cold soak filtration time (CSFT) below 360 s.

Precipitate formation is expected to be accelerated when biodiesel is subjected to low temperatures with a concomitant increase in CSFT. However, depending on the precipitate size and shape, plugging of the glass microfiber filter may occur during the cold soak filtration test. This may result in CSFT well above the ASTM

Please cite this article as: Mendoza Florez L.C., Plata V., Gauthier P.M., Avellaneda F., 2015, Characterization of precipitate formed above and below the cloud point of palm oil biodiesel, Chemical Engineering Transactions, 43, 475-480 DOI: 10.3303/CET1543080

limit, even though a small amount of precipitate has been formed during cold soak (Chupka et al., 2012). In addition, temperature may affect not only the amount of precipitate but also its nature. Precipitate formed above the cloud point of soybean oil biodiesel was found to be apparently different in nature from that formed below the cloud point (Tang et al., 2008). Therefore, the primary objective of this study was to investigate the effect of temperature on the nature of POB precipitate formed above and below the cloud point. A related objective was to investigate the effect of temperature on the precipitate content and CSFT.

2. Materials and methods

2.1 Materials

POB was supplied by Ecodiesel Colombia S.A. (Barrancabermeja, Colombia). The POB was obtained dynamically from a sampling loop in a distribution line in the processing facility. All solvents were Carlo Erba Reagents (Milan, Italy) ACS reagent grade. Monopalmitin standard was obtained from Nu-Chek Prep, Inc. (Elysian, MN) and was reported to be >99 % pure. FSG standard mixture was obtained from Matreya LLC. (Pleasant Gap, PA) and was reported to be >98 % pure.

2.2 Sample conditioning

POB was manually agitated for 5 min in accordance with the European Standard EN 12662 before withdrawing 300 mL samples. Each sample was placed in 500 mL bottles, then heated for 3 h at 40 °C under a dry nitrogen atmosphere to erase the thermal history of the sample, and then allowed to stand for 24 h at 25 °C before soaking at 18 or 4 °C for 16 h. 4 °C was chosen in accordance with the ASTM D7501, and 18 °C was chosen to improve our understanding of the temperature effect on the nature of POB precipitate formed above and below the cloud point.

2.3 Cold soak filtration test and isolation of precipitates

After soaking, the samples were allowed to warm to 25 °C and held at this temperature for 4 h. Some samples were then tested for CSFT in accordance with the ASTM D7501, and some samples were centrifuged as described below. Samples tested for CSFT were filtered through a 0.7 µm glass microfiber filter (Whatman GF/F, 47 mm diameter, Piscataway, NJ) under 70 to 80 kPa below atmospheric pressure. The filtration proceeded until all biodiesel had passed through the filter, in contrast to the ASTM D7501 where filtration is stopped after 720 s. The time required for the biodiesel to pass through the filter was recorded as CSFT. The precipitate content was determined in accordance with the ASTM D7321 Standard Test Method. Centrifugation was performed at 35 s^{-1} and 15 °C for 15 min. The POB supernatant was discarded, and 10 mL of hexane were added to the centrifugation tube to remove any excess biodiesel from the precipitate concentrated on the tube bottom. The precipitate was then centrifuged as described above, and the hexane supernatant was discarded. The precipitate was washed two more times, and then dried in an oven at 55 °C for 30 min to remove any excess hexane. The precipitate isolated from POB incubated at 4 °C was denominated as Hz1 and the precipitate isolated from POB incubated at 18 °C was denominated as Hz2.

2.4 Characterization

FTIR spectra were obtained using a Bruker Tensor 27 spectrometer equipped with an attenuated total reflectance (ATR) sampling accessory (with diamond crystal). All the spectra were obtained in the wavenumber range of 4000 to 400 cm^{-1} using an average of 16 scans, with a spectral resolution of 4 cm^{-1}, and air as the background.

DSC curves were obtained using a TA instrument model DSC Q10. Nitrogen as purge gas was passed through the measurement cell at 50 mL min^{-1}. Each sample (~ 5 mg) was sealed in aluminum Tzero pans, and an empty pan was used as reference. The samples were equilibrated at 20 °C for 1 min, and then heated at 5 °C min^{-1} to 110 °C. After remaining at this temperature for 1 min, the samples were cooled to -10 °C at the same rate, then held isothermally for 1 min, and then reheated to 110 °C at the same rate.

SEM/EDS analyses were performed on a Quanta 650 FEG equipment with 10 kV and magnification of up to 5000x.

3. Results and discussion

3.1 Influence of temperature on the precipitate content and CSFT

Investigating the effect of temperature on the nature of POB precipitate formed above and below the cloud point was the primary objective of this study. Investigating the effect of temperature on the precipitate content and CSFT was a related objective. As depicted in Figure 1, the precipitate content of POB incubated at 4 °C was more than two-fold higher than that of POB incubated at 18 °C, confirming that temperature has a marked effect on biodiesel precipitate formation. CSFT of POB incubated at 4 °C was also markedly higher. The increase in CSFT was most probably due to the increase in the precipitate content. This was consistent with Tang et al. (2008) in their finding that the precipitate content and CSFT of biodiesel from several feedstocks markedly increased with decreasing temperature.

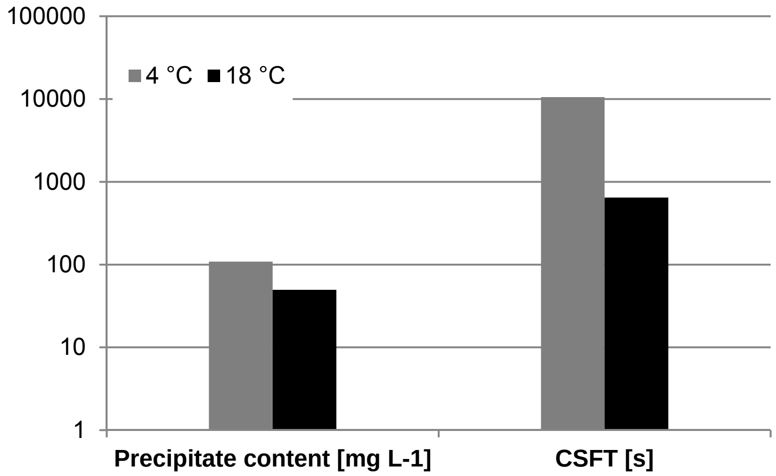

Figure 1: precipitate content and cold soak filtration time (CSFT) of palm oil biodiesel incubated at 4 or 18 °C for 16 h

3.2 Characterization

FTIR spectra of the precipitates were quite similar to each other. This suggested that the same compounds were present in both precipitates (Figure 2). In general, the same absorption peaks were observed in the spectra. A broad –OH stretching peak (3384 cm^{-1}) and peaks attributable to asymmetric and symmetric stretching of C–O–C (1262 and 1018 cm^{-1}) and asymmetric stretching of O–C–C in the glucoside moiety (1168 cm^{-1}), characteristic of FSG (Figure 3), indicated the presence of FSG in both precipitates. In addition, even though a doublet of –OH stretching peak was not observed in the spectra, and the series of strong peaks due to twisting and wagging bending of $–CH_2$ was apparently absent from the region referred as the "finger-print" (1300 to 900 cm^{-1}), the strong peaks due to $–CH_2$ asymmetric and symmetric stretching (2915 and 2850 cm^{-1}), –C=O stretching (1730 cm^{-1}), and $–CH_2$ rocking bending (719 cm^{-1}), characteristic of monoglycerides (Figure 3), indicated the presence of monoglycerides in both precipitates. This was consistent with Plata et al. (2015b) in their finding that POB precipitate is mostly composed of FSG and saturated monoglycerides, especially monopalmitin.

The aforementioned peaks, however, were more intense in the spectrum of Hz1, indicating that Hz1 contained a higher amount of FSG and monoglycerides. The limited solubility of FSG in POB (56 mg L^{-1} at 20 °C, Bondioli et al., 2008) was probably reduced to an even lower value by the reduction in temperature, more FSG being able to act as nucleators for precipitate formation. Similarly, the solubility of monoglycerides was probably reduced. Thus, more FSG and monoglycerides may have interacted to form the precipitate, and this may has been the cause for the increase in the precipitate content noted above. In summary, temperature was not found to have significant influence on the chemical constitution of POB precipitate, i.e. precipitates were composed of the same compounds, but on the concentration of precipitate constituents, i.e. precipitate formed below the cloud point contained a higher amount of FSG and monoglycerides.

DSC curves of the precipitates were also similar to each other (Figure 4). In general, a broad endothermic peak was observed during the heating step, followed by a series of exothermic peaks during the cooling step and a broad endothermic peak during the reheating step. This peak was similar to that observed during the heating step, which most probably corresponded to melting of the α form of the saturated monoglycerides present in both precipitates. Saturated monoglycerides may exist in several polymorphs, namely sub-α, α, and β forms (Vereecken et al., 2009); however, they precipitate in the α form in biodiesel and transform into the β form only after long-term storage (Chupka et al. 2011).

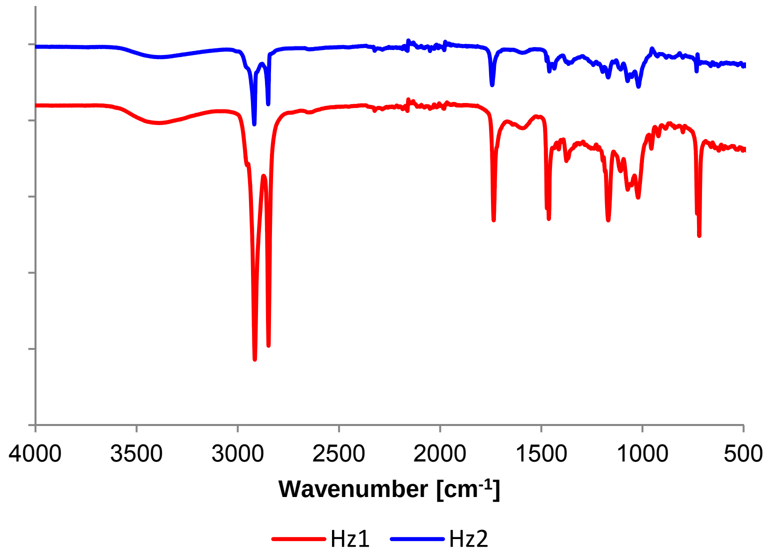

Figure 2: FTIR spectra of precipitate isolated from palm oil biodiesel incubated at 4 °C (Hz1) or 18 °C (Hz2) in the wavenumber range of 4000-400 cm^{-1}

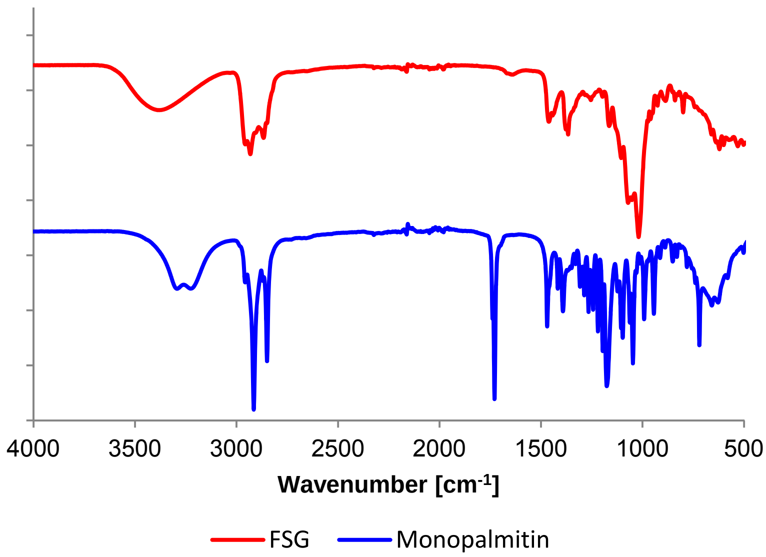

Figure 3: FTIR spectra of the FSG and monopalmitin standards in the wavenumber range of 4000-400 cm^{-1}

When sufficiently cooled, the α form undergo a polymorphic transition to the sub-α form (Vereecken et al., 2009). This is consistent with the series of exothermic peaks observed during the cooling step in the DSC curves. These peaks, however, were sharper for Hz1 than for Hz2. In addition, crystallization and melting temperatures along with enthalpies of crystallization and fusion differed between the precipitates. These differences in crystallization and melting behavior were consistent with the fact that the precipitates did not contain the same amount of FSG, as noted above. When present, impurities displace DSC peak temperatures (Romain et al., 2013) and affect enthalpies of crystallization and fusion (Vereecken et al., 2009). Therefore, temperature was not found to have significant influence on the overall thermal behavior of POB precipitate, but on crystallization and melting temperatures and enthalpies of crystallization and fusion.

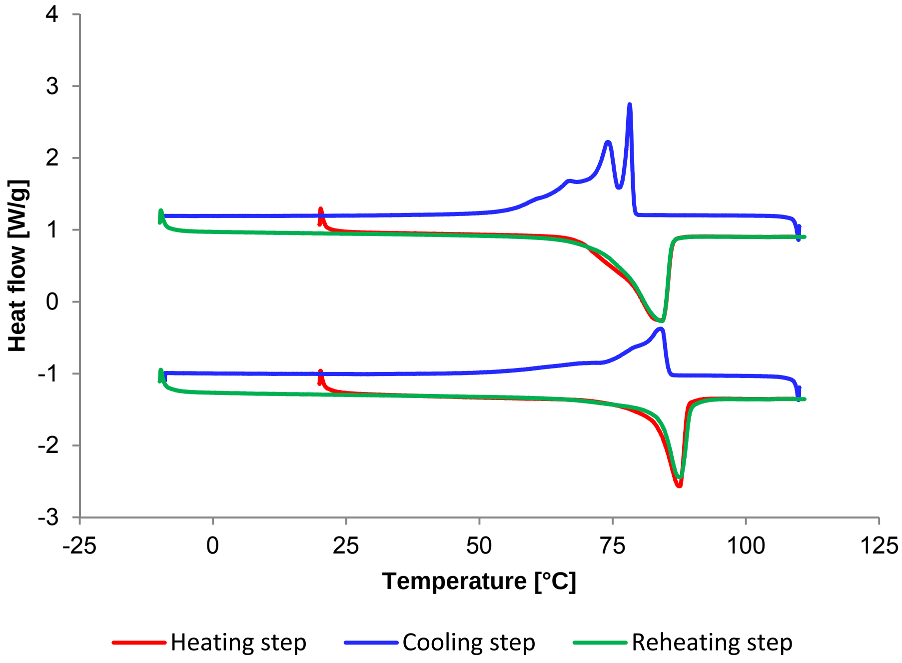

Figure 4: DSC curves of precipitate isolated from palm oil biodiesel incubated at 4 °C (Hz1, up) or 18 °C (Hz2, down)

SEM analyses revealed that the precipitates were physically equal (Figure 5). Corrugate spherical structures incorporated into a network of snowflake-like structures surrounded by amorphous structures were observed in both precipitates. EDS analyses revealed the preponderance of carbon and oxygen. Sodium was also found in the spherical structures, indicating the presence of fatty acid soaps in the precipitates. Fatty acid soaps have been demonstrated to contribute to precipitate formation because of their low solubility in biodiesel and the possibility of interacting with glycerin and glyceride species to generate a colloidal (Lin et al., 2011). When present in biodiesel feedstock, free fatty acids neutralize alkali catalyst (usually sodium methoxide) resulting in formation of fatty acids soaps (Dunn et al., 2009).

Average elemental composition of the snowflake-like structures (95 wt% C, 5 wt% O) was similar to that of monopalmitin (92 wt% C, 8 wt% O) while average elemental composition of the amorphous structures (80 wt% C, 20 wt% 0) was similar to that of β sitosteryl glucoside (83 wt% C, 17 wt%). β sitosteryl glucoside is the major FSG found in POB (Van Hoed at el., 2008). Thus, interaction of FSG, monoglycerides, and fatty acid soaps was found to result in complex networks of structures possessing different chemical composition and morphology. However, temperature was not found to have significant influence on these properties.

4. Conclusions

The precipitate content and CSFT of POB incubated at 4 °C were markedly higher than those of POB incubated at 18 °C, confirming that temperature has a marked effect on biodiesel precipitate formation. SEM analyses revealed that precipitates isolated from these biodiesels were physically equal. Although differing from each other in their elemental composition, corrugate spherical structures incorporated into a network of snowflake-like structures surrounded by amorphous structures were observed in the precipitates. FTIR spectra suggested that the precipitates were composed of the same compounds, namely FSG and monoglycerides. However, peaks characteristic of FSG were more intense in the spectrum of the precipitate formed at 4 °C. Crystallization and melting profiles obtained by DSC were similar to each other; however, crystallization and melting temperatures and enthalpies of crystallization and fusion were lower for the precipitate formed at 18 °C. Thus, the nature of POB precipitate was not found to be significantly affected by temperature because there were no marked differences in morphology, chemical constitution, and thermal profile between precipitates formed above and below the cloud point.

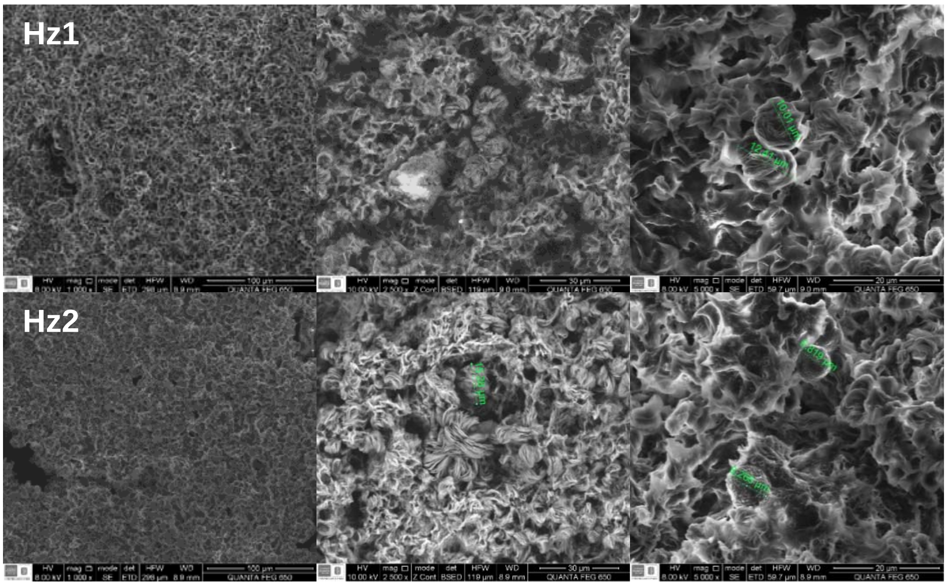

Figure 5: SEM images of precipitate isolated from palm oil biodiesel incubated at 4 °C (Hz1) or 18 °C (Hz2)

Acknowledgements

The authors gratefully acknowledge the support of the Departamento Administrativo de Ciencia, Tecnología e innovación, COLCIENCIAS, through the Jóvenes Investigadores e Innovadores training program; and the Virrectoría de Investigación y Extensión, Universidad Industrial de Santander (Project No. 5460). The authors also gratefully acknowledge Ecodiesel Colombia S.A. for providing the palm oil biodiesel for this study. Sincere appreciation is extended to Dr. Carlos Ríos from the Laboratorio de Microscopía, Parque Tecnológico de Guatiguará, Universidad Industrial de Santander, for his excellent assistance with SEM/EDS analyses.

References

Bondioli P., Cortesi N., Mariani C., 2008. Identification and quantification of steryl glucosides in biodiesel. European Journal of Lipid Science and Technology, 110, 120-126.

Chupka G.M., Yanowitz J., Chiu G., Alleman T.L., McCormick R.L., 2011. Effect of saturated monoglyceride polymorphism on low-temperature performance of biodiesel. Energy & Fuels, 25, 398-405.

Chupka G.M., Fouts L., McCormick R.L., 2012. Effect of low-level impurities on low-temperature performance properties of biodiesel. Energy & Environmental Science, 5, 8734-8742.

Dunn R.O., 2009. Effects of minor constituents on cold flow properties and performance of biodiesel. Progress in Energy and Combustion Science, 35, 481-489.

Lin H., Haagenson D.M., Wiesenborn D.P., Pryor S.W., 2011. Effect of trace contaminants on cold soak filterability of canola biodiesel. Fuel, 90, 1771-1777.

Plata V., Kafarov V., Castillo E., 2012. Improving the low-temperature properties and filterability of biodiesel. Chemical Engineering Transactions, 29, 1243-1248.

Plata V, Gauthier-Maradei P., Kafarov V., 2015a. Influence of minor components on precipitate formation and filterability of palm oil biodiesel. Fuel, 144, 130-136.

Plata V., Gauthier-Maradei P., Romero-Bohórquez A.R., Kafarov V., Castillo E., 2015b. Characterization of insoluble material isolated from Colombian palm oil biodiesel. Biomass and Bioenergy, 74, 6-14.

Romain V., Ngakegni-Limbili A.C., Mouloungui Z., Ouamba J.M., 2013. Thermal properties of monoglycerides from *Nephelium Lappaceum* L. oil, as a natural source of saturated and monounsaturated fatty acids. Industrial & Engineering Chemistry Research, 52, 14089-14098.

Tang H., Salley S.O., Ng K.Y.S., 2008. Fuel properties and precipitate formation at low temperature in soy-, cottonseed-, and poultry fat-based biodiesel blends. Fuel, 87, 3006-3017.

Van Hoed V., Zyaykina N., De Greyt W., Maes J., Verhé R., Demeestere K., 2008. Identification and occurrence of steryl glucosides in palm and soy biodiesel. Journal of the American Oil Chemists' Society, 85, 701-709.

Vereecken, J., Meeussen, W., Foubert, I., Lesaffer, A., Wouters, J., Dewettinck, K., 2009, Comparing the crystallization and polymorphic behaviour of saturated and unsaturated monoglycerides, Food Research International, 42, 1415-1425.