

## CHAPTER IV

### RESULT AND DISCUSSION

#### 4.1 Synthesis of Cycloalkyl Nitrate Compounds and Tetrahydrofurfuryl Nitrate

Cycloalkyl nitrate compounds and tetrahydrofurfuryl nitrate could be prepared by nitration of organic hydroxy compounds with concentrated nitric acid and concentrated sulfuric acid. The temperature of the reaction was maintained at  $0\pm 2^{\circ}\text{C}$  while the reaction temperature of tetrahydrofurfuryl nitrate was below  $-20^{\circ}\text{C}$ .

In this study, all products were obtained in high yield. Moreover, the products were substantially pure which was the benefit of this process.

#### 4.2 Characteristics of Synthesized Nitrate Compounds

##### 4.2.1 Cyclohexylmethyl Nitrate

The IR spectra of cyclohexylmethanol and cyclohexylmethyl nitrate were shown in Figures A1 and A2, respectively. The important absorption bands of cyclohexylmethyl nitrate were listed in Table 4.1.

**Table 4.1** The absorption assignments of cyclohexylmethyl nitrate.

Wave Number (cm <sup>-1</sup> )	Assignment
2852	C-H Stretching, Aliphatic
1630	NO <sub>2</sub> Asymmetric Stretching
1450	C-H Bending, Aliphatic
1280	NO <sub>2</sub> Symmetric Stretching
988	C-O Stretching
866	N-O Stretching Vibration

From the IR spectrum of cyclohexylmethyl nitrate (Figure A2) as comparing with of cyclohexylmethanol (Figure A1), it could be observed that there was no the absorption band of OH stretching 3200-3600 cm<sup>-1</sup> but the absorption bands of NO<sub>2</sub> (asymmetric and symmetric) stretching and NO stretching were clearly observed at 1630, 1280 and 866 cm<sup>-1</sup> respectively. The result was confirmed by using <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra.

The <sup>1</sup>H-NMR spectra of cyclohexylmethanol and cyclohexylmethyl nitrate were shown in Figures A3 and A4, respectively. The important signals of cyclohexylmethyl nitrate were shown in Table 4.2.

**Table 4.2** The assignments of <sup>1</sup>H-NMR spectrum of cyclohexylmethyl nitrate.

Chemical Shift (δ,ppm)	Multiplicity	Position of Proton	Number of Protons
0.96-1.27	<i>m</i>	a, b	6
1.62-1.77	<i>m</i>	c, d	5
4.23	<i>d</i> ( <i>J</i> = 6.00 Hz)	e	2

The  $^{13}\text{C}$ -NMR spectra of cyclohexylmethanol and cyclohexylmethyl nitrate were shown in Figures A5 and A6, respectively. The important signals of cyclohexylmethyl nitrate were shown in Table 4.3.

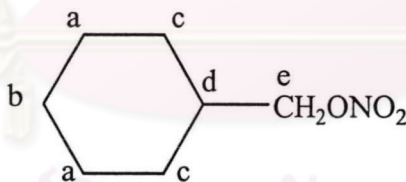
**Table 4.3** The assignments of  $^{13}\text{C}$ -NMR spectrum of cyclohexylmethyl nitrate.

Position of Carbon	Carbon Type*	Chemical Shift of Nitrate( $\delta$ ,ppm)	Chemical Shift of Alcohol( $\delta$ ,ppm)**
a	$\text{CH}_2$	25.60	25.81
b	$\text{CH}_2$	26.05	26.56
c	$\text{CH}_2$	29.43	29.55
d	CH	35.73	40.41
e	$\text{CH}_2$	78.19	68.56

\* It was determined by DEPT spectra as shown in Figure A31

\*\*The position of carbon of alcohol was referred by Ref. [26].

From the results of the spectral data, it could be concluded that the product was cyclohexylmethyl nitrate and its structure was as follow:



#### 4.2.2 2-Cyclohexylethyl Nitrate

The IR spectra of 2-cyclohexylethanol and 2-cyclohexylethyl nitrate were shown in Figures A7 and A8, respectively. The important absorption bands of cyclohexylmethyl nitrate were listed in Table 4.4.



**Table 4.4** The absorption assignments of 2-cyclohexylethyl nitrate.

Wave Number (cm <sup>-1</sup> )	Assignment
2852	C-H Stretching, Aliphatic
1630	NO <sub>2</sub> Asymmetric Stretching
1449	C-H Bending, Aliphatic
1280	NO <sub>2</sub> Symmetric Stretching
963	C-O Stretching
866	O-N Stretching Vibration

By comparing the IR spectra of (Fig- ) and - (Fig- )  
 From the IR spectrum of 2-cyclohexylethyl nitrate (Figure A8) as comparing with of 2-cyclohexylethanol (Figure A7), it could be observed that there was no the absorption band of OH stretching 3200-3600 cm<sup>-1</sup> but the absorption bands of NO<sub>2</sub> (asymmetric and symmetric) stretching and NO stretching were clearly observed at 1630, 1280 and 866 cm<sup>-1</sup>, respectively. The result was confirmed by using <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra. *in the first spectrum.*

The <sup>1</sup>H-NMR spectra of 2-cyclohexylethanol and 2-cyclohexylethyl nitrate were shown in Figures A9 and A10, respectively. The important signals of cyclohexylmethyl nitrate were shown in Table 4.5.

**Table 4.5** The assignments of <sup>1</sup>H-NMR spectrum of 2-cyclohexylethyl nitrate.

Chemical Shift (δ,ppm)	Multiplicity	Position of Proton	Number of Protons
0.94-1.50	<i>m</i>	a, b	6
1.53-1.72	<i>m</i>	c, d, e	7
4.5	<i>t</i> ( <i>J</i> = 8 Hz)	f	2

The  $^{13}\text{C}$ -NMR spectra of 2-cyclohexylethanol and 2-cyclohexylethyl nitrate were shown in Figures A11 and A12, respectively. The important signals of cyclohexylmethyl nitrate were shown in Table 4.6.

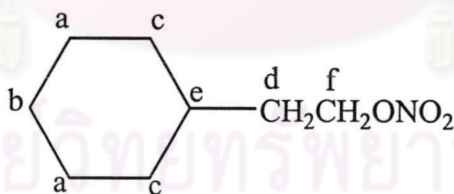
**Table 4.6** The assignments of  $^{13}\text{C}$ -NMR spectrum of 2-cyclohexylethyl nitrate.

Position of Carbon	Carbon Type*	Chemical Shift of Nitrate( $\delta$ ,ppm)	Chemical Shift of Alcohol( $\delta$ ,ppm)**
a	$\text{CH}_2$	26.04	26.23
b	$\text{CH}_2$	26.28	26.52
c	$\text{CH}_2$	33.01	33.32
d	$\text{CH}_2$	33.90	34.18
e	CH	34.30	40.19
f	$\text{CH}_2$	71.70	60.40

\* It was determined by DEPT spectra as shown in Figure A32

\*\*The position of carbon of alcohol was referred by Ref. [27].

From the results of the spectral data, it could be concluded that the product was 2-cyclohexylethyl nitrate and its structure was as follow:



#### 4.2.3 1,4-Cyclohexanedimethyl Nitrate

The IR spectra of 1,4-cyclohexanedimethanol and 1,4-cyclohexanedimethyl nitrate were shown in Figures A13 and A14, respectively. The important absorption bands of 1,4-cyclohexanedimethyl nitrate were listed in Table 4.7.

**Table 4.7** The absorption assignments of 1,4-cyclohexanedimethyl nitrate.

Wave Number (cm <sup>-1</sup> )	Assignment
2863	C-H Stretching, Aliphatic
1625	NO <sub>2</sub> Asymmetric Stretching
1451	C-H Bending, Aliphatic
1282	NO <sub>2</sub> Symmetric Stretching
946, 978	C-O Stretching
864	N-O Stretching Vibration

From the IR spectrum of 1,4-cyclohexanedimethyl nitrate (Figure A14) as comparing with of 1,4-cyclohexanedimethanol (Figure A13). It could be observed that there was no the absorption band of OH stretching 3200-3600 cm<sup>-1</sup> but the absorption bands of NO<sub>2</sub> (asymmetric and symmetric) stretching and NO stretching were clearly observed at 1625, 1282, and 864 cm<sup>-1</sup> respectively. The result was confirmed by using <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra.

The <sup>1</sup>H-NMR spectra of 1,4-cyclohexanedimethanol and 1,4-cyclohexanmethyl nitrate were shown in Figures A15 and A16, respectively. The important signals of cyclohexylmethyl nitrate were shown in Table 4.8.



**Table 4.8** The assignments of  $^1\text{H}$ -NMR spectrum of 1,4-cyclohexanedimethyl nitrate.

Chemical Shift ( $\delta$ ,ppm)	Multiplicity	Position of Proton	Number of Protons
1.01-1.16	<i>m</i>	f	4
1.42-1.88	<i>m</i>	c, d, e	16
4.24	<i>d</i> ( $J = 6$ Hz)	b	2
4.35	<i>d</i> ( $J = 6$ Hz)	a	6

The  $^{13}\text{C}$ -NMR spectra of 1,4-cyclohexanedimethanol and 1,4-cyclohexane dimethyl nitrate were shown in Figures A17 and A18, respectively. The important signals of cyclohexylmethyl nitrate were shown in Table 4.9.

**Table 4.9** The assignments of  $^{13}\text{C}$ -NMR spectrum of 1,4-cyclohexanedimethyl nitrate.

Position of Carbon	Carbon Type*	Chemical Shift of Nitrate( $\delta$ ,ppm)	Chemical Shift of Alcohol( $\delta$ ,ppm)**
a	$\text{CH}_2$	77.60	66.35
b	$\text{CH}_2$	75.57	63.84
c	CH	35.49	38.46
d	CH	32.87	35.94
e	$\text{CH}_2$	28.33	27.38
f	$\text{CH}_2$	25.02	23.61

\* It was determined by DEPT spectra as shown in Figure A33

\*\*The position of carbon of alcohol was referred by Ref. [28].

From the results of the spectral data, it could be concluded that the product was 1,4-cyclohexanedimethyl nitrate and its structure was as follow:





The  $^1\text{H-NMR}$  spectra of tetrahydrofurfuryl alcohol and tetrahydrofurfuryl nitrate were shown in Figures A21 and A22, respectively. The important signals of tetrahydrofurfuryl nitrate were shown in Table 4.11.

**Table 4.11** The assignments of  $^1\text{H-NMR}$  spectrum of tetrahydrofurfuryl nitrate.

Chemical Shift ( $\delta$ ,ppm)	Multiplicity	Position of Proton	Number of Protons
1.63-1.69	<i>m</i>	A	2
1.87-2.06	<i>m</i>	B	2
3.75-3.87	<i>m</i>	E	2
4.12-4.17	<i>m</i>	C	1
4.38-4.45	<i>m</i>	D	2

The  $^{13}\text{C-NMR}$  spectra of tetrahydrofurfuryl alcohol and tetrahydrofurfuryl nitrate were shown in Figures A23 and A24, respectively. The important signals of tetrahydrofurfuryl nitrate were shown in Table 4.12.

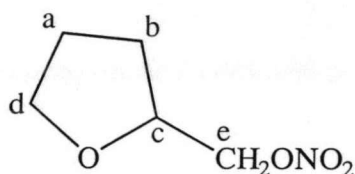
**Table 4.12** The assignments of  $^{13}\text{C-NMR}$  spectrum of tetrahydrofurfuryl nitrate.

Position of Carbon	Carbon Type*	Chemical Shift of Nitrate( $\delta$ ,ppm)	Chemical Shift of Alcohol( $\delta$ ,ppm)**
a	$\text{CH}_2$	25.54	25.89
b	$\text{CH}_2$	28.08	27.11
c	$\text{CH}$	74.72	64.74
d	$\text{CH}_2$	74.52	68.17
e	$\text{CH}_2$	68.60	79.58

\* It was determined by DEPT spectra as shown in Figure A34

\*\*The position of carbon of alcohol was referred by Ref. [29].

From the results of the spectral data, it could be concluded that the product was tetrahydrofurfuryl nitrate and its structure was as follow:



### 4.3 Characteristics of 2-Ethylhexyl Nitrate

The IR spectra of 2-ethyl-1-hexanol and 2-ethylhexyl nitrate were shown in Figures A25 and A26, respectively. The important absorption bands of 2-ethylhexyl nitrate were listed in Table 4.13.

**Table 4.13** The absorption assignments of 2-ethylhexyl nitrate.

Wave Number (cm <sup>-1</sup> )	Assignment
2868	C-H Stretching, Aliphatic
1634	NO <sub>2</sub> Asymmetric Stretching
1465, 1383	C-H Bending, Aliphatic
1275	NO <sub>2</sub> Symmetric Stretching
978	C-O Stretching
866	O-N Stretching Vibration

From the IR spectrum of 2-ethylhexyl nitrate (Figure A26) comparing with of 2-ethyl-1-hexanol (Figure A25), it could be observed that there was no the absorption band of OH stretching 3200-3500 cm<sup>-1</sup> but the absorption bands of NO<sub>2</sub> (asymmetric and symmetric) stretching and NO stretching were clearly observed at 1634, 1280 and 866 cm<sup>-1</sup> respectively. The result was confirmed by using <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra. The <sup>1</sup>H-NMR spectra of 2-ethyl-1-hexanol and 2-ethylhexyl nitrate were shown in Figures A27 and A28, respectively. The important signals of 2-ethylhexyl

nitrate were shown in Table 4.14.

**Table 4.14** The assignments of  $^1\text{H-NMR}$  spectrum of 2-ethylhexyl nitrate.

Chemical Shift ( $\delta$ ,ppm)	Multiplicity	Position of Proton	Number of Protons
1.60-1.78	<i>d</i> ( $J = 6$ Hz)	g	2
1.27-1.48	<i>m</i>	c, d, e, f	4
0.85-0.92	<i>m</i>	a, b	8
4.38	<i>m</i>	h	1

The  $^{13}\text{C-NMR}$  spectra of 2-ethyl-1-hexanol and 2-ethylhexyl nitrate were shown in Figures A29 and A30, respectively. The important signals of 2-ethylhexyl nitrate were shown in Table 4.15.

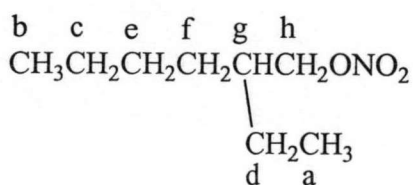
**Table 4.15** The assignments of  $^{13}\text{C-NMR}$  spectrum of 2-ethylhexyl nitrate.

Position of Carbon	Carbon Type	Chemical Shift of Nitrate( $\delta$ ,ppm)*	Chemical Shift of Alcohol( $\delta$ ,ppm)**
a	$\text{CH}_2$	25.60	25.81
b	$\text{CH}_2$	26.05	26.56
c	$\text{CH}_2$	29.43	29.55
d	CH	35.73	40.41
e	$\text{CH}_2$	78.19	68.56

\* The position of carbon of nitrate was referred by Ref. [30].

\*\*The position of carbon of alcohol was referred by Ref. [31].

From the results of the spectral data, it could be concluded that the product was 2-ethylhexyl nitrate and its structure was as follow:





#### 4.4 Determination of Cetane Index of Synthesized Nitrate Compounds in Base

##### Diesel Fuel.

Table 4.16 provided mid-boiling point, API gravity and cetane index as the results of 0.05% and 0.10% by weight of cyclohexylmethyl nitrate, 2-cyclohexylethyl nitrate, 1,4-cyclohexanedimethyl nitrate, tetrahydrofurfuryl nitrate and 2-ethylhexyl nitrate which were blended in base diesel fuel.

**Table 4.16** Cetane index of the blend of synthesized nitrate compounds with base diesel fuel.

Concentration (%weight)	Blended Composition	API Gravity @ 60 °F	Mid-Boiling Point (°F)	CCI	Improver Value	CCI Improved
None	Base	38.0	523.40	53.60	-	-
0.05	Base + CHMN	37.9	519.80	53.03	3.94	56.97
	Base + CHEN	37.9	523.40	53.43	3.97	57.40
	Base + CHDMN	37.9	519.80	53.03	3.94	56.97
	Base + THFN	38.0	523.40	53.60	3.98	57.58
	Base + EHN	37.9	519.80	53.03	3.94	56.97
0.10	Base + CHMN	37.9	521.60	53.23	6.36	59.59
	Base + CHEN	37.9	525.20	53.62	6.41	60.03
	Base + CHDMN	37.9	519.80	53.03	6.34	59.37
	Base + THFN	38.0	525.20	53.80	6.43	60.23
	Base + EHN	37.9	521.60	53.23	6.36	59.59

Note: CHMN = Cyclohexylmethyl Nitrate

CHEN = 2-Cyclohexylethyl Nitrate

CHDMN = Cyclohexanedimethyl Nitrate

THFN = Tetrahydrofurfuryl Nitrate

EHN = 2-Ethylhexyl Nitrate

CCI = Calculated Cetane Index

CCI Improver = CCI + Improver Value

From Table 4.16, it could be seen that mid-boiling point of all blended base diesel fuels at the concentrations of 0.05% and 0.10% by weight gave the values similar to base diesel fuel and there were the same API gravity values of 38.0. Therefore, it was found that calculated cetane index of these synthesized nitrate compounds did not give any change of these physical properties as compared with the value of base diesel fuel without cetane improver, on account of using only an equation according to the method of ASTM D976.

In fact, the calculated cetane index equation possesses certain inherent limitations which must be recognized in its application. There are

1. It is not applicable to fuels containing additives for raising cetane number.
2. It is not applicable to pure hydrocarbons, synthetic fuels, such as certain products derived from shale oils, tar sands, alkylates, or coal-tar products.

Therefore, another equation having additional value was considered. It was found that the improved equation for considering the improver value could be calculated by the following equation [17]:

$$\text{Improver value} = 0.1742(0.1G)^{1.4444}(0.01M)^{1.0052}(\ln(1+17.5534D))$$

where

G = API gravity at 60°F, determined by ASTM D1298

M = Mid-boiling point temperature (°F), determined by ASTM D86

D = Percent weight of cetane improver

By adding this equation to an equation in ASTM D976, the correct calculated cetane index of diesel fuel containing cetane improver could be determined as shown in Table 4.16. It could be seen that the calculated cetane index of all samples were increased by 3.9 units at the concentration of 0.05% by weight, and 6.4 units at the concentration of 0.10 % by weight, respectively, as compared with base diesel fuels.

From CCI improver values, it could be seen that the blended base diesel fuels with cycloalkyl nitrate compounds and tetrahydrofurfuryl nitrate gave higher CCI improver value than base diesel fuel and 2-ethylhexyl nitrate at the concentrations of 0.05% and 0.10% by weight. According to both concentrations, tetrahydrofurfuryl nitrate gave the highest CCI improver value as compared with the others. These results were observed that the compound, which had incorporated oxygen atom in hydrocarbon chain, could be improved greater cetane number. This pointed out that oxygen atom in the hydrocarbon chains enhanced the oxidation, which resulted in increasing of cetane number.

#### **4.5 Determination of Cetane Improvement of Synthesized Nitrate Compounds in Base Diesel Fuel.**

In this study, there was another method for calculation of cetane improvement. Cetane improvement of blended base diesel fuels could be determined by nomograph of Associated Octel Company Ltd. [10] and these results were shown in Table 4.17



**Table 4.17** Cetane improvement of the blend of synthesized nitrate compounds with base diesel fuel.

Concentration (%weight)	Blended Composition	Density @ 15°C	$\Delta$ CN	CN
None	Base	0.8344	-	54.00
0.05	Base + CHMN	0.8349	2.97	56.97
	Base + CHEN	0.8349	2.97	56.97
	Base + CHDMN	0.8349	2.97	56.97
	Base + THFN	0.8344	3.00	57.00
	Base + EHN	0.8349	2.97	56.97
0.10	Base + CHMN	0.8349	4.98	58.98
	Base + CHEN	0.8349	4.98	58.98
	Base + CHDMN	0.8349	4.98	58.98
	Base + THFN	0.8344	5.00	59.00
	Base + EHN	0.8349	4.98	58.98

Note:  $\Delta$ CN = Increase Cetane Number

CN = Cetane Number

From Table 4.14, it could be seen that cetane improvements of all samples were increased by 3.00 units at the concentration of 0.05% by weight and 5.00 units at the concentration of 0.10% by weight, as compared with base diesel fuel. These results gave the similar trend of cetane improvement as Calculated Cetane Index. It could be concluded that the cetane number could be increased by adding the nitrate compounds, such as these synthesized nitrate compounds of this study, to the base diesel fuel.

#### 4.6 Physical Properties of Synthesized Nitrate Compounds in Base Diesel Fuel

There were many properties that were considered to be most indicative of diesel fuel quality. Some diesel fuel properties were presented in Table 4.18 except mid-boiling point, API gravity and cetane index that were shown in Table 4.16

**Table 4.18** Physical properties of synthesized nitrate compounds in base diesel fuels.

Concentration (%weight)	Blended Composition	Flash Point (°C)	Pour Point (°C)	Viscosity @ 40 °C
Base	Base	73	0.0	3.059
0.05	Base + CHMN	72	1.0	3.070
	Base + CHEN	73	1.0	3.068
	Base + CHDMN	73	-2.0	3.066
	Base + THFN	73	0.0	3.061
	Base + EHN	70	0.0	3.060
0.10	Base + CHMN	76	1.0	3.068
	Base + CHEN	73	1.0	3.065
	Base + CHDMN	73	1.0	3.066
	Base + THFN	73	0.0	3.059
	Base + EHN	73	0.0	3.059

#### 4.7 Determination Effect of Tetrahydrofurfuryl Nitrate and 2-Ethylhexyl Nitrate on Base Diesel Fuel Properties

The addition of tetrahydrofurfuryl nitrate and 2-ethylhexyl nitrate had no measurable effect on diesel fuel properties other than cetane number. This was illustrated by the data in Table 4.19, which shown that even at additive concentrations

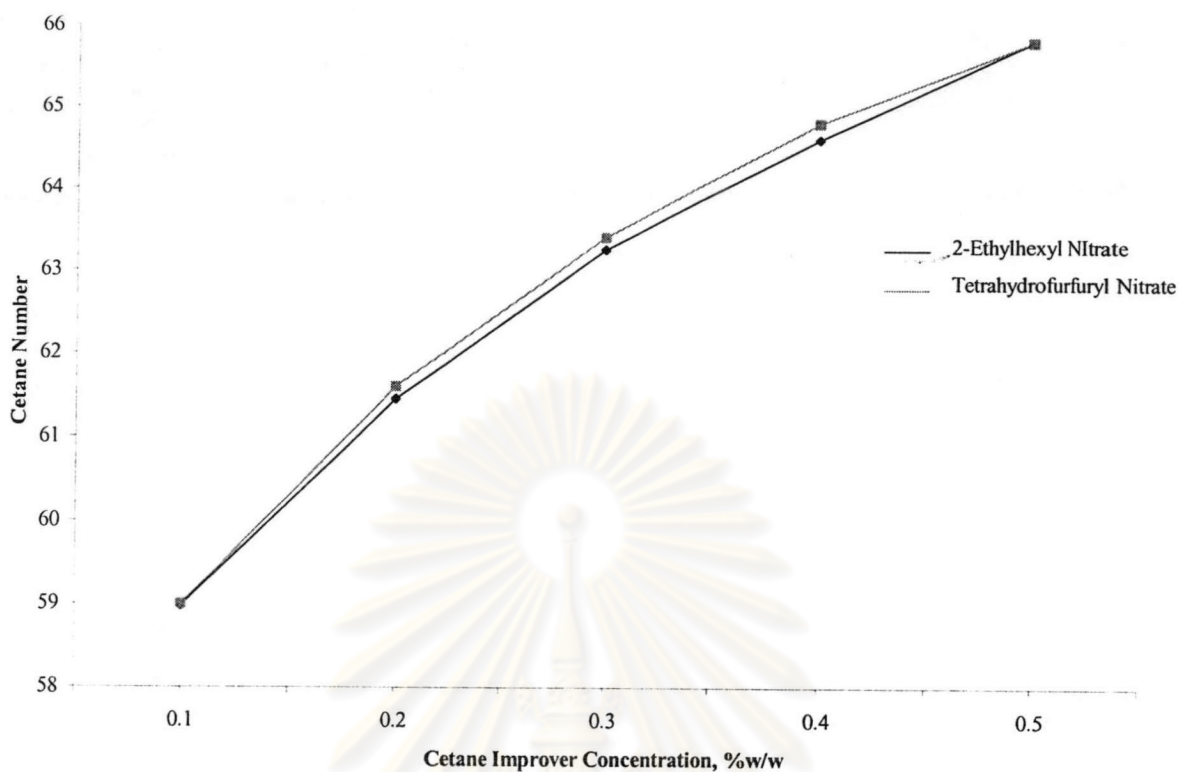
of 0.20%, 0.30%, 0.40% and 0.50% by weight no changed in properties such as mid-boiling point, API gravity, viscosity, flash point, pour point and density were evident.

**Table 4.19** Effect of tetrahydrofurfuryl nitrate and 2-ethylhexyl nitrate on diesel fuel properties.

Property	Tetrahydrofurfuryl Nitrate				2-Ethylhexyl Nitrate			
	Concentration (% wt.)				Concentration (% wt.)			
	0.20	0.30	0.40	0.50	0.20	0.30	0.40	0.50
Density at 15°C	0.834	0.834	0.834	0.834	0.835	0.835	0.835	0.835
Viscosity at 40°C	3.059	3.061	3.060	3.066	3.059	3.060	3.066	3.065
Pour Point(°C)	0.0	-1.0	0.0	-2.0	0.0	0.0	-2.0	-2.0
Flash Point(°C)	73	73	73	72	73	73	70	70
Mid-boiling Point(°C)	273	273	274	273	272	272	272	272
API Gravity at 60°F	38.0	38.0	38.0	38.0	37.9	37.9	37.9	37.9
Cetane Number[10]	61.60	63.40	64.80	65.80	61.45	63.25	64.60	65.80

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**Figure 4.1** Cetane response of tetrahydrofurfuryl nitrate and 2-ethylhexyl nitrate

From Tables 4.18 and 4.19, it could be seen that the synthesized nitrate compounds did not make any change to the physical properties of the base diesel fuel and all of blended base diesel fuels gave the similar value as base diesel fuel.

If the synthesized nitrate compounds did make any change to the physical properties of the base diesel fuel, these blended base diesel fuels could not be used according to the specification of diesel fuel.