CHAPTER IV

RESULTS AND DISSCUSION

Synthesis of metal dithiophosphates in this study was detailed in 3 step. First, the optimum condition for the synthesis of dialkylphosphorodithioic acid (DPDA) was studied, and then various types of metal oxide were used to prepare metal dithiophosphates. Second, the products were characterized by FT-IR, NMR, EA and XRF. Finally, the products from synthesis were mixed with lubricating base oil for testing oxidation property by TGA technique.

4.1 DPDA Synthesis

DPDA was synthesized by reacting isoamyl alcohol with P_2S_5 under various conditions to find the optimum conditions. Other alcohols were also used at the optimum conditions. The reaction is shown in Figure 4.1

$$4\ ROH + P_2S_5 \xrightarrow{60 - 110\ ^{\circ}C} \underset{\text{DPDA}}{2\ (RO)_2PSSH} + H_2S$$

Figure 4.1 The synthesis of DPDA

4.1.1 The effect of molar ratio of isoamyl alcohol and P_2S_5

Isoamyl alcohol and P_2S_5 were reacted with different molar ratio to obtain DPDA. The results are shown in Table 4.1 and in Figure 4.2.

Table 4.1 Yield of DPDA (percent) with various molar ratios of isoamyl alcohol and P_2S_5

DPDA	**Molar ratio of isoamyl alcohol : P_2S_5**			
	4:1.1	**4:1.2**	**4:1.3**	**4:1.4**
Weight(g)	45.89	49.81	49.89	48.96
% Yield	85	92	92	91

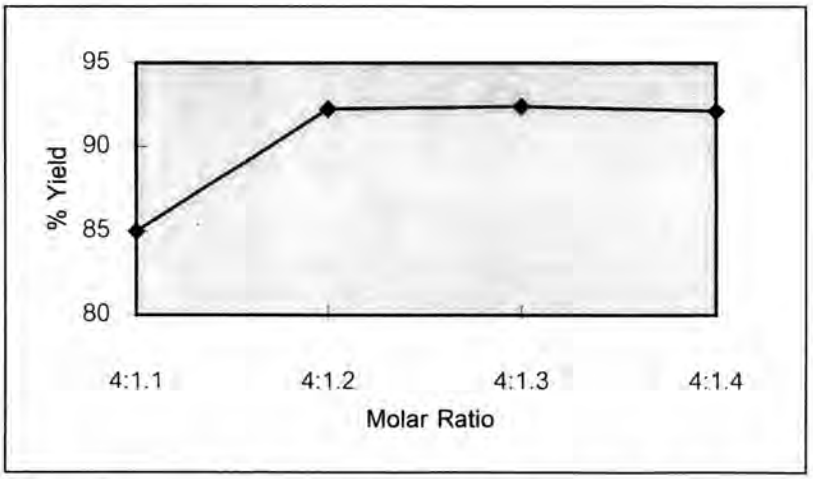


Figure 4.2 Percent yield of DPDA VS molar ratio of alcohol : P_2S_5

From the Figure 4.2, it was found that percentage yield was increased when the molar ratio was changed increasingly. But when the molar ratio was more than 4:1.2, percentage yield was steadied.

From the above data, it could be concluded that the molar ratio at 4:1.2 was the optimum proportion for the preparation of DPDA. Because P_2S_5 could form H_2S gas before reacted with alcohol. Therefore, a small excess of P2S5 must be used in the reaction **[18,19]**.

4.1.2 The effect of temperature

Isoamyl alcohol and P_2S_5 were reacted with different temperature to obtain DPDA. The results are shown in Table 4.2 and Figure 4.3

Table 4.2 Yield of DPDA (percent) in reaction in various temperature

DPDA	Temperature (°C)			
	60	**80**	**100**	**110**
Weight (g)	21.84	25.36	25.12	25.41
% Yield	81	94	93	94

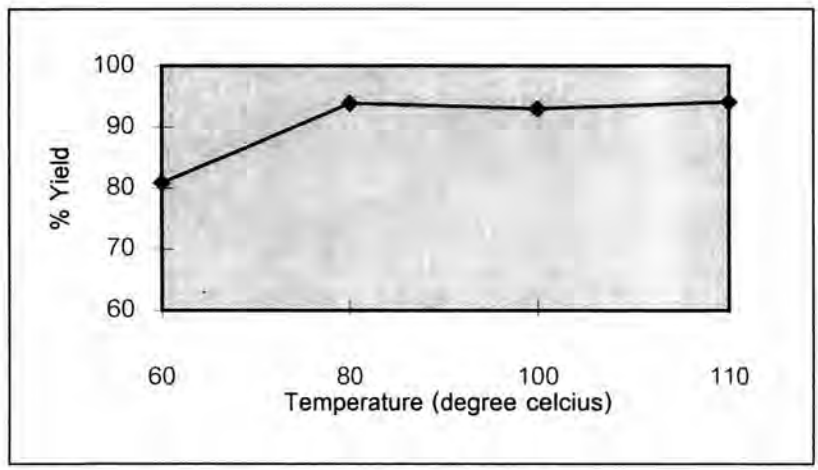


Figure 4.3 Percent yield of DPDA VS temperature

The graph indicated that at 60 °C, the reaction could occur but it gave a little yield of DPDA. At 80 °C, the higher yield of DPDA was occurred , and the yield was not increased at higher temperature. So, the optimum temperature for synthesis of DPDA was 80 °C.

4.1.3 The effect of reaction time.

The effect of the reaction time was shown in Table 4.3 and Figure 4.4.

Table 4.3 Yield of DPDA (percent) in reaction with various reaction times.

DPDA	Reaction Time (hours)			
	1	2	3	4
Weight (g)	15.08	20.81	25.63	25.58
% Yield	56	77	95	95

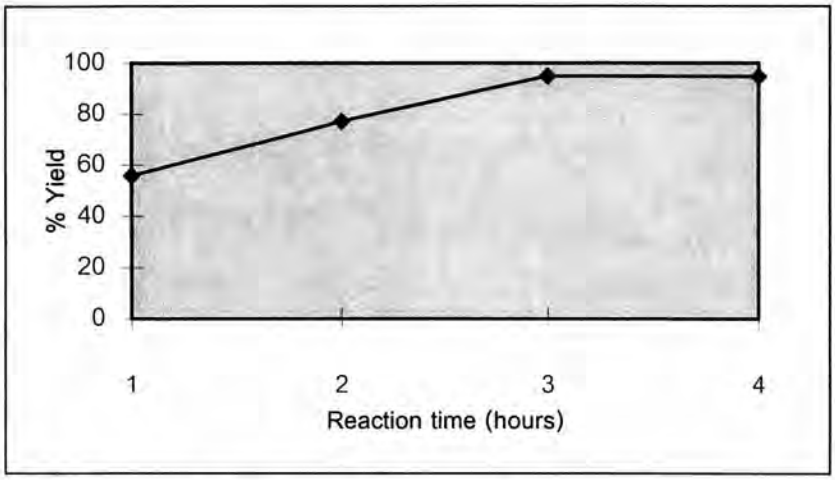


Figure 4.4 Percent yield DPDA VS temperature

From the Figure 4.4, the graph indicated that the percentage yield of DPDA was increased up to the reaction time until 3 hours the percentage yield of DPDA was steadied. Thus, the optimum reaction time was 3 hours.

For the synthesis of DPDA by reaction of alcohol with P_2S_5, the optimum conditions are as follow:

molar ratio isoamyl alcohol:P_2S_5 = 4:1.2

temperature = 80 °C

reaction time = 3 hours

For this condition the yield of DPDA was found to be 95%.

4.2 Synthesis of metal dithiophosphates (MDDP)

MDDP were synthesized by neutralizing DPDA with metal oxide, the reaction as shown in Figure 4.5

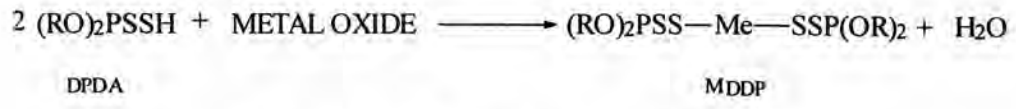


Figure 4.5 The synthesis of MDDP

4.2.1 Selection of metal oxide for metal dithiophosphates synthesis

In this study, zinc oxide(ZnO), cupric oxide(CuO), calcium oxide(CaO), magnesium oxide(MgO), molybdenum trioxide(MoO_3) and tin(II) oxide(SnO_2) were selected to react with DPDA. The results are shown in Table 4.4.

Table 4.4 Conversion of MDDP(percent) with various metal oxides

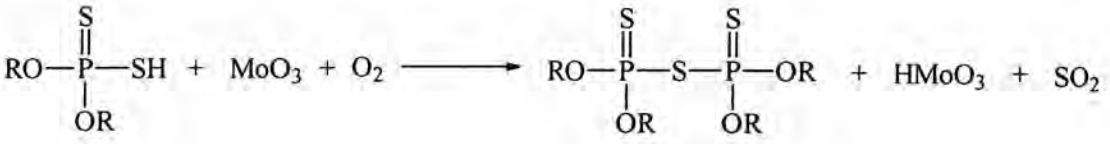
Water from reaction	**Metal oxides**					
	ZnO	**CuO**	**CaO**	**MgO**	**MoO_3**	**SnO_2**
Volume (ml)	1.7	1.6	0.6	0.8	ND	ND
% Conversion	94	83	33	44	-	-

ND = No detected volume

The above data showed that ZnO, CuO, CaO and MgO were reacted with DPDA, but MoO_3 and SnO_2 were not reacted.

The synthesis of CaDDP and MgDDP gave the poor %conversion that might due to the stability of product which produced from the hard base of CaO and MgO. In the acid-basic theory **[22,23]** indicated that DPDA was a borderline acid, it will be reacted with borderline basic, ZnO or CuO, better than the weaker base MoO_3, SnO_2 respectively.

The synthesis of MoDDP and SnDDP from this method were not accomplished because water was not found in Dean-Stark trap and acid gas from the reaction, tested by pH paper, was evolved. Because MoO_3 and SnO_2 had high oxidation state, it could be postulated that MoO_3 and SnO_2 might act as oxidizing agents, which reacted with DPDA to produce SO_2 **[23]**. The proposed reaction is shown below:



From the above data, the appropriate metal oxides for synthesizing MDDP by this method were zinc oxide and copper (II) oxide.

4.2.2 The effect of molar ratio of metal oxide and DPDA

Selected metal oxide from 4.2.1were used to synthesized MDDP. The molar ratio of metal oxide and DPDA were varied from 0.6:1, 0.8:1, 1:1, and 1.2 :1. The results are shown in Table 4.5 and Figure 4.6.

Table 4.5 Conversion of MDDP (percent) with various molar ratio of metal oxide and DPDA

Water from reaction	**Molar ratio of metal oxide and DPDA**			
	0.6:1	**0.8:1**	**1:1**	**1.2:1**
ZDDP				
Volume (ml)	1.3	1.5	1.7	1.7
% Conversion	72	83	94	94
CuDDP				
Volume (ml)	1.5	1.6	1.6	1.6
% Conversion	83	89	89	89

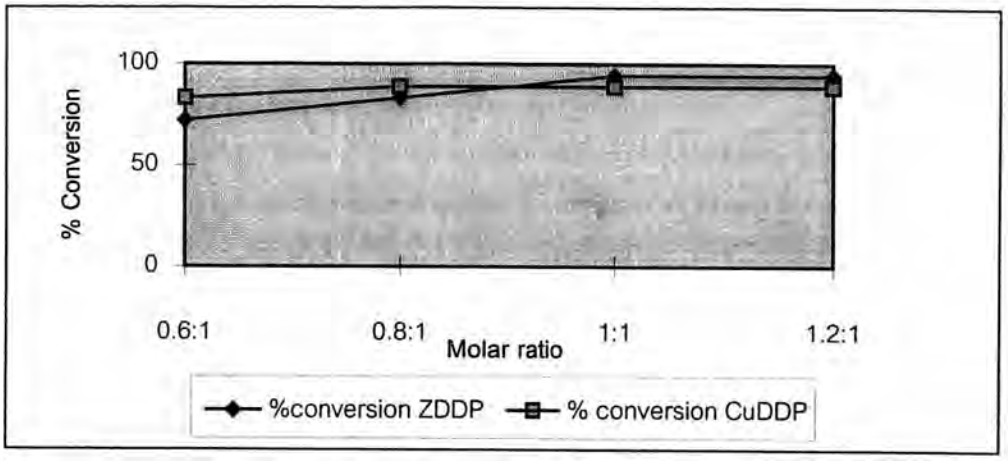


Figure 4.6 Percent conversion VS molar ratio of metal oxide and DPDA

The graph indicated that the optimum molar ratio of metal oxide and DPDA was 1:1 for ZDDP synthesis and 0.8:1 for CuDDP synthesis.

It was not necessary to vary reaction time because the progress of the reaction could be determined by the volume of water formed. At the above optimum condition, the conversion of DPDA to MDDP were found to be 94% for ZDDP and 89% for CuDDP.

4.3 Synthesis of MDDP with various alcohol.

In this study, the effect of various alcohols were also observed by using the optimum condition from 4.1 and 4.2

4.3.1 Synthesis of DPDA

The results are shown in Table 4.6

Table 4.6 Yield of DPDA (percent) with various alcohols

Alcohol	DPDA	
	Weight(g)	% Yield
n-Butanol	44.82	93
2-Ethyl hexanol	64.79	92
n-Octanol	63.37	90

The above results showed that the other alcohols could also be used to synthesize DPDA under the optimum condition of isoamyl alcohol. The results were indicated that when the longer hydrocarbon chain of alcohol was used, the lower percentage yield of products were observed. These results were similar to the results of Jacob and Armgrad. **[24-25]**.

4.3.2 Synthesis of MDDP

The results are shown in Table 4.7

Table 4.7 Conversion of MDDP (percent) with various alcohols

DPDA from alcohol	Water from reaction			
	ZDDP		CuDDP	
	Volume (ml)	%Conversion	Volume (ml)	%Conversion
n-Butanol	1.7	94	1.7	94
2-Ethyl hexanol	1.7	94	1.7	94
n-Octanol	1.6	89	1.6	89

The results showed that the percentage yields of ZDDP and CuDDP from other alcohol were not significantly difference with ZDDP and CuDDP from isoamyl alcohol. So, this condition could be used to prepare MDDP from other alcohol and metal oxide.

In contrast to previous research, Georges, Gunter, and Abbas were used acid catalyst in ZDDP synthesis**[11, 14, 18, 19]** but this study was not necessary used acid catalyst. Because, this method used Dean-Stark trap for driving the equilibrium shifted to the product side.

4.4 Products Characterization

The products from different alcohol and metal oxide were had different characteristic as showed in Table 4.8

Table 4.8 Characteristic of MDDP

MDDP	Characteristic of MDDP
ZDDP	
- Isoamyl alcohol	Clear yellow viscous product
- Butanol	Clear yellow viscous product
- 2-Ethyl hexanol	Clear yellow viscous product
- Octanol	Clear yellow viscous product
CuDDP	
- Isoamyl alcohol	Green solid (m.p. 95°C)
- Butanol	Green brown semisolid
- 2-Ethyl hexanol	Green brown viscous product
- Octanol	Green brown viscous product

The products were characterized by FT-IR, NMR, EA and XRF.

4.4.1 Functional group of products

The FT-IR spectrum of MDDP synthesized under the optimum condition are shown in Appendices A1.

By comparison with the IR spectrum from Aldrich Library **[26]**, the spectrum showed the disappearance of O-H stretching band. The C-O stretching at 1,100 cm^{-1} was changed to C-O-P stretching at a lower position. P-S stretching at 650 cm^{-1} was also apparent and the S-H stretching in region of 2400 cm^{-1} disappeared.

Important IR bands of MDDP are shown in Table 4.9

Table 4.9 Characterization of various MDDP

MDDP from alcohol	**IR characterize (cm^{-1})**
ZDDP	
-Isoamyl alcohol	973(a), 666(b)
-n-Butanol	978(a),666(b)
-2-Ethyl hexanol	1009(a),666(b)
-n-Octanol	978(a),666(b)
CuDDP	
-Isoamyl alcohol	988(a),630(b)
-n-Butanol	980(a),640(b)
-2-Ethyl hexanol	1014(a),650(b)
-n-Octanol	1019(a)645(b)

(a) C-O-P stretching (b) P-S stretching

4.4.2 The structure of products

The products were also characterized by ^{13}C-NMR (Appendices A2). A chemical shift of the CH_2-O-P group appeared at higher position than the CH_2-OH group from Sadtler standard **[27]**, because phosphorus atom was withdraw electron more than hydrogen atom; hence, chemical shift of the CH_2-O-P group appeared at lower-field position compared to the CH_2-OH group.

4.4.3 Total acid number (TAN)

The results are shown in Table 4.10

Table 4.10 TAN in mg KOH/g of MDDP

Reactant alcohol	TAN(ASTM D974)		
	DPDA	ZDDP	CuDDP
-Isoamyl alcohol	201.6	3.2	2.6
-n-Butanol	223.7	3.6	3.4
-2-Ethyl hexanol	163.2	1.9	1.8
-n-Octanol	154.2	2.2	2.1

Total acid number was used to indicate the complete reaction. The products in this study had nearly the theoretical TAN which is 0 mg of KOH/g of MDDP. So, MDDP from this synthesis was nearly pure.

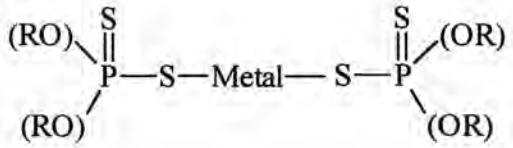
4.4.4 Composition of products

The composition of products were characterized by EA and XRF. The results are shown in Appendix A3.

In Appendix A3, it was shown that the composition of products had metal, phosphorus and sulfur. It indicated that the synthesis of MDDP was successful. In addition, the composition of the products were similar to the calculated. Thus, the product structure was similar to the estimated structure.

In case of the MoDDP and SnDDP synthesis, it was not found the metal composition from XRF. It can be concluded that the reaction of MoO_3 or SnO_2 with DPDA were not occurred.

From these results, NMR, FT-IR, EA and XRF, it can be summarized that the structure of products are as follows:



4.5 Performance evaluation of products

The synthetic MDDP was mixed with 150 SN mineral base oil to study antioxidant performance by TGA.

Thermogravimetric analysis

The antioxidant performance of synthesized products was determined by TGA . The results are shown in Table 4.10 , Figure 4.7 and Appendix A4.

Table 4.11 Effect of the percentage MDDP on Oxidation Temperature

%MDDP	Oxidation Temperature (°C)	
	ZDDP	CuDDP
0	601.3	601.3
0.5	606.0	638.4
1.0	622.7	672.7
1.5	620.7	685.4
2.0	637.2	693.7

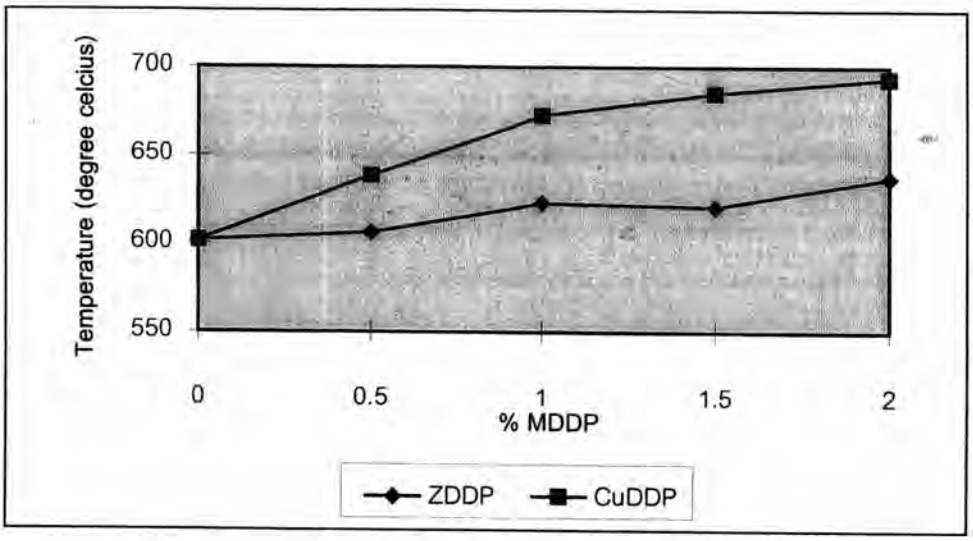


Figure 4.7 Antioxidant performance of MDDP

The results showed that ZDDP and CuDDP synthesized from isoamyl alcohol were good antioxidants. They increased the onset of the oxidation temperature by about 21-71 °C at 1 % concentration. The higher dosage (2% concentration) further increased the onset of the oxidation temperature by another 9-16 °C. Both of ZDDP and CuDDP showed the best performance at the 1% concentration. In the same concentration CuDDP showed a better antioxidant performance than ZDDP.

By comparison with commercial ZDDP, small amount of CuDDP showed the same anti-oxidation performance as commercial ZDDP package. 1% Concentration of CuDDP increased the oxidation temperature about 72 °C, whereas, commercial ZDDP was used 7.7% (Appendix A4-10).

Thus it may be concluded that CuDDP could be used to act as new antioxidant in lubricating oil.(The amount of MDDP for this study was 0.5-2 % by weight**[28]**.)