CHAPTER III

EXPERIMENT

3.1 Materials

3.1.1 Cashew Nut Shell was obtained locally.

3.1.2 1-Hexanol ($C_6H_{13}OH$) was obtained from Fluka.

3.1.3 Salicylic acid was obtained from J.T. Baker.

3.1.4 2-ethyl-1-hexanol was obtained from Fluka.

3.1.5 Methyl salicylate was obtained from J.T. Baker.

3.1.6 Hexane was obtained from Fluka.

3.1.7 Toluene was obtained from BDH.

3.1.8 Hydrochloric acid concentration (HCl) was obtained from BDH.

3.1.9 Aniline was obtained from Merck.

3.1.10 *o*- Toluidine was obtained from Merck.

3.1.11 *m*-Toluidine was obtained from Merck.

3.1.12 *p*-Toluidine was obtained from Merck.

3.1.13 Sodium nitrite ($NaNO_2$) was obtained from BDH.

3.1.14 Potassium Hydroxide (KOH) was obtained from BDH.

3.1.15 Methanol (CH_3OH) was obtained from J.T. Baker.

3.1.16 Ethylene glycol was obtained from J.T. Baker.

3.1.17 Morpholine was obtained from J.T. Baker.

3.1.18 Diisopropylamine was obtained from Merck.

3.1.19 Acetone was obtained from J.T. Baker.

3.2 Instruments and Apparatuses

3.2.1 FT-IR spectra

The FT-IR spectra were recorded on a Perkin Elmer model IR 2000 series (Double beam) using neat liquid. The working range 4000-400 cm^{-1} is used for characterization of functional groups.

3.2.2 Ultraviolet and Visible Spectra (UV and VIS)

The UV and VIS spectra were determined on a Perkin Elmer Spectrophotometer Model Lamda-2 at the maximum wavelength of each marker dyes.

3.2.3 Distillation

The distillation data was obtained by a Herzog Automatic distillation Model MP 626.

3.2.4 Flash Point

The flash point was obtained on a Pensky Martin Automatic Flash Point ISL, FP 93.

3.2.5 Pour Point

The pour point data was made by using a ISL, CPP 92

3.2.6 Viscosity

The kinematic viscosity data was carried out by using a Cannon automatic viscosity. The kinemetic viscosity of products was checked at 40, 50 and 100 °C

3.2.7 Color

The color was tested according to ASTM D 1500 to check color of dyed fuel oil.

3.2.8 Proton and Carbon-13 Nuclear magnetic Resonance (^{1}H NMR and ^{13}C NMR)

The ^{1}H and ^{13}C NMR were performed using a Bruker Spectrospin Model DPX-300. Tetramethylsilane (TMS) was used as an internal standard. The chemical shifts (δ) were given in ppm down field from the TMS.

3.3 Syntheses

3.3.1 Esterification of CNSL

Cashew nut shell extract (CNSL) was obtained by n-hexane extraction. The n-hexane was evaporated by rotary evaporator.

Procedure

CNSL 50 g, 1-hexanol 26 g, toluene 200 ml and concentrated sulfuric acid 3 ml were placed in a 500 ml round-bottomed flask. A dean-stark and condenser was attached and the mixture was refluxed for 10 hrs. on a hot-plate with magnetic stirrer.

The solution was cooled and transferred to a separatory funnel and the acid catalyst was washed with 30 ml cold water until the aqueous phase was not strongly acidic as judged by pH paper.

The crude ester was transferred to a round-bottomed flask, and toluene and unreacted alcohol were removed by distillation.

Structure of CNSL and esterified-CNSL were studied by FT-IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy and its physical properties tested according to standard ASTM testing methods as describe in Table 3.1.

Table 3.1: The ASTM testing methods of CNSL and esterified-CNSL.

Test item	ASTM
Specific Gravity @ 15.6/15.6°C	D 1298
Kinematic Viscosity @ 40 °C, cSt	D 445
@ 50 °C, cSt	D 445
@ 100 °C, cSt	D 445
Pour Point, °C	D 97
Flash Point, (P.M), °C	D 93

3.3.2 Preparation of 2-Ethyl-1-hexyl salicylate

Salicylic acid 6.9 g was dissolved in 20 ml of 2-ethyl-1-hexanol in a 250 ml a round-bottom flask. A 100 ml of toluene, 0.8 ml of concentrated sulfuric acid and a magnetic bar were sequentially added. A Dean-stark and condenser was fitted, and the mixture was refluxed for 10 hrs.

The mixture was cooled and transferred to a saparatory funnel. The acid catalyze and unreacted salicylic acid was washed with saturated sodiumhydrogencarbonate solution until the aqueous phase was not strong acid tested by pH paper. The crude ester was transferred to a round-bottomed flask, toluene and unreacted alcohol were removed by distillation.

Structure of 2-ethyl-1-hexyl salicylate was studied by FT-IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy.

3.3.3 Preparation of Diazonium Salt

Aniline

A solution of 0.91 ml (0.01 mole) of aniline (purified by redistillation) in 12.5 ml 2*N* hydrochloric acid was cooled in an Erlenmeyer flask immersed in an ice salt bath and stirred mechanically. Ten milliliters of 1*N* sodium nitrite solution was added dropwise while the temperature was controlled below 0°C. The mixture was stirred for about 10 minutes below 0°C after completing the addition of nitrite and tested with starch-iodide paper, which usually gave a weak blue color.

o-Toluidine and m-Toluidine

A mixture of 1.08 ml (0.01 mole) of *o*-toluidine or m-toluidine (purified by redistillation) and 12.5 ml 2*N* hydrochloric acid was cooled in an Erlenmeyer flask. After cooling in a freezing mixture (ice+NaCl) to 0°C, the content was diazotised by adding dropwise, with constant stirring, a cold solution of 10 ml of 1*N* $NaNO_2$. A clear solution of diazonium salt was obtained in about 15 minutes. The diazonium salt solution gave a weak blue color with starch-iodide paper.

p-Toluidine

To a well-stirred mixture of 1.07 g (0.01 mole) of *p*-toluidine and 12.5 ml of 2*N* hydrochloric acid in a flask, which was cooled in ice salt bath. Then, the mixture was added 10 ml of 1*N* sodium nitrite solution dropwise. Stirring was continued and the mixture was kept cold. The diazonium salt solution became clear and almost colorless, and remained clear on standing

3.3.4 Preparation of Phenolate Ions

Methyl salicylate

Potassium hydroxide 1.12 g was dissolved in 5ml of methanol with stirring. Then, methyl salicylate 1.28 ml was added while the solution was cooled in ice.

2-Ethyl-1-hexylsalicylate

Potassium hydroxide 1.12 g was placed in 5 ml of methanol with stirring, and 2.5 g of 2-ethyl-1-hexylsalicylate was added into the solution. The solution was allowed to cool to about 0-5°C.

Esterified-CNSL

Potassium hydroxide 1.12 g was dissolved in 5 ml of methanol and 5 g of esterified-CNSL was added with stirring and cool to about 0-5°C.

3.3.5 Preparation of Marker Dyes

Azo dyes useful for marking fuel oils were prepared by coupling reaction. Series of marker dyes were listed in Table 3.2

Table 3.2: The synthesized azo dyes

Marker dye	Phenolate ion	Diazonium salt
1	Methyl salicylate	Aniline
2		*o*-Toluidine
3		*m*-Toluidine
4		*p*-Toluidine
5	2-Ethyl-1-hexylsalicylate	Aniline
6		*o*-Toluidine
7		*m*-Toluidine
8		*p*-Toluidine
9	Esterified-CNSL	Aniline
10		*o*-Toluidine
11		*m*-Toluidine
12		*p*-Toluidine

The solution of diazonium salt was added into the phenolate ion solution. The temperature of the mixture was controlled so that it did not rise above 8°C. The coupling reaction was completed after stirring for about 1 hour and then the reaction mixture was transferred to a separatory funnel, the aqueous phase was separated. The oil phase was collected and characterized by spectroscopic methods (e.g. FT-IR, UV-VIS, ^{1}H-NMR and ^{13}C-NMR) and analyzed by reduction with stannous chloride.

3.4 Acid Reduction of Marker Dyes

Stannous chloride 0.5 g was dissolved in 1 ml of concentrated hydrochloric acid and then a few mg of azo dye was added to this solution. The mixture was heated on water bath for 10 min. A colorless solution confirmed the presence of azo dyes.

3.5 Physical Properties of Marked and Unmarked Diesel Fuel Oil

Physical properties of marked and unmarked diesel fuel oil were studied by the ASTM method as described in Table 3.3

Table 3.3: The ASTM testing method of marked and unmarked diesel fuel oil

Test item	ASTM
API Gravity @ 60 °F	D 1298
Calculated Cetane Index	D 976
Kinematic Viscosity @ 40 °C, cSt	D 445
Pour Point, °C	D 97
Sulfur Content, %wt	D 4294
Copper Strip Corrosion, Number (3 hrs , @ 50 °C)	D 130
Flash Point, (P.M), °C	D 93
Distillation : (Correct Temp)	D 86
Color, ASTM	D 1500

3.6 Preparation of Concentrated Marker Dyes 5 – 12

The concentrated marker dyes were prepared according to Table 3.4 and 3.5. Table 3.4 showed the amount of marker dye used for preparing stock solution and the stock solution was made up to volume (100 ml) with toluene in order to prepare 1000 ppm of marker dye solution

Table 3.4: Preparation of stock solution and 1000 ppm of marker dyes 5 – 12

Marker dye	Stock solution		1000 ppm
	%Concentration	Amount of Marker dye (g) in 25 ml of Toluene	Volume of Stock solution (ml)
5 – 8	1	0.25	10
9 - 12	10	2.5	1

The 1% stock solution of each marker dyes 5-8 in toluene were prepared by dissolving 0.25 g of each solution and diluting it to the mark with toluene in 25.00 ml volumetric flasks. The 1000 ppm of each marker dyes were prepared by pipetting 10 ml of 1% stock solution and put into 100.00 ml volumetric flasks and then diluting it to the mark with toluene.

The 10% stock solution of marker dyes 9-12 in toluene were prepared by dissolving 2.5 g of each solution and diluting it to the mark with toluene in 25.00 ml volumetric flasks. The 1000 ppm of each marker dyes were prepared by pipetting 1 ml of 1% stock solution and put into 100.00 ml volumetric flasks and then diluting it to the mark with toluene.

Table 3.5: Preparation of concentration of marker dyes 5 – 12

Marker dye	Volume of 1000 ppm in 100 ml of Toluene	Volume of 100 ppm in 100 ml of Diesel oil				
	100ppm	1ppm	2ppm	3ppm	4ppm	5ppm
5 – 12	10	0.1	0.2	0.3	0.4	0.5

Table 3.5 showed the volume of 1000 ppm of marker dyes 5 – 12 solution per in 100 ml of toluene to prepared 100 ppm solution and then this 100 ppm marker dyes solutions were used to prepare various concentration of marker dyes in diesel oil.

The 1000 ppm of marker dyes 5-12 in toluene were prepared by pipetting 10 ml of each solution and diluting it to the mark with toluene in 100.00 ml volumetric flasks. 1-5 ppm of marker dye solutions was prepared from the 100-fold dilution of 100 ppm of marker dye solution.

3.7 Extraction System for Detection of Marker Dyes in Fuel Oil

The solution systems, which will extract the marker dyes in this study from tagged high-speed diesel oil, may be prepared from a dilute alkali, such as NaOH or KOH, and a extraction solution. The extraction solution also included a water-miscible and petroleum-immiscible solvent, such as methanol or ethylene glycol. The phenolic group of the azo dye formed a salt with the base in the extraction solution and developed color in extracted phase.

Procedure

5 ppm solution of marker dye 9 was prepared by pipetting 0.5 ml of 100 ppm of marker dye solution and put into 100.00 ml volumetric flasks and then diluting it to the mark with high-speed diesel oil. 10% by weight KOH in ethylene glycol was prepared by dissolving 8 g of KOH in 50 ml of ethylene glycol and stirring to give a clear solution and then diluting it with ethylene glycol in 100.00 ml volumetric flask. After that the 5 ppm of marked dye 9 and extraction system were pipetted into a vial at 45 ml and 5 ml, respectively. The vial was capped and shaken for 30 seconds. In addition, diesel oil and extraction solution was mixed as described above, and the extraction procedure was carried out as a blank. After leaving until the two layers completely separated, the lower layer was transferred to the uv-visible spectroscopic measurement at the wavelength of 350 nm to 700 nm using the unmarked high-speed diesel oil as reference.

In addition, the four solutions of suitable solvent systems were choose to study for the visual color and absorption of extracted phase of each marker dye. The absorbance of each solution was measured at its λ maximum against the extracted phase of unmarked diesel oil. The optimal concentration of each marker dye in diesel oil was then concluded from all of results.

3.8 Quantitative Analysis of Marker Dyes

The concentrated marker dyes in commercial fuel oil was determined by the calibration method. The calibration curve was plotted between absorbance and concentration. Marker dye was added into commercial high-speed diesel oil at suitable concentration and quantitative analysis was carried out by measuring the absorption of extracted phase at λ maximum that were compared with the standard curve.

3.9 Stability Test for Marker Dyes in Commercial High-Speed Diesel Oil

The stability of marked diesel fuel oil was studied by monitoring the amount of marker dyes that added at the treat rate level after specific time of storage in a dark place. The concentration of marker dye in marked diesel fuel oil was calculated from the procedure described in Section 3.8.