

CHAPTER IV

RESULTS AND DISCUSSION

Dewaxing Process

Light distillate which was obtained from Fang Refinery was a solid at room temperature because of high quantities of wax content. The pour point of this distillate was about 50°C. It is necessary to remove wax to obtain low pour point oil. Methyl ethyl ketone was widely used as a solvent for dewaxing process because of its low wax solubility at dewaxing temperature and sufficiently low boiling point to facilitate removal from dewaxed oil. From the result of dewaxing, this distillate contained 47.7% by weight of wax and 52.3% by weight of oil as shown in Figure 4.1. The oil fraction was black viscous liquid and slack wax was a white solid. The physical and chemical properties of dewaxed oil are shown in Table 4.1.

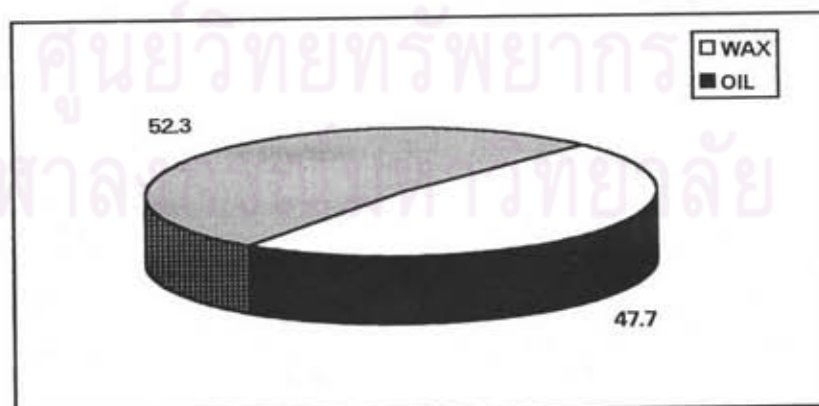


Figure 4.1 The percentages of wax and dewaxed oil from dewaxing process.

Table 4.1 The properties of Fang light distillate and dewaxed oil.

Properties	Fang light distillate	Dewaxed oil
Color ,Visual	> 8	> 8
Saybolt	< -16	< -16
Pour Point (°C)	50	4
API	36.7	32.5
Viscosity ,40°C (cSt)	-	28.13
100°C (cSt)	3.31	4.62
Viscosity Index	-	67.80
Sulfur Content (% wt)	-	0.309
% Ca	-	7.9
% Cp	-	65.9
% Cn	-	26.2
UV absorbance of DMSO*		
extract at		
280-400 nm	-	> 4.0
Direct UV absorptivity at		(all wavelengths)
275 nm	-	2.811
295 nm	-	2.682
300 nm	-	2.716
310 nm	-	2.784
320 nm	-	2.964

* DMSO is dimethyl sulfoxide

Table 4.2 The straight chain alkanes in light distillate and dewaxed oil.

A number of carbon	Molecular weight	Retention time (min)		
		Standard	Light distillate	Dewaxed oil
C13	184	6.545		
C14	198	8.105		
C15	212	9.645		9.621
C16	226	11.146		11.101
C17	240	12.526		12.521
C18	254	13.887	13.656	13.881
C19	268	15.167	14.939	15.181
C20	282	-	16.186	16.421
C21	296	17.865	17.598	17.861
C22	310	19.505	19.185	19.481
C23	324	21.411	21.289	21.282
C24	338	23.251	22.942	
C25	352	25.255	24.980	
C26	366	27.397	27.010	
C27	380	29.480	29.182	
C28	394	31.520	31.362	
C29	408	33.622	33.331	
C30	422	35.663	35.342	
C31	436	37.684		
C32	450	39.644		
C33	464	41.564		

The ^{13}C -NMR spectrum in Figure A1 showed three types of carbon present in dewaxed oil. Following ASTM D 2140, the chemical shifts from 110 to 160 ppm were aromatic carbons having integrated area of 9.817, the chemical shifts from 0 to 25 and resolved chemical shifts from 25-60 were paraffinic carbons having total integrated area of 83.210, and beside chemical shifts of paraffinic carbons from 25 to 60 was naphthenic carbons having integrated area of 33.026. This dewaxed oil contained 7.9 % by mole atom of aromatic carbon, 65.9 % by mole atom of paraffinic carbon, and 26.2 % by mole atom of naphthenic carbon.

The GC-MS chromatograms in Figure A2 showed components in light distillate and dewaxed oil. The retention times and/or mass spectra of each components were compared with the retention times of straight chain alkanes standard compounds (C13-C33) and mass spectra of standard compounds in library program. The retention times of straight chain alkanes in standard compounds, Fang light distillate and dewaxed oil are shown in Table 4.2. Most of the components of dewaxed oil in a retention time range from 9.210 to 21.281 minutes were straight chain alkanes between pentadecane and Docosane (C13-C22) and five main components were heptadecane, octadecane, nonadecane, eicosane, and docosane (C17-C21) which showed the retention times at 12.521, 13.881, 15.181, 16.421, and 17.841 minutes, respectively. But the retention times above 19.481 minutes were too difficult to identify actual components because of no clear separation of these components.

In Figure A3, the UV absorbances of DMSO extract of dewaxed at all wavelengths from 270 to 550 were more than 4.0, and direct absorptivities of dewaxed oil in iso-octane at all wavelengths from 275 to 320 nm were more than 2.6. These illustrated that dewaxed oil contained a large amount of impurities. Accordingly dewaxed oil contained 0.305% by weight of

sulfur content and 7.9 % by mole atom of aromatic carbon. (The details about UV absorption would explain in the results of hydrogenation stage in the page of 77).

Generally, after dewaxing, a pour point of dewaxed oil should be below about -15°C . [2] Because of the limit of cooling apparatus, the pour point of this dewaxed oil was 4°C .

It can be seen that dewaxing process only improved pour point of dewaxed oil. Aromatic compounds were not removed. Thus dewaxed oil was treated in the hydrodesulfurization process to remove sulfur.

Hydrodesulfurization Stage

The most important objective of this stage is to remove sulfur to give oil containing less than 0.001 % by weight of sulfur to prevent poisoning on platinum catalyst in hydrogenation stage. Also nitrogen compounds was eliminated. But it cannot detect a small amount of nitrogen compounds in this dewaxed oil..

Sulfur compounds in petroleum products are mainly aromatic compounds. [13] After they are removed to produce aromatic hydrocarbons, sulfur content in oil is decreased and its color will be lighter. This shows that the rate of hydrodesulfurization increases.

In conclusion, the best catalyst and the best parameters or conditions for hydrodesulfurization will improve the properties of hydrodesulfurized oil as follows:

1) low sulfur content- It is the most important property of hydrodesulfurized oil.

2) light color- This shows that most of aromatic compounds were removed from this stage.

3) low cracking products- Cracking reaction results in low yield of hydrodesulfurized oil and many peaks of low boiling point products in the GC-MS chromatogram.

The first study was to determine the suitable catalyst for hydrodesulfurization. Dewaxed oil was treated with hydrogen in the presence of various catalysts such as Raney nickel, NiMo/Al₂O₃, NiW/Al₂O₃ and prepared NiMoCo/Al₂O₃. The dewaxed oil was subjected to various catalysts at reaction temperature of 350°C, hydrogen pressure of 500 Psig, reaction time of 3 hours, agitation speed of 500 rpm, and catalyst concentration of 5% by weight of oil.

The GC-MS chromatograms of these hydrodesulfurized oils are shown in Figure A4. The results of hydrodesulfurization are shown in Table 4.3. The effect of catalyst type on color, sulfur content and percent yield of hydrodesulfurized oil are presented in Figure 4.2 to 4.4, respectively.

Table 4.3 The properties of hydrodesulfurized oils at various catalysts: reaction temperature 350°C, hydrogen pressure 500 Psig, reaction time 3 hours, catalyst concentration 5% by weight of oil, and agitation speed 500 rpm.

Properties	Dewaxed oil	Raney nickel	NiMo/Al ₂ O ₃	NiMoCo/Al ₂ O ₃	NiW/Al ₂ O ₃
Sulfur, %wt	0.309	0.256	0.201	0.121	0.116
Color, visual	> 8	4.5	4.0	3.0	3.0
% yield (> 330°C)		82.1	96.0	95.4	96.3

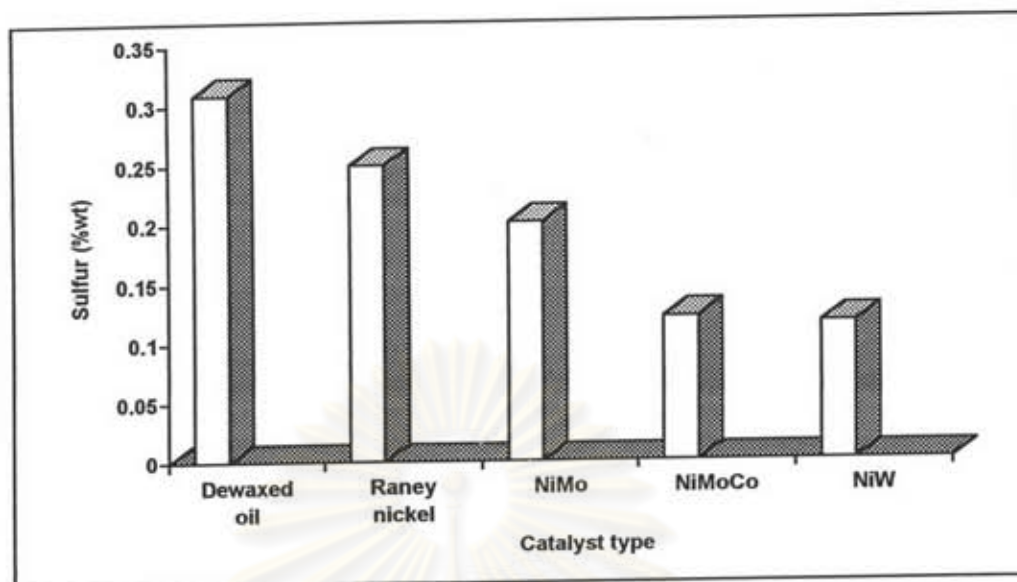


Figure 4.2 Effect of catalyst type on sulfur content of hydrodesulfurized oil.

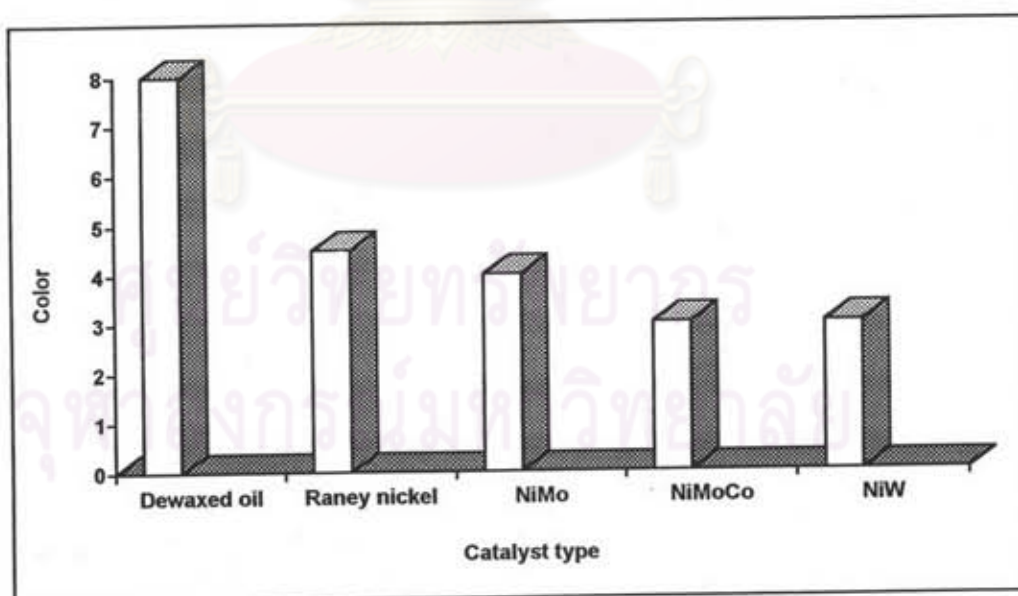


Figure 4.3 Effect of catalyst type on color of hydrodesulfurized oil.

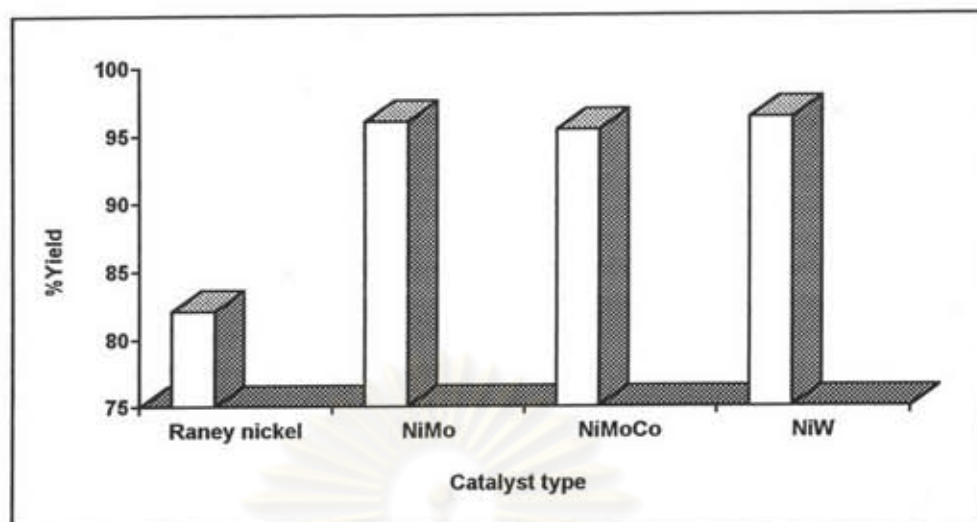


Figure 4.4 Effect of catalyst type on percent yield of hydrodesulfurized oil.

From the experiment, when Raney nickel was used as catalyst, the color of hydrodesulfurized oil was darkest and sulfur content was still high or only 17.15% by weight of sulfur of original sulfur were eliminated. The percent yield of hydrodesulfurized oil was lowest because of cracking reaction, and many low molecular weight or low boiling point components were observed in the GC-MS chromatogram of this oil in Figure A4. Thus Raney nickel was not a suitable catalyst for hydrodesulfurization stage. In comparison of treating with NiMo/Al₂O₃ and prepared NiMoCo/Al₂O₃ catalyst, the hydrodesulfurized oil performed with the prepared catalyst had better color, and contained lower sulfur compounds. Thus NiMoCo/Al₂O₃ was better the hydrodesulfurization catalyst than NiMo/Al₂O₃. From the result of using NiW/Al₂O₃ as a catalyst, the sulfur content of hydrodesulfurized oil was 0.116% by weight, which was slightly different from using NiMoCo/Al₂O₃ as a catalyst (0.121% by weight). This indicated that NiW/Al₂O₃ was as the good hydrodesulfurization catalyst as NiMoCo/Al₂O₃.

From this study, it could be seen that the prepared NiMoCo/Al₂O₃ catalyst exhibited more superior performance for hydrodesulfurization than NiMo/Al₂O₃ and Raney nickel catalysts, but was similar to NiW/Al₂O₃ catalyst. However, tungsten is more expensive than cobalt and molybdenum. Therefore, in this research, the prepared NiMoCo/Al₂O₃ catalyst was chosen as a suitable catalyst for the hydrodesulfurization stage.

This catalyst was optimized for the hydrodesulfurization stage by varying parameters as follows: reaction temperature, hydrogen pressure, catalyst concentration, and reaction time while fixing the percentages of molybdenum, nickel, and cobalt in this prepared catalyst.

The reaction temperatures were varied between 250°C and 400°C. The dewaxed oil was operated under hydrogen pressure of 500 Psig, reaction time of 3 hours, and catalyst concentration of 5% by weight of oil. The temperatures were operated at 250, 300, 350, and 400°C. When the temperature increased, the total pressure in reactor also increased to 820,950, 1010, and 1105 Psig, respectively.

The GC-MS chromatograms of these hydrodesulfurized oils are shown in Figure A5. The results of hydrodesulfurization are shown in Table 4.4. The effect of reaction temperature on color, sulfur content and percent yield of hydrodesulfurized oil are presented in Figure 4.5 to 4.7, respectively.

Table 4.4 The properties of hydrodesulfurized oils at various reaction temperatures: hydrogen pressure 500 Psig, reaction time 3 hours, catalyst concentration of 5% by weight of oil, and agitation speed 500 rpm.

Properties	Dewaxed oil	Reaction temperature (°C)			
		250	300	350	400
Sulfur, %wt	0.305	0.278	0.202	0.121	0.108
Color, visual	> 8	> 8	4.0	3.0	2.5
% yield (> 330°C)		98.3	96.2	95.4	85.7

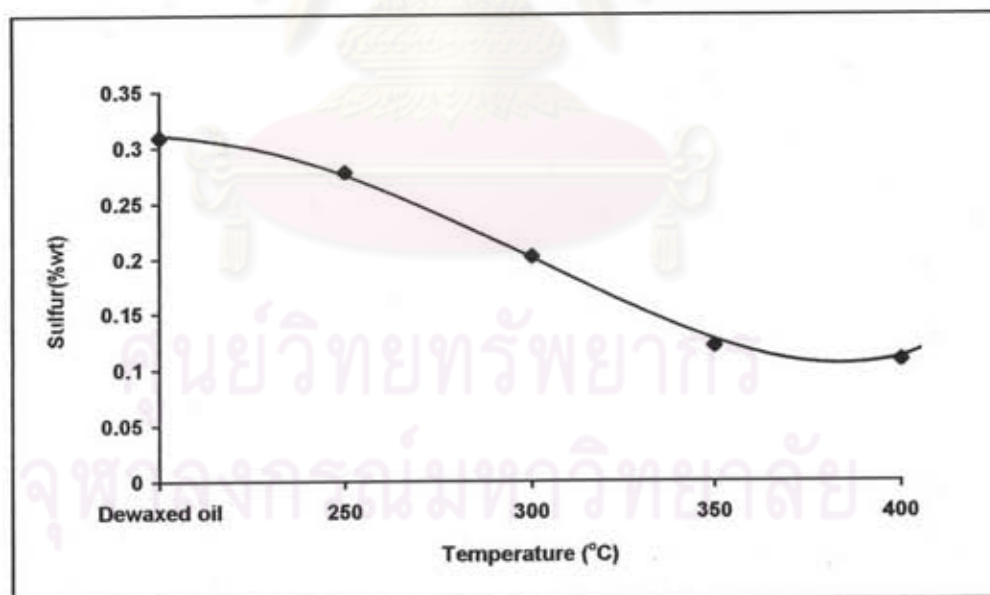


Figure 4.5 Effect of reaction temperature on sulfur content of hydrodesulfurized oil.

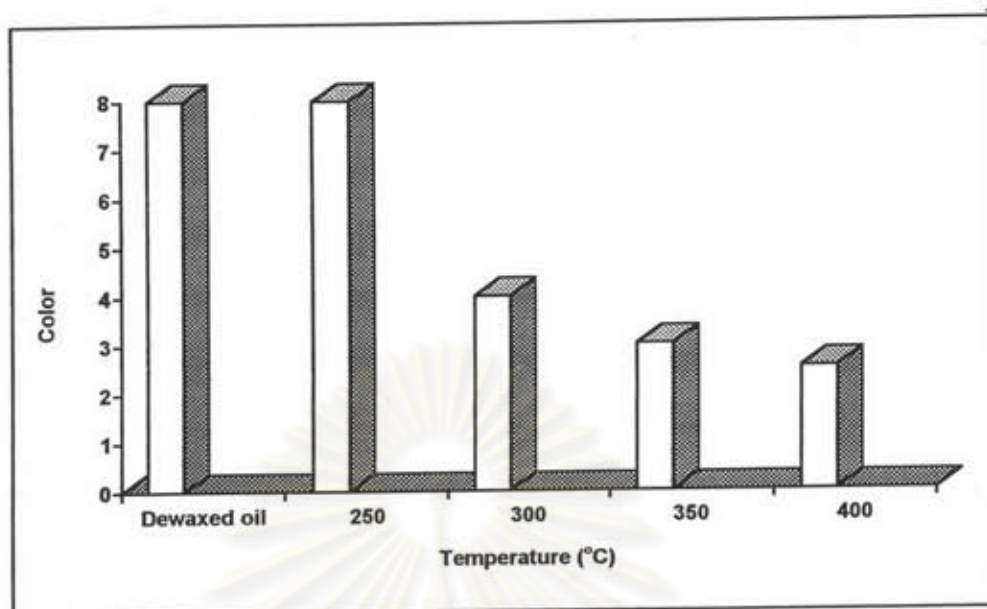


Figure 4.6 Effect of reaction temperature on color of hydrodesulfurized oil.

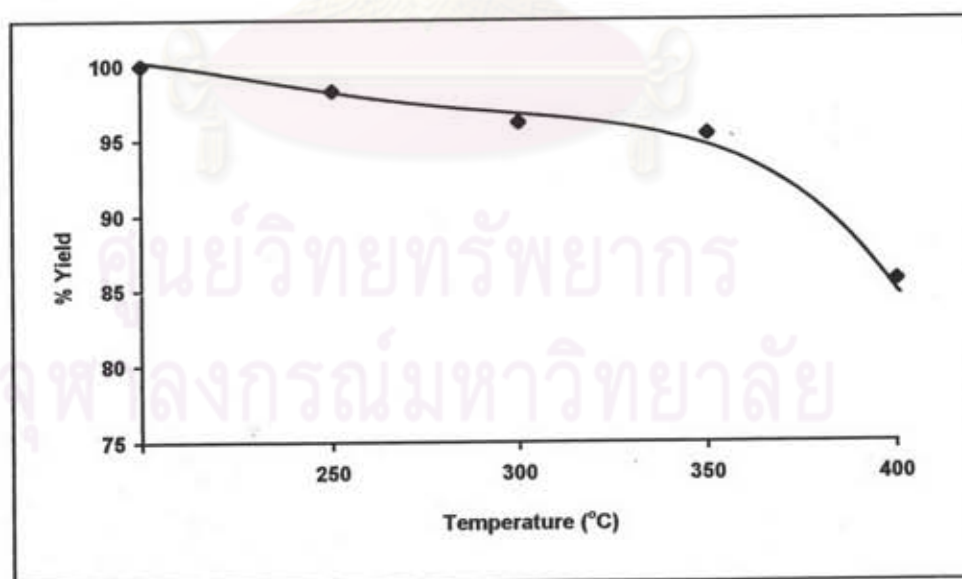


Figure 4.7 Effect of reaction temperature on percent yield of hydrodesulfurized oil.

From the results, when the reaction temperature was increased, the sulfur content, the color and percent yield of hydrodesulfurized oil were proportionally decreased. The sulfur content was decreased from 0.305 to 0.278, 0.202, 0.121, and 0.108% by weight, respectively, while the reaction temperatures were operated at 250, 300, 350, and 400°C. These showed that the effect of increasing reaction temperature was to increase the rate of hydrodesulfurization reaction. When reaction was operated at 250°C, a small amount of sulfur compounds were removed. Also the color of hydrodesulfurized oil was as dark as dewaxed oil. These indicated that the rate of hydrodesulfurization reaction was very low at 250°C. On the other hand at 400°C the yield was lowest in the range of these studied temperatures and there were many low boiling point products observed from peaks of these components at the retention times below 11.101 minutes in the GC-MS chromatogram in Figure A5. These components were straight and branch alkanes between octane and hexadecane (C8-C16). These were the result of thermal cracking at high temperature. The sulfur content in hydrodesulfurized oil operated at 300°C was higher and its color was darker than hydrodesulfurized oil operated at 350°C. The GC-MS chromatograms of hydrodesulfurized oils performed at 250°C, 300°C, and 350°C (Figure A5) were slightly different. Although hydrodesulfurized oil operated at 400°C would contain lower sulfur and has better color than that operated at 350°C, the temperature of 350°C was chosen as the optimum reaction temperature for hydrodesulfurization stage because of thermal cracking at 400°C

The third concerned variable parameter was the pressure of the process which was controlled by the hydrogen pressure. Dewaxed oil was carried out at reaction temperature of 350°C, reaction time of 3 hours, and

catalyst concentration of 5% by weight of oil. The hydrogen pressure was varied from 300, 400, 500, and 600 Psig.

The GC-MS chromatograms of these hydrodesulfurized oils are shown in Figure A6. The results of hydrodesulfurization are shown in Table 4.5. The effect of hydrogen pressure on color, sulfur content and percent yield of hydrodesulfurized oil are presented in Figure 4.8 to 4.10, respectively.

Table 4.5 The properties of hydrodesulfurized oils at various hydrogen pressures: reaction temperature 350°C, reaction time 3 hours, catalyst concentration 5% by weight of oil, and agitation speed 500 rpm.

Properties	Dewaxed oil	Hydrogen pressure (Psig)			
		300	400	500	600
Sulfur , %wt	0.305	0.201	0.159	0.121	0.101
Color , visual	>8.0	4.0	3.5	3.0	2.5
% yield (> 330°C)		96.3	95.8	95.4	94.1

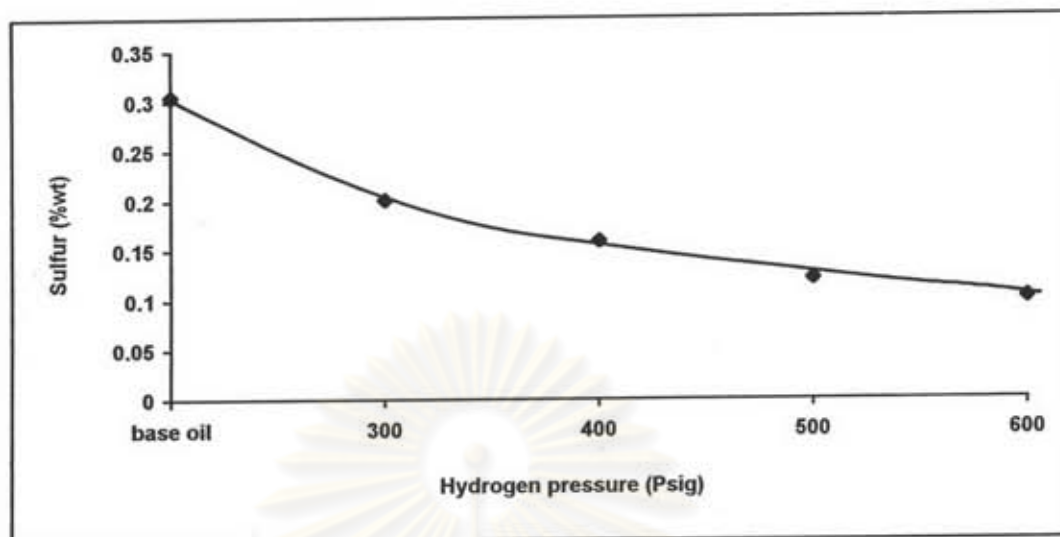


Figure 4.8 Effect of hydrogen pressure on sulfur content of hydrodesulfurized oil.

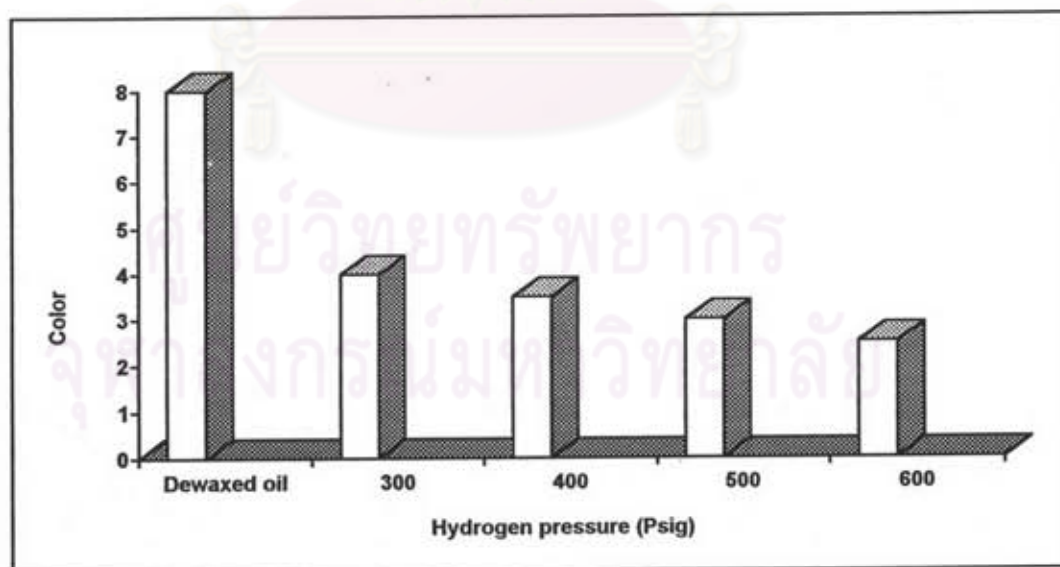


Figure 4.9 Effect of hydrogen pressure on color of hydrodesulfurized oil.

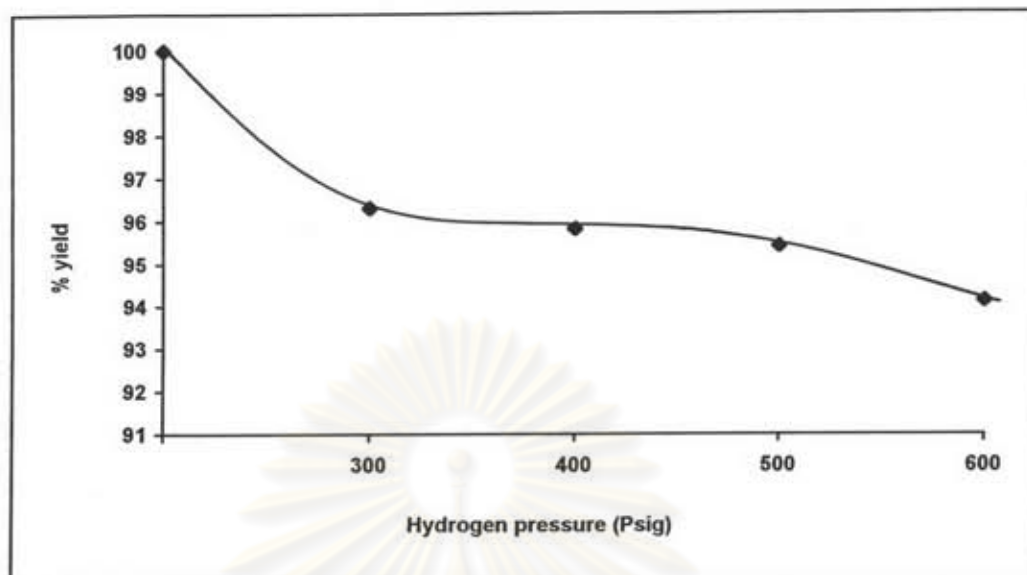


Figure 4.10 Effect of hydrogen pressure on percent yield of hydrodesulfurized oil.

It would be noted that increasing hydrogen pressure resulted in decreasing the color, and the sulfur content in hydrodesulfurized oil. These demonstrated that when the hydrogen pressure was increased, the rate of hydrodesulfurization reaction was increased. Unlike increasing temperature, increasing hydrogen pressure resulted in slightly different yield of hydrodesulfurized oil. This was confirmed by little difference of the GC-MS chromatograms of these hydrodesulfurized oils at various hydrogen pressures in Figure A6. It was concluded that the hydrogen pressure in the study range had no significant effect on cracking reaction. From Figure 4.8, it was estimated that the sulfur content in hydrodesulfurized oil could be reduced more than 0.101% if the reaction was operated at above 600 Psig. But the limit of the regulator of the hydrogen tank used could not be adjusted above 600 Psig.

Therefore, the hydrogen pressure of 600 Psig was chosen as the suitable pressure for this hydrodesulfurization stage.

The fourth variable parameter was the suitable quantity of catalyst for hydrodesulfurization reaction. It was varied in a concentration range from 1 to 7 % by weight of oil. Dewaxed oil was carried out at reaction temperature of 350°C, hydrogen pressure of 600 Psig, reaction time of 3 hours, and catalyst concentration of 1, 3, 5, and 7% by weight of oil, respectively.

The GC-MS chromatograms of these hydrodesulfurized oils are shown in Figure A7. The results of hydrodesulfurization are shown in Table 4.6. The effect of catalyst concentration on color, sulfur content and percent yield of hydrodesulfurized oil are shown in Figure 4.11 to 4.13, respectively.

Table 4.6 The properties of hydrodesulfurized oils at various catalyst concentrations: reaction temperature 350°C, hydrogen pressure 600 Psig, reaction time 3 hours, and agitation speed 500 rpm.

Properties	Dewaxed oil	Catalyst concentration by weight of oil (%)			
		1	3	5	7
Sulfur , %wt	0.305	0.135	0.110	0.101	0.096
Color , visual	> 8	3.5	3.0	2.5	2.5
% yield (>330°C)		96.0	95.2	94.1	90.2

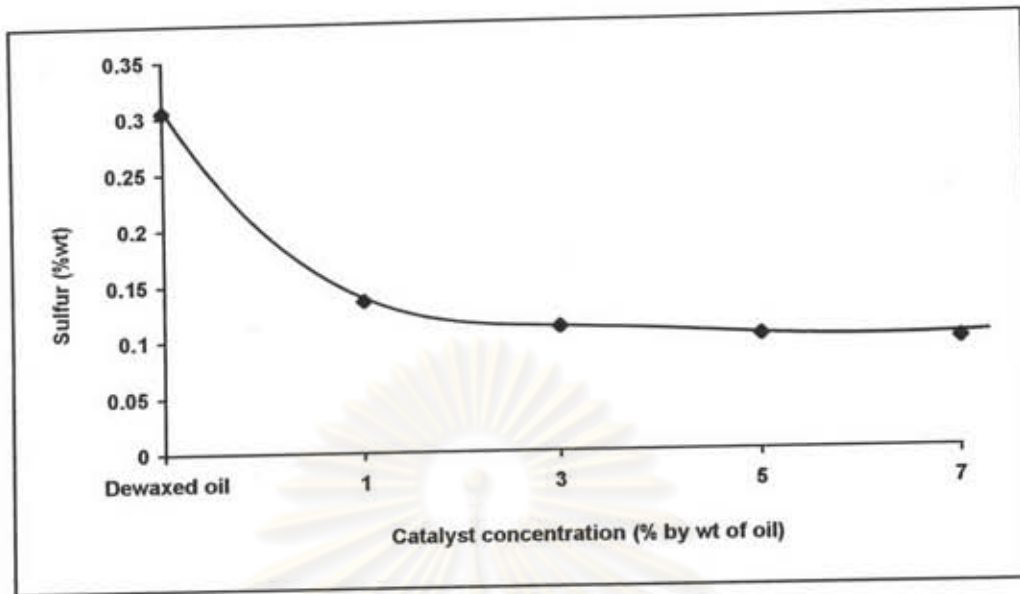


Figure 4.11 Effect of catalyst concentration on sulfur content of hydrodesulfurized oil.

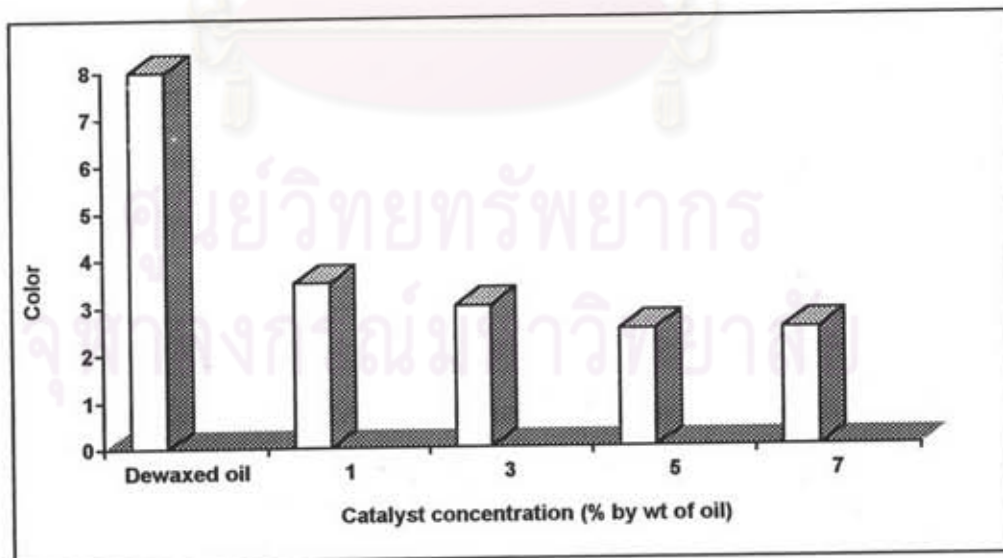


Figure 4.12 Effect of catalyst concentration on color of hydrodesulfurized oil.

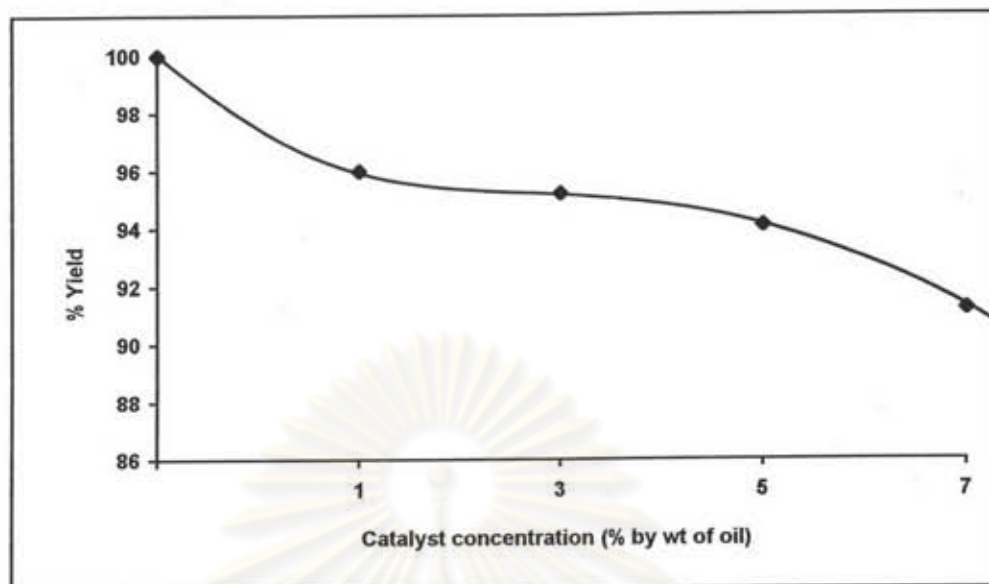


Figure 4.13 Effect of catalyst concentration on percent yield of hydrodesulfurized oil.

From data of this experiment, when the catalyst concentration was increased, sulfur content, and percent yield of hydrodesulfurized oils were slightly decreased. In Figure A7, GC-MS chromatograms of hydrodesulfurized oils at various catalyst concentrations were slightly different. When adding 5% to 7% catalyst concentration, they were not significantly effected on color and sulfur content of hydrodesulfurized oils but percent yield of hydrodesulfurized oil was rapidly reduced. This showed that increasing catalyst concentration would increase catalytic cracking. Moreover, the catalyst is costly, and it is not essential to use excess amount of the catalyst. In this operation, the decision was made to choose the 5% as the suitable catalyst concentration due to economic aspect.

The last variable parameter is the reaction time in a range of 2 to 6 hours. The dewaxed oil was carried out at reaction temperature of 350°C, hydrogen pressure of 650 Psig, and catalyst concentration of 5% by weight of oil. The reaction time was varied from 2, 3, 4, 5, and 6 hours.

The GC-MS chromatograms of these hydrodesulfurized oils are shown in Figure A8. The results of hydrodesulfurization are shown in Table 4.7. The effect of catalyst concentration on color, sulfur content and percent yield of hydrodesulfurized oil are presented in Figure 4.14 to 4.16, respectively.

Table 4.7 The properties of hydrodesulfurized oils at various reaction times: reaction temperature 350°C, hydrogen pressure 600 Psig, catalyst concentration 5% by weight of oil, and agitation speed 500 rpm.

Properties	Dewaxed oil	Reaction time (hours)				
		2	3	4	5	6
Sulfur, %wt	0.305	0.131	0.101	0.082	0.068	0.061
Color, visual	> 8	3.0	2.5	2.5	2.5	2.5
% yield (>330°C)		95.3	94.1	92.5	90.3	87.1

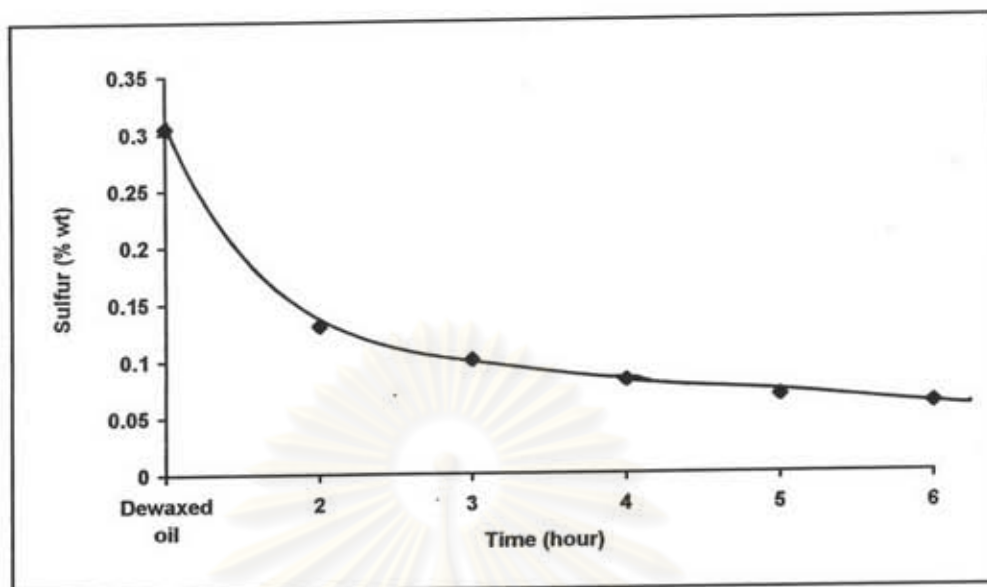


Figure 4.14 Effect of reaction time on sulfur content of hydrodesulfurized oil.

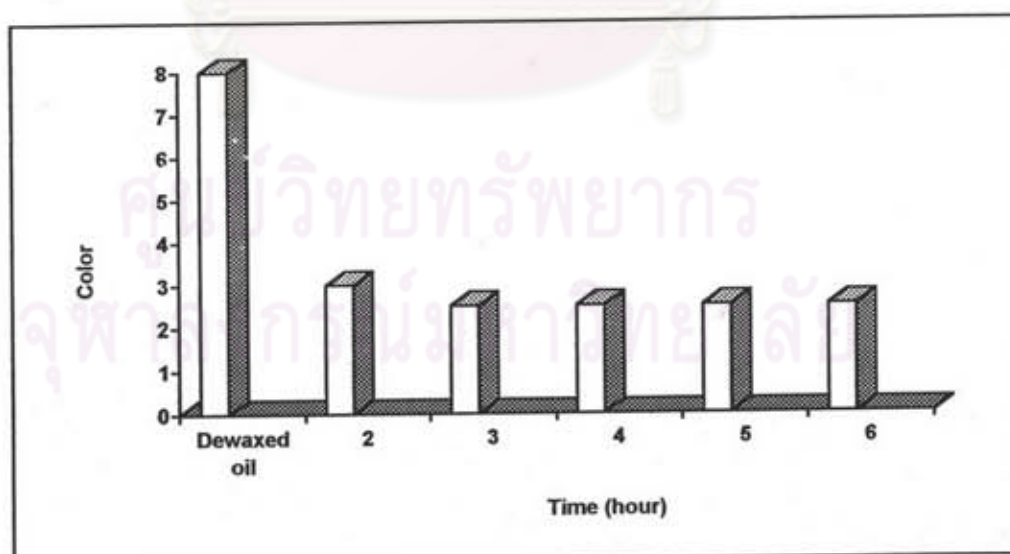


Figure 4.15 Effect of reaction time on color of hydrodesulfurized oil.

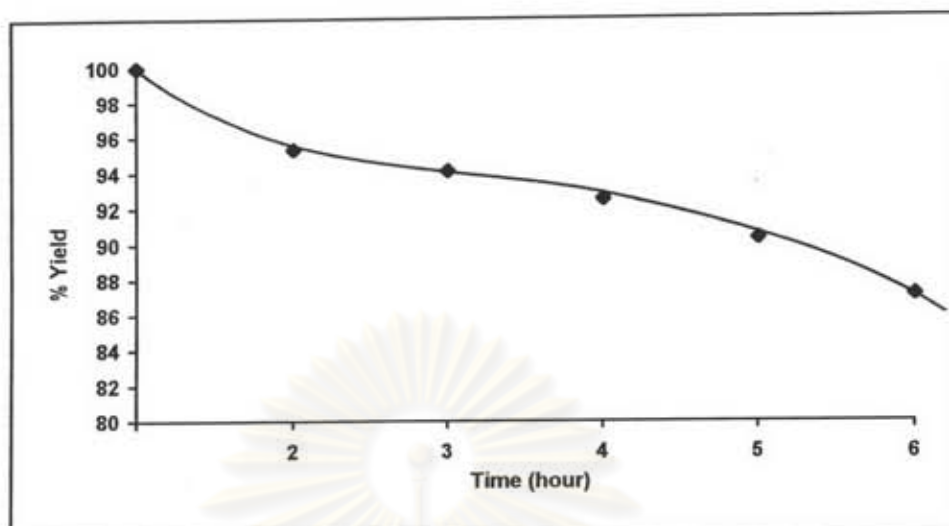


Figure 4.16 Effect of reaction time on percent yield of hydrodesulfurized oil.

From this experiment, It was noted that the sulfur contents in hydrodesulfurized oils were 0.131, 0.101, 0.082, 0.68 and 0.061 when the reaction time was 2, 3, 4, 5, and 6 hours, respectively. While the longer reaction time was performed, the sulfur content of hydrodesulfurized oil was proportionately decreased and slightly decreased when the reaction time was operated more than 4 hours. But The color of these oils remained constant if the time was spent more than 3 hours. Thus the reaction time more than 4 hours resulted in slightly increasing the rate of hydrodesulfurization. It was expected that while the sulfur compounds was removed to give hydrogen sulfide and coke that caused the deactivation of catalyst. The longer reaction time did not increase the rate of hydrodesulfurization. From Figure 14.16, the percent yield of hydrodesulfurized oil was rapidly decreased when the reaction time was longer and the GC-MS chromatogram in Figure A8 showed peaks of low boiling point products after operating at 6 hours. These indicated that more oil

was cracked more when the longer time was spent. Thus operating at longer time was not suitable for hydrodesulfurization stage.

However, sulfur contents in hydrodesulfurized oils at the reaction time of 2, 3, and 4 hours were more than 0.001% by weight. The sulfur content was too high to treat with the platinum catalyst in the hydrogenation stage. Thus the sulfur compounds in the hydrodesulfurized oil were removed again in the second step of hydrodesulfurization following the procedure 5.6 (p.46).

The results of the double hydrodesulfurization are shown in Table 4.8. The effect of the double hydrodesulfurization on color, sulfur content and percent yield of the second hydrodesulfurized oils compared with the first hydrodesulfurized oil operated at 4 and 6 hours are presented in Figure 4.17 to 4.18, respectively.

Table 4.8 The properties of the second hydrodesulfurized oils at various reaction times: reaction temperature 350°C, hydrogen pressure 600 Psig, the catalyst concentration of 5% by weight of oil, and agitation speed 500 rpm.

Properties	Reaction time (hours)		
	2	3	4
Color, visual	1.5	1.5	1.5
Sulfur, %wt	0.020	0.005	0.003

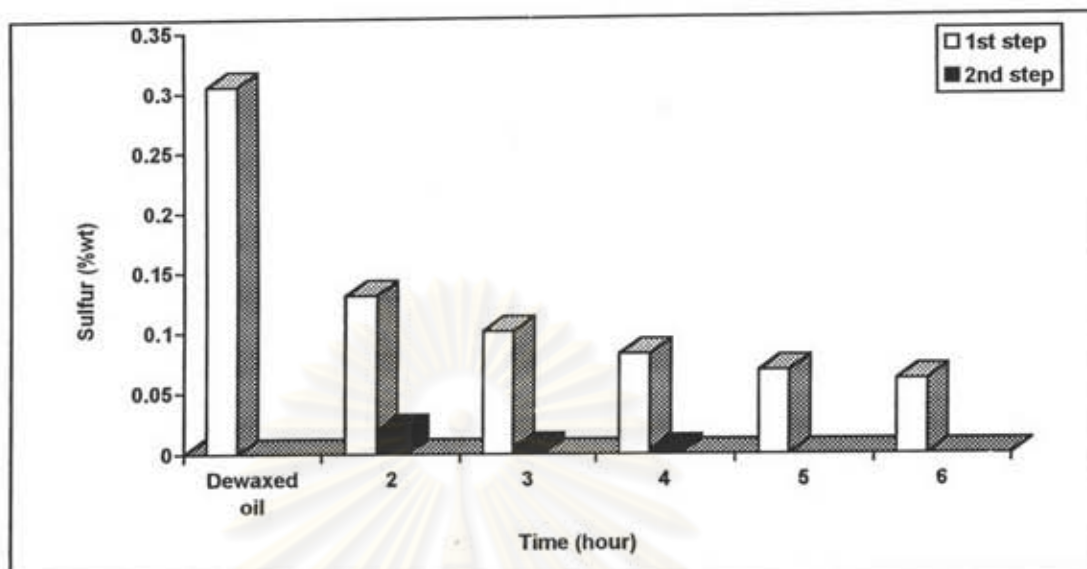


Figure 4.17 Effect of the double hydrodesulfurization at various reaction times on sulfur content of the second hydrodesulfurized oil.

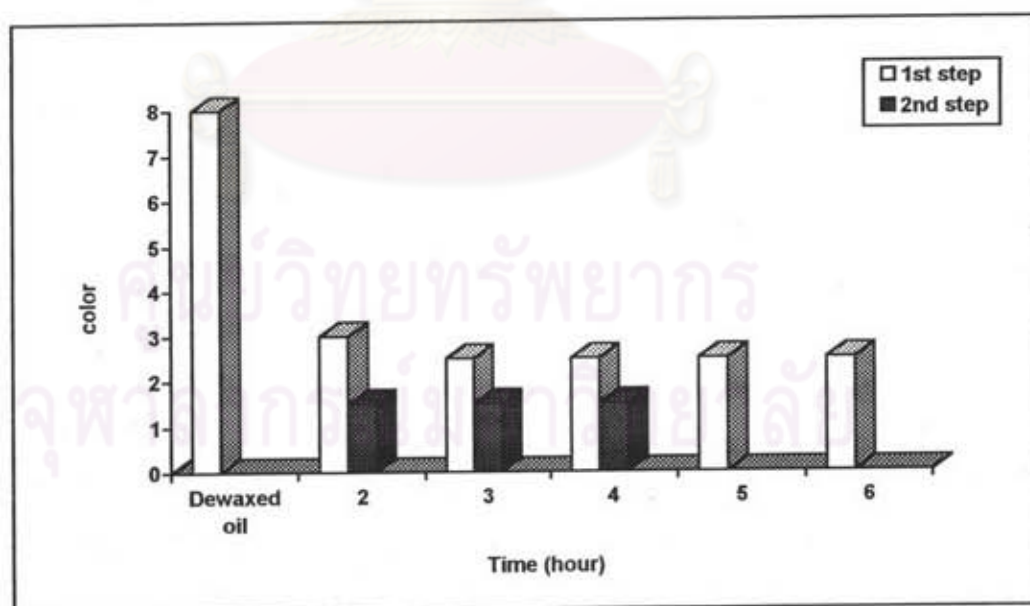


Figure 4.18 Effect of the double hydrodesulfurization at various reaction times on color of the second hydrodesulfurized oil.

From the result, the color of the second hydrodesulfurized oils at the various reaction times remained the same and sulfur contents at the reaction time of 3 and 4 hours were slightly different (0.005 and 0.003 % by weight, respectively) while sulfur content of this oil at the reaction time of 2 hours was still high (0.020 % by weight). The sulfur contents of the second hydrodesulfurized oils were lower than those of the first hydrodesulfurized oils that were treated at the reaction times of 5 and 6 hours. These showed that two hydrodesulfurization steps were better than the one hydrodesulfurization step at longer reaction times. The double hydrodesulfurization about 3 hours of both steps was chosen as suitable condition for hydrodesulfurization stage.

Although operating the double hydrodesulfurization at reaction time of 3 hours would give hydrodesulfurized oil having more than 0.001% by weight of sulfur content, it was expected that sulfur content would be lower if this hydrodesulfurized oil was distilled at reduced pressure to obtain the products in a boiling range of 330°C to 450°C. From the result of distillation, this hydrodesulfurized oil fraction contained less than 0.001% by weight of sulfur.

The GC-MS chromatogram of the hydrodesulfurized oil (a boiling range of 330°C to 450°C) compared with other oils is shown in Figure A9. The ¹³C-NMR spectrum of hydrodesulfurized oil is shown in Figure A10. The comparison of UV spectrum of DMSO extract of hydrodesulfurized oil and that of dewaxed oil is shown in Figure A11. The UV spectrum of hydrodesulfurized oil in iso-octane and that of dewaxed oil in iso-octane are presented in Figure A12, and other physical and chemical properties of hydrodesulfurized oil and those of dewaxed oil are shown in Table 4.9.

Table 4. The properties of dewaxed oil and hydrodesulfurized oil (330-450°C).

Properties	Dewaxed oil	Hydrodesulfurized oil
Color, Visual	> 8	1.0
Saybolt	< -16	< -16
Pour Point (°C)	4	2
API	32.5	32.7
Viscosity , 40°C (cSt)	28.13	24.06
100°C (cSt)	4.62	4.32
Viscosity index	67.8	75.7
Sulfur content (%wt)	0.309	< 0.001
%Ca	7.9	5.3
%Cp	65.9	65.2
%Cn	26.2	29.5
UV absorbance of DMSO		
at 280-289 nm	>4.0	2.706
290-299 nm	>4.0	2.715
300-309 nm	>4.0	2.819
310-319 nm	>4.0	3.035
320-329 nm	>4.0	3.072
330-330 nm	>4.0	3.081
340-349 nm	>4.0	2.998
350-359 nm	>4.0	2.761
360-370 nm	>4.0	2.743
Direct UV absorptivity at		
275 nm	2.811	2.689
295 nm	2.682	2.545
300 nm	2.716	2.504
310 nm	2.784	1.732
320 nm	2.964	1.044
% Yield (330-450°C)		85.3

Before distillation, sulfur content in hydrodesulfurized oil was 0.005% by weight, and after distillation the fraction with a boiling range of 330 °C to 450°C contained less than 0.001% by weight of sulfur. It was assumed that the higher boiling point products were sulfur containing compounds.

The light fraction products with a boiling range below 330°C was colorless. From the GC-MS chromatogram in the Figure A9, it showed that this fraction contained hydrocarbons from C8 to C22 and four main components were heptadecane, octadecane, nonadecane, and eicosane (C17-C20). Another fraction with a boiling range above 450°C was black color, high pour point and high viscosity oil.

In summary, the suitable condition for hydrodesulfurization stage in the batch reaction in the presence of catalyst comprising %5 nickel, 10% molybdenum and 5% cobalt supported was the double hydrodesulfurization at reaction temperature of 350°C under hydrogen pressure of 600 Psig, catalyst concentration of 5% by weight of oil, and reaction time about 3 hours for each step. After dewaxed oil was treated at the optimum condition and then distilled, hydrodesulfurized oil with a boiling range of 330°C to 450°C contained less than 0.001% by weight of sulfur, and 5.3% by mole carbon atom of aromatic carbon. The visual color of this oil was 1 and the pour point was 2°C. The viscosity of this oil was 24.06 cSt at 40°C and 4.32 cSt at 100°C, having viscosity index of 75.7. The UV absorbances of DMSO extract of this hydrodesulfurized oil in a wavelength range of 280 to 370 nm were more than 2.7, and direct absorbivities in a wavelength range of 275 to 300 nm were more than 2.5 while those of 300 to 320 nm were more than 1.0. This dewaxed oil gave 85.3% yield of hydrodesulfurized oil and 7.1% of light oil, 4.0% of gas, and 3.6% of residual fraction.

Hydrogenation Stage

In this stage, the second hydrodesulfurized oil with a boiling range of 330°C to 450°C was contacted in the batch reactor with the presence of hydrogen and the catalyst comprising of 0.3% platinum supported on alumina to determine the optimum conditions for hydrogenation stage.

In this study, the three important criteria to determine the properties of hydrogenated oil were color, UV absorption of DMSO extract, and direct UV absorptivity.

Because the color of hydrogenated oil was too light to determine by visual color test, it was measured as Saybolt color. But hydrodesulfurized oil was too dark to determine by Saybolt color test, it was reported to have Saybolt color below -16. If oil is colorless, Saybolt color is +30.

The UV absorption is the method for testing purity of white oil. [2] The impurities are aromatic compounds such as aromatic hydrocarbons, and aromatic sulfur and nitrogen compounds. The examples of UV absorption of these compounds are presented in Figure A24-A27. It is noted that UV absorption of monoaromatic compounds is in a wavelength range of 250 to 300 nm, that of diaromatic compounds is in a wavelength range of 250 to 320 nm, and that of polyaromatic compounds is in a wavelength range of 250 to 400 nm. Aromatic sulfur and nitrogen compounds, and polyaromatic compounds are soluble in DMSO. Following ASTM D 2269-73, when extract hexane solution of hydrogenated oil or white oil with DMSO, most of aromatic nitrogen and sulfur components are in DMSO and aromatic hydrocarbons are in both DMSO and hexane. Thus measuring UV absorption of DMSO extract of hydrogenated oil or white oil will indicate these impurities in oils. Another method for testing purity of oil is direct absorptivity of oil following ASTM D 2008. Generally, hydrogenated oil and white oil contain aromatic hydrocarbons more than other aromatic compounds. This method will detect aromatic hydrocarbons in these

oils. The concentration of 1 g/l of oil in iso-octane was subjected to UV absorption measurement by using 1 cm of cell path length, thus the absorptivity is equal absorbance.

In hydrogenation stage the hydrogen pressure was preferably operated at about 2200 to 5000 Psig- higher than in hydrodesulfurization stage. Because of the limit of the hydrogen pressure in this research, the hydrogen pressure of 600 Psig was chosen as the suitable pressure for hydrogenation stage.

The first parameter studied was the reaction temperature at 275, 300 and 350°C. The hydrodesulfurized oil was hydrogenated at hydrogen pressure of 600 Psig, reaction time of 3 hours, catalyst concentration of 5% by weight of oil, and various reaction temperatures.

The UV spectra of DMSO extracts of hydrogenated oils and hydrogenated oils in iso-octane at various reaction temperatures are presented in Figure A13 and A14, respectively. The color, the sulfur content, and the percent yield of these hydrogenated oils are recorded in Table 4.10. The effect of reaction temperature on UV absorption of DMSO extract and direct UV absorptivity of hydrogenated oil are shown in Figure 4.19 and 4.20, respectively.

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

Table 4.10 The properties of hydrogenated oil at various reaction temperatures: hydrogen pressure 600 Psig, reaction time 3 hours, catalyst concentration of 5% by weight of oil, and agitation speed 500 rpm.

Properties	HDS oil	Hydrogenated oil at temperature (°C)			Spec. of technical white oil
		275	300	350	
Color , Saybolt	< -16	+ 21	+28	+ 28	+ 20 min
Sulfur, % by weight	<0.001	< 0.001	<0.001	< 0.001	
UV absorbance of DMSO extract at					
280-289 nm	2.706	2.254	2.482	2.523	4.0 max
290-299 nm	2.715	2.351	2.493	2.576	3.3 max
300-309 nm	2.819	2.502	2.633	2.668	2.3 max
310-319 nm	3.035	2.726	2.851	2.849	2.3 max
320-329 nm	3.072	2.785	2.923	2.883	2.3 max
330-339 nm	3.081	2.792	2.935	2.545	0.8 max
340-349 nm	2.998	2.724	2.834	1.866	0.8 max
350-359 nm	2.761	2.409	2.239	1.175	-
360-370 nm	2.743	2.464	1.138	0.44	-
Direct UV absorptivity at					
275 nm	2.689	2.665	2.319	2.135	-
295 nm	2.545	1.750	1.334	1.324	-
300 nm	2.504	1.540	1.081	1.059	-
310 nm	1.732	0.983	0.505	0.522	-
320 nm	1.044	0.475	0.154	0.191	-
% Yield (330-450°C)		96.5	94.3	91.1	

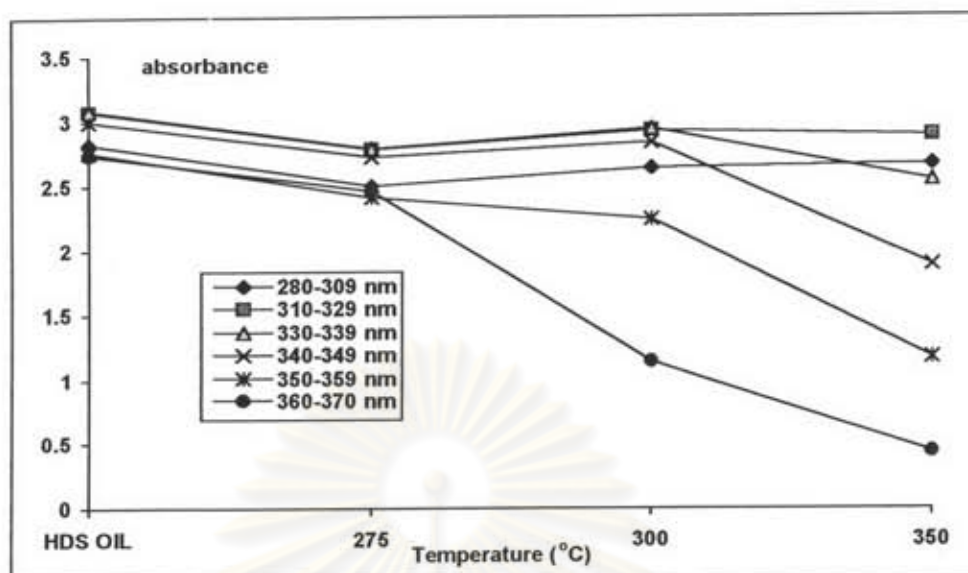


Figure 4.19 Effect of the reaction temperature on UV absorption of DMSO extract of hydrogenated oil.

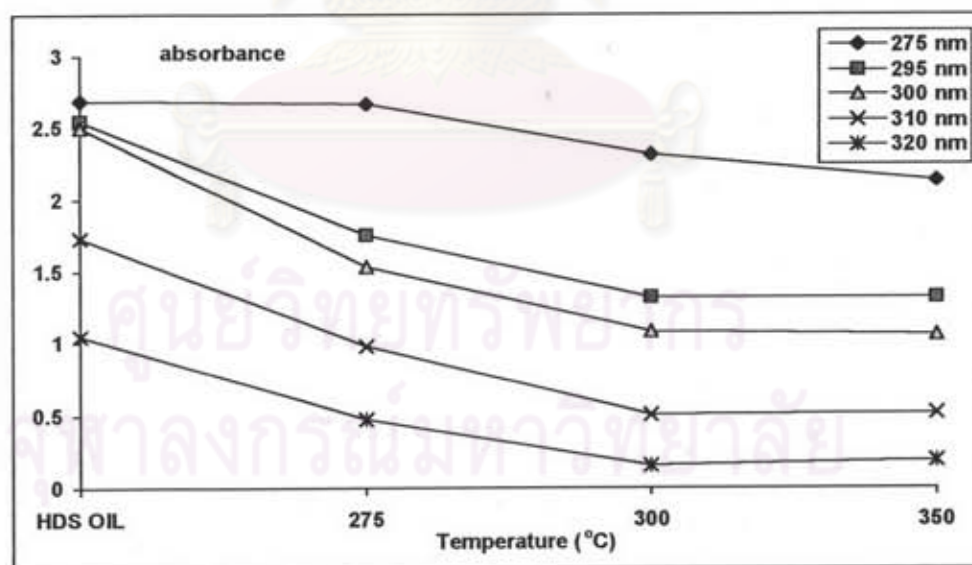


Figure 4.20 Effect of the reaction temperature on direct UV absorptivity of hydrogenated oil in iso-octane.

From data in Table 4.10, the sulfur contents of hydrogenated oils was lower than 0.001%. The color of hydrogenated oils at 350°C and 300°C was almost colorless (Saybolt color of +28), while the color of hydrogenated oil at 275°C was slightly yellow (Saybolt color of +21). This showed that operating hydrogenation at 350°C and 300°C improved color better than that at 275°C.

Although the color of these hydrogenated oils would pass the specification of technical white oil, the impurities in these oils are still high. From Figure A13 and 4.19, when compared UV absorption of DMSO extracts of hydrogenate oil at three temperatures, absorbances in a wavelength range of 260-360 nm were slightly different, but absorbances in a wavelength range of 360-400 nm were rapidly decreased, especially absorbance at 360 nm decreased from 2.743 (HDS oil) to 1.918, 1.515 and 1.452 at 270, 300, and 350 °C, respectively. According to direct absorptivities of hydrogenated oils in iso-octane (Figure A14 and 4.20), absorptivities of hydrogenated oil at 275°C were rapidly decreased from original and slightly decreased when temperature increased. These indicated that the hydrogenation reaction was more effective when the temperature increased from 275°C to 350°C. Because of slightly yellow color of hydrogenated oil at 275°C and a large number of thermal cracking products at 350°C, therefore 300°C was chosen the suitable reaction temperature for hydrogenation stage. Although UV absorbances of DMSO extract in a range wavelength of 280 to 299 nm were less than specification of technical white oil, the hydrogenated oil at 300°C did not give white oil because of high absorbances in a wavelength range of 300 to 350 nm.

Next, the reaction time for hydrogenation stage was varied. The hydrodesulfurized oil was hydrogenated at temperature of 300°C, hydrogen pressure of 600 Psig, catalyst concentration of 5%, and agitation speed of 500 rpm. The UV spectra of DMSO extracts of hydrogenated oils and hydrogenated

oils in iso-octane at various reaction temperatures are presented in Figure A15 and A16, respectively. The color, the sulfur content, and the yield of these hydrogenated oils are recorded in Table 4.11. The effect of reaction time on UV absorption of DMSO extract and direct UV absorptivity of hydrogenated oil are shown in the Figure 4.21 and 4.22, respectively.

Table 4.11 The properties of hydrogenated oil at various reaction times: reaction temperature 300°C, hydrogen pressure 600 Psig, catalyst concentration 5% by weight of oil and agitation speed 500 rpm.

Properties	HDS oil	Hydrogenated oil at reaction time (°C)			Spec. of technical white oil
		3	6	9	
Color , Saybolt	< -16	+28	+ 30	+ 30	+ 20 min
Sulfur, % by weight	<0.001	<0.001	< 0.001	<0.001	
UV absorption of DMSO extract at					
280-289 nm	2.706	2.482	2.362	2.340	4.0 max
290-299 nm	2.715	2.493	2.342	2.406	3.3 max
300-309 nm	2.819	2.633	2.532	2.455	2.3 max
310-319 nm	3.035	2.851	2.757	2.574	2.3 max
320-329 nm	3.072	2.923	2.761	2.804	2.3 max
330-339 nm	3.081	2.935	2.804	2.810	0.8 max
340-349 nm	2.998	2.834	2.743	2.725	0.8 max
350-359 nm	2.761	2.239	2.386	2.381	-
360-370 nm	2.743	1.918	1.515	1.452	-
Direct UV absorptivity at					-
275 nm	2.689	2.319	2.187	2.093	-
295 nm	2.545	1.334	1.248	1.113	-
300 nm	2.504	1.081	0.970	0.891	-
310 nm	1.732	0.505	0.443	0.434	-
320 nm	1.044	0.154	0.090	0.122	-
% Yield (330-450°C)		94.3	92.7	89.5	

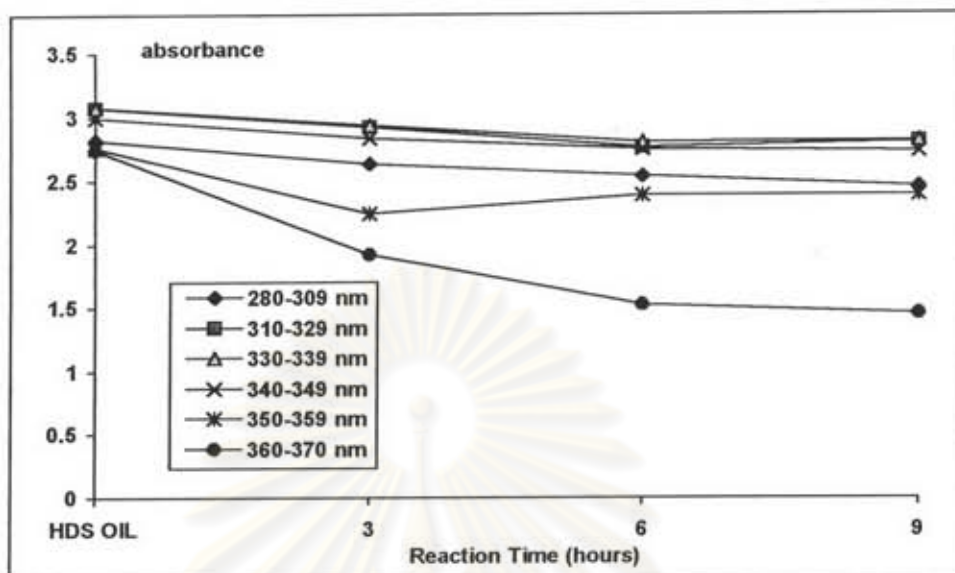


Figure 4.21 Effect of the reaction time on UV absorption of DMSO extract of hydrogenated oil.

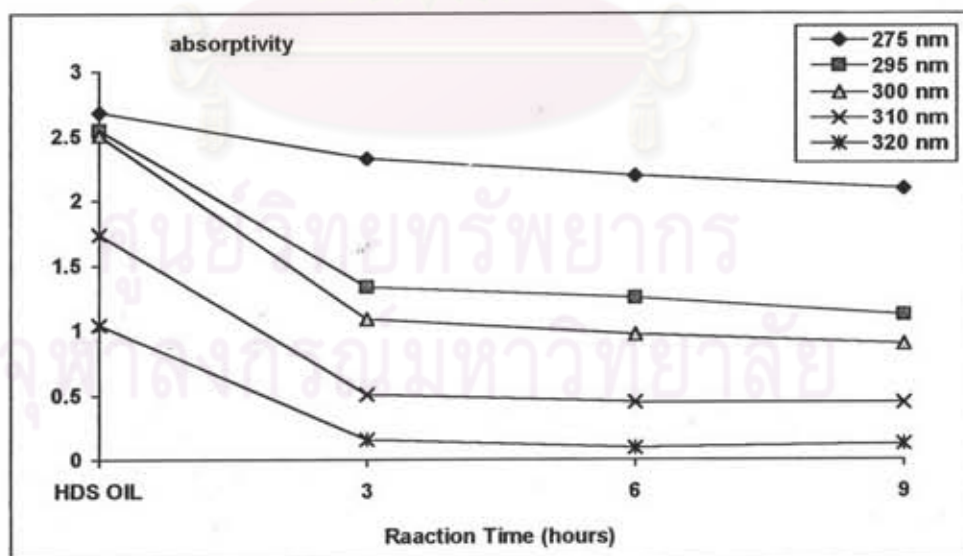


Figure 4.22 Effect of the reaction time on direct absorptivity of hydrogenated oil in iso-octane.

From the data, when the longer time was spent more than 3 hours, the color of hydrogenated oils were colorless (Saybolt color of +30) but UV absorbances of DMSO extract and UV absorptivities of hydrogenated oils were not significantly changed. It was concluded that the reaction time more than 3 hours had no significant effect on hydrogenation reaction. It was expected that hydrogen sulfide which was generated from residual sulfur compounds in hydrodesulfurized oil may cause the deactivation of platinum catalyst. In this experiment, the process was a batch process. When hydrogen sulfide was generated, it was still in the reactor. Thus it was difficult to hydrogenate aromatic compounds.

To solve the problem of hydrogen sulfide and other impurities gas generated during the reaction, the multiple step hydrogenation following a procedure in the experiment 6.3 (p.49) was carried out. In each step, the reaction was performed at temperature of 300°C, hydrogen pressure of 600 Psig, catalyst concentration of 5% by weight of oil, and agitation speed of 500 rpm during 4 cycles of hydrogenation.

The UV spectra of DMSO extracts of hydrogenated oils and hydrogenated oils in iso-octane are presented in Figure A17 and A18. The color, the sulfur content, and the percent yield of hydrogenated oil are recorded in Table 4.12. The effect of the multiple hydrogenation on UV absorption of DMSO extract of hydrogenated oil and direct UV absorptivity of hydrogenated oil are shown in Figure 4.23 and 4.24, respectively.

Table 4.12 The properties of hydrogenated oils at multiple hydrogenation: reaction temperature 300°C, hydrogen pressure 600 Psig, reaction time of each steps for 3 hours, catalyst concentration 5% by weight oil, and agitation speed 500 rpm.

Properties	HDS oil	Hydrogenated oil of the				Spec. of technical white oil
		first step	second steps	third step	forth step	
Color, Saybolt	< -16	+ 28	+ 30	+ 30	+30	+ 20 min
Sulfur, % by wt	<0.001	<0.001	< 0.001	<0.001	<0.001	
UV absorbances of DMSO extract at						
280-289 nm	2.706	2.496	2.336	2.471	2.460	4.0 max
290-299 nm	2.715	2.525	2.317	2.486	2.370	3.3 max
300-309 nm	2.819	2.641	2.398	2.579	2.11	2.3 max
310-319 nm	3.035	2.857	2.524	2.626	1.19	2.3 max
320-329 nm	3.072	2.876	2.704	2.530	0.33	2.3 max
330-339 nm	3.081	2.876	2.323	1.750	0.208	0.8 max
340-349 nm	2.998	2.787	1.963	1.150	0.138	0.8 max
350-359 nm	2.761	2.443	1.445	0.771	0.023	-
360-370 nm	2.743	1.998	0.497	0.459	0.008	-
Direct UV absorptivity at						
275 nm	2.689	2.135	1.688	1.021	0.444	-
295 nm	2.545	1.324	0.850	0.414	0.168	-
300 nm	2.504	1.059	0.670	0.318	0.130	-
310 nm	1.732	0.522	0.343	0.153	0.067	-
320 nm	1.044	0.191	0.108	0.026	0.017	-

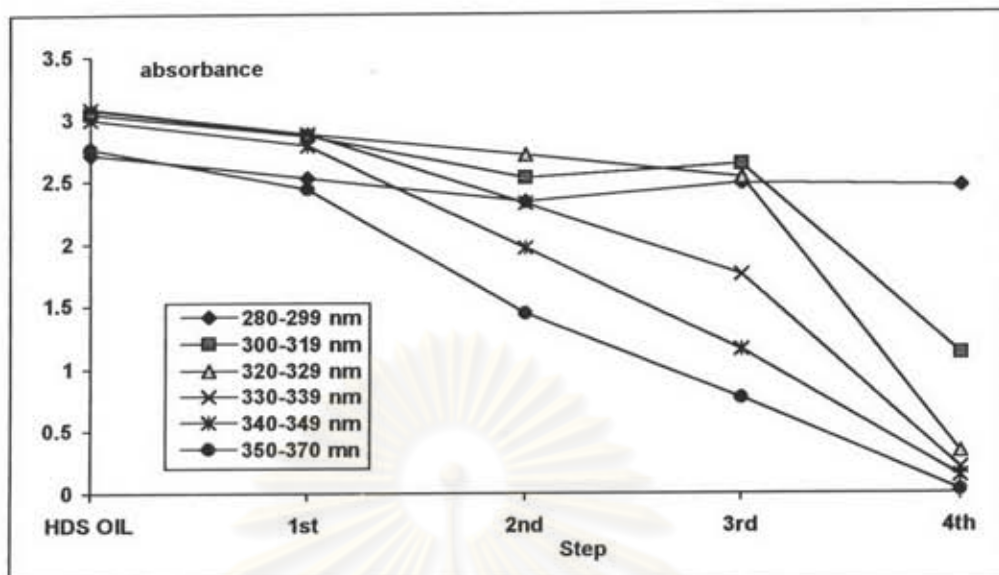


Figure 4.23 Effect of multiple hydrogenation on UV absorption of DMSO extract of hydrogenated oil.

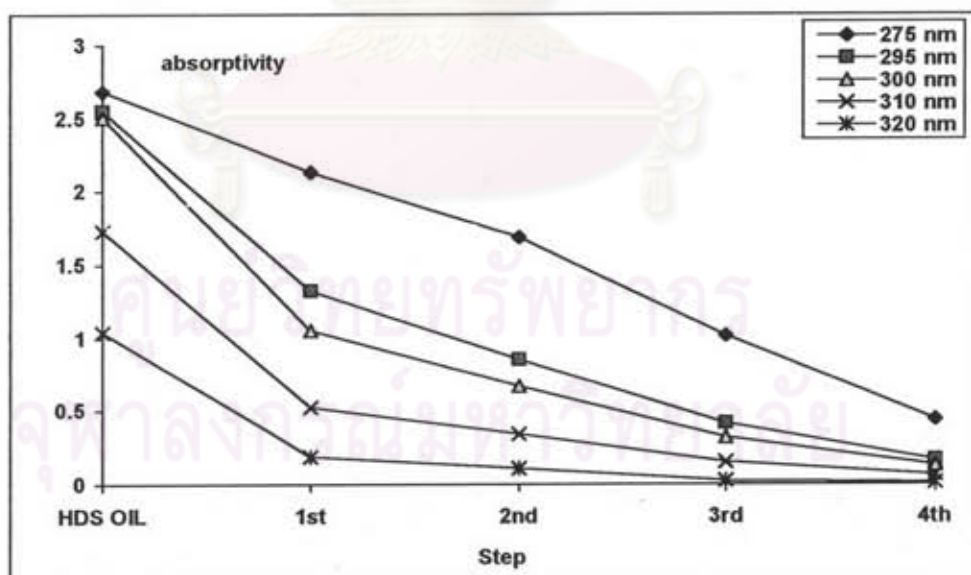


Figure 4.24 Effect of multiple hydrogenation on direct absorptivity of hydrogenated oil in iso-octane.

From this experiment, the color of the second, the third and the fourth hydrogenated oils were colorless (Saybolt color of +30). When multiple hydrogenation was carried out, UV absorbances of DMSO extracts of hydrogenated oils (Figure A17, Figure 4.23) at wavelengths above 330 nm were rapidly reduced. Although absorbances at a wavelength range of 280 to 310 nm were slightly reduced, they were lower than those specification of technical white oils. In Figure A18 and 4.24, when multiple hydrogenation was carried out, UV absorptivities of hydrogenated oils at wavelength range above 275 nm were rapidly decreased.

It was clear that only the fourth hydrogenated oil met all requirements for technical white oil, particularly the maximum UV absorbances of produced white oil were 2.460, 2.370, 2.110, and 0.208, while the specification of technical white oil are 4.0, 3.3, 2.3, and 0.8 in a range wavelength of 280-289, 290-299, 300-329, and 330-350 nm, respectively. Moreover it passed direct UV absorptivity test for medicinal and food grade white oil of Germany. If hydrogenation was carried out more than four times, it is expected that this white oil would have higher purity. The other properties of the fourth hydrogenated oil or white oil were compared with original oil, and commercial technical white oil as shown in Table 4.12.

This technical white oil was transparent, colorless, almost odorless, having API of 33.1, viscosity of 21.15 and 4.03 cSt at 40°C and 100 °C, respectively, and viscosity index of 77.0. Moreover it passed UV absorption of DMSO extract and direct UV absorptivity test.

Hydrodesulfurized oil gave 85.1 % yield of technical white oil, 8.4 % of light oil, and 6.5 % of gas. When calculated from dewaxed oil, it gave 72.6% yield of technical white oil, 14.3% of light oil, 9.5% of gas and 3.6% of residual fraction, and when calculated from light distillate, it gave 34.6% yield of technical white oil, 6.8% of of light oil, 4.5% of gas and 1.7% of residual fraction, .

Table 4.12 The properties of dewaxed oil, hydrodesulfurized oil and white oil.

Properties	Dewaxed oil	HDS oil	White oil	Specification of technical white oil
Color, Visual	> 8	1.0	-	-
Saybolt	< -16	< -16	+ 30	+20 min.
Pour Point (°C)	4	2	0	-
API	32.5	32.7	33.1	
Viscosity , 40°C (cSt)	28.13	24.06	21.15	> 5.0
100°C (cSt)	4.62	4.32	4.03	-
Viscosity index	67.80	75.7	77.0	-
Sulfur content (%wt)	0.309	<0.001	< 0.001	-
UV absorbance of DMSO extract at				
280-289 nm	> 4.0	2.706	2.460	4.0 max
290-299 nm	> 4.0	2.715	2.370	3.3 max
300-329 nm	> 4.0	3.072	2.110	2.3 max
330-350 nm	> 4.0	2.792	0.208	0.8 max
Direct UV absorptivity at				
275 nm	2.689	2.665	0.444	1.6 max ^a
295 nm	2.545	1.750	0.168	0.20 max ^a
300 nm	2.504	1.540	0.130	0.15 max ^a
%Ca	7.9	5.3	ND ^b	
%Cp	65.9	65.2	61.1	
%Cn	26.2	29.5	38.9	
% yield		85.3 ^c	72.6 ^c	
		40.7 ^d	34.6 ^d	

^aspecification of medicinal and food grade white oils of Germany ^b ND = none detect

^c compare with dewaxed oil

^d compare with light distillate