

CHAPTER III

EXPERIMENTAL

3.1 Chemicals

3.1.1. Isoamyl alcohol (C₅H₁₁OH)

Isoamyl alcohol was obtained from distilled alcoholic refinery by-product.

2.1.2 n- Butyl alcohol (C₄H₉OH)

analytical grade; J.T. Baker Inc.

3.1.3 2-Ethyl-hexyl alcohol (C₈H₁₇OH)

analytical grade; J.T. Baker Inc.

3.1.4 n-Octyl alcohol (C₈H₁₇OH)

analytical grade; J.T. Baker Inc.

3.1.5 Phosphorus pentasulfide (P₂S₅)

reagent grade; Merck

3.1.6 Zinc oxide (ZnO)

analytical grade; Merck

3.1.7 Cupric oxide (CuO)

analytical grade; J.T. Baker Inc.

3.1.8 Calcium oxide (CaO)

analytical grade; J.T. Baker Inc.

3.1.9 Magnesium oxide

analytical grade; J.T. Baker Inc.

3.1.10 Molybdenum trioxide (MoO₃)

analytical grade; J.T. Baker Inc.

3.1.11 Toluene

analytical grade; J.T. Baker

3.2 Instruments and apparatus

3.2.1 Apparatus for synthesis of DPDA and MeDDP

- Four necked round bottom glass reactor with thermometer, gas inlet, gas scrubber and dropping funnel was used to synthesize DPDA.
- A Dean-Stark trap was used to synthesize MeDDP.

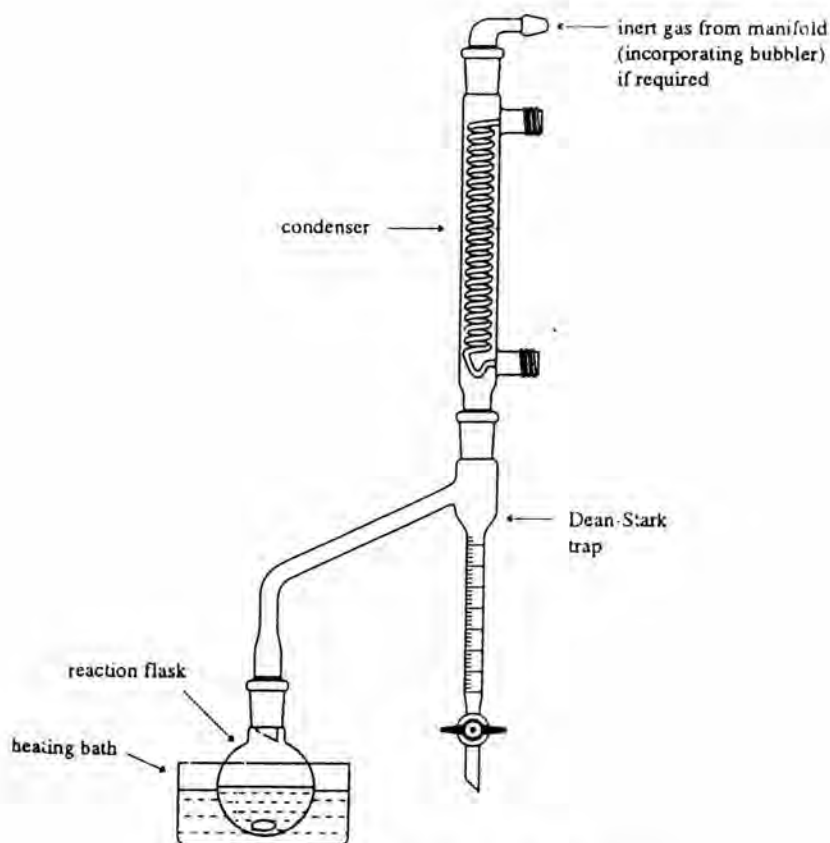


Figure 3.1 A Dean-Stark trap

3.2.2 *Fourier Transform Infrared Spectrophotometer* (*FT-IR Spectrometer*)

The FT-IR model 1760x from Perkin Elmer was used.

3.2.3 *Nuclear Magnetic Resonance Spectrometer* (*NMR Spectrometer*)

The NMR model AC-F 200 from Bruker at 50 MHz for ^{13}C spectra was used.

3.2.4 X-ray Fluorescence

The x-ray fluorescence model ED-2000 from Oxford was used.

3.2.5 CHNS/O analyzer (EA)

The elemental analyzer model PE2400 Series 2 from Perkin was used.

3.2.6 Thermal gravimetric analyzer (TGA)

TGA model STA 409 from Netzsch was used.

3.3 Procedure

Preparation of metal dithiophosphate

Metal dithiophosphate was prepared by a 2-step method. First, phosphorus pentasulphide was reacted with alcohol to form dithiophosphoric acid. Next, metal dithiophosphate was prepared from the dithiophosphoric acid synthesised in step 1.

Step 1 Preparation of dithiophosphoric acid

Into a 1 liter, 4-necked flask equipped with a magnetic bar, condenser, dropping funnel, gas inlet and thermometer was added a slurry of phosphorus pentasulfide (P_2S_5) in toluene, It was purged with nitrogen gas and the contents were heated to 60 °C. The alcohol (0.4 mol) was added dropwise over 1 hour

with agitation. After all of alcohol was introduced, the temperature was raised to reaction temperature and held for 1-4 hours. Hydrogen sulfide gas was trapped by a caustic scrubber. The reaction was then allowed to cool to ambient temperature under nitrogen and the solution was filtered to remove the unreacted P_2S_5 , then the filtrate was evaporated under reduced pressure. The dithiophosphoric acid was neutralized with metal oxide according to the procedure of step 2.

In this step, mole ratio of alcohol and P_2S_5 , reaction temperature and reaction time were varied to given highest % yield(The operating condition are shown in Table 3.1).

Table 3.1 The various conditions for preparation of DPDA

Parameter studied	i-amyl alcohol: P_2S_5 ratio	Reaction temperature ($^{\circ}C$)	Reaction time (hours)
1	4 : 1.1	110	4
2	4 : 1.2	110	4
3	4 : 1.3	110	4
4	4 : 1.4	110	4
5	4 : 1.2	60	4
6	4 : 1.2	80	4
7	4 : 1.2	100	4
8	4 : 1.2	110	4
9	4 : 1.2	80	1
10	4 : 1.2	80	2
11	4 : 1.2	80	3
12	4 : 1.2	80	4

Step 2 Preparation of metal dithiophosphate

In a round bottom flask having a Dean-Stark trap with a condenser and magnetic stirrer, was placed the dithiophosphoric acid (DPDA) prepared in step 1 (0.2 mol.), toluene and metal oxide. The temperature rose from ambient temperature to 50 °C and after 30 minutes under agitation, the temperature was raised to 110 °C. The water produced by the reaction was removed, by azeotropic distillation. The mixture was maintained at reflux temperature until the water volume from the reaction was constant then the reaction was allowed to cool.

The solution was filtered and then evaporated under reduced pressure to a constant weight. In this step, metal oxides were zinc oxide, cupric oxide, calcium oxide, magnesium oxide, molybdenum trioxide and tin(II) oxide.

3.4 Characterization

The products was characterized by various techniques as shown below:

3.4.1 Determination of the functional group

Metal dithiophosphate was prepared in a form of KBr pellet for CuDDP from isoamyl alcohol and prepared by casting on KBr cell for other MDDP. The functional group of the sample was determined by FT-IR.

3.4.2 Product characterization

3.4.2.1 Deuterated chloroform (CDCl₃) was used to dissolve metal dithiophosphate. The structure of the sample was analysed by ¹³C-NMR.

3.4.2.2 Elemental analyzer was used to measure the amount of C/H/O/S in samples.

3.4.2.3 X-ray fluorescence was used to measured the amount of metal , phosphorus and sulfur in sample.

3.4.2.4 Total acid number (TAN) of products was determined by ASTM D974

Into a 250 ml Erlenmeyer flask, a weighed quantity of the sample (DPDA : 0.2 g and MDDP : 2.0 g) was placed. 100 ml of the titration solvent and 0.5 ml of indicator solution was added, and without stoppering, the sample was swirled until entirely dissolved by the solvent. It was titrated immediately at a temperature below 30 °C. Then 0.1 M KOH solution was added ,consider the end point definite if the color change . A blank titration on 100 ml of titration solvent and 0.5 ml of indicator solution, then 0.1 m KOH solution was added and recorded the quantity of KOH solution required to reach the end point.

3.4.3 Determination of thermal stability of metal dithiophosphates

The thermal stability was measured by differential thermogravimetric analysis. Temperature ranges began from room temperature to 800°C with an oxygen flow rate of 20 ml/min and the sample weight was 46 mg. The sample of products was measured the oxidation point contrast to the sample of commercial ZDDP.