

CHAPTER 4

RESULTS AND DISCUSSION

The catalysts used in this process were prepared by using alumina supports type CS-303 which was commercially available from United Catalyst Inc.,. The pore volume of this alumina supports was measured by using distilled water before impregnation (18). The pore volume of alumina support CS-303 was $0.27 \text{ cm}^3/\text{g}$.

These hydrogenation catalysts were prepared by dry impregnation (19). The alumina supports were impregnated with nickel nitrate solution, followed by drying and calcination. The amount of nickel in the catalysts were analyzed by atomic absorption. The results obtained from atomic absorption were shown in Table 3.2.

The catalysts activity were evaluated by hydrogenation of standard cyclohexene. Standard cyclohexene was treated with hydrogen in the present of these nickel catalysts at 100°C , 200 psig, about 2 hours. The hydrogenated products of cyclohexene were purified by usual manner and were identified by Infrared Spectrophotometer. The IR spectrum of cyclohexene and hydrogenated product were shown in Fig. 4.1 and 4.2. Fig. 4.1 showed the absorption band of unconjugated C=C double bond at wavenumber 1640 cm^{-1} . IR spectrum of hydrogenated product (fig. 4.2) did not show the absorption band at 1640 cm^{-1} .

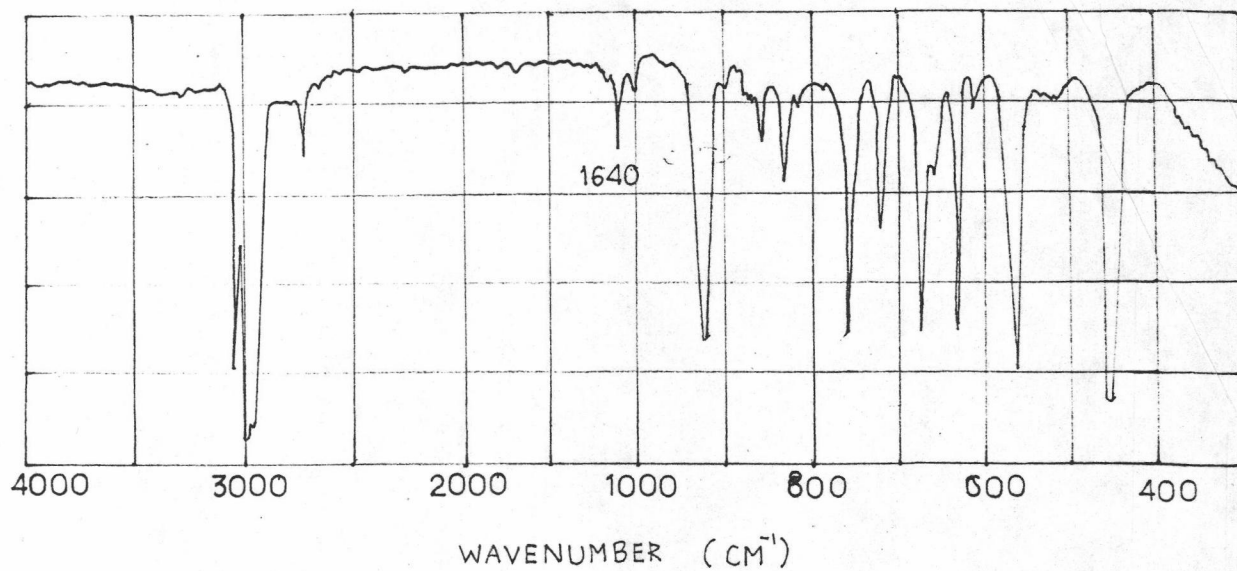


Fig. 4.1 The spectrum of cyclohexene

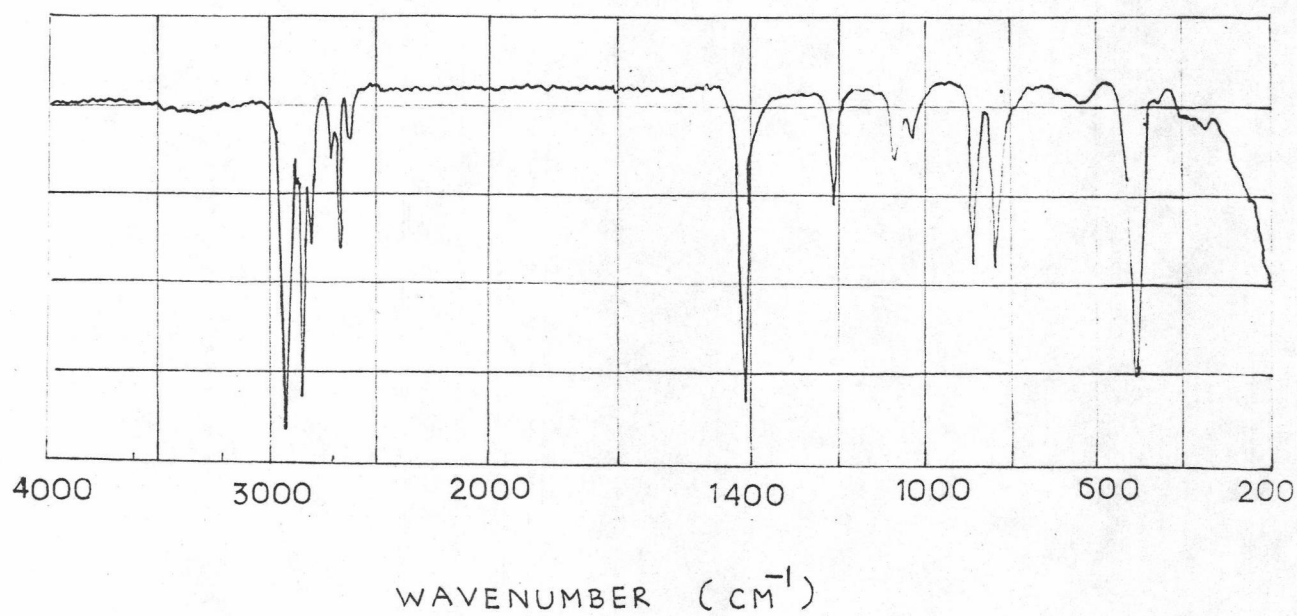


Fig. 4.2 The IR spectrum of cyclohexene after hydrogenation

This result indicated that the prepared catalyst was as good as the catalysts which were commercially available.

The physical and chemical properties of lubricating oil (150 BS, SHELL and PTT) were determined before hydrogenation as shown in Table 3.3. The following physical properties were as determined: The American Petroleum Institute (API) gravity, flash point, colour, pour point, kinematic viscosity and sulfur content. The aromatic carbon content ($\%C_A$), paraffinic carbon content ($\%C_P$) and naphthenic carbon content ($\%C_N$) of lubricating base oils were determined by C^{13} -NMR and the percentages of oxidative compounds were analyzed by thermal gravimetric balance.

The nickel catalysts were optimized for the hydrogenation of lubricating base oil by varying the following parameters: percentages of nickel on alumina supports, catalyst concentration, reaction time and reaction temperature with constant pressure at 250 psig.

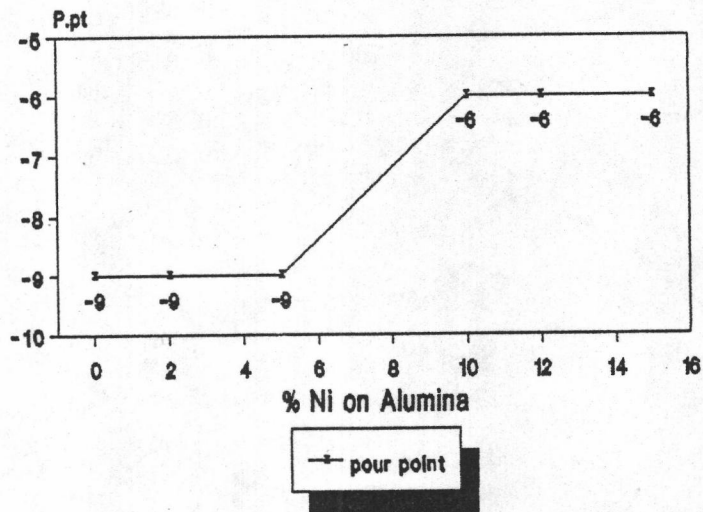
The optimum operating conditions were determined and the results shown in Table 4.1-4.4.

This catalytic hydrogenation was operated at temperatures between 200 °C and 350 °C. Reactions were performed under pressures of 200 psig because the hydrogenator could not operate at pressure higher than 200 psig. The nickel content in this catalysts were 2% to 15% based the total catalyst weight. The

Table 4.1 Hydrogenation of lubricating base oil using different %Ni/Al₂O₃:
 Cat.conc. 1% oil, Reaction temperature 200 °C, Reaction time 1 hr.,
 reaction pressure 200 psig., agitation speed 300 rpm.

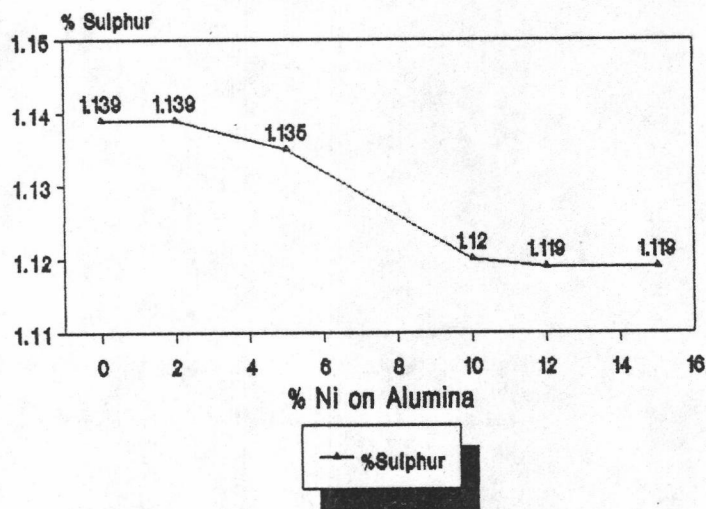
Properties	Base	% Nickel on alumina support				
	150					
	BS	2	5	10	12	15
Colour, Visual						
ASTM	3.5	3.5	3.5	3.5	3.5	3.5
Flash Point, (C.O.C), °C	>243	>243	>243	>243	>243	>243
Pour Point, (C.O.C), °C	-9	-9	-9	-6	-6	-6
Viscosity Kinematic,						
@ 40 °C, cSt	478.90	510.95	482.12	480.92	501.50	481.41
@100 °C, cSt	31.46	32.84	31.66	31.46	32.63	31.50
Viscosity Index	96	96	96	96	96	96
Sulphur, %wt	1.139	1.139	1.135	1.120	1.119	1.119
%C _A	18.41	18.41	18.40	17.35	17.34	17.25
%C _P	47.14	47.14	47.14	47.15	47.15	47.18
%C _N	34.45	34.45	34.46	35.50	35.51	35.57
Oxidation point (°C)	390	390	390	390	390	390
Oxidative Compound,						
%wt	38	38	38	38	38	38

FIGURE 4.3
EFFECT OF %Ni/ALUMINA ON POUR Pt.



Cat. Conc. 1% oil, Temp. 200 C,
Time 1 hr., P 200 psig and Speed 300 rpm.

FIGURE 4.4
EFFECT OF %Ni/ALUMINA ON %S



Cat. Conc. 1% oil, Temp. 200 C
Time 1 hr., P 200 psig. and speed 300 rpm

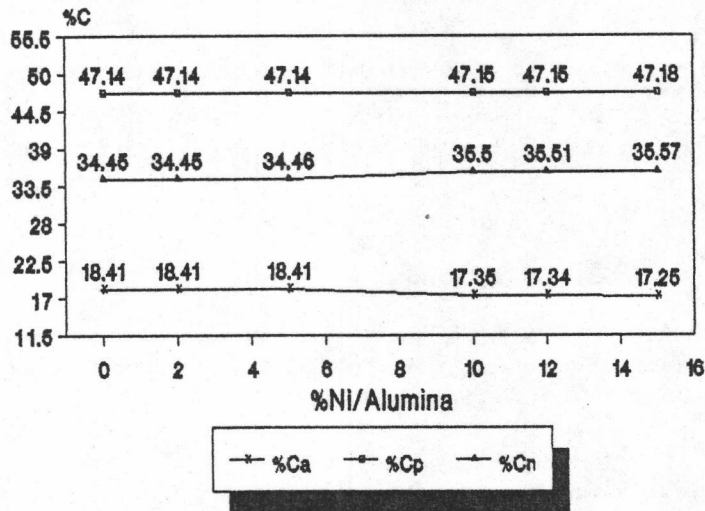
catalyst concentration were 1.0-3.0% by weight based on an oil.

The properties of lubricating base oils were improved after hydrogenation. Pour point and viscosity index were increased by 8 and 44 unit when compared to lubricating base oil before hydrogenation. The sulfur content was also reduced. The aromatic compounds were converted to saturated and naphthenic compounds.

The results from hydrogenation of lubricating base oils using different percentages of nickel of 2, 5, 10, 12 and 15% on alumina supports were shown in Table 4.1. The catalyst content were 1% by weight based on an oil. This reaction was performed at 200 °C and 1 hour.

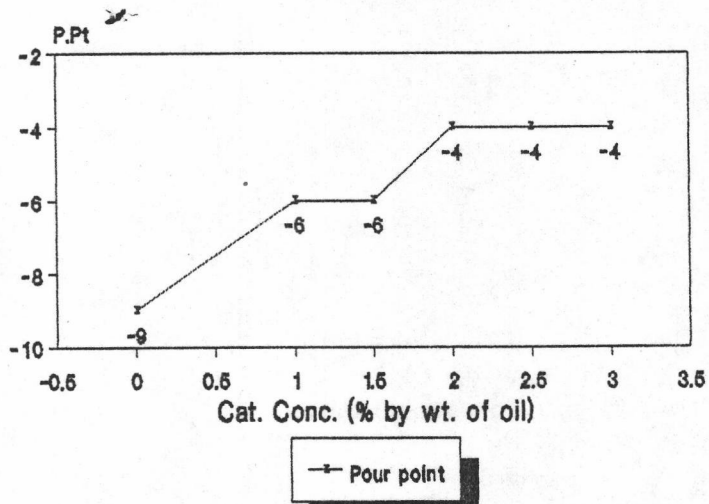
The effect of percentages of nickel on pour point, sulfur content, aromatic carbon content, paraffinic carbon content and naphthenic carbon content were shown in Fig. 4.3, 4.4 and 4.5 respectively. From Fig 4.3, it demonstrated that pour point was increased from -9 °C when reaction was operated with 5% Ni/Al₂O₃ to -6 °C when reaction was operated with 10% Ni/Al₂O₃ and began constant at 10% Ni/Al₂O₃. Fig 4.4 indicated that the sulphur content was decreased from 1.139% to 1.120% at 10% Ni/Al₂O₃. Fig 4.5 showed that aromatic carbon content were decreased from 18.41% to 17.38%. Viscosity Index and oxidative compounds were not changed, while naphthenic carbon content was increased from

FIGURE 4.5
EFFECT OF %Ni/ALUMINA ON %CARBON



Cat. Conc. 1% oil, Temp 200 C
Time 1 hr., P 200 psig and speed 300 rpm

FIGURE 4.6
EFFECT OF CAT.CONC. ON POUR POINT



10% Ni/Alumina, Temp. 200 C,
Time 1 hr., P 200 psig. and Speed 300 rpm

and began constant at 250 °C.

From this experimental results, it indicated that the optimum reaction temperature was 250 °C.

The experimental results obtained from hydrogenation of lubricating base oils which were operated at various temperature showed that pourpoint, viscosity index and paraffinic carbon content were increased but aromatic and naphthenic carbon content were decreased. Because hydrogenation with increasing temperature was effective for opening aromatic rings to paraffinic compounds.

Also, oxidative compounds were reduced because unsaturated linkages were hydrogenated. Saturated linkages were less readily oxidized than unsaturated linkages. Lubricating base oil after hydrogenation at 250 °C had better stability.

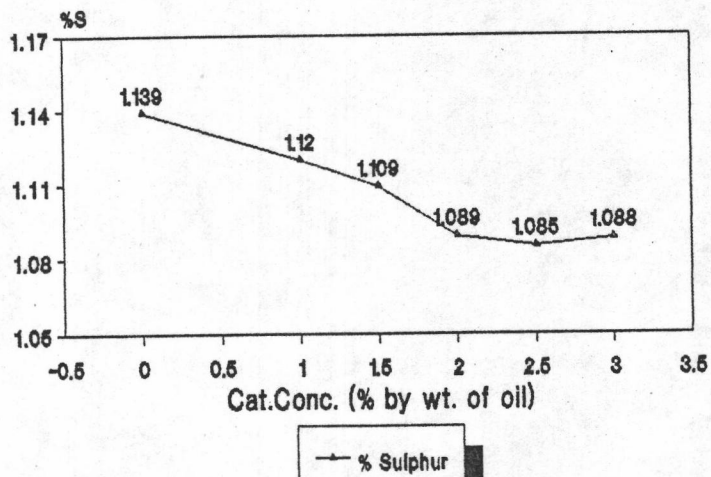
The results were confirmed on hydrogenation of SHELL and PTT lubricating oil which commercially available. The optimum operating conditions (Table 4.5) were 10% Ni/Al₂O₃, catalyst concentration 2% by weight based on an oil, reaction time 2 hours and reaction temperature 250 °C.

The results showed that pour point of hydrogenated SHELL lubricating oil was increased from -7 °C to -5 °C. Viscosity index was increased from 95 to 111. The sulfur content was not changed. The aromatic carbon content was decreased from 21.91% to 18.35%. The paraffinic and naphthenic carbon content were increased from

Table 4.2 Hydrogenation of lubricating base oil using different concentration of catalyst(% by weight of oil): 10 %Ni/Al₂O₃, Reaction temperature 200 °C, Reaction time 1 hr., reaction pressure 200 psig., agitation speed 300 rpm.

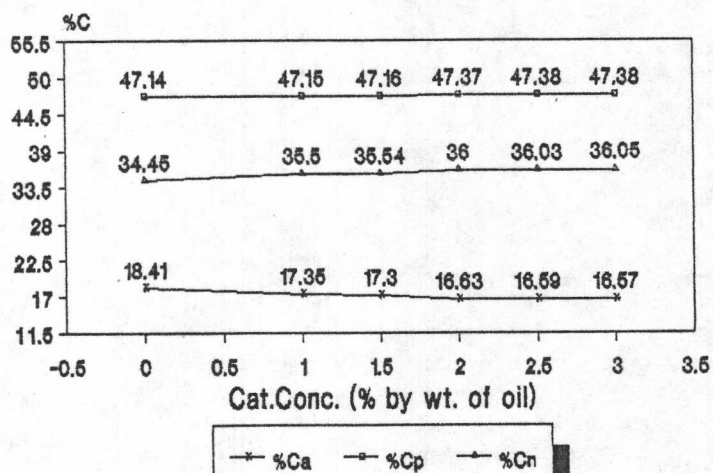
Properties	Base	Catalyst Concentration (% by weight of oil)				
	150					
	BS	1.0	1.5	2.0	2.5	3.0
Colour, Visual						
ASTM	3.5	3.5	3.5	3.5	3.5	3.5
Flash Point, (C.O.C), °C	>243	>243	>243	>243	>243	>243
Pour Point, (C.O.C), °C	-9	-6	-6	-4	-4	-4
Viscosity Kinematic,						
@ 40 °C, cSt	478.90	480.92	500.22	497.84	501.51	412.40
@100 °C, cSt	31.46	31.46	32.33	32.68	32.59	28.64
Viscosity Index	96	96	96	96	96	96
Sulphur, %wt	1.139	1.120	1.109	1.089	1.085	1.088
%C _A	18.41	17.35	17.30	16.63	16.59	16.57
%C _P	47.14	47.15	47.16	47.37	47.38	47.38
%C _N	34.45	35.50	35.54	36.00	36.03	36.05
Oxidation point (°C)	390	390	390	390	390	390
Oxidative Compound,						
%wt	38	38	37	37	37	37

FIGURE 4.7
EFFECT OF CAT. CONC. ON %S



10% Ni/Alumina, Temp. 200 C
Time 1 hr., P 200 psig and Speed 300 rpm

FIGURE 4.8
EFFECT OF CAT. CONC. ON %CARBON



10% Ni/Alumina, Temp 200 C
Time 1 hr., P 200 psig and Speed 300 rpm

points were increased but aromatic carbon content were decreased because unsaturated linkages were hydrogenated. Hydrogenation was effective for the saturation of aromatic compounds to naphthenic compounds because naphthenic carbon content were increased while paraffinic carbon content were not changed. The sulphur content was also reduced.

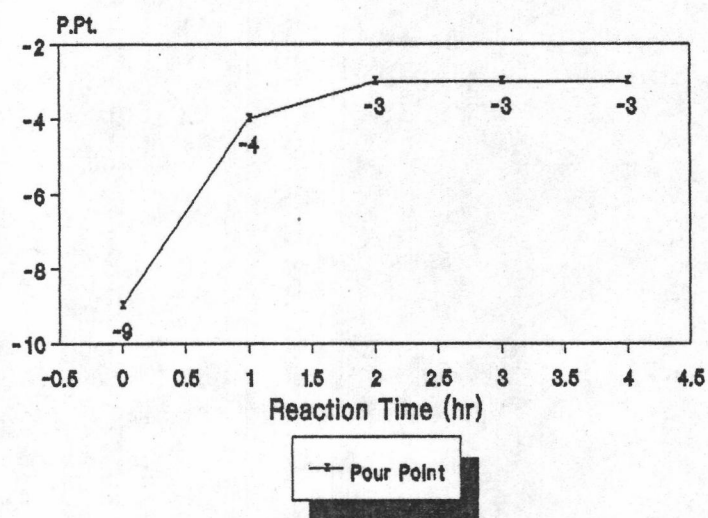
The results from hydrogenation of lubricating base oils when performed at various reaction time of 1, 2, 3 and 4 hours with constant 10% Ni/Al₂O₃, catalyst concentration 2% by weight based on an oil, and reaction temperature at 250 °C, were shown in Table 4.3. These results showed that pour point of reaction product was increased from -9 °C to -3 °C while viscosity index was not changed. Sulphur content and aromatic carbon content was also decreased from 1.139% to 1.049% and from 18.41% to 14.30% respectively. The paraffinic carbon content and naphthenic carbon content were increased from 47.14% to 48.02% and 34.45% to 37.68%. Oxidative compounds was decreased from 37% to 35%.

The effect of time on pour point, sulfur content, aromatic carbon content, paraffinic carbon content and naphthenic carbon content were determined to give the results that showed in Fig. 4.9, 4.10 and 4.11. From Fig. 4.9, it indicated that pour point was increased and began constant (-3 °C) when the reaction was operated at about 2 hours. In Fig. 4.10, it indicated that

Table 4.3 Hydrogenation of lubricating base oil at various
 Reaction Time: 10 %Ni/Al₂O₃, Cat.conc. 2% oil,
 Reaction temperature 200 °C, reaction pressure 200 psig.,
 agitation speed 300 rpm.

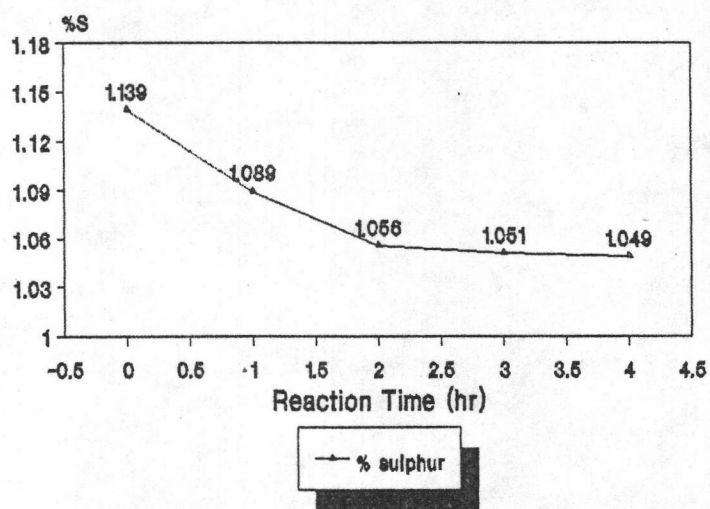
Properties	Base	Reactime Time			
	150	(hr)			
	BS	1	2	3	4
Colour, Visual					
ASTM	3.5	3.5	3.5	3.5	3.5
Flash Point, (C.O.C), °C	>243	>243	>243	>243	>243
Pour Point, (C.O.C), °C	-9	-4	-3	-3	-3
Viscosity Kinematic,					
@ 40 °C, cSt	478.90	497.84	481.41	483.39	517.84
@100 °C, cSt	31.46	32.68	31.50	31.19	33.02
Viscosity Index	96	96	96	96	96
Sulphur, %wt	1.139	1.089	1.056	1.051	1.049
%C _A	18.41	16.63	14.54	14.33	14.30
%C _P	47.14	47.37	48.01	48.02	48.02
%C _N	34.45	36.00	37.45	37.65	37.68
Oxidation point (°C)	390	390	390	390	390
Oxidative Compound,					
%wt	37	37	35.5	35	35

FIGURE 4.9
EFFECT OF TIME ON POUR POINT



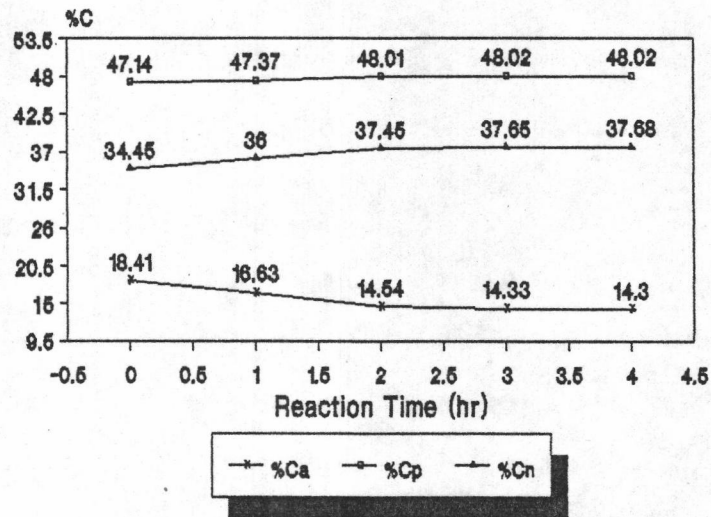
10% Ni/Alumina, Cat. Conc. 2%,
Temp 200 C, P 200 psig and Speed 300 rpm

FIGURE 4.10
EFFECT OF TIME ON %SULPHUR



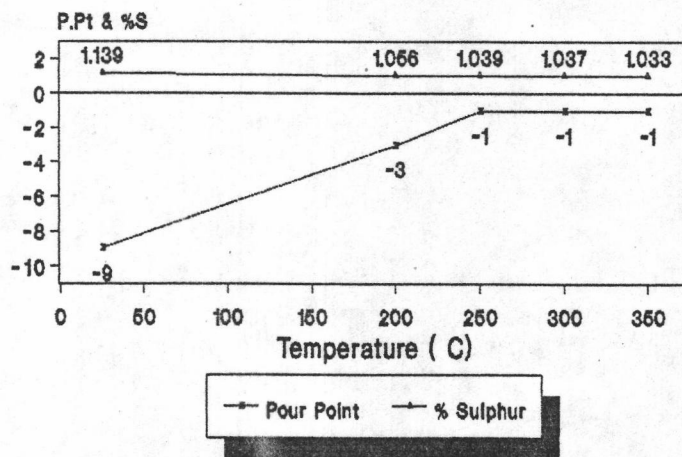
10 %/Alumina, Cat.Conc. 2%,
Temp 200 C, P 200 psig and Speed 300 rpm

FIGURE 4.11
EFFECT OF TIME ON %CARBON



10% Ni/Alumina, Cal.Conc 2%,
Temp 200 C,P 200 psig. and Speed 300 rpm

FIGURE 4.12
EFFECT OF TEMPERATURE ON
POUR POINT AND % SULPHUR



10% Ni/Alumina, Cal.Conc 2%,
Time 1 hr.,P 200 psig. and Speed 300 rpm

sulphur content was decreased with increasing time. In Fig 4.11, %C_A was decreased and began constant (14.54) at 2 hours reaction time. The paraffinic carbon content and naphthenic carbon content were increased and began constant at 2 hours reaction time.

From this experimental results, it indicated that the optimum reaction time was 2 hours.

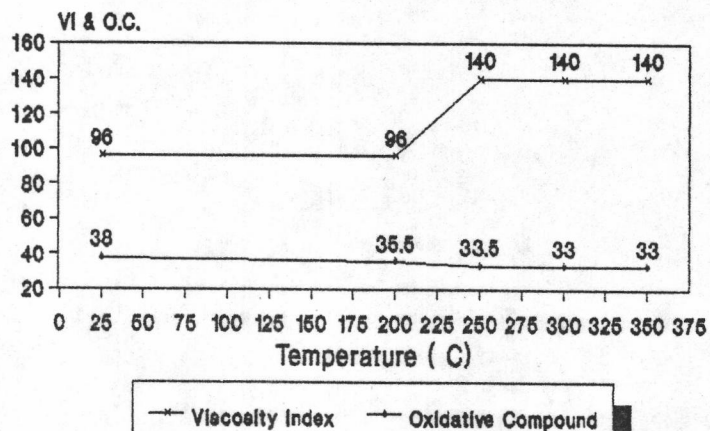
The results from hydrogenation of lubricating base oils which operated at various reaction temperature of 200, 250, 300 and 350 °C, were shown in Table 4.4. The results showed that pour point of reaction product was increased from -9 °C to -1 °C. Viscosity index was increased from 96 to 140. Sulphur content was not changed. The aromatic carbon content and naphthenic carbon content were decreased from 18.41% to 12.95% and from 34.45% to 33.08% respectively. Oxidative compounds were decreased from 38% to 33%.

The effect of temperature on pour point, sulphur content, viscosity index, oxidative compounds, aromatic carbon content, paraffinic carbon content and naphthenic carbon content were shown in Fig 4.12, 4.13 and 4.14. In Fig 4.12, the results indicated that pour point of treated product was increased and began constant (-1 °C) at 250 °C. The sulphur content was not changed. In Fig 4.13, it showed that viscosity index was increased and began constant (140) at 250 °C. Oxidative compounds were decreased

Table 4.4 Hydrogenation of lubricating base oil at various
 Reaction Temperature: 10% Ni/Al₂O₃, Cat.conc. 2% oil,
 Reaction time 2 hr., Reaction pressure 200 psig.,
 agitation speed 300 rpm.

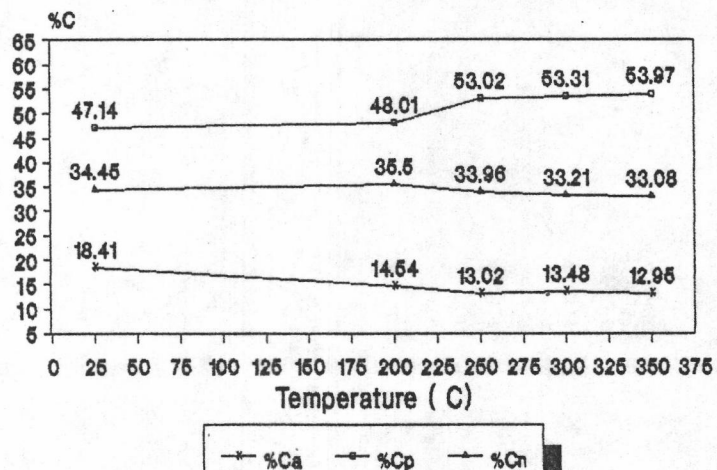
Properties	Base 150 BS	Reaction Temperature (°C)			
		200	250	300	350
		Colour, Visual			
ASTM	3.5	3.5	3.5	3.5	3.5
Flash Point, (C.O.C), °C	>243	>243	>243	>243	>243
Pour Point, (C.O.C), °C	-9	-3	-1	-1	-1
Viscosity Kinematic, @ 40 °C, cSt	478.90	481.41	404.03	350.50	403.89
@100 °C, cSt	31.46	31.50	38.26	34.19	38.25
Viscosity Index	96*	96	140	140	140
Sulphur, %wt	1.139	1.056	1.039	1.037	1.033
%C _A	18.41	14.54	13.02	13.48	12.95
%C _P	47.14	48.01	53.02	53.31	53.97
%C _N	34.45	35.50	33.96	33.21	33.08
Oxidation point (°C)	390	390	390	390	390
Oxidative Compound, %wt	38	35.5	33.5	33	33

FIGURE 4.13
EFFECT OF TEMPERATURE ON VISCOSITY INDEX AND OXIDATIVE COMPOUND



10% Ni/Alumina, Cat. Conc. 2%,
 Time 1 hr., P 200 psig. and Speed 300 rpm

FIGURE 4.14
EFFECT OF TEMPERATURE ON % CARBON



10% Ni/Alumina, Cat. Conc. 2%,
 Time 1 hr., P 200 psig and Speed 300 rpm

and began constant at 250 °C.

From this experimental results, it indicated that the optimum reaction temperature was 250 °C.

The experimental results obtained from hydrogenation of lubricating base oils which were operated at various temperature showed that pourpoint, viscosity index and paraffinic carbon content were increased but aromatic and naphthenic carbon content were decreased. Because hydrogenation with increasing temperature was effective for opening aromatic rings to paraffinic compounds.

Also, oxidative compounds were reduced because unsaturated linkages were hydrogenated. Saturated linkages were less readily oxidized than unsaturated linkages. Lubricating base oil after hydrogenation at 250 °C had better stability.

The results were confirmed on hydrogenation of SHELL and PTT lubricating oil which commercially available. The optimum operating conditions (Table 4.5) were 10% Ni/Al₂O₃, catalyst concentration 2% by weight based on an oil, reaction time 2 hours and reaction temperature 250 °C.

The results showed that pour point of hydrogenated SHELL lubricating oil was increased from -7 °C to -5 °C. Viscosity index was increased from 95 to 111. The sulfur content was not changed. The aromatic carbon content was decreased from 21.91% to 18.35%. The paraffinic and naphthenic carbon content were increased from

Table 4.5 Hydrogenation of lubricating oil SHELL and PTT:
 10% Ni/Al₂O₃, Cat.conc. 2% oil, Reaction Temperature 250 °C,
 Reaction time 2 hr., Reaction pressure 200 psig.,
 agitation speed 300 rpm.

Properties	BASE		BASE		BASE	
	150 BS	150 BS	SHELL	SHELL	PTT	PTT
Colour, Visual						
ASTM	3.5	3.5	Std. red	Std. red	Std. green	Std. green
Flash Point, (C.O.C), °C	>243	>243	>243	>243	>243	>243
Pour Point, (C.O.C), °C	-9	-1	-7	-5	-6	-5
Viscosity Kinematic,						
@ 40 °C, cSt	478.90	404.03	137.99	117.61	144.27	150.78
@100 °C, cSt	31.46	38.26	13.89	13.48	14.32	16.29
Viscosity Index	96	140	95	111	96	114
Sulphur, %wt	1.139	1.039	1.037	1.018	0.934	0.911
%C _A	18.41	13.02	21.91	18.35	17.46	15.04
%C _P	47.14	53.02	57.14	60.00	55.55	58.87
%C _N	34.45	33.96	20.95	21.65	26.99	26.09
Oxidation point (°C)	390	390	360	360	360	360
Oxidative Compound,						
%wt	38	33.5	27.5	26.0	26.0	24.5

57.14% to 60% and from 20.95% to 21.65%. Oxidation point was 360 °C and oxidative compounds were decreased from 27.5% to 26.0%.

The results showed that pour point of hydrogenated PTT lubricating oil was increased from -6 °C to -5 °C. Viscosity index was increased from 96 to 114. The sulphur content was not changed. The aromatic carbon content was decreased from 17.46% to 15.04%. The paraffinic and naphthenic carbon content were increased from 55.55% to 58.87% and from 26.99% to 26.09% respectively. Oxidation point was 360 °C and oxidative compounds were decreased from 26.0% to 24.5%.