

CHAPTER IV

RESULTS AND DISCUSSION

This research was intended to improve the quality of used marine lubricating oil by means of the catalytic hydrogenation method. Because of the physical and chemical treatment method gave high waste byproduct and disposal problem. Then this research was studied closely to solve this undesirable problem and to reduce the step of treatment by treating the used lubricating oil directly with the catalytic hydrogenation method.

The goal of this research was to study the optimum condition in hydrogenation of used lubricating oil by using the hydrotreating catalyst such as Raney nickel, Nickel oxide/tungsten oxide/alumina and Nickel oxide/molybdenum oxide/alumina. The studying in each type of catalyst was tried to find the suitable condition which used the least reaction time and concentration of catalyst that gave oil having desirable properties in order to make it possible use in the industrial way and to save cost.

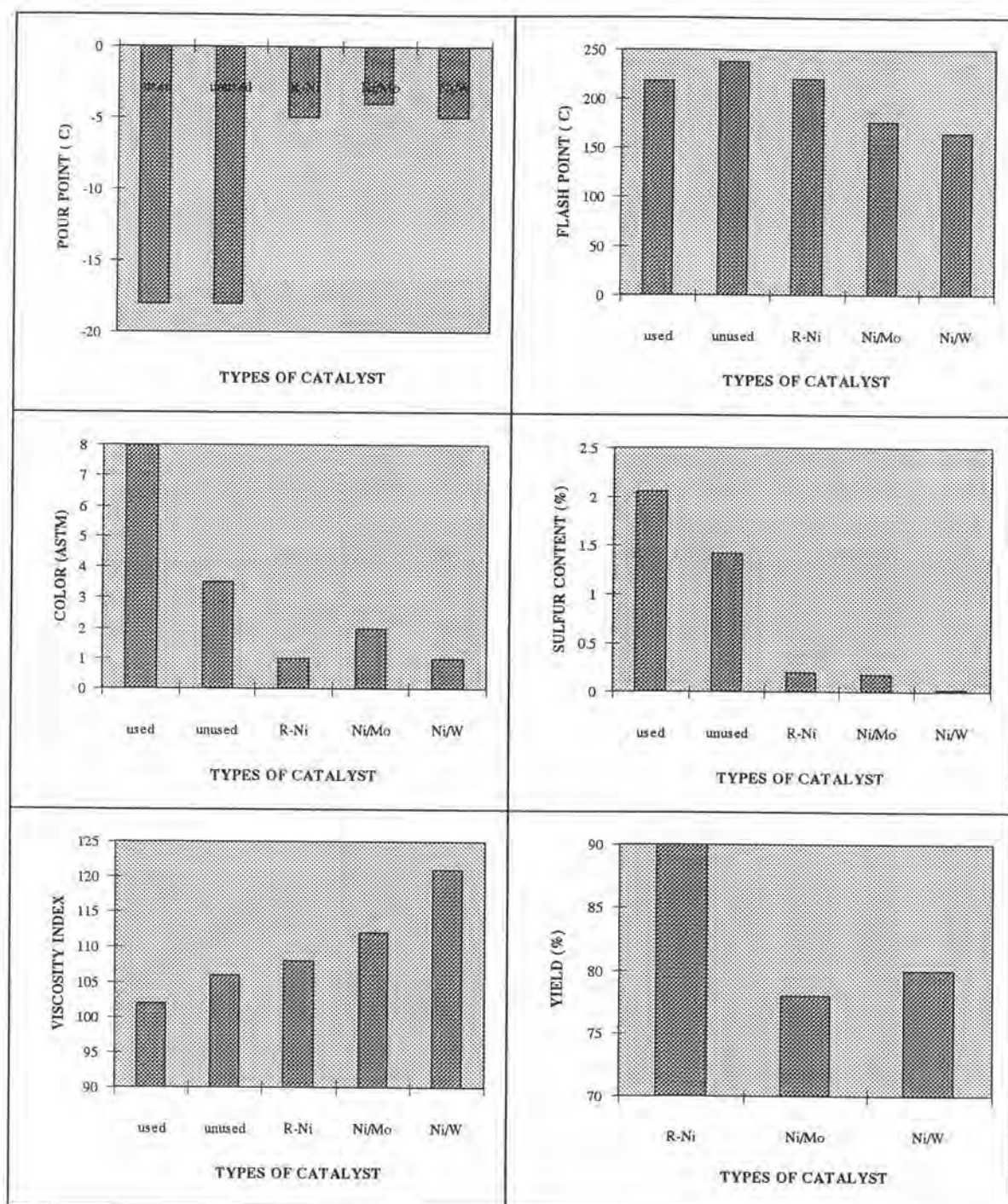


Figure 4.1 Effect of catalyst types on properties of hydrogenated oils compared with original used oil and unused oil.

Table 4.1 and Figure 4.1 showed that pour point of hydrogenated oil receiving from using three types of catalyst was higher than used oil ($-18\text{ }^{\circ}\text{C}$). This result from deteriorating of pour point depressant which was remained in used oil, when the hydrogenation of used oil was operated at the temperature of $350\text{ }^{\circ}\text{C}$. When $\text{NiO}/\text{WO}_3/\text{Al}_2\text{O}_3$ and Raney nickel was used in the reaction, the pour point value were $-5\text{ }^{\circ}\text{C}$, whereas in use of $\text{NiO}/\text{MoO}_3/\text{Al}_2\text{O}_3$ the pour point value was $-4\text{ }^{\circ}\text{C}$.

In term of color, when $\text{NiO}/\text{WO}_3/\text{Al}_2\text{O}_3$ and Raney nickel was used in the reaction, the color were 1, whereas in use of $\text{NiO}/\text{MoO}_3/\text{Al}_2\text{O}_3$ the color was 2. However, color of hydrogenated oils were better than used oil (>8) and unused oil (3.5). This result from the decreasing of viscosity, causing assembled of contaminants, settled down and separated of hydrogenated oil from contaminants and waste byproduct.

In term of flash point, there was only the use of Raney nickel that gave flash point ($220\text{ }^{\circ}\text{C}$) higher than used oil ($218\text{ }^{\circ}\text{C}$). On the other hand the hydrogenated oil obtaining from the use of $\text{NiO}/\text{MoO}_3/\text{Al}_2\text{O}_3$ and $\text{NiO}/\text{WO}_3/\text{Al}_2\text{O}_3$ had flash point of 176 and $164\text{ }^{\circ}\text{C}$, respectively. This result from, $\text{NiO}/\text{MoO}_3/\text{Al}_2\text{O}_3$ and $\text{NiO}/\text{WO}_3/\text{Al}_2\text{O}_3$ might have been occurred another reaction such as hydrocracking. Hydrocracking gave hydrogenated oils having constituent of small alkane contents.

The best catalyst in sulfur removal was $\text{NiO}/\text{WO}_3/\text{Al}_2\text{O}_3$ that gave oil having sulfur content of 0.021 %. The second and third to the best were $\text{NiO}/\text{MoO}_3/\text{Al}_2\text{O}_3$ and Raney nickel, that gave oil having sulfur content of 0.181 and 0.202 %, respectively. However, the hydrogenated oil which obtained from using of all types of hydrotreating catalysts had lower sulfur content than used oil (2.065 %) and unused oil (1.414 %).

Yield obtained from the use of Raney nickel, $\text{NiO}/\text{WO}_3/\text{Al}_2\text{O}_3$ and $\text{NiO}/\text{MoO}_3/\text{Al}_2\text{O}_3$ were 90, 80 and 78 %, respectively.

These three types of catalyst gave oil which had similar properties in terms of pour point and color. In terms of viscosity index and sulfur removal, the best catalyst was NiO/WO₃/Al₂O₃, NiO/MoO₃/Al₂O₃ and Raney nickel respectively. On the other hand, Raney nickel was the best catalyst in terms of flash point and yield.

In comparison among hydrogenated oil, used lubricating oil and unused lubricating oil, hydrogenated oil had more desirable properties than used and unused lubricating oil in terms of viscosity index, color and sulfur content.

In the next experiment it would be studied in each type of catalyst to try to find the condition which used the least reaction time and concentration of catalyst that gave oil having desirable properties in order to make it possible use in the industrial way and to save cost.

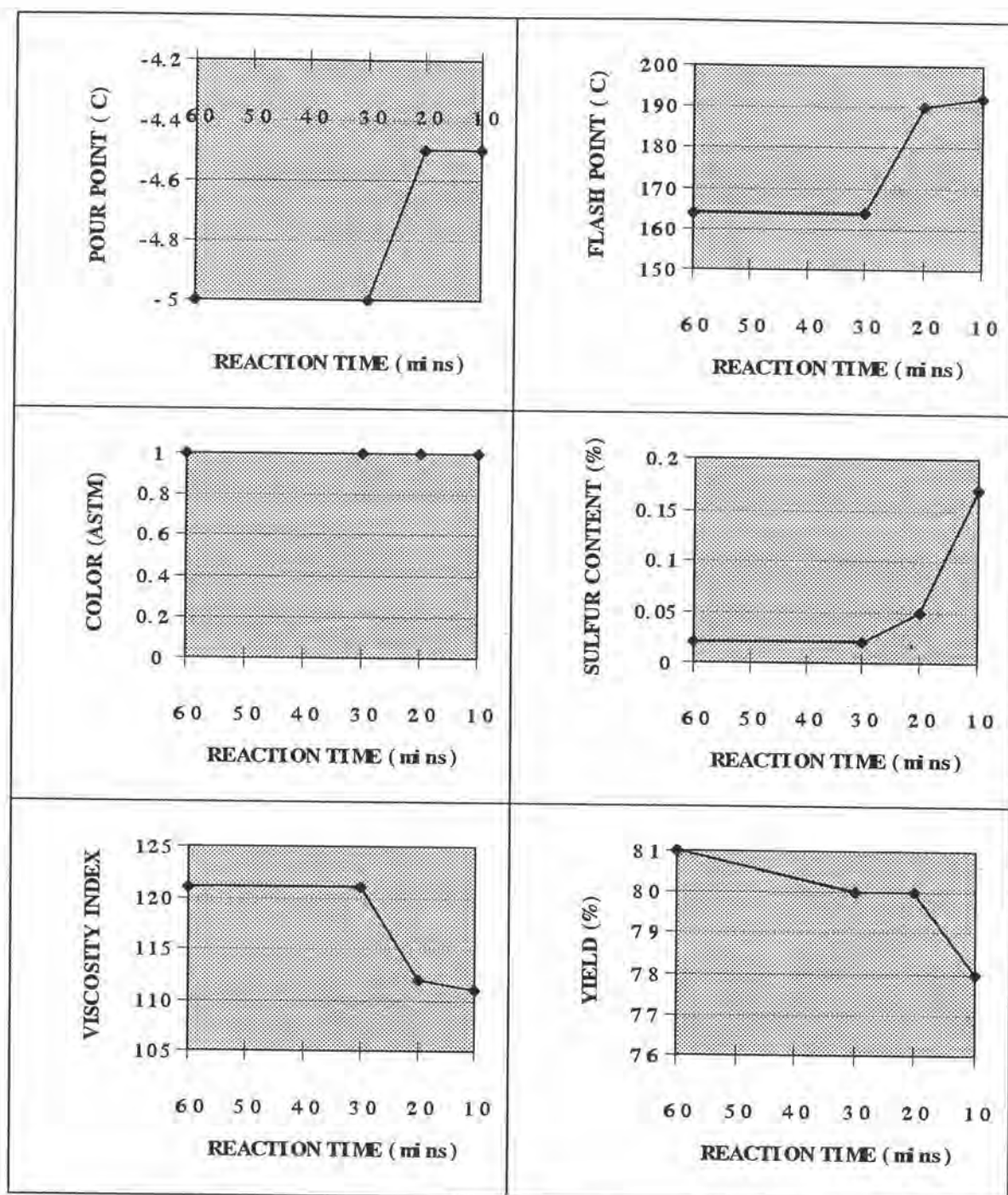


Figure 4.2 Effect of time on properties of hydrogenated oil by using $\text{NiO}/\text{WO}_3/\text{Al}_2\text{O}_3$ catalyst at the constant concentration (40 %) and various reaction times.

From Table 4.2 and Figure 4.2, the decreasing of reaction time would gave the oil having higher pour point from -5°C to -4.5°C , and higher than used oil (-18°C). This result from deteriorating of pour point depressant which was remained in used oil, when the hydrogenation of used oil was operated at the temperature of 350°C .

In term of color, the result showed that hydrogenated oil had the same color (1) although the reaction time was decreased. Hydrogenated oil had better color than used oil (>8).

In term of viscosity, the result showed that decreasing reaction time decreased the rate of hydrocracking and hydrogenation resulting in decreasingly higher molecular weight hydrocarbon compounds. Hydrogenated oil obtaining from operating at short reaction time had more viscosity than operating at long reaction time.

In term of VI, at the reaction time of 60 and 30 minutes, the value of VI was the same (121). When the reaction time was decreased to 20 and 10 minutes, the VI value was decreased to 112 and 111, respectively. This result from, hydrogenated oil obtaining in use of long reaction time had more constituent of paraffinic hydrocarbons. However, the VI value of hydrogenated oil obtaining from every reaction time were higher than used oil (102).

In term of flash point, at the reaction time of 60 and 30 minutes, the flash point of hydrogenated oils were the same. The decreasing of reaction time from 30 to 20 and 10 minutes would gave the oils having higher flash point from 164°C to 190 and 192°C , respectively. This result from, the increasing reaction time increased the rate of hydrocracking and hydrogenation resulting in increasingly lower molecular weight hydrocarbon compounds. Hydrogenated oil which obtained from operating at long reaction time had lower flash point than operating at short reaction time.

The effective in sulfur removal was decreased when the reaction time was decreased. The hydrogenated oil had the sulfur content of 0.17, 0.05 and 0.02 %, when the reaction time was increased from 10 to 20 and 30 minutes, respectively. Increasing of reaction time from 10 to 20 and 30 minutes, and 60 minutes, the slightly increased yield from 78 % to 80, 80 and 81 %, respectively.

The objective of this experiment was to find the least reaction time which gave oil which had desirable properties. From table 4.2, the increasing of reaction time would gave oil which had similar properties in terms of pour point and color. In terms of viscosity index sulfur removal and yield, the best reaction time was 60 minutes. The obtained hydrogenated oil at the reaction time of 10 minutes was desirable properties. In term of flash point, the best reaction time was 10 minutes.

The result indicated that 10 minutes of reaction time gave oil having desirable properties. So, it was not necessary to operate at the reaction time over 10 minutes.

In some cases, the used lubricating oil had better properties than hydrogenated oil such as pour point. This can be explained that used oil might have some available additives to maintain the good result of oil.

In the next experiment, it would be studied the least concentration of catalyst which gave oil having had desirable properties.

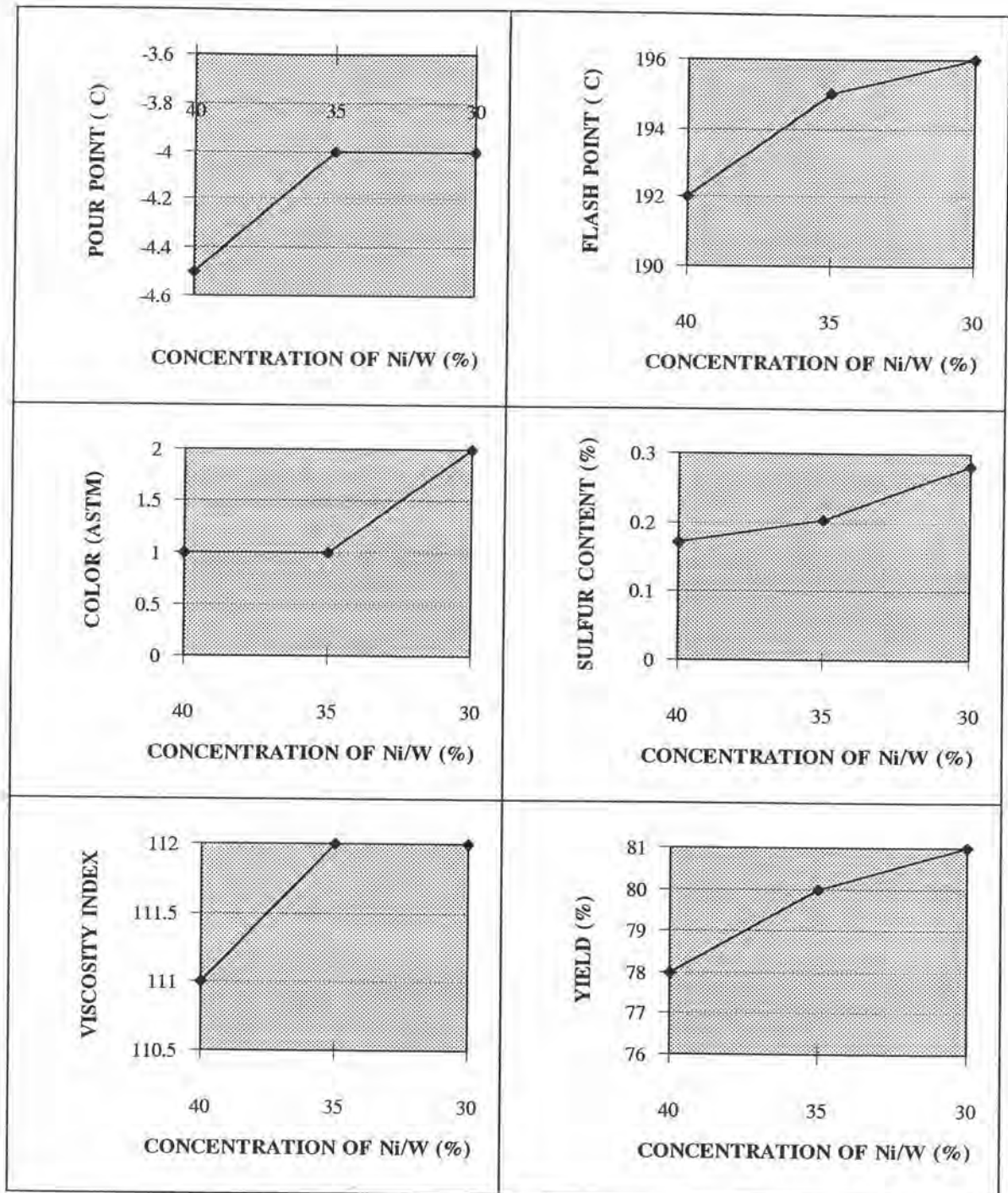


Figure 4.3 Effect of concentration of hydrogenated oil by using constant reaction time (10 minutes) and various concentration of $\text{NiO}/\text{WO}_3/\text{Al}_2\text{O}_3$ catalyst.

Effect of concentration of catalyst on hydrogenation of used lubricating oil were investigated by varying the catalyst concentration of 40, 35, 30 and 20 % by weight of used oil. The objective of this experiment was to study the least concentration of catalyst which gave oil which had desirable properties.

Table 4.3 and Figure 4.3 showed that when the reaction was operated at the concentration of 20 % catalyst, the color of hydrogenated oil was as black as the color of used oil (>8). This showed that hydrotreating reaction was less active at this condition.

When the concentration of catalyst was decreased from 40 % to 35 and 30 %, the slightly change of pour point of hydrogenated oil. The pour point of hydrogenated oils were slightly increased from -4.5°C to -4°C , which was higher than that of used oil (-18°C). This result from deteriorating of pour point depressant which was remained in used oil, when the hydrogenation of used oil was operated at the temperature of 350°C . Concentration of catalyst had a little effect to the pour point of hydrogenated oils.

Color of hydrogenated oil at the concentration of 40 and 35 % catalyst were not different, whereas in use of concentration of catalyst of 30 % the color of hydrogenated oil was increased to 2.

When decreased the concentration of catalyst from 40 % to 35 and 30 %, the viscosity was increased, this result from increasing of paraffinic hydrocarbons. In term of VI, when the concentration of catalyst was decreased from 40 % to 35 and 30 %, hydrogenated oil had the value of VI slightly increased from 111 to 112. This result from slightly increased of paraffinic hydrocarbon. At the concentration of 35 and 30 % catalyst, the value of VI were the same (112).

In term of flash point and sulfur content, the data showed that flash point of hydrogenated oil was increased from 192°C to 195 and 196°C and the sulfur content of hydrogenated was increased from 0.172 % to 0.204 and 0.282

%, when the concentration of catalyst was decreased from 40 % to 35 and 30 %, respectively. This result from increasing of concentration of catalyst increased the rate of hydrocracking, hydrodesulfurization and hydrogenation, resulting in increasingly lower molecular weight hydrocarbon compounds and effective of sulfur removal.

The decreasing of concentration of catalyst from 40 % to 35 and 30 %, the slightly increased yield from 78 to 80 and 81 %, respectively.

From data above, when the reaction was operated at the concentration of 20 % catalyst, the color of the hydrogenated oil was as black as the color of the used oil. This showed that hydrotreating reaction was less active at this condition. The properties and yields of hydrotreated oils at the concentration of 40, 35 and 30 % catalyst were no significant difference except the sulfur content. However, the sulfur content of hydrotreated oil was desirable when concentration of 30 % catalyst was operated. It was not necessary to use the concentration of catalyst upto 40 %.

In some cases, the used lubricating oil had better properties than hydrogenated oil such as pour point. This can be explained that used oil might have some available additives to maintain the good result of oil.

Finally, this experiment was tried to decrease the reaction time less than 10 minutes in order to apply to use in the industrial way. It was possible to decrease the reaction time to 5 and 2 minutes. The data are shown in the Table 4.4.

Table 4.4 Physical and chemical properties of hydrogenated oil at constant concentration of NiO/MoO₃/Al₂O₃ (30 %) and various reaction time.

Physical and Chemical Properties		Reaction Time (mins)							
		10			5			2	
		#1	#2	#3	#1	#2	#3	#1	#2
Pour point	(°C)	-4	-6	n.a.	-6	-5.5	n.a.	-5.5	n.a.
Color	(ASTM)	2	2	>8	2	2	>8	2	>8
Viscosity, Kin @	40 °C (cSt)	58.30	35.56	n.a.	55.09	27.37	n.a.	55.71	n.a.
	@ 100 °C (cSt)	8.22	6.12	n.a.	8.02	5.24	n.a.	8.03	n.a.
Viscosity Index		112	119	n.a.	113	125	n.a.	112	n.a.
Flash point	(°C)	196	164	n.a.	200	144	n.a.	206	n.a.
Sulfur content	(%)	0.282	0.319	n.a.	0.326	0.363	n.a.	0.356	n.a.
Yield	(%)	81	83	n.a.	80	82	n.a.	81	n.a.

= The number of time which catalyst was used again without regenerating.

From Table 4.4 and Figure 4.4, the decreasing of reaction time from 10 minutes to 5 and 2 minutes causing the slightly decreased of pour point from -4 °C to -6 and -5.5 °C, respectively. This result from the operating at short reaction time took a chance of less deteriorating of pour point depressant than the operating at long reaction time.

When the catalyst was used two times without regenerating, the pour point of hydrogenated oil operating at 10 minutes of reaction time was decreased from -4 to -6 °C. This result from the operating at long reaction time in first time causing the catalyst broke into dust, flowed and assembled with hydrogenated oil and byproduct. This caused the decreasing of surface area and active site of catalyst in the operating at second time. The pour point of hydrogenated oil operating at 5 minutes of reaction time was increased from -6 to -5.5 °C. This result from the operating at 5 minutes of reaction time in first

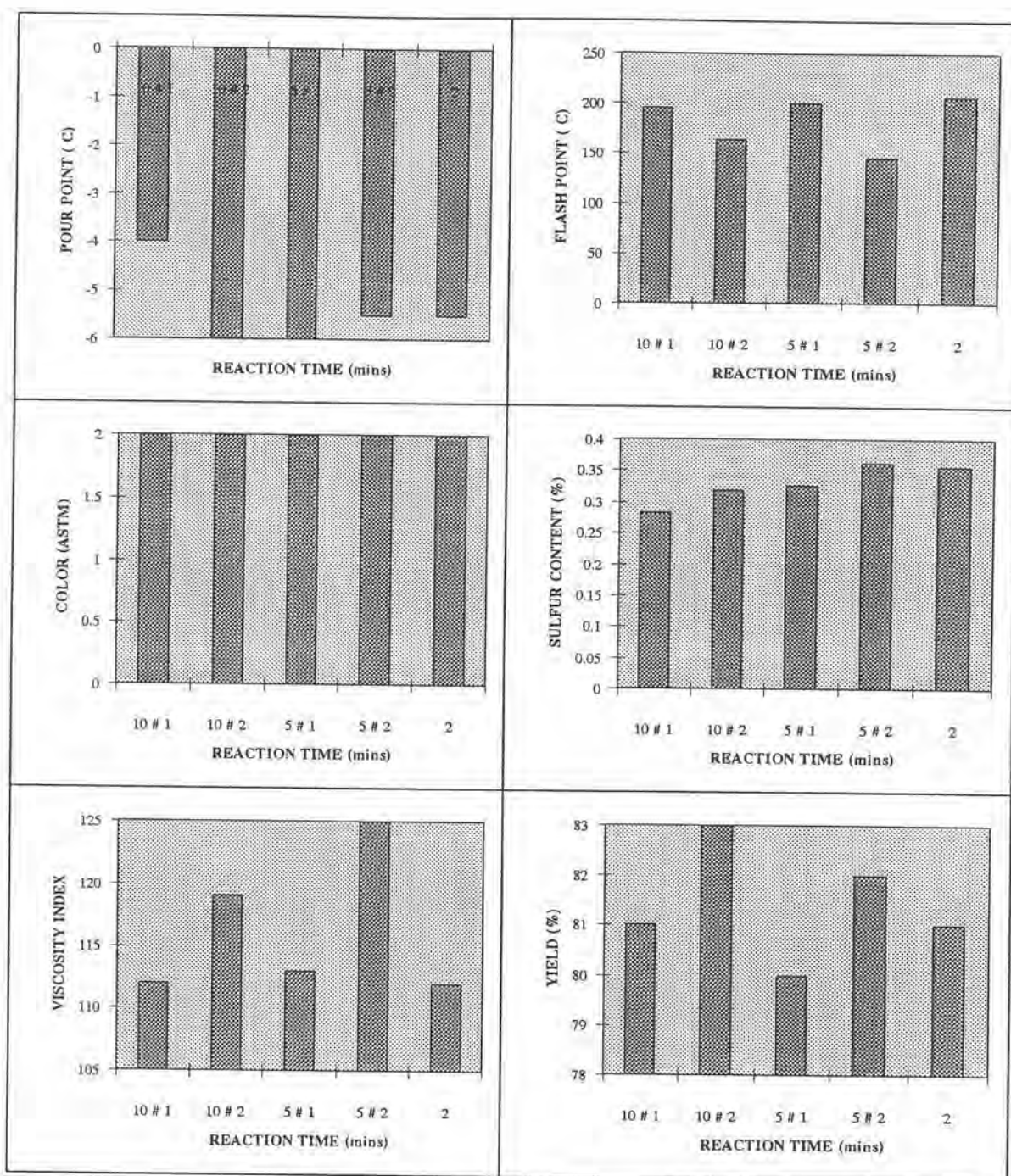


Figure 4.4 Effect of reaction time on properties of hydrogenated oils by using NiO/WO₃/Al₂O₃ catalyst at the constant concentration (30 %) and various reaction times.

time causing the catalyst broke into dust less than at 10 minutes. The lost of catalyst in form of dust was less together, causing more active site to take a chance of deteriorating of pour point depressant so the pour point was slightly increased. The operating at 2 minutes of reaction time in two times and at 10 and 5 minutes in three times gave the oil having color as black as used oil. This showed that the catalyst was less effective.

In term of color, it was found that the decreasing of reaction time would gave the hydrogenated oil having the same color (2) included in the operating in the second time.

In term of viscosity, it was found that there was a little changed in viscosity when the reaction time was decreased. But at the operating in the second time, the viscosity was decreased both in the reaction time of 10 and 5 minutes. This result from the catalyst was broken into dust causing more active site to increase the rate of hydrocracking resulting in higher paraffinic hydrocarbons.

In term of VI, when decreasing the reaction from 10 minutes to 5 and 2 minutes at the operating in first time, there was a slightly changed of VI value (112-113). On the other hand when operating at the second time, it was found that the VI value was increased to 119 (10 minutes) and 125 (5 minutes). This result from the same reason in term of viscosity. The operating at 2 minutes of reaction time in two times and at 10 and 5 minutes in three times gave the oil having color as black as used oil. This showed that the catalyst was less effective.

When decreasing the reaction from 10 minutes to 5 and 2 minutes at the operating in first time, the flash point of hydrogenated oil was increased from 196 to 200 and 206 °C. This result from the increasing reaction time increased the rate of hydrocracking resulting in increasingly lower molecular weight hydrocarbon compounds. At the operating in second time, it was found

that the flash point was decreased from 196 to 164 °C (10 minutes) and was decreased from 200 to 144 °C (5 minutes). This result from the breaking of catalyst gave more surface area and active site causing increased the rate of hydrocracking resulting in lower molecular weight hydrocarbon compounds.

In term of sulfur content, when decreasing the reaction from 10 minutes to 5 and 2 minutes at the operating in first time, the effective of sulfur removal was decreased. The sulfur content of hydrogenated oil was increased from 0.282 to 0.326 and 0.356 %. This result from the increasing reaction time increased the rate of hydrodesulfurization. At the operating in second time, it was found that the sulfur content was increased from 0.282 to 0.319 % (10 minutes) and was increased from 0.326 to 0.363 % (5 minutes). This result from, it might have been left of sulfur in catalyst behind the first time of operation.

There was a little effect of time in yield of hydrogenated oil. Yield was in range of 80-81 %. At the operating in second time, it was found that the yield was increased from 81 to 83 % (10 minutes) and was increased from 80 to 82 % (5 minutes). This result from sulfur which left in catalyst behind the first time of operation causing more active of catalyst in increasingly in yield of hydrogenated oil.

From data above, the properties of oils by using less reaction time than 10 minutes were desirable. At each reaction time of 10 and 5 minutes, when the catalyst was used two times without regenerating, the properties of the resulting oils were still desirable. The catalyst could not be used at the three times because the color of hydrogenated oil was as black as the used oil. This resulted from no or less active sites on catalysts. However, at the reaction time of 2 minutes, when the catalyst was used two times, the color of resulting oil

was undesirable. The optimum reaction time for 30 % NiO/WO₃/Al₂O₃ catalyst was 2 minutes.

Table 4.5 Properties of hydrogenated oil obtained from suitable condition by using NiO/WO₃/Al₂O₃ catalyst compare with specification of re-refined base oil (150 SN) and finished petroleum base oil (150 SN)

Properties	Hydrogenated oil (suitable condition)	Re-refined base oil	Base oil
Viscosity at 100 °C	8.03	5.0±0.2	4.55
Viscosity Index	112	90-110	98
Color (ASTM)	2	3	-
Flash point (°C)	206	210	-
Pour point (°C)	-5.5	-9	-23

From Table 4.5, it was showed that hydrogenated oil had more desirable properties than quality acceptance oil of re-refined base oil (150 SN) and inspection characteristics of finished petroleum base oil (150 SN), especially in terms of viscosity at 100 °C, viscosity index and color. Hence, the hydrogenated oil could be used as marine lubricating oil by adding less additives than in petroleum base oil.

D. Effect of Reaction Time on Hydrogenation of Used Oil by using Nickel oxide/molybdenum oxide/alumina (NiO/MoO₃/Al₂O₃) catalyst.

This section was studied the hydrogenation of used lubricating oil by using the constant concentration of Nickel oxide/molybdenum oxide/alumina catalyst (40 %) but varying the reaction times. Reaction times for this experiment were 60, 30, 20 and 10 minutes respectively. Used oils were carried out at the hydrogen pressure of 500 psig and the reaction temperature of 350 °C. By this way, all data obtained from this experiment are shown in the Table 4.6

Table 4.6 Physical and chemical properties of hydrogenated oils at the constant concentration of NiO/MoO₃/Al₂O₃ catalyst (40 %) and various reaction times.

Physical and Chemical Properties	Reaction Time (minutes)			
	60	30	20	10
Pour Point (°C)	-4.5	-4	-4	-4
Color (ASTM)	1.5	2	2	2
Viscosity, Kin @ 40 °C (cSt)	51.67	49.66	52.29	52.78
@ 100 °C (cSt)	7.65	7.45	7.68	7.71
Viscosity Index	112	112	111	110
Flash point (°C)	180	186	190	196
Sulfur Content (%wt)	0.111	0.181	0.187	0.208
Yield (%)	76	75	75	75

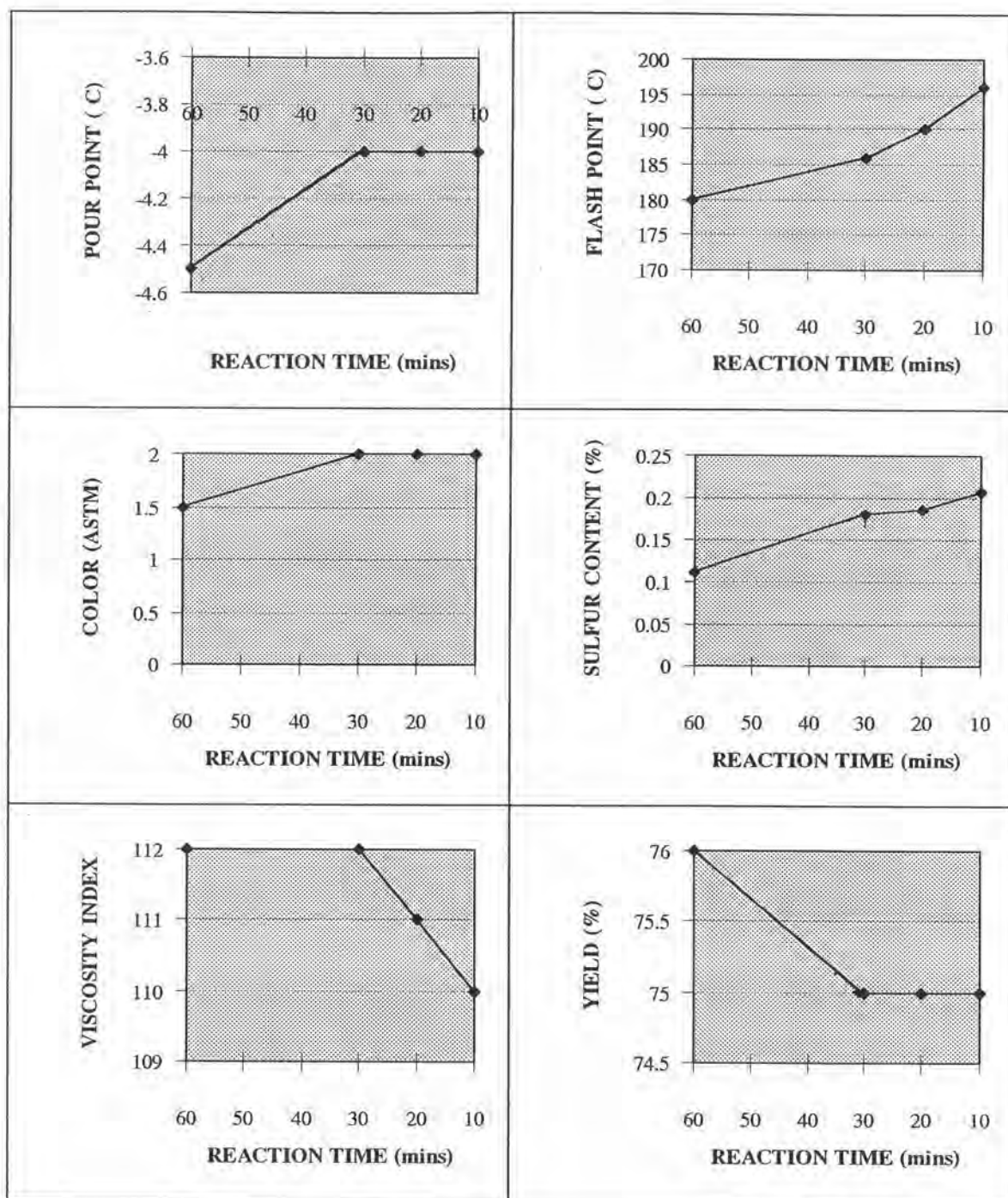


Figure 4.5 Effect of reaction time on properties of hydrogenated oils by using NiO/MoO₃/Al₂O₃ catalyst at the constant concentration (40 %) and various reaction times.

Effect of reaction time on hydrogenation of used lubricating oil was tried out by varying the reaction time of 60, 30, 20 and 10 minutes respectively. The objective of this experiment was to try to optimize reaction time for desirable properties of hydrogenated oil.

From Table 4.6 and Figure 4.5, the decreasing of reaction time from 60 to 30 minutes would give the oil having higher pour point from -4.5°C to -4°C , the pour point at the reaction time of 30, 20 and 10 minutes was the same (-4°C). The pour point of hydrogenated oil at every reaction time was higher than used oil (-18°C). This result from deteriorating of pour point depressant which was remained in used oil, when the hydrogenation of used oil was operated at the temperature of 350°C .

The color of hydrogenated oil was increased from 1.5 to 2 when the reaction time was increased from 60 to 30 minutes. At the reaction time of 30, 20 and 10 minutes, the color of hydrogenated oil were the same (2). Hydrogenated oil had better color than used oil (>8).

There was a little change in viscosity when the reaction time was decreased. In term of VI, at the reaction time of 60 and 30 minutes, the value of VI was the same (112). When the reaction time was decreased to 20 and 10 minutes, the VI value was decreased to 111 and 110, respectively. This result from, hydrogenated oil obtaining in use of long reaction time had more constituent of paraffinic hydrocarbons. However, the VI value of hydrogenated oil obtaining from every reaction time were higher than used oil (102).

In term of flash point, the decreasing of reaction time from 60 to 30, 20 and 10 minutes would give the oils having higher flash point from 180°C to 186 , 190 and 196°C , respectively. This result from, the increasing reaction time increased the rate of hydrocracking and hydrogenation resulting in increasingly lower molecular weight hydrocarbon compounds. Hydrogenated oil which

obtained from operating at long reaction time had lower flash point than operating at short reaction time.

The effective in sulfur removal was decreased when the reaction time was decreased. The hydrogenated oil had the sulfur content of 0.208, 0.187, 0.181 and 0.111 %, when the reaction time was increased from 10 to 20, 30 and minutes, respectively. This result from the rate of hydrodesulfurization was increased when the reaction time was increased.

Yield of hydrogenated oils at the reaction time of 10, 20 and 30 minutes were the same (75 %). Decreasing of reaction time from 60 minutes to 30 minutes, the slightly decreased yield from 76 to 75 %.

From Table 4.6, the oil obtained by using more reaction time had better properties than less reaction time in terms of pour point, viscosity index, color and sulfur content. But the flash point was low when the reaction time were increased. This resulted from cracking reaction.

The result demonstrated that reaction time of 10 minutes gave oil having desirable properties. So, it was not necessary to use more reaction time than this. In the next experiment, it would be studied the least concentration of catalyst which gave oil having desirable properties.

Effect of concentration of catalyst on hydrogenation of used lubricating oil were investigated by varying the catalyst concentration of 40, 35 and 30 % by weight of used oil. The objective of this experiment was to study the least concentration of catalyst which gave oil which had desirable properties.

Table 4.7 showed that when that the reaction was operated at the and 30 % concentration of catalyst, the color of hydrogenated oil was as black as the color of used oil (>8). This showed that hydrotreating reaction was less active at this condition.

When the concentration of catalyst was decreased from 40 to 35 %, the pour point of hydrogenated oils was decreased from -4 °C to -5.5 °C, which was higher than that of used oil (-18 °C). This result from deteriorating of pour point depressant which was remained in used oil, when the hydrogenation of used oil was operated at the temperature of 350 °C. Concentration of catalyst had a little effect to the pour point of hydrogenated oils.

Color of hydrogenated oil at the catalyst concentration of 40 and 35 % were not different (2).

When decreased the concentration of catalyst from 40 to 35 %, the viscosity was slightly increased, this result from increasing of paraffinic hydrocarbons. In term of VI, when the concentration of catalyst was decreased from 40 to 35 %, hydrogenated oil had the value of VI increased from 110 to 117. This result from increased of paraffinic hydrocarbons.

In term of flash point and sulfur content, the data showed that flash point of hydrogenated oil was increased from 170 to 207 °C and the sulfur content of hydrogenated was increased from 0.208 to 0.279 %, when the concentration of catalyst was decreased from 40 to 35 %. This result from increasing of concentration of catalyst increased the rate of hydrocracking,

hydrodesulfurization and hydrogenation, resulting in increasingly lower molecular weight hydrocarbon compounds and effective of sulfur removal.

The decreasing of concentration of catalyst from 40 to 35 %, the slightly increased yield from 75 to 77 %.

From Table 4.7, the using NiO/MoO₃/Al₂O₃ catalyst in less concentration was more active in hydrogenation of used oil. But the concentration of 30 % catalyst gave no or less reaction. At the concentration of 35 % catalyst, the resulting oil had desirable properties. The oil obtained from concentration of catalyst at 35 % had better properties than used oil in terms of viscosity index, color and sulfur content. The catalyst which was used in first time without regenerating could not be used in the second time because the color of hydrogenated oil was as black as used oil. This resulted from no or less active sites on catalyst. The yield of hydrogenated oil was 77 %.

The reaction time was decreased less than 10 minutes but the color of the resulting oils were not better than that of used oil. The suitable condition for 35 % NiO/MoO₃/Al₂O₃ catalyst was 10 minutes.

Table 4.8 Properties of hydrogenated oil obtained from suitable condition by using NiO/MoO₃/Al₂O₃ catalyst compare with specification of re-refined base oil (150 SN) and finished petroleum base oil (150 SN)

Properties	Hydrogenated oil (suitable condition)	Re-refined base oil	Base oil
Viscosity at 100 °C	8.11	5.0±0.2	4.55
Viscosity Index	117	90-110	98
Color (ASTM)	2	3	-
Flash point (°C)	207	210	-
Pour point (°C)	-5.5	-9	-23

From Table 4.8, it was showed that hydrogenated oil had more desirable properties than quality acceptance oil of re-refined base oil (150 SN) and inspection characteristics of finished petroleum base oil (150 SN), especially in terms of viscosity at 100 °C, viscosity index and color. Hence, the hydrogenated oil could be used as marine lubricating oil by adding less additives than in petroleum base oil.

F. Effect of Reaction Time on Hydrogenation of Used Oil by using Raney Nickel catalyst.

This section was studied the hydrogenation of used lubricating oil by using the constant concentration of Raney nickel catalyst (40 %) but varying the reaction times. Reaction times for this experiment were 30, 20 and 10 minutes respectively. Used oils were carried out at the hydrogen pressure of 500 psig and the reaction temperature of 350 °C. By this way, all data obtained from this experiment are shown in the Table 4.9

Table 4.9 Physical and chemical properties of hydrogenated oils at the constant concentration of Raney nickel catalyst (40 %) and various reaction times.

Physical and Chemical Properties	Reaction Time (minutes)		
	30	20	10
Pour Point (°C)	-5	-5	-5
Color (ASTM)	1	1	1
Viscosity, Kin @ 40 °C (cSt)	60.22	64.65	63.59
@ 100 °C (cSt)	8.33	8.59	8.55
Viscosity Index	108	105	105
Flash point (°C)	218	220	220
Sulfur Content (%wt)	0.202	0.265	0.287
Yield (%)	93	92	92

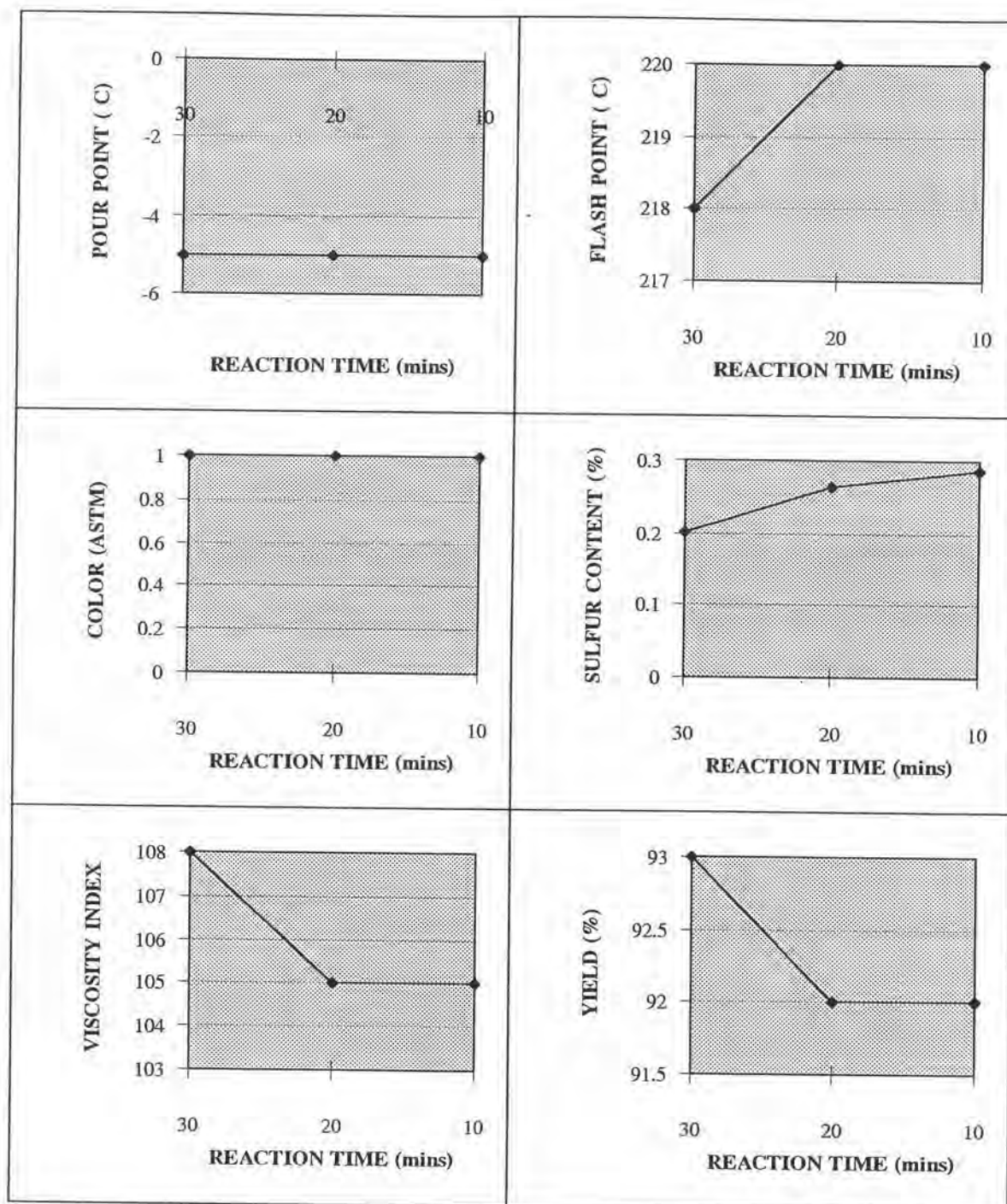


Figure 4.6 Effect of reaction time on properties of hydrogenated oils by using Raney nickel catalyst at the constant concentration (40 %) and various reaction times.

Effect of reaction time on hydrogenation of used lubricating oil was investigated by varying the reaction time of 30, 20 and 10 minutes respectively. The objective of this experiment was to try to determine the least reaction time which gave oil having desirable properties.

From Table 4.9 and Figure 4.6, the decreasing of reaction time from 30 to 20 and 10 minutes would give the oil having the same pour point ($-5\text{ }^{\circ}\text{C}$). There was no effect of reaction time on pour point of hydrogenated oil. The pour point of hydrogenated oil at every reaction time was higher than used oil ($-18\text{ }^{\circ}\text{C}$). This result from deteriorating of pour point depressant which was remained in used oil, when the hydrogenation of used oil was operated at the temperature of $350\text{ }^{\circ}\text{C}$.

The color of hydrogenated oil was the same (1), although the reaction time was decreased from 30 to 20 and 10 minutes. Hydrogenated oil had better color than used oil (>8).

There was a slightly increased in viscosity when the reaction time was decreased. In term of VI, when the reaction time was decreased from 30 to 20 minutes, the VI value was decreased from 108 to 105. At the reaction time of 20 and 10 minutes, the value of VI was the same (105). However, the VI value of hydrogenated oil obtaining from every reaction time were higher than used oil (102).

In term of flash point, the decreasing of reaction time from 30 to 20 minutes would give the oils having higher flash point from 218 to $220\text{ }^{\circ}\text{C}$, respectively. This result from, the increasing reaction time increased the rate of hydrocracking and hydrogenation resulting in increasingly lower molecular weight hydrocarbon compounds. Hydrogenated oil which obtained from operating at long reaction time had lower flash point than operating at short reaction time. At the reaction time of 20 and 10 minutes, flash point of hydrogenated oil was the same ($220\text{ }^{\circ}\text{C}$).

The effective in sulfur removal was decreased when the reaction time was decreased. The hydrogenated oil had the sulfur content of 0.202, 0.265 and 0.287 %, when the reaction time was decreased from 30 to 20 and 10 minutes, respectively. This result from the rate of hydrodesulfurization was decreased when the reaction time was decreased.

Yield of hydrogenated oil at the reaction time of 10 and 20 minutes were the same (92 %). Decreasing of reaction time from 30 to 20 minutes, the yield were slightly decreased from 93 to 92 %.

From data above, the oil obtained at more reaction time had better properties than done at less reaction time in terms of viscosity index and sulfur content. The other properties such as pour point, color and flash point was no significant differences although the reaction time were decreased.

The result showed that the properties of hydrogenated oil at reaction time of 10 minutes were desirable. In the next experiment, it was planned to study the least concentration of catalyst that still gave desirable properties of oil.

G. Effect of Concentration of Catalyst on Hydrogenation of Used Oil by using Raney Nickel catalyst.

The aim of this experiment was to compare the properties of resulting oil when the concentration of Raney nickel catalyst were varied (40, 35, and 30 % by weight of used oil). Used oils were carried out at the hydrogen pressure of 500 psig, the reaction temperature of 350 °C, and the reaction time of 10 minutes. The data obtained from this experiment are shown in the Table 4.10

Table 4.10 Physical and chemical properties of hydrogenated oils at the constant reaction time (10 minutes) and various concentration of Raney nickel catalyst.

Physical and Chemical Properties	Concentration of R-Ni (%)		
	40	35	30
Pour Point (°C)	-5	-5	n.a.
Color (ASTM)	1	3	>8
Viscosity, Kin @ 40 °C (cSt)	63.59	65.12	n.a.
@ 100 °C (cSt)	8.55	8.83	n.a.
Viscosity Index	105	109	n.a.
Flash point (°C)	220	220	n.a.
Sulfur Content (%wt)	0.287	0.306	n.a.
Yield (%)	92	93	very low

Effect of concentration of catalyst on hydrogenation of used lubricating oil were investigated by varying the catalyst concentration of 40, 35 and 30 % by weight of used oil. The objective of this experiment was to study the least concentration of catalyst which gave oil which had desirable properties.

Table 4.10 showed that when that the reaction was operated at the and 30 % concentration of catalyst, the color of hydrogenated oil was as black as the color of used oil (>8). This showed that hydrotreating reaction was less active at this condition.

When the concentration of catalyst was decreased from 40 to 35 %, the pour point of hydrogenated oils was the same (-5 °C), which was higher than that of used oil (-18 °C). This result from deteriorating of pour point depressant which was remained in used oil, when the hydrogenation of used oil was operated at the temperature of 350 °C. Concentration of catalyst had no effect to the pour point of hydrogenated oils.

Color of hydrogenated oil was increased from 1 to 3 when the concentration of catalyst was decreased from 40 to 35 %.

When decreased the concentration of catalyst from 40 to 35 %, the viscosity was slightly increased, this result from increasing of paraffinic hydrocarbons. In term of VI, when the concentration of catalyst was decreased from 40 to 35 %, hydrogenated oil had the value of VI increased from 105 to 109. This result from increased of paraffinic hydrocarbon.

In term of flash point and sulfur content, the data showed that flash point of hydrogenated oil was the same (220 °C) although the concentration of catalyst was decreased from 40 to 35 %. The sulfur content of hydrogenated was increased from 0.287 to 0.306 %, when the concentration of catalyst was decreased from 40 to 35 %. This result from increasing of concentration of catalyst increased the rate of hydrodesulfurization resulting in increasingly effective of sulfur removal.

The decreasing of concentration of catalyst from 40 to 35 %, the slightly increased yield from 92 to 93 %.

From data above, the concentration of 30 % catalyst gave no or less reaction. At the concentration of 35 % catalyst, the resulting oil had desirable properties. The oil obtained from concentration of 35 % catalyst had better properties than used oil in terms of viscosity index, color and sulfur content. The catalyst which was used in the first time without regenerating could not be used in the second time because the color of hydrogenated oil was as black as used oil. This resulted from no or less active sites on catalyst. The yield of hydrogenated oil was 93 %.

The reaction times were decreased less than 10 minutes but the color of the resulting oils were not better than that of used oil. The suitable condition for 35 % Raney nickel was 10 minutes.

Table 4.11 Properties of hydrogenated oil obtained from suitable condition by using Raney-Ni catalyst compare with specification of re-refined base oil (150 SN) and finished petroleum base oil (150 SN)

Properties	Hydrogenated oil (suitable condition)	Re-refined base oil	Base oil
Viscosity at 100 °C	8.83	5.0±0.2	4.55
Viscosity Index	109	90-110	98
Color (ASTM)	3	3	-
Flash point (°C)	220	210	-
Pour point (°C)	-5	-9	-23

From Table 4.11, it was showed that hydrogenated oil had more desirable properties than quality acceptance oil of re-refined base oil (150 SN) and inspection characteristics of finished petroleum base oil (150 SN), especially in terms of viscosity at 100 °C, viscosity index, color and flash point. Hence, the hydrogenated oil could be used as marine lubricating oil by adding less additives than in petroleum base oil.