

## CHAPTER III

### EXPERIMENTAL

#### 3.1 Apparatuses

1. Fourier-Transform NMR Spectrometer : Model AC-F 200  
(200MHz); Bruker Spectrospin
2. Fourier-Transform Infrared Spectrophotometer : Model Impact410;  
Nicolet
3. Automatic Distillation Apparatus : Model MP626; Herzog
4. Pensky-Martens Closed Flash Tester : Model ISL(PMFP93); Perzoo
5. Automatic Pour Point Tester : Model ISL(CPP97-6); ISL
6. Cannon Automatic Viscometer : Model CAV-3; Cannon
7. Apparatus for API Gravity

### 3.2 Chemicals

1. Cyclohexylmethanol: analytical grade; Merck
2. 2-Cyclohexylethanol: analytical grade; Merck
3. 1,4-Cyclohexanedimethanol: analytical grade; Merck
4. Tetrahydrofurfuryl Alcohol: analytical grade; Merck
5. 2-Ethyl-1-hexanol: analytical grade; Fluka
6. Dichloromethane: analytical grade; Lab-Scan
7. 96% Sulfuric Acid: analytical grade; Merck
8. 65% Nitric Acid: analytical grade; Lab-Scan
9. Sodium Hydrogen Carbonate: analytical grade; Merck
10. Anhydrous Sodium Sulfate: analytical grade; Merck
11. Chloroform-D1: NMR spectroscopy grade; Merck
12. Base Diesel Fuels; Petroleum Authority of Thailand

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

#### 3.3.1 Synthesis of Cyclohexylmethyl Nitrate

The solution of cyclohexylmethanol (2.28 g., 0.02 moles) in dichloromethane (30 ml.) was added dropwise into a stirred mixture of 65% nitric acid (4.85 g., 0.05 moles) and 96% sulfuric acid (10.21 g., 0.10 mole) within 30 minute and cooled in ice-bath at about  $0 \pm 2^\circ\text{C}$ . The solution was stirred for over a one hour. At the point, the stirring was stopped and then the solution was allowed to separate. The organic layer was washed with 20 ml. of water, 10 ml. of 10% sodium hydrogen carbonate and 20 ml. of water, respectively. The solution was dried over anhydrous sodium sulfate. The solution was the concentrate on a rotary evaporator at  $60^\circ\text{C}$  to give 2.91 g. of cyclohexylmethyl nitrate (91.51% yield) as a pale yellow liquid. [8, 23]

#### 3.3.2 Synthesis of 2-Cyclohexylethyl Nitrate

The solution of cyclohexylethanol (3.84 g., 0.03 moles) in dichloromethane (30 ml.) was added dropwise into a stirred mixture of 65% nitric acid (4.85 g., 0.05 moles) and 96% sulfuric acid (10.21 g., 0.10 mole) within 30 minute and cooled in ice-bath at about  $0 \pm 2^\circ\text{C}$ . The solution was stirred for over a one hour. At the point, the stirring was stopped and then the solution was allowed to separate. The organic layer was washed with 20 ml. of water, 10 ml. of 10% sodium hydrogen carbonate and 20 ml. of water, respectively. The solution was dried over anhydrous sodium sulfate. The solution was the concentrate on a rotary evaporator at  $60^\circ\text{C}$  to give 4.69 g. of cyclohexylmethyl nitrate (90.37% yield) as a pale yellow liquid.

### 3.3.3 Synthesis of Cyclohexanedimethyl Nitrate

The solution of 1,4-cyclohexanedimethanol (2.88 g., 0.02 moles) in dichloromethane (30 ml.) was added dropwise into a stirred mixture of 65% nitric acid (9.70 g., 0.10 moles) and 96% sulfuric acid (15.31 g., 0.15 mole) within 30 minute and cooled in ice-bath at about  $0 \pm 2^\circ\text{C}$ . The solution was stirred for over a one hour. At the point, the stirring was stopped and then the solution was allowed to separate. The organic layer was washed with 20 ml. of water, 10 ml. of 10% sodium hydrogen carbonate and 20 ml. of water, respectively. The solution was dried over anhydrous sodium sulfate. The solution was the concentrate on a rotary evaporator at  $60^\circ\text{C}$  to give 4.27 g. of cyclohexylmethyl nitrate (91.24% yield) as a white solid.

### 3.3.4 Synthesis of Tetrahydrofurfuryl Nitrate

In a reactor was placed and stirred 65% nitric acid (3.88 g., 0.04 moles). The nitric acid was cooled to  $0 \pm 2^\circ\text{C}$  and then 96% sulfuric acid (6.13 g., 0.06 moles) and 0.2 g. urea was added. The mixture was stirred and cooled below  $-20^\circ\text{C}$  and then 2.04 g. (0.02 moles) of tetrahydrofurfuryl alcohol was added over a one hour. The solution was stirred for 1 hour more, 10 ml. of dichloromethane was added and the mixture was stirred for another five minutes. The two phase system was then poured into 200 g. of crushed ice layered with 50 ml. of dichloromethane. The organic layer was separated, washed with 20 ml. of water, 10% sodium hydrogen carbonate and 20 ml. of water, respectively. The solution was dried over anhydrous sodium sulfate. The dichloromethane solvent was removed by rotary evaporator at  $60^\circ\text{C}$  to give 2.06 g. of tetrahydrofurfuryl nitrate (70.07% yield) as a pale red liquid [9, 23].



### 3.4 Synthesis of 2-Ethylhexyl Nitrate

50 ml. Dichloromethane were added 96% sulfuric acid (6.13 g., 0.06 moles) and 65% nitric acid (3.88 g., 0.04 moles). 2-Ethyl-1-hexanol (2.6 g., 0.02 moles) were then slowly added to the well-agitated mixture whilst maintaining the temperature between 0 °C and 5 °C. The mixture was stirred for over a one hour. Stirring was stopped, and allowed the mixture to separate. The lower spent acid (comprising mainly strong sulfuric acid) was removed. The organic layer was washed with water to remove the excess nitric acid, then washed with sodium hydrogen carbonate, after which it was neutral. Solvent was removed on a rotary evaporator at 60 °C, to give 3.26 g. of 2-Ethylhexyl nitrate (93.14% yield) as a colorless liquid [25].

### 3.5 Characterization and Determination of the Synthesized Nitrate Compounds

#### 3.5.1 Characterization of the Synthesized Nitrate Compounds

The synthesized nitrate compounds were characterized by using instruments as follows:

1. Fourier-Transform Infrared Spectrophotometer
2. Fourier-Transform NMR Spectrometer

The result was shown in appendix A.

#### 3.5.2 Determination of Properties and Cetane Index of Base Diesel Fuel Blended with Synthesized Nitrate Compounds

Blended base diesel fuels containing with 0.05% and 0.10% by weight of synthesized nitrate were determined of their properties and cetane index.

1. The blended base diesel fuels were prepared by blending synthesized nitrate compounds (0.50 g. and 0.25 g.) in base diesel fuel (500 g.). The synthesized nitrate compounds were as follow.

- 1) Cyclohexylmethyl nitrate
- 2) 2-Cyclohexylethyl nitrate
- 3) 1,4-Cyclohexanedimethyl nitrate
- 4) Tetrahydrofurfuryl nitrate
- 5) 2-Ethylhexyl nitrate

2. The physical properties of the blended base diesel fuels were determined as shown in Table 3.1

**Table 3.1** Test method of the blended base diesel fuels

Property	Method
Mid-boiling point	ASTM D86
API gravity	ASTM D1298
Pour point	ASTM D97
Flash point	ASTM D93
Viscosity	ASTM D445
Cetane index	ASTM D976

### 3.5.3 Determination of Cetane Improvement of Synthesized Nitrate Compounds in Base Diesel Fuel

Blended base diesel fuels containing with 0.05% and 0.10% by weight of synthesized nitrate compounds were determined of their cetane numbers. Apart from cetane number testing according to ASTM D613 CFR engine technique, there is the other method for prediction of cetane number of diesel fuel. It is the calculation of

cetane improvement from the alignment chart of the Associated Octel Company Ltd. [10], as follows.

1. Density at 15°C (which correlated with API gravity at 60°C) of blended base diesel fuels were measured at 0.05% and 0.1% concentration.

2. Cetane improvement was calculated by nomograph for the calculation of cetane improvement which given in Figure 3.1 by using density data and the cetane number of the known base diesel fuel.

#### **Method of Using Nomograph in Figure 3.1**

1. Identifying the base fuel cetane number and density on the appropriate axes and draw a line joining these two points.

2. Where this line intersects the pivot line, either

a) Connecting the pivot point to the cetane number increase ( $\Delta CN$ ) that is desired and extend the line to the concentration axis to predict the additive concentration, or

b) Connecting the pivot point to the chosen concentration and read back along the line to the predicted cetane number increase.

#### **3.5.4 Determination of Effect and Cetane Improvement of Tetrahydrofurfuryl Nitrate and 2-Ethylhexyl Nitrate in Base Diesel Fuel**

Blended base diesel fuels containing with 0.20%, 0.30%, 0.40% and 0.50% by weight of tetrahydrofurfuryl nitrate and 2-ethylhexyl nitrate were determined of their properties and cetane numbers [10].



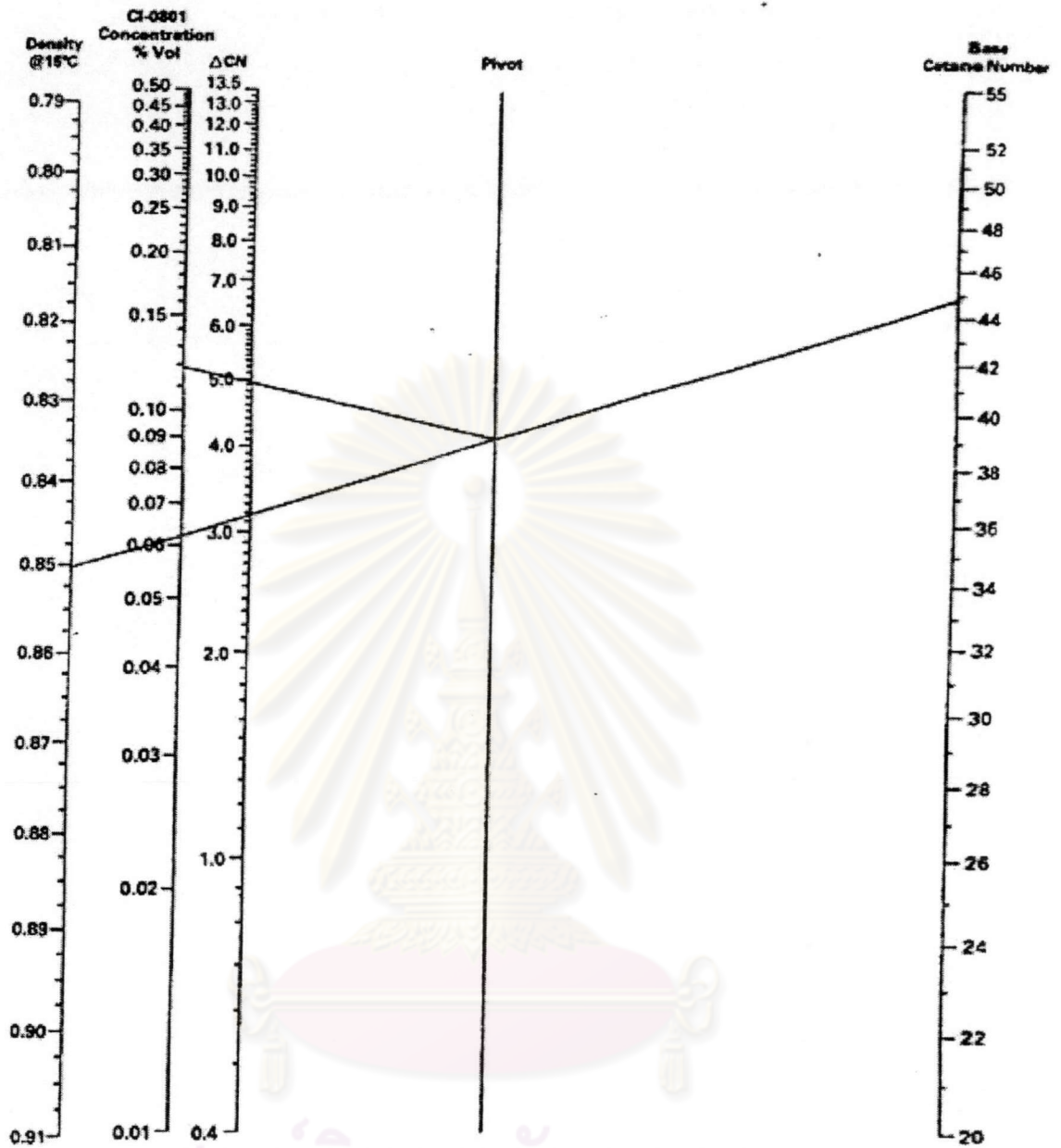


Figure 3.1 Nomograph for the calculation of cetane improvement from cetane improver additions. (Source: The Associated Octel Company Ltd.)