Effects of Fatty Acid Derivatives on the Ignition Quality and Cold Flow of Diesel Fuel

S. Stournas*, E. Lois and A. Serdari
Laboratory of Fuel Technology and Lubricants, National Technical University of Athens,
Zografou Campus, Athens, Greece

ABSTRACT: The biodiesel that is considered as a possible substitute or extender of conventional automotive diesel fuel is commonly composed of fatty acid methyl esters that are prepared from the glycerides in vegetable oils by transesterification with methanol. This form of biodiesel is compatible with diesel fuel but offers no improvement in its ignition quality. This work describes the results of a series of experiments aimed at assessing other common fatty acid derivatives that could provide the desired biofuel component and, at the same time, improve the performance of the fuel. It was found that tertiary fatty amines and amides are significantly more effective than methyl esters in enhancing the ignition quality of the finished diesel fuel without having any negative effect on its cold flow properties.
JAOCS 72, 433–437 (1995).

KEY WORDS: Biodiesel, blending cetane numbers, cold flow properties, fatty alcohols, fatty amides, fatty amines, fatty esters,

Carbon dioxide emissions from fuel usage are generally considered a major contributor to global warming. As a means to alleviate the problem, the possibility of using biomass-derived fuel components in gasoline and diesel fuel is being pursued in many part of the world. The European Community has set an objective to secure for motor biofuels a market share of 5% of total motor fuel consumption by 2005; it is expected that a significant portion of this total amount will be biodiesel, and a Council Directive that sets down its specification is currently under discussion (1). In a similar vein, the U.S. Department of Energy (2) estimates that up to 50% of the total U.S. diesel fuel consumption could be replaced with biodiesel, defined as "a substitute for, or an additive to, diesel fuel that is derived from the oils and fats of plants."

Accepted sources of biodiesel are various types of vegetable oils (3–7), which are generally transesterified to a mixture of fatty acid methyl esters to reduce viscosity and improve combustion behavior. The resulting biodiesel is quite similar to conventional diesel fuel in its main characteristics; it has a cetane number (CN) of around 50, while its sulfur content is close to zero. Biodiesel is also compatible with conventional diesel, and the two can be blended in any proportion; the ignition quality of the blends, however, remains essentially the same as that of the conventional diesel.

This paper describes some of the recent work in our laboratory regarding other derivatives of fatty acids, which can be blended with conventional diesel fuel and furnish the desired biomass-derived component, while at the same time enhancing the ignition quality and other characteristics of the fuel. The materials that were examined include fatty acid ethyl esters and diethylamides, along with the corresponding primary and tertiary fatty amines, fatty alcohols and their acetate esters.

EXPERIMENTAL PROCEDURES

Most of the components that were used in this study (fatty acid methyl and ethyl esters, fatty alcohols and primary fatty amines) were obtained from Fluka Chemical Co. (Buchs, Switzerland), and they were used as received; the purity of most of them was 97% or better, except for oleic acid derivatives, which were of technical grade.

The acetate esters were prepared by treatment of the corresponding fatty alcohols with excess acetic anhydride; after a reaction time of 24 h at room temperature, the mixtures were washed with water and 5% aqueous sodium bicarbonate, dried over anhydrous magnesium sulfate and vacuum-distilled to furnish the desired materials, whose properties corresponded to those reported in the literature.

The N,N-diethylamides of lauric and palmitic acids were prepared by dissolving the corresponding acid chlorides (also obtained from Fluka and distilled prior to use) in toluene, followed by gradual addition of 2.2 molar equivalents of diethylamine with continuous stirring and cooling. The mixtures were stirred at room temperature for 24 h, the precipitated diethylamine hydrochloride was filtered off, the solvent and excess amine were removed by distillation at atmospheric pressure, and the residue was distilled *in vacuo* to furnish the desired amides.

The N,N-dimethyl tertiary fatty amines were prepared from the corresponding primary amines by reductive alkylation with formaldehyde in the presence of formic acid (Leuckart–Wallach reaction). As an example, the preparation of N,N-dimethyl–dodecylamine is described:

---

*To whom correspondence should be addressed at Laboratory of Fuel Technology and Lubricants, National Technical University of Athens, Zografou Campus, Athens, Greece.

TABLE 1
Base Fuel Properties

Property		Method
Density, kg/L (15°C)	0.8543	ASTM D-1298[a]
Viscosity, cSt (40°C)	3.4	ASTM D-445[a]
Sulfur content (wt%)	0.14	IP 336[b]
Pour point (°C)	−12	ASTM D-97[a]
Cloud point (°C)	−10	ASTM D-2500[a]
CEPP (°C)	−10	IP 309[b]
Cetane number	47.7	DIN 51773[c]
Distillation (°C)		ASTM D-86[a]
Initial boiling point	174	
10%	206	
50%	284	
90%	356	
Final boiling point	382	
Water (ppm)	68	ASTM D-1744[a]
Aromatics (vol%)	35.5	ASTM D-1319[a]
Copper corrosion	1A	ASTM D-130[a]

[a] Reference 10.
[b] Reference 11.
[c] Reference 9.

Dodecylamine (111 g, 0.6 moles) was added dropwise with stirring and cooling to 172 g of 98% formic acid. After the addition was complete, 120 g of 37% aqueous formaldehyde was added, and the mixture was heated under reflux until the evolution of carbon dioxide ceased (*ca.* 24 h). Concentrated hydrochloric acid was added to the residue to bind the amine, and the excess formic acid and water were distilled off; the residue was treated with 20% aqueous sodium hydroxide until strongly basic, whereupon two phases were formed. Ether was then added, the phases were separated, the aqueous phase was washed with fresh ether, the organic phases were combined, and the ether was distilled off. Vacuum distillation of the residue furnished the desired amine at 131–135°C/15 mmHg, n_D^{18} 1.4382 [lit. (8) b.p. 110–112°C/3 mmHg, n_D^{26} 1.4345]. Yield: 84.3 g (66%).

The base fuel that was employed in the relevant tests was typical of the commercial diesel fuels available in the Athens area, and its properties are shown in Table 1, along with the standard methods that were used in their determination.

For CN determinations, the various fatty acid derivatives were added to the base diesel fuel at a concentration of 5% by weight. CNs were measured by employing a BASF single-cylinder CI engine, according to the standard DIN procedure (9), which is similar to ASTM D-613 (10) and slightly better in accuracy. All reported CNs are the averages of three determinations and are considered accurate to within ±0.5 units; the CN of the base fuel was measured more than ten times and is considered accurate to within ±0.2 units.

Pour points and cloud points were measured by the relevant ASTM procedures [D-97 and D-2500 (Ref. 10), respectively], whereas the standard method IP 309 (11) was employed for measurements of the cold filter plugging point (CFPP).

RESULTS AND DISCUSSION

The measure that was used to compare the ignition improving efficiency of the various components that were added to diesel fuel was the blending cetane number (BCN) (12), which is defined as:

$$\text{BCN} = [A - (1 - x)B]/x \qquad [1]$$

where A = the measured CN of the blend; B = the CN of the base fuel; and x = the concentration of the added component (weight fraction).

The accuracy of BCN determinations depends both on the accuracy of the CN determination and on the concentration of the added component; in our case, with a constant concentration of 5% by weight and an in-house CN repeatability of about ±0.5 units, the BCN accuracy is estimated to be around ±10 units.

To serve as a reference point, the blending CNs of a series of saturated fatty acid methyl esters were measured; they are shown in Table 2, along with the reported (13,14) CNs of the neat esters. There is a fairly good correspondence between actual and blending CNs, both of them increasing as the alkyl chain of the fatty acid becomes longer. In a similar vein, Table 3 depicts the blending CNs that were determined for a number of saturated linear fatty alcohols, along with the reported (14) CNs of the neat materials; a fairly good correspondence of the two sets of values can again be observed.

The effects of the addition to diesel fuel of saturated alcohols with carbon chainlengths from C_4 to C_{16} are shown schematically in Figure 1, which shows an almost linear rela-

TABLE 2
Cetane Numbers of Saturated Methyl Esters

Ester	Blending cetane number	Neat cetane number	
		Reference 13	Reference 14
Methyl caprylate	46 ± 10	33.6	—
Methyl caprate	61 ± 10	47.2	47.9
Methyl laurate	70 ± 10	61.4	60.8
Methyl myristate	72 ± 10	66.2	73.5
Methyl palmitate	80 ± 10	74.5	74.3
Methyl stearate	81 ± 10	86.9	75.6

TABLE 3
Cetane Numbers of Saturated Alcohols

Alcohol	Blending cetane number	Neat cetane number[a]
1-Hexanol	23 ± 10	23.3
1-Octanol	48 ± 10	39.1
1-Decanol	62 ± 10	50.3
1-Dodecanol	67 ± 10	63.6
1-Tetradecanol	90 ± 10	80.8
1-Hexadecanol	117 ± 10	—

[a] Values from Reference 14.

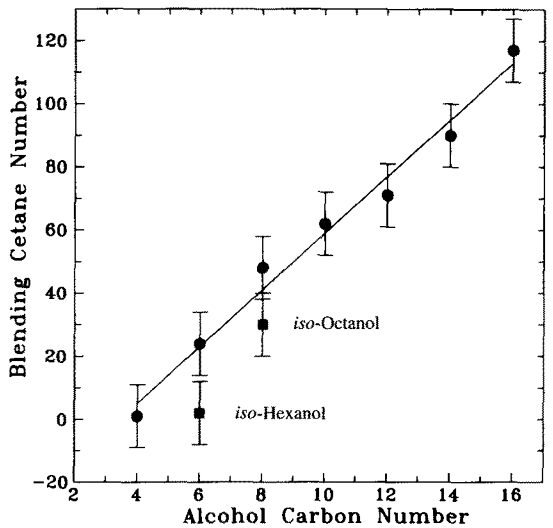

FIG. 1. Blending cetane number of saturated alcohols.

tionship between blending CN and chainlength of normal alcohols, in agreement with the behavior that has been reported for the CN of the neat alcohols (14). The two branched alcohols that were also measured, i.e., 2-ethyl-1-butanol (isohexanol) and 2-ethyl-1-hexanol (isooctanol), had a lower blending CN than their straight-chain isomers, as expected.

All BCN values that were determined for derivatives of fatty acids from C_8 to C_{18} are shown in Table 4. Only small differences were observed between equivalent methyl and ethyl esters, and even the slightly higher BCN values of the acetates of fatty alcohols are within the experimental accuracy of BCN determinations. The derivatives that are clearly superior in ignition performance are the fatty amines, particularly the tertiary amines; the tertiary amides occupy an intermediate position between esters and amines. These general trends of the various derivatives as a function of chainlength are shown in Figure 2 as shaded areas because of the BCN uncertainties that were mentioned previously.

Another observation that can be made from the data in Table 4 is that the presence of a double bond in the fatty acid chain leads to a lowering of ignition quality; this is shown more clearly in Figure 3, where BCN of all oleate derivatives is noticeably lower than that of the corresponding stearates.

In addition to ignition quality, another important property of diesel fuel is its flow behavior at low temperatures. Because the diesel fuel that is produced in many refineries cannot perform adequately in colder regions or during the winter months, it is a frequent practice to add cold flow-improving additives. Given this situation, it is important that any fatty acid component that is added to diesel fuel should not compromise its performance at low temperatures and, if possible, should improve it.

The common criteria that are used to gauge cold flow performance are the pour point (ASTM D-97), the cloud point (ASTM D-2500) (10), the CFPP, and the low-temperature flow test (LTFT). The CFPP, as described in standard method IP-309, has become increasingly popular in Europe and is frequently the only cold flow performance criterion that is included in diesel fuel specifications (15); the situation is different in North America, where LTFT (ASTM D-4539) is the more common cold flow performance test (10).

Pour point and CFPP measurements were taken for 5% solutions in base diesel fuel of the various fatty acid derivatives that have already been mentioned; the results are shown in Tables 5 and 6, respectively.

Given the ±3°C repeatability of pour point determinations, most of the added components did not appear to affect the −12°C pour point of the base fuel to a significant degree. The major exceptions are the saturated fatty alcohols with C_{12} and longer alkyl chains, which increase the pour point substantially; minor negative effects were also observed with some of the longer-chain esters. It is worth noticing that the presence of the double bond in all oleate derivatives sharply improves their cold flow behavior in comparison to the corresponding stearates. The only added component that appeared to marginally decrease the pour point was ethyl laurate. To check the validity of this observation, a solution of 20% ethyl laurate in diesel fuel was prepared, and its pour point was −17°C; it thus appears that this material behaves as a weak pour point depressant in diesel fuel.

For CFPP, whose repeatability is ±1°C in the region −1 to −25°C, the worst performers are again the longer fatty alcohols. Some of the esters, particularly the methyl esters above C_{12}, also degrade the CFPP, whereas smaller negative effects

TABLE 4
Blending Cetane Numbers of Fatty Acid Derivatives

Fatty acid (RCOOH)	Methyl ester (RCOOMe)	Ethyl ester (RCOOEt)	Diethylamide ($RCONEt_2$)	Alcohol (RCH_2OH)	Acetate ester (RCH_2OCOCH_3)	Primary amine (RCH_2NH_2)	Tertiary amine (RCH_2NMe_2)
C_8:0 (caprylic)	46	50	—	48	48	156	177
C_{10}:0 (capric)	61	64	—	62	62	175	195
C_{12}:0 (lauric)	70	73	147	67	77	190	217
C_{14}:0 (myristic)	72	75	—	90	81	196	233
C_{16}:0 (palmitic)	80	80	179	117	86	211	245
C_{18}:0 (stearic)	81	86	—	insoluble	90	215	247
C_{18}:1 (oleic)	71	72	—	65	78	162	181

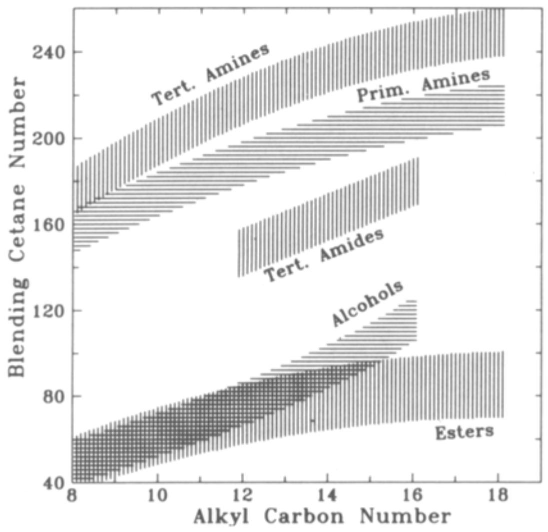

FIG. 2. Blending cetane number of fatty acid derivatives as a function of chainlength; Tert., tertiary; Prim, primary.

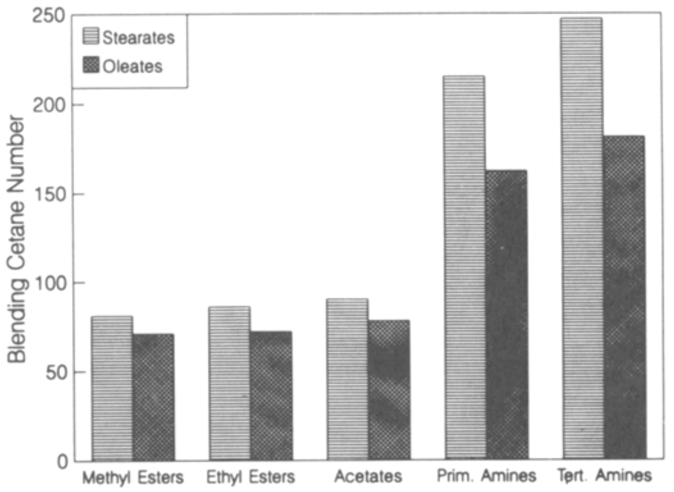

FIG. 3. Comparison of blending cetane number of oleic and stearic acid derivatives. See Figure 2 for abbreviations.

TABLE 5
Pour Points of Fatty Acid Derivatives (5% concentration in diesel fuel)

Fatty acid (RCOOH)	Methyl ester (RCOOMe)	Ethyl ester (RCOOEt)	Diethylamide ($RCONEt_2$)	Alcohol (RCH_2OH)	Acetate ester (RCH_2OCOCH_3)	Primary amine (RCH_2NH_2)	Tertiary amine (RCH_2NMe_2)
C_8:0 (caprylic)	−10	−12	—	−12	−12	−12	−12
C_{10}:0 (capric)	−10	−12	—	−12	−12	−12	−12
C_{12}:0 (lauric)	−10	−14	−12	+2	−12	−12	−12
C_{14}:0 (myristic)	−9	−10	—	+14	−12	−12	−12
C_{16}:0 (palmitic)	−9	−8	−12	+16	−10	−12	−12
C_{18}:0 (stearic)	−9	−6	—	insoluble	−8	−9	−12
C_{18}:1 (oleic)	−12	−12	—	−12	−12	−12	−12

TABLE 6
Cold Filter Plugging Point of Fatty Acid Derivatives (5% concentration in diesel fuel)

Fatty acid (RCOOH)	Methyl ester (RCOOMe)	Ethyl ester (RCOOEt)	Diethylamide ($RCONEt_2$)	Alcohol (RCH_2OH)	Acetate ester (RCH_2OCOCH_3)	Primary amine (RCH_2NH_2)	Tertiary amine (RCH_2NMe_2)
C_8:0 (caprylic)	−8	−10	—	−10	−10	−9	−11
C_{10}:0 (capric)	−9	−10	—	−10	−10	−9	−10
C_{12}:0 (lauric)	−5	−9	−10	+2	−10	−8	−12
C_{14}:0 (myristic)	0	−8	—	+16	−10	−7	−10
C_{16}:0 (palmitic)	+6	−8	−10	+20	−8	−6	−10
C_{18}:0 (stearic)	+7	−4	—	insoluble	−6	−6	−9
C_{18}:1 (oleic)	−10	−11	—	−10	−10	−9	−11

are observed with the longer primary amines. On the contrary, the tertiary amines and amides, along with all the oleic acid derivatives, do not appear to affect the CFPP of the fuel.

When both ignition quality and cold flow behavior are taken into account, the tertiary dimethylamines are the best performers; however, the tertiary amides also appear to be interesting prospects, in that their preparation from the glycerides of natural vegetable oils may be much simpler than that of the amines, as some recent studies have shown. An important question that has to be answered regarding these nitrogen-containing derivatives, however, is whether they affect exhaust emissions and particularly nitrogen oxides (NO_x). We have initiated a series of exhaust measurements from various diesel engines to answer this question, and preliminary results do not show an increase in exhaust NO_x; this may be due to the fact that an increase in the CN of the fuel lowers NO_x emissions (16,17). Detailed results from these experiments will be reported in a separate communication.

ACKNOWLEDGMENTS

We thank Hellenic Aspropyrgos Refinery for making available to us their Cetane Engine and for supplying us with the automotive diesel fuel that was used in all experiments. Financial support for this work was supplied by the Greek Ministry of Energy in the frame of the EEC "VALOREN" Program.

REFERENCES

1. *Proposal for a Council Directive Concerning the Specifications for Vegetable Oil Methylesters (biodiesel) as a Motor Fuel,"* Commission of the European Communities (DG XVII), Brussels, May 1993.
2. *Biofuels for Transportation*, U.S. Department of Energy (National Renewable Energy Laboratory), Washington, D.C., NREL/SP-420-5439, August 1993.
3. Pischinger, G.H., R.W. Siekman and A.M. Falcon, SAE Paper 82039, 1982.
4. Gateau, P., J.C. Guibot and R. Stern, *Rev. Fr. Corps Gras 31*:77 (1984).
5. Pryde, E.H., *J. Am. Oil Chem. Soc. 61*:1609 (1984).
6. Clark, S.J., L. Wagner, M.D. Schrock and P.G. Piennaar, *Ibid. 61*:1632 (1984).
7. Mittelbach, M., and P. Tritthart, *Ibid. 65*:1185 (1988).
8. Shinyo, S., *J. Agric. Chem. Soc. Japan 33*:362 (1959) [*Chem. Abstr. 58*:4447b (1963)].
9. *Bestimmung der Zündwilligkeit von Diesel-kraftstoffen*, DIN 51773 (1971).
10. *Annual Book of ASTM Standards*, vol. 05.04, American Society for Testing and Materials, Philadelphia, 1988, ASTM D-86, D-97, D-130, D-445, D-613, D-1298, D-1319, D-1744, D-2500, D-4539.
11. *Methods for Analysis and Testing*, Vol. 2, The Institute of Petroleum, London, 1979, IP 309.
12. Pecci, G.C., M.G. Clerici and F. Giavazzi, in *Proceedings, IX International Symposium on Alcohol Fuels*, Florence, vol. I, 1991, p. 321.
13. Klopfenstein, W.E., *J. Am. Oil Chem. Soc. 62*:1029 (1985).
14. Freedman, B., and M.O. Bagby, *Ibid. 67*:565 (1990).
15. Brown, G.I., and J.E. Chandler, SAE Paper 932769 (1993).
16. Lois, E., and S. Stournas, *Preprints, Div. Fuel Chem. ACS 37*:25 (1992).
17. Lange, W.W., A.A. Reglitzky, A. LeJeune, A. Schaefer, D. Naber and M. Gairing, SAE Paper 932685 (1993).

[Received March 17, 1994; accepted December 19, 1994]