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The Synthesis of Alkane Dinitrates and Theirs Efficiency for Cetane Improver[1]

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Abstract—Dinitrate compounds was prepared from alkane diols; 1,6-hexane diol, 1,8-octane diol, 1,10-decane diol, and 2-methyl-2,4-pentane diol using nitration reaction. These dinitrate compounds were used as cetane improver for diesel fuel. Results showed that the cetane number values has increased about 1 and 3 units for 0.05 and 0.10% by weight of dinitrate compounds, respectively, compared with base oil. Their efficiency is higher than commercial cetane improver, 2-ethylhexyl nitrate.

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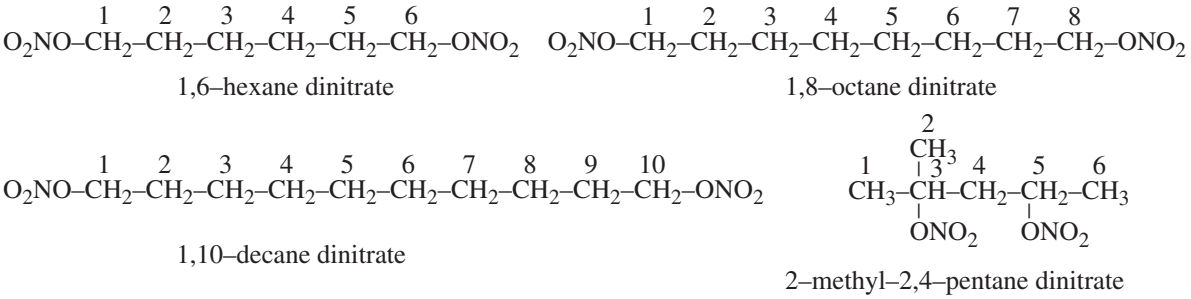
When a fine spray of fuel is injected into a combustion chamber of a diesel engine, ignition does not occur immediately. The heat produced by compression varies from about 440.5°C at 10 : 1 compression ratio to about 565.5°C at 15 : 1 compression ratio, and is the sole source of ignition. The interval between the beginning of the fuel injection and ignition is called the ignition delay period. If the delay is long, the engine may be hard to start. When the accumulated fuel ignites, the excessive energy released causes the engine to knock. The shorter the delay, the easier the engine is to start and the smoother it operates [1]. Ignition delay is measured by the Cetane Number (CN) test [2], which uses a single-cylinder, variable compression ratio engine analogous to the Octane Number engine. In this case, the ignition delay of the test fuel is measured at a fixed compression ratio. This result is compared with the results from standard reference fuels consisting of blends of n-cetane and methylnaphthalene. Normal cetane has a short delay period and ignites readily. It has a cetane number of 100. Heptamethylnonane has a long delay period and does not ignite readily. It has a cetane number of 0. The cetane number of a diesel fuel is the percentage by the volume of normal cetane in a blend with methylnaphthalene that matches the ignition quality of a reference fuel with known cetane number.

Cetane number improvers [3, 4] can reduce combustion noise and smoke. The magnitude of the benefit varies among engine designs and operating modes, ranging from no effect to readily perceptible improvement. 2-Ethylhexyl nitrate (EHN) or octyl nitrate is the most widely used as cetane number improver [5]. EHN is thermally unstable and decomposes rapidly at high temperatures in the combustion chamber. The products of decomposition help initiate fuel combustion and, thus, shorten the ignition delay period from that of the fuel without additive.

An increase in cetane number from a given concentration of EHN varies from one fuel to another. It is greater for a fuel whose natural cetane number is already relatively high. The incremental increase gets smaller as more EHN is added, so there is little benefit to exceeding a certain concentration. EHN typically is used in the concentration range of 0.05 to 0.40% wt./wt. and may yield a 3 to 8 cetane number benefit. Other alkyl nitrates, as well as ether nitrates and some nitroso compounds, also have been found to be effective cetane number improvers, but they are not currently used commercially. Di-tertiary butyl peroxide has been recently introduced as a commercial cetane number improver. One of the disadvantages of EHN is that EHN decreases the thermal stability of some fuels [6, 7]. The effect of the other cetane number improvers on thermal stability is unknown, but it seems likely that they will be similarly disadvantaged. Consequently, new cetane improvers are required. The mechanism of cetane improver involved the nitrate group so dinitrate compound, which contain two group of nitrate, are consider an effective cetane improver.

In this work, alkyl dinitrates as cetane improvers were synthesized by nitration of alkane diols using a mixture of cone. H_2SO_4 and cone. HNO_3. The properties of the blend between diesel base oil and prepared alkyl dinitrates have been investigated.

[1] The article is published in the original.



Schematic of alkane dinitrates.

EXPERIMENTAL

Preparations of Alkyl Dinitrates from Alkane Diols

All four alkyl dinitrates were prepared from alkyl diol; 1,6-hexane diol, 1,8-octane diol, 1,10-decane diol, and 2-methyl-2,4-pentane diol, using the same protocol as described below. A mixture of 65% HNO_3 7 ml, 96% H_2SO_4 12 ml and water 7 ml was placed in a round bottom flask, then well stirred, and maintained at the temperature of 23°C. Urea 1.36 g was added to the mixture, and the solution was stirred for a half an hour. Then, a solution of alkyl diol 2.5 g and $CHCl_3$ 30 ml was slowly added to a reactor while maintained the temperature of 23°C for an hour. The mixture was then allowed to warm at room temperature and then organic phase was separated. The organic phase was washed with 4×30 ml of an aqueous saturated sodium chloride solution and then dried over anhydrous sodium sulphate.

Characterization and detennination of the products were carried on the Nicolet Fourier-Transform Infrared Spectroscopy model Impact 410 and Brucker Nuclear-Magnetic Resonance Spectroscopy model AC-F 200 (200 MHz).

Determination of properties and Cetane Number of blended base diesel fuel containing dinitrate compounds Blended base diesel fuels containing 0.05, 0.10, 0.15, and 0.20% by weight of dinitrate compounds were prepared and their properties were determined using the following protocols. The values of Cetane Number were measured using ASTM D613 [8] using PetroSpec model Cetane 2000.

RESULTS AND DISCUSSION

Synthesis of Dinitrate Compounds

Dinitrated compounds were synthesized by nitration reaction using cone, nitric acid and cone, sulphuric acid. In this study, all four alkyl dinitrates; 1,6-hexanediol, 1,8-octanediol, 1,10-decanediol, and 2-methyl-2,4-pentanediol, were prepared. The yield of 1,6-hexane dinitrate (HDN); colourless liquid, 1,8-octane dinitrate (ODN); colourless liquid, 1,10-decane dinitrate (DDN); colourless liquid, and 2-methyl-2,4-pentane dinitrate (MPDN); yellow liquid, were 80, 86.9 88.5 and 53.2%, respectively. Most of products were very high yield about 95%, except, 2-methyl-2,4-pentane dinitrate that might be due to its sensitivity to autooxidation. Additionally, 2-methyl-2,4-pentane dinitrate was hygroscopic and sensitive to air.

Structure Elucidation of Alkane Dinitrate

The IR spectrum of 1,6-hexanediol and 1,6-hexane dinitrate were compared. No sign of absorption bands of OH stretching group of 1,6-hexanediol (3500 cm^{-1}) in IR spectrum of 1,6-hexane dinitrate. Additionally, there were the absorption bands of NO_2 stretching (asymmetric and symmetric) and NO stretching at 1630, 1287, and 871 cm^{-1}, respectively. Moreover, the structure of 1,6-hexane dinitrate was confirmed using ^{1}H-NMR and ^{13}C-NMR spectra. The ^{1}H-NMR spectrum showed a 4 protons (δ 4.36 (t)) which concerns with I3C-NMR absorption at 5 73.36 (C-1 and C-6). Other 4 proton (δ 1.65 (q)) which located on C-3 and C-4 (8 26.38) were also recorded. Finally, the last 4 protons of 1,6-hexane dinitrate were recorded at δ 1.36 (t) and these proton belong to C-2 and C-5 (δ 25.08). ^{1}H and ^{13}C-NMR spectra together with IR spectrum allowed the complete structure of 1,6-hexane dinitrate to be established (Fig. 1).

The product of nitration of others alkane diols were studies using the same techniques. All results suggested that all alkane diols were converted to dinitrate compounds (see spectroscopic data in Tables 1 and 2).

Properties Determination of Blended Base Diesel Fuel Oil Containing Dinitrate Compounds

The dinitrate compounds were blended with base oil fuels. Each of 0.05 and 0.10% by weight of HDN, ODN, DDN, and MPDN, respectively, were used and their properties were determined and compared with EHN. The results were shown in Table 3.

From the results suggested that the physical properties of blended base diesel fuels with alkane dinitrate did not change compared with base diesel fuel.

Table 1. The IR spectrum data of alkane dinitrates

Assignment	Wave number, cm^{-1}			
	HDN	ODN	DDN	MPDN
C–H stretching, aliphatic	2941, 2878	2931, 2859	2936, 2863	2991, 2935
NO_2 asymmetric stretching	1630	1625	1630	1634
C–H bending, aliphatic	1471, 1393	1471, 1383	1471, 1388	1460, 1393
NO_2 symmetric stretching	1287	1282	1287	1280
C–O stretching	967	982	982	1280
N–O stretching	871	861	861	871

Note: HDN = 1,6-hexane dinitrate, ODN = 1,8-octane dinitrate, DDN = 1,10-decane dinitrate, and MPDN = 2-methyl-2,4-pentane dinitrate.

Determination of Cetane Number (CN) of Blended Base Diesel Fuel Containing Dinitrate Compounds

The Cetane Number each blended base diesel fuels was determined according to ASTM D613 [3]. All alkane dinitrates gave a higher improvement compared with EHN (commercial additive). It might be due to these compound contain 2 nitrate group which more enhance the ignited-oxidation. The chain length of hydrocarbon did not have an effect on the increasing of cetane number value since HDN, ODN, and DDN show a similar results. Moreover, the increasing of concentration of alkane dinitrate did not show any effect on the improving of cetane number value.

CONCLUSIONS

The alkane dinitrate compound could be easily prepared by direct nitration using alkane diols and conc. HNO_3 and conc. HCl. The blended diesel fuel with containing alkane dinitrate at 0.05 and 0.10% by weight did not change any specification of physical properties. Calculated cetane index values of blended diesel fuels were determined and found to be higher than base diesel fuel alone; about 4 units. Moreover, alkane dinitrates show the similar CN value than 2-ethylhexyl nitrate (common commercial cetane improver). Then these alkane dinitrate compounds had a potential to be use for improving of cetane number in base oil fuel.

Table 2. The ^{1}H-NMR and ^{13}C-NMR spectrum data of alkane dinitrates

Chemical shift (δ, ppm)								
	^{1}H-NMR				^{13}C-NMR			
Position	HDN	ODN	DDN	MPDN	HDN	ODN	DDN	MPDN
1	4.36(t)	4.36(t)	4.36(t)	1.47(m)	73.36	73.40	73.44	31.12
2	1.65(q)	1.65(q)	1.64(q)	1.47(m)	26.38	28.72	29.14	27.40
3	1.36(t)	1.25–1.40(m)	1.25–1.37(m)	2.14(d)	25.08	26.48	26.26	48.96
4	1.36(t)	1.25–1.40(m)	1.25–1.37(m)		25.08	25.35	25.52	65.00
5	1.65(q)	1.25–1.40(m)	1.25–1.37(m)		26.38	25.35	25.52	23.93
6	4.36(t)	1.25–1.40(m)	1.25–1.37(m)		73.36	26.48	25.52	70.95
7		1.65(q)	1.25–1.37(m)			28.72	25.52	
8		4.36(t)	1.25–1.37(m)			73.40	26.26	
9			1.64(q)				29.14	
10			4.36(t)				73.44	

Note: 1. m = multiplet, q = Quintet, and t = triplet.
2. Chemical shifts are relative to solvent signal ($CDCl_3$).

Table 3. Cetane number of base oil and blended base oil

	% Additive							
	0.05	Δ	0.10	Δ	0.15	Δ	0.20	Δ
EHN	46.5	1.4	48.3	3.2	49.3	4.2	50.6	5.5
HDN	47.4	2.3	49.2	4.1	51.0	5.9	52.8	7.7
ODN	47.4	2.3	49.4	4.3	50.9	5.8	52.6	7.5
DDN	47.6	2.5	49.4	4.3	50.1	5.0	52.8	7.7
MPDN	46.0	1.1	46.9	1.8	48.2	3.1	49.7	4.6

Note: 1. Cetane number of base oil = 45.1.
2. All cetane number is measured using ASTM613.
3. A is the in creasing values of cetane number from base oil.

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REFERENCES

1. D. S. Moulton and N. R. Sefer, *Diesel Fuel Quality and Effects of Fuel Additives* (Transportation Research Board, National Research Council, Washington, 1984).
2. *Standard Test Method for Cetane Number of Diesel Fuel Oil* [ASTM D613-01] (Annual Book of ASTM Standards, 2001).
3. M.-A. Poirier, D. E. Steere, and J. A. Krogh, US Patent No. 348,528 (1995).
4. R. F. Purcell and L. L. Hallock, US Patent No. 563,124 (1985).
5. G. J. Suppes, Y. Rui, A. C. Rome, and Z. Chen, Ind. Eng. Chem. Res. **36**, 4397 (1997).
6. H. Bornemann, F. Scheidt, and W. Sander, Int. J. Chem. Kinet. **34**, 34 (2002).
7. J. C. Oxley, J. L. Smith, and E. Rogers, Energy Fuels **15**, 1194 (2001).
8. *Standard Test Method for Cetane Number of Diesel Fuel Oil* [D613-03b] (Annual Book of ASTM Standards, 2003).