CHAPTER III

EXPERIMENTAL

3.1 Apparatus

1. Fourier-Transform Infrared Spectrophotometer: Model Impact 410; Nicolet
2. Fourier-Transform NMR Spectrometer: Model AC-F 200 (200MHz); Bruker Spectrospin
3. Cetane – 2000 Diesel Fuel Analyzer; Petrospec
4. Automatic Distillation Apparatus: Model MP626; Herzog
5. Pensky-Martens Closed Flash Tester: Model ISL(PMFP93); Perzoo
6. Automatic Pour Point Tester: Model ISL(CPP97-6); ISL
7. Cannon Automatic Viscometer: Model CAV-3; Cannon
8. Apparatus for API Gravity

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3.2 Chemicals

1. Hexane: analytical grade; Lab-Scan
2. Dichloromethane: analytical grade; Lab-Scan
3. Methanol: analytical grade; Merck
4. 50% Hydrogen Peroxide: analytical grade; Merck
5. 96% Sulfuric Acid: analytical grade; Merck
6. 65% Nitric Acid: analytical grade; Merck
7. 37% Hydrochloric acid: analytical grade; Merck
8. Glacial Acetic Acid: analytical grade; Merck
9. Sodium Hydrogen Carbonate: analytical grade; Merck
10. Anhydrous Sodium Sulfate: analytical grade; Merck
11. Chloroform-D: NMR spectroscopy grade; Merck
12. Based Diesel Fuel; Petroleum Authority of Thailand
13. Palm oil; Morakot Industry Co., Ltd.
14. Soybean oil; Thanakorn Vegetable Oil Products Co., Ltd.

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3.3 Synthesis of Nitrate Compounds from Palm Oil

3.3.1 Synthesis of Palm Oil Methyl Ester

In the 500 ml of 2-neck round bottom flask equipped with thermometer and reflux condenser, palm oil (100 g.), methanol (224 g.) and 96% sulfuric acid (6.72 g.) were added. The mixture was refluxed at 80°C for 12 hours. After the reaction completed, the mixture was allowed to separate. After the aqueous layer was removed, the organic layer was washed with water (100 ml), 10% sodium hydrogen carbonate solution (100 ml), water (100 ml) and saturated sodium chloride solution (100 ml), respectively. The solution was dried over anhydrous sodium sulfate. The organic solvent was removed on rotary evaporator at 60°C to give 96.26 g. of palm oil methyl ester as a yellow liquid.

3.3.2 Synthesis of Palm Oil Epoxide

In the 500 ml of 3-neck round bottom flask equipped with thermometer and reflux condenser, palm oil methyl ester (100 g.), hexane (100 g.), glacial acetic acid (14.2 g.) and 50% sulfuric acid (2.1 g.) were added. The mixture was then heated to 55-65°C. Then 50% hydrogen peroxide (38.59 g.) was slowly added over 1 hour period. The temperature was then maintained between 60 to 65°C for 6 hours. After the reaction completed, the mixture was allowed to separate. After the aqueous layer was removed, the organic layer was washed with water (100 ml), 10% sodium hydrogen carbonate solution (100 ml), water (100 ml) and saturated sodium chloride solution (100 ml), respectively. The solution was dried over anhydrous sodium sulfate. The organic solvent was removed on rotary evaporator at 60°C to give 98.08 g. of palm oil epoxide as a pale yellow liquid.

3.3.3 Synthesis of Palm Oil Diol

In the 500 ml of 2-neck round bottom flask equipped with thermometer and reflux condenser, palm oil epoxide (90 ml), 1 N hydrochloric acid (270 ml) and 96% sulfuric acid (72 drops) were added. The mixture was refluxed at 90°C for 4 hours. After the reaction completed, the mixture was allowed to separate. After the aqueous layer was removed, the organic layer was washed with water (100 ml), 10% sodium hydrogen carbonate solution (100 ml), water (100 ml) and saturated sodium chloride solution (100 ml), respectively. The solution was dried over anhydrous sodium sulfate. The organic solvent was removed on rotary evaporator at 60°C to give 83.96 g. of palm oil diol as a pale yellow liquid.

3.3.4 Synthesis of Palm Oil Nitrate

In the 250 ml of round bottom flask, 65% nitric acid (4.85 g.) and 96% sulfuric acid (10.20 g.) were added. The mixture was stirred on ice-bath while maintaining temperature at 0±2°C. The palm oil diol (5.54 g.) in dichloromethane (30 ml) was added dropwise to the flask and the temperature was kept at 0± 2°C. The reaction was stirred for 5 hours and maintained the temperature at 0± 2°C. After the reaction completed, the mixture was allowed to separate. After the aqueous layer was removed, the organic layer was washed with water (75 ml), 10% sodium hydrogen carbonate solution (75 ml), water (75 ml) and saturated sodium chloride solution (75 ml), respectively. The solution was dried over anhydrous sodium sulfate. The organic solvent was removed on rotary evaporator at 60°C to give 5.36 g. of palm oil nitrate as a yellow liquid.

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3.4 Synthesis of Nitrate Compounds from Soybean Oil

3.4.1 Synthesis of Soybean Oil Methyl Ester

By starting with soybean oil (100 g.) using a process analogous to that described in 3.3.1, the subtitle 98.86 g. of soybean oil methyl ester as a yellow liquid was obtained.

3.4.2 Synthesis of Soybean Oil Epoxide

By starting with soybean oil methyl ester (100 g.) using a process analogous to that described in 3.3.2, the subtitle 97.24 g. of soybean oil epoxide as a pale yellow liquid was obtained.

3.4.3 Synthesis of Soybean Oil Diol

By starting with soybean oil epoxide (90 ml.) using a process analogous to that described in 3.3.3, the subtitle 94.72 g. of soybean oil diol as a pale yellow liquid was obtained.

3.4.4 Synthesis of Soybean Oil Nitrate

In the 250 ml of round bottom flask, 65% nitric acid (4.85 g.) and 96% sulfuric acid (10.20 g.) were added. The mixture was stirred on ice-bath while maintaining temperature at $0\pm2^{\circ}$C. The soybean oil diol (5.54 g.) in dichloromethane (30 ml) was added dropwise to the flask and the temperature was kept at $0\pm2^{\circ}$C. The reaction was stirred for 6 hours and maintained the temperature at $0\pm2^{\circ}$C. After the reaction completed, the mixture was allowed to separate. After the aqueous layer was removed, the organic layer was washed with water (75 ml), 10% sodium hydrogen carbonate solution (75 ml), water (75 ml) and saturated sodium chloride solution (75 ml), respectively. The solution was dried over anhydrous sodium sulfate. The organic

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solvent was removed on rotary evaporator at 60°C to give 5.29 g. of soybean oil nitrate as a brown liquid.

3.5 Synthesis of 2-Ethylhexyl Nitrate

In the 250 ml of round bottom flask, dichloromethane (50 ml), 96% sulfuric acid (6.13 g.) and 65% nitric acid (3.88 g.) were added. The mixture was stirred on ice-bath and maintained temperature between 0-2°C. 2-Ethyl-1-hexanol (2.60 g.) was then slowly added to the well-agitated mixture while maintaining the temperature between 0-2°C. The mixture was stirred for one hour. Stirring was stopped, and allowed the mixture to separate. The lower spent acid (comprising mainly sulfuric acid) was removed. The organic layer was washed with water (100 ml.), 10% sodium hydrogen carbonate solution (100 ml.), water (100 ml.) and saturated sodium chloride solution (100 ml.), respectively. The solution was dried over anhydrous sodium sulfate. Solvent was removed on rotary evaporator at 60 °C, to give 3.26 g. of 2-ethylhexyl nitrate (93.14% yield) as a colorless liquid [5].

3.6 Characterization and Determination of the Synthesized Nitrate Compounds

3.6.1 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.

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3.6.2 Determination of Cetane Number of Base Diesel Fuel Blended with Synthesized Nitrate Compounds

Blended base diesel fuels containing with 0.05%, 0.10%, 0.25%, 0.50%, 0.75% and 1.00% by weight of synthesized nitrate were determined of cetane number using Cetane – 2000 Diesel Fuel Analyzer.

1. The blended base diesel fuels were prepared by blending synthesized nitrate compounds (0.05 g., 0.10 g., 0.25 g., 0.50 g., 0.75 g. and 1.00 g.) in base diesel fuel (100 g.). The synthesized nitrate compounds were as follows.

1) Palm oil nitrate
2) Soybean oil nitrate
3) 2-Ethylhexyl nitrate

2. The physical properties of the base diesel fuel blended with synthesized nitrate compounds were determined as shown in Table 3.1.

Table 3.1 Test method of the blended base diesel fuel.

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

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