Use of Branched-Chain Esters to Reduce the Crystallization Temperature of Biodiesel

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ABSTRACT: To reduce the tendency of biodiesel to crystallize at low temperatures, branched-chain alcohols were used to esterify various fats and oils, and the crystallization properties of the branched esters were compared with those of methyl esters by using differential scanning calorimetry (DSC), cloud point, and pour point. Compared with the methyl esters that are commonly used in biodiesel, branched-chain esters greatly reduced the crystallization onset temperature (T_{CO}) of neat esters and their corresponding ester diesel fuel blends. Isopropyl and 2-butyl esters of normal (~10 wt% palmitate) soybean oil (SBO) crystallized 7–11 and 12–14°C lower, respectively, than the corresponding methyl esters. The benefit of the branched-chain esters in lowering T_{CO} increased when the esters were blended with diesel fuel. Esters made from a low-palmitate (3.8%) SBO crystallized 5–6°C lower than those of normal SBO. Isopropyl esters of lard and tallow had T_{CO} values similar to that of methyl esters of SBO. DSC provided an accurate means of monitoring crystallization, and the DSC results correlated with cloud and pour point measurements.

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KEY WORDS: Biodiesel, branched-chain esters, 2-butyl esters, cloud point, crystallization, differential scanning calorimetry, isopropyl esters, pour point, soydiesel.

The history of alternative fuels for powering diesel engines goes back to the late 1800s, when the compression ignition engine was first invented and powered on peanut oil (1). Recently, there has been growing interest in biodiesel, that is, diesel fuels based on fats and oils. Methyl esters and, sometimes, ethyl esters of vegetable oils have been considered in this application because their viscosities and resulting engine performances are comparable with conventional petroleum-based diesel fuels (1–3). Remarkable reductions in emissions, other than nitrogen oxides, have been reported with neat methyl soyate or methyl soyate/diesel fuel blends (2,4,5). Biodiesel has the additional advantage of being made from renewable resources.

However, one disadvantage of biodiesel is its performance at temperatures below ~0°C. Methyl or ethyl esters of vegetable oils have considerably higher crystallization temperatures than diesel fuel; thus, the vegetable oil esters, especially saturated fatty acid esters, crystallize and separate from diesel fuel at temperatures often experienced in wintertime operation. Such crystals can plug fuel lines and filters, causing problems in fuel pumping and engine operation (6,7).

Crystal growth inhibitors, commercially available as additives for diesel fuels, have been reported to reduce the pour points of biodiesel fuels; however, these additives do not reduce the cloud point nor improve the filterability of biodiesel (7).

Crystallization involves the arrangement of molecules in an orderly pattern. When branches are introduced into linear, long-chain esters, intramolecular associations should be attenuated and crystallization temperatures reduced (8). Thus, the crystallization temperature of biodiesel should be improved by replacing the methyl or ethyl ester with a branched moiety such as isopropyl. In this study, we assessed the potential of using esters made with branched-chain alcohols, such as isopropyl or 2-butyl, to reduce the crystallization temperature of biodiesel.

EXPERIMENTAL PROCEDURES

Materials. Refined, bleached, and deodorized soybean and canola oils (Hunt-Wesson, Inc., Fullerton, CA) were purchased locally. Refined low-palmitate soybean oil (LPSBO) was obtained from Pioneer Hi-Bred International, Inc. (Johnston, IA). Bleachable fancy-grade crude tallow was obtained from Feed Energy (Des Moines, IA), and edible-grade crude lard was obtained from Excel Corporation (Wichita, KS). No. 1 and No. 2 diesel fuels were obtained from a local oil company. Neopentyl alcohol (2,2-dimethyl-1-propanol) was purchased from Aldrich Chemical Co. (Milwaukee, WI). Other anhydrous alcohols and sodium were purchased from Fisher Scientific (Pittsburgh, PA). Fatty acids (99% purity) were purchased from Sigma Chemical Co. (St. Louis, MO).

Refining. The lard was refined by adding 25.6 g of 12 Baumé (8.0 wt%) NaOH solution to 350 g lard, agitating the mixture with a magnetic stirrer at high speed for 20 min at 40°C and then at low speed for 60 min at 70°C, and followed by filtering (Whatman No. 4 filter paper) in an oven at 65°C. Tallow, which was refined as described for lard, had a free

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fatty acid content of 0.51% and was subjected to a second treatment with 12 g of 24 Baumé (17.9 wt%) NaOH solution for 260 g of tallow. The refined lard and tallow had free fatty acid contents of 0.03%.

Preparation of esters. Esters of various fats and oils were prepared by transesterification between refined oils and various anhydrous alcohols with the corresponding sodium alkoxides of the alcohols as catalysts. The molar ratio of triglyceride to alcohol was 1:66. The sodium alkoxides were prepared as 1M solutions by reacting sodium metal with the appropriate alcohol and were used at the rate of 0.185 meq/g of oil (1 wt% of oil in esterification with methanol). Boiling with reflux was needed to prepare catalysts with branched-chain moieties. During interesterification, the reactants and catalyst were stirred vigorously at room temperature, except for lard and tallow, which were kept at 40°C. Boiling with reflux was needed for *tert*-butyl and neopentyl esterification. Transesterification was monitored by thin-layer chromatography (TLC). After interesterification, the reaction mixture was extracted with hexane and washed with water, and the solvents were evaporated under vacuum until no change in the weight of the residue was observed. For differential scanning calorimetry (DSC) analysis, the esters were purified further by TLC.

Esters of pure fatty acids were prepared by reacting the fatty acids with appropriate alcohols and concentrated sulfuric acid (4.5 wt% of fatty acids) as a catalyst. The molar ratio of fatty acid to alcohol was 1:22. The reactants and catalyst were refluxed for 2 h, and the reaction mixture was extracted with hexane. The hexane extract was washed with 5% aqueous sodium bicarbonate solution and with additional water, and the hexane was evaporated under vacuum.

Measurement of crystallization properties. The crystallization properties of esters and esters/diesel fuel blends were characterized by cloud point (9) and pour point (10) according to the methods of the American Society for Testing and Materials (ASTM) and by the crystallization onset temperature (T_{CO}) from DSC analysis.

A differential scanning calorimeter (DSC7) equipped with Intracooler System II (Perkin Elmer, Norwalk, CT) was used to obtain cooling and heating thermograms of the esters and blends of esters with diesel fuel. Approximately 7.5-mg samples were weighed into aluminum pans, and an empty aluminum pan was used as a reference. Both cooling and melting thermograms were examined, and various heating and cooling rates were tested to observe their effects on T_{CO}. For cooling thermograms, the samples were first heated to 100°C for 2 min, cooled to 30°C at 200°C/min, and then held until the heat flow stabilized. Further cooling from 30 to −70°C was carried out at 0.1, 5, or 20°C/min. For melting thermograms, samples were cooled to −70°C at 200°C/min and held until the heat flow stabilized. Then, samples were heated from −70 to 60°C. After comparing various heating rates, 5°C/min was selected. Samples, which were solid at room temperature, were melted completely before weighing into a sample pan.

T_{CO} was determined as the end point (where the transition curve deviates from the baseline at the high-temperature side) of the highest melting transition, that is, the lowest temperature at which the sample was completely liquid. The temperatures were calibrated by measuring each day the T_{CO} of cyclohexane (6.54°C).

TLC. For monitoring transesterification, 5 µL of the reaction mixture after alcohol removal was spotted on silica gel plates (0.25 mm, Type K5; Whatman LabSales, Hillsboro, OR), and the plates were developed in hexane/diethyl ether/acetic acid solvent systems of 90:10:1 (vol/vol/vol) or 50:50:1 (vol/vol/vol). The former was used to resolve esters and triacylglycerols; the latter, partial glycerides. The separated spots were visualized in an iodine chamber. For further purification of esters, about 250 mg of the prepared esters diluted with 250 µL hexane was applied to a 1-mm thick TLC plate. The plates were developed in hexane/diethyl ether/acetic acid (90:10:1), and the bands were visualized by spraying with 0.2% dichlorofluorescein in ethanol and by viewing under ultraviolet light. Esters were eluted from the plates with hexane, and the solvent was evaporated under vacuum.

Fatty acid analysis. Fats and oils were transesterified by the method of Frey and Hammond (11), and the methyl esters were analyzed isothermally at 200°C for fatty acid composition by using a Hewlett-Packard Model 5890 gas chromatograph (Kennet Square, PA) equipped with a J&W (Folsom, CA) DB-23 fused-silica column (15-m length, 0.25-mm i.d., 0.25-µm film thickness) and a flame-ionization detector.

Statistical analysis. Each datum on crystallization properties is the average of duplicate measurements carried out on duplicate preparations. Statistical analyses were done by using the analysis of variance and Duncan's Multiple Range Test procedures of SAS 6.06 (12).

RESULTS AND DISCUSSION

Conditions for DSC analysis. One might expect that the cooling thermograms would represent the crystallization process of esters better than melting thermograms, but T_{CO} values determined from cooling thermograms varied significantly with cooling rate in our studies, as well as in previous reports (13), probably because of nucleation effects. The cooling rate did not significantly affect T_{CO} from the melting thermogram, and T_{CO} determined from a melting thermogram is typically higher than that from a cooling thermogram (13). Figure 1 compares the melting and cooling thermograms of methyl soyate when both cooling and heating rates were 5°C/min. T_{CO} from a cooling thermogram was −3.5°C, whereas that from a melting thermogram was 5.2°C. T_{CO} increased ~1.6°C when methyl soyate was heated at 10°C/min instead of 5°C/min. The higher T_{CO} from the melting transition is a safer indicator of the lowest temperature suitable for cold-temperature operations, and 5°C/min is a convenient and reliable rate to use.

Melting transitions of esters. Figure 1 also shows the melting transition of TLC-purified isopropyl soyate (c) and its T_{CO}. Figure 2 shows the thermograms of some mixtures pre-

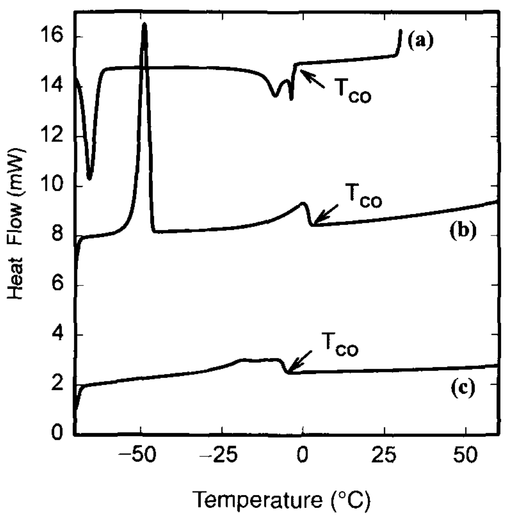

FIG. 1. Thermograms of thin-layer chromatography-purified methyl soyate and isopropyl soyate: (a) cooling thermogram of methyl soyate, (b) melting thermogram of methyl soyate, and (c) melting thermogram of isopropyl soyate, T_{CO}, temperature of crystallization onset.

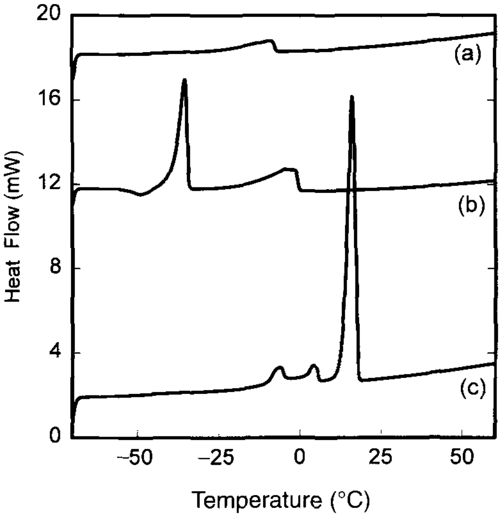

FIG. 2. Thermograms of mixtures of isopropyl esters with the ratio resembling fatty acid composition of soybean oil: (a) palmitate/stearate = 11:4, (b) palmitate/stearate/oleate = 11:4:25, and (c) palmitate/stearate/oleate/linoleate = 11:4:25:60.

pared from the isopropyl esters of pure fatty acids combined in ratios resembling soybean oil (SBO). Isopropyl palmitate/isopropyl stearate 11:4 (c) had one major and two minor melting transitions. When the lower-melting isopropyl oleate was added to the saturated esters (b), the transition for the saturates moved to a lower temperature range, and oleate had a separate transition peak. When the even lower-melting linoleate was added (a), the transition peak of unsaturated esters was not observed, probably because its crystallization temperature was lower than −70°C, and that of saturated esters again moved to a lower range. However, the melting transition of the unsaturates was observed in methyl soyate (Fig. 1b) because of the higher melting temperatures of the unsaturated methyl esters compared with those of isopropyl esters. Seemingly, methyl oleate and methyl linoleate, which have melting points at −19.9 and −35.5°C (14), respectively, present only one transition in the temperature range that we tested.

The melting point of a mixture generally is lower than those of its individual components. The component proportion that gives the lowest crystallization temperature is termed a "eutectic mixture," and its melting temperature is called the "eutectic temperature" (15). Thus, the T_{CO} of the mixture of isopropyl palmitate and isopropyl stearate (11:4) was 6.3°C lower than that of pure isopropyl palmitate and 9.8°C lower than isopropyl stearate. Obviously, the eutectic composition for isopropyl esters, especially those of palmitate and stearate mixtures, should be ideal for optimizing the melting behavior of biodiesel.

Crystallization properties of esters from various fats and oils. The esters of branched alcohols had significantly lower T_{CO} than those of the unbranched methyl or ethyl alcohols. Table 1 shows the T_{CO} of TLC-purified esters of various fats and oils as determined by DSC, and Table 2 lists the fatty acid compositions of these fats and oils.

Replacement of the propyl moiety of soy esters with its branched-chain isomer, isopropyl, reduced T_{CO} by 5.5°C. T_{CO} of soybean isopropyl and 2-butyl esters were −6.0 and −9.0°C, which were 11.2 and 14.2°C lower than those of methyl esters, respectively. In the preliminary studies, isobutyl (2-methylpropyl) stearate had a higher T_{CO} than isopropyl stearate. Isobutyl alcohol also is more expensive than isopropyl, so its use was not considered further.

The highly branched *tert*-butyl or neopentyl esters had T_{CO} higher than that of 2-butyl esters. The reactions for producing the more highly branched esters also gave lower yields, and significant portions of incomplete reaction products were detected in the final reaction mixtures by TLC. Probably, the lower yields (i.e., about 8–9% crystalline material comprised of partial glycerides and entrained esters was removed from the isopropyl ester preparations vs. no impurity removal for methyl esters) resulted from steric hindrance by the bulky branched alcohol moieties (16).

The use of branched esters of fats and oils other than SBO gave similar reductions in T_{CO}. Esters of LPSBO, which had 6.7% saturates instead of the 14.5% in normal SBO, had significantly reduced T_{CO} compared with those of normal SBO, regardless of the alcohol with which it was esterified. When esterified with isopropyl alcohol, T_{CO} of LPSBO was −12°C instead of −6°C of SBO; and with 2-butyl esters, T_{CO} was −18.5°C instead of −9°C, respectively. Canola oil, which had a level of saturates similar to LPSBO, did not perform as well as the LPSBO but performed similarly to normal SBO. Probably this was because of significantly greater amounts of arachidate and behenate in canola oil than in SBO.

The lard esters, which were considerably more saturated

TABLE 1
Crystallization Onset Temperatures of Thin-Layer Chromatography-Purified Esters from Various Fats and Oils and No. 2 Diesel Fuel Determined by DSC

	Crystallization onset temperature (°C)					
Esters	Soybean oil	Low-palmitate soybean oil	Canola	Lard	Tallow	No. 2 diesel
Methyl	5.2^a	−0.2^a	—	17.7^a	17.8^a	
Ethyl	1.4^b	−3.8^b	0.4^a	12.1^b	—	
Propyl	−0.5^c	—	—	—	—	
Isopropyl	−6.0^d	−12.0^c	−6.8^b	4.0^c	6.6^b	
2-Butyl	−9.0^e	−18.5^d	−8.1^c	0.5^d	—	
tert-Butyl	−8.0^f	—	—	—	—	
Neopentyl	−1.2^c	—	—	—	—	
						−11.9

$^{a–f}$Values in the same column with different superscripts are significantly different ($P < 0.05$).

TABLE 2
Fatty Acid Compositions of Various Fats and Oils Used for Esters Preparation

	Fatty acid (%)															
Fats and oils	14:0	15:0	15:1	16:0	16:1	17:0	17:1	18:0	18:1	18:2	18:3	20:0	20:1	20:4	22:0	22:1
Soybean oil	—	—	—	10.3	—	—	—	3.8	22.7	55.1	7.5	0.4	0.2	—	—	—
Low-palmitate soybean oil	—	—	—	3.8	—	—	—	2.7	20.3	62.0	10.6	0.2	0.4	—	—	—
Canola oil	—	—	—	3.9	0.3	—	—	1.6	58.4	22.2	9.9	0.8	1.8	—	0.3	0.8
Lard	1.5	—	—	23.3	2.9	0.4	0.4	12.7	45.1	10.9	0.8	0.3	1.2	0.5	—	—
Tallow	3.2	0.3	0.1	23.7	3.8	1.5	0.8	18.4	44.1	2.9	0.4	0.2	0.5	—	—	—

than the vegetable oils, had a T_{CO} about 10°C higher than normal soy esters regardless of the type of ester. But isopropyl esters of lard had a T_{CO} lower than that of methyl esters of SBO. The tallow esters had a slightly higher T_{CO} than lard esters because of the greater amount of stearic acid that they contained; however, the isopropyl esters of tallow had a T_{CO} comparable to that of the methyl esters of SBO. The use of branched-chain esters may make animal fats, which are more saturated but cheaper than SBO, attractive as biodiesel in warm temperature service.

No. 2 diesel fuel began to crystallize at −11.9°C; thus, the branched-chain esters of SBO crystallize at temperatures approaching that of No. 2 diesel fuel. If LPSBO is used, T_{CO} of the branched esters are as low or lower than that of No. 2 diesel fuel.

Cloud and pour points often are used to establish the suitabilities of fuels for use at low temperature. The cloud point is defined as the temperature at which a cloud of crystals first appears when a fuel oil is cooled under standard conditions (9), and the pour point is the lowest temperature at which the fuel oil is pourable (10). Table 3 shows the cloud and pour points of various esters of SBO and LPSBO. The cloud points were 2 to 7°C lower than the T_{CO} measured by DSC, which indicated that DSC was capable of determining the presence of crystals before they could be observed as a cloud of crystals in the cloud point measurements. The difference between the two determination procedures was less with the branched-chain esters than with the straight ones. The cloud points for isopropyl and 2-butyl esters of SBO were −9 and −12°C, which were 7 and 10°C lower, respectively, than that of the corresponding methyl esters. Esters of LPSBO had cloud points about 5°C lower than those of SBO.

In preparing the branched-chain esters for cloud point determinations, some crystalline material was removed before the measurement by allowing the preparations to stand overnight at ambient temperature. These impurities were shown by TLC to be partial glycerides, mostly monoglycerides. The preparations of 2-butyl esters had more monoglycerides than the isopropyl esters. Even after removal of these solids from the 2-butyl preparation by settling at room temperature, the remaining impurities interfered with observing the cloud point. However, the impurities did not interfere with pour point measurement.

Isopropyl and 2-butyl esters of normal SBO had pour points 9 and 12°C lower, respectively, than that of methyl esters. Again, the esters of LPSBO had pour points 6 to 9°C lower than those of SBO. 2-Butyl esters of LPSBO performed comparably with No. 2 diesel fuel in terms of cloud and pour points, despite the presence of impurities.

It has been reported that the flow tests, such as the Low-Temperature Flow Test or the European Cold Filter Plugging Point, tend to correspond with cloud points (7). Also, good correlation has been reported between T_{CO} from DSC and cloud points with petroleum distillate products (17). However, it is difficult to say which test best predicts the actual low-temperature performance of fuel. Crystals were observed

TABLE 3
Cloud and Pour Points (°C) of Various Esters of Normal and Low-Palmitate Soybean Oil Compared with Those of Diesel Fuel

Material	Normal soybean oil		Low-palmitate soybean oil		Diesel fuel	
	Cloud point	Pour point	Cloud point	Pour point	Cloud point	Pour point
Methyl	−2[a]	−3[a]	−7[a]	−9[a]		
Ethyl	−2[a]	−6[b]	−8[b]	−12[b]		
Isopropyl	−9[b]	−12[c]	−14[c]	−21[c]		
2-Butyl	−12[c]	−15[d]	NA[e]	−24[d]		
No. 2 diesel					−17	−24

[a–d] Values in the same column with different superscripts are significantly different ($P < 0.05$).
[e] Not available.

when methyl soyate, which has a T_{CO} and cloud point at 5.2 and −2°C, respectively, was stored at 2.2°C for extended periods.

Crystallization properties of esters/diesel fuel blends. The reduced T_{CO} of branched-chain esters also was manifested in SBO ester/diesel fuel blends (Table 4). No. 1 diesel fuel, which had a T_{CO} of −43°C, and TLC-purified esters were used for DSC analysis of the blends containing 30 or 50 wt% esters. T_{CO} of blends containing 30 wt% isopropyl and 2-butyl esters were 14.9 and 16.0°C lower, respectively, than that of the 30% methyl ester blend. The T_{CO} of 2-butyl esters was not significantly lower than that of the isopropyl esters in this blend. Seemingly, the benefits of branched-chain esters increased when the esters were blended with diesel fuel. The 30% isopropyl soy ester blend had a cloud point of −28°C compared with −18°C for that of methyl esters. As before, impurities in the 2-butyl esters interfered with the observation of the cloud point determinations of its blends. Pour points were generally 0 to 5°C below the cloud points.

In the ASTM specification for diesel fuel oils, a limit is not specified for the cloud point, but the specification states that satisfactory operation should be achieved in most cases if the cloud point is less than 6°C above the "tenth percentile minimum ambient temperature for the area" (18). The tenth percentile minimum ambient temperature is defined as the "lowest temperature that will occur 90% of the time" and is derived from an analysis of the history of hourly temperature readings for the area. Those of several states in the United States are shown in Table 5. Thus, one can conclude that the 30% isopropyl soyate blend, which has a cloud point at −28°C, should perform satisfactorily in January weather in Minnesota.

Although using branched-chain esters is a technically feasible method for making soydiesel blends usable in cold climates, it entails extra costs because of the higher prices and greater molecular weight of the branched alcohols compared with methanol. The current price of isopropanol is $0.62/L, compared with $0.34/L for methanol (19). Considering material balances of the transesterification reactions, isopropyl soyate costs about 5¢/L more than methyl soyate. The premium would only be about 2¢/L on a 30% isopropyl soyate/diesel fuel blend, which would have a 15°C lower T_{CO}. Other branched alcohols do not seem economically feasible because they are more expensive than isopropanol, and their transesterification gave lower yields and more impurities than that of isopropanol.

In conclusion, replacing the methyl esters with esters of branched alcohols greatly reduced T_{CO}, and T_{CO} of the branched-chain SBO esters were comparable with that of No. 2 diesel fuel. The benefits of branched-chain esters increased when the esters were blended with diesel fuel. Isopropyl and 2-butyl esters of SBO had T_{CO} that were 7–11 and 12–14°C lower, respectively, than methyl esters, depending upon the comparison method used. LPSBO esters had significant advantages over SBO in crystallization onset. The use of branched esters may also make the use of animal fats in biodiesel application more feasible. DSC provided accurate crystallization data in a relatively fast and easy way that corresponded well with the conventional cloud and pour points.

TABLE 4
Crystallization Onsets and Cloud and Pour Points (°C) of Normal Soy Esters/Diesel Fuel Blends[a]

	50% Esters			30% Esters		
	Methyl	Isopropyl	2-Butyl	Methyl	Isopropyl	2-Butyl
Crystallization[b] onset	−5.7	−19.4	−23.1	−14.2	−29.1	−30.2
Cloud point	−12	−23	NA[c]	−18	−28	NA
Pour point	−15	−24	−27	−18	−33	−36

[a] No. 1 diesel fuel was used.
[b] Thin-layer chromatography-purified esters were used.
[c] Not available.

TABLE 5
Tenth Percentile Minimum Ambient Temperatures (°C)

State	Nov.	Dec.	Jan.	Feb.	Mar.
Minnesota	−18	−30	−34	−31	−24
Iowa	−13	−23	−26	−22	−16
Missouri	−7	−14	−16	−13	−8
Arkansas	−4	−7	−11	−7	−3
Louisiana	−1	−3	−4	−2	1

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