Fast Gas Chromatographic Separation of Biodiesel

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Abstract

A high-speed gas chromatographic method has been developed to determine the FAME distribution of B100 biodiesel. The capillary column used in this work has dimensions of 20 m × 0.100 mm and is coated with a polyethylene glycol film. Analysis times are typically on the order of 4–5 min depending upon the composition of the B100. The application of this method to a variety of vegetable and animal derived B100 is demonstrated. Quantitative results obtained with this method were in close agreement with those obtained by a more conventional approach on a 100 m column. The method, coupled with solid-phase extraction, was also found suitable to determine the B100 content of biodiesel–diesel blends.

Introduction

Biodiesel is a blend of conventional diesel fuel with fatty acid methyl esters (FAME). Pure FAME is referred to as B100, and blends of B100 in conventional diesel fuels are referred to as Bx (i.e., a 5% mixture of FAME in diesel would be called B5). The FAMEs employed in biodiesel are produced by transesterification of biologically derived triglycerides with methanol. In some areas of the world, such as Brazil, where ethanol is more cost effective, ethyl esters may be produced in place of methyl esters. The triglycerides are commonly obtained from vegetable oils, but triglycerides obtained from animal sources are also employed. The predominant plant derived FAMEs employed in the biodiesel industry are from soy, rapeseed, and palm (1).

Often the source and FAME distribution of the B100 blended into diesel is of interest for quality control purposes. In addition, a rapid chromatographic method to determine the B100 source and content of biodiesel–diesel blends is required. The most straightforward way to identify the source of B100 is to determine the distribution of the FAME components as the fatty acid composition of vegetable derived oil differs with the source and is usually fixed within narrow boundaries for any given source. The distribution of FAMEs is commonly determined by capillary gas chromatography (GC) (2–4). A number of different columns can be employed for the separation of FAME mixtures. For example, EN 14103, an EU method to determine the fatty acid content of B100, specifies use of a polyethylene glycol stationary phase (5). This widely used phase provides separation of FAMEs with different carbon numbers and a degree of unsaturation. It is more limited in its ability to separate cis/trans isomers. Biscyanopropyl siloxane columns are also widely employed for FAME separation especially when the separation of cis/trans isomers is of interest (6). Recently a number of workers have begun to apply fast GC methods to the determination of FAME distributions (7–12).

In this work, we have explored the use of GC with narrow bore (0.100 mm internal diameter) columns for the rapid characterization of B100. The use of long, narrow diameter columns, compared to other approaches for achieving high speed GC separations, allows for the simultaneous achievement of high resolution and fast analysis times (13,14). This methodology has been applied to determine both the composition of B100 and to determine the amount of B100 in biodiesel blends. In the latter case, solid-phase extraction (SPE) was employed in the sample pretreatment to isolate B100 from diesel components. The use of this high speed method was evaluated for a number of B100s from different sources including soy, rapeseed, palm, coconut, mustard seed, and animal fat. For soy and rapeseed FAMEs, GC analysis times are on the order of 4–5 min.

Experimental

Analyses with narrow bore columns were performed on an Agilent 6890 GC equipped with a split injector and a flame ionization detector. A 20 m × 0.100 mm capillary column containing a 0.1 µm film of polyethylene glycol was employed (J&W Scientific). Helium carrier gas was employed. The analysis was performed under isothermal conditions at 245°C with a column head pressure of 90 psi (constant pressure mode). This generated a linear velocity of 28 cm/s. An injection volume of 0.2 µL was employed. The split ratio was 500:1. Samples were prepared for analysis by dissolving 0.2 g of B100 into 10 mL of dichloromethane solvent. Area percents were taken directly as wt% except as discussed later. Solvents were reagent grade and used as received.

Additional analyses were performed on the same GC with a 100 m × 0.25 mm Rtx 2560 (biscyanopropyl) column with a 0.20 mm film. The oven temperature was programmed from 100 to 240°C at 3°C/min after an initial hold of 4 min. The final temperature was held for 10 min. The column head pressure was 35 psi. The injection volume was 1 µL, and the split ratio was 50:1. Sample preparation was as described earlier.

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Solid-phase extraction analyses were performed on silica gel cartridges containing 690 mg of adsorbent (Waters WAT051900, Palo Alto, CA). Samples were prepared by weighing approximately 1 gram of diesel sample into 5 mL of internal standard solution (4.00 mg/mL methyl pentadecanoate in heptane). Approximately 1 mL of this solution was applied to the head of the silica gel cartridge followed by 5 mL of heptane. This fraction was discarded. The FAME components were then eluted with 3 mL of dichloromethane. This fraction was then examined on the 0.100 mm polyethylene glycol column as described earlier. For samples containing greater than 10 wt% B100, the sample size was reduced proportionately. A commercial diesel fuel was employed to prepare known B100-diesel blends. The peak area from all FAME components excluding the internal standard was summed together to calculate the B100 concentration. Equivalent response between the FAME components and the internal standard was assumed.

Results and Discussion

Biodiesel characterization

Figure 1 contains a chromatogram of a soy-derived B100 biodiesel (100% FAME) obtained on the 0.100 mm capillary column coated with a 0.10 µm film of polyethylene glycol. In subsequent discussions, separations performed on this column will be referred to as fast GC analyses. Major FAME peaks are identified in the figure by their carbon number and number of double bonds. Minor components are not labeled on the Figure. The separation was performed isothermally at 245°C with a head pressure of 90 psi. Note the analysis time is on the order of 4.5 min for the principal FAME's present in soy (up to C22:0). Minor components of biodiesel such as mono-, di-, and triacylglycerols and free fatty acids are not detected by this method. These components are present at lower concentrations compared to FAME components and are either too polar or have too high a boiling to elute from the PEG column. Because only the more volatile FAME components in the B100 are of interest, split injection was sufficient for this analysis.

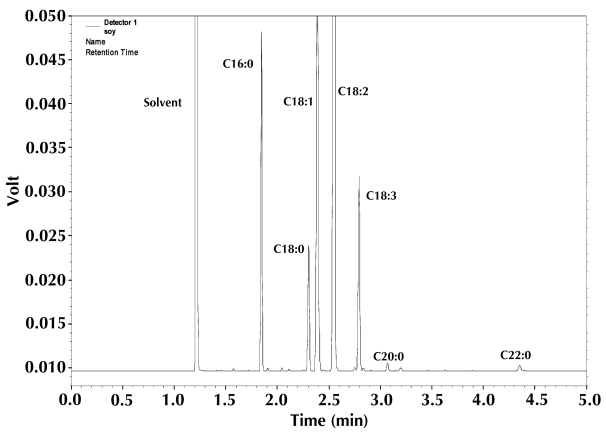

Figure 1. High-speed chromatogram of soy B100. See text for conditions.

The criteria used to select chromatographic parameters were two-fold. The carrier gas linear velocity was limited by the choice of carrier gas and the available head pressure. Helium was chosen for convenience and the head pressure was limited to 100 psi by the instrument. A value of constant pressure at 90 psi generating a linear velocity of 28 cm/s was selected for these reasons. The column temperature was optimized to minimize analysis time while still maintaining adequate resolution of the C18 components. Isothermal operation, in preference to temperature programming, was selected to minimize between run times. A temperature of 245°C was found suitable. This temperature is near the maximum for this stationary phase. While not in use, the column temperature was maintained at a lower temperature (100°C) to minimize column bleed.

For comparison purposes, Figure 2 contains a chromatogram of a soy B100 obtained under higher resolution condition; a 100 m column containing a biscyanopropyl phase. The first 20 min of the chromatogram are not shown in the figure. This separation employed temperature programming conditions, and the analysis time was 60 min. Two major differences can be noted between the two chromatograms. First, a minor C18:1 isomer peak observed in Figure 2 is not resolved from the major peak C18:1 under fast GC conditions. Second, under the fast GC isothermal conditions, the C24 isomer observed on the longer column does not elute in a reasonable time and is not observed in the time frame shown on Figure 1. It can be observed at longer times. However, in the context of biodiesel analysis, resolution of the minor C18:1 isomer is not critical, and the C24 isomer is present at low concentrations in soy and other common vegetable derived oils, typically on the order of 0.1 wt% (15).

Table I contains a summary of results from replicate analyses (five injections) of a soy B100 sample using the fast GC conditions. In this table, as in all those that follow, all isomeric peaks have been summed together. Thus all C18:3 isomers have been added together to provide a sum. For major components such as C18:1 and C18:2, the relative standard deviations are under 0.1%. For lower level components reported in Table I, such as C20:0, the relative standard deviation are on the order of 1–2%.

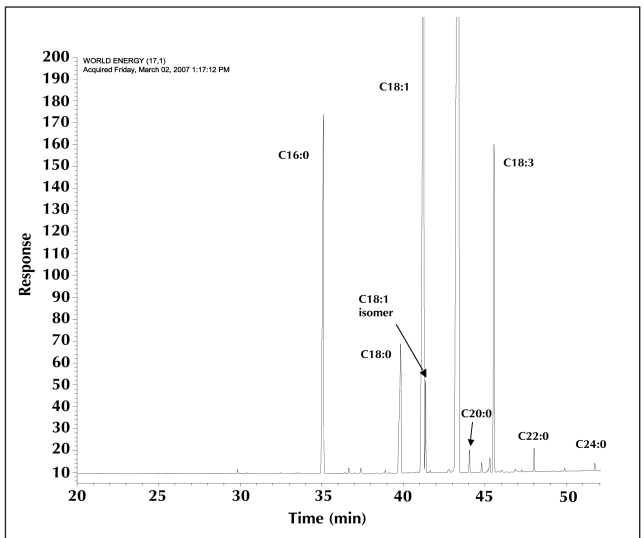

Figure 2. Chromatogram of soy B100 on 100 m biscyanopropyl column. See text for conditions.

Figure 3–5 show chromatograms of rapeseed, coconut, and mustard seed FAMEs obtained under identical conditions to the soy FAME shown in Figure 1. Rapeseed contains FAMEs of similar carbon number to soy, although the component distribution differs. Coconut contains a greater proportion of lower carbon number FAMEs, while mustard seed contains a great proportion of higher carbon number FAMEs. For example, mustard seed contains high levels of C22:1 FAME, while coconut contains high levels of C8-C14 FAMEs not commonly found in the other vegetable derived oils examined here. The presence of higher carbon number components in the mustard required longer analysis times (8 min) compared to the other materials. In all cases, the separations appeared to provide adequate separation of the major components. Use of hydrogen as carrier gas should provide even shorter analysis times because a higher linear velocity could be achieved at the head pressure employed in this work. In addition, the optimal flow rate for hydrogen occurs at higher velocities (14). The use of hydrogen was not explored in this study.

Tables II and III, respectively, contain a summary of the distribution of FAMEs in the various vegetable derived B100s that were obtained on the fast GC column and on the 100 m biscyanopropyl column. FAMEs from five different sources are included in the tables. Excellent agreement was noted between the two sets of data. Figure 6 contains a plot of the C18:1 results from the two different analyses. The slope of 0.99 and small

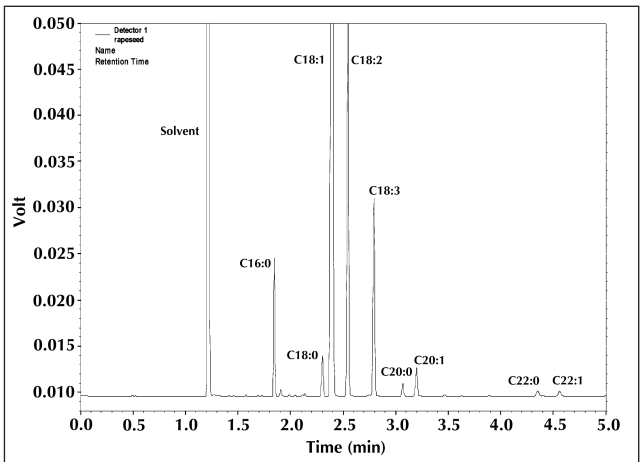

Figure 3. High-speed chromatogram of rapeseed B100. See text for conditions.

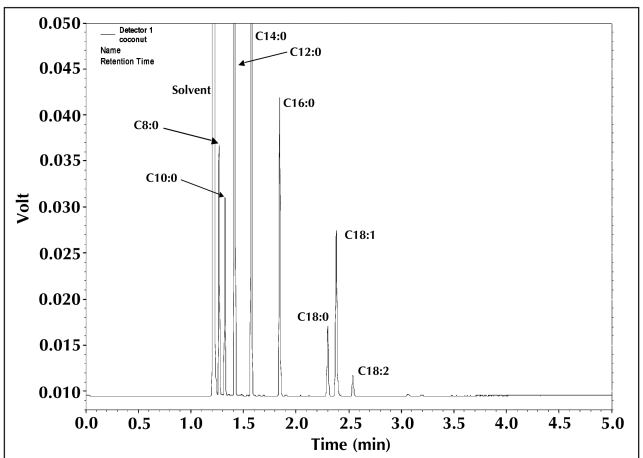

Figure 4. High-speed chromatogram of coconut B100. See text for conditions.

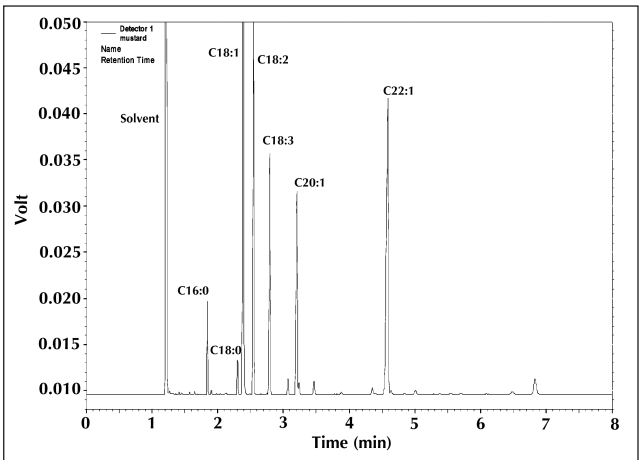

Figure 5. High-speed chromatogram of mustard seed B100. See text for conditions.

Table I. Results from Replicate Analyses of Soy FAME on 0.100 mm Column

FAME	Average (wt%)	Standard Deviation (wt%)	Relative Standard Deviation (%)
C14:0	0.08	0.008	9.7
C16:0	10.16	0.022	0.2
C16:1	0.14	0.007	4.9
C17:0	0.14	0.003	2.4
C17:1	0.08	0.003	3.4
C18:0	4.71	0.001	0.0
C18:1	22.16	0.025	0.1
C18:2	53.01	0.023	<0.1
C18:3	8.05	0.010	0.1
C20:0	0.36	0.008	2.1
C20:1	0.19	0.006	3.2
C22:0	0.36	0.004	1.2
C22:1	0.03	0.002	6.9
Unknowns	0.51	0.038	9.5

Table II. Composition (wt%) of FAME from Different Sources on 0.100 mm Column

	Soy	Rapeseed	Palm	Coconut	Mustard
C8:0		0.03	0.06	7.03	0.06
C10:0			0.04	5.76	0.02
C12:0	0.02	0.02	0.52	46.1	0.07
C14:0	0.07	0.06	1.03	19.0	0.10
C16:0	10.2	4.50	41.9	10.5	3.08
C16:1	0.14	0.30	0.20	0.04	0.22
C17:0	0.13	0.06	0.10		0.05
C17:1	0.08	0.20	0.03	0.02	0.12
C18:0	4.71	1.74	5.28	2.93	1.45
C18:1	22.1	62.3	39.2	7.20	24.4
C18:2	53.0	18.9	10.6	0.91	15.9
C18:3a	8.02	8.49	0.20		11.0
C20:0	0.37	0.61	0.38	0.10	0.81
C20:1a	0.20	1.48	0.14	0.07	10.9
C22:0	0.36	0.34	0.06	0.06	0.50
C22:1	0.04	0.37	0.03	0.05	26.3
misc pks.	0.55	0.68	0.26	0.22	5.17

intercept demonstrate that results obtained under the faster analysis times were comparable with those obtained with higher resolution and the corresponding longer analysis time.

The fast GC column was also useful to determine the composition of animal derived B100. Figure 7 contains a chromatogram of the FAME found in beef tallow derived B100. As can be seen from Figure 7, animal derived FAME contains a larger number of minor components compared to the vegetable oils discussed earlier. The figure demonstrates that adequate resolution of major and minor components in these more complex mixtures was also possible with the short run times afforded by the narrow diameter column.

Although not specifically explored in this work, this fast GC approach should also be applicable to measure the composition of fatty acid ethyl esters although some of the higher carbon number ethyl esters such as that derived from the C24 fatty acid may not elute in a reasonable time.

In all quantitative work cited here, equivalent response was used with normalization to calculate the concentration of different FAME components. This assumption may be valid for oils that contain a narrow carbon range such as soy or rapeseed, but may not be appropriate for other vegetable oils. A number of workers have reported on the calculation of theoretical flame ionization response factors for a variety of compound classes including FAME (16–18). Many of these are based on the effective carbon number concept (ECN). These approaches take into account by the effect of functional groups and unsaturation. The ECN approach described by Scanlon (16) was used to calculate FID response factors for the FAME's found in the materials examined in this study. These factors were then used to calculate component concentrations for the five vegetable oils. For palm, soy, and rapeseed, average differences between results using equivalent response factors and those using the ECN response factors were less than 1% relative. As expected the largest difference was noted for coconut, which contains a wider range of carbon numbers. The average difference between the values calculated with equivalent response factors and those calculated with ECN response factors was 5% relative for the C8-C18 even number coconut FAMEs. Thus for coconut and other B100s containing a wide range of carbon number FAMEs, it will be necessary to employ response factors for reasonable quantitation.

Table III. Composition (wt%) of FAME from Different Sources on Biscyanopropyl Column

	Soy	Rapeseed	Palm	Coconut	Mustard
C8:0	0.02	0.01	0.05	6.62	0.01
C10:0		0.01	0.03	5.58	0.01
C12:0		0.01	0.47	45.8	0.03
C14:0	0.08	0.05	1.01	19.2	0.06
C16:0	10.1	4.39	41.7	10.7	2.89
C16:1	0.09	0.22	0.13	0.02	0.13
C17:0	0.11	0.05	0.10	0.01	0.03
C17:1	0.05	0.07	0.02		0.04
C18:0	4.74	1.75	5.33	3.03	1.41
C18:1	22.3	62.6	39.4	7.27	23.7
C18:2	53.1	18.9	10.3	0.95	16.2
C18:3a	8.21	8.47	0.37	0.04	12.3
C20:0	0.37	0.63	0.39	0.10	0.81
C20:1a		1.46			10.8
C22:0	0.38	0.36	0.06	0.02	0.51
C22:1		0.38	0.01		26.7
C24:0	0.11	0.14	0.07	0.04	0.29
misc pks	0.48	0.55	0.47	0.71	4.03

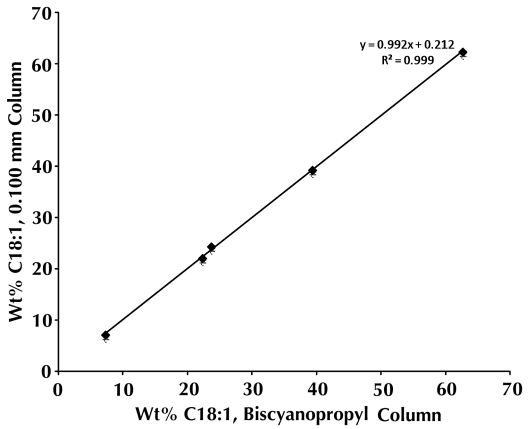

Figure 6. Comparison of C18:1 results between high speed and 100 m biscyanopropyl columns for five different B100's.

Biodiesel-diesel blends

The fast GC approach was also applied to determine the total amount and distribution of FAME in B100-diesel blends. Spectroscopic methods such as FTIR, NIR, and Raman are gaining favor for the analysis of the B100 content of biodiesel blends because of their speed and portability advantages compared to chromatographic methods. However, they can be limited in identifying the source of the FAME and in many cases require extensive development of chemometric models to effectively measure blends containing FAME from different sources (19).

The method described here, which couples a rapid SPE separation followed by fast GC, offers a useful alternative. Prior to GC analysis, the diesel was rapidly separated from FAME components by solid-phase extraction using silica gel. This approach is well established and serves as the basis for a European Union Method (20). The separation described here is a modification of that method. Preliminary studies were performed using a mixture of naphthalene (a surrogate for di-aromatic compounds in diesel) and methyl oleate in order to optimize the separation of

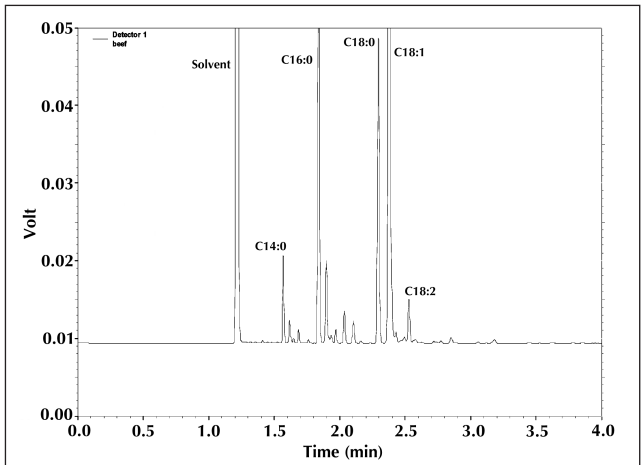

Figure 7. High-speed chromatogram of beef tallow B100. See text for conditions.

diesel from FAME. After heptane elution of diesel components, B100 was eluted from the SPE cartridge with dichloromethane as described in the experimental section. Figure 8 shows a chromatogram of a rapeseed FAME isolated from a diesel blend that contained approximately 9 wt% B100. As noted in the experimental section, it was necessary to reduce the sample size of blends with greater than 10% B100 to prevent breakthrough of the FAME on the silica gel column.

Methyl pentadecanoate was added as internal standard prior to the solid phase extraction. In these analyses, all FAME components were assumed to have the same response factor and were summed to give a B100 concentration.

Table IV contains a summary of results from the analysis of several B100-diesel blends containing known amounts of B100. A number of different B100 sources were employed. The known B100 content ranged from approximately 2.5 to 10 wt%. The average recovery (calculated as the ratio of the determined to prepared concentrations expressed as a percent) was 98 %. Triplicate analyses of two diesel blends spiked with approximately 9 wt% each of a rapeseed and a soy B100 gave average and standard deviation values of 9.42 ± 0.16 wt% and 9.18 ± 0.04 wt%, respectively.

Summary

A high-speed GC method has been developed to determine the FAME distribution of B100 biodiesel. The capillary column used in this work has dimensions of 20 m × 0.100 mm and is coated with a polyethylene glycol film. Isothermal conditions are employed. Analysis times are on the order of 4–5 min for the major FAME components depending upon the composition of the B100. Longer analysis times were required to elute C24 FAME components. Resolution of isomeric compounds is typically less than that obtained on longer columns, but appears to be sufficient to screen B100 for composition and to identify its source. The application of this method to a variety of vegetable and animal materials was demonstrated.

Results obtained with this method were in close agreement with those obtained by a more conventional approach on a 100 m column. That analysis required approximately 1 h to complete. The precision of the high-speed analysis was also comparable to those previously found using conventional approaches. The method, coupled with solid-phase extraction, was also found suitable to rapidly determine the B100 content of biodiesel-diesel blends.

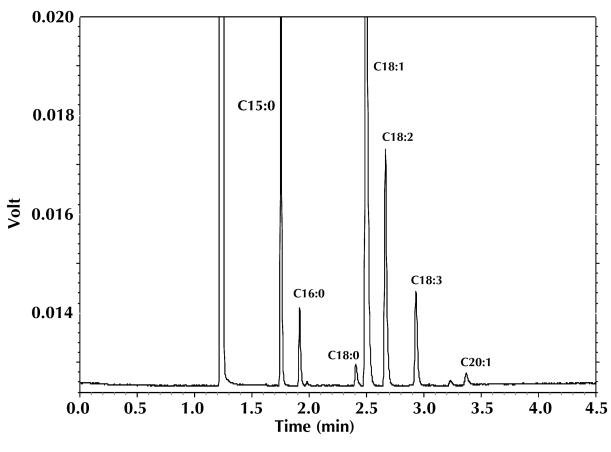

Figure 8. Chromatogram of rapeseed FAME isolated from a B100 diesel blend. Blend contained approximately 9 wt% B100.

Table IV. Determination of B100 in Biodiesel Blends.

B100 Source	Prepared Conc. (wt%)	Determined Conc. (wt%)	Recovery (%)
Rapeseed	2.61	2.56	98
Rapeseed	5.08	4.96	98
Rapeseed	9.65	9.27	96
Soy	9.59	9.21	96
Palm	9.52	9.66	101

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Manuscript received June 7, 2010;
revision received September 20, 2010.