

CHAPTER III

EXPERIMENTAL

3.1 Materials

- 3.1.1 Cashew Nut Shell liquid (CNSL) was obtained locally.
- 3.1.2 Toluene ($C_6H_5CH_3$) was obtained from BDH.
- 3.1.3 Hexanol ($C_6H_{13}OH$) was obtained from Fluka.
- 3.1.4 Sulfuric acid (H_2SO_4) was obtained from BDH.
- 3.1.5 Chloroanilines was obtained from Merck.
- 3.1.6 Sodium nitrite ($NaNO_2$) was obtained from BDH.
- 3.1.7 Potassium Hydroxide (KOH) was obtained from BDH.
- 3.1.8 Methanol (CH_3OH) was obtained from J.T. Baker.
- 3.1.9 Acetone (CH_3COCH_3) was obtained from J.T. Baker.

3.2 Instruments and Apparatuses

3.2.1 FT-IR Spectrophotometer

The FT-IR Spectrophotometer Model 2000 series (Double Beam) from Perkin Elmer is used for characterization at the working range $400-4000\text{ cm}^{-1}$

3.2.2 UV/VIS-Spectroscopy

The UV/VIS-Spectroscopy Model Lamda-2 from Perkin Elmer was used to quantify at the maximum wavelength each marker dye.

3.2.3 Automatic Distillation

The automatic distillation apparatus model MP 626 from Herzog was used for distillation of dyed and undyed gasoline or high speed diesel products.

3.2.4 Automatic Flash Point (Pensky Martin)

The ISL,FP 93 automatic flash point apparatus was used to check the flash point of products conform to ASTM D 93.

3.2.5 Automatic Pour Point Apparatus

The ISL, CPP 92 automatic pour point apparatus was used to determine the pour point of products conform by ASTM D 92.

3.2.6 Automatic Viscosity

The Cannon automatic viscosity was used to check the kinematic viscosity of products at the 40, 50 and 100 °C.

3.2.7 Colorimeter

The ASTM D 1500 method was used to check color of dyed fuel oil.

3.2.8 Total Acidity Number Apparatus

To determine the total acidity of CNSL and the other product, the ASTM D 974 was used.

3.2.9 Nuclear Magnetic Resonance Spectrometer

The FT-NMR spectrometer model DPX-300 from Bruker Switzerland, was used to characterize the products at 75 Hz. for ^{13}C -NMR and 300 Hz. for ^1H -NMR.



3.3 Experimental

3.3.1 Syntheses

3.3.1.1 Esterification of CNSL [18]

The esterification of CNSL was done by the following procedure. A portion of 51.00 g. (0.15 mol) of CNSL and 46.0 g. (0.45 mol) of n-Hexanol were placed into the 500 ml two-neck round bottom flask. Then, 150 ml of toluene was added and 4 ml (0.04 mol) of concentrated sulfuric acid was added into the flask and fitted this flask with condenser and then heated the mixture under reflux for 10 hrs. The reaction was cooled to room temperature. The product was washed 3-4 times with 20 ml. distilled water in a separation funnel. The two phases were allowed to separate and the aqueous layer was discarded. The upper phase was returned into the round bottom flask and the solvent and unreacted alcohol was evaporated until temperature reached 162 °C and then cooled down.

The properties of CNSL and Esterified-CNSL were investigated by spectroscopic methods (e.g. FT-IR, UV / VIS, ¹³C - NMR) and the ASTM Testing methods as described in Table 1.

Table 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

3.3.1.2 Diazotization of chloroaniline salts**3.3.1.2.1 Diazotization of 2-chloroaniline salt**

A portion of 1.02 ml (0.01 mol) of 2-chloroaniline was added into of 0.42 ml (0.0075 mol) of 50% sulfuric acid in distilled water. Then, the mixture was stirred vigorously while cooled down to 0-5 °C. A portion of 0.72 g (0.01 mol) of sodium nitrite was dropwise added into chloroaniline sulfuric solution under the diazotization temperature condition. The undissolved material was filtered off with filter paper under the same condition. The pale-yellow solution of 2-chloroaniline diazonium salt was kept under the same temperature condition.

3.3.1.2.2 Diazotization of 3-chloroaniline salt

The procedure in 3.3.1.2.1 was repeated except that 1.02 ml (0.01 mol) of 3-chloroaniline was used. The clear pale-yellow-green solution of 3-chloroaniline diazonium salt was obtained.

3.3.1.2.3 Diazotization of 4-chloroaniline salt

The procedure in 3.3.1.2.1 was repeated except that 1.24 g. (0.01 mol) of 4-chloroaniline was used. The clear pale-yellow solution of 4-chloroaniline diazonium salt was obtained.

3.3.1.2.4 Diazotization of 2,3-dichloroaniline salt.

The procedure in 3.3.1.2.1 was repeated except that 1.02 ml. (0.01 mol) of 2,3-dichloroaniline was used. The clear pale-yellow solution of 2,3-dichloroaniline diazonium salt was obtained.

3.3.1.2.5 Diazotization of 2,5 -dichloroaniline salt.

The procedure in 3.3.1.2.1 was repeated except that 1.6 g. (0.01 mol) of 2,5-dichloroaniline was used. The clear pale-yellow solution of 2,5-dichloroaniline diazonium salt was obtained.

3.3.1.2.6 Diazotization of 3,4-dichloroaniline salt

The procedure in 3.3.1.2.1 was repeated except that 1.6 g. (0.01 mol) of 3,4-dichloroaniline was used. The clear pale-yellow solution of 3,4-dichloroaniline diazonium salt was obtained.

3.3.1.3 Coupling of chloroaniline diazonium salt and alkyl phenolate ion

The alkyl phenolate ion used in the coupling reaction was prepared by the following procedure. Place 0.84 g (0.01 mol) of potassium hydroxide in 3.0 ml methanol with swirling at 0-5 °C. A few drops of distilled water was added to help dissolution. Then, 4.24 g (0.01 mol) of esterified CNSL (Section 3.3.1.1) was added into the solution and a red-brown oil was obtained.

3.3.1.3.1 2-chloroaniline diazonium salt

The pale-yellow solution of 2-chloroaniline diazonium salt (Section 3.3.1.2.1) was added into alkyl phenolate ion solution obtained according to 3.3.1.3 under cold temperature (0-5 °C) and the two phase were allowed to separate. The product was washed 2-3 times with 10 ml distilled water. The upper oil phase gave a deep yellow-brown of 2-chloroaniline diazonium salt with esterified-CNSL azo dye.

3.3.1.3.2 3-chloroaniline diazonium salt

The procedure in 3.3.1.3.1 was repeated except that 3-chloroaniline diazonium salt (Section 3.3.1.2.2) was used.

3.3.1.3.3 4-chloroaniline diazonium salt

The procedure in 3.3.1.3.1 was repeated except that 4-chloroaniline diazonium salt (Section 3.3.1.2.3) was used.

3.3.1.3.4 2,3-dichloroaniline diazonium salt

The procedure in 3.3.1.3.1 was repeated except that 2,3-dichloroaniline diazonium salt (Section 3.3.1.2.4) was used.

3.3.1.3.5 2,5-dichloroaniline diazonium salt

The procedure in 3.3.1.3.1 was repeated except that 2,5-chloroaniline diazonium salt (Section 3.3.1.2.5) was used.

3.3.1.3.6 3,4 –dichloroaniline diazonium salt.

The procedure in 3.3.1.3.1 was repeated except that 3,4-dichloroaniline diazonium salt (Section 3.3.1.2.6) was used.

3.3.1.4 Coupling of chloroaniline diazonium salt and methyl salicylate.

3.3.1.4.1 2-chloroaniline diazonium salt

The pale-yellow solution of 2-chloroaniline diazonium salt was added into methyl salicylate solution prepared according to 3.3.1.3 at the temperature between 0-5⁰C and allow the two phases to separate. The product was washed 2-3 times with 10 ml distillation water. The upper oil phase gave a red-color of 2-chloroaniline methyl salicylate azo dye.

3.3.1.4.2 3-chloroaniline diazonium salt

The procedure in 3.3.1.4.1 was repeated except that 3-chloroaniline diazonium salt was used.

3.3.1.4.3 4-chloroaniline diazonium salt

The procedure in 3.3.1.4.1 was repeated except that 4-chloroaniline diazonium salt was used.

3.3.1.4.4 2,3-dichloroaniline diazonium salt

The procedure in 3.3.1.4.1 was repeated except that 2,3-dichloroaniline diazonium salt was used.

3.3.1.4.5 2,5-dichloroaniline diazonium salt

The procedure in 3.3.1.4.1 was repeated except that 2,5-dichloroaniline diazonium salt was used.

3.3.1.4.6 3,4-dichloroaniline diazonium salt

The procedure in 3.3.1.4.1 was repeated except that 3,4-dichloroaniline diazonium salt was used.

3.3.2 Treatment of marker dyes in Fuel oil

The marker dyes synthesized in section 3.3.1.3.1 to 3.3.1.3.6 were characterized by spectroscopic techniques and they were tested for physical properties according to the ASTM testing methods described in Table 2

Table 2 : The ASTM Testing methods for physical properties of marker dyes

Test items	ASTM
Density @ 15 °C , g/cm ³	D 1298
Specific Gravity @ 15.6/15.6 °C	D 1298
Kinematic Viscosity @ 50 °C, cSt	D 445

The marker dyes synthesized from coupling processes were prepared as stock solution before adding into fuel oils by the following procedure. A portion of 5.0-6.0 g. of each marker dye (Section 3.3.5) was added into 25 ml. volumetric flask and diluted to make volume with toluene. The content was mixed well and it represented 20-24% stock solution of each marker dyes.

The undyed diesel fuel oil was placed into 100 ml volumetric flask and then 3 µl of stock marker dye solution was added and shaken. It gave 30 ppm of marker dye in fuel oil. For undyed gasoline the same procedure for undyed diesel fuel oil was used.

3.3.3 Extraction solution system

The extraction solution systems were prepared from various suitable bases. For example, The KOH was dissolved with various concentration in ethylene glycol, NH₄OH, acetone, methanol and water. Then, the absorbance of lower phase containing marker dye was measured to find out the suitable extraction system.

3.3.4 Determination of marker dyes in added fuel oil

3.3.4.1. Standard Calibration Curve for diesel fuel oil

The new standard calibration curve was prepared from 20 to 60 ppm of marker dye by following procedure. The undyed diesel fuel oil was placed into 100 ml volumetric flask and 2 μ L, 4 μ L, 6 μ L of marker dye was added to it, respectively. The volume was made to level with undyed diesel fuel oil and was shook well. A 15 ml of the mixture was transferred to 25 ml glass vial and then 5 ml of 10% KOH in methanol (Extraction Solution) was added. The vial was capped with capper and shook. The two phases were allowed to separate for 3 minutes. The lower phase was pipetted into 1 cm UV cuvette and the absorbance was measured at the maximum absorption wavelength. The calibration curve was then obtained.

3.3.4.2 Determination marker dyes in dyed diesel fuel oil

A 15 ml of dyed diesel fuel oil was pipetted into 25 ml glass vial and then 5 ml of extraction solution (10% KOH in methanol) was added. The vial was capped and shaken. The two phases were allowed to separate. The lower phase was pipetted into 1 cm UV cuvette and the absorbance was measured. The concentration of dye was obtained from calibration curve.

3.3.4.3. Standard Calibration Curve for gasoline

The procedure in 3.3.4.1 were repeated except dyed gasoline was used with the same as a concentration and solution ratio.

3.3.4.4. Determination marker dyes in dyed gasoline

The procedure in 3.3.4.2 were repeated except dyed gasoline was used.

3.3.5 Physical properties of dyed and undyed fuel oil

3.3.5.1 Physical properties of dyed and undyed diesel fuel oil

The physical properties were studied by the ASTM method as described in

Table 3

Table 3 : The ASTM Testing method of dyed and undyed diesel fuel oil

Test item	ASTM
API Gravity @ 60 °F	D 1298
Specific Gravity @ 15.6/15.6 °C	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
Total Acid Number, mg KOH/g	D 974

3.3.5.2 Physical properties of dyed and undye gasoline

The physical properties were studied by the ASTM method as described in

Table 4

Table 4 : The ASTM Testing methods of dyed and undye gasoline

Test item	ASTM
API Gravity @ 60 °F	D 1298
Specific Gravity @ 15.6/15.6 °C	D 1298
Octane Number	
- Research Method (RON)	D 2699
Reid Vapor Pressure @ 37.8 °C, kpa	
- Oxygenated Blends	D 5191
Copper Strip Corrosion, Number	D 130
(3 hrs, 50 °C)	
Distillation : (Correct Temp)	D 86
Total Acid Number, mg KOH/g	D 974

3.4 Stability of marker dyes in fuel oil

The stability of marker dyes in fuel oil were studied by monitoring the amount of marker dyes which extracted from marked fuel oil after storage in a dark area and determined by UV/Vis-spectroscopic technique.