Fuel Properties of Tallow and Soybean Oil Esters

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ABSTRACT: Fuel properties of beef tallow, soybean oil, their esters, and blends with No. 2 diesel fuel and ethanol were determined. Fuel properties tested were viscosity, specific gravity, API gravity, distillation ranges, calculated cetane index, energy content, flash point, water content, sulfur content, carbon residue, particulate matter, acid value, copper-strip corrosion test, ash content, melting point, cloud point, and pour point. Gas-chromatographic analyses of tallow, soybean oil, and their esters were performed to determine their major constituents. Viscosities of soybean oil and tallow were significantly reduced by esterification. Other fuel properties of the esters and their blends with No. 2 diesel fuel and ethanol were similar to the properties of No. 2 diesel fuel.

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KEY WORDS: Fatty acid content, fuel property, gas-chromatographic (GC) analysis, methyl soyate, methyl tallowate, No. 2 diesel fuel, soybean oil, tallow.

Vegetable oils and animal fats can be used as alternative fuels for the compression-ignition diesel engine. They possess certain physical and fuel properties that are comparable to diesel fuel, but their use in the direct-injection-type diesel engine is limited by at least one physical property, i.e., viscosity. Viscosities of oils and fats are 10 to 20 times that of No. 2 diesel fuel (1). Apart from viscosities, oils and fats are considered to be low in total energy content and high in density, carbon residue, and particulate matter. The fuel properties of these oils and fats can be improved by processes such as dilution, microemulsification, pyrolysis, and transesterification (2).

Transesterification of oils and fats is the most common process for using oils and fats as fuel. In this process, oils and fats can be converted into glycerol and fatty methyl or ethyl esters; the latter have viscosities low enough to be used as diesel fuel but still three or four times greater than No. 2 diesel fuel. Ali and Hanna (3) attempted to reduce the viscosity of methyl tallowate by blending it with ethanol, and they recommended that methyl tallowate be blended with ethanol in a ratio of 65:35 (vol/vol) to reduce its viscosity to that of diesel fuel. Goering *et al.* (1) studied fuel properties of 11 vegetable oils and concluded that vegetable oils were much more viscous, were much more reactive to oxygen, and had much higher cloud-point and pour-point temperatures. Schwab *et al.* (4) determined fuel properties of soybean oil esters and found that methyl, ethyl, and butyl esters of soybean oil had properties that compared reasonably well with those of No. 2 diesel fuel. They concluded that these esters had slightly lower (12% less) energy contents than diesel fuel, but had higher gum contents, higher flash points, higher cetane numbers, and higher viscosities.

Recently, there has been considerable worldwide research on alternative diesel fuel qualities, with emphasis on finding the key fuel properties that influence emissions, so that fuels that help improve air quality can be formulated. Understanding the physical and fuel properties of esters of oils and fats will aid in the development of alternate fuels for diesel engines. These properties can assist the user, the refiner, and the formulator to define a consistently uniform product. Also, these properties are often used to establish acceptable levels of additive components in the finished fuels. Therefore, this research was undertaken to study fuel properties of raw tallow and soybean oil, their methyl esters, and their blends with No. 2 diesel fuel and ethanol.

METHODS AND MATERIALS

The beef tallow used in this study was provided by Excel Corp. (Schuyler, NE). The soybean oil was provided by Archer Daniels Midland Co. (Lincoln, NE). Tallow esters (methyl tallowate) and soybean oil esters (methyl soyate) were obtained from Interchem Environmental, Inc. (Overland Park, KS). The fuel-grade ethanol used in this study was obtained from Whitehead Oil Co. (Lincoln, NE), and the Amoco brand No. 2 diesel fuel was obtained from Salem Oil Co. (Lincoln, NE).

Fuel blend preparation. Eighteen fuel samples, including raw beef tallow and soybean oil, their methyl esters, and blends with No. 2 diesel fuel and ethanol in different proportions, were prepared. Table 1 presents the complete list of all fuel blends used in this study.

Free fatty acid (FFA) content of both tallow and soybean oil was determined by American Association of Cereal Chemists (AACC) Method 58-15 (5). Total FFA content of raw tallow and soybean oil, which is indicative of their quality, was less than 2%.

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TABLE 1
Fuel Blends Used

Blend number	Beef tallow (%)	Soybean oil (%)	No. 2 diesel fuel (%)	Methyl tallowate (%)	Methyl soyate (%)	Ethanol (%)
1	100	0	0	0	0	0
2	0	100	0	0	0	0
3	0	0	100	0	0	0
4	0	0	0	0	0	100
5	0	0	0	100	0	0
6	0	0	0	0	100	0
7	0	0	0	65	0	35
8	0	0	0	0	65	35
9	0	0	0	32.5	32.5	35
10	0	0	80	13	0	7
11	0	0	70	19.5	0	10.5
12	0	0	60	26	0	14
13	0	0	80	6.5	6.5	7
14	0	0	70	9.75	9.75	10.5
15	0	0	60	13	13	14
16	0	0	80	20	0	0
17	0	0	70	30	0	0
18	0	0	60	40	0	0

Fatty acid composition determination. Fatty acid compositions of raw beef tallow, soybean oil, and their esters were determined by gas chromatography (GC). Raw tallow and soybean oil were esterified before GC analyses by using the method described by Morrison and Smith (6). Samples of 0.0625 to 0.25 g were placed in a 5-mL reaction bottle, and 1 mL BF_3/methanol was added. N_2 was used to purge the air from the bottles. The bottles were tightly covered and heated at 100°C for 30 min so that a reaction could take place. After 30 min, the mixtures were cooled, 1 mL hexane was added to each bottle to extract the methyl esters, and 1 mL distilled water was added to stop the esterification reaction and to allow phase separation. The mixture was then stirred well and centrifuged to separate the hexane and aqueous phases. The top portion was collected and used for GC analysis.

A Hewlett-Packard (Avondale, PA) 5890 Series II gas chromatograph was used to analyze the samples. The capillary column was purchased from Alltech Associates, Inc. (Deerfield, IL). It had a Carbowax phase, 30-m long with a 0.32-mm inside diameter and 0.25-μm film thickness. N_2 was used as carrier gas with a split ratio of 2 to 200. The head pressure was 0.14 mPa. GC injector temperature was 200°C, flame-ionization detector (FID) temperature was 350°C, and column temperature (oven temperature) was kept at 180°C during the test. A Hewlett-Packard HP 3396A integrator was used to record the results. Attenuation was set at −1 while the chart speed was 1.25 cm/min. At the end of each run, the integrator automatically gave individual peak retention times, peak areas, and area percentages of each peak.

Physical properties determination: viscosity. Viscosities of fuel blends were determined at 40°C. A Brookfield Synchro-Lectric LV Viscometer (Brookfield Engineering Laboratories, Inc., Stoughton, MA) with UL adapter was used. Temperatures of the samples were maintained within ±0.5°C by submerging the sample cup in a temperature bath (Tamson Neslab Instruments, Inc., Portmouth, NH). Samples (16 mL) were placed in the UL adapter cup, which was then fixed to the viscometer. The cup was dipped in the constant-temperature bath for a few minutes before taking the viscosity measurements.

Specific gravity. The specific gravities of the fuel blends were determined by use of a hydrometer, as given in American Society for Testing and Materials (ASTM) Method D1298-85 (7). The fuel temperature was 15.6°C (60°F). The specific gravity (sp. gr.) for each fuel blend was used to calculate the API gravity from the relationship (7) as follows:

$$\text{API gravity, (deg)} = \{141.5/(\text{sp. gr. } 60/60°\text{F})\} - 131.5 \qquad [1]$$

Distillation range. All fuel samples, except ethanol, were sent to Professional Service Industries, Inc. (Omaha, NE) to determine the distillation ranges by ASTM Method D86-93 (7). The distillation range for each fuel blend was used to determine the calculated cetane index (CCI). CCI is based on specific gravity and the 10, 50, and 90% distillation temperatures of the fuels, and it gives numbers that correlate with the engine-testing method. The relationship is given by the following four-variable equation (8):

$$\begin{aligned} \text{CCI} = {} & 45.2 + (0.0892)(T_{10N}) + [0.131 + (0.901)(B)][T_{50N}] \\ & + [0.0523 - (0.42)(B)][T_{90N}] \\ & + [0.00049][(T_{10N})^2 - (T_{90N})^2] + (107)(B) + (60)(B)^2 \qquad [2] \end{aligned}$$

where CCI = calculated cetane index by the four-variable equation; $T_{10N} = T_{10} - 215$ (°C); T_{10} = 10% distillation temperature, °C, determined by ASTM Method D86-93 and corrected to standard barometric pressure; $T_{50N} = T_{50} - 260$ (°C); T_{50} = 50% distillation temperature, °C, determined by ASTM Method D86-93 and corrected to standard barometric pressure; $T_{90N} = T_{90} - 310$ (°C); T_{90} = 90% distillation temperature, °C, determined by ASTM Method D86-93 and corrected to standard barometric pressure; $B = [e^{(-3.5)(DN)}] - 1$; $DN = D - 0.85$; and D = specific gravity at 15°C determined by ASTM Method D1298-85.

Ali and Hanna (3) determined the cetane number of a blend of 80:13:7% (vol/vol/vol) diesel/methyl tallowate/ethanol by cetane method ASTM D613-86 (7) and reported that the cetane index determined by the four-variable equation was close to that determined by the cetane method. The cetane number by cetane method ASTM D613-86 was 48.9 as opposed to the CCI value of 48.17.

Energy content. Gross energy content or heat of combustion of all fuel blends was determined by following standard ASTM Method D240-92 (7). A Parr 1241 automatic adiabatic oxygen bomb calorimeter (Parr Instrument Co., Moline, IL) was used.

Melting point. Melting points of all fuel blends were determined by the capillary method given in standard AACC Method 58-40 (5). Capillary tubes of 5-mm internal diameter were filled to approximately 1-cm depth with fuel and then fused at the bottom. The tubes were held overnight at −30°C. The tubes were taped to the bulb of a thermometer with 0.2°C graduation and immersed into a saturated $CaCl_2$ solution at −18°C. The temperature of the solution was increased slowly, and the melting point of each sample was determined.

Cloud point. Cloud point is the temperature at which a cloud of crystals first appears in a liquid when cooled under conditions as described in ASTM Method D2500-91 (7). Three cooling baths with different cooling temperatures were used. The −1 to −3°C temperature bath was prepared by mixing saturated NaCl solution with crushed ice. A second bath, with a temperature of −15 to −18°C, was made with a saturated $CaCl_2$ solution and crushed ice. The third bath, with a temperature of −35 to −40°C, was made by cooling acetone with solid CO_2 (dry ice). Samples were put in jars, as prescribed in ASTM Method D2500 (7), so that the thermometers touched the jar bottoms, and were subsequently moved from one cooling bath to the next (higher to lower temperature) until clouds of crystals appeared in the bottom of the jars.

Pour point. Pour point of petroleum oil is an index of the lowest temperature at which it has utility in certain applications. The pour points of all fuel blends were determined by ASTM Method D97-93 (7). The test apparatus and system were the same as that used to determine the cloud point, except that the thermometers were positioned so that just their bulbs were immersed in the fuel.

Flash point. Flash point is the temperature at which the fuel will start burning when it comes in contact with fire. All fuel samples, except ethanol, were sent to Professional Service Industries, Inc. to determine the flash points by use of the Pensky–Martens closed tester and ASTM Method D93-90 (7).

Ash content. Ash content of the samples of fuel blends was determined by ASTM Method D482-91 (7). Samples of approximately 100 g were burned in crucibles, and the charred samples with crucibles were placed in a muffle furnace at 780°C for about 4 h to determine the ash content of the fuel samples.

Other properties. A sample of each fuel blend was prepared and sent to Professional Service Industries, Inc. to determine sulfur content by ASTM Method D129-91 (7), Ramsbottom carbon residue by ASTM Method D524-88 (7), particulate matter by ASTM Method D2276-93 (7), acid value by potentiometric titration after ASTM Method D664-89 (7), and copper-strip corrosion test by ASTM Method D130-88 (7).

Water content. A sample each of methyl tallowate, methyl soyate, and diesel fuel was sent to Professional Service Industries, Inc. to determine water content by ASTM Method D1796-94 (7). It was assumed that water content of each blend was in proportion to its components, i.e., methyl tallowate, methyl soyate, ethanol, and/or diesel fuel.

RESULTS AND DISCUSSION

Fatty acid composition. Fatty acid compositions of raw beef tallow, soybean oil, and their esters are presented in Table 2. The total saturated and unsaturated fatty acid compositions of edible tallow were 48.2 and 51.8%, respectively, whereas those of inedible tallow were 39.8 and 60.2%, respectively. The increase in unsaturated fatty acids in inedible tallow was due to the fact that it was a mixture of fats, oils, and lard from all sources.

Physical properties. Tables 3–5 give a summary of the physical and fuel properties of tallow, soybean oil, their esters, diesel fuel, ethanol, and their blends.

Viscosity. Proper operation of an engine depends on the proper viscosity of the liquid fuel. The viscosity of liquid fuel is important to its flow through pipelines, injector nozzles, and orifices, and for atomization of fuel in the cylinder. Thus

TABLE 2
Average Composition of Fatty Acids (wt%) in Edible and Inedible Beef Tallow and Soybean Oil and Their Esters

Carbon chain	Edible tallow[a] (%)	Edible tallow ester[a] (%)	Inedible tallow[a] (%)	Inedible tallow ester[b] (%)	Soybean oil[c] (%)	Soy ester[b] (%)	Inedible tallow ester + soy ester (%)
$C_{8:0}$	—	—	0.02	0.07	0.04	0.07	—
$C_{9:0}$	—	—	0.10	—	—	—	—
$C_{10:0}$	—	—	0.10	0.09	—	—	—
$C_{11:0}$	—	—	—	—	—	—	—
$C_{12:0}$	—	—	0.05	0.28	—	0.36	0.31
$C_{14:0}$	4.89	2.59	1.85	1.35	—	0.25	0.81
$C_{16:0}$	28.43	23.69	23.87	23.76	10.74	9.65	16.71
$C_{16:1}$	4.63	2.96	3.30	2.60	—	—	1.20
$C_{18:0}$	14.86	19.86	13.84	13.79	3.84	4.39	8.75
$C_{18:1}$	44.55	48.91	47.38	48.18	20.96	23.10	34.25
$C_{18:2}$	2.64	1.99	9.49	9.88	56.56	53.93	33.56
$C_{18:3}$	—	—	—	—	7.86	8.25	4.41
Sat.[d]	48.18	46.14	39.83	39.34	14.62	14.72	26.58
Unsat.[d]	51.82	53.86	60.17	60.66	85.38	85.28	73.42

[a]Excel Corporation (Schuyler, NE). [b]Interchem Environmental, Inc. (Overland Park, KS). [c]Archer Daniels Midland Co. (Decatur, IL). [d]Sat., saturated; Unsat., unsaturated.

TABLE 3
Fuel Properties of Tallow, Soybean Oil, Their Esters, and Diesel Fuel and Ethanol

Fuel properties	ASTM method[a]	Raw tallow	Methyl tallowate	Soybean oil	Methyl soyate	Ethanol	Diesel fuel
Viscosity, mP–s @ 40°C		51.15	4.11	28.05	4.06	0.91	2.07
Specific gravity @ 15.5°C	D1298-85	0.9198	0.8772	0.926	0.887	0.7947	0.8383
API gravity	D1298-85	22.34	29.81	21.31	28.03	46.55	37.29
Distillation range	D86-93						
IBP, °C (°F)		279 (535)	218 (424)	220 (428)	265 (509)		179 (355)
10% Point, °C (°F)		319 (607)	323 (613)	320 (608)	329 (625)		212 (414)
50% Point, °C (°F)		329 (625)	331 (629)	(336 (638)	335 (635)		262 (504)
90% Point, °C (°F)		351 (665)	353 (667)	364 (688)	313 (595)		326 (619)
FBP, °C (°F)		3512 (665)	354 (669)	375 (708)	337 (639)		326 (619)
Calculated cetane index	J313[b]	40.15	57.78	38.90	51.61		50.34
Energy content, kJ/kg	D240-92	40,054	39,949	39,280	40,080	28,322	45,509
Melting point, °C (°F)		45 (113)	13.5 (56)	–3.5 (26)	–3 (27)		<–10 (14)
Cloud point, °C (°F)	D2500-91	—	12 (54)	–9 (16)	3 (37)		–15 (5)
Pour point, °C (°F)	D97-93	—	9 (48)	–16 (3)	–7 (19)		–28 (–18)
Flash point, °C (°F)	D93-90	201 (395)	96 (205)	174 (345)	127 (260)		54 (130)
Water content, %	D1796-94	—	<0.05	—	<0.05		<0.05
Sulfur content, %	D129-91	—	0.05	—	<0.05		0.24
Ash content, %	D482-91	0.04	<0.01	0.12	<0.01	<0.005	<0.001
Carbon residue, %	D524-88	6.21	1.83	4.01	1.74		0.18
Particulate matter, mg/100 mL	D2276-93	—	5.56	—	5.61		0.39
Acid value, mg KOH/g	D664-89	—	0.82	—	0.29		0.23
Copper-strip corrosion	D130-88	—	1a	—	1a		1a

[a] *Annual Book of ASTM Standards,* American Society for Testing and Materials, Philadelphia, 1994.
[b] *SAE Handbook of Engines, Fuels, Lubricant, Emissions, and Noise,* Society of Automotive Engineers, Inc., Warrendale, 1989.

accurate measurement of viscosity is essential to many product specifications.

The viscosity data presented in Tables 3–5 show that raw tallow and soybean oil are extremely viscous compared to No. 2 diesel fuel. Esterification of tallow and soybean oil significantly reduced their viscosities; however, Ali and Hanna (3) reported the viscosity of methyl tallowate as a function of temperature. They reported that viscosity of methyl tallowate and methyl soyate decreased with increasing temperatures and by blending with ethanol. As presented in Tables 3–5, blending methyl tallowate and ethanol in a 65:35 (vol/vol) ratio reduced the viscosity to that of No. 2 diesel fuel. Viscosities of the blends that contained diesel, methyl tallowate, and/or methyl soyate and ethanol were basically the same as the viscosity of diesel fuel.

Specific gravity. Accurate determinations of the density, specific gravity, and API gravity of petroleum products are necessary for the conversion of measured volumes to volumes at standard temperatures of 15°C (60°F). These factors govern the quality of crude petroleum. These properties, however, are uncertain indications of fuel quality unless correlated with other properties. Mullins (9) correlated fuel density with particulate emissions and concluded that increasing density gave increasing particulate emissions.

The specific gravity data presented in Tables 3–5 show that converting tallow and soybean oil to esters reduced their specific gravities from 0.92 to about 0.88, which was still a little higher than the 0.84 for No. 2 diesel fuel. The specific gravities of blends of tallow and soybean oil esters with ethanol were further reduced to approximately 0.85. The specific gravities of all tested blends were within 2.3% range of No. 2 diesel fuel.

Distillation property. The distillation characteristics of hydrocarbons often have an important effect on their safety and performance, specifically for fuels and solvents. Volatility is the major determinant of the tendency of a hydrocarbon to produce potentially explosive vapors. It also is critically important to an engine's start and warm-up. The presence of high-boiling point components in fuels can significantly affect the degree of formation of solid combustion deposits.

The distillation characteristics data for raw beef tallow, soybean oil, their esters, and blends with No. 2 diesel fuel and ethanol are presented in Table 3 and Figure 1. Both tallow and soybean oil, as well as their esters, had higher distillation temperatures (Fig. 1A and B) than did No. 2 diesel fuel. Tallow decomposed at 351°C, the temperature at which there was 90–95% recovery. Similarly, soybean oil decomposed at 364°C, with about 90% recovery. At that temperature, the sample foamed excessively, and temperature became unstable due to evolution of volatiles. Methyl soyate decomposed at 84% recovery, and the temperature dropped to 313°C at 90% recovery. Typically, it was not possible to distill all of the tallow and soybean oil, and some residue remained in the distillation flask. These results are in general agreement with Goering *et al.* (1).

The rest of the fuel blends, which contained ethanol, had low initial boiling points of about 78°C. Because of the fact that ethanol boils at 77°C, 10% condensate also was collected at 78°C, and, once the ethanol evaporated from the sample,

TABLE 4
Fuel Properties of Blends of Diesel Fuel (D), Methyl Tallowate (MT), Methyl Soyate (MS), and Ethanol (E)

Fuel properties	ASTM method[a]	D/MT/E (80:13:7)	D/MT/E (70:19.5:10.5)	D/MT/E (60:26:14)	D/MT/MS/E (80:6.5:6.5:7)	D/MT/MS/E (70:9.75:9.75:10.5)	D/MT/MS/E (60:13:13:14)
Viscosity, mP–s @ 45°C		1.98	1.97	2.01	2.09	2.09	2.10
Specific gravity, @ 15.5°C	D1298-85	0.8392	0.8403	0.8412	0.8395	0.8410	0.8425
API gravity	D1298-85	37.11	36.89	36.71	37.09	36.75	36.45
Distillation range	D86-93						
IBP, °C (°F)		77 (171)	78 (172)	78 (172)	78 (172)	78 (172)	78 (172)
10% Point, °C (°F)		200 (392)	79 (174)	79 (174)	184 (364)	78 (173)	79 (174)
50% Point, °C (°F)		270 (518)	276 (529)	279 (534)	268 (515)	273 (523)	278 (532)
90% Point, °C (°F)		345 (624)	334 (634)	333 (631)	328 (622)	330 (627)	334 (633)
FBP, °C (°F)		335 (636)	338 (640)	341 (636)	340 (644)	340 (644)	342 (648)
Calculated cetane index	J313[b]	50.35	49.15	49.19	48.89	48.28	48.48
Energy content, kJ/kg	D240-92	42,288	40,997	39,148	42,803	41,522	38,350
Melting point, °C (°F)		–5 (23)	–5 (23)	–5 (23)	<–10 (14)	<–10 (14)	<–10 (14)
Cloud point, °C (°F)	D2500-91	–8 (18)	–5 (23)	–4 (25)	–11 (12)	–10 (14)	–10 (14)
Pour point, °C °F)	D97-93	–15 (5)	–14 (7)	–13 (9)	–16 (3)	–14 (7)	–13 (9)
Flash point, °C (°F)	D93-90	27 (80)	27 (80)	27 (80)	27 (80)	27 (80)	27 (80)
Water content, %	D1796-94	—	—	—	—	—	—
Sulfur content, % D129-91	0.12	0.10	0.10	0.13	0.11	0.11	—
Ash content, %	D482-91	—	—	—	—	—	—
Carbon residue, %	D524-88	0.13	0.14	0.14	0.03	0.14	0.15
Particulate matter, mg/100 mL	D2276-93	1.39	1.66	1.69	1.24	2.21	2.68
Acid value, mg KOH/g	D664-89	0.27	0.36	0.32	0.33	0.22	0.30
Copper-strip corrosion	D130-88	1a	1a	1a	1a	1a	1a

[a] *Annual Book of ASTM Standards,* American Society for Testing and Materials, Philadelphia, 1994.
[b] *SAE Handbook of Engines, Fuels, Lubricant, Emissions, and Noise,* Society of Automotive Engineers, Inc., Warrendale, 1989.

the temperatures quickly rose above those for diesel fuel (Fig. 1C, D, and F). Samples of diesel fuel and methyl tallowate blends had similar distillation curves as those for No. 2 diesel fuel (Fig. 1E).

Based on the distillation ranges of the fuel blends, CCI was determined and presented in Tables 3–5. Raw tallow and soybean oil had CCI lower than that of No. 2 diesel fuel, but, after esterification, the CCI of both esters was greater than that of No. 2 diesel fuel. The CCI of all other blends was generally the same as that of No. 2 diesel fuel, except for the blends containing no ethanol. The CCI of these blends was greater than that of No. 2 diesel fuel.

This CCI is useful for estimating ASTM cetane numbers when a test engine is not available for direct measurement, and it may be conveniently employed for estimating cetane number when the quantity of sample available is too small for an engine rating.

Many researchers have concluded that the cetane number influences both gaseous and particulate emissions, with higher cetane numbers giving lower emissions. Cowley *et al.* (10) confirmed these observations and also investigated the influence of cetane number on particulate emissions. They found that an increase in cetane number did not generally lead to a reduction in light-duty vehicle particulate emissions. The situation for heavy-duty engines was different, however: there was a small reduction in particulates with higher-cetane fuels, but the size of the effect was engine-dependent. Mullins (9) emphasized that cetane number had a major influence on cold starting and on subsequent white smoke and noise emissions in both heavy- and light-duty vehicles. Thus an increase in cetane number can be beneficial to modern engines.

Energy content. Heat of combustion is a measure of the energy available in a fuel. It is a critical property of fuel intended for use in weight-limited vehicles.

The energy content of raw tallow, soybean oil, their esters, and blends with diesel fuel and ethanol is presented in Tables 3–5. The gross energy content of both methyl tallowate and methyl soyate is approximately 12% lower than that of No. 2 diesel fuel. Goering *et al.* (1) also reported that gross heat content of differently processed vegetable oils was less than that of No. 2 diesel fuel. The energy content of the methyl tallowate/ethanol blend was further reduced by 8%. Overall, the energy content of 65:35 blends of methyl tallowate or methyl soyate and ethanol were about 20% less than that of No. 2 diesel fuel. The energy content of all other blends decreased as the amount of methyl tallowate, methyl soyate, and ethanol content increased.

Melting point. Natural fats and oils from animal and vegetable origins are mixtures of triglycerides composed of a variety of fatty acids. They do not exhibit definite or sharp melting points. Therefore, the term "melting point" does not imply the same characteristics that it does with pure substances of a definite crystalline nature. Fats pass through a stage of gradual softening before they become completely liquid. The melting point then must be defined by the specific conditions of the method by which it is determined, and, in this case, it is the temperature at which the sample becomes totally liquid and perfectly clear.

TABLE 5
Fuel Properties of Blends of Diesel Fuel (D), Methyl Tallowate (MT), Methyl Soyate (MS), and Ethanol (E)

Fuel properties	ASTM method[a]	MT/E 65:35	MS/E 65:35	MT/MS/E 32.5:32.5:35	D/MT 80:20	D/MT 70:30	D/MT 60:40
Viscosity, mP–s @ 40°C		2.03	2.13	2.14	2.40	2.61	2.87
Specific gravity, @ 15.5°C	D1298-85	0.8480	0.8577	0.8495	0.8460	0.8500	0.8540
API gravity	D1298-85	35.36	33.48	35.07	35.76	34.97	34.19
Distillation range	D86-93						
IBP, °C (°F)		77 (171)	77 (171) 77 (171)	175 (347)	182 (359)	183 (361)	
10% Point, °C (°F)		78 (172)	78 (172)	78 (172)	213 (416)	218 (424)	226 (439)
50% Point, °C (°F)		321 (610)	333 (631)	329 (625)	278 (532)	291 (555)	302 (575)
90% Point, °C (°F)		342 (647)	342 (647)	339 (643)	329 (624)	333 (631)	335 (635)
FBP, °C (°F)		342 (648)	348 (658)	347 (657)	340 (644)	341 (645)	353 (650)
Calculated cetane index	J313[b]	52.40	48.69	52.67	53.43	55.14	56.34
Energy content, kJ/kg	D240-92	36158	34,096	35,560	43,616	43,147	42,807
Melting point, °C (°F)		9.5 (49)	−3 (26)	7 (45)	−3 (27)	−1.5 (29)	−0.25 (32)
Cloud point, °C (°F)	D2500-91	8 (46)	−4 (25)	4 (39)	−7 (19)	−6 (21)	−4 (25)
Pour point, °C (°F)	D97-93	3 (37)	−10 (14)	1 (34)	−11 (12)	−9 (16)	−6 (21)
Flash point, °C (°F)	D93-90	27 (80)	27 (80)	27 (80)	52 (125)	57 (135)	66 (150)
Water content, %	D1796-94	—	—	—	—	—	—
Sulfur content, %	D129-91	<0.05	<0.05	<0.05	0.14	0.15	0.12
Ash content, %	D482-91	—	—	—	—	—	—
Carbon residue, %	D524-88	0.50	0.35	0.27	0.16	0.21	0.21
Particulate matter, mg/100 mL	D2276-93	—	—	—	2.58	8.17	3.48
Acid value, mg KOH/g	D664-89	0.67	0.17	0.37	0.18	0.39	0.12
Copper-strip corrosion	D130-88	1a	1a	1a	1a	1a	1a

[a] *Annual Book of ASTM Standards,* American Society for Testing and Materials, Philadelphia, 1994.
[b] *SAE Handbook of Engines, Fuels, Lubricant, Emissions, and Noise,* Society of Automotive Engineers, Inc., Warrendale, 1989.

Melting point data, presented in Tables 3–5, show that the melting point of raw tallow was markedly reduced by esterification. Melting points of soybean oil and its esters were much lower than those of tallow and its esters. Melting points of both esters were high compared to that of No. 2 diesel fuel. When 35% (vol/vol) ethanol was added to the esters, melting points were reduced further.

Melting points of methyl tallowate blended with diesel fuel in ratios varying from 40:60 to 20:80 (vol/vol) were intermediate and a function of the blend formulation. Addition of ethanol to the blends further reduced melting points. When 50% of the methyl tallowate was replaced with methyl soyate, melting points were well below −10°C.

Cloud point. Cloud point of petroleum products is the temperature at which a cloud of wax crystals first appears in the liquid when it is cooled. Cloud point is generally determined for products that are transparent in a 40-mm–thick layer and have cloud points below 49°C.

The trends in the cloud point values of methyl tallowate, methyl soyate, and their blends with diesel fuel and ethanol were the same as those observed with melting points (see Tables 3–5). Methyl tallowate and methyl soyate had significantly higher cloud points than did No. 2 diesel fuel. When ethanol was blended with the esters, cloud-point temperatures were reduced. When 50% of the methyl tallowate was replaced with methyl soyate, cloud point of the blend was 4°C.

Addition of ethanol with methyl tallowate reduced cloud point. If 50% of the methyl tallowate was replaced with methyl soyate, cloud point was further reduced, and a blend of diesel, methyl tallowate, methyl soyate, and ethanol reduced cloud point to within 4 or 5°C of the cloud point of diesel fuel.

Pour point. The trends in pour points of all blends were similar to those observed with melting and cloud points (see Tables 3–5). Pour points of methyl tallowate and methyl soyate were significantly higher than that of No. 2 diesel fuel. Once again, when ethanol was added to the esters, pour points were reduced, and, when 50% of the methyl tallowate was replaced with methyl soyate, pour point was 1°C.

Blends of diesel fuel and methyl tallowate in the range from 60:40 to 80:20 (vol/vol) had pour points ranging from −6 to −11°C. The blends of diesel, methyl tallowate, and ethanol had pour points ranging from −13 to −15°C. As shown in Table 3, there was no noticeable difference in pour point when 50% of the methyl tallowate was replaced with methyl soyate. Therefore, it was concluded that the addition of ethanol with methyl tallowate reduced pour point. Pour points of diesel fuel, methyl tallowate, methyl soyate, and ethanol blends were within 12°C of the pour point of No. 2 diesel fuel.

Flash point. Flash point measures the tendency of the sample to form a flammable mixture with air under controlled laboratory conditions. This is the only property that must be considered in assessing the overall flammability hazard of a material. It is used in shipping and safety regulations that define flammable and combustible materials. Flash point can indicate the possible presence of highly volatile and flammable materials in relatively nonvolatile or nonflammable material.

Flash points of raw tallow and soybean oil were far greater than that of No. 2 diesel fuel (see Tables 3–5). Flash points of

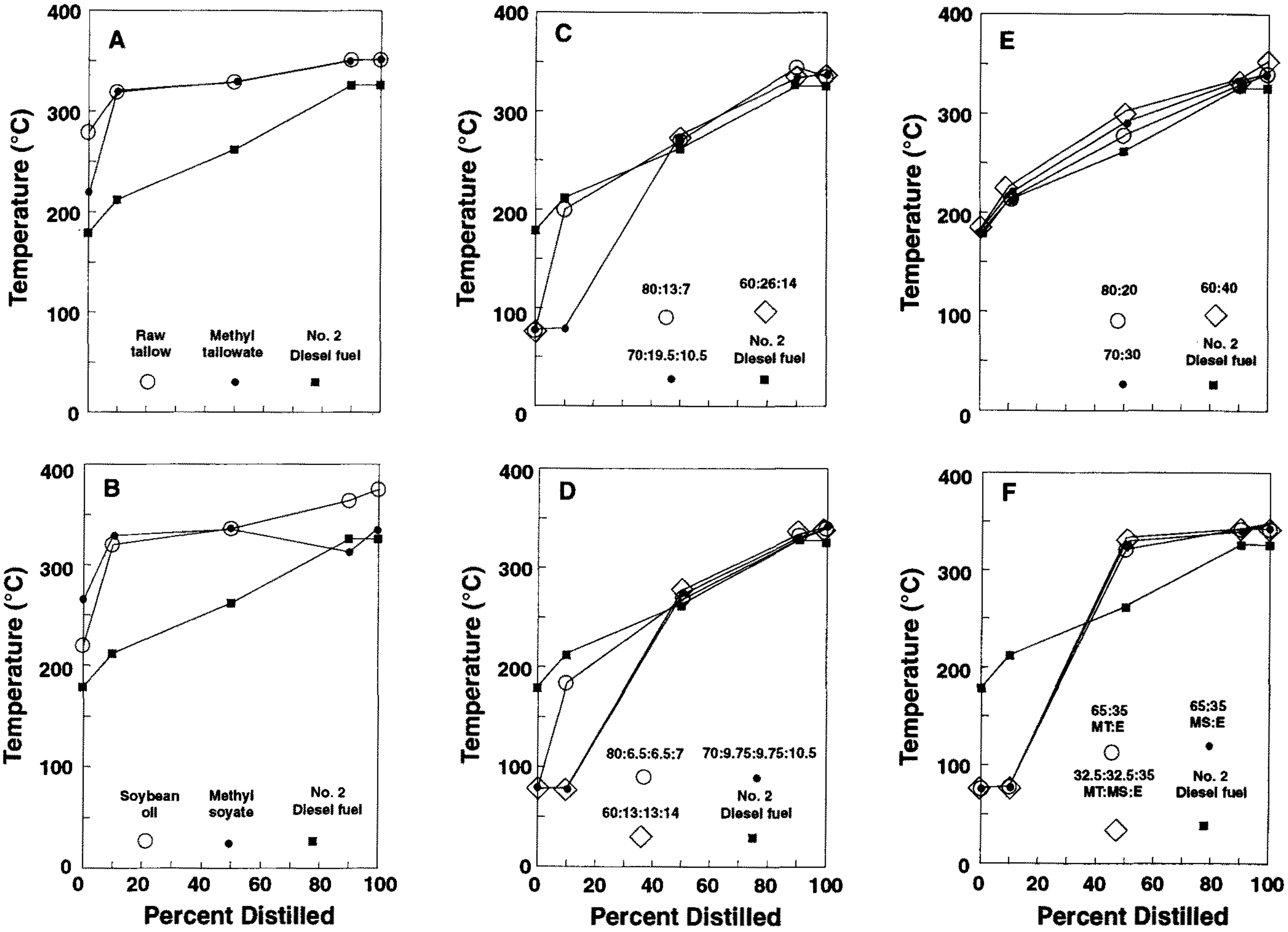

FIG. 1. Distillation curve for tallow, soybean oil, their esters and blends with ethanol and No. 2 diesel fuel.

tallow and soybean oil were reduced after esterification, but were still higher than that of diesel fuel. Flash points increased with increasing methyl tallowate in the blends. Flash points of blends containing ethanol were reduced to 27°C, which corresponded to the flash point of ethanol.

Water content. Water and sediment content of fuel oil are important because they cause corrosion of equipment and problems in processing. Determination of water and sediment content is also required to accurately measure net volumes of actual fuel oil in sales, taxation, exchanges, and custody transfer (7).

Water content of methyl tallowate, methyl soyate, and No. 2 diesel fuel was determined (see Tables 3–5). Water content was less than 0.05%. It was assumed that the water content of the blends prepared from these three fuels would also be less than 0.05%.

Sulfur content. Sulfur compounds pose a dual problem: they not only cause environmental pollution from their combustion products, but these products are also naturally corrosive and cause severe physical problems to engine parts. Sulfur pollution and corrosion were problems long before the NO_X were known to affect the atmosphere. The general availability of low-sulfur fuels, however, diminished the concern with respect to the sulfur (11).

Sulfur contents of both methyl tallowate and methyl soyate were less than 0.05% (see Tables 3–5). High-sulfur (0.24%) diesel fuel was used in this study. It was assumed that the sulfur content of the blends would vary according to the diesel and methyl tallowate/soyate content of the blends.

Ash content. Knowledge of the amount of a product's ash-forming material can provide information on whether the product is suitable for use in a given application. Ash can result from oil, water-soluble metallic compounds, or extraneous solids, such as dirt and rust.

Ash content of raw tallow, soybean oil, their esters, ethanol, and No. 2 diesel fuel was determined. Ash content of the blends was assumed to vary in proportion to the ash content of their individual components.

Tables 3–5 shows the ash content of raw tallow, methyl tallowate, soybean oil, methyl soyate, ethanol, and No. 2 diesel fuel. Except for raw tallow and soybean oil, the ash content was less than 0.01%. Ash content of soybean oil was 0.12%;

tallow was 0.04%; esters were less than 0.01%; ethanol was less than 0.005%; and diesel fuel was less than 0.001%. Therefore, it was concluded that ash content was low enough not to cause any problems when used as fuel.

Carbon residue content. The carbon residue value of diesel fuel correlates with the amount of carbonaceous deposits the fuel will form in the combustion chamber of the engine. The higher the carbon residue value, the greater the expected carbon deposits in the combustion chamber.

Carbon residue content of raw tallow and soybean oil wasreduced by the process of esterification (see Tables 3–5). All other fuel blends had carbon residue content within 16% of the carbon residue content of No. 2 diesel fuel, except for the blends of diesel and methyl tallowate, which had carbon residue content 2 to 3 times greater than that of No. 2 diesel fuel.

Particulate matter content. Particulate matter contains primarily carbon particles. Carbonaceous particulates that form from gas-phase processes are generally referred to as soot, and those that develop from pyrolysis of liquid hydrocarbon fuels are generally referred to as coke or cenospheres (11). Because soot particulates can absorb and carry carcinogenic materials into the environment as emission, they can cause an ill effect on human health. Determination of particulate matter in the fuel blends will give a potential comparison of the emission of particulate matter with diesel fuel.

Particulate matter content of methyl tallowate and methyl soyate differed markedly from that of No. 2 diesel fuel at 5.56, 5.61, and 0.39 mg/100 mL, respectively (see Tables 3–5). Particulate matter content of all blends varied according to the diesel and ester content.

Acid value. New and used petroleum products may contain acidic constituents present as additives or as degradation products, such as oxidation products, formed during service. The relative amount of these materials can be determined by titrating with alkali. Acid value is a measure of the amount of acidic substances in the fuel. This can also be defined as the amount of potassium hydroxide, in mg, necessary to neutralize the FFA in a 1-g sample of oil or esters. This number is used as a guide in the quality control of fuels, per ASTM Method D664-89 (7).

Acid values of methyl tallowate, methyl soyate, and No. 2 diesel fuel were 0.82, 0.29, and 0.23 mg KOH/g, respectively (see Tables 3–5). Acid values of all other blends varied according to their methyl tallowate and diesel content.

Copper-strip corrosion. Petroleum products contain sulfur compounds, most of which are removed during refining. Of the sulfur compounds remaining in the petroleum product, however, some can have a corroding effect on various metals. This corrosivity is not necessarily directly related to the total sulfur content, however. The effect can vary according to other chemicals and types of sulfur compounds present.

Copper-strip corrosion tests were performed on each fuel blend to assess relative degree of corrosivity and each strip was compared with the data in ASTM Method D130-88 (7). The classification code indicates that numbers 1, 2, 3, and 4 designate slight tarnish, moderate tarnish, dark tarnish, and corrosion, respectively. Subscripts a–e describe a standard color reproduction in the standard chart. In this case, all copper strips obtained for different fuel blends showed a classification code of 1a, which indicates slight tarnish with a light orange color, almost the same as the freshly polished strip. These results indicate that the fuel blends would not cause corrosion.

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