CHAPTER IV

RESULTS AND DISCUSSION

This study utilized hydroisomerization of wax from heavy distillate to produce a high quality purified wax and a high viscosity index lubricating base oil. Heavy distillate obtained from Fang refinery is a solid at room temperature because it contains large quantities of associate wax or high paraffin hydrocarbon. Fang heavy distillate was characterized by GC/MS. The GC/MS chromatogram is shown in Figure A1 and the molecular weight distributions are reported in Table A1. This result demonstrates that Fang heavy distillate consists of C_{14}-C_{40} hydrocarbons with the main components being C_{24}-C_{32}. Its pour point was 51 °C. The properties of this distillate are shown in Table 4.1.

API gravity and molecular weight distributions of Fang heavy distillate show that this distillate is light vacuum gas oil (compare API 30.5 for Fang heavy distillate to API gravity of light vacuum gas oil of 30 in Table 2.5).

High quantities of waxes and contaminants in Fang heavy distillate lead to poor pour point (51 °C) and dark color (> 8), respectively. In order to improve wax properties, oils and contaminant compounds have to be separated by a solvent deoiling process. Methyl ethyl ketone (MEK), the widest used dewaxing solvent in the industry, was selected because of its low wax solubility at the deoiling temperature and its low boiling point which facilitates its removal from the deoiled wax. The deoiling process was performed at a filter temperature of 0 °C using a solvent to heavy distillate crude ratio of 3:1. The result of the deoiling process is shown in Figure 4.1.

Table 4.1 The properties of Fang heavy distillate.

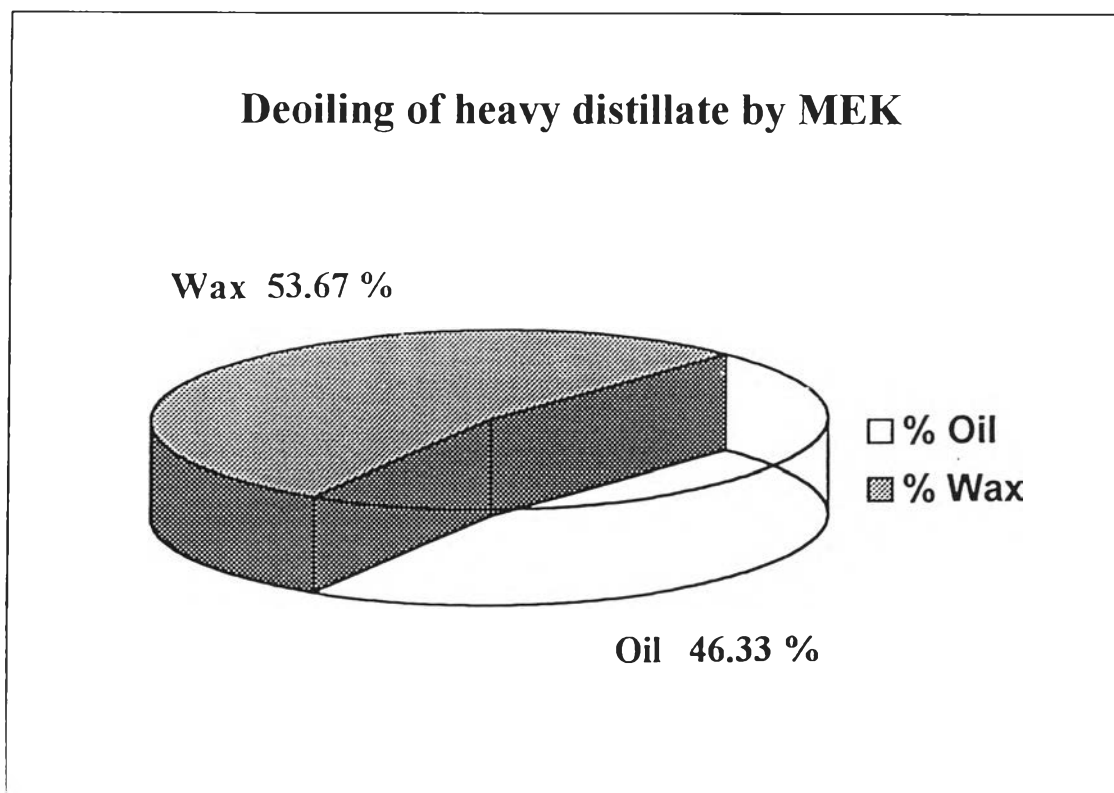| Properties	Test method	Determined Value
API gravity	ASTM D 1298	30.5
Color	ASTM D 1500	>8
Pour point, °C	ASTM D 97	51
Kinematic viscosity @ 40°C , cSt. @ 100°C , cSt.	ASTM D 445	- 6
Sulfur content, wt%	ASTM D229 (X-ray)	0.418
Carbon distribution	GC/MS	C_{14}-C_{40}

Figure 4.1 The percents by weight of wax and oil separated
by the deoiling process

Figure 4.1 showed that the deoiling process could extract up to 53.67 % by wt of slack wax and 46.33 % by wt of oil. Slack wax or deoiled wax from the deoiling process, after solvent removal, was a brown solid. The oil fraction was a black viscous liquid.

The physical and chemical properties of slack wax are differrent from those of heavy distillate, as shown in Table 4.2. The GC/MS chromatogram of slack wax is shown Figure A2 and the molecular weight distribution of slack wax is shown in Table A1. It indicates that the molecular weight distribution of n-alkanes is the same as that of heavy distillate crude but the composition of slack wax (C_{17}-C_{38}) has fewer than crude (C_{14}-C_{40}).

Table 4.2 The properties of slack wax from the deoiling process.

Properties	Fang HD	Slack wax
Color	> 8	5.5
Melting point, $^{\circ}$C by cooling curve	51.0	52.5
Congealing point, $^{\circ}$C	-	51.0
Sulfur content, %wt	-	0.14
Oil content, %wt	-	35.1
Molecular weight distribution	C_{14}-C_{40}	C_{17}-C_{38}

The oil content of the slack wax was 35.1 %wt. This wax can be classified as a petrolatum wax type. The melting point and congealing point were 52.5 °C, and 51.0 °C, respectively.

Although the sulfur content and the color of the slack wax from the dewaxing process as shown in Table 4.2 was decreased 0.418 to 0.14%wt and from above 8 to 5.5, respectively, both the sulfur content and the color were still unsuitable for usage. The color of the slack wax come from color substances or chromophores, such as aromatic compounds, unsaturated compounds, and sulfur compounds, which are not removed completely by the deoiling process. Further refining to improve the color and sulfur content of slack wax using a hydrotreating process, hydrodesulfurization, and hydroisomerization were studied.

In the first process, slack wax was hydrodesulfurized using various group VIIIB and GroupVIB metal combination. The most important objectivity of this stage was to remove the sulfur to give wax containing less than 10 ppm of since sulfur compounds from the petroleum source could adversely affect the lifetime and activity of the platinum hydroisomerization catalyst in the next step. The hydrodesulfurized wax was hydroisomerized in the second process to give high purity wax and/or high viscosity index lubricating base oil. The suitable catalyst for this process was low Pt content on alumina doped with fluoride.

In this research, the MoCoNi on alumina type CS331-3, having pore volume about 0.64 ml/g, hydrodesulfurization catalyst was prepared by impregnating method. First the alumina was soaked with ammonium thiosulfate solution then dried for improving crush strenght. This impregnation was achieved in a single wetting. Citric acid was added to the solution of molybdenum, cobalt, and nickel salts to stabilized it against precipitation. The impregnetion was carried out by wetting the ammonium thiosulfate treated alumina with a citric acid/metal salts solution followed by drying then

calcining. The catalyst prepared in this manner contained 10 %Mo, 5 %Co, and 5 %Ni and had a surface area of 141.05 m^2/g.

To select a suitable hydrodesulfurization catalyst, the conventional hydrotreating catalyst, MoCoNi metal sulfide on alumina prepared catalyst, and commercial catalysts identified as C20-7-06 ($MoNi/Al_2O_3$ metal oxide catalyst), T-2563(NiW/Al_2O_3 metal oxide catalyst) and Raney nickel, were employed to treat slack wax under fixed conditions of temperature 350 °C, hydrogen pressure 500 psig, reaction time 4 hours, catalyst concentration 5 % wt of slack wax and agitation speed 500 rpm in a stirred autoclave reactor.

The results of hydrodesulfurization using the various catalyst types are summarized in Table A2 and the molecular weight distributions are shown in Table A3. To establish the oily product from hydrodesulfurized waxes, the products were deoiled with a press device (procedure 3) to the obtain the oil fraction. The physical properties, sulfur content, and color, of this desulfurized waxes are plotted against catalyst types as illustrated in Figure 4.2 and 4.3, respectively. The oil contents were determined and results are summarized in Table A2 and Figure 4.4, respectively.

This experiment shows that these catalysts all improve the color and sulfur content properties. Comparing color after the different catalyst treatments, NiW/Al_2O_3 catalyst gives the best color. On the other hand, $MoNi/Al_2O_3$ catalyst was the worst catalyst for improving color.
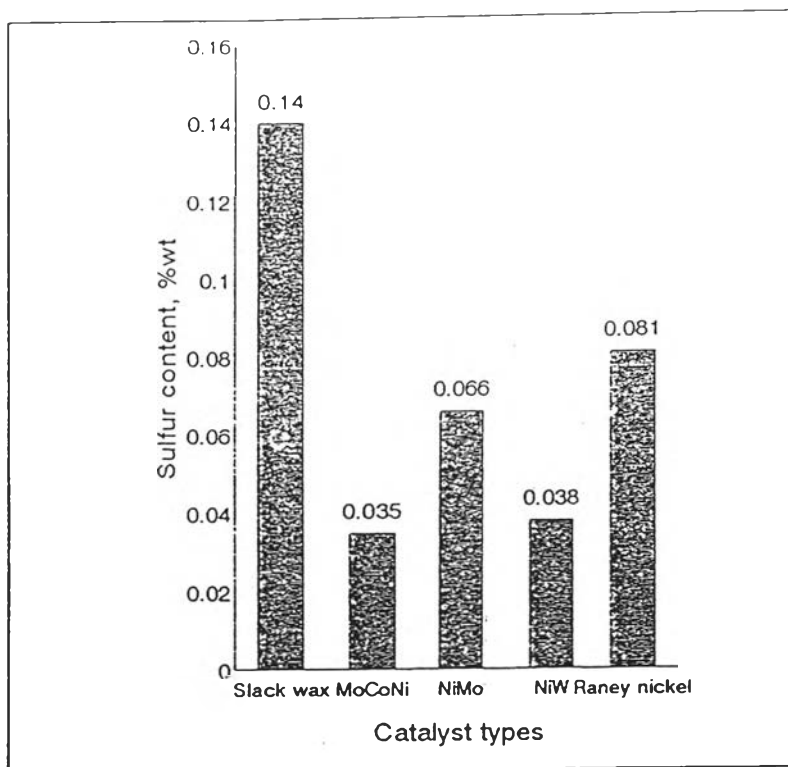
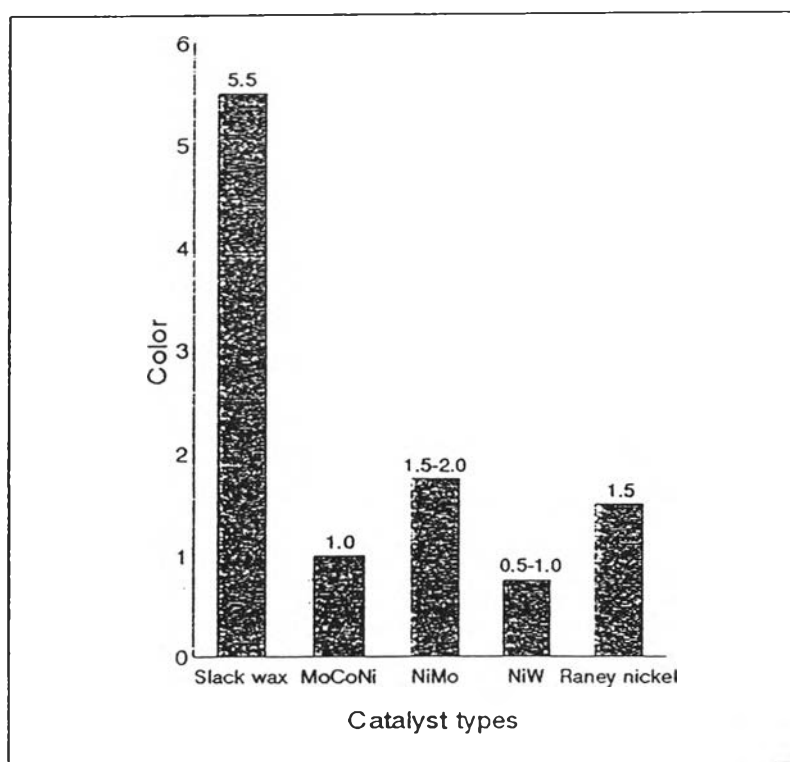**Figure 4.2** Effect of catalyst types on sulfur content of desulfurized wax

Figure 4.3 Effect of catalyst types on color of desulfurized wax

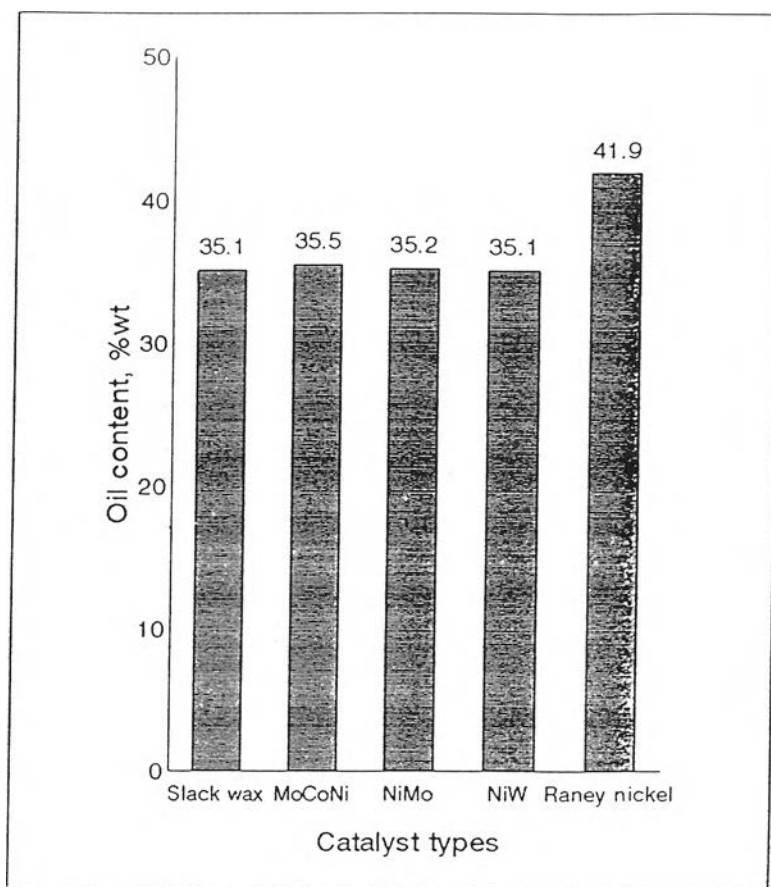**Figure 4.4** Effect of catalyst types on oil content of desulfurized wax

It is found from this experiment that the results from T-2563 (NiW/Al$_2$O$_3$) and prepared MoCoNi/Al$_2$O$_3$ catalyst are quite similar. Both decreased sulfur content about 75 % (from 0.14 %wt to 0.038 %wt and 0.035 % wt, respectively). Only 42 % of the sulfur was removed by Raney nickel catalyst and only 53 % by the NiMo catalyst.

GC/MS chromatograms in Figure A3 and the molecular weight distributions in Table A2 show that the composition are not significantly altered for C20-7-06 (MoNi/Al$_2$O$_3$), T-2563 (NiW/Al$_2$O$_3$), and prepared MoCoNi/Al$_2$O$_3$ catalyst, but Raney nickel induced some cracking of hydrocarbons to smaller molecules at these experiment conditions.

The results in Table A2 and A3 indicate that the prepared MoCoNi/Al$_2$O$_3$ catalyst had the best performance for the hydrodesulfurization

process as compared to T-2563, C20-7-06 and Raney nickel catalyst. It gives greatest improvement in color and sulfur content of slack wax and at the same time it has high crush strength (thereby resisting attrition due to crushing) in hydrodesulfurization process, making this catalyst recoverable and thus usable for a longer time. Other catalysts were not suitable because their crush strengths were too low. Even though Raney nickel is a simple economic catalyst, its performance in reducing sulfur content was actually not very good. This experiment also demostrated that Raney nickel is the better catalyst for hydrocracking because the low boiling point compounds were observed when Raney nickel was used.

After the catalyst had been chosen, the optimum condition using prepared $MoCoNi/Al_2O_3$ catalyst was determined by varying the operating parameters: reaction temperature, hydrogen pressure, reaction time and catalyst concentration. The first parameter varied was reaction temperature. The hydrodesulfurization reaction was carried out under hydrogen pressure of 500 psig, a reaction time of 4 hours, and a catalyst concentration of 5 % by wt of oil. The temperature was varied from 200 to 400 $^{\circ}$C in 50 $^{\circ}$C steps.

The results from hydrodesulfurization performed at various temperatures of 200, 250, 300, 350 and 400 $^{\circ}$C are shown in Table A4. The effect of temperature variation on sulfur content, color and oil content of treated wax are illustrated in Figure 4.5, 4.6, and 4.7, respectively.

The results from this experiment indicate that temperature affects color, sulfur content, and oil content. Color was improved with increasing reaction temperature. The best color was obtained at temperature 350 $^{\circ}$C and 400 $^{\circ}$C which was determined to be 0.5 by ASTM D 1500. But at low reaction temperatures, 200 and 250 $^{\circ}$C, the color of hydrodesulfurized slack wax was 2.5 and 2.0, respectively. While sulfur content in slack wax was decreased from 0.140 to 0.080, 0.060, 0.046, 0.035 and 0.017 %wt when performed at the various temperatures of 200, 250, 300, 350 and 400 $^{\circ}$C, respectively. GC/MS

chromatograms in Figure A4 and molecular weight distributions in Table A5 illustrate that the lower molecular weight components were favored by increasing temperatures. The cracking of higher molecules was more induced at higher temperatures. While hydrocracking was increased, the color of the slack wax decreased. This result shows that the hydrogenation activity greatly increased as well as the hydrocracking activity when the temperature was increased from 300 °C to 400 °C. The first cracking of hydrocarbon appeared at 300 °C and the smallest molecule which was cracked out was about C_{14} n-alkane. At maximum operation temperature (400 °C) slack wax was cracked more than under other conditions and small hydrocarbon molecules of product, about C_9 n-alkane, were produced.
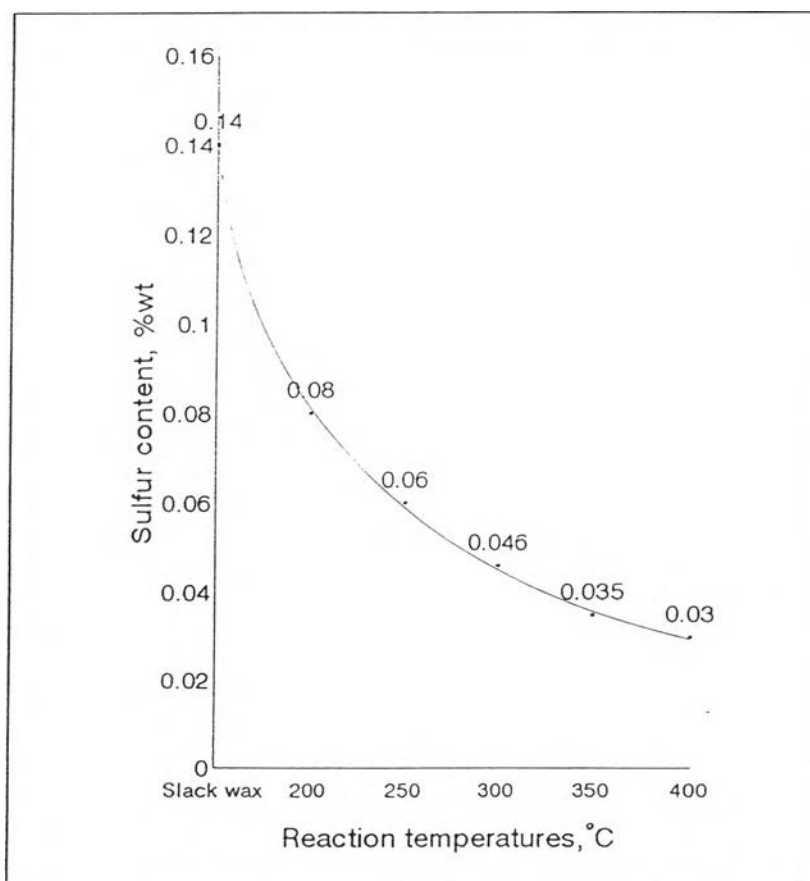
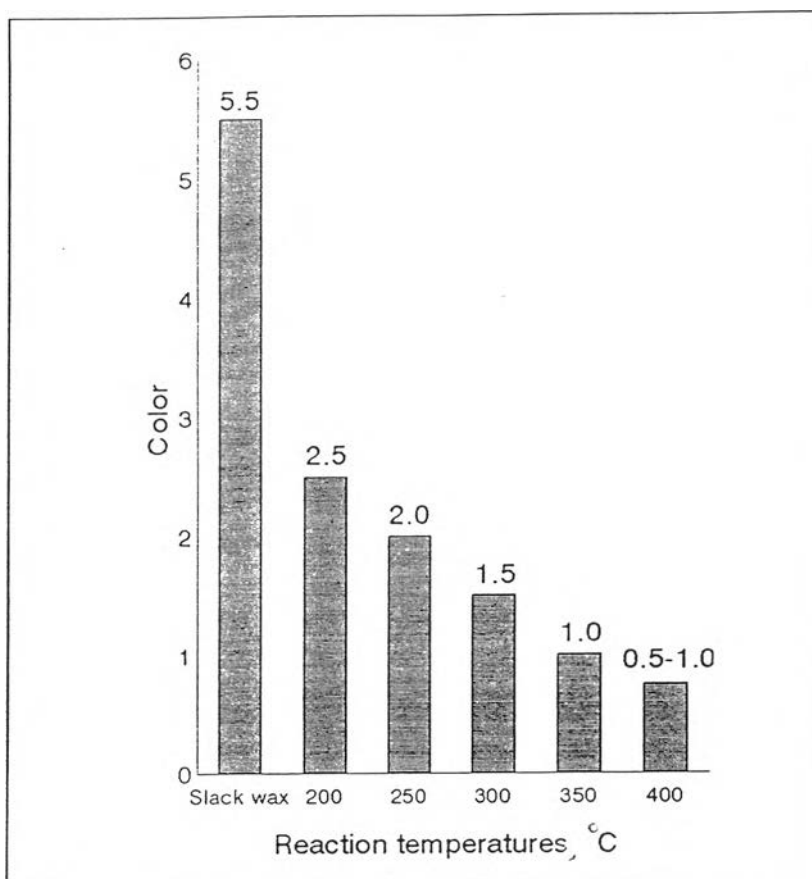**Figure 4.5** Effect of reaction temperature on sulfur content of desulfurized wax

Figure 4.6 Effect of reaction temperature on color of desulfurized wax
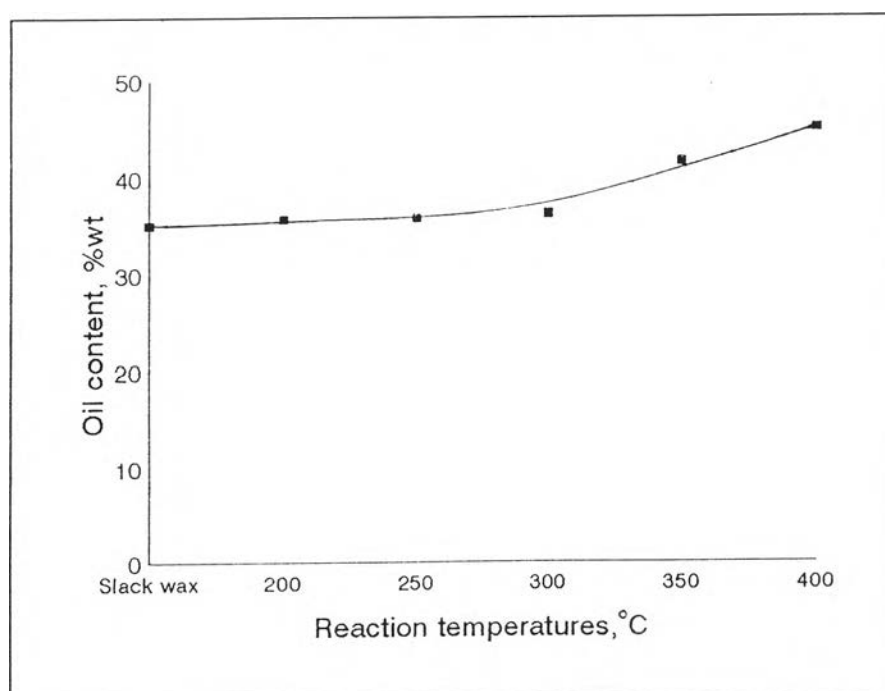

Figure 4.7 Effect of reaction temperature on oil content of desulfurized wax

These results show that increasing reaction temperature increases the rate of hydrocracking, hydrodesulfurization, and hydrogenation. Meanwhile, as the temperature was increased, those reactions involving cleavage of carbon-carbon bonds and carbon-sulfur bonds were increased resulting in increasingly lower molecular weight hydrocarbon compounds.

Within the range of the studied temperature, when the temperature was increased, more and more unsaturated compounds were hydrogenated and other color substances were removed. The evidence could be seen by decreasing in color and sulfur content. According to the result in Table A4, the properties of slack wax treated at 400 °C were the best. therefore, the optimum reaction temperature is 400 °C.

However, in the determination of optimum operating condition, other parameters were considered. Thus futher study looked for the most suitable hydrogen pressure. The hydrogen pressure was varied from 300, 400, 500, and 600 psig. The results from hydrodesulfurization of slack wax under different hydrogen pressures are recorded in Table A6. The sulfur content, color, and oil content of desulfurized wax were plotted against hydrogen pressure as shown in Figure 4.8, 4.9, and 4.10, respectively.

From this experiment, the color of hydrodesulfurized slack wax was improved. It was decreased from 5.5 to 1.5-2.0, 1.5-1.0, 0.5-1.0 and 0.5-1.0 when hydrogen pressures were increased from 300, 400, 500 and 600 psig, respectively. Sulfur content decreased with increasing hydrogen pressure, the same as color. The result of sulfur content, as shown in Figure 4.6, would be reduced slowly. At optimum hydrogen pressure (600 psig), sulfur content was the lowest (0.027 %wt). The carbon distributions of these experiments, observed by GC/MS, are illustrateded in Figure A5 and the molecular weight distributions are summarized in Table A7.
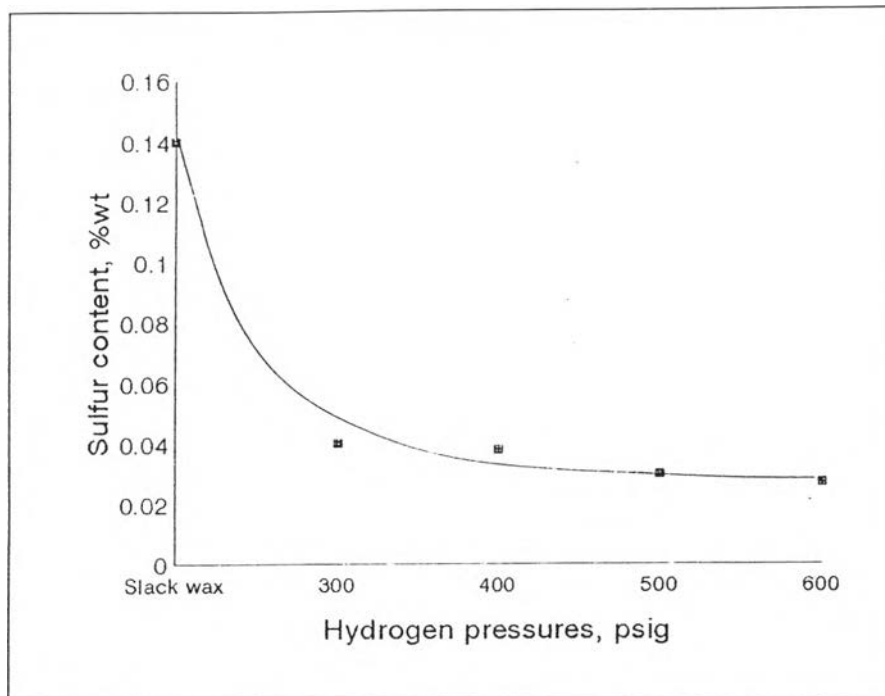
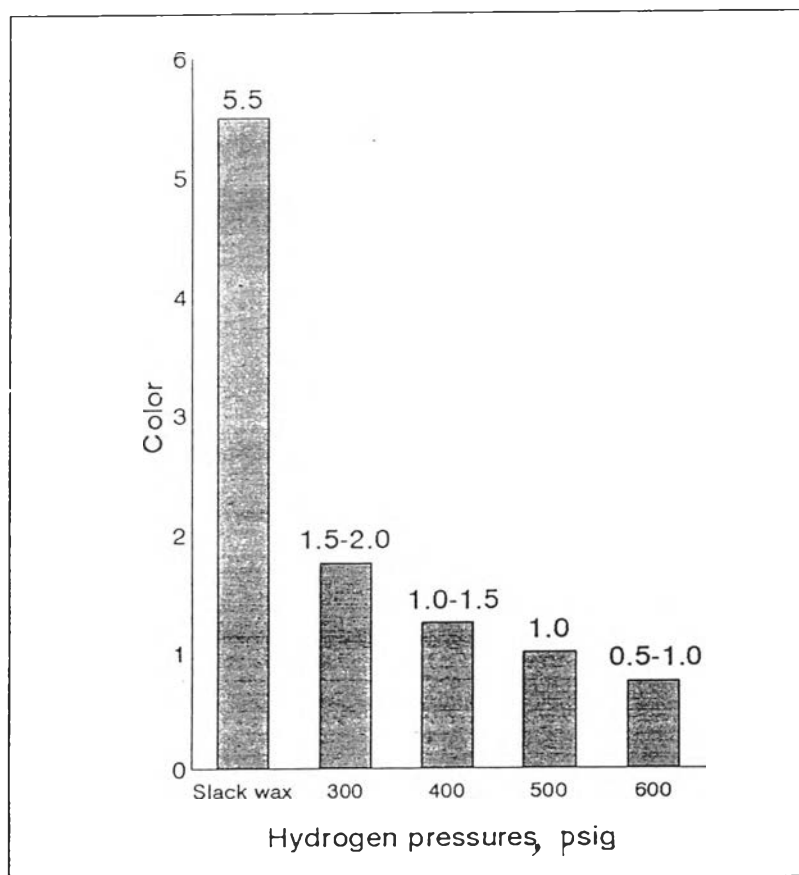**Figure 4.8** Effect of hydrogen pressure on sulfur content of desulfurized wax.

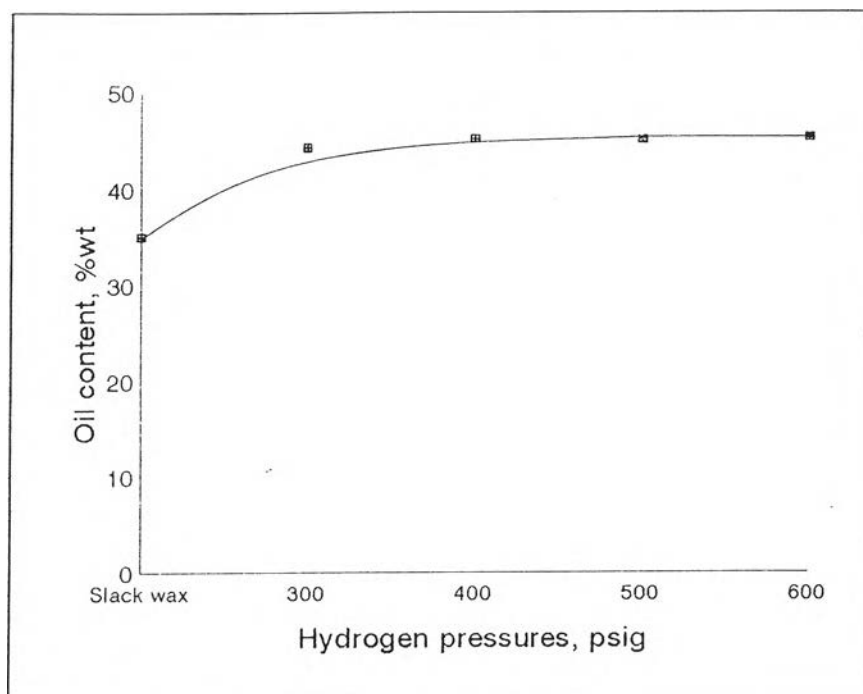**Figure 4.9** Effect of hydrogen pressure on color of desulfurized wax

Figure 4.10 Effect of hydrogen pressure on oil content of desulfurized wax

The results from the GC/MS chromatograms illustrate that hydrogen pressure does not significantly effect on cracking of hydrocarbon molecules under various hydrogen pressures from 300 to 600 psig.

thus, it is seen that increasing hydrogen pressure affects the rate of desulfurization and the hydrogenation of unsaturated compounds but not the rate of cracking. Therefore, these observations suggest that the optimum hydrogen pressure is 600 psig.

As previously studied, reaction temperature and hydrogen pressure were considered while the reaction time was kept constant at 4 hours. Thus the reaction time was the next parameter of interest. Reaction time of the hydrodesulfurization of slack wax was studied at 4, 6, 8, and 10 hours holding

other parameters constant: reaction temperature of 400 $^{\circ}$C, hydrogen pressure of 600 psig, and concentration catalyst of 5 %.

The results from hydrodesulfurization performed at the various reaction times of 4, 6, 8, and 10 hours are shown in Table A8. The effect of reaction time on sulfur content, color and oil content of treated are shown in Figures 4.11, 4.12, and 4.13, respectively.

The result of this experiment show that reaction time affected color, sulfur content, and carbon distribution. The effect on color could be seen in Table A8. The color of the slack wax was reduced to 0.5 at reaction times 8 and 10 hours. From Figure 4.10, sulfur content was also redued from 0.140 to 0.027 %wt when the reaction time was 4 hours. Sulfur content could be reduced still further when reaction time was increased.

The GC/MS analysis (Figure A6) and molecular weight distributions (Table A9) indicated that the cracking of hydrocarbon molecules was increased when the reaction was performed for a longer period. Therefore, these observations suggested that the optimum time, at the fixed parameter value, is about 8 hours.
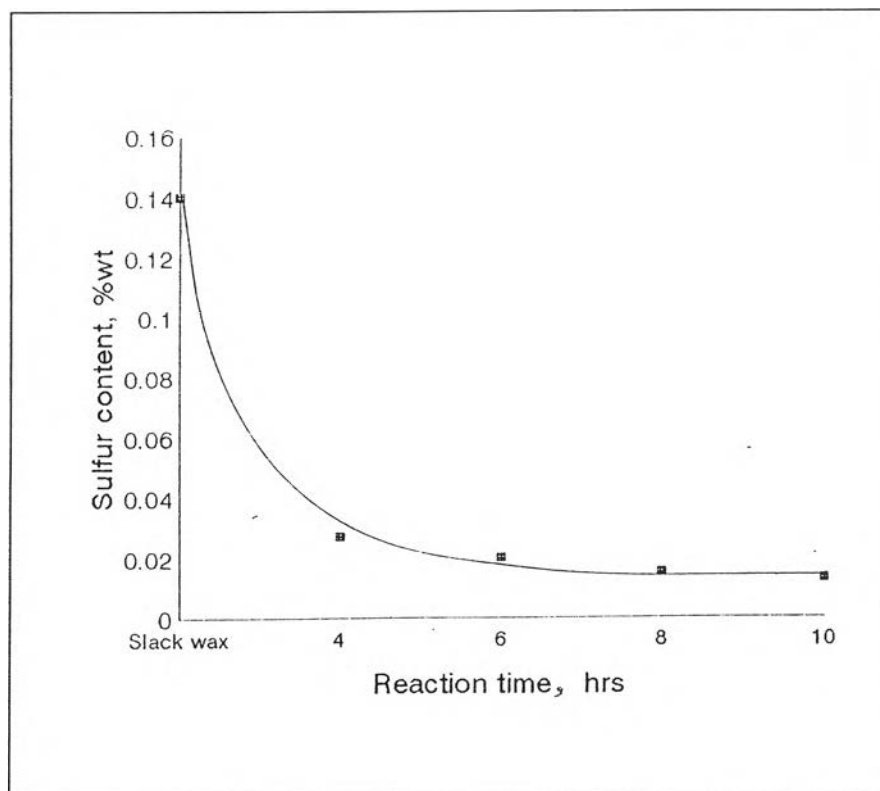
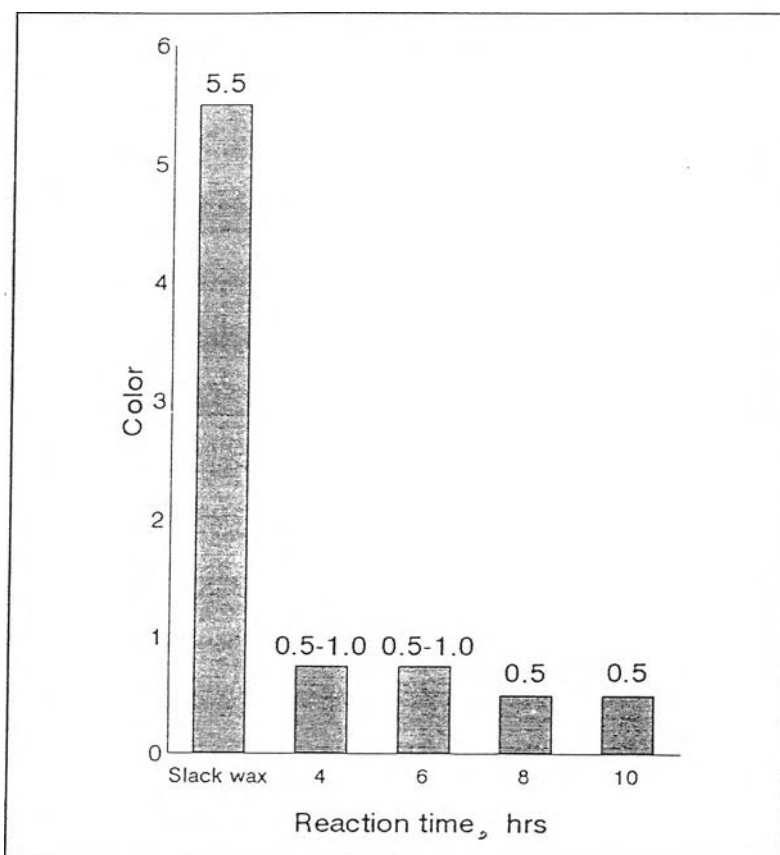**Figure 4.11** Effect of reaction time on sulfur content of desulfurized wax

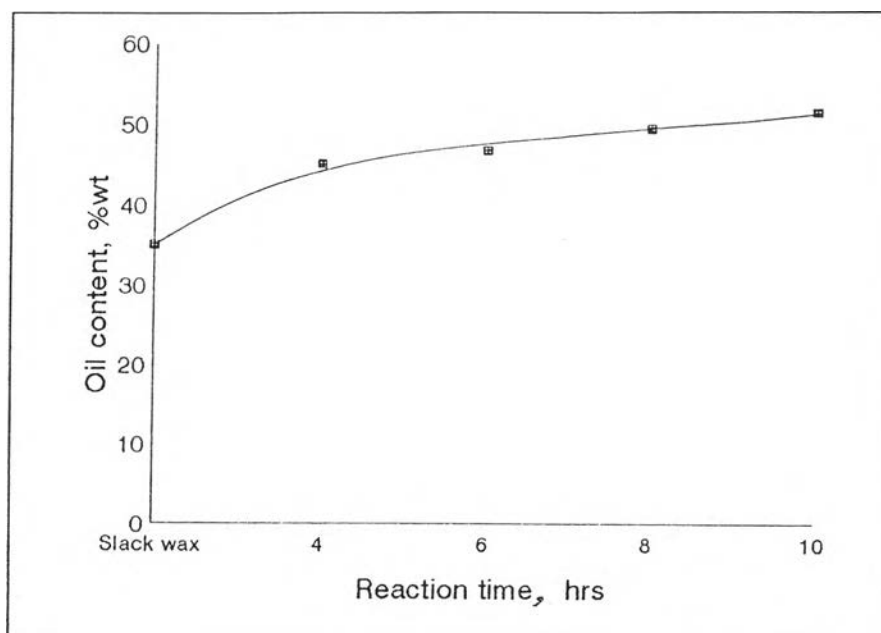**Figure 4.12** Effect of reaction time on color of desulfurized wax.

Figure 4.13 Effect of reaction time on oil content of treated wax.

The last variable to be considered for the hydrodesulfurization reaction was catalyst concentration. The hydrodesulfurization reaction was studied at constant parameters (400 °C, 8 hours, and 600 psig) with different catalyst concentrations of 5, 2, 1, 0.5, and 0.2 %wt of wax. The results are reported in Table A10. The sulfur content, color, and oil content are plotted against catalyst concentration in the reaction as shown in Figure 4.14, 4.15 and 4.16, respectively. The results presented show that the greatest effect of catalyst concentration is on the sulfur content in slack wax. The sulfur content of slack wax was reduced as catalyst concentration was decreased. The color of slack wax was affected in the opposite direction to the sulfur content in the product. At low catalyst concentration, color was increased. From these results, it suggested that the rate of desulfurization reaction, at low concentration, occurred more actively than hydrogenation reaction.

GC-MS chromatograms in Figure A7 and molecular weight distributions in Table A11 show that the cracking process is not depent upon the catalyst concentration as it is varied from 0.2 %wt to 5.0 %wt. In this process, the main criterion for selecting optimum conditions is the sulfur content in the treated product. A secondary criterion in this step is color reduction since hydroisomerization in the last process will be favored when low sulfur wax is used in the final step. Therefore, the optimum catalyst concentration to be used is about 0.5 %wt of wax.

In conclusion, the best catalyst of those studied for hydrodesulfurization of slack wax was the prepared MoCoNi/Al$_2$O$_3$ catalyst which contained 10 %Mo, 5 %Co and 5 %Ni. The optimum condition (reaction temperature, hydrogen pressure, reaction time, and catalyst concentration) were 400 °C, 600 psig, 0.5 % wt of wax, and 8 hours, respectively. The sulfur content and color of the wax treated at the optimum conditions were less than 0.001 %wt and 1.0-1.5, respectively.
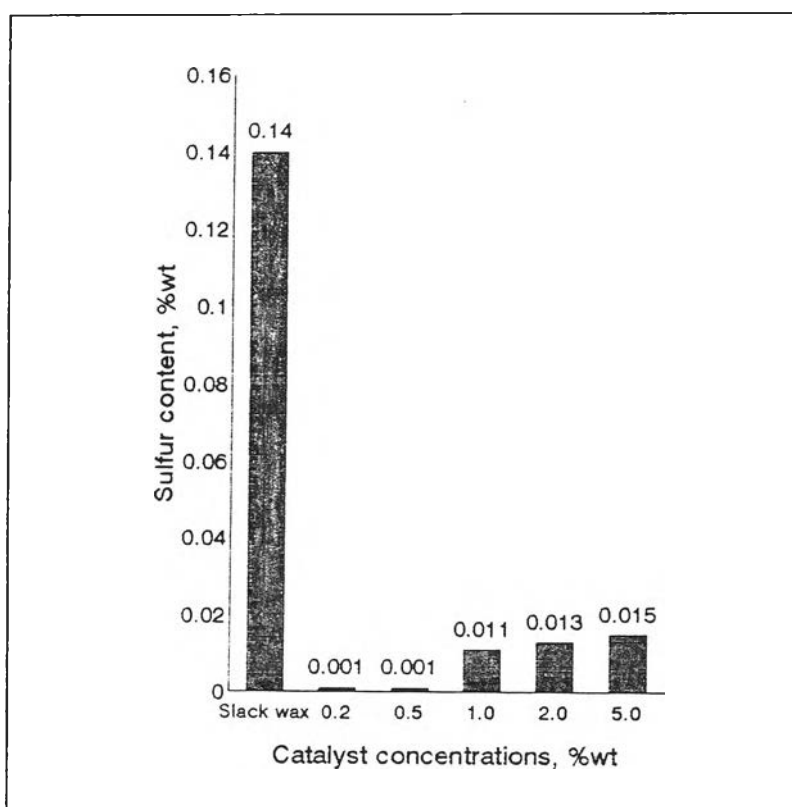

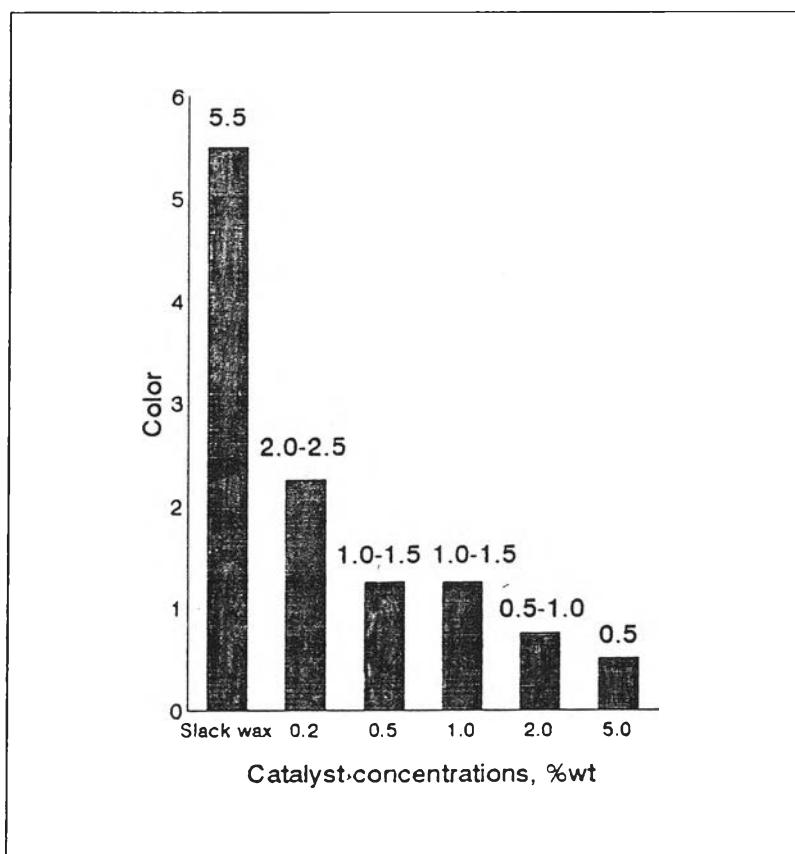**Figure 4.14** Effect of catalyst concentration on sulfur content of desulfurized wax

Figure 4.15 Effect of catalyst concentration on color of desulfurized wax
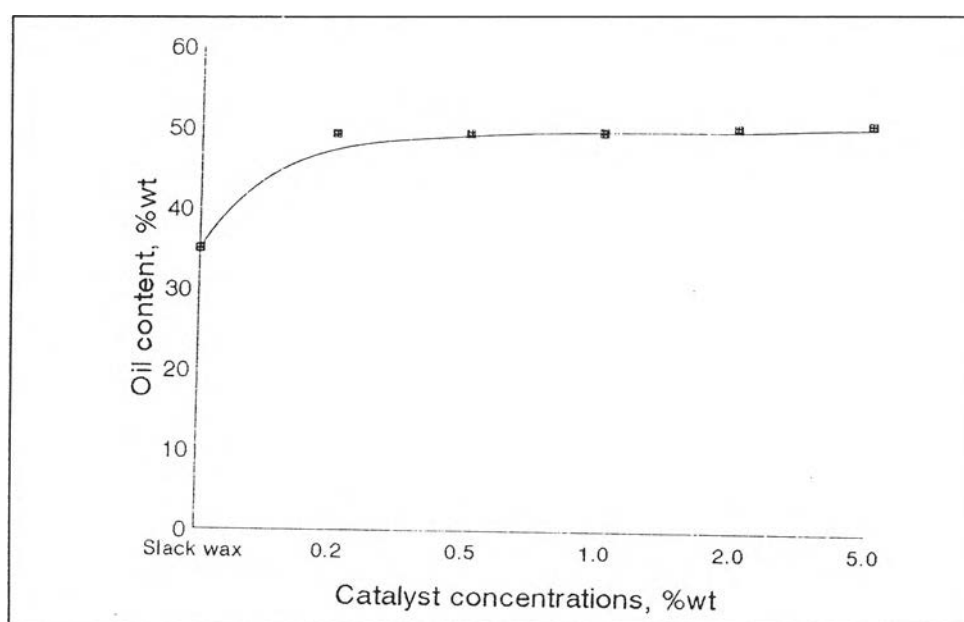

Figure 4.16 Effect of catalyst concentration on oil content of desulfurized wax

After slack wax is desulfurized, it is satisfactory for the hydroisomerization process. The next part of this study was to determine suitable parameters (reaction temperature, hydrogen pressure, reaction time, and concentration of catalyst) for the $Pt/F/Al_2O_3$ catalyzed hydroisomerization reaction. The first parameter was reaction temperature which was studied at 250, 300, 350, and 400 °C. The reaction was carried out under hydrogen pressure of 600 psig, reaction time of 4 hours and catalyst concentration of 2 % wt of wax. The results of these experiments are reported in Table A12. The color and the oil content of the isomerization products are plotted against temperature to give the curves illustrated in Figure 4.17 and 4.18, respectively. These results showed that the color of the isomerized wax is improved with increasing temperature. The big increase in oil content occurs going from 350 to 400 °C (4%) compare to only 2% going from 250 to 350 °C. The maximum oil was obtained at 400 °C for 4 hours

The results from GC/MS analysis in Figure A8 and Table A13, indicated that when the reaction was operated at higher temperature, the increasing of low molecualr weight distribution components was detected. This result illustrates that the cracking process is induced at higher temperature. In order to maximize the conversion of wax to high viscosity index base oil and lower melting point wax, a degree of carbon to carbon cleavage typical of hydrocracking, and production of substantial amounts of lower boiling point material is not required. Thus, the temperature in this process was selected at 300 °C.
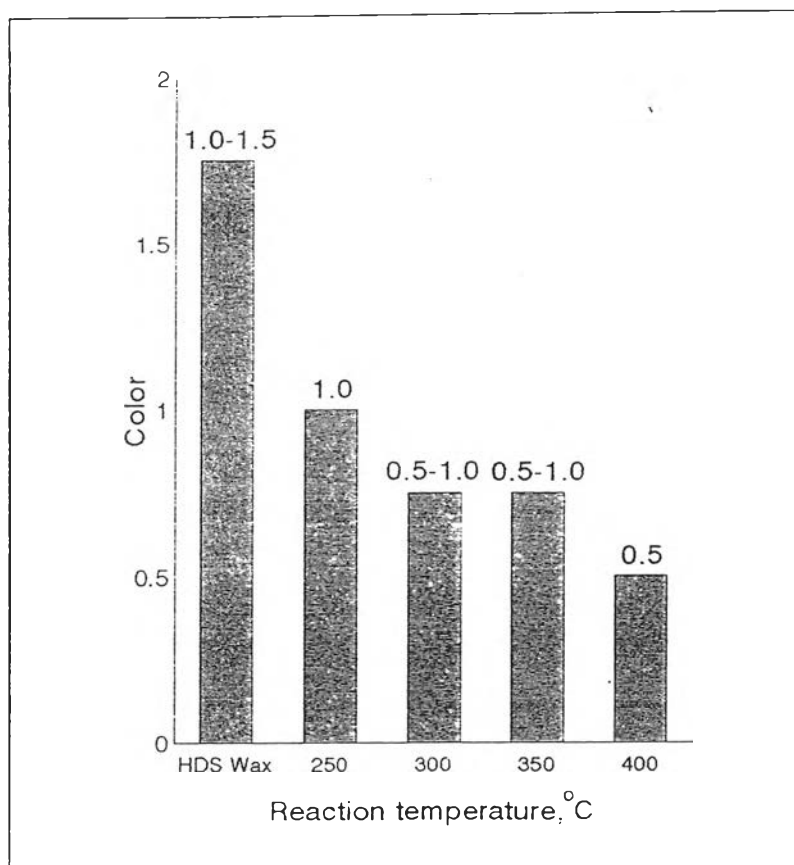
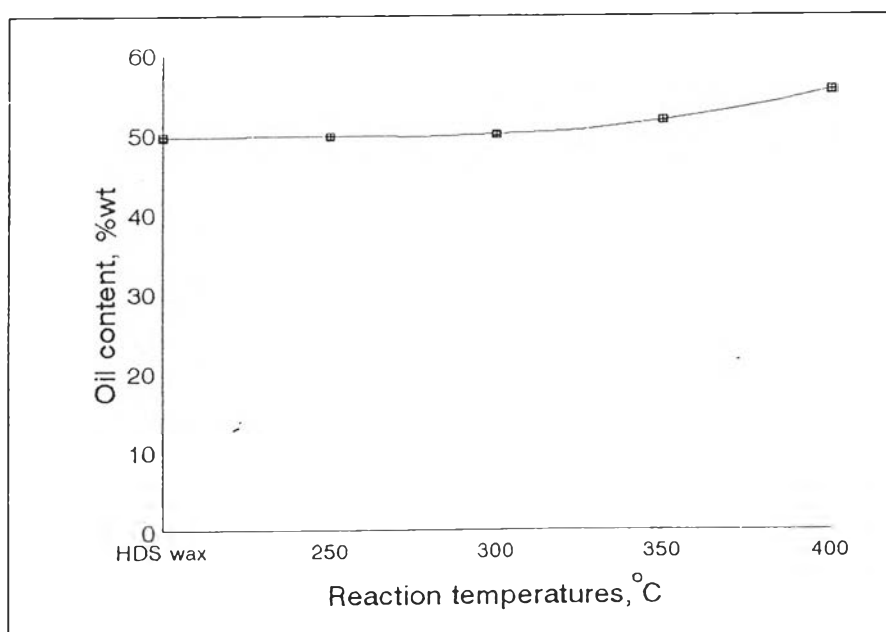**Figure 4.17** Effect of reaction temperature on color of isomerized wax

Figure 4.18 Effect of reaction temperature on oil content of isomerized wax

The second parameter considered was hydrogen pressure which was varied from 300, 400, 500, and 600 psig. The results are reported in Table A12. The changing of color and oil content are plotted against hydrogen pressure in the reaction as shown in Figure 4.19 and 4.20, respectively. These results show that the color and the oil content were changed when hydrogen pressure was increased. It was found that the best performance isomerized wax was obtained after treating at 600 psig. The carbon distribution of each product wax was observed by GC/MS and the results are presented in Figure A9. The molecular weight distributions are summarized in Table A14. The results from GC/MS observation illustrate that the hydrocarbon cracking is not dependent on the hydrogen pressure variation in the range of 300 to 600 psig. These observations that the optimum hydrogen pressure, at fixed parameters (300 $^{\circ}$C, 4 hours and catalyst concentration 2 %wt) is 600 psig.
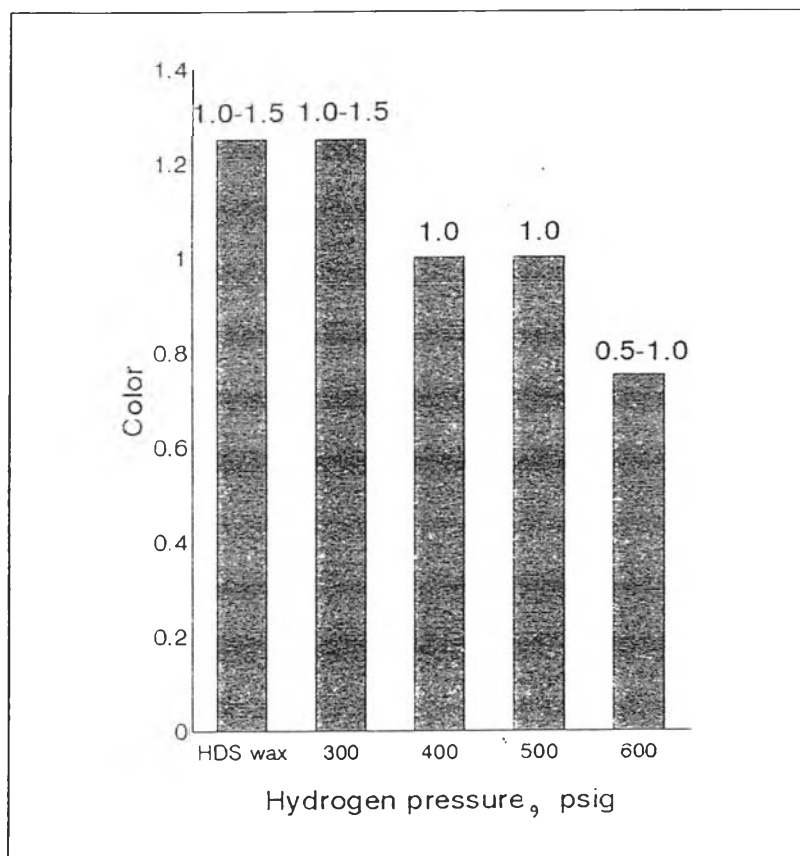
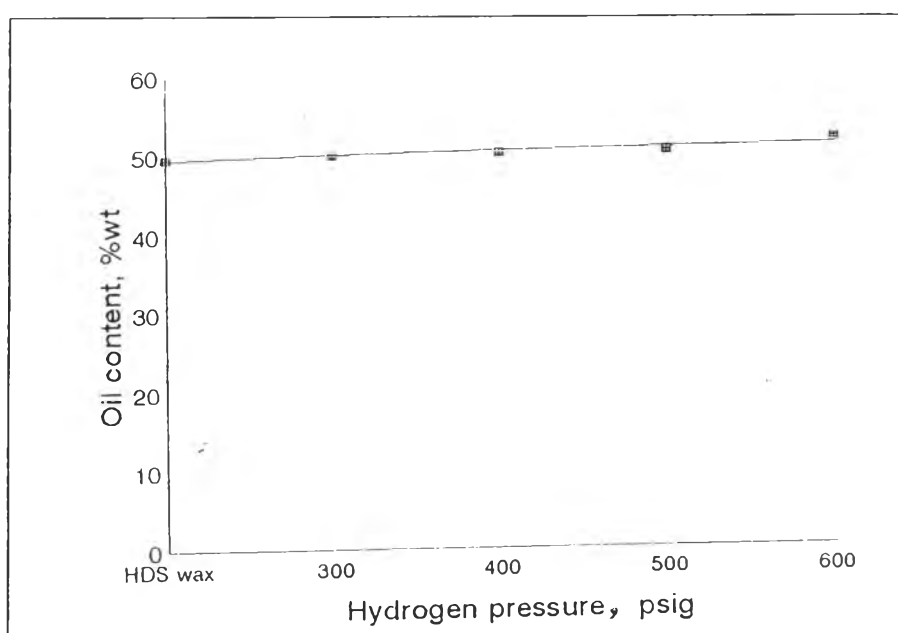**Figure 4.19** Effect of hydrogen pressure on color of isomerized wax

Figure 4.20 Effect of hydrogen pressure on oil content of isomerized wax

The next parameter was the catalyst concentration which was studied at 2.0, 4.0, 6.0, and 7.0 %wt. The results of these experiments are presented in Table A12. The changing of color and oil content of the isomerized wax are plotted against the concentration of catalyst to give curves as shown in Figures 4.21 and 4.22 respectively.

These results show that oil content increases with increasing concentration of catalyst. In this experiment, it was found that the color of isomerized wax was constant (0.5-1.0) by using catalyst concentration 2, 4 and 5 %wt of wax. The color was improved when catalyst concentration was increased to 6 %wt of wax.

The results of GC/MS analysis (Figure A10) show that the catalyst concentration does not significantly affect the carbon distribution of isomerized wax at fixed parameters (300 °C, 600 psig, and 4 hours). The molecular weight distributions are reported in Table A15. These observations suggest that the suitable concentration of catalyst is 6 %wt of wax because it was economic. The color of isomerized wax was constant at 0.5.
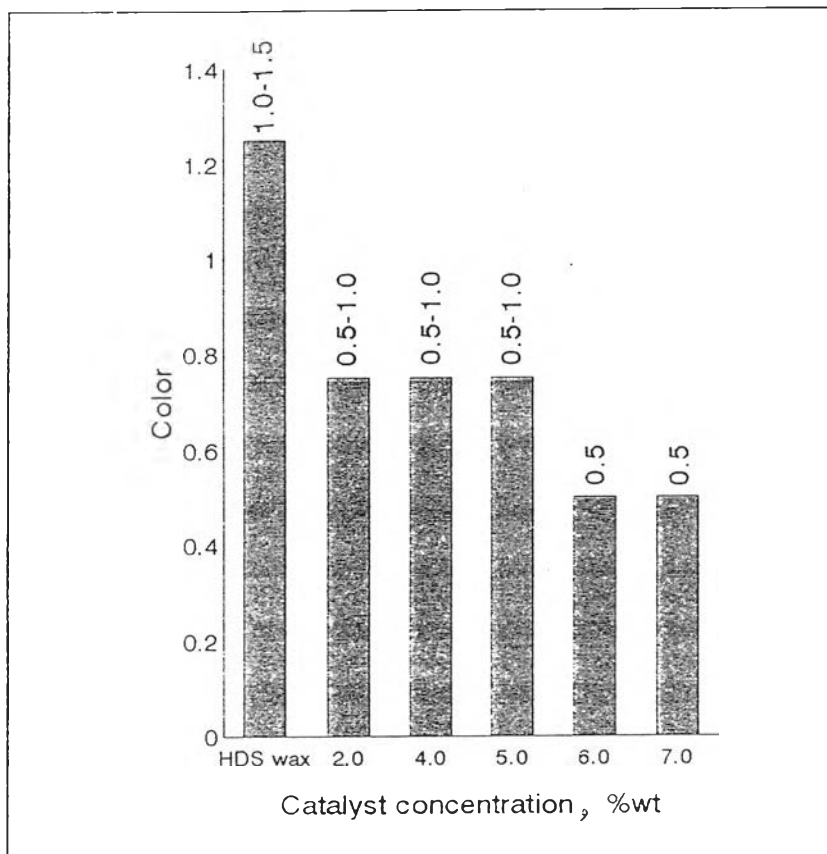
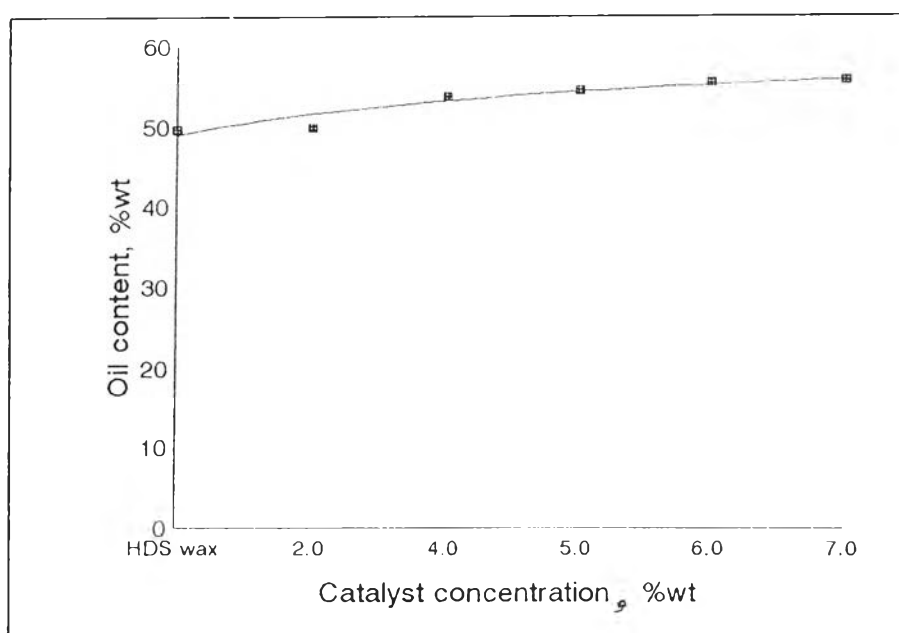**Figure 4.21** Effect of catalyst concentration on color of isomerized wax

Figure 4.22 Effect of catalyst concentration on oil content of isomerized wax

The last parameter considered was reaction time which was performed with reaction times from 4, 6, 8, 10, and 12 hours. The results of these experiments are presented in Table A12. The changing of color and oil content are plotted against reaction time as illustrated in Figures 4.13 and 4.14 respectively.

These results show the oil content increases with increasing time and the color of the isomerized wax was improved to nearly colorless (~ 0) after the reaction was operated for 12 hours. The result of GC/MS analysis (Figure A11) and molecular weight distribution (Table A16) indicate that reaction time does not significantly affect the cracking process.

According to the former result, it was found that the properties of the isomerized wax after a reaction time of 12 hours was the best because its color was good and its oil content was high. Therefore, the decision was made to select a reaction time of 12 hours as the optimum condition due to safe energy.

In summary, the best conditions (reaction temperature, hydrogen pressure, catalyst concentration and reaction time) for hydroisomerization of desulfurized wax using 0.3 %Pt and 0.5 %F on alumina support catalyst were 300 °C, 600 psig, 6 % by weight of wax and 12 hours, respectively. After the desulfurized wax was treated in the above optimum conditions, color and the oil yield content of the isomerate were ~ 0 and 69.1 %wt respectively.
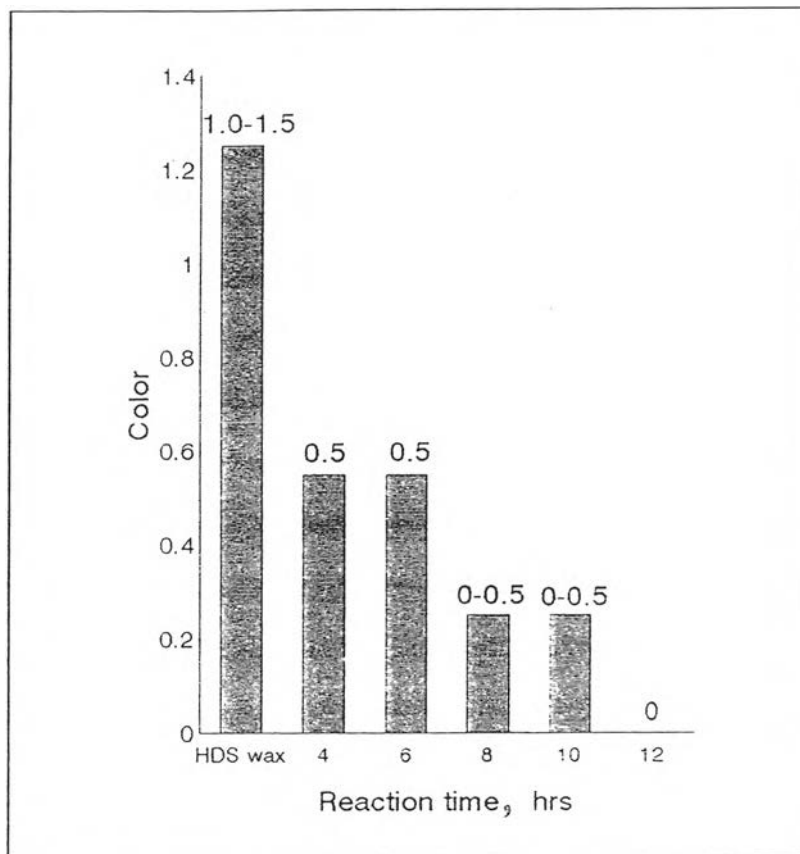
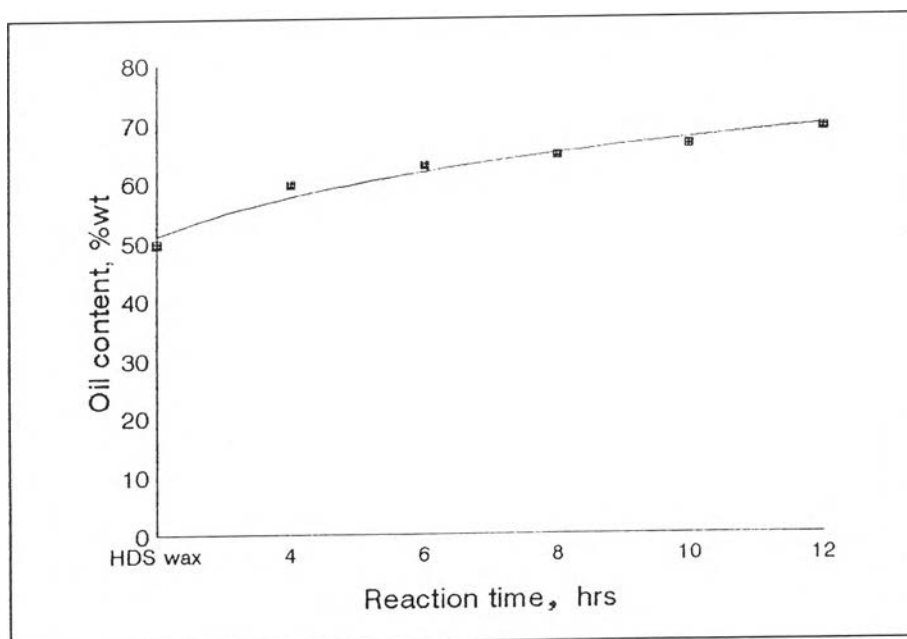**Figure 4.23** Effect of reaction time on color of isomerized wax

Figure 4.24 Effect of reaction time on oil content of isomerized wax

The properties of untreated slack wax, desulfurized wax, and isomerized wax at optimum condition are summarized in Table 4.3. The properties of deoiled wax from desulfurization and isomerization were reported in Table 4.4.

The oil fraction obtained from the deoiling process was distilled under reduced pressure to give light fraction (boiling point below 330 °C) and lube fraction (or oil fraction 330 °C+). The lube fraction was dewaxed using MEK as described in procedure 9 to give lube base oil. From these results, the percentage of light fraction, lube base oil, and lube fraction residue are recorded in Table 4.5. The properties of lube base oil from the isomerization process, color, pour point, viscosity, viscosity index, oxidation point, and oxidative compound, are presented in Table 4.6. The comparison of UV absorption of these waxes in Table A18 showed that they met all requirements for the food or pharmaceutical grade wax.

The GC/MS analysis of the isomerized waxes are shown in Figure A12 and the molecualr weight distribution of each fraction is reported in Table A17.

Table 4.3 The properties of untreated slack wax, desulfurized wax and isomerized wax

Properties	Untreated slack wax	Desulfurized wax	Hydroisomerized wax
Color (ASTM D 1500)	5.5	1.5	~ 0
Sulfur content, %wt	0.140	< 0.001	< 0.001
Deoiled wax, %wt	64.9	48.6	30.9
Oil content, %wt	35.1	51.4	69.1

Table 4.4 The properties of wax from untreated slack wax, desulfurized wax, and hydroisomerized wax

Properties	Untreated slack wax	Desulfurized wax	Hydroisomerized wax
Color (ASTM D 1500)	1.5	0 (> +17 Saybolt)	0 (> +17 Saybolt)
Melting point, °C (by cooling curve)	52.0	59.8	60.0
Congealing point, °C	51.0	58.5	58.5
max. UV absorption of wax at 250-300 nm, absorbance.[#]	0.200	0.020	0.015

[#] 100 mg of wax in 100 ml isooctane was used for determination.

Table 4.5 The percentage of hydroisomerized products

Fractions	Untreated slack wax	Desulfurized wax	Hydroisomerized Wax
Deoiled wax	64.9	48.6	39.2
Oil fraction	35.1	51.4	63.8
- light fraction	-	25.2	24.8
- lube base oil	-	18.4	20.6
- lube fraction residue[@]	-	7.8	15.4

[@] The lube fraction residue was a mixture, comprising wax .and oil from dewaxing process after deoiling by pressing hydroisomerized wax which comprised oil and small wax.

Table 4.6 Properties of lube base oil from the hydroisomerization process

Physical properties	Untreated slack wax	Hydrodesulfurized slack wax	Hydroisomerized slack wax
Color	-	1.0-1.5	0.5
Pour point	-	-5	-5
Viscosity			
@ at 40 °C, cSt	-	79.44	72.20
@ at 100 °C,cSt	6	8.52	8.50
Viscosity index	-	70	85
Sulfur content, %wt	0.140	< 0.001	< 0.001
Oxidation point, °C	-	-	375
Oxidative compound, %wt	-	-	15

In this study, we found that the hydroisomerization of waxes has advantages over other wax purification treatments such as the acid-clay treatment process and adsorbent material treatment, because this process produces a high quality product and does not make pollute. Each product in this process can be used in several industies. The waste from the process is hydrogen sulfide which can be convert to free sulfur completely by an oxidizing agent while the other processes produce many wastes. The acid-clay treatmentis especcially dirty, making large qualities of acid sludge, and pollution problems.

The products in each steps of the hydroisomerization of Fang heavy distillate waxes are shown in Figure 4.25 and the products from the hydroisomerized wax are shown in Figure 4.26.

Figure 4.25 Fang heavy distillate, untreated wax (slak wax), desulfurized wax, and hydroisomerized wax

Figure 4.26 The products from hydroisomerized wax