CHAPTER III

EXPERIMETAL

3.1 Materials and chemicals

1. Base Diesel Fuel
   Petroleum Authority of Thailand.
2. Palm Oil Soapstock
   Siam Union Sahamitr Co., Ltd.
3. Rice Bran Oil Soapstock
   Thai edible oil Co., Ltd.
4. n-Hexane
   Analytical grade; Lab-Scan, Ireland
5. Sulfuric Acid (96%)
   Analytical grade; Carlo Erba, Italy
6. Phosphoric Acid (85%)
   Analytical grade; Carlo Erba, Italy
7. Dichloromethane
   Analytical grade; Lab-Scan, Ireland
8. Methanol
   Analytical grade; Merck, Germany
9. Sodium Hydrogen Carbonate
   Analytical grade; Merck, Germany
10. Sodium Chloride
    Analytical grade; Merck, Germany
11. Anhydrous Sodium Sulfate
    Analytical grade; Merck, Germany
12. Chloroform-D : NMR
    Spectroscopy grade; Merck, Germany

13. Di-n-Butyl Sulfide (21.9%)
14. Oleum

3.2 Instruments and apparatus

1. Fourier-Transform Infrared Spectrophotometer
   Nicolet Impact 410
2. Fourier-Transform NMR Spectrometer
   Varian Mercury 400
4. X-ray fluorescence spectrometer (XRF)
   Bruker AXS S4Explorer
5. X-ray fluorescence spectrometer (XRF)
   Oxford MDX 1000
6. High Frequency Reciprocating Rig
7. Automatic Distillation Apparatus
   Herzog MP626
8. Pensky-Martens Closed Flash Tester
   Perzoc ISL (PMFP 93)
9. Automatic Pour Point Tester
   ISL (CPP97-6)
10. Cannon Automatic Viscometer
    Cannon CAV-3
11. Apparatus for API Gravity
12. Dean Stark Apparatus

3.3 Experimental procedure

3.3.1 Synthesis of palm oil sulfonated methyl ester [30]

3.3.1.1 Synthesis of palm oil methyl ester

Palm oil soapstock (218 g), methanol (780 g), dichloromethane (200 g) and 96% sulfuric acid (20 ml) were added into 2000 ml of two-neck round bottom flask

equipped with thermometer, reflux condenser and dean stark apparatus. The mixture was refluxed at 65°C for10 hours. After reaction was completed, the mixture was allowed to separate and removed the aqueous layer and washed the organic layer with (200 ml) water, 10% sodium hydrogen carbonate solution (200 ml), water (200 ml) and saturated sodium chloride solution (200 ml), respectively. The solution was dried over anhydrous sodium sulfate. The organic solvent was removed on rotary evaporator at 60°C to give 211.49 g (97.01 % yield) of palm oil methyl ester as a yellow liquid.

3.3.1.2 Synthesis of palm oil sulfonated methyl ester

Palm oil methyl ester (150 g), dichloromethane (150 g) were added into beaker equipped with ice bath and hotplate stirrer. Then oleum 30 g was slowly added by dropper. The temperature was then maintained between 30-35 °C for 3 hours, the mixture was allowed to separate. The aqueous layer was removed and the organic layer was washed with water until the layer had neutral condition. The solution was dried over anhydrous sodium sulfate. The organic solvent was removed on rotary evaporator at 60 °C to give 127.46 g (84.97 %yield) of palm oil sulfonated methyl ester as brown liquid.

3.3.2 Synthesis of rice bran oil sulfonated methyl ester

3.3.2.1 Degumming of rice bran oil soapstock

Rice bran oil soapstock was added with phosphoric acid and washed many times with water. Dicholoromethane was added after remove the aqueous layer and the organic layer was washed with water. The organic solvent was removed on rotary evaporator at 60°C to give a brown oil of rice bran oil soapstock.

3.3.2.2 Synthesis of rice bran oil methyl ester

Rice bran oil soapstock (214 g), methanol (680 g), dichloromethane (200 g) and 96% sulfuric acid (20 ml) were added into 2000 ml of two-neck round bottom flask equipped with thermometer, reflux condenser and dean stark apparatus. The mixture was refluxed at 65°C for10 hours. After reaction completed, the mixture was

allowed to separate and removed the aqueous layer and washed the organic layer with 200 ml water, 10% sodium hydrogen carbonate solution (200 ml), water (200 ml) and saturated sodium chloride solution (200 ml), respectively. The solution was dried over anhydrous sodium sulfate. The organic solvent was removed on rotary evaporator at 60°C to give 205.82 g (96.18 % yield) of rice oil methyl ester as a yellow liquid.

3.3.2.3 Synthesis of rice bran oil sulfonated methyl ester

Rice bran oil methyl ester (150 g), dichloromethane (150 g) were added into beaker equipped with ice bath and hotplate stirrer. Then oleum 30 g was slowly added by dropper. The temperature was then maintained between 30-35 °C for 3 hours. After reaction completed, the mixture was allowed to separate. The aqueous layer was removed and the organic layer was washed with water until the layer had neutral condition. The organic solvent was removed on rotary evaporator at 60 °C to give 120.67 g (80.51 %yield) of rice bran oil sulfonated methyl ester as brown liquid.

3.3.3 Characterization and determination of the synthesized vegetable oil soapstocks sulfonated methyl ester compound

3.3.3.1 Characterization of the synthesized vegetable oil soapstocks sulfonated methyl ester compound

The synthesized vegetable oil soapstocks sulfonated methyl ester compounds were characterized by using instruments as follows:

1. Fourier-Transform Infrared Spectrophotometer
2. Fourier-Transform NMR Spectrometer
3. Gas Chromatrography - Mass Spectrometry
4. X-Ray Fluorescence Spectrometer

The results were shown in appendix A

3.3.3.2 Determination of sulfur in sulfonated methyl ester compound

The sulfur in sulfonated methyl ester were determination sulfur by using X-ray fluorescence spectrometer. The calibration curve were established by using Di n-butyl sulfide standard in the concentration range of 0.0004-0.0020%, 0.0021-0.0105 %, and 0.0357-0.1783 % by volume. The conditions of XRF were shown in Table 3.1.

Table 3.1 The conditions of X-Ray Fluorescence

Parameter	**Conditions**
Preparation	Mylar 6 μm
Method	Liquid
Spectrometer condition	Helium
Peak Measurements	Peak Measurements : Measure at fixed positions Background Measurements : Measure at fixed
Measuring Time	Automatic optimization
Lines	S LA1-HS-Min

3.3.3.3 Determination of physical properties of base diesel fuel blended with sulfonated methyl ester

1. The physical properties of blended base diesel fuels containing of 0.05% to 10% by weight of sulfonated methyl ester were determined as shown in Table 3.2.

Table 3.2 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
Sulfur Content	ASTM D2622
Total Acid Number	ASTM D664

2. The lubricity performance of the base diesel fuels blended with 5 % by weight sulfonated methyl ester compound was determined by using High Frequency Reciprocating Rig Method.