CHAPTER IV

RESULTS AND DISCUSSION

This study aimed to upgrade the heavy distillate (HD) fraction, obtained from Fang Refinery Plant, to be suitable for using as a lubricating base oil by hydroisomerization process. The HD is a solid at room temperature because of the high dissolved paraffin wax content. The original heavy distillate was characterized as shown in Table 4.1 and Figure A1.

Table 4.1 Properties of the original heavy distillate

Properties	Fang heavy distillate (HD)
Color, ASTM 1500	>8
Pour point (^{0}C)	51
Kinematic viscosity	
@ 40 ^{0}C, cSt	-
@ 100 ^{0}C, cSt	6.00
Viscosity index	-
API gravity @ 15.6 ^{o}C	30.5

From Table 4.1, the API gravity indicated that the Fang heavy distillate was not a heavy distillate because its gravity was approached the gravity of light vacuum gas oil (API 30). Figure A1 and Table A1 demonstrate that this distillate contained 14-40 carbon atoms and the main compositions were C_{24}-C_{32} paraffin hydrocarbons. Its boiling range was within the lubricating oil

range (330-600 °C). High quantities of waxes and contaminants led to poor pour point and dark color, respectively. In order to improve the flow characteristics of HD, these waxes had to be removed and the selected solvent dewaxing process was necessary for base oil producing process. Methyl ethyl ketone (MEK), the widest used dewaxing solvent in the industry, was selected as the solvent due to the low wax solubility at the dewaxing temperature and its sufficiently low boiling point to facilitate removal from the dewaxed oil. The dewaxing process was performed on a portion of HD using MEK at a 3:1 solvent:oil ratio and a filter temperature of 0 °C. The result from dewaxing of HD is shown in Figure 4.1.
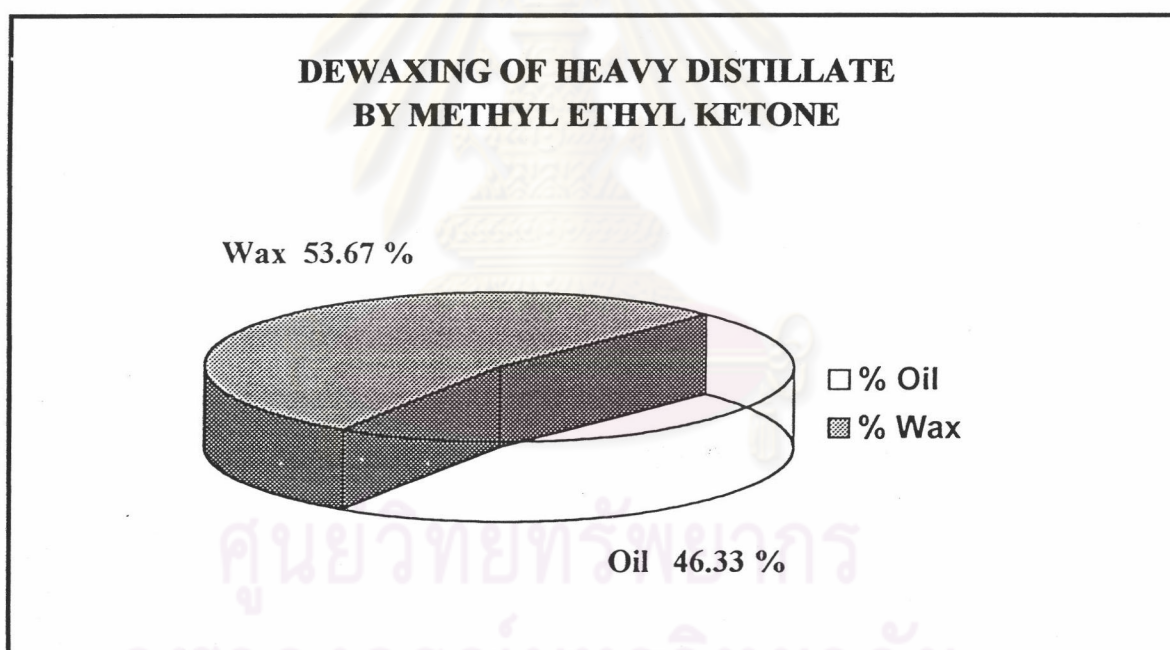

DEWAXING OF HEAVY DISTILLATE BY METHYL ETHYL KETONE

Wax 53.67 %

☐ % Oil
▨ % Wax

Oil 46.33 %

Figure 4.1 The percents by weight of oil and wax separated by solvent dewaxing process

Figure 4.1 indicated that MEK extracted 53.67% by weight of slack wax leaving 46.33% by weight of dewaxed oil. The wax was a white crystalline solid and the dewaxed oil was a black viscous liquid. The dewaxed oil's

properties are summarized in Table 4.2 and its GC-MS chromatogram is shown in Figure A1. The ^{13}C-NMR spectrum and thermogram are shown in Figure A2 and A3, respectively.

Table 4.2 The properties of the dewaxed oil

Properties	Dewaxing Process	
	HD before dewaxing	dewaxed oil
Color	>8	>8
Pour point (°C)	51	6
Kinematic viscosity		
@ 40 °C, cSt	-	159.69
@ 100 °C, cSt	6.00	11.10
Viscosity index	-	22
Sulfur, %wt	-	0.338
Component:		
%C_a	-	8.54
%C_n	-	18.67
%C_p	-	72.79
Flash point (°C)	-	236
Oxidation point (°C)	-	350
Oxidative compound, %wt	-	18.09

The results from Table 4.2 illustrate that the pour point of the dewaxed oil is 6 °C as compared to 51 °C for HD. Because of the wax removal, the viscosity at 100 °C of the dewaxed oil was higher than that of the original HD. The color remained higher than 8. The sulfur content, oxidative compounds and viscosity index were 0.338 %, 18.09 %, and 22, respectively. The aromatic,

paraffinic and naphthenic contents were 8.54, 72.79 and 18.67 % by mole atom of carbon, respectively.

Although the dewaxing process improved the pour point of the oil, 10.52 % of paraffin waxes remained in the dewaxed oil and the oil's color was still dark. The color of the oil came from color substances such as aromatic compounds, which also created poor viscosity index, unsaturated compounds and sulfur compounds which were not removed by the dewaxing process. To achieve the desired base oil properties, further refining process was incorporated in this study.

Catalytic hydroisomerization process was effective for converting remained waxy components, comprising straight chain and slightly branched chain paraffins, in the dewaxed oil to relatively less waxy isoparaffins and more highly branched aliphatics.

Dewaxed oil from natural petroleum sources contains numerous molecular species such as sulfur compounds and aromatic materials which are detrimental to the life and activity of platinum isomerization catalysts. Consequently, this heteroatom should be removed prior to contact with the hydroisomerization catalyst by using a hydrodesulfurization process. This pretreating process was conducted under typical hydrotreating conditions to reduce sulfur contents to levels of 10 ppm or less. The hydrodesulfurization catalyst (Mo/Ni/Co on alumina type CS331-3 having pore volume about 0.64 ml/g) was prepared by the dry impregnation method. The first step was to soak the alumina with ammonium thiosulfate solution to improve crush strength. [24] This impregnation was achieved in one single wetting by adding citric acid to the solution of molybdenum, cobalt and nickel salts. As a result, this solution was stable for a long time before a precipitate of Mo/Ni/Co was formed, then the impregnated alumina was dried and calcined. The catalyst prepared in this manner containing 10% Mo, 5% Ni and 5% Co, had a surface area of 141.05 m^2/g.

For selecting a suitable hydrodesulfurization catalyst, several conventional hydrotreating catalysts, such as Mo/Ni/Co metal sulfide on alumina prepared catalyst and commercial catalysts identified as C20-7-06 (Mo/Ni/Al$_2$O$_3$ metal oxide catalyst), T-2563 (Ni/W/Al$_2$O$_3$ metal oxide catalyst) and Raney nickel, were employed to treat the dewaxed oil under the same conditions at temperature 350 ^{0}C, hydrogen pressure 500 psig, reaction time 4 hrs, catalyst concentration 5% by weight of oil and agitation speed 500 rpm in a stirred autoclave reactor.

The molecular weight distributions of the components in desulfurized oil and the GC-MS chromatograms at various catalyst types are shown in Table A2 and Figure A4, respectively. The sulfur content was measured and the results are summarized in Table A3. To establish the properties of the oily component of this desulfuried oil, the total liquid product was distilled under reduced pressure to obtain lube cut ($\geq$ 330 ^{o}C) and distillate cut ($<$ 330 ^{o}C). The physical properties of this desulfurized lube cut were determined and the results are summarized in Table A3. The sulfur content, color, viscosity index and pour point were plotted against catalyst types and shown as bar graph in Figure 4.2, 4.3, 4.4, and 4.5, respectively.

From this experiment, the results showed that the prepared Mo/Ni/Co catalyst exhibited superior performance for desulfurizing as compared to Ni/W, Ni/Mo and Raney nickel catalyst. Raney nickel is a simple inexpensive catalyst. However, the performance of Raney nickel in reducing sulfur content was very poor, when compared with the other catalysts. The mass spectral analysis also demonstrates that when the Raney nickel was used in the hydrodesulfurization process, lower boiling compounds were produced.

From this study, it can be seen that the color and VI improvement results of Ni/W catalyst were better than Mo/Ni/Co catalyst. However, we found that during the reaction took place the cylindrical structure of the Ni/W catalyst was broken to the powder, so it could not be reused while the

cylindrical structure of the Mo/Ni/Co catalyst was preserved. Thus, Mo/Ni/Co catalyst was selected for use in the hydrodesulfurization process.
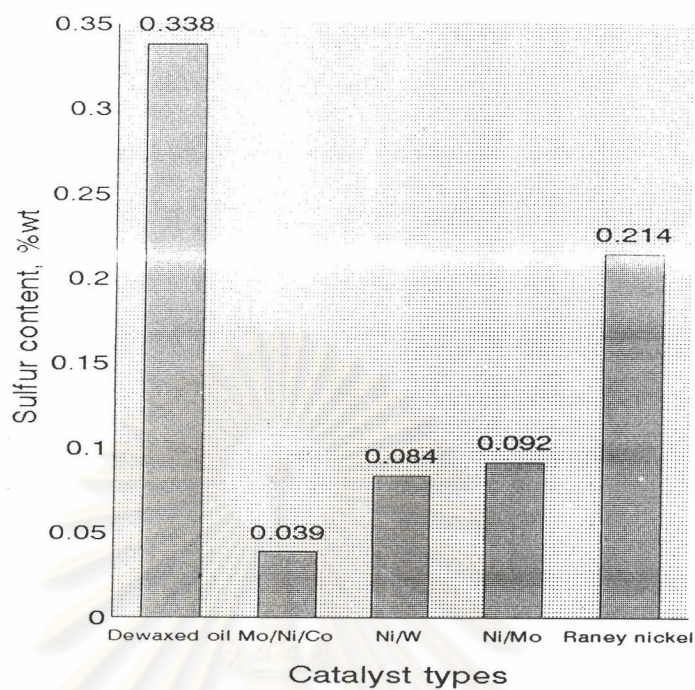
Figure 4.2 Effect of catalyst types on sulfur content of desulfurized oil
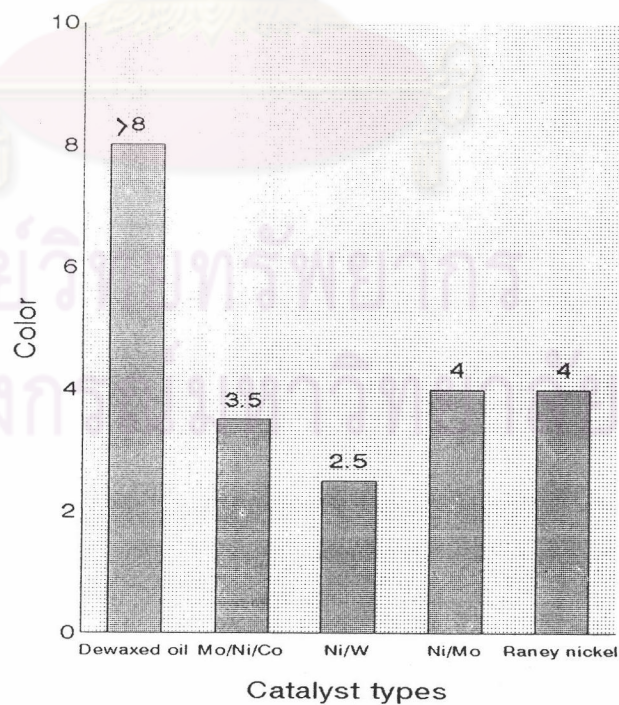

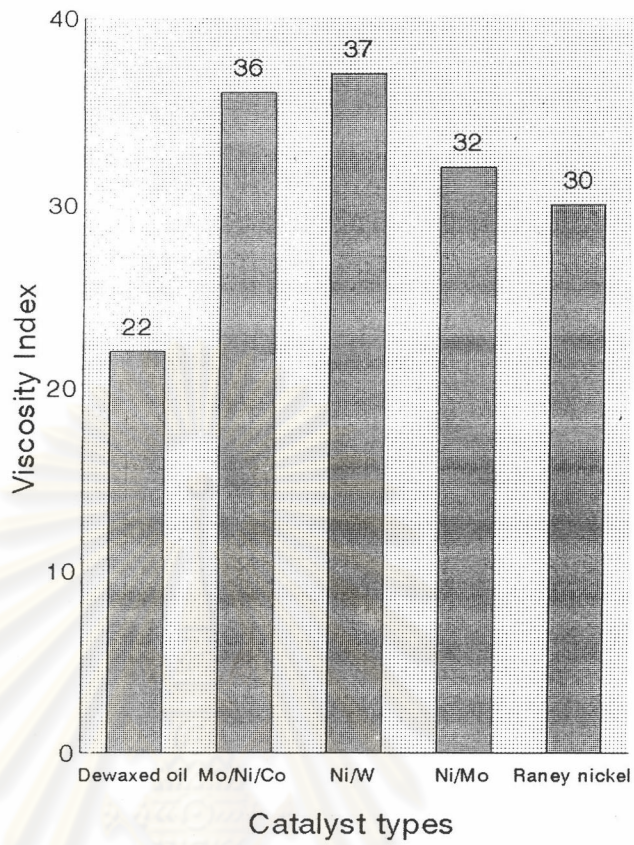**Figure 4.3** Effect of catalyst types on color of desulfurized oil

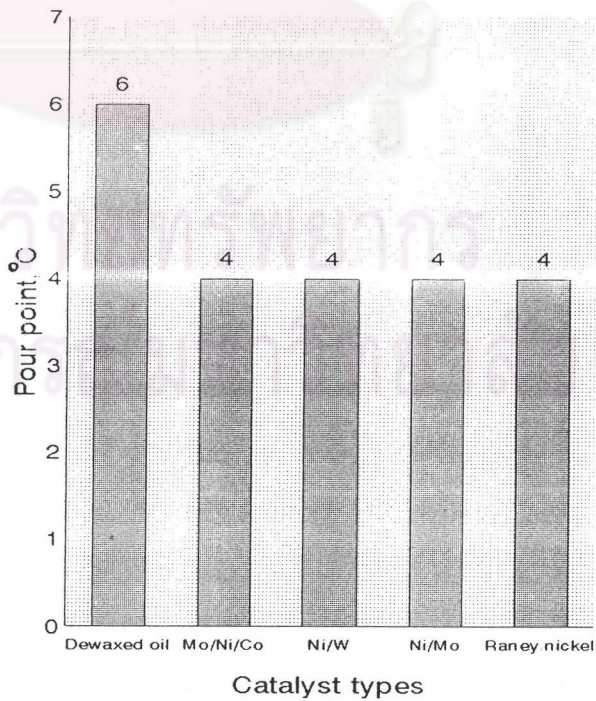**Figure 4.4** Effect of catalyst types on viscosity index of desulfurized oil

Figure 4.5 Effect of catalyst types on pour point of desulfurized oil

Optimized conditions for use of the prepared Mo/Ni/Co catalyst for hydrodesulfurization were determined by varying the several operating parameters: reaction temperature, hydrogen pressure, reaction time, and catalyst concentration.

The first parameter to be varied in the hydrodesulfurizing process was reaction temperature. It was varied from 200 to 400 in 50 °C steps. The GC-MS chromatograms (Figure A5) and Table A4 illustrate that the molecular weight distributions of the products are changed by increasing temperature. When the reaction was operated at a higher temperature, lower molecular weight components were increased. This result demonstrates that the cracking process occurs more at higher temperature. It was expected that naphthenic hydrocarbons would be reformed to paraffinic hydrocarbons by cracking process and desulfurized oil's properties, especially viscosity index were also improved.

The sulfur content of the resulting desulfurized oils and the physical properties of their respective lube cuts were determined and the results are reported in Table A5. The sulfur content, color, VI and pour point were plotted against temperature variation in Figures 4.6, 4.7, 4.8, and 4.9, respectively.

The results from this experiment show that sulfur content of desulfurized oil decreases with increasing operating temperature. This result also showed that optimum temperature for reducing sulfur content from desulfurized oil was 400 °C. Moreover, the physical properties, color, VI and pour point were improved with increasing the temperature. The temperature resulted in the desired optimum physical properties was 400 °C. At this temperature, the percentage yield of lube fraction was 92.53, indicating that cracking was increased at this temperature.
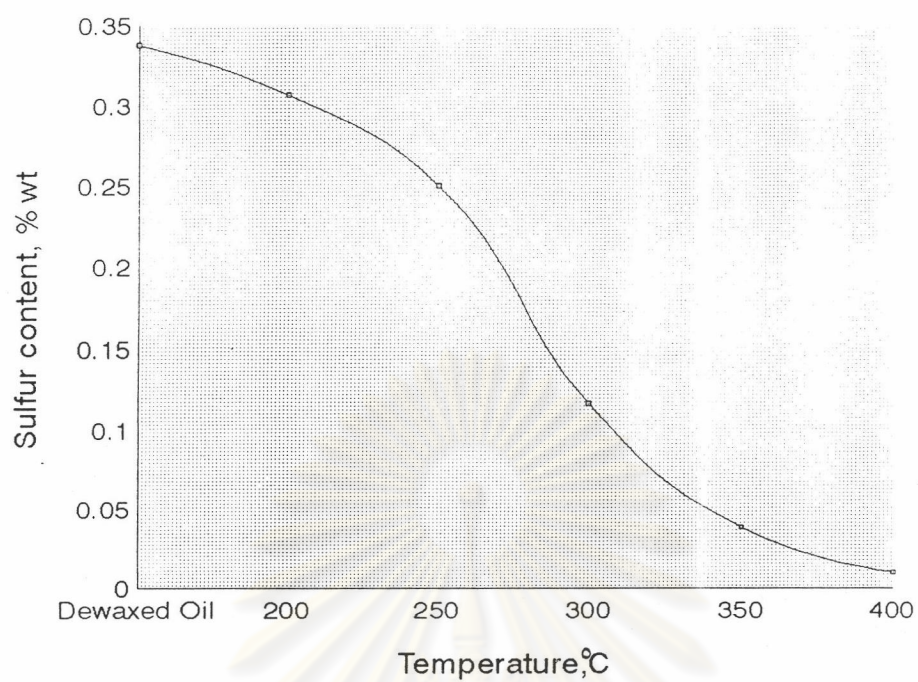
Figure 4.6 Effect of reaction temperature on sulfur content of desulfurized oil
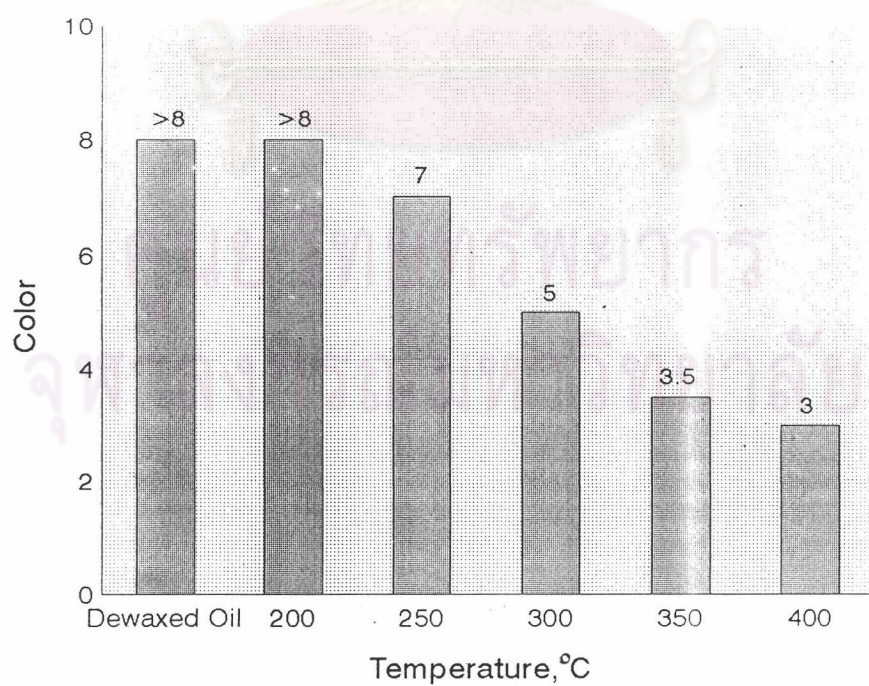

Figure 4.7 Effect of reaction temperature on color of desulfurized oil
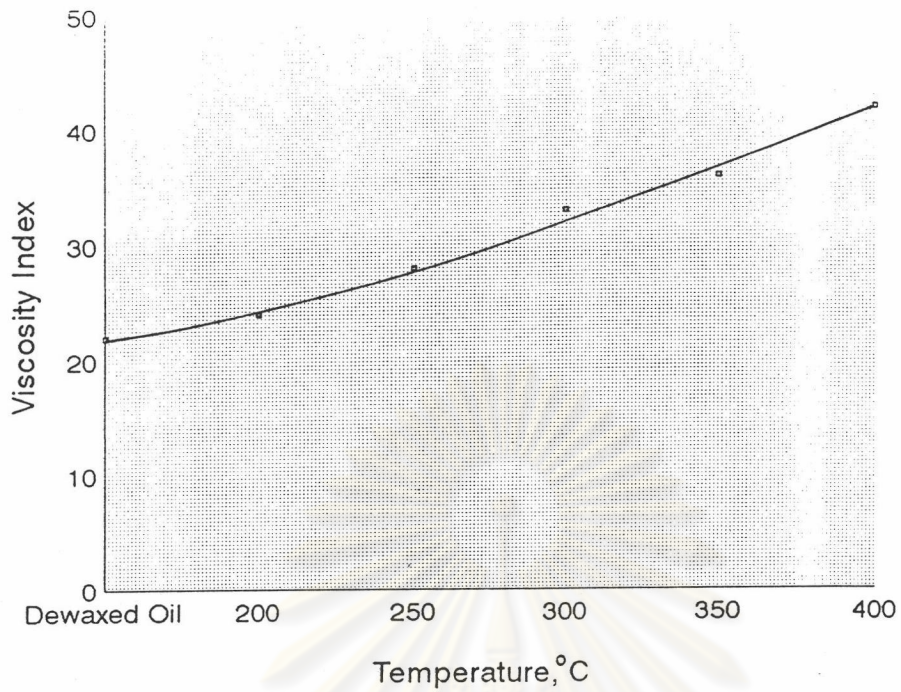
Figure 4.8 Effect of reaction temperature on viscosity index of desulfurized oil
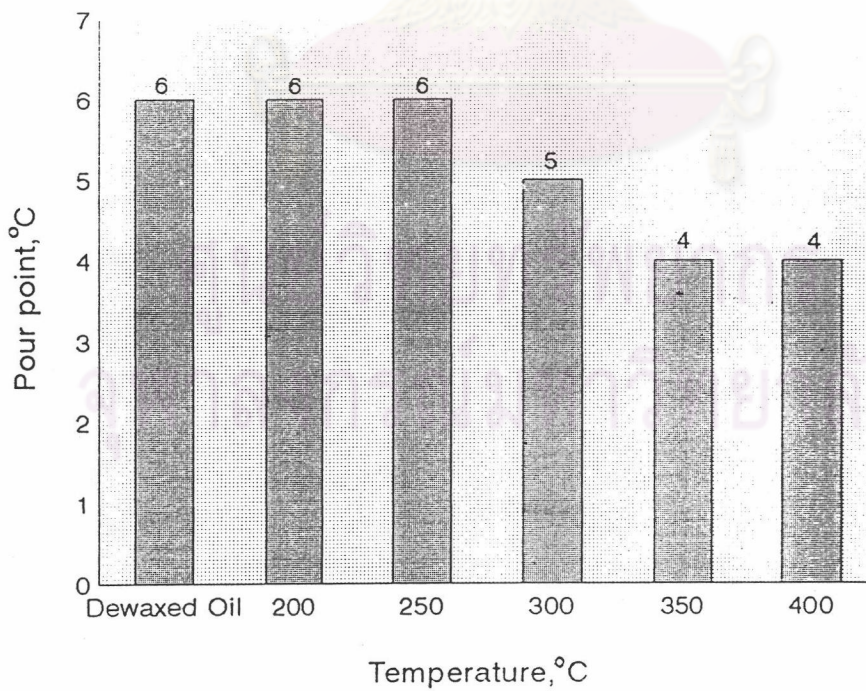

Figure 4.9 Effect of reaction temperature on pour point of desulfurized oil

The second parameter studied for the hydrodesulfurization reaction was hydrogen pressure. The reaction was performed with hydrogen pressures of 200, 300, 400, 500 and 600 psig. The molecular weight distributions of the products were observed by GC-MS and the results are presented in Figure A6. The molecular weight distributions are summarized in Table A6. The results from GC-MS show that the cracking process does not depend on the hydrogen pressure variation from 200 to 600 psig.

The sulfur content and the physical changes are plotted against hydrogen pressure in Figures 4.10, 4.11, 4.12 and 4.13. The experiment results in Table A7 showed that the sulfur content was decreased from 0.338, to 0.193, 0.098, 0.057, 0.010 and 0.005%wt, respectively when the reactions were operated under hydrogen pressure at 200, 300, 400, 500 and 600 psig, respectively. The result from the increasing of hydrogen pressure showed that the rate of desulfurization and hydrogenation of unsaturation were increased. These results suggest that the optimum hydrogen pressure is 600 psig.
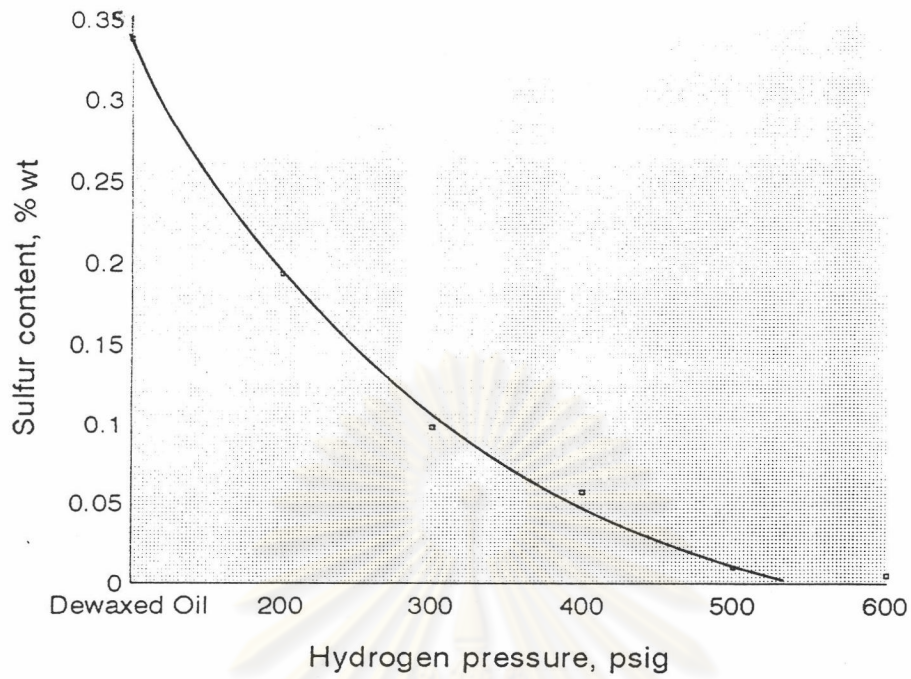
Figure 4.10 Effect of hydrogen pressure on sulfur content of desulfurized oil
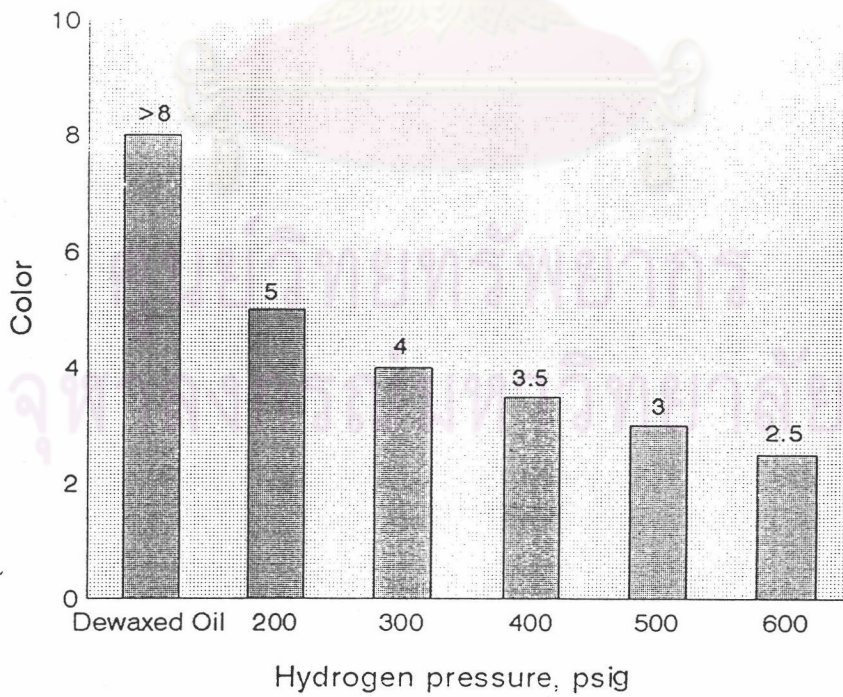

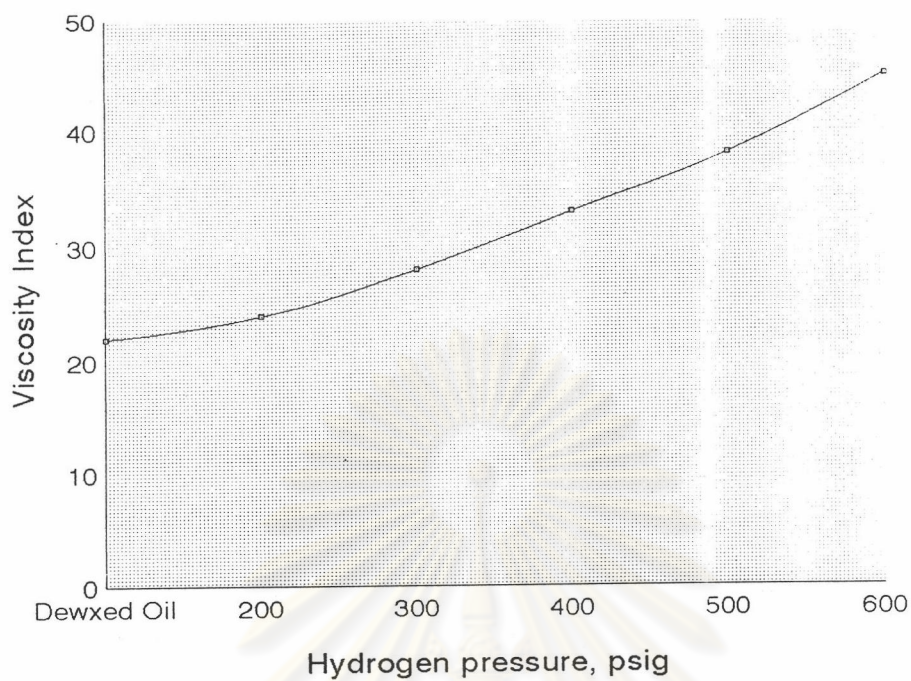**Figure 4.11** Effect of hydrogen pressure on color of desulfurized oil

Figure 4.12 Effect of hydrogen pressure on viscosity index of desulfurized oil
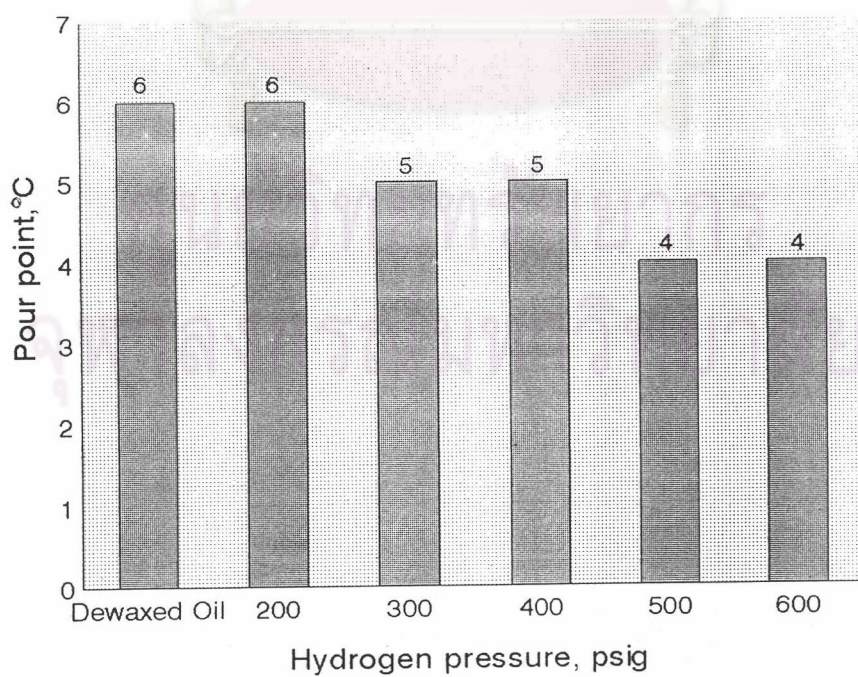

Figure 4.13 Effect of hydrogen pressure on pour point of desulfurized oil

The next parameter of interest was reaction time in which the reaction was performed with varying reaction times of 2, 4, 6, 8 and 10 hrs. The GC-MS analysis (Figure A7) and molecular weight distributions (Table A8) indicated that cracking increased when the reaction was performed for a longer time.

The Mo/Ni/Co catalyst was used and the reaction was operated at 400 °C and 600 psig. The results of these experiments are presented in Table A9. The sulfur content and physical properties were plotted against reaction time to give the curves shown in Figures 4.14, 4.15, 4.16 and 4.17.

The results from these experiments (with similar condition; 400 °C, 600 psig, Mo/Ni/Co catalyst) show that the sulfur content decreases rapidly from 0.338 to 0.017% in first 2 hrs when the experiments were performed at optimum amount of catalyst, temperature, and hydrogen pressure. After that, the sulfur content decreased slowly from the second hrs to the fourth hrs. The minimum sulfur content (less than 0.001% or 10 ppm) was achieved after the reaction was performed for 6 hrs and after this time the sulfur content remained unchanged. The physical properties (color, VI and pour point) of these reaction products also improved rapidly in the first two hours and improved slowly after the second hours. There was no significant experiment in the physical properties for reaction time longer than six hours. The results from Table A9 show that % yield of desulfurized oil was decreased when the reaction was operated at a longer time. These observations suggest the optimum reaction time, under these conditions, was 6 hrs.
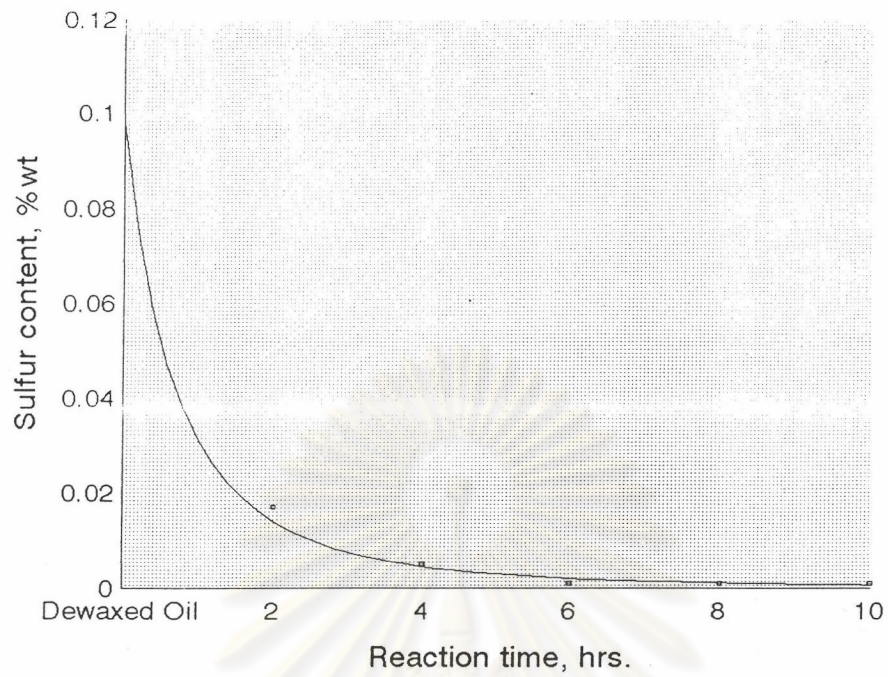
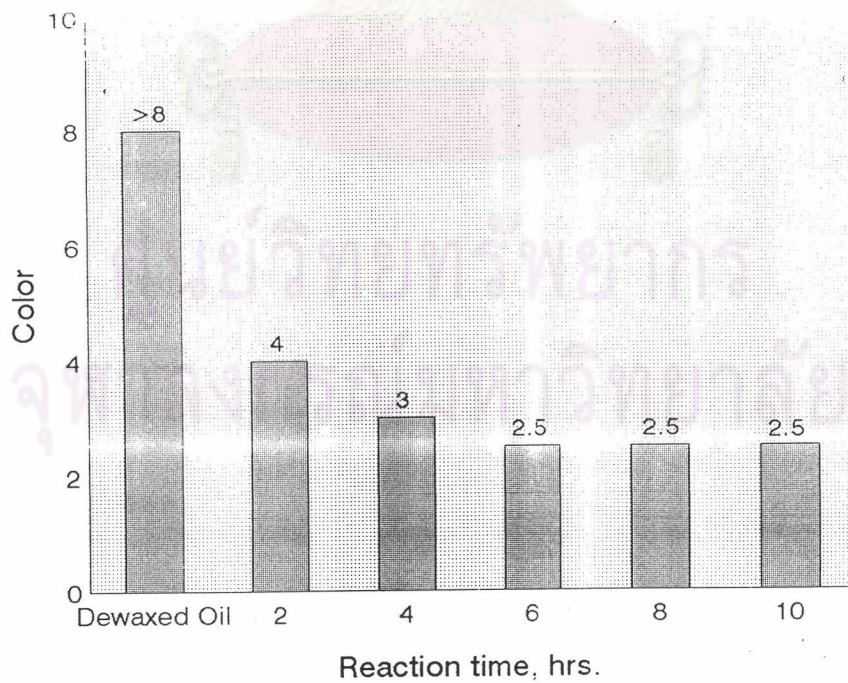**Figure 4.14** Effect of reaction time on sulfur content of desulfurized oil

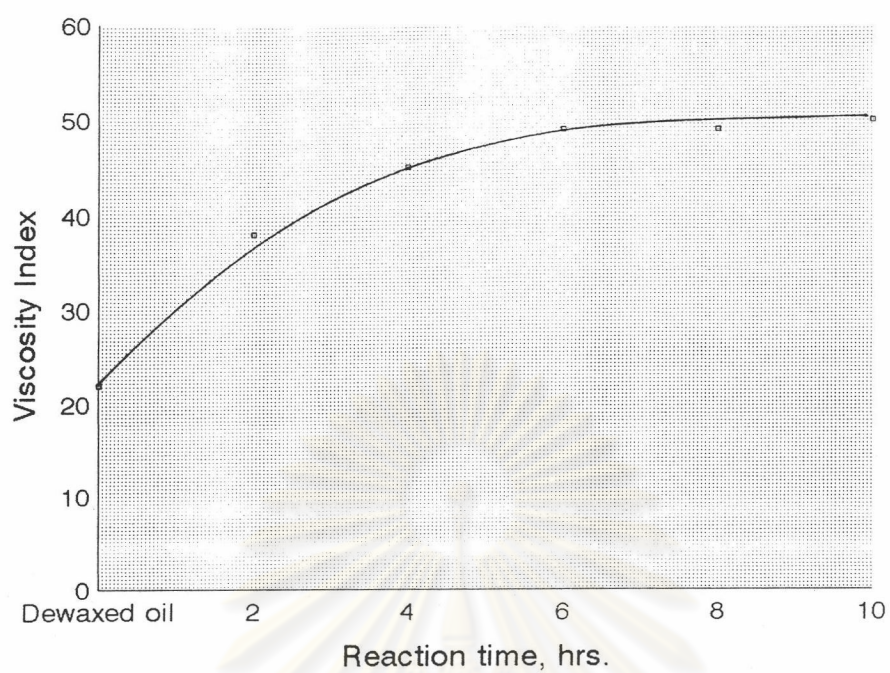**Figure 4.15** Effect of reaction time on color of desulfurized oil

Figure 4.16 Effect of reaction time on viscosity index of desulfurized oil
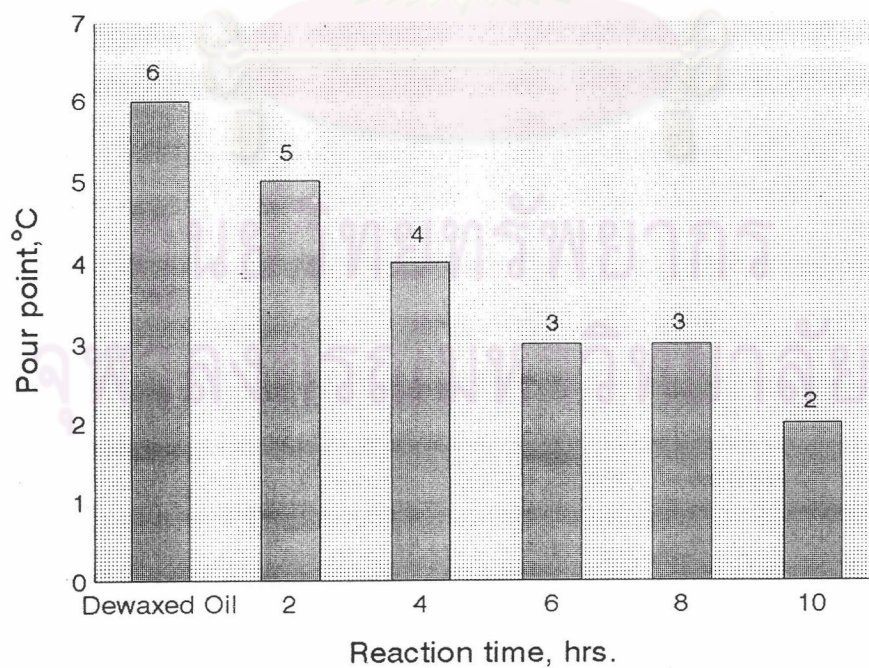

Figure 4.17 Effect of reaction time on pour point of desulfurized oil

The last parameter varied was catalyst concentration. The reaction was operated at the optimized condition (400 °C, 600 psig, and 6 hrs) with varying catalyst concentration of 1, 2, 3, 4 and 5 % by weight of oil. The GC-MS analysis in Figure A8 indicated that the molecular weight distribution (Table A10) remained unchanged when the amount of catalyst was varied. This observation shows that the extent of cracking is not dependent on catalyst quantity.

The physical and chemical results are presented in Table A11. The sulfur content and physical property changes are plotted against amount of catalyst used in the reaction in Figures 4.18, 4.19, 4.20 and 4.21. The results from these experiments show that color, VI, and pour point are scarcely changed when the amount of catalyst was increased. However, it was found that the maximum VI (49, in this case) was observed when the amount of catalyst was 4% by weight of oil. It was also found that there was no significant change in sulfur content when the amount of catalyst was decreased from 5% to 4%, but, the sulfur content was drastically increased when the amount of catalyst was decreased below 4%. Therefore, the preferred optimum catalyst concentration was about 4% by weight of oil.

In summary, the best catalyst and the optimum conditions (temperature, hydrogen pressure, reaction time and catalyst concentration) for hydrodesulfurization of dewaxed oil are Mo/Ni/Co catalyst (10% Mo, 5% Ni, and 5% Co), and 400 °C, 600 psig, 6 hrs, and 4% by weight of oil, respectively. After the dewaxed oil was treated in the above optimum condition, the sulfur content and physical properties (VI, color, and pour point) were less than 0.001%, 49, 2.5 and 3, respectively. The chemical properties (oxidation point, oxidative compound, aromatic carbon content, paraffinic carbon content and naphthenic carbon content) were 345 °C, 13.40%, 6.26%, 51.74% and 42.0%, respectively. The ^{13}C-NMR spectrum and thermogram are shown in Figure A9 and A10, respectively.
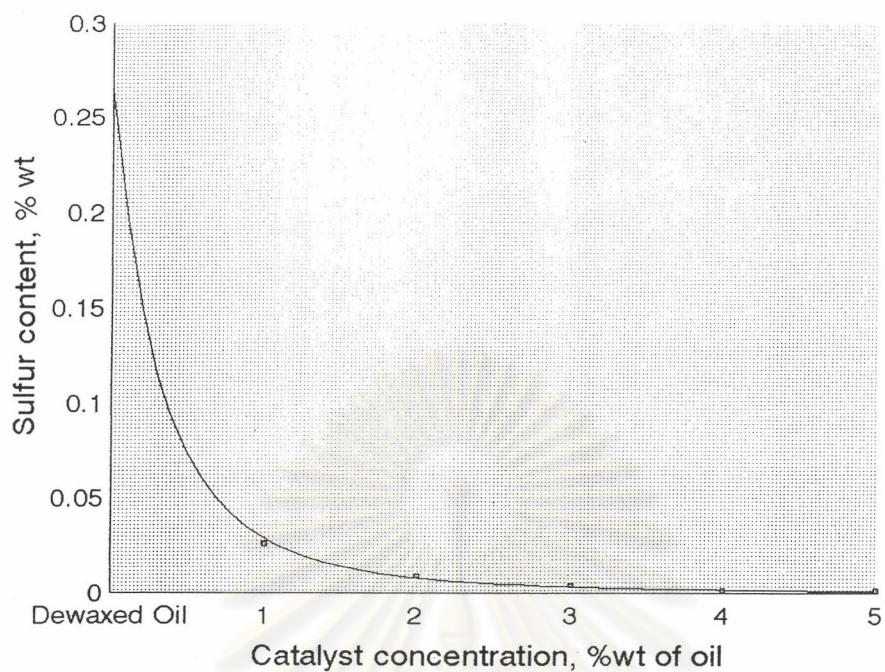
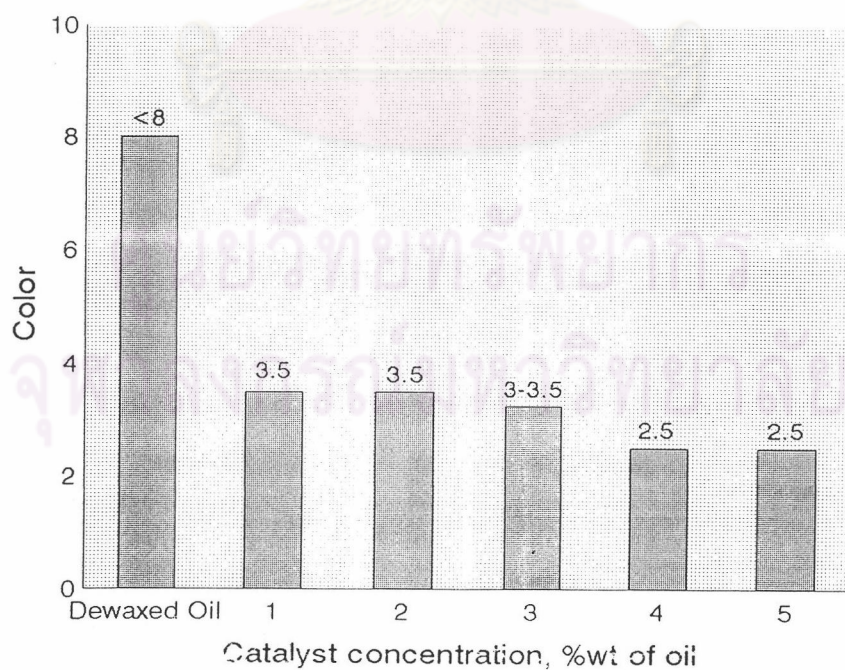**Figure 4.18** Effect of catalyst concentration on sulfur content of desulfurized oil

Figure 4.19 Effect of catalyst concentration on color of desulfurized oil
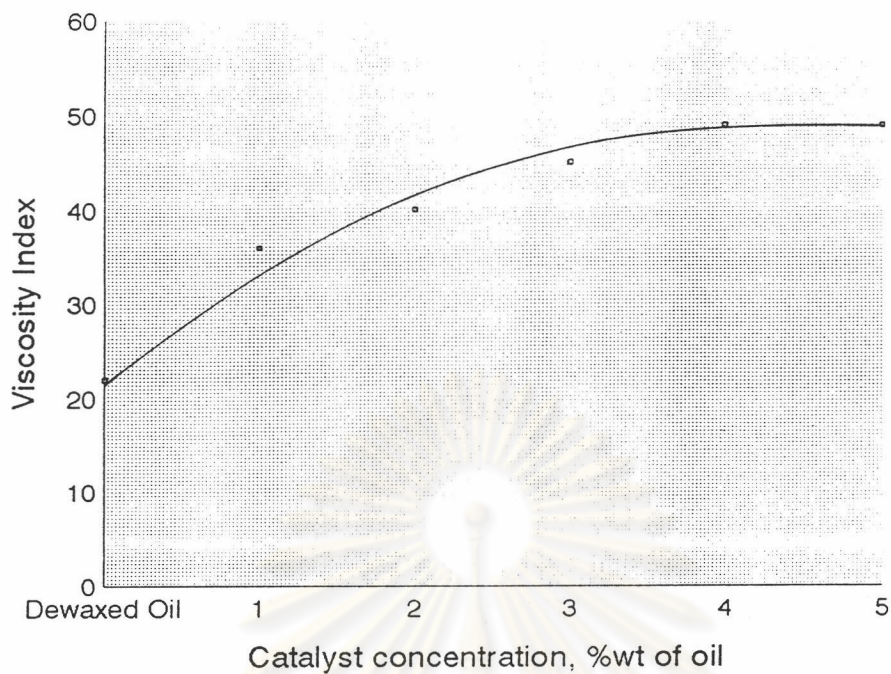
Figure 4.20 Effect of catalyst concentration on viscosity index of desulfurized oil
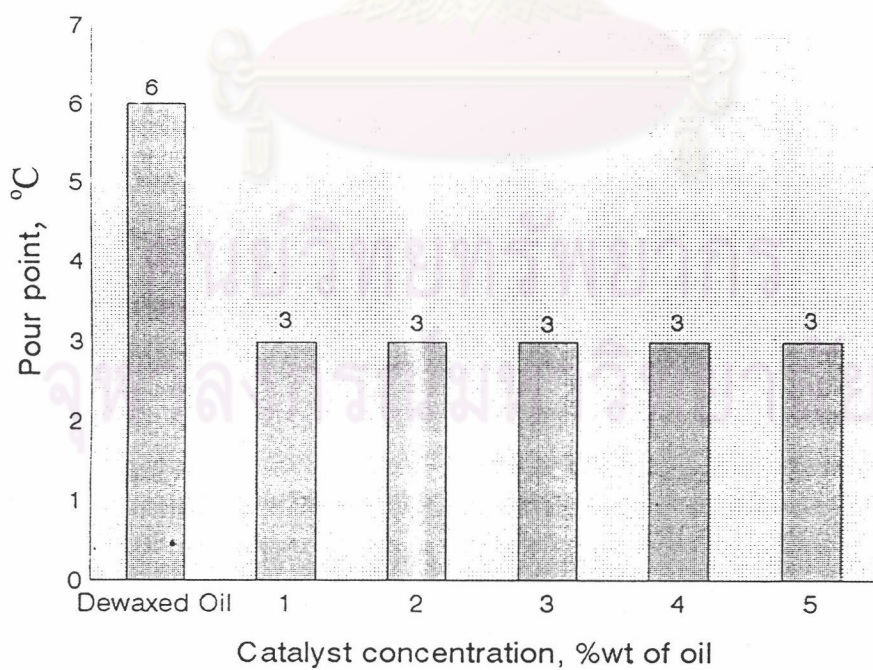

Figure 4.21 Effect of catalyst concentration on pour point of desulfurized oil

The two refining processes, dewaxing and hydrodesulfurization, improved the VI, pour point, color, sulfur content, and stability of the oil (Figure A3 and Figure A10), however, the desulfurized oil could not be used as lubricating base oil since its viscosity index was still quite low while the percentage of oxidative compounds and the pour point were still quite high. These properties of the desulfurized oil would be improved by hydroisomerization.

The goal of this study was to convert the paraffin wax into lube base oil, having low pour point and high VI. In this research, the desulfurized oil was isomerized with a prepared hydroisomerization catalyst containing 0.3% Pt and 0.5% F and having surface area of 184.68 m^2/g. It was demonstrated that the isomerization reaction was promoted by a few percent of fluoride containing in the catalyst [17-19]. The effectiveness of the catalyst on the hydroisomerization of desulfurized oil was studied by varying the condition parameters of temperature, hydrogen pressure, reaction time, and catalyst concentration.

The first parameter varied was reaction temperature, which was varied from 250 to 400 $^{\circ}$C in steps of 50 $^{\circ}$C. The isomerate was distilled under reduced pressure so as to remove cracked product (below 330 $^{\circ}$C) prior to the characterization. The results from GC-MS analysis (Figure A11) and Table A12 indicated that when the reaction was operated at higher temperature, the quantities of lower molecular weight components were increased. This result demonstrates that the cracking process is increased at higher temperature.

The results of these experiments are summarized in Table A13. The physical properties are plotted against temperature as illustrated in Figures 4.22, 4.23 and 4.24. These results show that the physical properties (color, VI, and pour point) are improved with increasing temperature. The VI was proportionated with elevated temperature. It was found that the improvement of VI increased rapidly in the temperature range from the beginning to 300 $^{\circ}$C. It

was also observed that when the reactions were performed at higher temperature, 350 and 400 $^{\circ}$C, the VI was slowly improved. The maximum VI (74) was obtained after the reaction was operated at 400 $^{\circ}$C.

The preferred optimum reaction temperature was 350 $^{\circ}$C in order to maximize the conversion of wax to oils, reduce a degree of random carbon to carbon cleavage typical of hydrocracking and minimize production of substantial amounts of lower boiling material.
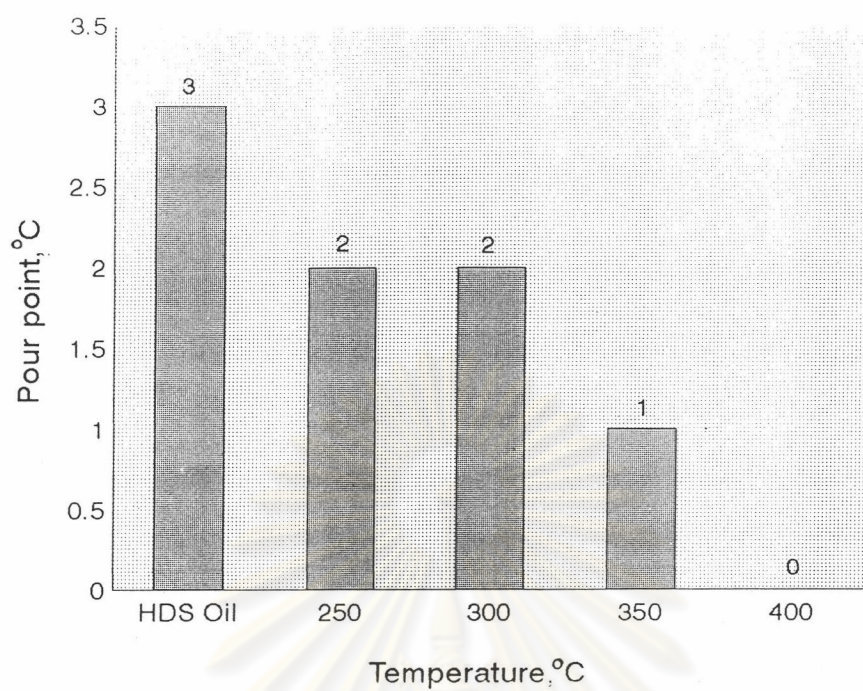
Figure 4.22 Effect of reaction temperature on pour point of isomerized oil
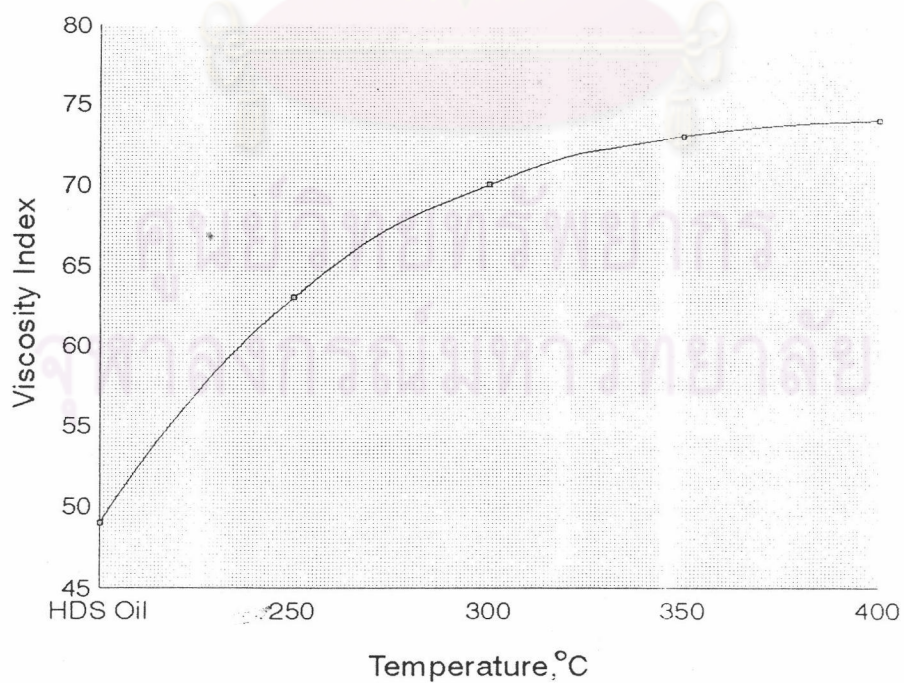

Figure 4.23 Effect of reaction temperature on viscosity index of isomerized oil
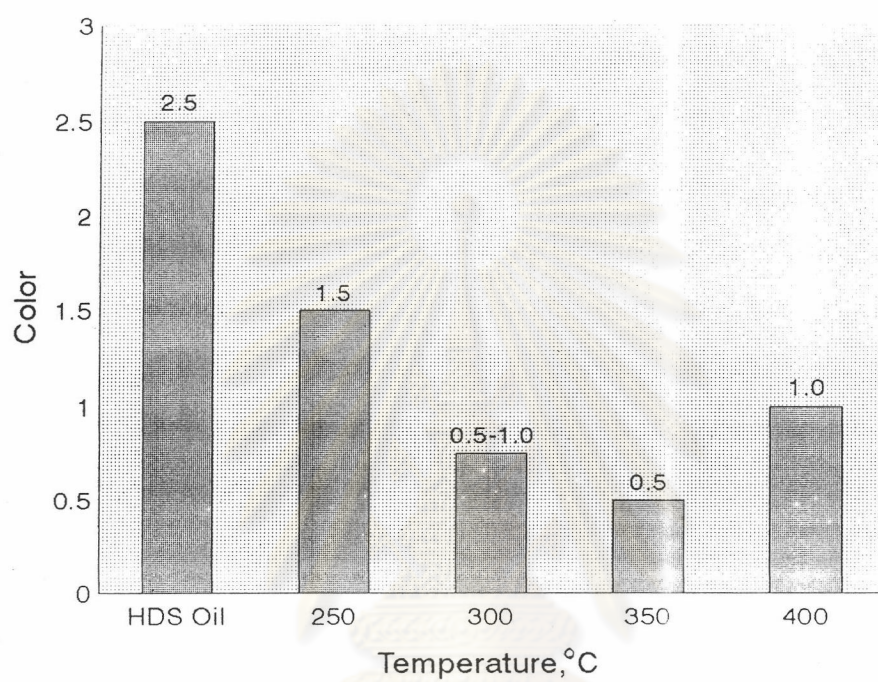
Figure 4.24 Effect of reaction temperature on color of isomerized oil

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The second important parameter studied was hydrogen pressure which was varied from 300 to 600 psig in steps of 100 psig. The molecular weight distributions of each experiments were observed by GC-MS and the results are illustrated in Figure A12 and the molecular weight distributions are summarized in Table A14. The results from GC-MS observation show that the cracking process does not depend on the hydrogen pressure variation from 300 to 600 psig.

The result of the experiments are presented in Table A15. The physical property changes are plotted against hydrogen pressure in Figures 4.25, 4.26 and 4.27. The experimental results in Table A15 show that the VI was scarcely changed when increasing the hydrogen pressure. However, it was found that the maximum VI (73, in this case) was obtained when the hydrogen pressure was 600 psig. Figure 4.27 show that color of products remains the same at 0.5 after the reaction was operated at 400 psig. At hydrogen pressure above 500 psig, the pour point also remained constant. The cracking reaction and percentage yield of the isomerized lube cut did not change significantly as a function of hydrogen pressure. Therefore, these observations suggested that the optimum hydrogen pressure at fixed parameter (350 °C) was 600 psig.
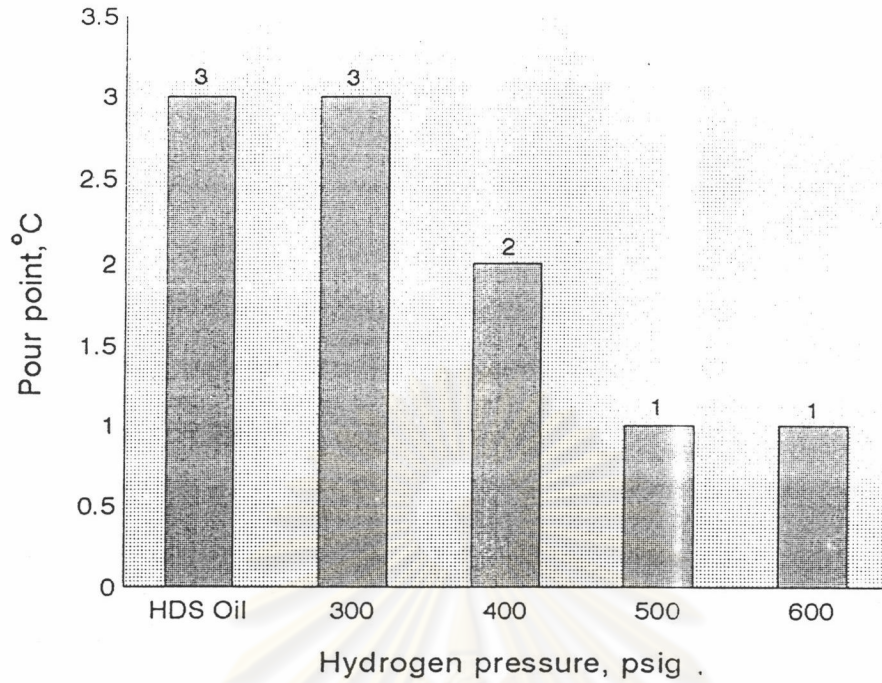
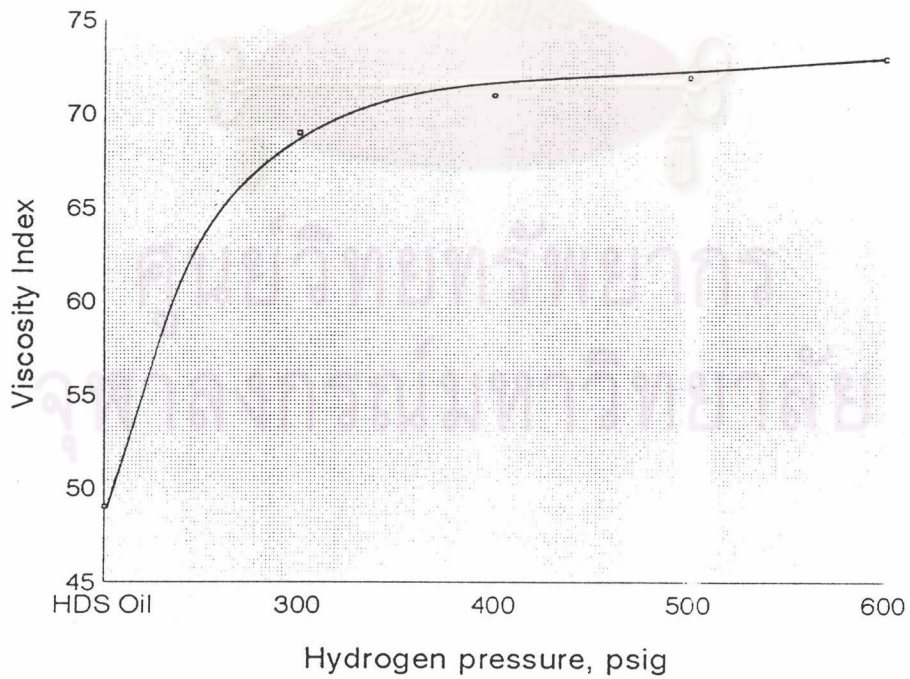**Figure 4.25** Effect of hydrogen pressure on pour point of isomerized oil

Figure 4.26 Effect of hydrogen pressure on viscosity index of isomerized oil
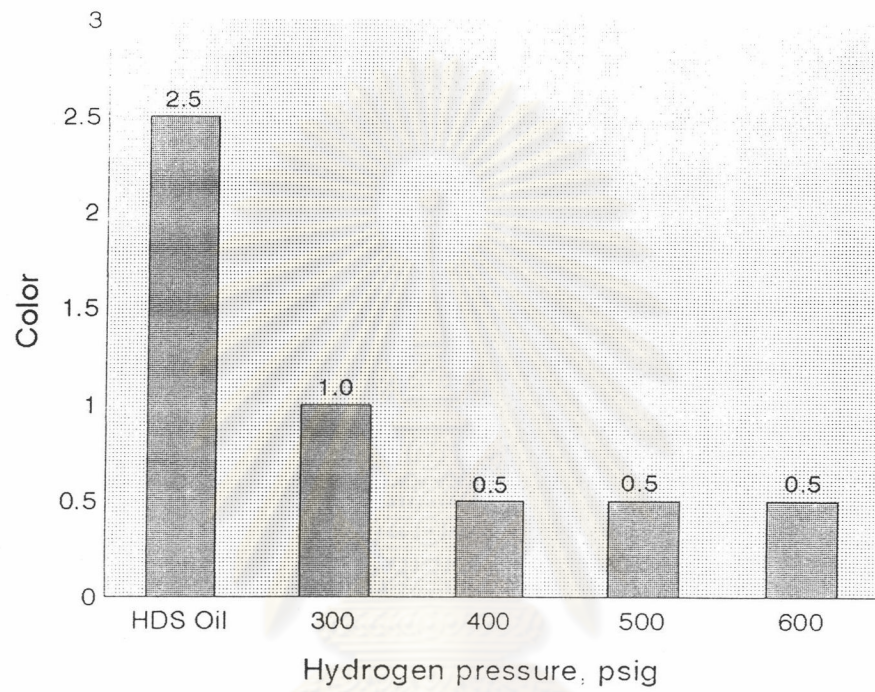
Figure 4.27 Effect of hydrogen pressure on color of isomerized oil

The next parameter of interest was reaction time which was studied at 4, 8, 12 and 16 hrs. The results of GC-MS analysis (Figure A13) indicate that cracking process was increased and the molecular weight distribution was changed (Table A16) when the reaction was performed with the longer time.

The results of these experiments are presented in Table A17. The physical changes are plotted against reaction time as illustrated in Figure 4.28, 4.29 and 4.30. This experiments (with the same condition; 350 $^{\circ}$C and 600 psig) show that the viscosity index increased with increasing reaction time. This result also indicated that the viscosity index remained constant after the reaction was operated for 12 hrs. Other physical properties (color and pour point) of these reaction products were lowest at 12 hrs and 16 hrs. Therefore, these observation suggested that the optimum reaction time at the same said parameter was 12 hrs.
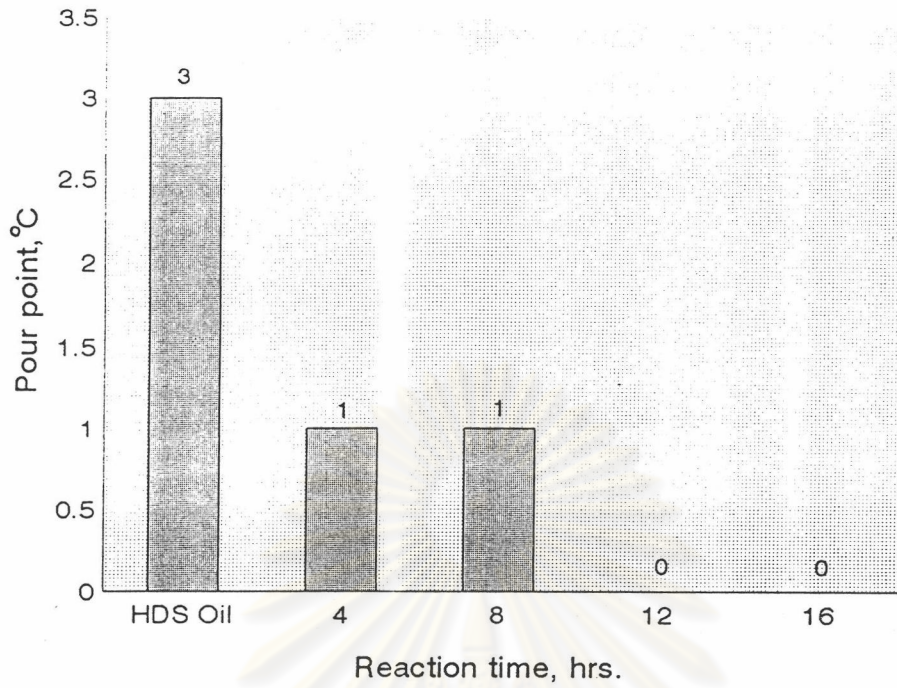
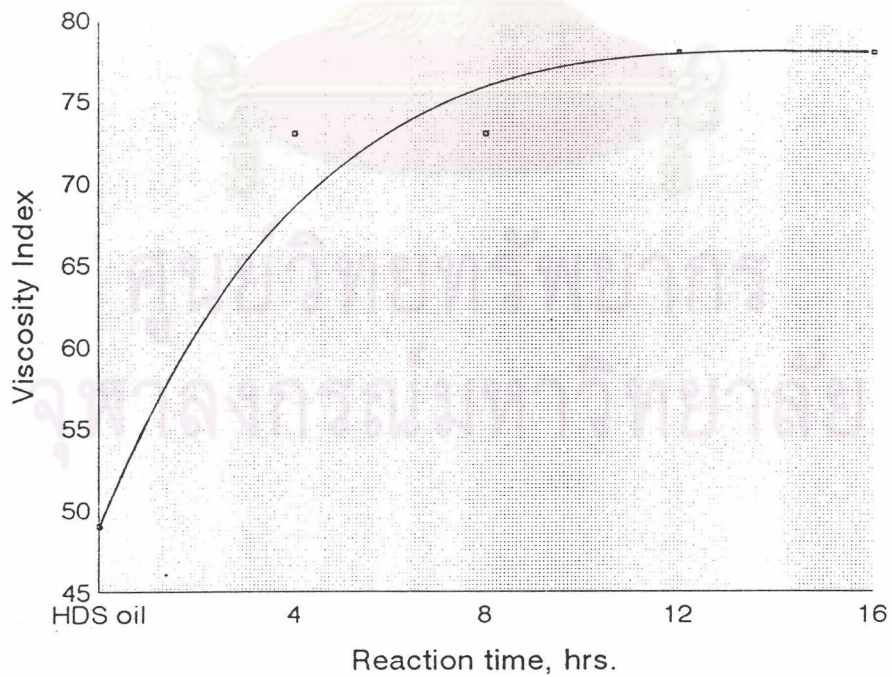**Figure 4.28** Effect of reaction time on pour point of isomerized oil

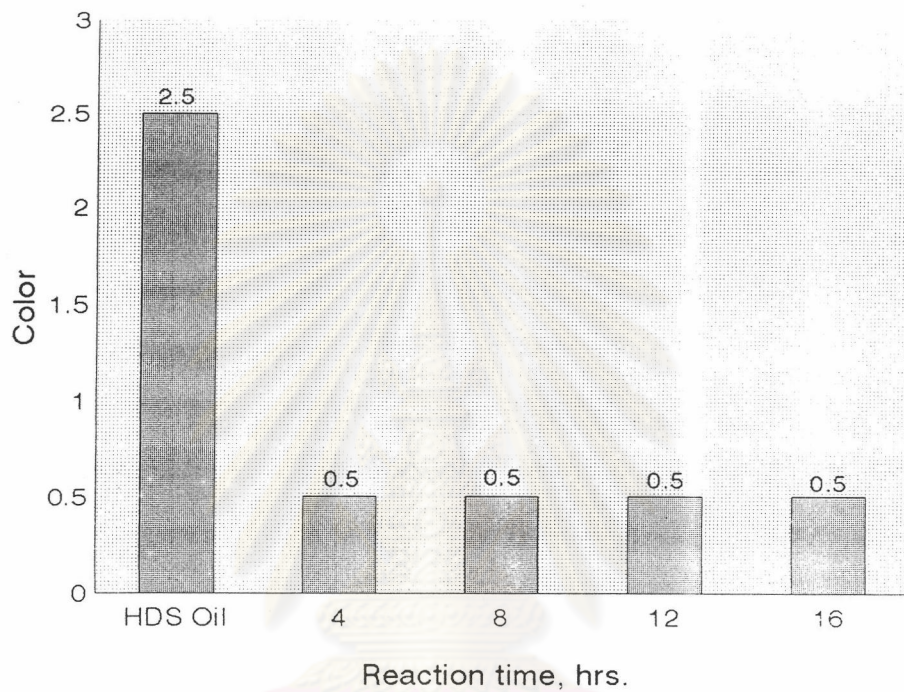**Figure 4.29** Effect of reaction time on viscosity index of isomerized oil

Figure 4.30 Effect of reaction time on color of isomerized oil

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The last parameter varied was the concentation of catalyst, which was studied at 2, 4, 6 and 8% by weight of oil. The GC-MS analysis as illustrated (Figure A14 and Table A18) indicate that the molecular weight distribution remaines unchanged when the amount of catalyst is varied. This result shows that catalyst concentration in the range of 2-8% by weight of oil had no signifiant cracking.

The results of these experiments are shown in Table A19. The physical properties are plotted against catalyst concentration as shown in Figures 4.31, 4.32 and 4.33. From this experiment, it is clear that the VI of isomerate was improved when the catalyst concentration is increased. As could be seen in Figure 4.32 that the VI was increased from 49 to 78 at 6% catalyst and to 79 at 8% catalyst. From the data in Table A19, other results had little or no change when increasing the catalyst concentration from 2-8% by weight of oil. The best color and pour point were 0.5 and 0, respectively.

According to the former result, it was found that the properties of isomerate which performed at 8% of catalyst concentration was the best. However, the decision was made to select the 6% catalyst as the optimum catalyst concentration due to the higher yield.

In summary, the best conditions of temperature, hydrogen pressure, reaction time, and catalyst concentration for hydroisomerization of desulfurized oil using 0.3% Pt and 0.5% F on alumina as catalyst were 350 ^{0}C, 600 psig, 12 hrs, and 6% by weight of oil, respectively. After desulfurized oil was treated under the above optimum conditions, color, sulfur content, pour point, viscosity index, oxidation point, and oxidative compounds of the isomerate were 0.5, less than 0.001%, 0 ^{0}C, 78, 330 ^{0}C, and 9.47%, respectively. The aromatic, paraffinic, and naphthenic content were 2.66%, 89.67%, and 7.67 % by mole atom of carbon, respectively.
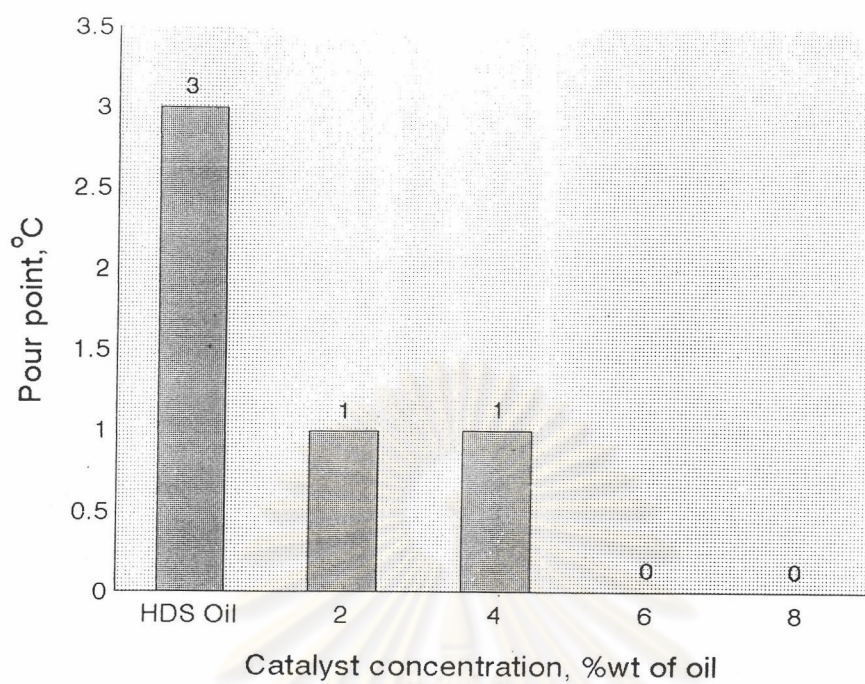
Figure 4.31 Effect of catalyst concentration on pour point of isomerized oil
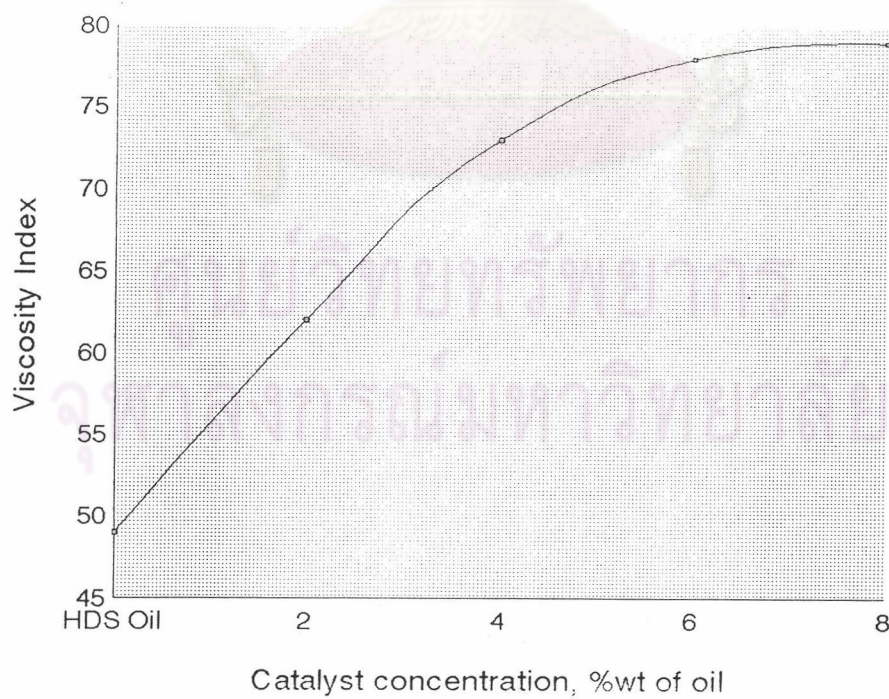

Figure 4.32 Effect of catalyst concentration on viscosity index of isomerized oil
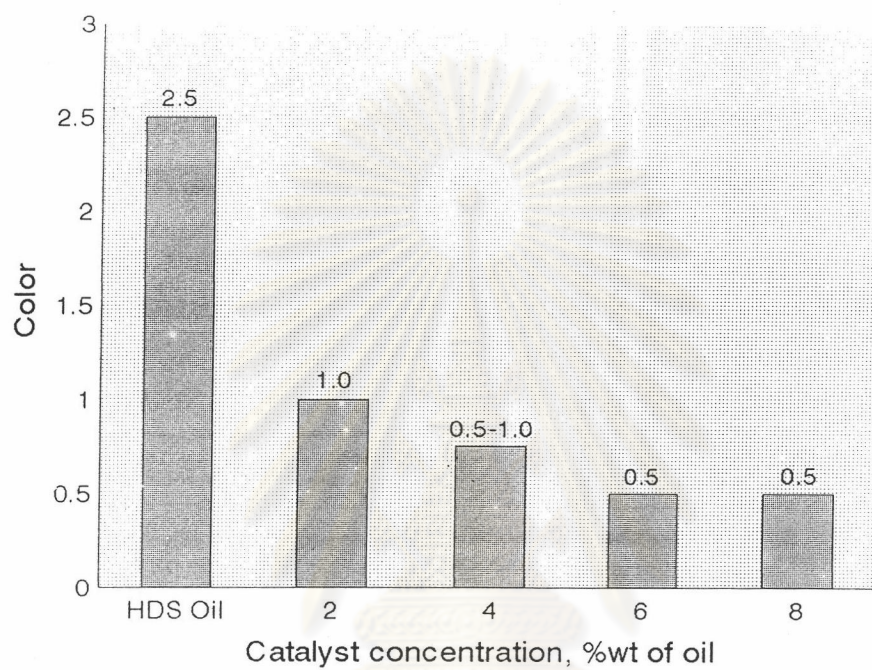
Figure 4.33 Effect of catalyst concentration on color of isomerized oil

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The properties of heavy distillate, dewaxed oil, desulfurized oil and isomerized oil at the optimum conditions for each processing step are summarized in Table 4.3. These oils are shown in Figure 4.34. The ^{13}C-NMR spectrum and thermooxidation stability curve for the isomerized oil are shown in Figures A15 and A16, respectively.

Table 4.3 The properties of heavy distillate, dewaxed oil, desulfurized oil and isomerized oil

Properties	Fang heavy distillate (HD)	Dewaxed oil	Desulfurized oil	Isomerized oil
Color	>8	>8	2.5	0.5
Pour point (^{o}C)	51	6	4	0
Kinematic Viscosity				
@ 40°C, cSt	-	159.69	81.44	54.78
@ 100°C, cSt	6.00	11.10	8.06	6.98
Viscosity Index (VI)	-	22	49	78
Sulfur, % wt	0.304	0.338	< 0.001	< 0.001
Component				
%C_a	-	8.54	6.26	2.66
%C_n	-	18.67	42.00	7.67
%C_p	-	72.79	51.74	89.67
Flash point (°C)	-	236	245	245
Oxidation point (°C)	-	350	345	340
Oxidative compound (% wt)	-	18.09	13.40	9.47
% yield of lube cut	-	46.33	91.04	81.49

Figure 4.34 Heavy distillate, dewaxed oil, desulfurized oil distillate cut, and
isomerized oil at the optimum conditions for each processing step

From this study, there were several limitations of the experimental conditions which could not make lubricating base oil with better properties than this. First of all, the pressure reactor used in this experiment was a batch type reactor with the working pressure of 600 psig and temperature of 400 °C. Therefore, the pressure and temperature of the reaction could not go beyond these limits. If the pressure and temperature could go beyond these limits, it was likely that we could see more isomerization of waxes. Secondly, the continuous reactor should be implemented in order to understand more of the reaction under continuous condition which should be useful in scale up in the later stage. Thirdly, different types of catalysts should be investicated to select the best one.