Chapter IV

Results and Discussions

In this chapter, experimental results are presented and compared with specification of base lube oil. Lubricating oils are usually a mixture of different grades of base lube oil and additives. Several types of base oil stocks are used in Thailand. Their properties depend on sources and companies who sell lubricating oil. Table 4.1 shows examples of base lube oil specifications normally used in Thailand.

Table 4.1   The Specification Properties of Base Lube Oil

Properties	Test Method	Limit		
		No.1	No.2	No.3
1. COLOR	ASTM D1500	max 1.5	max 3.5	max 6.0
2. SULFUR (wt%)	ASTM D4294	0.2-0.8	0.2-0.8	0.5-1.7
3. Viscosity (cSt)	ASTM D445			
40°C		Report	Report	Report
100°C		4.8-5.4	10.0-12.0	30.0-34.0
4. Viscosity Index	ASTM D2270	min 95	min 95	min 95
5. FLASH POINT (°C)	ASTM D92	min 200	min 220	min 260
6. TAN (mgKOH/g)	ASTM D974	max 0.05	max 0.05	max 0.05
7. WATER :CRACKLE	AMS 150.09	nil	nil	nil

Lubricating oils are classified on the basis of
their viscosities. Viscosity grading of automotive oils
by Society of Automotive Engineers (SAE) is given in
Table 4.2 (Becker, 1982). The viscosity of the oil is
inversely proportional to temperature. At low
temperature, viscosity is high and the engine is
difficult to start. At high temperature, insufficient
lubrication may be occurred because of lower viscosity
and causes the engine to be worn out. Thus, only one SAE
grade can not serve over a wide range of temperature.
Addition of viscosity-index improvers, oils that meet the
requirement of more than one SAE grade are available.

Table 4.2   SAE Automotive-Lubricant Viscosity
            Classifications

SAE viscosity grade	Viscosity range		
	mPa.s(cP)[1] (at −18°C)	mm^2/s (cSt) (at 100°C)	
	Max	Min	Max
5W	1,250	3.8	
10W	2,500	4.1	
20W	10,000	5.6	
20		5.6	< 9.3
30		9.3	< 12.5
40		12.5	< 16.3
50		16.3	< 21.9

[1] cP = centipoise = cSt x density of oil

Common automobile lubricating oil in Thailand is
SAE20W-50 which combine the low temperature viscosity of
the SAE20W classification for easy low temperature
strating with SAE50 high viscosity for better load
capacity at the normal engine running temperature. It
has viscosity in a range of 16.3 to 21.6 cSt at 100°C and
less than 10000 cP at -18°C (Table 4.2).

Commercial lubricating oils grade SAE20W-50 which
are avaiable in market are sampled and analyzed to find
properties of commercial lubricating oil. Table 4.3
shows properties of sample commercial lubricating oils
grade SAE20W-50.

Lubricating oil can be deteriorated by external
contaminants such as dust, dirt, metal paticles, water,
acids, soot, sludge, unburned fuel and oxidation
products. Dust and dirt get into the engine by
inefficient and leakage in air cleaning systems. They
contaminate the oil and result in an increase in
viscosity of the oil. Normal wear of the engine produces
small metal particles. The abrasive material causes
rapid wear and generates larger metal particles which are
in themselves quite abrasive. Water and acid materials
are produced during combustion. When the temperature of
the engine is high, most of the water and acid vapors
leave the engine through exhaust. However, when the
engine temperature is low, during start-up and warm-up,
these vapors are condensed on cylinder walls and are
picked up by the oil. Water is generally a component of

Table 4.3 Properties of Sample Commercial Lubricating Oil Grade 20W-50.

Properties	Test Method	Analytical Result							
		No.1	No.2	No.3	No.4	No.5	No.6	No.7	No.8
1.COLOR	ASTM D1500	2.0	2.0	2.0	2.0	2.0	L3.0	L3.0	L3.0
2.SULFUR (wt%)	ASTM D4294	0.54	0.51	0.56	0.43	0.70	0.40	0.50	0.50
3.Viscosity (cSt)	ASTM D445								
40°C		172.34	168.26	172.80	172.92	166.10	156.40	156.40	154.00
100°C		18.88	18.35	18.83	18.82	18.43	18.06	18.23	18.09
4.Viscosity Index	ASTM D2270	124	122	123	123	124	128	130	130
5.FLASH POINT (°C)	ASTM D92	243	241	237	246	231	224	248	234
6.TBN (mgKOH/g)	ASTM D974	10.44	10.58	10.40	10.63	10.50	8.60	8.61	8.82
7.WATER :CRACKLE	AMS 150.09	DRY	DRY	DRY	DRY	DRY	DRY	DRY	DRY

crankcase sludge and causes rusting to engine parts. The acid materials combine any water present and cause corrosion of engine parts. Incomplete combustion produces soot, vanish and other deposit forming materials. Rich mixture during starting and warm-up periods increases amount of such materials formed. Deposits are formed when oil becomes saturated with these contaminants. In addition, unburned fuel is drained from combustion chamber into the crankcase where it dilutes the lubricating oil. Severe dilution of the oil can bring serious result in reducing the viscosity and flash point of the oil below desirable level. Consistent and extremely high-speed driving, especially at high temperature, promotes oil oxidation. Oil oxidation is harmful because products of oil oxidation interfere with lubrication by forming sludge and corrosive by-products. Thus, properties of the used oil depend on lubricating oil grade, operating condition and serviced period. In this study, used lubricating oils are collected from several service stations and are blended. A sample is taken for analysis. Properties of the sample used oil are shown in Table 4.4.

Table 4.4   The Properties of A Sample Used Lubricating
            Oils

Properties	Test Method	Result
1. COLOR	ASTM D-1500	D 8
2. SULFUR (wt%)	ASTM D-4294	1.20
3. Viscosity (cSt)	ASTM D-445	
40°C		142.60
100°C		16.70
4. Viscosity Index	ASTM D-2270	126
5. FLASH POINT (°C)	ASTM D-92	210
6. TAN (mgKOH/g)	ASTM D-664	4.30
7. Neutralization (mgKOH/g)	ASTM D-974	3.40
8. WATER :CRACKLE	AMS 150.09	DRY

Tables 4.3 and 4.4 demonstrate that after use, viscosity and flash point of the oil decrease while the ASTM color, acidity and sulfur content increase. As previously described, viscosity and flash point of the oil are decreased by dilution with unburned fuel and acidity is increased by acid meterials which are produced by a combustion process. Color becomes darker by contamination with soot, carbon and oxidation product. Increasing of sulfur content in the used oil is expected to come from sulfur compounds in fuel. Fuel usually contains small amount of sulfur compounds. When fuel burns in combustion process, by-product gas which includes sulfur is produced. Similar to water and acid vapors, the sulfur compounds condense on cylinder walls at cold engine temperatures and are picked up in the oil.

In this study, solvent extraction is selected to remove most of contaminants and additives from used lubricating oil because it is easier to operate in laboratory than vacuum distillation. A solvent mixture of 1-butanol, 2-propanol and methylethyl ketone at a ratio of 2:1:1, by volume, is used as solvent in the extraction step. This solvent mixture provides a high percentage of oil recovery while maintains the natural lubricity and other desirable qualities of base oil. Furthermore, the required solvent-to-oil ratio of this solvent is less than other solvents and the sludge which has a neutral pH does not affect environment. After the solvent is separated from the oil, the solvent-extracted oil is hydrotreated with hydrogen. Average properties of solvent-extracted oils are shown in Table 4.5.

After extraction, it is observed that viscosity, flash point and acidity of the oil decrease while ASTM color and sulfur content are unchanged. The decreasing of viscosity may result of selectivity of solvent extraction. The solvent generaly dissolve only base lube oil but can not dissolve synthetic base lube oil. Wishman et al. (1978) treated dried used oil with the same solvent mixture and followed by vacuum distillation to split the oil into four fractions. They found that sulfur content and acidity of the oil decreased after extraction.

Table 4.5   The Average Physical Properties of
            Solvent-Extracted Oils

Properties	Test Method	Result
1. COLOR	ASTM D-1500	D 8
2. SULFUR (wt%)	ASTM D-4294	1.30
3. Viscosity (cSt)	ASTM D-445	
40°C		61.05
100°C		8.45
4. Viscosity Index	ASTM D-2270	110
5. FLASH POINT (°C)	ASTM D-92	181
6. TAN (mgKOH/g)	ASTM D-664	3.50
7. Neutralization (mgKOH/g)	ASTM D-974	2.00
8. WATER :CRACKLE	AMS 150.09	DRY

In this study, effects of temperature and liquid
space velocity on catalytic hydrotreatment of
solvent-extracted oil are studied. The temperatures are
varied in the range of 320°C and 380°C. The liquid space
velocities are varied between 0.5 hr^{-1} and 1.5 hr^{-1}. The
catalysts are commercial CoMo, NiMo and NiW. There are
total of 27 experiments in this study. Detials of each
experiment are given in Table 4.6

During each experiment, liquid samples are taken
every 12 hours. The properties of the liquid sample such
as sulfur content, ASTM color, acidity, flash point,
viscosity and viscosity index are analyzed by ASTM
methods. The results of each experiment are shown in
Table 4.7 and sulfur content of liquid sample are
represented as percent sulfur removal in Table 4.8.

Error of Sample Analysis and Repeatability of Experiments

When conducting experiments, two sources of error
can be introduced to the experimental results,
experimental error and analysis error. The error
introduced by sample analysis was found by three
consecutive tests of the same sample and three separate
experiments were conducted at the same conditions in
order to study the repeatability of the experiments. A
reference experiment is conducted over NiW catalyst at a
pressure of 5.51 MPa (800 psig), a temperature of 350°C
(662°F) and a liquid space velocity of 0.5 hr^{-1}. The
product oil of the reference experiment is used as a
reference sample to find the analytical error.
Analytical results of reference experiment are shown in
Table 4.6. The results show that the analytical error is
in the range of ±5% except the acidity of product oils
which exhibit the analytical error in the range of ±22%.
Two additional experiments are conducted at the same
conditions as the referance experiment and the results of
these three experiments are shown in Table 4.7. The
results are reproducible within an accuracy of 5%.
Although, the acidity of product oils illustrate the
experiment error in the range of ±16%. This error is
within the analytical error.

Table 4.6 Operating Condition in Each Experiment.

Experiment No.	Catalyst	Temperature (°C)	LHSV (hr^{-1})
1	NiW	320	0.5
2	NiW	320	1.0
3	NiW	320	1.5
4	NiW	350	0.5
5	NiW	350	1.0
6	NiW	350	1.5
7	NiW	380	0.5
8	NiW	380	1.0
9	NiW	380	1.5
10	NiMo	320	0.5
11	NiMo	320	1.0
12	NiMo	320	1.5
13	NiMo	350	0.5
14	NiMo	350	1.0
15	NiMo	350	1.5
16	NiMo	380	0.5
17	NiMo	380	1.0
18	NiMo	380	1.5
19	CoMo	320	0.5
20	CoMo	320	1.0
21	CoMo	320	1.5
22	CoMo	350	0.5
23	CoMo	350	1.0
24	CoMo	350	1.5
25	CoMo	380	0.5
26	CoMo	380	1.0
27	CoMo	380	1.5

Table 4.7   Properties of Product Oils from Each Experiment.

Experiment Condition			Analytical Result						
Catalyst	Temp. (°C)	LHSV (hr⁻¹)	ASTM Color	Sulfur Content (wt%)	Viscosity (cSt) 40°C	Viscosity (cSt) 100°C	V.I.	Flash Point (°C)	Acidity (mgKOH/g)
NiW	320	0.5	D 8.0	0.453	62.15	8.44	102	230	1.05
		1.0	D 8.0	0.657	63.98	8.44	106	213	1.14
		1.5	D 8.0	0.863	68.04	8.44	100	235	1.78
	350	0.5	L 8.0	0.192	54.71	7.85	108	227	0.32
		1.0	D 8.0	0.336	61.73	8.38	105	226	0.67
		1.5	D 8.0	0.478	67.68	8.35	105	232	1.04
	380	0.5	L 3.0	0.000	21.83	4.58	126	134	0.07
		1.0	6.0	0.134	44.40	6.86	110	198	0.19
		1.5	D 8.0	0.387	40.36	6.45	110	202	0.64
NiMo	320	0.5	D 8.0	0.379	49.64	7.36	106	222	0.47
		1.0	D 8.0	0.442	50.73	7.46	109	190	0.41
		1.5	D 8.0	0.500	55.26	7.80	109	124	0.59
	350	0.5	D 8.0	0.220	48.60	7.12	106	172	0.05
		1.0	D 8.0	0.259	48.70	7.21	107	178	0.08
		1.5	D 8.0	0.310	50.93	7.40	104	190	0.17
	380	0.5	3.0	0.018	34.69	5.93	115	164	0.10
		1.0	4.0	0.176	43.70	6.74	108	182	0.22
		1.5	5.5	0.193	53.00	7.52	104	212	0.21
CoMo	320	0.5	D 8.0	0.344	36.99	6.18	115	182	0.31
		1.0	D 8.0	0.495	37.17	7.20	115	192	0.51
		1.5	D 8.0	0.594	48.75	7.24	108	193	0.70
	350	0.5	L 2.5	0.098	50.48	7.29	104	196	0.02
		1.0	L 5.5	0.279	49.25	7.05	105	186	0.03
		1.5	L 8.0	0.354	32.54	6.41	118	198	0.10
	380	0.5	L 2.5	0.058	34.40	5.74	121	110	0.16
		1.0	4.5	0.133	39.30	6.01	109	128	0.30
		1.5	4.0	0.172	46.52	6.22	114	172	0.28

Table 4.8   Percent Sulfur Removal of Product Oils from Each Experiment.

Temp. (°C)	CoMo catalyst LHSV (hr⁻¹)			NiMo catalyst LHSV (hr⁻¹)			NiW catalyst LHSV (hr⁻¹)		
	0.5	1.0	1.5	0.5	1.0	1.5	0.5	1.0	1.5
320	66.86	52.31	42.78	63.39	57.61	51.83	56.36	36.71	16.86
350	90.56	73.12	65.90	78.81	74.95	70.14	81.50	67.63	53.95
380	94.41	87.19	83.43	98.07	82.66	81.70	100.00	87.09	62.72

Table 4.9   The Repeatability of Analyze Instrument on The Product Oils of Referance Experiment

TEST ITEM	354/350/0.5				%Deviation	
	1	2	3	Avg	Max.	Min.
Sulfur Content, wt%	0.192	0.182	0.199	0.191	4.19	4.71
Viscosity at 40°C, cSt.	56.25	55.86	55.96	56.02	0.41	0.29
Viscosity at 100°C, cSt.	7.91	7.97	7.91	7.93	0.50	0.25
Viscosity Index	106	110	108	108	1.85	1.85
Flash Point, °C	223	220	227	223.3	1.64	1.49
Neutralization, mgKOH/g	0.39	0.31	0.27	0.32	21.88	15.63

Table 4.10   Results of Three Experimental Runs.

Test Item	Ref. Exp. No.				% Deviation	
	1	2	3	Avg.	Max.	Min.
Sulfur Content, wt%	0.191	0.184	0.193	0.189	3.65	4.17
Viscosity at 40°C, cSt.	56.02	55.04	53.13	54.73	2.36	2.92
Viscosity at 100°C, cSt.	7.93	7.85	7.66	7.81	1.49	1.96
Viscosity Index	108	108	108	108	0.00	0.00
Flash Point, °C	223.3	236	222	227.1	3.92	2.25
Neutralization, mgKOH/g	0.32	0.29	0.38	0.33	15.15	12.12

Hydrodesulfurization

Hydrodesulfurization is a reaction between organosulfur compounds and hydrogen gas resulting on the formation of hydrogen sulfide and hydrocarbon without sulfur element as major products. Figures 4.1 to 4.3 show comparison of percent sulfur removal by each catalyst at diffent LHSVs and temperatures. The results show that percent sulfur removal increases with increasing reaction temperature for all catalysts. It indicates that the hydrodesulfurization activity increases with increasing temperature.

Similar results were observed by Bethea et al. (1973) and Bahn et al. (1982). Bahn et al. (1982) showed that the sulfur content of product oils decreased from approximately 0.21 wt% to about 0.01 wt% for the temperature increase from 285°C to 375°C. Bethea et al.
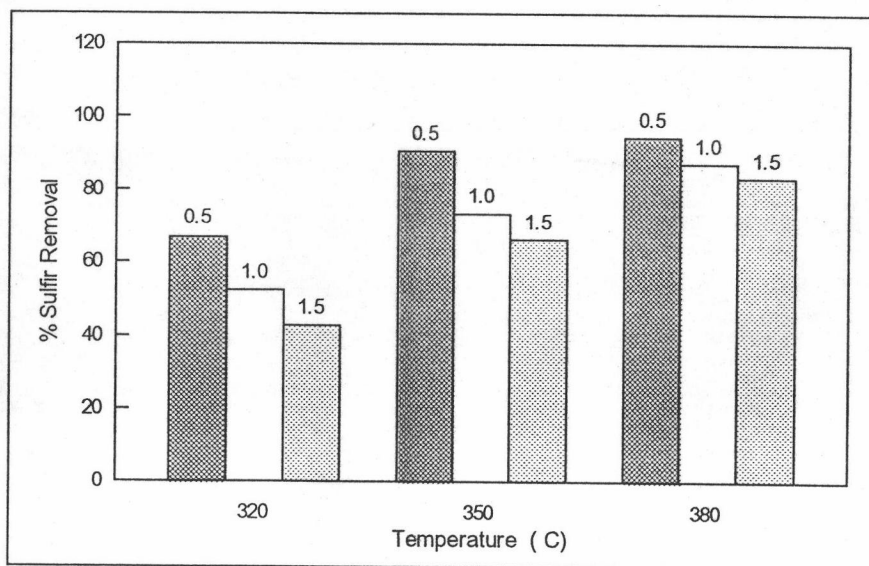
Figure 4.1 Percent Sulfur Removal of CoMo Catalyst at Various LHSV and Temperature.
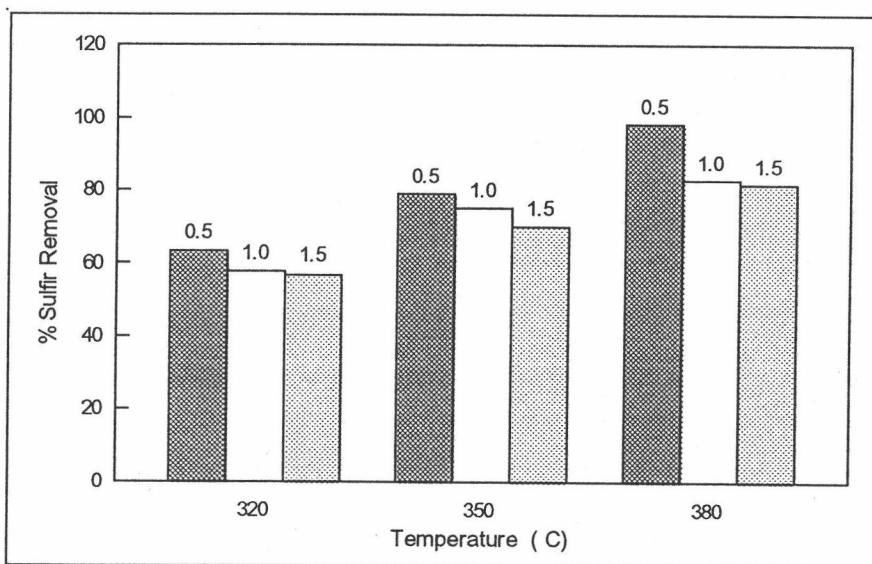
Figure 4.2   Percent Sulfur Removal of NiMo Catalyst at Various LHSV and Temperature.
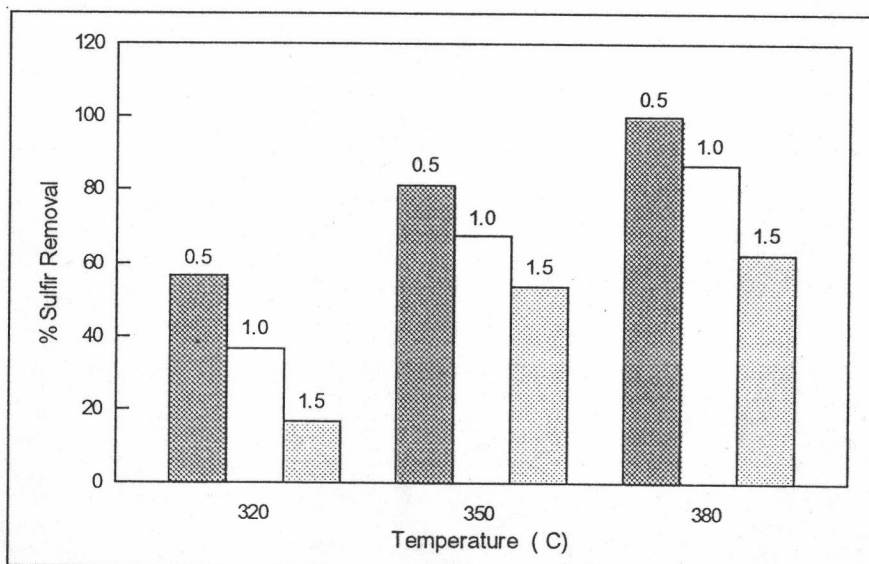
Figure 4.3   Percent Sulfur Removal of NiW Catalyst at Various LHSV and Temperature.

(1973) showed that sulfur content of oil product decreased from 0.053 to 0.012 wt% when the temperature was rised from 288°C (550°F) to 343°C (650°F). Gary and Handwark (1984) also reported that increasing temperature increases sulfur removal.

This result also agreed with a document of Meketta et al. (1982) who reported that a higher temperature increases the rate of desulfurization and a study of Campagna et al. (1985) who study effect of temperature and space velocity on residuum hydrotreating. They showed that percent suflfur removal of product oils increased from 55.16 to 86.17 when the reaction temperature was increased from 320 to 400°C.

Figures 4.1 to 4.3 also illustrate that the sulfur removal decreases with increasing LHSV because the contact time between hydrogen and sulfur compound decreased. This result agreed with the work of Mohammed et al. (1985) who showed that percent sulfur removal of products decreased from 82.21 to 63.83 for the LHSV rise from 0.84 to 2.60 hr^{-1}.

Figures 4.4 to 4.6 demonstrate the comparison of catalyst activity on sulfur removal of product oils for tmeperature of 320, 350 and 380°C, respectively. The results showed that for low temperatures of 320°C and 350°C, NiMo gave the best HDS activity at LHSVs of 1.0 and 1.5 hr^{-1} while CoMo catalyst gave the best activity at a LHSV of 0.5 hr^{-1}. At a high temperature, all catalysts show closed activity at LHSVs of 0.5 and 1.0 hr^{-1}.
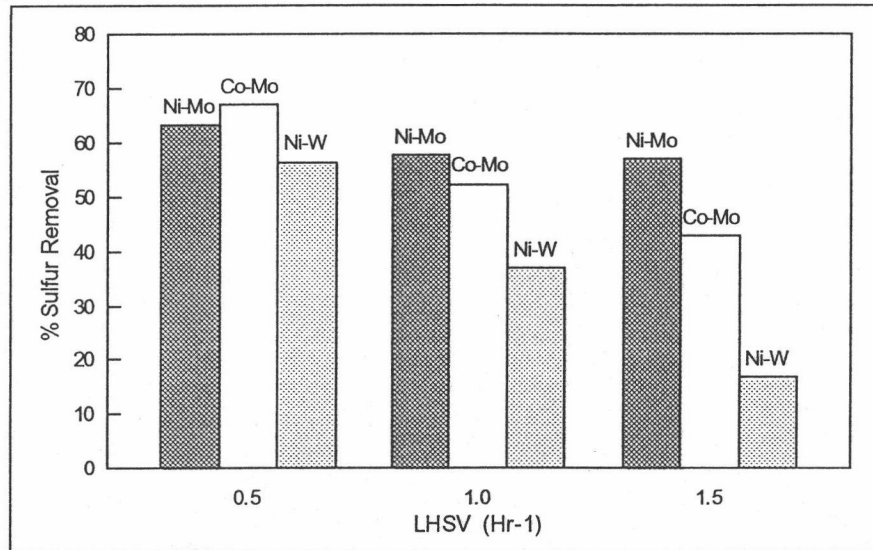
Figure 4.4   The Comparison of Catalyst Activity on Sulfur Removal
at Temperature of 320°C.
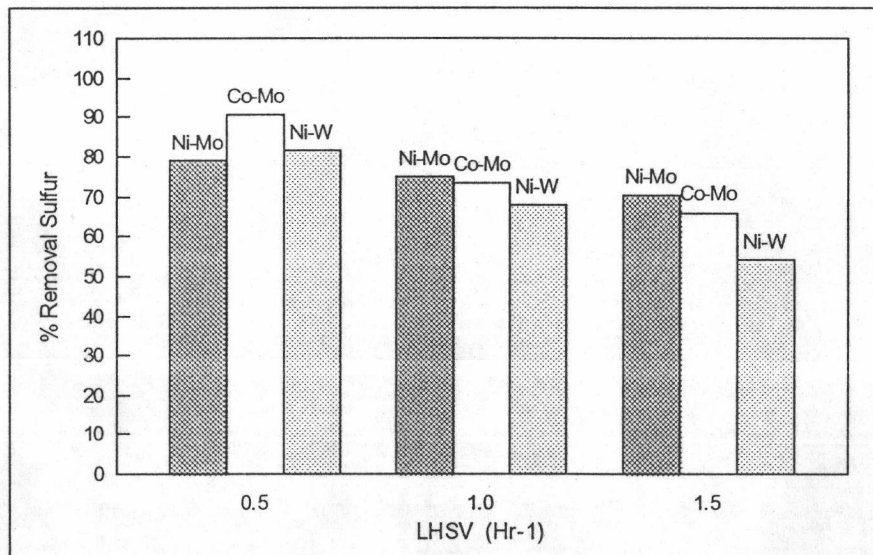
Figure 4.5   The Comparison of Catalyst Activity on Sulfur Removal
at Temperature of 350°C.
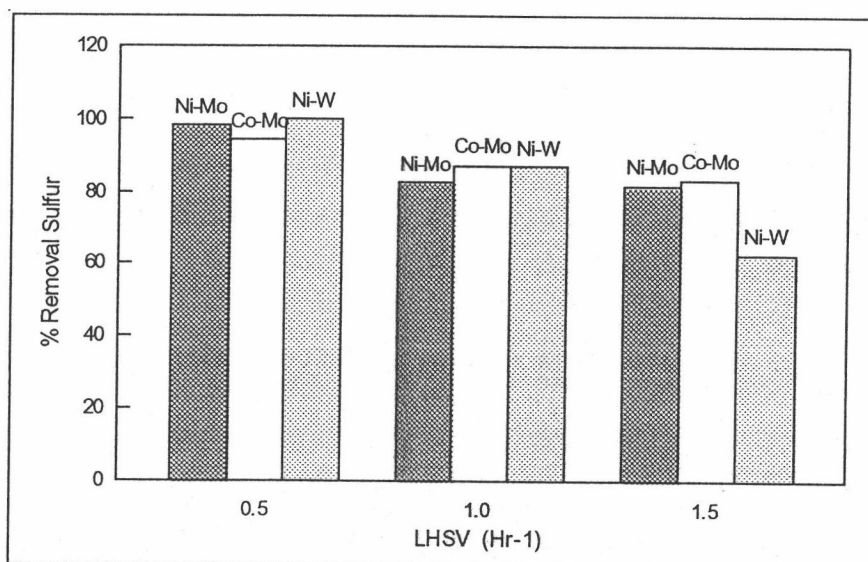
Figure 4.6   The Comparison of Catalyst Activity on Sulfur Removal
             at Temperature of 350°C.

Sulfur content of the product oils meet the specification of base lube oil at all operating conditions and catalysts. Product oils have sulfur content in the range of 0.000 to 0.863 wt% while sulfur content of base lube oil is limited at a range of 0.2 to 1.7 wt%.

ASTM Color

ASTM color is the color of petroleum products that closely matches the color of a specified glass standard. Table 4.11 shows the ASTM color of the product oils at various temperatures and LHSVs. The results show that the ASTM color of the product oils decrease with increasing hydrotreating temperatures, especially the product oils that were reacted at LHSVs of 0.5 and 1.0

hr^{-1} using CoMo catalyst. The results agreed with the
study of Bahn et al. (1982) which used NiMo catalyst.
They found that the ASTM color of their liquid product
decreased from 1.5 to 1.0 when the reaction temperature
was increased from 285 to 325°C.

Table 4.11   The ASTM Color of Product Oils for All
             Catalyst at Various Temperatures and LHSVs.

Hydrotreating Temperature (°C)	CoMo Catalyst			NiMo Catalyst			NiW Catalyst		
	LHSV (hr^{-1})			LHSV (hr^{-1})			LHSV (hr^{-1})		
	0.5	1.0	1.5	0.5	1.0	1.5	0.5	1.0	1.5
320	D8.0	D8.0	D8.0	D8.0	D8.0	D8.0	D8.0	D8.0	D8.0
350	L2.5	L5.5	D8.0	D8.0	D8.0	D8.0	L8.0	D8.0	D8.0
380	L2.5	4.0	4.5	3.0	4.0	5.5	L3.0	6.0	D8.0

Table 4.11 also shows that the ASTM color
decrease with a decrease in LHSV. This result differs
from the study of Bahn et al. (1982) who reported that
the space velocity of the liquid did not affect the color
of liquid product significantly. It is difficult to
explain why the ASTM color of product oils decrease with
a temperature increase and increase with a LHSV increase.
Because no evidence has been reported to show for dark
color substance and for process that produced dark color
substance. However, many documents (Soudek M., 1974;
Waddams A.L., 1980; Bahn et al., 1982; Gary J.H. and
Harwerd G.E., 1984) reported that the dark color of the
oil related with organic nitrogen compounds and
decreasing of nitrogen content improved the oil color.
Thus, the effect of hydrotreating on the ASTM color of
product oils should have the similar result. At the low

temperatures (320 and 350°C) and high LHSV (1.0 and 1.5 hr^{-1}), no appreciable change in the ASTM color was observed for all catalysts. This result may due to the severity of hydrotreating condition which was not enough to remove the dark color substances in the oil.

Comparison of catalyst activity on the product oil color is shown in Table 4.11. CoMo catalyst gives the best ASTM color of product oils while NiW catalyst shows the least performance.

The maximum acceptable ASTM color of the base lube oil is 6.0. The result in Table 4.11 shows that the ASTM color of the product oils is in the range of L2.5 to D8.0. At a low operating temperature (320°C), the product oils did not meet all of the base lube oil specifications. When operating temperature was increased, some operating conditions produced product oils that have acceptable ASTM color. However, the ASTM color of the product oils that produced from these conditions also depends on catalyst types. CoMo catalyst can produce the acceptable ASTM color at a temperature of 380°C and LHSVs of 0.5-1.5 hr^{-1} and at a temperature of 350°C and LHSVs of 0.5-1.0 hr^{-1}. NiMo catalyst can produce the same result at a temperature of 380°C for all LHSV and NiW catalyst can produce at a temperature of 380°C for LHSV 0.5 and 1.0 hr^{-1}.

Acidity

Acidity of the product oils was analyzed by ASTM D974 and presented in form of total acid number. The total acid number is the quantity of base, expressed in milligrams of potassium hydroxide (KOH), that is required to titrate all acidic constituents present in 1 gram of sample.

The effect of operating conditions on acidity of product oils is given in Figures 4.7 to 4.9. The figures show that acidity of the product oils decrease with a temperature rise and increase with a LHSV increase for all catalysts. Although the study of Bethea et al. (1973) reported the acidity of product oils at different operating temperatures it can not conclude the effect of
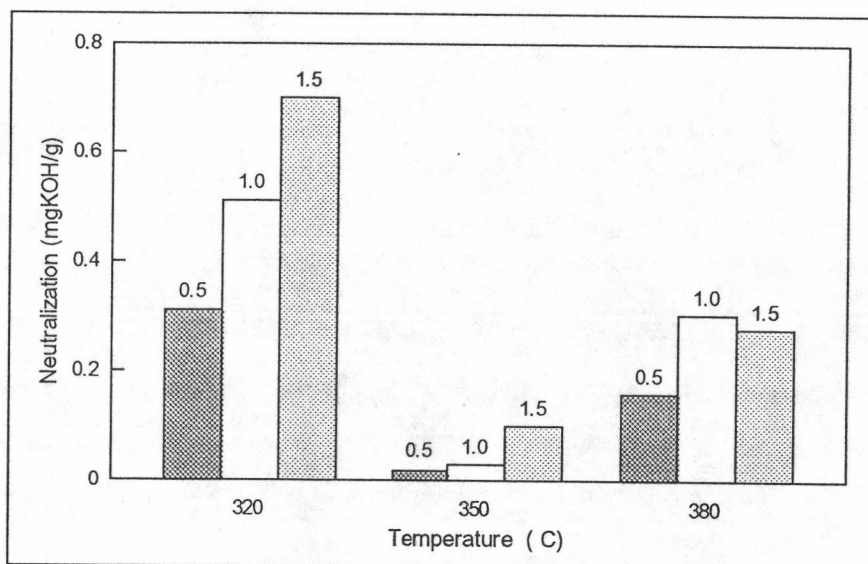
Figure 4.7 The Effect of Operating Conditions on Acidity of Product Oils for CoMo Catalyst.
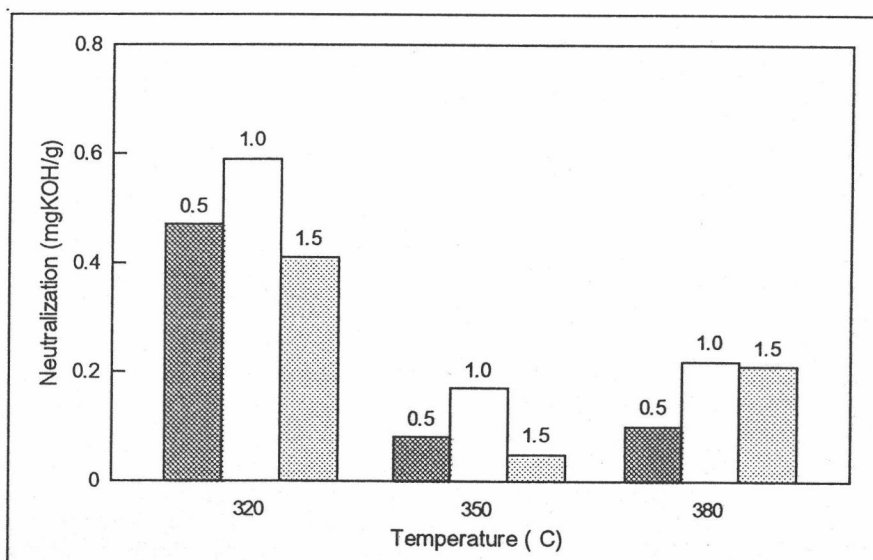
Figure 4.8   The Effect of Operating Conditions on Acidity of
Product Oils for NiMo Catalyst.
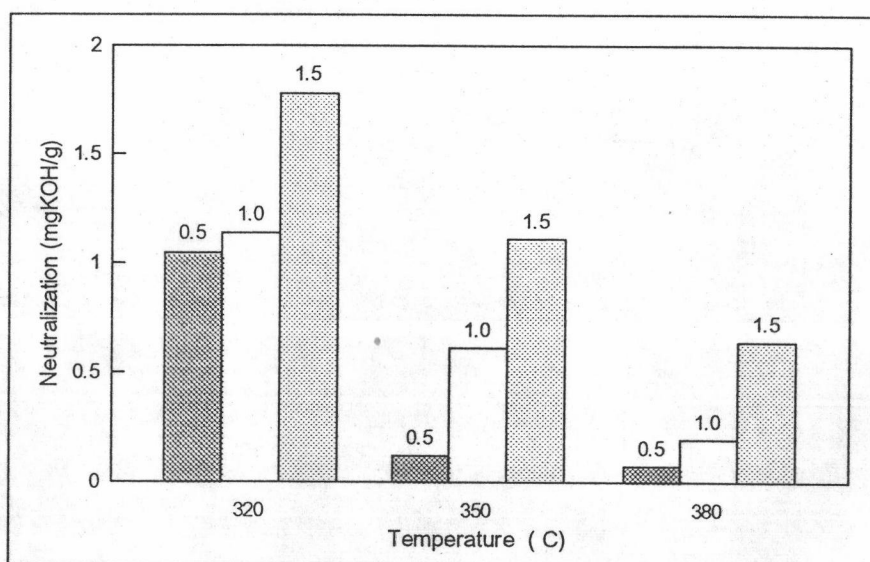
Figure 4.9   The Effect of Operating Conditions on Acidity of
Product Oils for NiW Catalyst.

temperature on acidity of product oils. Because the
acidity of the product oils in their study was reduced
from 0.51 to 0.0 mgKOH/g for all operating temperature.
It is difficult to clarify the decreasing of acidity in
used oils. Because acid compounds in used lubricating
oils are produced by several reactions that occurred
during oil oxidation and during fuel combustion.

Figures 4.10 to 4.12 show comparison of catalyst
activity on acidity of product oils at temperature of
320, 350 and 380°C, respectively. Figures 4.10 and 4.11
show CoMo catalyst give the best activity at LHSVs of 0.5
and 1.0 hr^{-1} and NiMo catalyst give the best at a LHSV of
1.5 hr^{-1}, while NiW catalyst shows the least activity to
reduce acidity of product oils for all LHSV. Figure 4.12
shows different result from Figures 4.10 and 4.11.
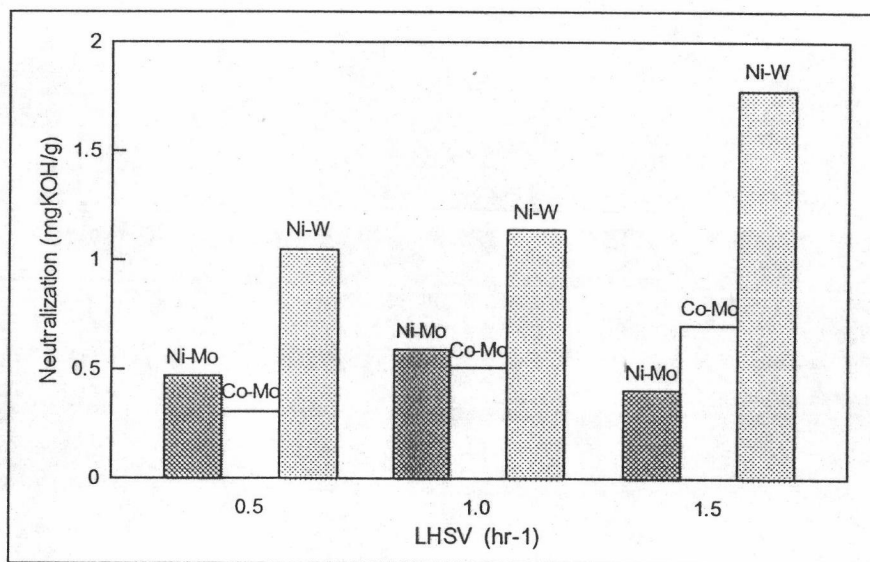
Figure 4.10   The Comparison of Catalyst Activity on Acidity of
Product Oils at Temperature of 320°C.
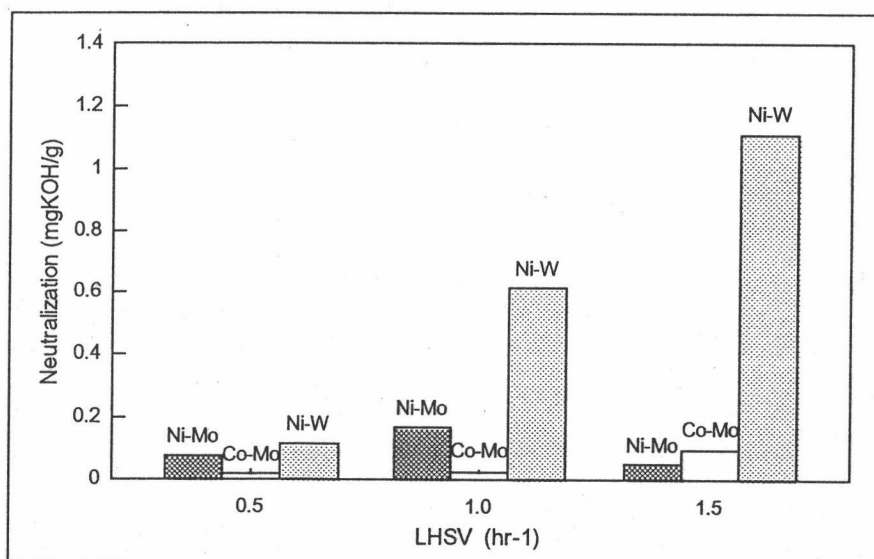
Figure 4.11   The Comparison of Catalyst Activity on Acidity of
Product Oils at Temperature of 350°C.
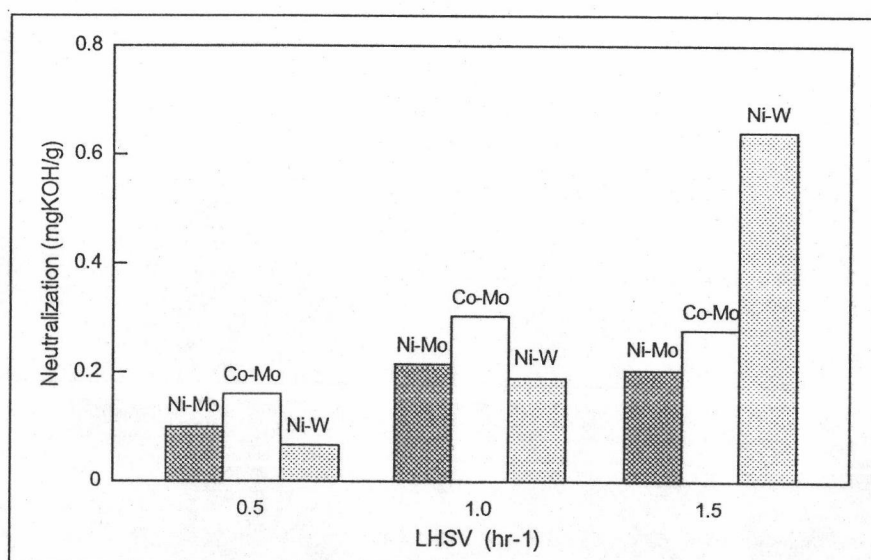
Figure 4.12   The Comparison of Catalyst Activity on Acidity of
Product Oils at Temperature of 380°C.

The result in Figure 4.12 shows that NiW catalyst exhibit the best activity at LHSVs of 0.5 and 1.0 hr^{-1} while CoMo catalyst shows the least activity.

When the acidity of the product oils is compared with specification of base lube oil, it was found that the most of the product oils did not have the acidity meeting the specification of base lube oil. The maximum of acidity in base lube oil is set up at 0.05 mgKOH/g while the acidity of product oils is in a range of 0.02 to 1.78 mgKOH/g. The product oils that have acidity below the limit were produced by using CoMo catalyst at a temperature of 350°C and LHSVs of 0.5 and 1.0 hr^{-1} and by using NiMo catalyst at a temperature of 350°C and LHSVs of 0.5 hr^{-1}. Besides these conditions, the product oils can not acceptably to use as base lube oil. However, the other product oils that have acidity closed to the limit of base lube oil can use as base lube oils by mixing with corrosion inhibitor additives that are highly alkaline compounds.

Viscosity Index

The viscosity index is an arbitrary number indicating the effect of change of temperature on the kinematic viscosity of an oil. A high viscosity index signifies a relatively small change of kinematic viscosity with temperature.
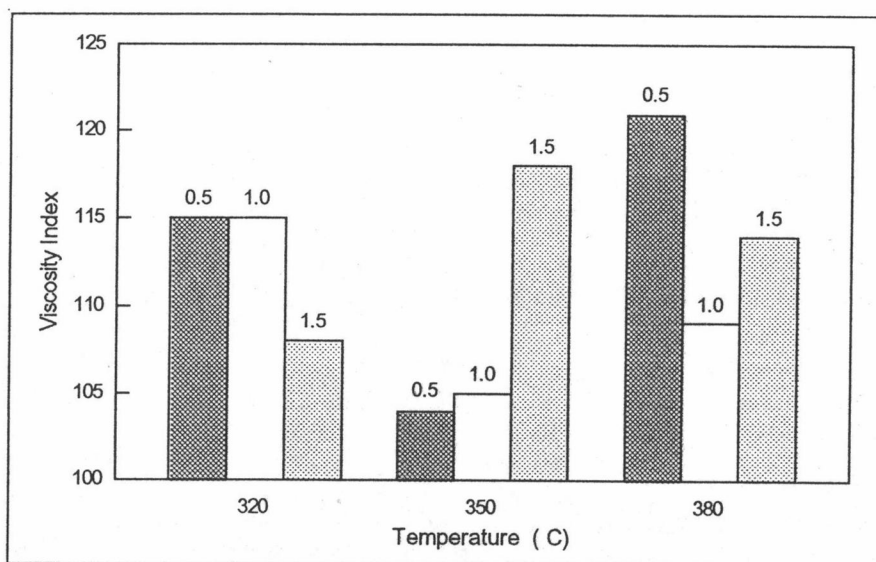
Figure 4.13   Viscosity Index of Product Oil for CoMo Catalyst at
Various Temperature.
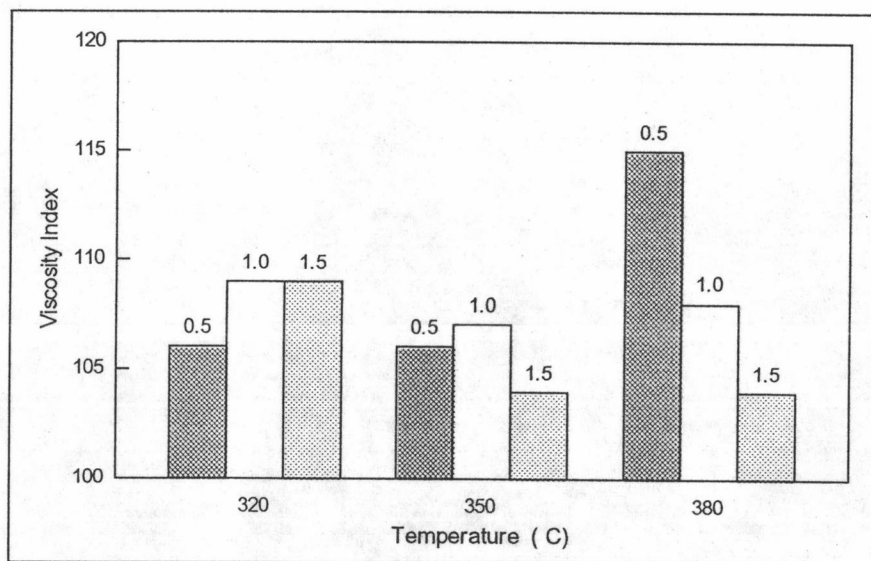
Figure 4.14   Viscosity Index of Product Oil for NiMo Catalyst at
Various Temperature.
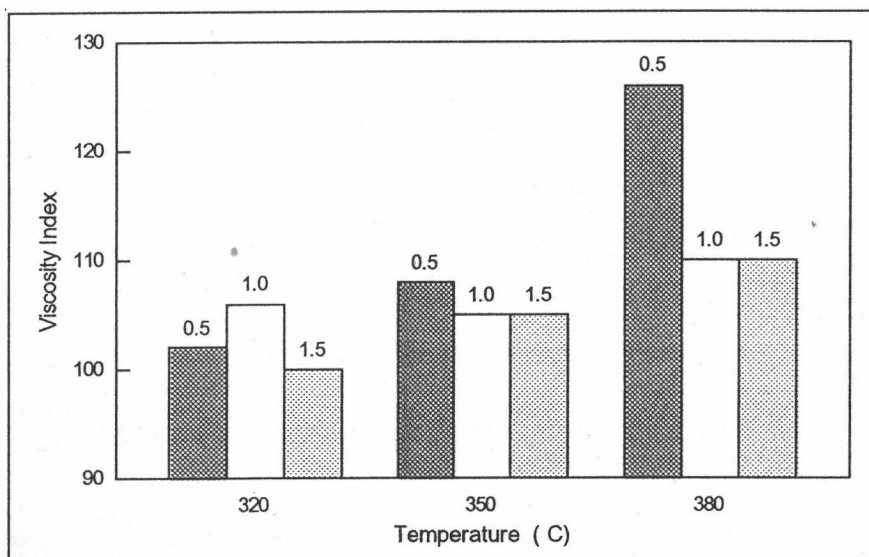
Figure 4.15 Viscosity Index of Product Oil for NiW Catalyst at
            Various Temperature.

        The effect of operating conditions on viscosity
index of the product oils for CoMo, NiMo and NiW
catalysts is shown in Figures 4.13 to 4.15, respectively.
The figures show that the viscosity index increases with
increasing temperatures and decreases with increasing
LHSVs. This result differs from the study of Bethea et
al. (1973) who observed that the temperature did not have
any significant effect on the viscosity index of product
oils. They showed that the viscosity index of product
oils changed from 101 to 103 when temperature was
increased from 288°C (550°F) to 343°C (650°F).

        The document of Billon et al. (1975) shows that
the viscosity index depended on the chemical structure of
the oil and this structure was changed by hydrogenation,
hydrodecyclization and hydroisomerization reactions. For
example, hydrogenation of polyaromatic into polynapthenes

changed viscosity index from approximately -60 to approximately 20 (Figure 4.16). Hydrodecyclization of polyaromatic and polynaphthenoaromatic into mononaphthens improved viscosity index from about 20 to a range of 110 to 140 (Figure 4.17). Hydroisomerization of n-paraffins into isoparaffins changed viscosity index from 125 to 119 (Figure 4.18). These reactions can occur in hydrotreating process. Thus, the hydrotreating reactions which change the chemical structure of the oil from low
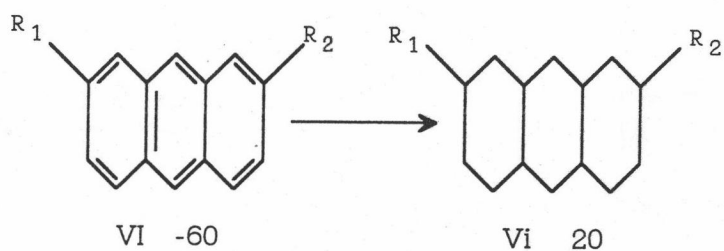
Figure 4.16 Hydrogenation of Polyaromatics into Polynaphthenes.
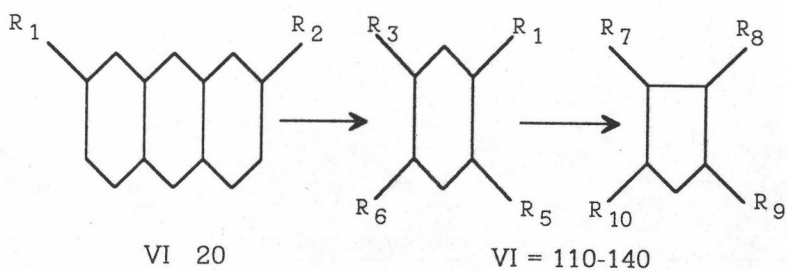
Figure 4.17 Hydrodecyclization of Polyaromatic and Polynaphtheno-
aromatics into Mononaphthenes.
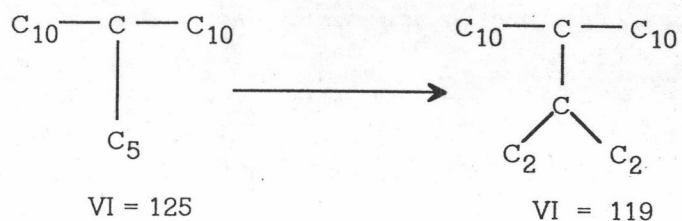
Figure 4.18 Hydroisomerization of n-paraffins into isoparaffins.

viscosity index to high viscosity index were promoted by
increasing hydrotreating temperature and/or decreasing
LHSV.

Figures 4.19 to 4.21 show comparison of catalyst
activity on viscosity index of product oils at
temperature of 320, 350 and 380°C, respectively. This
result shows that CoMo catalyst give the best viscosity
index.

Viscosity index of the product oils shows a
better value than the limit of the base lube oil
specification. While the specification of the base lube
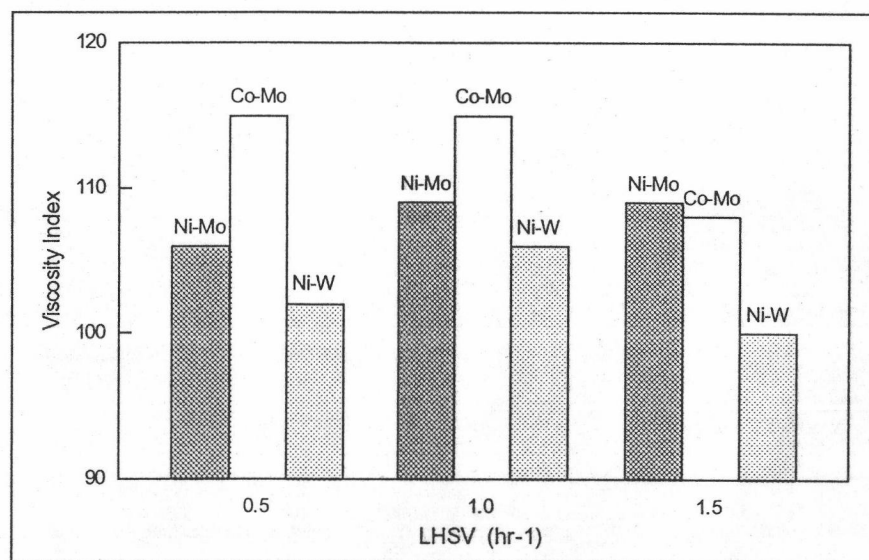
Figure 4.19 The Comparison of Catalyst Activity on Viscosity Index
of Product Oils at Temperature of 320°C.

61
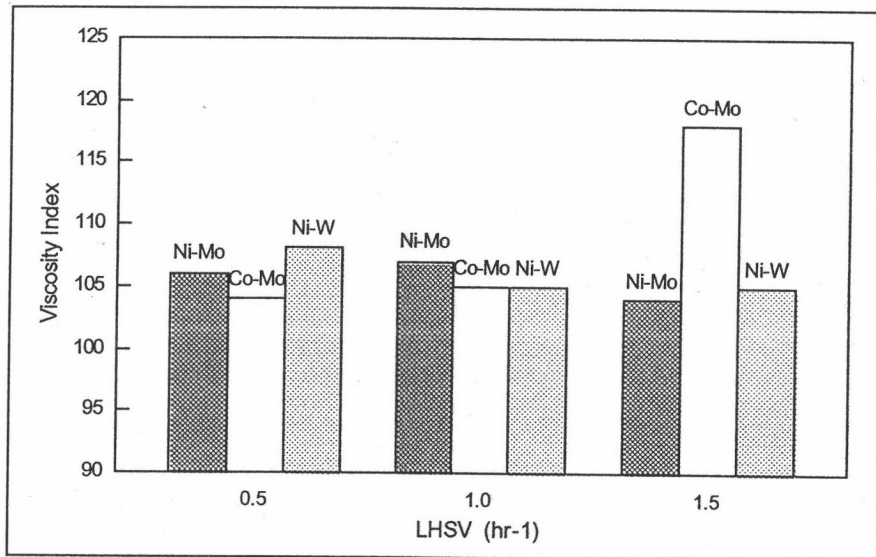
Figure 4.20   The Comparison of Catalyst Activity on Viscosity Index
of Product Oils at Temperature of 350°C.
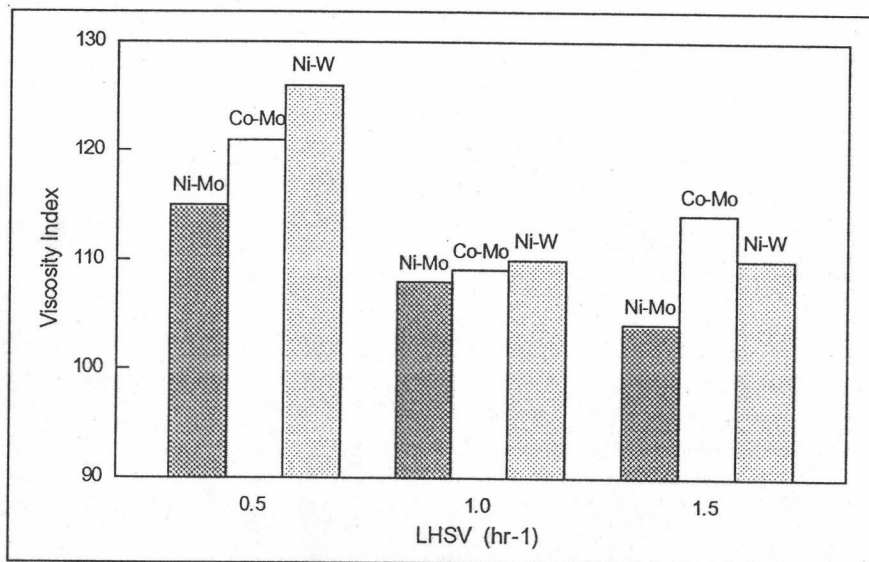
Figure 4.21   The Comparison of Catalyst Activity on Viscosity Index
of Product Oils at Temperature of 380°C.

oil limits the value of viscosity index at more than 95, the viscosity index of the product oils is in a range of 100 to 126.

Vicosity

Viscosity is the most important physical property of lubricating oil. It is a measure of the lubricating oil's internal friction or the resistance of the flow. The viscosity of lubricating oil changes with temperatures; it increases as the temperature decreases and decreases as the temperature increases.

The effect of operating conditions on viscosity at 100°C of the product oils for CoMo, NiMo and NiW catalyst is given in Figures 4.22 to 4.24, respectively.
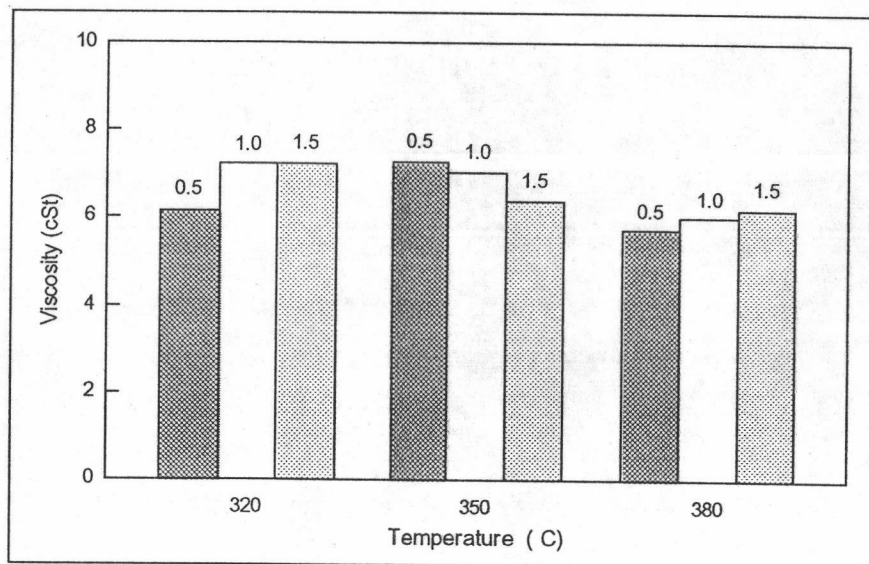
Figure 4.22 The Effect of Operating Conditions on Viscosity at 100°C of Product Oils for CoMo Catalyst.
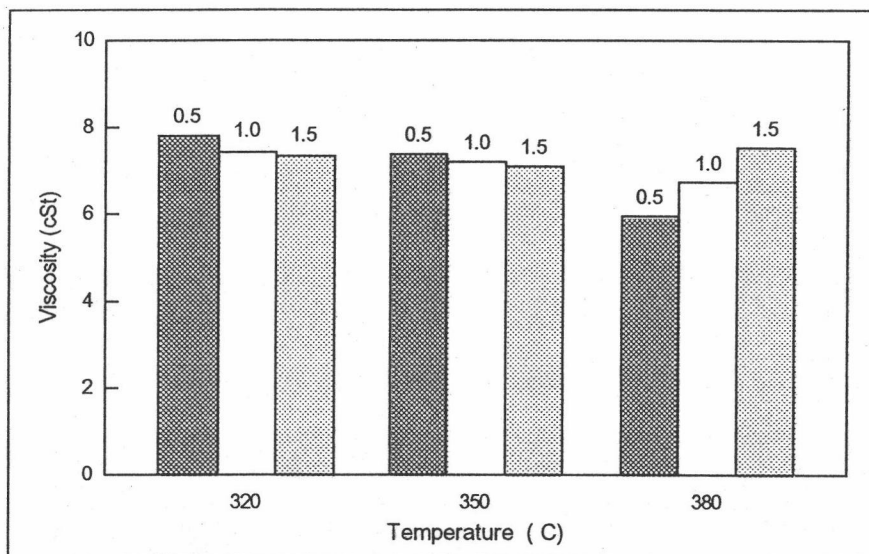
Figure 4.23   The Effect of Operating Conditions on Viscosity at
100°C of Product Oils for NiMo Catalyst.
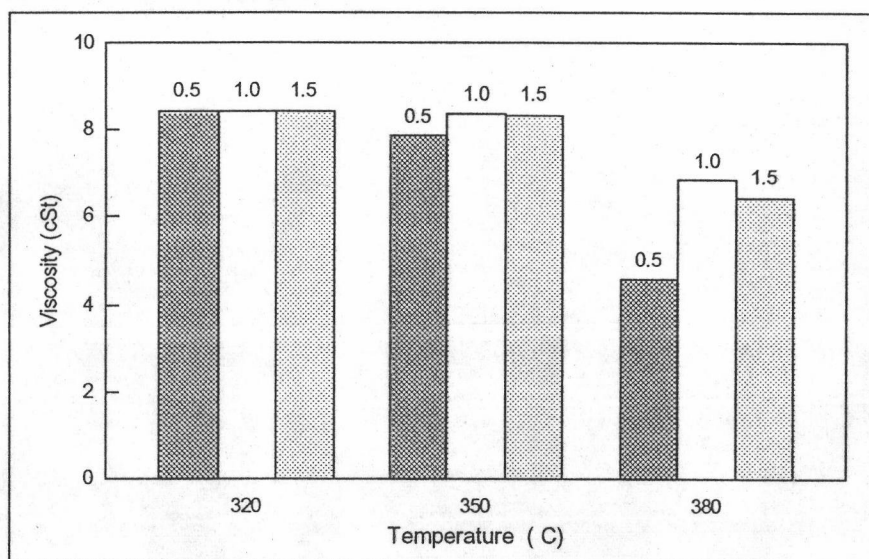
Figure 4.24   The Effect of Operating Conditions on Viscosity at
100°C of Product Oils for NiW Catalyst.

The figures show that the viscosity decrease with a temperature increase for all catalysts. This trend is similar to Bahn et al. (1982) who used NiMo catalyst. They found that the viscosity at 100°C of the oil product decreased from 6.56 to 6.21 centipoise for temperature increase from 285 to 345°C.

These figures also illustrate that the viscosity at 100°C of the product oils increase with increasing LHSV. From the knowledge, the viscosity of hydrocarbon depends on the chemical structure (Ellis L.,1945). It was confirmed by Hegel et al. (1931) who observed that for the same molecular weight hydrocarbons, the viscosity of cyclic hydrocarbons is greater than the viscosity of paraffins. Introduction of side chains, as well as unsaturation, had little effect on the viscosity of acryclic hydrocarbons. With cyclic hydrocarbons, the introduction of side chains, particularly methyl group, had a specific effect though not always in the same direction. Thus, the decreasing of viscosity of the oil indicated that the chemical structure of the oil was changed.

The structural change of used oil can be caused by reactions that occurred during hydrotreating the feedstock such as HDS, HDN, HDO and hydrogenation. Thus, this result indicated that the hydrotreating activity of the oil was more pronounced at a higher temperature.
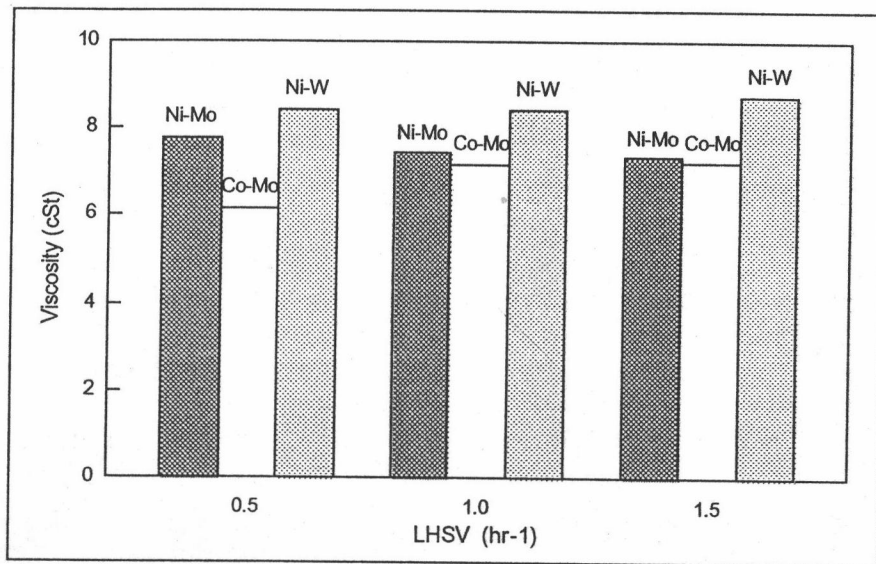
Figure 4.25   The Comparison of Catalyst Activity on Viscosity at
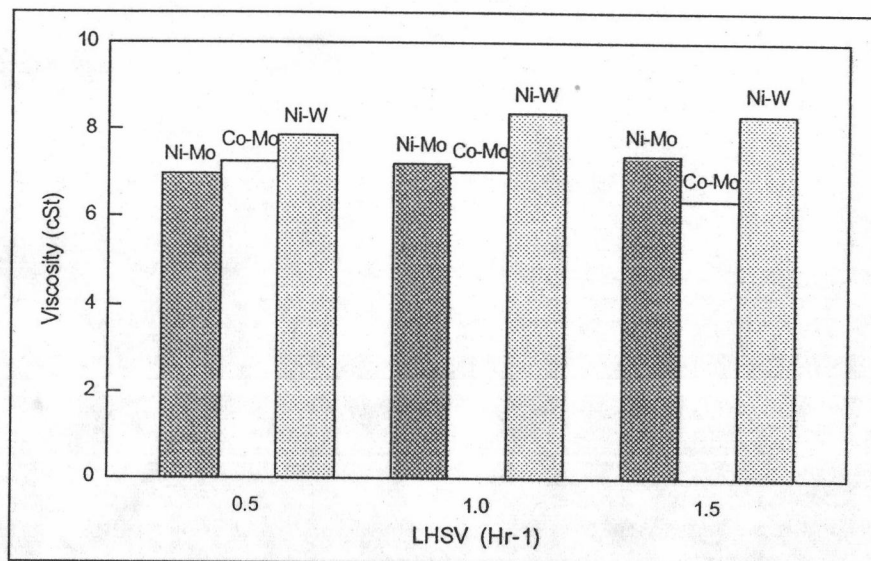100°C of Product Oils at Temperature of 320°C.

Figure 4.26   The Comparison of Catalyst Activity on Viscosityat
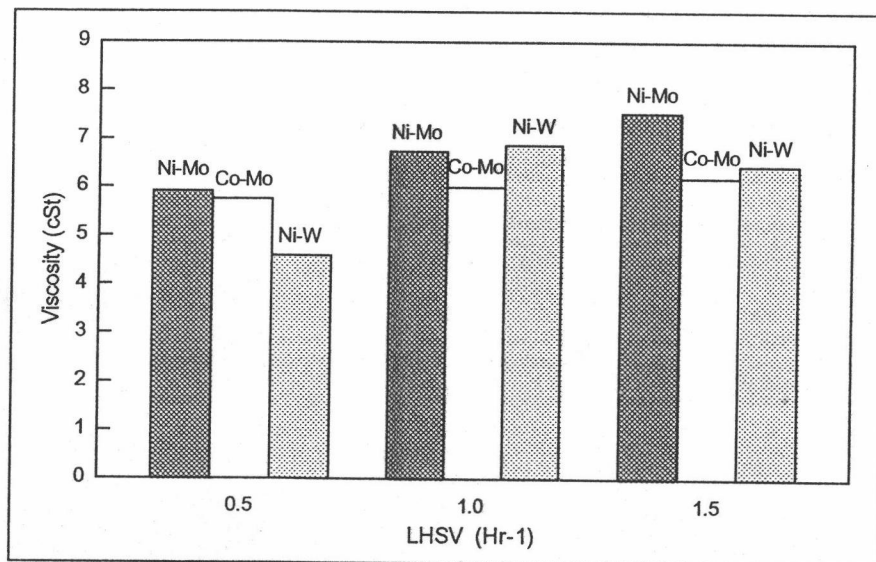100°C of Product Oils at Temperature of 350°C.

Figure 4.27 The Comparison of Catalyst Activity on Viscosity at

100°C of Product Oils at Temperature of 380°C.

Figures 4.25 to 4.27 show the comparison of
catalytic activity on the viscosity of the product oils
at temperatures of 320, 350 and 380°C, respectively. The
results show that CoMo catalyst gives the best
hydrotreating activity while NiW catalyst shows the least
activity. However, at the temperature of 380°C, NiW
catalyst gives a better activity than NiMo catalyst.

Table 4.7 shows that viscosity of the product
oils is in a range of 5.98 to 8.44 cSt. This range is
between the base lube oil grade No. 1 (4.8-5.4 cSt) and
No. 2 (10.0-12.0 cSt). Although these results did not
match with any grade of base lube oil in Table 4.1, it
may use as base lube oil. Because in lubricating oil
production, the viscosity of the base lube oil was
adjusted to meet the SAE grades by blending with other
base lube oil grades that have different viscosity.

However, other properties of product oils such as sulfur content, viscosity index, acidity and flash point were considered together.

Flash point

The flash point of oils is the temperature at which the oil releases enough vapor at its surface to ignite when an open flame is applied. The flash point of oils varies according to the degree of viscosity; higher viscosity oils tend to have higher flash points.

The effect of operating conditions on flash point of product oils for CoMo, NiMo and NiW catalyst is given in Figures 4.28 to 4.30. The results show that flash points of the product oils decrease with a temperature
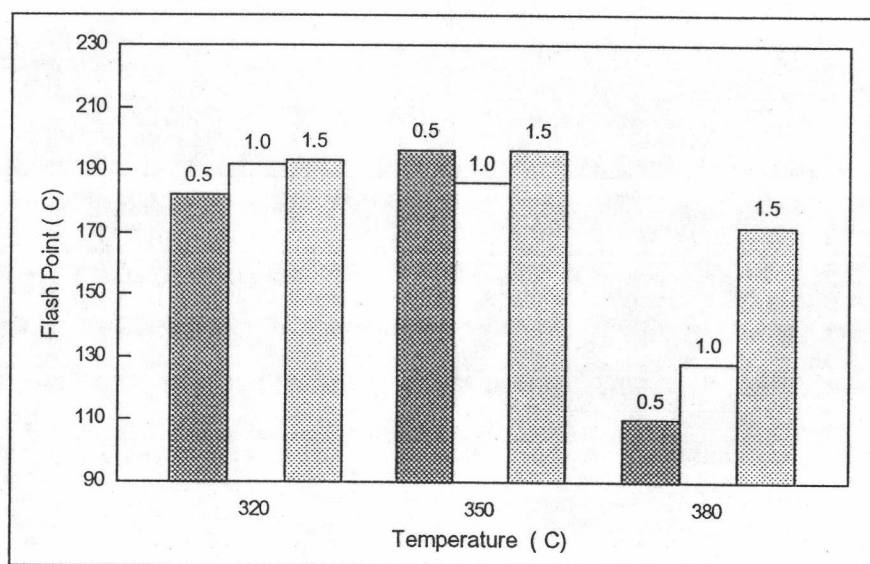
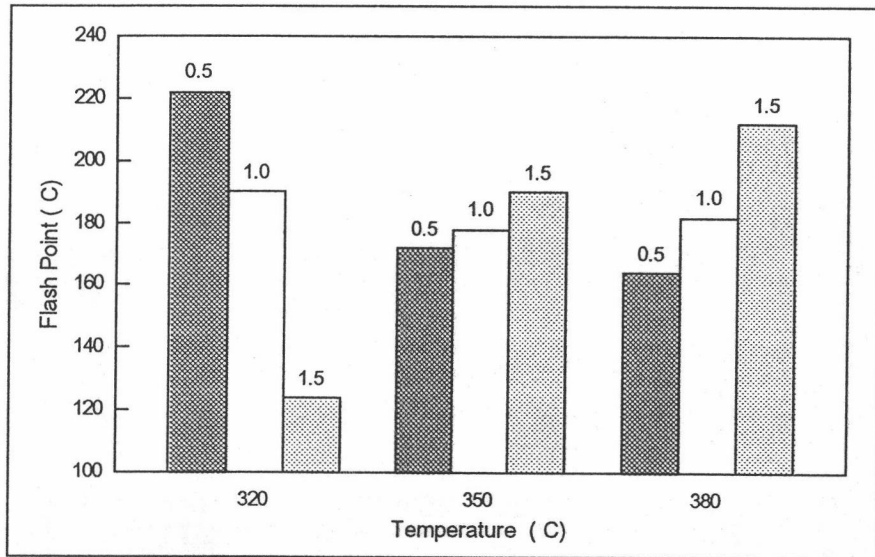Figure 4.28   The Effect of Operating Conditions on Flash Point of Product Oils for CoMo Catalyst.

Figure 4.29 The Effect of Operating Conditions on Flash Point of Product Oils for NiMo Catalyst.
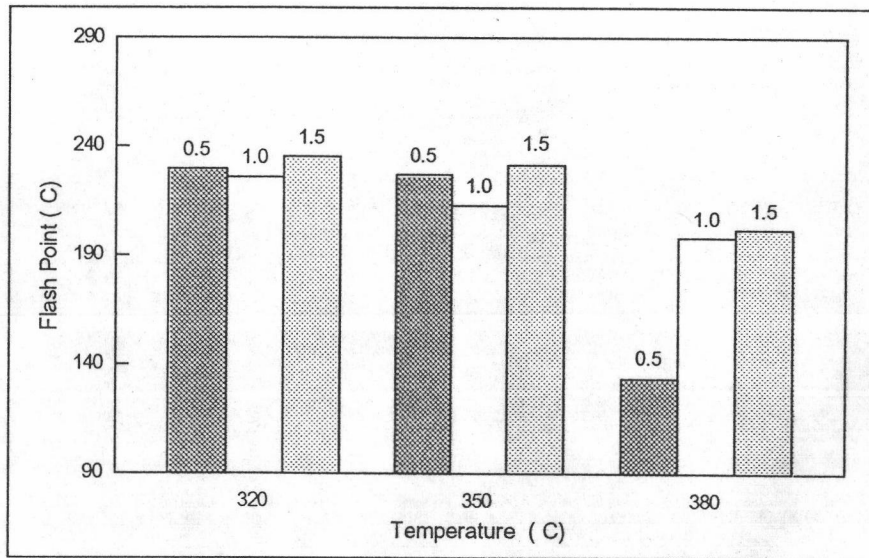

Figure 4.30 The Effect of Operating Conditions on Flash Point of Product Oils for NiW Catalyst.

increasing. This result differs from the study of Bethea
et al. (1973) who observed that change in the temperature
did not affect the flash point of product oils
significantly. They illustrated that the flash point of
product oils at temperatures of 288°C (550°F), 316°C
(600°F) and 343°C (650°F) is 216°C (420°F), 221°C (430°F)
and 210°C (410°F), respectively.

These figures also show that the flash point of
product oils increases with a LHSV increase.
Hydrotreating not only occurs structure changing but also
produces light hydrocarbons by hydrocracking reaction.
The increasing of light hydrocarbon in the oils decreases
the flash point of the oils. Thus, this result indicate
that the hydrotreating activity increase with increasing
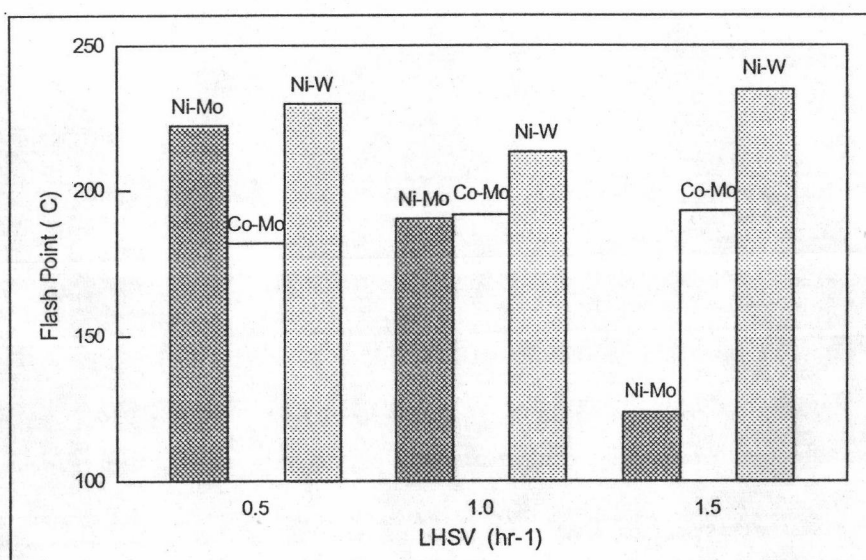temperaturea and/or decreasing LHSVs.

Figure 4.31 The Comparison of Catalyst Activity on Flash Point of
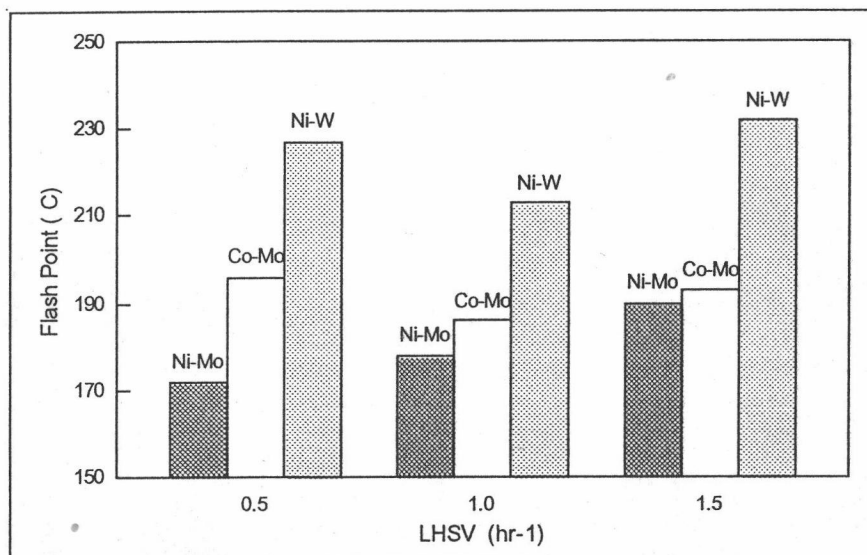Product Oils at Temperature of 320°C.

Figure 4.32   The Comparison of Catalyst Activity on Flash Point of
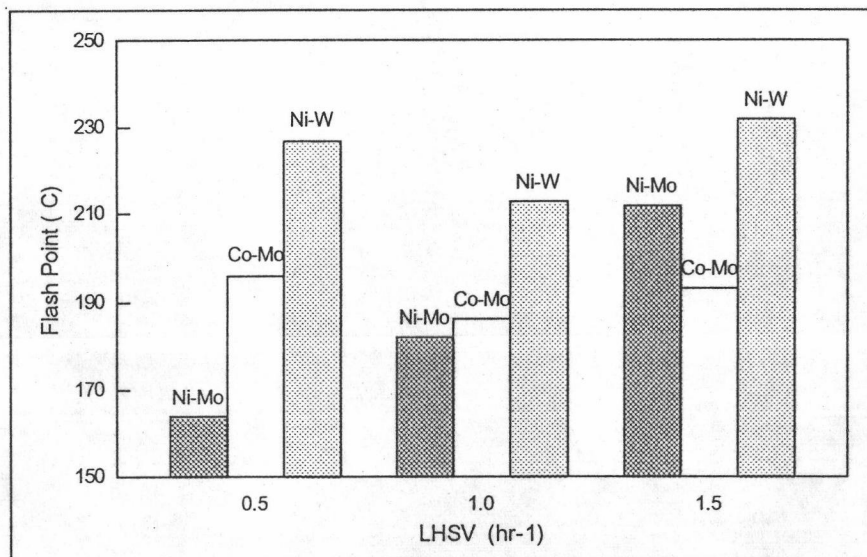Product Oils at Temperature of 350°C.

Figure 4.33   The Comparison of Catalyst Activity on Flash Point of
Product Oils at Temperature of 380°C.

The comparison of catalyst activity on flash point of product oils at temperature of 320, 350 and 380°C is shown in Figure 4.31 to 4.33, respectively. The results show that NiW catalyst gives the best performance for all conditions while CoMo catalyst shows the least performance at temperature of 320°C and NiMo catalyst gives the least performance at temperatures of 350 and 380°C.

Flash point of product oils did not meet the specification of base lube oil. The specification of base lube oil is limited the minimum flash point at a temperature of 200°C while the flash point of product oils is in a range of 110-235°C. This result is almost below the limit except the product oils that were producrd by using NiW catalyst. The flash point of product oils due to light compounds that were occurred by hydrotreating the oil. However, low flash point of product oils is improved by stripping the product oils to remove the light compounds. This method is used by KTI process to produce the product with the right specifications. Therefore, these product oils can use as base lube oil if the oils were stripped.