



# Hydrolysis of soybean oil

## in a subcritical water flow reactor

Jerry W. King,\* Russell L. Holliday and Gary R. List

Food Quality and Safety Research Unit, National Center for Agricultural Utilization Research, Agricultural Research Service/USDA, 1815 N. University Street, Peoria, Illinois 61604, USA.

E-mail: kingjw@mail.ncaur.usda.gov

Received 8th November 1999

### Summary

Subcritical water has been recently demonstrated to be a viable medium for conducting hydrolysis reactions on a variety of organic compounds. In this study, the hydrolysis of triglycerides in soybean oil to their respective free fatty acids has been affected using a flow reactor. The flow reactor permits hydrolysis to be accomplished without the need of a catalyst but requires higher temperatures than previously used in a static system to attain >97% product conversion. Using a high pressure view cell as a diagnostic aid, it was found that the oil miscibility with water is crucial to attaining a high conversion to the free fatty acids. Water to oil ratios of 2.5:1–5:1 were found to optimal for high conversions as well as residence time between 10–15 minutes in the open tubular reactor. Such rapid hydrolysis times contrast with multi-hour conversions utilized industrially to achieve a 96–98% fatty acid yield. Although conversion of the all natural *cis* forms of the fatty acids to some *trans* form occurred, the isolated products were clear and free of degradation products, unlike previous results reported for the reaction run in a closed vessel under static conditions at these elevated temperatures (>300 °C). Determination of the *trans* fatty acid content of aqueous hydrolyzed oils has not been previously reported, however they are of minor importance since the produced fatty acid mixtures are primarily intended for industrial utilization and not for food consumption.

### Introduction

The exploration of new reaction media and conditions to yield environmentally-benign manufacturing processes offers new challenges and opportunities under the name of 'green chemistry'.<sup>1</sup> Reviews of such 'green' options have been summarized by several authors<sup>2,3</sup> and the synthetic possibilities using critical fluid media by others.<sup>4–6</sup> Such fluids avoid many of the problems associated with organic solvents, including flammability, product contamination, and the costs associated with solvent disposal. To date, many of these critical fluid processes have utilized supercritical carbon dioxide (SC-CO<sub>2</sub>), due to its low cost, attractive critical constants, and relative inertness.<sup>7,8</sup>

Water, in its supercritical region (SC-H<sub>2</sub>O), and its subcritical analogue, have also receiving increasing interest as an alternative to using organic solvents.<sup>9</sup> The critical properties of SC-H<sub>2</sub>O are higher ( $T_c = 374$  °C,  $P_c = 24.2$  MPa and  $\rho_c = -0.32$  g mL<sup>-1</sup>), relative to those for SC-CO<sub>2</sub>. Water has the capability of dissolving a variety of organic solutes, since its dielectric constant (permittivity) can be adjusted as a function of temperature while under external pressure. Under appropriate conditions, pressurized water can solubilize even the most nonpolar, hydrophobic organic compounds.<sup>10,11</sup> This property of sub- and SC-H<sub>2</sub>O has

been exploited since the early 1980s for the destruction of hazardous waste,<sup>12</sup> and more recently for selective and controlled degradative synthesis of organic compounds.<sup>13–15</sup> Recently, Clifford and co-workers have demonstrated the potential of subcritical water as an extraction agent, and shown it to be competitive with steam distillation for the processing of natural products.<sup>16,17</sup>

Specific synthetic organic reactions have been conducted using water in its near-critical or critical state. The oxidation of alkyl aromatics,<sup>18</sup> metal-catalyzed organic transformations,<sup>19</sup> acylation of phenols,<sup>20</sup> as well as the dehydration of alcohols<sup>21</sup> are but a few examples of synthetic possibilities. Recently, Aleman *et al.*<sup>22</sup> have utilized subcritical water for the hydrolysis and saponification of benzoate esters.

Hydrolysis reactions have also been important for many years in the oleochemical industry. Name processes/reactions, such as the Twitchell process,<sup>23</sup> or Colgate-Emery synthesis<sup>24</sup> of complex mixtures of fatty acids have historically been conducted at low pressures and elevated temperatures; although the Eisenlohr<sup>25</sup> process utilized pressures up to 24.2 MPa. It is interesting to note that processes like the Colgate-Emery synthesis are conducted at subcritical conditions with respect to the physical state of water (250 °C and 5.0 MPa), although historically they have not been interpreted as such because the oil to water ratio is usually 2:1, suggesting more of a steam-based hydrolysis, than a subcritical process. The above processes are generically referred to as 'fat

### Green Context

**Fatty acids form an important group of products, which are used in a range of applications. Their production from sustainable resources is thus a worthwhile venture, with triglycerides being an obvious source. The hydrolysis of these natural products, without the use of acids or alkalis, which lead to salt streams upon neutralisation, is a particularly attractive route. This paper describes the use of sub-critical water as an efficient reagent and reaction medium for the preparation of fatty acids. (See also *Green Chemistry*, 1999, 1, 65 for other work with sub-critical water). One of the key variables in high pressure water is the increased miscibility of organics, even hydrophobic materials such as oils. This miscibility is shown to be very important for a rapid and complete hydrolysis. While some isomerisation of the double bond is seen in unsaturated fatty acids, the route described represents an attractive new route with minimal waste generation.**

*DJM*

splitting' and a patent application<sup>26</sup> cites the use of subcritical water for affecting this reaction, although the given examples, degree of hydrolytic efficiency, and reaction conditions in this patent would not necessarily be attractive to industry.

Previously we have demonstrated that hydrolysis of vegetable oils can be rapidly achieved in a closed reactor without the need for a catalyst.<sup>27</sup> In this study we have extended the concept using a flow reaction system similar to that used in conventional fat splitting. Hydrolysis is conducted in an open tube without internal mixing elements or catalytic agents, at volumetric proportions where the water content in the reactor exceeds that of the vegetable oil. Reaction conditions have been studied at temperatures between 250–340 °C in the above reactor and in a sight glass to visually observe the process.

## Results and discussion

Residence time (flow rate), temperature, pressure and the water to oil ratio were all studied to find the conditions where the hydrolysis yields would be optimal with limited degradation of the oils. Consequently, the majority of the reactions were run with a residence time between 7 and 15 minutes and in the temperature range of 270–340 °C.

Table 1 illustrates some of the conditions that were determined to be appropriate for quantitative conversion of the oil to the free

**Table 1** Comparison of results for the subcritical water flow reactor system

Residence time/min	14.8	12.6	9.9	7.8	14.8
<i>T</i> /°C	338	338	338	338	330
<i>P</i> /MPa	13.1	13.1	13.1	13.6	13.1
Water:Oil	5:1	2.5:1	5:1	2.5:1	5:1
Free fatty acid (%) <sup>a</sup>	99	98	100	90.4	99
Monoglyceride				6.1	
Diglyceride				1.7	
Triglyceride				trace	

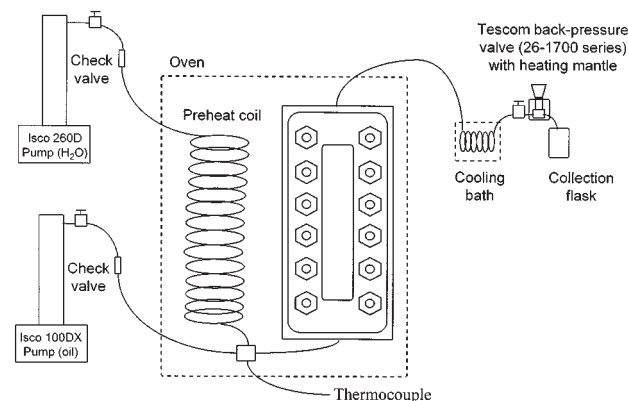
<sup>a</sup> Normalized percent free fatty acid based on GC analysis.

fatty acids. The hydrolysis of soybean oil; whose fatty acid composition was: palmitic (12.6%), stearic (4.6%), oleic (26.0%), linoleic (51.0%), and linolenic (5.8%), readily occurred between 10 to 15 minutes of residence time at 330–340 °C in the flow system. Optimal results were obtained at water to oil ratios between 2.5:1 and 5:1. Lower water/oil ratios produced incomplete hydrolysis, while higher ratios produced no improved conversion. Under the above conditions, reaction times shorter than ten minutes resulted in reduced yields of the free fatty acids, but in all cases, hydrolysis was completed in 15 minutes. Analysis of the incomplete reaction product mixtures by supercritical fluid chromatography indicated the presence of intermediate hydrolysis products, such as mono- and di-glycerides, as well as trace amounts of the starting triglycerides, as indicated by hydrolysis with the shortest residence time (7.8 min) in Table 1.

In all of the experiments, the collected water phase was milky white in appearance, consisting of an emulsion containing the free fatty acids. Initial experiments utilized temperatures starting at 270 °C, based on previous studies on the hydrolysis of triglycerides in a static, batch reactor system.<sup>27</sup> However, in contrast to the previous study, reactions at 270 °C, using the flow reactor and a residence time of 30 minutes, yielded only 22% conversion to free fatty acids.

To try and answer the disparity between the two studies (static vs. flow hydrolysis methods), the reaction chamber was replaced with the a high pressure view cell. This arrangement, shown in

Fig. 1, permitted observation of the oil and water phases under hydrolysis conditions. The conditions of the flow view cell were



**Fig. 1** Schematic of a view cell for subcritical water vegetable oil hydrolysis flow studies.

set such that the water/oil would have a residence time of 14 minutes and sufficient back pressure to keep the water from boiling (12.1–15.2 MPa). When hydrolysis was performed at 300 °C, a mixture was obtained consisting of 34% free fatty acids and significant amounts of mono- and di-glyceride. Under these conditions, it was observed that the soybean oil moved slowly up the window as a sphere, in which, a white solid initially formed, and then the solid slowly dissolved as it travelled on through the cell. Although flow conditions were set to assure an oil residence time of 14 minutes, the residence time in the cell of the oil was less than 2 minutes. This was due to the fact that it was not completely soluble with water at 300 °C, and the oil being less dense than the water, quickly gravitated to the top of the cell, thereby not allowing complete hydrolysis to be achieved.

When the water temperature was increased to 325 °C, the free fatty acid yield increased to 56%, although the water and oil had not become totally miscible. Then as the temperature of the water was slowly increased towards 340 °C, the reaction was closely watched, and at 339 °C, the oil droplets totally disappeared, indicating complete miscibility of the oil and water. At this temperature, the hydrolysis of the oil was complete indicating that for fast and complete hydrolysis, the oil needs to become totally miscible with the water.

Gas chromatographic fatty acid methyl ester (GC-FAME) analysis was also performed on all samples to determine if any degradation or isomerization occurred to the constituent fatty acids during hydrolysis. The major saturated acids, palmitic and stearic, were stable and unaffected under the above described conditions. The principle unsaturated fatty acids in soybean oil, oleic and linoleic, and linolenic acid did not degrade but did undergo some isomerization from the *cis* (*c*) to the *trans* (*t*) isomer. Migration of double bonds was also further verified by the formation of conjugated linoleic acid.

Table 2 lists the fatty acid isomers produced in the hydrolysis reaction as well as the minimum and maximum percentage for each in the completed reactions (> 97% hydrolysis). The variation in the observed conversion of *cis* to *trans* isomers proved to be dependent on the time and temperature that the hydrolysis was conducted under. The minimum conversions were observed at lower temperatures or short residence times, while the maximum conversion was attained at higher temperatures or longer reaction times. This isomerization of the free fatty acids, also occurred for incomplete hydrolysis conducted between 270 to 320 °C, although not to as great an extent as seen at 330 to 340 °C. The *c*, *t*, *t* and *t*, *c*, *t* as well as the *c*, *t*, *c*

**Table 2** Isomerization of soybean oil in flow system

Isomer	Minimum (%) <sup>a</sup>	Maximum (%) <sup>a</sup>
<i>t</i> 9-Oleic	1.9	6.1
<i>t</i> 11-Oleic	0.7	3.2
<i>t,t</i> Linoleic	1.0	5.0
<i>c,t</i> Linoleic	2.2	10.3
<i>t,c</i> Linoleic	1.9	10.1
<i>c,t,t</i> & <i>t,c,t</i> Linolenic	Trace	0.9
<i>t,t,c</i> Linolenic	Trace	1.1
<i>c,t,c</i> & <i>c,c,t</i> Linolenic	Trace	0.5
<i>t,c,c</i> Linolenic	Trace	0.8
conjugated Linoleic	0.7	2.6

<sup>a</sup> Normalized percent free fatty acid based on GC analysis.

and *c, c, t* linolenic acids could not be separated under the reported GC conditions and are reported as a sum for the above isomers. These isomer distribution patterns were found to be consistent during the course of the hydrolysis studies. Gas chromatographic analysis of the starting soybean oil contained none of the *trans*-containing acids reported in Table 2, which indicates that formation of *trans* fatty acids is entirely due to the hydrolysis process.

Since in traditional oleochemical synthetic methods, application of high pressure tends to decrease isomerization, several reactions were performed at higher pressures to test its effect on the resultant products. The use of higher pressures (up to 40.4 MPa) showed no appreciable reduction in the isomerization of the fatty acids, as can be seen in Table 3. In fact the results in Table 3 indicate a small decrease in the amount of *c,c*-linoleic acid that is present as pressure is increased.

**Table 3** Effect of increased pressure on isomerization

<i>P</i> /MPa	16.2	20.2	30.5	40.4
<i>T</i> /°C	330	330	330	330
% <i>c,c</i> Linoleic <sup>a</sup>	35.0	32.2	31.9	30.4

<sup>a</sup> The initial soybean oil contained 50% *c,c* linoleic acid. Normalized percent free fatty acid based on GC analysis.

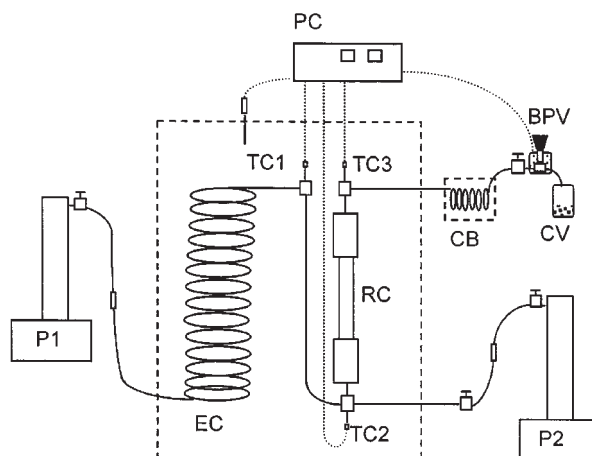
## Conclusions

The use of a subcritical water flow reactor has proven to be an effective means of hydrolyzing soybean oil to free fatty acids. Hydrolysis occurs rapidly, within 10 to 15 minutes at temperatures between 330 and 340 °C yielding 97% or better conversion; without the need for catalysts, emulsifying agents, or any reactor internals. These conversion times and corresponding yields are improvements over those currently used in the fat splitting industry, and are partially achieved by using a high water:oil ratio to suppress glycerol formation in the aqueous phase which inhibits fatty oil hydrolysis. Hydrolysis under these conditions does produce some isomerized fatty acids from the all natural *cis* (*c*) form to *trans* (*t*) isomer, data heretofore unreported, and which unfortunately do not exist for fatty acids produced under conventional industrial hydrolysis procedures. The quoted hydrolysis conditions differ from those previously determined to be optimal for a batch reaction, suggesting caution in extrapolating batch reactor conditions into flow reactor systems.

## Experimental

The soybean oil [refined, bleached, deodorized (RBD)] used in these studies was obtained from Archer Daniels Midland, Granite

City, IL. Deionized water was used without further purification. The high pressure flow reaction system, Fig. 2, consisted of an



**Fig. 2** Schematic of subcritical water flow reaction system in an oven. P1 and P2 are pumps, TC1–3 are thermocouples, EC is a equilibration coil, PC is process controller, RC is the reaction chamber, CB is a cooling bath, BPV is a back pressure regulating valve, and CV is the collection vial.

Isco 260D syringe pump (Isco, Inc., Lincoln, NE) for the water which then entered an oven (Model 3710A, ATS, Inc., Butler, PA) in 1/8" o.d. by 0.30" i.d. Hastelloy-C tubing. The preheated water from the coil went through a tee and then to a cross (all fittings and tubing from High Pressure Equipment, Erie, PA), both of which were equipped with a thermocouple (Type K, 1/16" inconel sheath, Omega Engineering, Stamford, CT). At the cross, the soybean oil was introduced to the system from a Isco 100DX syringe pump. The water–oil mixture then passed through the reaction chamber which consisted of a Hastelloy-C, 8" long, coned and threaded tube (1" o.d., 9/16" i.d., internal volume of 35.5 mL and a pressure rating of 138 MPa), fitted with 1" to 1/8" unions at both ends. The water/oil mixture continued to another tee fitted with a thermocouple, then out to the reservoir of a cooling bath (Model 801, PolyScience, Inc., Niles, IL), through a back pressure relief valve (Model 26-1722, Tescom Corp., Elk River, MN), and finally into a beaker for collection. The first thermocouple was connected to a controller (Part No. CN4800, Omega Engineering, Stamford, CT) which regulated the oven temperature, while the other thermocouples were connected to a digital meter to obtain an accurate reading of the water temperature, both before and after the reaction chamber.

Supercritical fluid chromatographic (SFC) analysis of the reaction products was performed on a Dionex Model 600 SFC (Dionex Corporation, Sunnyvale, CA). The SFC unit was equipped with a timed injector (200 nL injection loop) which was held open for 0.5 seconds; and a Dionex SB-Phenyl-50 capillary column (10 m × 50 μm i.d., 0.25 μm film thickness). The flame ionization detector (FID) was operated at 350 °C and an integrator (Data Jet-CH2, Spectra-Physics, San Jose, CA) was used for data acquisition. The capillary column was held at a constant temperature of 100 °C. The carrier gas was carbon dioxide (SFC/SFE grade, Air Products, Allentown, PA). The column pressure program utilized was as follows: an isobaric hold at 10.1 MPa for 5 minutes, then increased to 24.2 MPa at 0.404 MPa min<sup>-1</sup>, followed by another increase to 32.3 MPa at 1.01 MPa min<sup>-1</sup>.

GC-FAME analyses were performed according to previously described methods<sup>28</sup> on a HP5890 Series II GC using a FID

detector (Hewlett Packard Company, Wilmington, DE) and a 100% poly(biscyanopropylsiloxane) column (SP-2340, Supelco, Inc., Bellefonte, PA, 60 m × 0.25 mm, 0.20 μm thickness). The GC oven parameters were modified slightly for better separation of the standards. The oven was held at 100 °C for 5 minutes, then increased to 190 °C at 3 °C min<sup>-1</sup>, then increased at 1 °C min<sup>-1</sup> to 200 °C and held for 15 minutes, followed by a final increase at 50 °C min<sup>-1</sup> to 250 °C, where it was held for 1 minute. GC-MSD (mass selective detector) analysis of the FAMES were performed on a HP5890 Series II Plus GC interfaced with a HP5971A MSD using the same column as described above. The precision of the FAME analysis was 0.1% relative standard deviation.

For a typical reaction, the oven was set to a temperature between 250–340 °C, the water pump was then set to a constant flow of 2.0 mL min<sup>-1</sup>, and then water flow was commenced as the oven was heated. The back pressure regulator was set for an overall system pressure of 15.2 MPa (just enough pressure to keep the water from boiling) and the cooling bath was operated at 80 °C. Once the water had reached the desired temperature, the oil pump was set to a constant flow of 0.4 mL min<sup>-1</sup> and oil pumped into the system, yielding a total flow in the system of 2.4 mL min<sup>-1</sup>, and approximately a 15 minute residence time in the reaction chamber. After hydrolysis, the water–oil stream was cooled and depressurized, and collected in a beaker, to which sodium chloride had been added to break any emulsions that formed. The oil was initially pumped into the reactor for approximately 30 minutes before being shut off. However, the flow of water was allowed to continue until there was no visible oil/product being collected, at which time, the reaction was stopped.

The resultant water–product mixture was separated by pouring the mixture into a separatory funnel and extracting with diethyl ether. The ether was then evaporated to leave an oil or a solid consisting of the hydrolyzed fatty acids and any unreacted triglycerides. This extract was then subjected to SFC to determine the degree of hydrolysis. GC-FAME analysis was then utilized to determine if the triglyceride-derived fatty acid composition had been altered during the reaction.

In some experiments, a view cell was placed downstream rather than the tubular reactor. This was contained in an GC oven, that had been modified to include a window in the oven door, for viewing the cell. The view cell consisted of a 316 SS chamber (ca. 59 mL volume), tempered transparent glass, and grafoil gasket, (Model 17-R-40, Jergunson Gage and Valve, Strongsville, OH). The cell had a recommended rating of 22.2 MPa at 316 °C for liquids under pressure and a 3.03 MPa rating for steam. We exceeded this maximum temperature rating, but only with extreme caution, and at a reduced pressure relative to its maximum rating (152 MPa at 340 °C), making sure that the cell contents always remained in the liquid state. Residence times of the oil mixture in the high pressure view cell and the unpacked tubular reactors was calculated from a knowledge of the total metered flow rates through the devices. In the case of the view cell, individual segments of emulsified fat were timed during transit through the cell and gave good agreement with those calculated from flow rate measurement.

### Acknowledgments

The assistance of Mr Jeffrey Teel in the assembly of the experimental apparatus is gratefully acknowledged. Ms Angela Neese was responsible for performing some of the analysis that provided the experimental data.

### References

- 1 J. H. Clark, *Green Chem.*, 1999, **1**, 1.
- 2 *Green Chemistry*, ed. P. T. Anastas and T. C. Williamson, American Chemical Society, Washington, D.C., 1996.
- 3 R. Noyori, *Chem. Rev.*, 1999, **99**, 353.
- 4 D. A. Morgenstern, R. M. LeLacheur, D. K. Morita, S. L. Borkowsky, S. Feng, G. H. Brown, L. Luan, M. F. Gross, M. J. Burk and W. Tumas, in *Green Chemistry*, ed. P. T. Anastas and T. C. Williamson, American Chemical Society, Washington, D.C., 1996, pp. 132–151.
- 5 *Chemical Synthesis Using Supercritical Fluids*, ed. P. G. Jessop and W. Leitner Wiley-VCH, Weinheim, 1999.
- 6 E. Dinjus, R. Fornika and M. Scholz, in *Chemistry Under Extreme or Non-Classical Conditions*, ed. R. van Eldik and C. D. Hubbard, John Wiley, New York, 1997, p. 219.
- 7 *Supercritical Fluid Technology in Oil and Lipid Chemistry*, ed. J. W. King and G. R. List, AOCS Press, Champaign, IL, 1996.
- 8 H. Schmieder, N. Dahmen, J. Schon and G. Wiegand, in *Chemistry Under Extreme or Non-Classical Conditions*, ed. R. van Eldik and C. D. Hubbard, John Wiley, New York, 1997, p. 273.
- 9 C.-J. Li and T.-H. Chan, *Organic Reactions in Aqueous Media*, John Wiley, New York, 1997.
- 10 J. F. Connolly, *J. Chem. Eng. Data*, 1966, **11**, 13.
- 11 J. Gao, *J. Am. Chem. Soc.*, 1993, **115**, 6893.
- 12 M. Modell, *Chem. Phys. Process Combust.*, 1989, E1.
- 13 A. R. Katritzky, S. M. Allen and M. Siskin, *Acc. Chem. Res.*, 1996, **29**, 399.
- 14 L. J. Sealock, Jr., D. G. Elliott, E. G. Baker, A. G. Fassbender and L. J. Silva, *Ind. Eng. Chem. Res.*, 1996, **35**, 4111.
- 15 P. E. Savage, *Chem. Rev.*, 1999, **99**, 603.
- 16 A. Basile, M. M. Jimenez-Carmona and A. A. Clifford, *J. Agric. Food Chem.*, 1998, **46**, 5205.
- 17 A. A. Clifford, A. Basile, M. M. Jimenez-Carmona and S. H. R. Al-Saidi, *Proceedings of the 6th Meeting on Supercritical Fluid—Chemistry and Materials*, ISASF, Nancy, France, p. 485.
- 18 R. L. Holliday, B. Y. M. Jong and J. W. Kolis, *J. Supercrit. Fluids*, 1998, **12**, 255.
- 19 E. J. Parsons, *Chemtech*, 1996, **26**, 30.
- 20 J. Brown, D. Lamb, S. Nolen, R. Glaser, C. L. Liotta and C. A. Eckert, *Abstracts of the 2nd World Congress on Environmental Catalysts*, AIChE, p. 571.
- 21 X. Xu, C. De Almeida and M. J. Antal, Jr., *Ind. Eng. Chem. Res.*, 1991, **30**, 1478.
- 22 P. A. Aleman, C. Boix and M. Poliakov, *Green Chem.*, 1999, **1**, 65.
- 23 N. O. V. Sonntag, *J. Am. Oil Chem. Soc.*, 1979, **56**, 729A.
- 24 H. L. Barneby and A. C. Brown, *J. Am. Oil Chem. Soc.*, 1948, **25**, 95.
- 25 G. W. Eisenlohr, *US Pat.*, 2 154 835, 1939.
- 26 P. A. Moller, *Int. Pat.*, WO 97/07187, 1997.
- 27 R. L. Holliday and J. W. King and G. R. List, *Ind. Eng. Chem. Res.*, 1997, **36**, 932.
- 28 S. D. House, P. A. Larson, R. R. Johnson, J. W. DeVries and D. L. Martin, *J. Assoc. Off. Anal. Chem.*, 1994, **77**, 960.

Names are necessary to report factually on data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by the USDA implies no approval of the product to the exclusion that others might be suitable.

Paper 9/08861J