

Diethyl Ether (DEE) as a Renewable Diesel Fuel

Brent Bailey

National Renewable Energy Laboratory

James Eberhardt

Steve Goguen

U.S. Department of Energy

Jimell Erwin

Southwest Research Institute

ABSTRACT

Producing and using renewable fuels for transportation is one approach for a sustainable energy future for the United States, as well as the rest of the world. Renewable fuels may also substantially reduce contributions to global climate change. In the transportation sector, ethanol produced from biomass shows promise as a future fuel for spark-ignited engines because of its high octane quality. Ethanol, however, is not a high-quality compression-ignition fuel. Ethanol can be easily converted through a dehydration process to produce diethyl ether (DEE), which is an excellent compression-ignition fuel with higher energy density than ethanol. DEE has long been known as a cold-start aid for engines, but little is known about using DEE as a significant component in a blend or as a complete replacement for diesel fuel. Dimethyl ether, the methanol analog to DEE, was recently reported to be a low-emission, high-quality diesel fuel replacement, but similar engine testing and process information on DEE is limited. To identify the potential of DEE as a transportation fuel, we conducted a comprehensive literature review of its utilization in engines and also conducted limited laboratory experiments. This paper presents the findings on fundamental engine and emissions performance of DEE, along with an estimated cost of producing DEE from biomass ethanol.

INTRODUCTION

To determine the potential of diethyl ether (DEE) for use as a transportation fuel, it is necessary to understand its engine and emissions performance characteristics, as well as what it might cost. Although DEE has long been known as a cold-start aid for engines, knowledge about using DEE for other applications, such as a significant component of a blend, or as a complete replacement for diesel fuel, is limited. To evaluate the potential of DEE as a transportation fuel, we conducted a literature survey and limited laboratory tests.

LITERATURE SURVEY METHODOLOGY

The survey examined the technical literature back to the earliest dates available on the topic of using DEE as a transportation fuel. The specific terms searched were "diethyl ether," "ethyl ether," or "ether" (if mentioned in relationship to engines or fuels). References to methyl tertiary butyl ether (MTBE) or ethyl tertiary butyl ether (ETBE) were eliminated from the final listing.

The databases searched included:

- Chemical Abstracts (CAS, a division of the American Chemical Society): 1967 to date
- Energy Science and Technology (U.S. Department of Energy): 1974 to date
- Compendex (Engineering Information, Inc.): 1970 to date

- Mobility (Society of Automotive Engineers International): 1906 to date

In the search, 49 references with abstracts were identified, and we obtained complete papers for 16 of those.

LITERATURE SURVEY RESULTS

FUEL PROPERTIES OF DEE - General fuel properties of DEE and several other potential diesel fuels are presented in Table 1. As a compression-ignition fuel, DEE has several favorable properties, including an outstanding cetane number and reasonable energy density for on-board storage. Based on a measurement of ignition delay in a combustion bomb compared to known reference fuels, Southwest Research Institute (SwRI) reported that the cetane number of DEE is higher than 125 [1]. Others have reported lower equivalent cetane numbers based on blending values, as discussed below.

DEE is a liquid at ambient conditions, which makes it attractive for fuel handling and infrastructure requirements. Storage stability of DEE and blends of DEE are of concern because of a tendency to oxidize, forming peroxides in storage. Windholz et al. [2] suggested that antioxidant additives may be available to prevent storage oxidation. Concerns about detrimental impacts on air quality from DEE are related to its volatility and to its propensity toward peroxidation, although peroxidation in the liquid phase follows a different mechanism than that which occurs in the atmosphere.

Flammability limits for DEE are broader than those of many fuels, but the rich flammability limit of DEE is in question (see Table 1). DEE is widely known as an anesthetic, which may be of concern for direct human health impacts. DEE's lubrication properties are unknown, but these probably pose less of a problem than expected for dimethyl ether. In summary, DEE has some attractive fuel properties relative to use in compression-ignition engines, but its properties also raise some concerns. The concerns do not appear to be seriously limiting in nature and may be addressed through appropriate fuel handling provisions.

COMBUSTION QUALITY MEASUREMENTS - In a study performed for the Coordinating Research Council, Friedman et al. [3] reported the relative burning velocities, ignition energies, and flame-quenching distances for 12 fuels, including DEE. Their results showed that the burning velocity of DEE is 13% greater than normal heptane, about the same as benzene, and much less than that of propyne. DEE therefore falls in a typical burning velocity range with other hydrocarbons. The relative spark energy for DEE is much less than most of the hydrocarbons tested, but not as low as propyne. Quenching distance (ability of a flame to pass through a narrow passage) for DEE is similar to that of other hydrocarbons.

Ohta and Takahashi [4] reported stages of flame propagation for DEE. DEE has low heat-release rates during early cool flame generation, but has typical heat-release rates for a mid-stage blue flame oxidation. The blue flame is followed by a conventional red flame with constant heat release during full combustion. Heat-release rates were confirmed in both a bench test combustor and a single-cylinder engine. Analysis identified combustion products including ethylene, methane, carbon monoxide, hydrogen, formaldehyde, acetaldehyde, and unburned DEE. Primary combustion products observed in their lean combustion studies were methane, carbon monoxide, and hydrogen. Ohta and Takahashi [5] continued their study of DEE combustion with a comparison to normal heptane in a single-cylinder engine and found similar results in all runs regardless of whether DEE or normal heptane was the test fuel. They observed uniform development of a cool flame during onset of combustion, but with very slow flame speeds. Intermediate blue flame propagation was not uniform, but progressed with typical engine flame speeds of 2.5 meters per second (m/s).

Inomata et al. [6] reported on the comparison of isopropyl nitrate, di-t-butyl peroxide, acetaldehyde, and DEE as ignition improvers for normal butane. The nitrate and the peroxide performed well as ignition improvers, but the aldehyde and DEE did not provide an additive-type boost to ignition quality at low concentrations. Acetaldehyde (ethanal) and DEE "were extremely reactive when compressed in a stoichiometric mixture with air, and each yielded an ignition delay time that decreased monotonically as the compressed gas temperature was raised." Ignition delay times for DEE were slightly less than the aldehyde and approached just 2 to 3 milliseconds at 625° Kelvin. The researchers concluded that DEE aided the starting of a diesel engine by acting as the primary fuel.

Clothier et al. [7] reported that DEE ignition is inhibited by diesel fuel and that adding DEE to diesel fuel will actually decrease the cetane number of the diesel fuel. Experiments suggested that DEE may interact with aromatics in diesel fuel, delaying the onset of ignition. A mixture of 4% toluene in DEE resulted in an ignition delay of 4 to 5 milliseconds before the ether ignited, as illustrated in Figure 1. Used as a cold-starting aid, DEE apparently acts as a neat fuel and not in combination with the diesel fuel.

In a single ignition delay experiment with an equal volume blend of DEE and ethanol, Erwin and Moulton [1] determined an estimated cetane number of 19. This value is much less than would be predicted from the neat DEE cetane value, estimated at greater than 125.

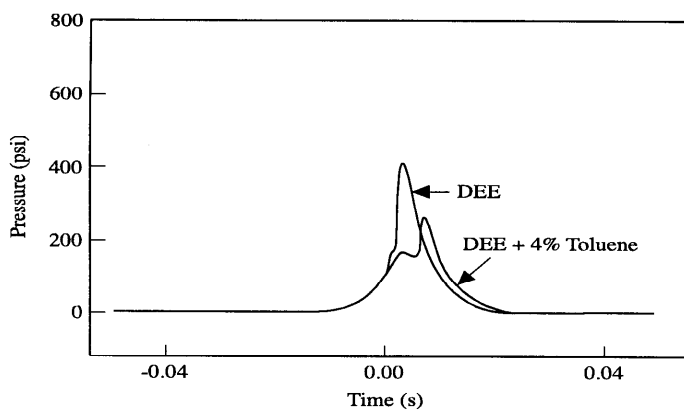
BLENDS OF DEE FOR SPARK-IGNITION ENGINES - From 1919 to 1923, alcohol motor fuel was manufactured

Table 1. Comparison of Properties of Potential Diesel Fuel Components*

Property	DF-2 Diesel	Fischer-Tropsch	Bio-diesel	Gasoline	CNG	Propane HD-5 ^h	Methanol	Ethanol	Methylal	Dimethyl ether	Diethyl ether
Formula	Hydrocarbons -C10 - -C21	Principally C _n H _{2n+2}	Various oils and esters	Hydrocarbons C4 - C9	Principally CH ₄	Principally C ₃ H ₈	CH ₃ OH	C ₂ H ₅ OH	CH ₃ OCH ₂ OCH ₃	CH ₃ OCH ₃	C ₂ H ₅ OC ₂ H ₅
Boiling Point, °F	370 - 650	350 - 670	360 - 640	80 - 437	n.a.	n.a.	149	172	107	-13	94
Reid Vapor Pressure, psi @ 100°F	<0.2	n.a.	n.a.	8 -15	n.a.	170	4.6	2.3	12.2°	116	16.0
Cetane Number	40 - 55	>74	>48	13 - 17	low	low	low	<5 ^b	49	>55	>125 ^a
Autoignition Temperature, °F	~600	~600	-	495	990	870	867	793	459	662	320
Stoichiometric Air/Fuel Ratio, Wt./Wt.	15.0	15.2	13.8	14.5	16.4	15.7	6.45	9.0	7.1	8.9	11.1
Flammability Limits, Vol. %: Rich	7.6	-	-	6.0	13.9	9.5	36.9	19.0	14.9°	27.0 ^d	9.5 36.0 ^d
Flammability Limits, Vol. %: Lean	1.4	-	-	1.0	5.0	2.4	7.3	4.3	3.3°	3.4 ^d	1.9 ^d
Lower Heating Value, Btu/lb	18,500	18,600	16,500	18,500	20,750	19,940	8,570	11,500	10,202	12,120	14,571
Lower Heating Value, Btu/gal	126,900	121,300	120,910	114,000		83,900	56,800	76,000	73,067	66,615	86,521
Lower Heating Value, Btu/SCF					1,033						
Viscosity, centipoise at (temp)°F	40(68)	2.1(100)	3.5(100)	3.4 (68)	-	-	0.59 (68)	1.19(68)	-	-	0.23(68)
Specific Gravity @ 60°F	0.860	0.783	0.880	0.750	-	0.506	0.796	0.794	0.86	0.66	0.714
Density, lb/gal	7.079	6.520	7.328	6.246	-	4.21	6.629	6.612	8.33	5.50	5.946
Note (See below)	e	h	b	e	f	h	e	e	c	b	b

* **Table compiled by N.R. Sefer, Southwest Research Institute.**

- a. Inferred from ignition delay
- b. Recent measurement at Southwest Research Institute
- c. Naegeli, D. W. ,and Weatherford, W. D. Jr. "Practical Ignition Limits for Low Molecular Weight Alcohols," Fuel 68, 45 (1989)
- d. NFPA 325 M, *Fire Hazard Properties of Flammable Liquids, Gases, Volatile Solids* (1977), Copyright 1977 National Fire Protection Association, Inc., Batterymarch Park, Quincy, MA 02269
- e. Table on gasoline and gasohol from *Alcohols and Ethers*, API Publication 4261, second edition, (July 1988).
- f. Liss, W.E., et al., "Variability of Natural Gas Composition in the US", GRI 92/0123, (March 1992).
- g. *Alternative Fuels Special Report, Diesel Progress, Engines and Drives*, (December 1993).
- h. Composition information from ASTM D 1635 Standard Specification for LPG. Calculations after *Perry's Chemical Engineers' Handbook*, 6th ed., (1984).



Source: P.Q.E. Clothier, et al. (1990) P227-B217809

Figure 1 Ignition Delay Impact from Toluene Blended with DEE [7]

from sugarcane molasses in British Guiana [8]. This fuel consisted of approximately 63% ethanol, 35% DEE, and 1% gas oil and pyridine. The fuel was produced by first fermenting cane molasses into ethanol. DEE was then manufactured by treating a part of the ethanol with sulfuric acid. This fuel, called alcolene, was sold for several years and used successfully in many types of gasoline engines with very little engine adjustment. Alcolene resulted in approximately 20 miles per gallon fuel economy compared to 22.5 miles per gallon for gasoline. The motor engines remained in good condition while the fuel was used. (Alcolene probably had a low octane number, but the engines of that era required only a 60 octane fuel or less.)

A series of technical reports prepared under direction of the U.S. Naval Technical Mission to Japan in December 1945 covered Japanese aviation fuel research during World War II. Because of the scarcity of petroleum aviation fuel near the end of the war, ethanol was investigated as a replacement fuel in Japan. However, performance problems developed, which resulted from low fuel volatility, poor fuel distribution among cylinders (which caused autoignition and detonation), and corrosion. Low volatility of neat ethanol made engine starting difficult, especially at low temperatures. This property also inhibited even fuel distribution to cylinders in carburetted engines. After investigation, adding DEE to ethanol was demonstrated as an acceptable method to improve performance. DEE blending in ethanol for this purpose was limited to 3% by volume because of reduced octane of the DEE/ethanol blends. The octane ratings of ethanol/DEE blends were 92, 90, 89, and 89 for 0%, 5%, 10%, and 20% volume DEE blends in ethanol, respectively. Details of these activities are reported by Neely [9], Yamamoto [10], Tsunoda [11], Kondo and Soma [12], and Yamamoto [13]. More recent work by Gulyamov et al. [14] in Russia also suggests DEE for use as a starting additive for alcohol-based synthetic motor fuels.

DEE AS A COMPRESSION-IGNITION FUEL - Antonini [15] reported on DEE as a new option for diesel engine fuels. This paper defends the use of DEE as an option for diesel engines mixed with vegetable oil and/or diesel fuel, and presents a case for Brazil using alcohol in diesel

engines instead of Otto cycle engines. The paper lists the advantages of using DEE; for example, it is the simplest way to transform alcohol to any other derivative. This transformation could be achieved by dehydration with solid fixed-bed catalysts instead of the standard process using sulfuric acid. DEE's advantages over ethanol include its noncorrosive nature and its greater heating value. Production safety standards are already established for handling DEE, and it can be mixed in any proportion in diesel fuel or vegetable oils. This paper also indicates that DEE can be produced economically.

Yamamoto and Matsumoto [16] reported on gas oil (distillates) blended with alcohols and ethers. They concluded that blending complex ethers such as diethyl carbitol (carbitol is a polyether ethanol derivative) in gas oil remarkably improves cetane number and engine performance. For example, blends of 40% diethyl carbitol in a gas oil of 49 cetane number raised the cetane number to 91.5. However, this paper makes no direct mention of DEE blends.

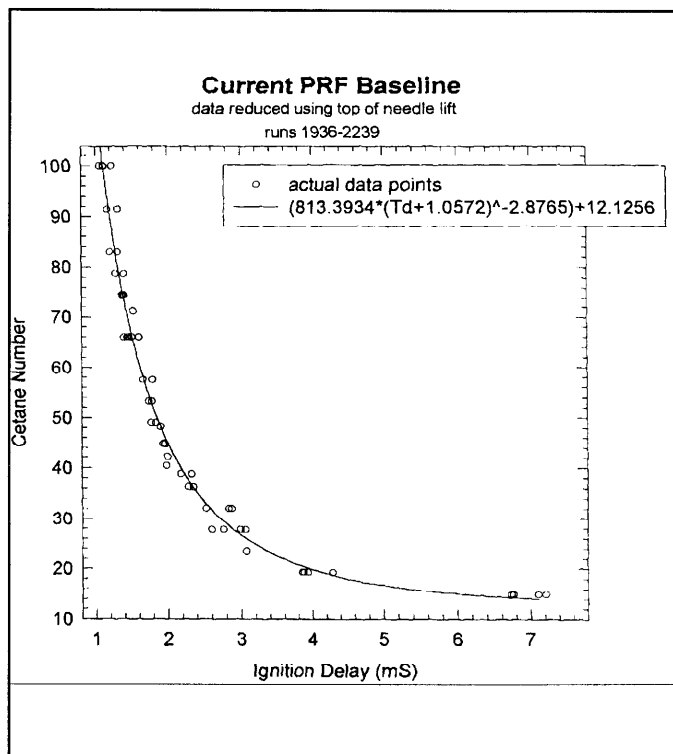


Figure 2 CVCA Ignition Delay Calibration Curve

COMBUSTION QUALITY OF DEE BLENDS - Cetane number was estimated in laboratory tests by combusting small-volume blends of the neat materials in a Constant Volume Combustion Apparatus (CVCA) [17]. The CVCA is a heated reaction chamber that holds a charge of air into which the sample to be rated is injected. The ignition delay time for the pressure and temperature rise is related to the cetane number as shown in Figure 2. Cetane number on this plot is the ASTM D 613 value for the blends of reference fuel. The CVCA is described in previous work [18,19,20].

Phillips Chemical Company 0.05 Sulfur Diesel Fuel Lot S-464			
Tests	Results	Specifications	ASTM Method
Specific Gravity, 60/60	0.8466	Report	D-4052
API Gravity	35.6	32–37	D-1298
Corrosion, 50°C, 3 h	1b	Report	D-130
Sulfur, wt%	0.033	0.03–0.05	D-2622
Flash Point, °F, PM	152	130 min	D-93
Viscosity, cs 40°C, 104°F est 210°F	2.7 1.12	2.0–3.4	D-445
Particulate Matter (mg/L)	1.77	15 Max	D-2276
Net Heat of Combustion, Btu/lb	18,452	Report	D-3338
Cetane Index	47.7	40–48	D-976
Cetane Number	46.7	40–48	D-613
Cloud Point, °F	+6	Report	D-2500
Pour Point, °F	-10	Report	D-2500
Carbon, wt%	86.8		
Hydrogen, wt%	13.2		
Carbon Density, g/gal	2,776	Report	
Distillation, °F			D-86
IBP	369	340–400	
5%	416		
10%	431	400–460	
15%	442		
20%	451		
30%	471		
40%	489		
50%	507	470–540	
60%	523		
70%	545		
80%	568		
90%	597	560–630	
95%	622		
EP	640	610–690	
Loss	1.3		
Residue	1.0		
Hydrocarbon Type, vol%			D-1319
Aromatics	29.9	27 min	
Olefins	3.9		
Saturates	66.2		

The materials used for the tests included Baker Chemical reagent-grade DEE and absolute alcohol (EtOH). The properties of the D-2 component appear in Table 2. The blends percentages are shown in Table 3.

Item	Description	Example for 100 mL
1	DEE	100 mL DEE
2	75% DEE/Ethanol	75 mL DEE/25 mL EtOH
3	50% DEE/Ethanol	50 mL DEE/50 mL EtOH
4	25% DEE/Ethanol	25 mL DEE/50 mL EtOH
5	0% DEE/Ethanol	100 mL EtOH
6	75% DEE/D-2	75 mL DEE/25 mL D-2
7	50% DEE/D-2	50 mL DEE/50 mL D-2
8	25% DEE/D-2	25 mL DEE/50 mL D-2
9	0% DEE/D-2	100 mL D-2

The results of the CVCA cetane number determinations are given in Table 4. The sets of results for the following combinations:

- Diethyl ether with D-2
- Diethyl ether with ethanol

appear in Figures 3 and 4. The blends were all miscible; no phase separation was noted.

Vol% Diethyl Ether	Vol% D-2	Cetane Estimate
100	0	158.2
75	25	102.2
50	50	68.5
25	75	51.5
0	100	42.9
Vol% Diethyl Ether	Vol% Ethanol	Cetane Estimate
75	25	61.1
50	50	19.0
25	75	12.2
0	100	12.1

The cetane number of hydrocarbon blends can usually be predicted on a linear volumetric basis. The blends of DEE with diesel fuel and with ethanol, respectively, show a nonlinear bias in the direction of the low cetane number component. The extremely high estimated cetane number

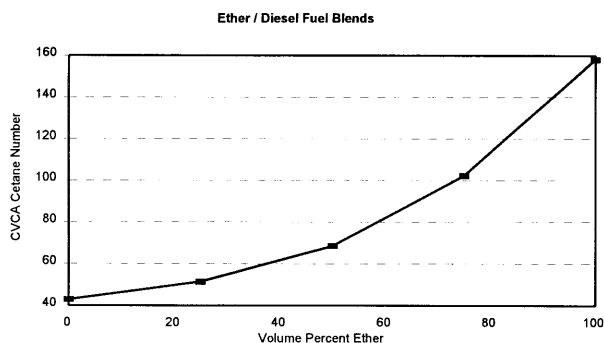


Figure 3 Diethyl ether-Diesel Fuel Blends

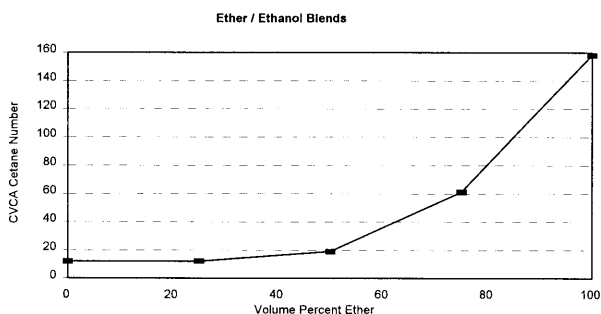


Figure 4 Diethyl ether-Ethanol Blends

of DEE does have a significant impact in the high concentration blends, however. A blend of 75% DEE and 25% ethanol produces a fuel with an estimated cetane number above 60.

AIR QUALITY IMPACTS OF DEE - Wallington et al. [21] reported on the reactivity of a series of ethers with respect to hydroxyl radical attack in simulated atmospheric conditions. The reactivity of DEE is predicted to be about 5 times the rate of MTBE. DME, considered quite chemically inert under ambient conditions, is predicted to be stable in the atmosphere for a period of approximately 5 days; MTBE is predicted to be stable for just less than 4 days; and DEE is estimated to be stable for about 19 hours.

COST OF DEE PRODUCTION - The work reported by the Technical Mission to Japan just after World War II indicated that DEE was easily manufactured by using an acid clay catalyst with 90% conversion of ethanol. The Japanese made ethanol from grains and sweet potatoes and even investigated the hydrolysis of wood, but did not build a production plant for cellulose conversion. Antonini [15] indicates that DEE could be easily produced from local ethanol sources in Brazil. However, no specific cost data are included in these papers.

The National Renewable Energy Laboratory (NREL) conducted a process simulation exercise which showed that hydrous ethanol (ethanol diluted with water) could be

converted to DEE. The simulation also showed that the resulting liquid/liquid phases of water-ethanol/ethanol-DEE could be separated in a simple decanter separator. Ideally, the hydrous ethanol would be generated at the end of the biomass ethanol production process, so that the ether conversion would take place before the final distillation or molecular sieve drying step in that process. The process simulation is illustrated in Figure 5.

The analysis shows that the net conversion cost for producing DEE in this manner is similar to that of the final drying process step, which means that the cost of fuel-

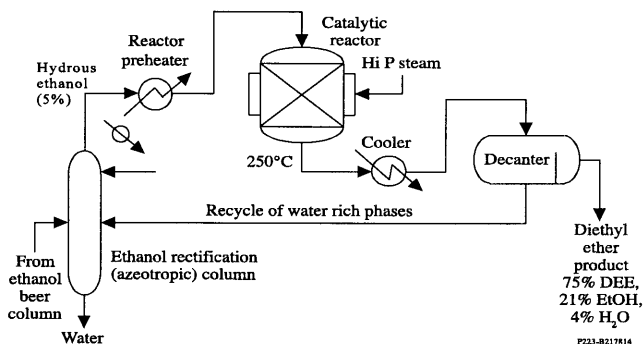


Figure 5 Production of Diethyl Ether from Biomass Ethanol

grade DEE would be only slightly higher than that of anhydrous ethanol.

CONCLUSION

This literature survey and brief laboratory analysis were insufficient for a comprehensive evaluation of DEE as a transportation fuel. The literature search results indicate the promise of DEE as a potential replacement fuel for compression-ignition engines. Additional information is needed on the emissions performance of DEE as a neat fuel and in blends when used in modern diesel engines. Storage and fuel handling requirements for DEE, including fuel additives and hardware systems, need to be identified. Direct impacts on human health and on atmospheric reactions need to be further explored and, finally, more detailed cost analyses for DEE production are needed.

ACKNOWLEDGEMENTS

Dr. Robert J. Wooley of the NREL Biofuels Program coordinated the ether conversion cost estimate.

REFERENCES

1. J. Erwin and S. Moulton. *Maintenance and Operation of the U.S. DOE Alternative Fuel Center*. Subcontract XS-2-12130-1. San Antonio, TX: Southwest Research Institute, Project No. 01-5151. November 1996.

2. G. Windholz, ed. *The Merck Index, An Encyclopedia of Chemicals, Drugs and Biologicals*, Tenth Edition, 1983.
3. R. Friedman, R.E. Albright, and H.F. Calcete. Relative Burning Velocities, Ignition Energies, and Quenching Distance for Twelve Fuels. Coordinating Research Council Report No. CRC-271, March 1953.
4. Y. Ohta and H. Takahashi. *Temperature and Pressure Effects in Cool and Blue Flames*. Nagoya Institute of Technology, Nagoya, Japan, 1981.
5. Y. Ohta and H. Takahashi. Homogeneity and Propagation of Autoignited Cool and Blue Flames. In *Progress in Astronautics and Aeronautics*. New York: AIAA, pp. 236–247, 1983.
6. T. Inomata, J.F. Griffiths, and A.J. Pappin. The Role of additives as sensitizers for the spontaneous ignition of hydrocarbons. In *Proceedings of the Twenty-third Symposium (International) on Combustion*. Pittsburgh, PA: Combustion Institute, pp. 1759–1766, 1991.
7. P.Q.E. Clothier, A. Moise, H.O. Pritchard. Effect of free-radical release on diesel ignition delay under simulated cold-starting conditions. *Combust Flame* 81:3–4, pp. 242–250, Sept. 1990.
8. E.C. Freeland. The use of cane molasses for the manufacture of motor fuels as experienced in the early 1920s. *Alternative Energy Sources* 3(3), 357–361 1983.
9. G.L. Neely. *Japanese Fuels and Lubricants, Article 3: Naval Research on Alcohol Fuel*. Report No. TOM-231-559-569. Department of the Navy, Washington, D.C. February 1946.
10. T. Yamamoto. *Studies on the Utilization of Alcohol for Aviation Fuel*. Report No. TOM-231-698-701. Texas A&M University, College Station, TX: December 1945.
11. K. Tsunoda. *Engine Test of Alcohol As Aviation Fuel*. Report No. TOM-231-689-697. Texas A&M University, College Station, TX: undated.
12. T. Kondo and S. Soma. *Alcohol Fuel Utility Test as Aeroengine Fuel*. Report No. TOM-231-721-726. Texas A&M University, College Station, TX: December 1945.
13. Yamamoto, T. *Summary of the Alcohol Research Program at the First Naval Fuel Depot*. Report Number TOM-231-571-573. Texas A&M University, College Station, TX: December 1945.
14. Y.M. Gulyamov, V.A. Gladkikh, Y.V. Shtefan, and V.D. Malykhin. Antiknock rating of alcohol-based synthetic motor fuels. *Chem. Technol. Fuels Oils* 27(3–4), pp. 184–187, November 1991.
15. R.G. Antonini. Ethyl ether, a new option for diesel engine fuels. Increased use of diesel engines for higher fuel availability. *Rev. Quim. Ind.* 50(593), pp. 10–12, 1981.
16. T. Yamamoto and I. Matsumoto. Fuel performance of gas oil containing alcohols and ethers. *Nenryo Kyokai Shi* 62(669), pp. 32–42, January 1983.
17. J. Erwin. Investigation of the Ignition Quality of Blends of Diethylether with D-2 Diesel Fuel and Ethanol. Special Report Prepared by Southwest Research Institute for the National Renewable Energy Laboratory, Golden, CO, January 1997.
18. T.W. Ryan III. Correlation of physical and chemical ignition delay to cetane number. SAE Paper No. 852103, 1985.
19. T.W. Ryan III and B. Stapper. Diesel fuel ignition quality as determined in a constant volume combustion bomb. SAE Paper No. 870586, 1987.
20. T.W. Ryan III and T.J. Callahan. Engine and constant volume bomb studies of diesel ignition and combustion. SAE Paper No. 881626, 1988.
21. T.J. Wallington, J.M. Andino, L.M. Skewes, W.O. Siegl, and S.M. Japar. Kinetics of the reaction of OH radicals with a series of ethers under simulated atmospheric conditions at 295 K. *Int J Chem Kinet* 21(11), pp. 993–1001, November 1989.