

## CHAPTER 4

### RESULT AND DISCUSSION

#### 4.1 Dewaxing of Light Distillate

This research was aimed to prepare chlorinated paraffins from light distillate and convert them to semi-synthetic lubricating oil. Light distillate which was obtained from Fang Oil Refinery was a solid at room temperature because it contained high quantities of long chain paraffin wax. Dewaxing was necessary to remove this dissolved wax. The selected method for separating wax was solvent dewaxing process. Methyl ethyl ketone was used as solvent because of its low wax solubility at dewaxing temperature and sufficiently low boiling point to facilitate removal from dewaxed oil.

From the experiment, methyl ethyl ketone could extract up to 56.42 % by weight of slack wax and 43.58 % by weight of oil. Slack wax was a white crystalline solid and the remaining oil fraction was a black viscous liquid.

The physical and chemical properties of dewaxed oil were shown in table 4.1. The physical properties were as follow: color, pour point, kinematic viscosity and viscosity index. The main structure was determined by  $^{13}\text{C}$ -NMR and GC-MS. The paraffinic carbon content (%Cp), naphthenic carbon content (%Cn) and aromatic carbon content (%Ca) were determined by



$^{13}\text{C}$ -NMR. The oxidation point and the percentages of oxidative compounds were analyzed by the thermogravimetric analyzer. The  $^{13}\text{C}$ -NMR spectrum, GC-MS chromatogram and thermogram were shown in figure A1, A2 and A3, respectively.

Table 4.1 The physical and chemical properties of dewaxed oil.

Properties	Dewaxed oil
<b>Physical:</b>	
Color, visual	>8
Pour point ( $^{\circ}\text{C}$ )	4
Kinematic viscosity	
@ 40 $^{\circ}\text{C}$ , cSt	31.88
@ 100 $^{\circ}\text{C}$ , cSt	4.91
Viscosity index	62
<b>Chemical:</b>	
%Cp	74.73
%Cn	25.20
%Ca	0.07
Sulfur content (%wt)	0.269
Oxidation point ( $^{\circ}\text{C}$ )	265
Oxidative compound (%wt)	11.58

The results from table 4.1 presented that pour point of dewaxed oil was reduced to 4  $^{\circ}\text{C}$ , because dissolved wax which caused high pour point was removed from dewaxing process..



The  $^{13}\text{C}$ -NMR spectrum in figure A1 showed that in dewaxed oil there were paraffinic, naphthenic and small amount of aromatic hydrocarbons. Characterization of dewaxed oil with GC-MS illustrated that main compositions contained in dewaxed oil were paraffins varying from  $\text{C}_{17}$  to  $\text{C}_{22}$  and the mass spectrum of nonadecane( $\text{C}_{19}$ ) was shown in figure A4. Although dewaxing process improved pour point of dewaxed oil, the oil color was still dark. The color of oil came from the containing color substances such as aromatic compounds, unsaturated compounds and sulfur compounds which were not removed by dewaxing process.

#### 4.2 Chlorination of paraffin oil and dewaxed oil

Commercial paraffin oil was used as a model to study the effect of temperature on properties of products. The temperature was varied at 60, 80, 100 and 120  $^{\circ}\text{C}$ , respectively. The viscosity and chlorine content were determined and shown in table 4.2 and figure 4.1. The structure was characterized by  $^{13}\text{C}$ -NMR.

Table 4.2 The effect of reaction temperature on properties of chlorinated products.

Temperature ( $^{\circ}\text{C}$ )	Flow rate of chlorine gas (lb/24hrs)	Time (hrs)	Chlorine content (%wt)	Viscosity (poise)
60	2.5	6	18.17	15.20
80	2.5	6	20.42	16.10
100	2.5	6	19.81	15.70
120	2.5	6	21.20	16.30



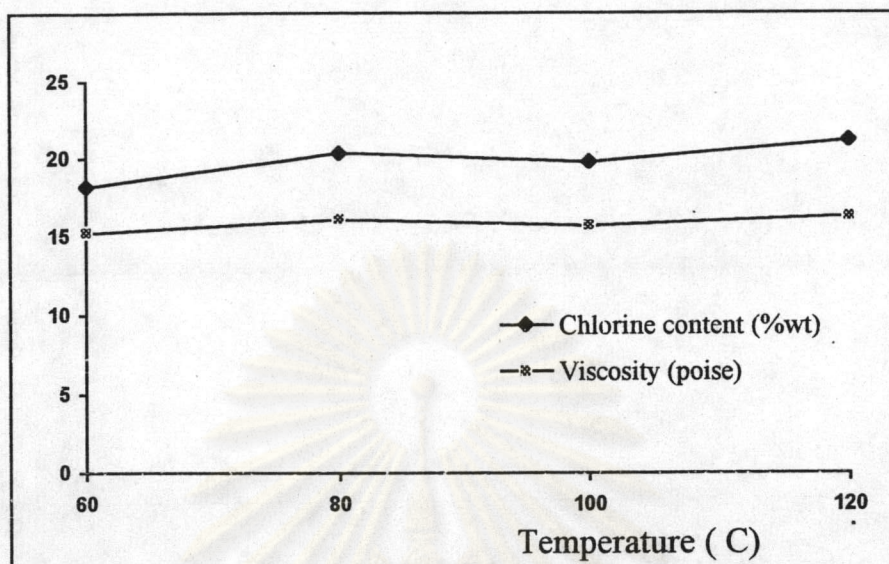


Figure 4.1 The effect of reaction temperature on properties of chlorinated products.

From table 4.2 and figure 4.1, it can be seen that reaction temperature had no significantly effect on chlorine content and viscosity of chlorinated products. The color of paraffin oil after chlorination was changed from colorless to dark brown. From the starting paraffin oil 250 g, chlorinated products about 335 g were obtained. Due to the same level of chlorine content of chlorinated products, their weight were not different at various temperatures. The  $^{13}\text{C}$ -NMR spectrum of paraffin oil before and after chlorination were illustrated in figure A5 and A6. There were group of C-Cl peaks at  $\delta$  58-70 ppm in the spectrum of paraffin oil after chlorination. Therefore, it indicated that paraffin oil was already chlorinated.



On the basis of these results, the temperature at 80 °C was used in all chlorination process of paraffin oil and dewaxed oil because it was easy and convenient to maintain the temperature during the reaction. Due to the limitation of chlorinator used in this study, flow rate of chlorine gas at 2.5 lb/hrs was the minimum which can be adjusted for chlorination process.

Paraffin oil and dewaxed oil were chlorinated at 80 °C. Flow rate of chlorine gas was constant at 2.5 lb/24hrs. The effect of reaction time on properties of products was studied by varying time from 3, 6, 9, 12 and 15 hrs, respectively. The results were presented in table 4.3-4.4 and figure 4.2-4.3.

Table 4.3 The effect of reaction time on properties of chlorinated products from paraffin oil.

Temperature (°C)	Flow rate of chlorine gas (lb/24hrs)	Time (hrs)	Chlorine content (%wt)	Viscosity (poise)
80	2.5	3	12.32	10.20
80	2.5	6	18.13	15.50
80	2.5	9	23.48	20.80
80	2.5	12	25.11	21.20
80	2.5	15	25.87	21.30



Table 4.4 The effect of reaction time on properties of chlorinated products from dewaxed oil.

Temperature (°C)	Flow rate of chlorine gas (lb/24hrs)	Time (hrs)	Chlorine content (%wt)	Viscosity (poise)
80	2.5	3	14.74	17.30
80	2.5	6	20.32	23.10
80	2.5	9	25.89	24.20
80	2.5	12	26.44	25.80
80	2.5	15	26.98	25.90

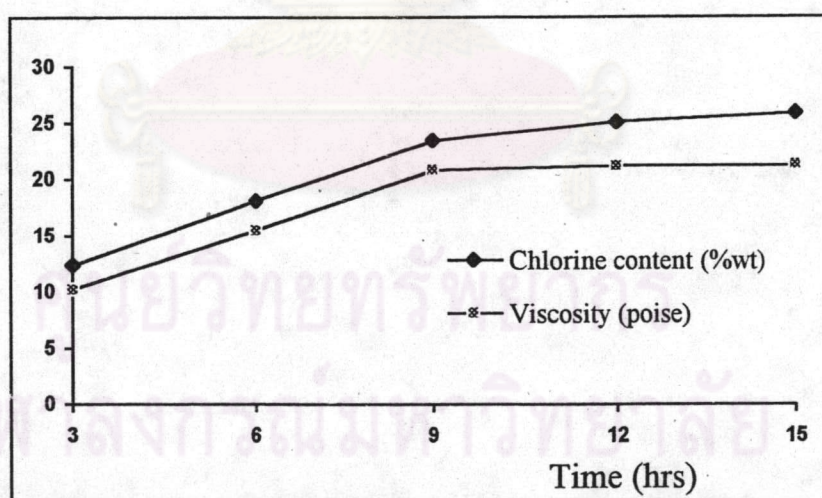


Figure 4.2 The effect of reaction time on properties of chlorinated products from paraffin oil.



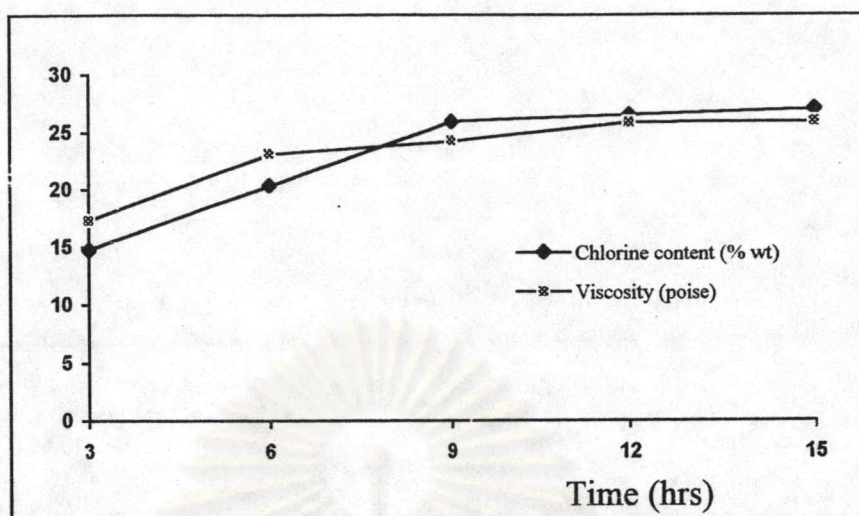


Figure 4.3 The effect of reaction time on properties of chlorinated products from dewaxed oil.

The observed data from table 4.3-4.4 and figure 4.2-4.3 indicated that the effect of reaction time on properties of chlorinated products from paraffin oil had direct effect to the chlorinated products from dewaxed oil. Chlorine content was increased when reaction time was longer, until the time was 12 hrs, chlorine content tend to stop increasing. It might be the level of maximum absorption of chlorine.

This finding supported the theory that viscosity of chlorinated paraffins increased with increasing the chlorine content. However, the color of both chlorinated paraffins from paraffin oil and dewaxed oil was undesirable. Chlorinated paraffins from dewaxed oil was darker and more viscous than chlorinated paraffins from paraffin oil. It was suspected that dewaxed oil might have more varieties of hydrocarbon than paraffin oil. In addition, dewaxed oil also had sulfur compounds resulting in dark color.



Because of the color of chlorinated paraffins from dewaxed oil, they could not be used as secondary plasticizer for PVC or other direct utilizations. Several attempts had been made to decolorize the chlorinated paraffins obtained from dewaxed oil, for example, bleaching with fullers earth, clay, activated charcoal and vacuum distillation, but none of these attempts gave satisfactory results. Thus, the further studies were tried to convert chlorinated paraffins to semi-synthetic lubricating oil.

### 4.3 Converting chlorinated paraffins to semi-synthetic lubricating oil

#### 4.3.1 Chlorinated paraffins obtained from TPC

There were two methods in this study that converted chlorinated paraffins to semi-synthetic lubricating oil. The first method was alkylation of chlorinated paraffins with toluene by using anhydrous aluminum chloride as catalyst. The amount of toluene were varied as mole ratio with chlorine content of chlorinated paraffins as follow: 1:1, 1:2 and excess toluene. The other was self-condensation of chlorinated paraffins in the presence of anhydrous aluminum chloride. The commercial available of chlorinated paraffins from TPC were first used as a model to find optimum conditions that gave desirable properties of lubricating oil.

After the alkylation and self-condensation reactions, the prepared oils were distilled under reduced pressure, 68% and 72% of prepared oil were obtained, respectively. The physical properties of the prepared oils from the two method were presented in table 4.5. Their structures were confirmed by  $^{13}\text{C}$ -NMR which were shown in figure A8-A9.



Table 4.5 The physical properties of the prepared oil from two methods.

Properties	Alkylation with toluene			Self-condensation
	1:1	1:2	excess	
Color, visual	3	3	3	2.5-3
Pour point (°C)	<-15	<-15	<-15	<-15
Kinematic viscosity				
@40 C, cSt	45.17	16.56	74.91	14.64
@100 C, cSt	4.65	2.89	5.84	3.21
Viscosity index	*	*	*	72

\* Viscosity index can not determine from table

The results from table 4.5 demonstrated that the color of all the prepared oils was in the same level and improved from dewaxed oil. Interestingly, all of them had excellent low pour points. However, the prepared oils from alkylation with toluene could not determine the viscosity index because their kinematic viscosities significantly changed when the temperature changed. It was hypothesized that they contained many aromatics and hydrogenation was required to improve their properties.

The prepared oil from self-condensation gave desirable properties, excellent low pour point and fairly well viscosity index. However, it still had some unsaturations, as shown in <sup>13</sup>C-NMR spectrum in figure A9.



Based on these results, the further studies were carried out to hydrogenate of all the prepared oils.

The prepared oils from alkylation with toluene were hydrogenated at vigorous condition because their structures were quite stable. They were hydrogenated for 6 hrs under hydrogen pressure 500 psi, 350 °C and 3% platinum on alumina was used as catalyst. The structure were characterized by  $^{13}\text{C}$ -NMR, The prepared oil from self-condensation was hydrogenated for 4 hrs under hydrogen pressure of 400 psi, 300 °C and 3%platinum on alumina was used as catalyst. Its structure was also confirmed by  $^{13}\text{C}$ -NMR. The percentage yield of both hydrogenated oils from alkylation and self-condensation was about 95%.

The  $^{13}\text{C}$ -NMR spectrum in figure A8 and A10 illustrated the structure of oils before and after hydrogenation, respectively. The results clearly indicated that hydrogenation didn't occur because the group of aromatic peaks still remained. The aromatics were difficult to hydrogenate because of their stable structure. Because of the limitation of the maximum operating capability of the apparatus in this study, no attempt was made to hydrogenate them.

From the theory as mentioned in chapter 2, if chlorine atom in the structure of chlorinated paraffins was replaced by toluene, the product should gave an excellent viscosity index. The results obtained clearly showed that the reaction couldn't occur in an expected way. It was believed that chlorinated paraffins from TPC wasn't suitable for this process because of its high content of chlorine. Therefore, and toluene could randomly replace more than one chlorine atom per chain of chlorinated paraffin.



The physical properties of oils from self-condensation after hydrogenation were shown in table 4.6. Its structure was characterized by  $^{13}\text{C}$ -NMR, as presented in figure A11.

Table 4.6 The physical properties of oils from self-condensation after hydrogenation.

Properties	
Color, visual	1-1.5
Pour point ( $^{\circ}\text{C}$ )	<-15
Kinematic viscosity	
@ 40 C, cSt	14.67
@ 100 C, cSt	3.21
Viscosity index	73

The data obtained from table 4.6 showed that hydrogenated oil's color was reduced to 1-1.5 while the pour point and viscosity index were basically the same. From figure A9, unsaturation peaks disappeared and it still remained C-Cl in structure. It may not necessary to eliminate all C-Cl bond because in commercial lubricating cutting oils, chlorinated paraffins are commonly used as additive. Therefore, the products from self-condensation may be suitable to use as cutting oils in metal industries. From this method, 65 % of lubricating oil were obtained.



On the basis of these results, it can be summarized that alkylation of chlorinated paraffins with toluene couldn't be achieved to give an expected products by using condition and equipments in this study and self-condensation method was suitable to convert chlorinated paraffins to lubricating oil. Thus, the further study would prepare semi-synthetic lubricating oil from dewaxed oil by this method.

#### 4.3.2 Chlorinated paraffins from dewaxed oil

Chlorinated paraffins from dewaxed oil contain ~26 % of chlorine were used to convert to semi-synthetic lubricating oil. They were refluxed with aluminum chloride 2.5 % by weight of dewaxed oil at 60 °C for 4 hrs and hexane are used as solvent. The products were worked up as usual.

The physical and chemical properties of finished oil obtained from dewaxed oil and dewaxed oil itself were shown in table 4.7. The oxidation point and the percentages of oxidative compound were analyzed by Thermogravimetric analyzer. Changing in its structure was characterized by  $^{13}\text{C}$ -NMR and GC-MS. The  $^{13}\text{C}$ -NMR spectrum, GC-MS chromatogram and thermogram were illustrated in figure A12, A13 and A14, respectively.



Table 4.7 The physical and chemical properties of dewaxed oil and finished oil.

Properties	Dewaxed oil	Finished oil
<b>Physical:</b>		
Color, visual	>8	2
Pour point (°C)	4	2
Kinematic viscosity		
@ 40 °C, cSt	31.88	14.45
@ 100 °C, cSt	4.91	3.21
Viscosity index	62	77
<b>Chemical:</b>		
%Cp	74.73	61.15
%Cn	25.20	38.80
%Ca	0.07	0.05
Sulfur content (%wt)	0.269	0.250
Oxidation point (°C)	265	282
Oxidative compound (%wt)	11.58	9.57

Table 4.7 compared the physical and chemical properties between dewaxed oil and finished oil. It showed that the properties of finished oil were improved from dewaxed oil. The viscosity index was enhanced from 62 to 77. The sulfur content and the amount of oxidative compound were not significantly changed. The finished oil obtained was 68 % of dewaxed oil.



Beside the condensation, other different reactions might take place during reaction. The lower hydrocarbons were formed from the cracking reaction. In addition, the original paraffinic hydrocarbon used for chlorination was reformed by the elimination of hydrogen chloride and simultaneous hydrogenation.

However, to compare with imported lubricating oils, the prepared oil was relatively low in viscosity index and the percentages of sulfur was relatively high. From this reasons, the prepared oil was still not good for automobiles, because of its low viscosity index. The oil may be usable as a lubricating base oil in industrial engines especially as turbine oil and hydraulic oil where the high viscosity index is not demanded. The production of any types of lubricating oils whether in engine service or in industrial service, the blending of several grades of base oils and additives is required in order to improve the overall properties. The choices of the additives are depending upon the application. From this study, in order to obtain the desirable properties of finished oil, purification of dewaxed oil such as desulfurization and vacuum distillation before chlorination was required and recommended for the further study.