

Upgrading of Light Dewaxed Oil through Hydrofinishing and Additives Blending for Producing Automatic Transmission Fluid

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Abstract: Light dewaxed oil was produced through dewaxing process of the light waxy distillate raffinate of crude oil from Western Desert of Egypt using methyl ethyl ketone/toluene mixed solvent. Hydrofinishing process was used to remove the non-hydrocarbon constituents and to improve the physicochemical properties of the produced oils such as color, viscosity index, inhibition responses, oxidation and thermal stability. The operating parameters which affected the quality of the hydrofinished oils were studied separately at different values that including reactor temperature, reactor pressure, liquid hourly space velocity and hydrogen to hydrocarbon ratio. The optimum operating conditions to be adopted for producing high quality automatic transmission fluid base oil were reactor temperature 290 °C, pressure 130kg cm⁻², liquid hourly space velocity 0.4 h⁻¹ and hydrogen/hydrocarbon ratio 800 Nm³ M⁻³. The effect of changing hydrofinishing temperature and liquid hourly space velocity on the hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) reactions as well as their thermodynamic parameters were estimated. Calculations of activation energy (Ea) and free energy of activation (ΔG) indicated that HDS was easier to occur than HDN and these reactions are more faster at higher temperatures. The effect of commercial and formulated additives on the quality of the hydrofinished oil was also studied. Automatic transmission fluid possessing the Dexron IID specification was produced by adding 7 wt% from Inferium T442 additive or by adding 9 wt% from Lubrizol ® 6701 D additive to the hydrofinished light dewaxed oil. Oils with the same efficiency were also produced using a formulated additive containing 4% viscosity index improver, 1.5% anti-oxidant and 1% anti-wear. The effect of increasing Inferium T442, Lubrizol R 6701 D and formulated additive percents on the protection efficiency of the automatic transmission fluid was studied through AC impedance technique. According to this technique, the effect of these additives on the corrosion rate of carbon steel coupons can be negligible.

Key words: Light dewaxed oil, raffinate, hydrodesulfurization, hydrodenitrogenation, automatic transmission fluid

INTRODUCTION

Lubricating oils play a crucial role in both domestic and industrial processes. Proper applications of lubricants increase the lifetime and efficiency of machinery and decrease long-term costs in terms of energy consumption, maintenance requirements and reduce operating temperatures. Lubricants are used for the following requirements: minimizing frictions at the interfaces, protection of the sensitive surfaces from rust and corrosion, the dissipation of the heat generated in the interfaces, help in the creation of seals, neutralize residues and removal or prevention of the interference of foreign matters into the interfaces. Lubricants selection depends upon the type of equipment, temperature range, loading, oxidation stability, volatility, system compatibility, foaming potential,

dispersant, detergency requirements, as well as demulsification or emulsification properties^[1-5].

Petroleum mineral oils, which have many applications, are produced from the residue of atmospheric distillation. The initial process that determine the grade of the produced base oil is the refining of feedstocks through vacuum distillation of fuel oils^[6-8]. Spindle oil, light waxy distillate (LWD), medium waxy distillate (MWD) and heavy waxy distillate (HWD) are used to produce special and neutral oils, while the vacuum residue is used to produce bright stock oil after propane deasphalting^[9-11].

The automatic transmission fluids (ATFs) are the most important lubricating oils which are used in many purposes, including heat dissipation, wear protection, lubrication, foam inhibition and shift quality. It is usually produced by hydrofinishing the light dewaxed

oil (LDWO) to remove the trace amounts of sulfur, oxygen, nitrogen and organometallic compounds as well as aromatic contents which affect the oil properties during applications and result in rapid darkening, oxidation and sludging in service^[12].

Most base oil additives are chemical compounds of non-petroleum origin. They are frequently used either to reinforce existing properties or create additional properties^[13,14]. However, individual base oils have different response to particular additives and it is necessary to search for additives which give the maximum performance^[15].

In view of these considerations, the LDWO of Egyptian crude oils produced from Western Desert region were hydrofinished using catalyst mixtures of NiO and MoO₃ supported on alumina where NiO acts as a promoter on crystallites of MoO₃. The effects of the reactor temperature, pressure, space velocity and hydrogen to hydrocarbon ratio on the quality of the hydrofinished oil in the presence of this type of catalyst were investigated in order to reach the best operating conditions. The compatibility and the effect of commercial and formulated additives on the physicochemical properties of the Western Desert LDWO were also studied. The objective of adding these specified materials to the hydrofinished oil is to produce ATF Dexron IID which is recommended for passenger car. ATF Dexron IID is characterized by excellent oxidation stability and deposit control under very high temperature and severe operating conditions, excellent antiwear properties, good antifoam, antirust and anticorrosion properties, low volatility to provide minimum evaporation loss and compatible with severe types of synthetic rubber^[16-19].

DATA AND METHODOLOGY

The LDWOs of a crude oils from the Western Desert of Egypt were used in this investigation. Table 1 lists the physicochemical properties of the feedstock tested according to ASTM and IP standard methods^[20,21]. The hydrofinishing process of LDWO were carried out in plant designed by Institute Francias Dupetrol (IFP) (Fig. 1). In this process, the LDWO is mixed with hydrogen, heated to the reaction temperature and passed down flow over the fixed bed of catalyst. Hydrogen quench is used to remove the generated heat and control the reaction temperature. The reactor effluent passes through a series of separators to remove the hydrogen and other light gases from the hydrofinished light dewaxed oil^[22, 23]. An industrial NiO-MoO₃/Al₂O₃ catalyst, supplied by Procatalyse-France, was presulfided in presence of hydrogen. Sulfiding process is carried out with dimethyl disulfide, which easily decomposed into hydrogen sulfide, in order to convert the catalyst to its active form. Operating without sulfiding process will cause feedstock cracking as well as coke deposition and

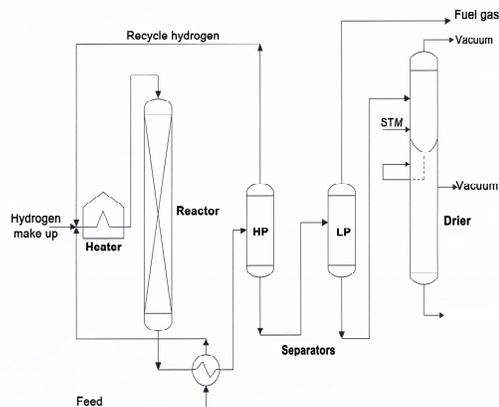


Fig. 1: Process flow for the hydrofinishing plant designed by the Institute Francais Dupetrol

rapid deactivation of the catalyst. The effect of reactor temperature, the applied pressure, liquid hourly space velocity and hydrogen to hydrocarbon ratio on the physicochemical properties of the products were studied^[24].

The hydrofinished LDWO was mixed with the multipurpose ATF additives; InfeniumT442 and Lubrizol ® 6701 D by the percentage of 5, 6, 7, 8, 9, 10, 11, 12 and 13%, wt for both. Infenium T442 is lubricant additive containing polyolefin amide alkyleneamine, poly long chain alkylmethacrylate, zinc alkyl dithiophosphate and other components dissolved in highly refined mineral oil, supplied by Infenium UK Limited, Abingdon, Oxfordshire. Lubrizol ® 6701D is a multipurpose package for automatic transmission fluids supplied from a local company ACPA, Cairo, Egypt. The formulated additive was prepared by adding different percentages of viscosity index (VI) improver (ACPA, SV 261) namely ; 2, 2.5, 3, 3.5, 4, 4.5, 5, 5.5 and 6% wt, 1.5% wt anti-oxidant (Vanlube R 961) and 1 % wt anti-wear (Angalamole 6085).

AC impedance technique was applied to study the effect of the increased sulfur and total acidity, due to increasing additive percents, on the corrosion rates of carbon steel coupons that may be contact the ATF during use.

METHODS OF CALCULATIONS

Calculation of activation energy and thermodynamic parameters of HDS and HDN reactions:

The effect of temperature on the rate of hydrogenation reactions according to the integrated form of the Arrhenius equation^[25, 26]:

$$K = A e^{-E_a/RT} \quad (1)$$

A= factor in the Arrhenius equations

E_a= apparent activation energy (K J mol⁻¹)

R= universal gas constant (J K⁻¹ mol⁻¹)

T= absolute reaction temperature (K)

The values for the enthalpy of activation ΔH, entropy of activation ΔS and free energy of activation

Table 1: Effect of the hydrogen/feed ratio, pressure, temperature and LHSV on the hydrofinishing of LDWO

Properties	Feed	Hydrogen / feed ratio (Nm ³ /M ³)						Pressure (kg/cm ²)				
		400	600	800	1000	1200	1400	100	110	120	130	135
Sp. gr. at 60/60 °F,	0.8699	0.8671	0.8662	0.8647	0.8638	0.8631	0.8624	0.8681	0.8669	0.8658	0.8647	0.8640
Refractive index at 70°C	1.4598	1.4582	1.4566	1.4555	1.4547	1.4540	1.4533	1.4586	1.4578	1.4566	1.4555	1.4549
Saybolt color	< 1.5 (ASTM)	+ 14	+ 18	+ 24	+ 26	+ 28	+ 30	+ 8	+ 14	+ 20	+ 24	+ 28
Kin.vis. at 100 °C, cSt	3.86	3.84	3.81	3.78	3.73	3.69	3.67	3.85	3.83	3.81	3.78	3.75
Kin.vis. at 40 °C, cSt	18.66	18.45	18.36	17.92	17.47	17.06	16.91	18.58	18.37	18.21	17.92	17.63
Viscosity index	96	97	97	98	99	101	101	96	97	97	98	98
Sulfur content, ppm	8800	480	390	310	240	190	170	570	440	360	310	270
Nitrogen content, ppm	57	27	19	13	10	7	5	31	24	19	13	12
Pour point, °C	- 30	- 30	- 27	- 27	- 24	- 24	- 21	- 30	- 30	- 27	- 27	- 27
Acidity, mg KOH/gm	0.021	0.017	0.014	0.012	0.01	0.007	0.005	0.018	0.016	0.013	0.012	0.012
Carbon residue, wt %	0.072	0.068	0.062	0.059	0.055	0.049	0.046	0.067	0.064	0.061	0.059	0.057
UV absorbance@275nm	1.153	0.711	0.561	0.447	0.338	0.253	0.184	0.731	0.562	0.432	0.347	0.321
VGC at 70 °C	0.8219	0.8187	0.8179	0.8164	0.8157	0.8152	0.8146	0.8198	0.8186	0.8174	0.8164	0.8158
Average M.wt	380	375	370	360	350	345	340	375	370	365	360	350
C _A %	5.97	5.33	3.32	2.76	2.30	1.74	1.18	5.31	4.91	3.74	2.76	2.50
C _N %	25.39	28.22	31.27	32.50	33.88	34.99	36.11	28.56	29.17	30.97	32.50	33.66
C _P %	68.64	66.45	65.41	64.65	63.82	63.27	62.71	66.13	65.92	65.29	64.65	63.84

Table 1: Contd.

Properties	Temperature (°C)						LHSV(h ⁻¹)				
	250	270	290	310	330	350	0.6	0.5	0.4	0.3	0.25
Sp. gr. at 60/60 °F,	0.8668	0.8659	0.8647	0.8636	0.8629	0.8638	0.8664	0.8656	0.8647	0.8634	0.8647
Refractive index at 70°C	1.4581	1.4569	1.4555	1.4543	1.4536	1.4549	1.4579	1.4566	1.4555	1.4538	1.4547
Saybolt color	+ 6	+ 18	+ 24	+ 28	+ 30	+ 22	+ 12	+ 18	+ 24	+ 30	+ 22
Kin.vis. at 100 °C, cSt	3.83	3.80	3.78	3.74	3.70	3.76	3.82	3.80	3.78	3.73	3.79
Kin.vis. at 40 °C, cSt	18.37	18.12	17.92	17.55	17.14	17.71	18.34	18.13	17.92	17.42	17.94
Viscosity index	97	97	98	99	101	99	96	97	98	100	99
Sulfur content, ppm	460	370	310	265	220	360	495	390	310	275	240
Nitrogen content, ppm	24	18	13	11	8	6	26	20	13	11	9
Pour point, °C	- 30	- 27	- 27	- 24	- 21	- 24	- 30	- 27	- 27	- 24	- 24
Acidity, mg KOH/gm	0.016	0.014	0.012	0.009	0.008	0.015	0.015	0.013	0.012	0.010	0.008
Carbon residue, wt %	0.065	0.061	0.059	0.048	0.041	0.049	0.063	0.060	0.059	0.045	0.042
UV absorbance@275nm	0.723	0.591	0.347	0.311	0.272	0.525	0.697	0.481	0.347	0.291	0.416
VGC at 70 °C	0.8185	0.8176	0.8164	0.8152	0.8146	0.8155	0.8181	0.8173	0.8164	0.8153	0.8163
Average M.wt	370	365	360	350	340	360	375	370	360	345	365
C _A %	5.50	4.19	2.76	1.75	1.34	1.64	5.31	3.75	2.76	1.17	1.23
C _N %	28.24	30.34	32.50	34.61	36.06	34.25	27.87	30.37	32.50	35.94	34.30
C _P %	66.26	65.47	64.65	63.64	62.60	64.11	66.82	65.88	64.65	62.84	64.47

ΔG can be calculated by using the following equations^[25, 26]:

$$\Delta H = E - RT \tag{2}$$

$$\Delta S/R = \ln A - \ln BTe/h \tag{3}$$

$$\Delta G = \Delta H - T\Delta S \tag{4}$$

Where, B is Boltzman constant, 1.3805x 10⁻¹⁶ erg

H is plank's constant, 6.6242 x 10⁻²⁷ erg

e = 2.7183

Calculation of the protection efficiency through impedance measurements: The protection efficiency P, of any particular compound was calculated from the impedance data by applying the following relation^[27]:

$$P = 100 \left[1 - \frac{(1/R_p)}{(1/R_p)_0} \right] \tag{5}$$

Where (1/R_p)₀ and (1/R_p) are reciprocal of the charge transfer resistance in the absence and presence of a certain concentration of the additive respectively.

RESULTS AND DISCUSSION

Hydrofinishing operating parameters and the production of ATF: The production of ATF from LDWO through the catalytic hydrofinishing process and the influence of different operating parameters on the process have been studied.

Table 2: Effect of hydrofinishing temperature and LHSV on the sulfur and nitrogen contents of LDWO. Hydrofinishing conditions: hydrogen to feedstock ratio= 800Nm³/M³, pressure = 130 kg/cm², sulfur of feed (S_{in}) = 8800 ppm, nitrogen of feed (N_{in}) = 57 ppm

T, °C	LHSV(h ⁻¹)	S ^(a) _{out} (ppm)	S _{in} /S _{out}	N ^(a) _{out} (ppm)	N _{in} /N _{out}	T, °C	LHSV(h ⁻¹)	S ^(a) _{out} (ppm)	S _{out} /S _{in}	N ^(a) _{out} (ppm)	N _{in} /N _{out}
190	0.6	695	12.662	40	1.425	250	0.6	550	16.000	31	1.839
	0.5	525	16.762	34	1.677		0.5	435	20.230	26	2.192
	0.4	455	19.341	29	1.966		0.4	355	24.789	21	2.714
	0.3	390	22.564	27	2.111		0.3	315	27.937	18	3.167
	0.25	350	25.143	22	2.591		0.25	280	31.429	14	4.071
210	0.6	640	13.750	37	1.541	270	0.6	520	16.923	28	2.036
	0.5	490	17.959	31	1.839		0.5	410	21.463	23	2.478
	0.4	420	20.953	26	2.192		0.4	325	27.077	17	3.353
	0.3	365	24.110	23	2.478		0.3	290	30.345	14	4.071
	0.25	325	27.077	19	3.000		0.25	255	34.510	12	4.750
230	0.6	590	14.915	33	1.727	290	0.6	495	17.778	26	2.192
	0.5	460	19.130	29	1.966		0.5	390	22.564	20	2.850
	0.4	380	23.158	24	2.375		0.4	310	28.387	13	4.385
	0.3	335	26.269	20	2.850		0.3	275	32.000	11	5.182
	0.25	300	29.333	17	3.353		0.25	240	36.667	9	6.333

Table 2: Contd.

T, °C	LHSV(h ⁻¹)	S ^(a) _{out} (ppm)	S _{in} /S _{out}	N ^(a) _{out} (ppm)	N _{in} /N _{out}
310	0.6	470	18.723	23	2.478
	0.5	375	23.467	17	3.353
	0.4	290	30.345	11	5.182
	0.3	255	34.510	9	6.333
	0.25	210	41.905	7	8.143
330	0.6	445	19.775	19	3.000
	0.5	360	24.444	13	4.385
	0.4	265	33.207	9	6.333
	0.3	230	38.261	7	8.143
	0.25	195	45.128	5	11.400
350	0.6	410	21.463	15	3.800
	0.5	330	26.667	11	5.182
	0.4	245	35.918	8	7.125
	0.3	210	41.905	5	11.400
	0.25	180	48.889	4	14.250

S^(a)_{out}, N^(a)_{out} = sulfur and nitrogen of hydrofinished LDWO

Table 3: Thermodynamic parameters of the HDS and HDN reactions for the hydrofinished LDWO. Ea of HDS = 8.601 K. J.mol⁻¹Ea of HDN 14.271 K. J.mol⁻¹

T, °C	1/T, K ⁻¹ x 10 ³	HDS			HDN				
		Rate constant (h ⁻¹)	ΔG K. J.mol ⁻¹	ΔH K. J.mol ⁻¹	- ΔS J.mol ⁻¹ .K ⁻¹	Rate constant (h ⁻¹)	ΔG K. J.mol ⁻¹	ΔH K. J.mol ⁻¹	- ΔS J.mol ⁻¹ .K ⁻¹
190	2.16	0.1148	122.116	4.750	253.49	0.0998	126.140	10.420	249.939
210	2.07	0.1137	127.188	4.583	253.84	0.1147	131.145	10.254	250.291
230	1.99	0.1146	132.270	4.417	254.180	0.1209	136.154	10.088	250.628
250	1.91	0.1153	137.357	4.251	254.504	0.1386	141.169	9.921	250.953
270	1.84	0.1221	142.449	4.084	254.816	0.1535	146.192	9.755	251.265
290	1.78	0.1240	147.549	3.918	255.117	0.1888	151.221	9.589	251.566
310	1.72	0.1390	152.654	3.752	255.407	0.2101	156.254	9.422	251.856
330	1.66	0.1458	157.764	3.585	255.688	0.2303	161.294	9.256	252.136
350	1.61	0.1568	162.882	3.419	255.960	0.2445	166.340	9.090	252.408

The studies were conducted with the aim of reaching the optimum operating conditions that would lead to the production of high quality ATF oil from LDWO.

Effect of hydrogen/feedstock ratio on the hydrofinished lubricating oil properties: The effect of H₂/feedstock ratio on the physicochemical properties of the hydrofinished LDWO of WD origin has been studied by increasing H₂/HC ratio from 400 to 1400 Nm³/M³ gradually. Other operating conditions were kept at constant values, (temperature = 290 °C, pressure = 130 kg cm⁻² and LHSV = 0.4 h⁻¹).

The increase in the H₂ to HC feed ratio from 400 to 800 Nm³ M⁻³ is apparently decreased the nitrogen, sulfur and acidity contents of the hydrofinished oil. These observation are probably due to the hydrogenation of nitrogen, sulfur and oxygen containing compounds with the liberation of NH₃, H₂S and H₂O. On the other hand, the specific gravity, refractive index, UV absorbance at 275 nm and the aromatic carbon, C_A% are decreased leading to a lighter oil with HCs of lower aromaticity. The viscosity of the hydrofinished oil is remained nearly constant while the VI is slightly increased. These results are associated with an increase in the C_N% confirming that naphthenic

hydrocarbons are characterized by better viscosity-temperature properties than their corresponding aromatics^[28,29].

The comparison between the different technological parameters which are affecting the hydrofinishing process. Table 1 shows that the increase of H₂/HC ratio has the most influential contribution on the process in terms of sulfur, nitrogen and acidity contents of the product. Further increase in H₂/HC feed ratio over did not significantly improve the quality of the hydrofinished oils. However, it will lead to an increase in the cost of the process with respect to hydrogen consumption and its recycling facilities^[30].

Effect of reactor pressure on the hydrofinished lubricating oil properties: The effect of reactor pressure on the physicochemical properties of the hydrofinished lubricating oil has been studied at five operating pressures ranging from 100 to 135 kg cm⁻², meanwhile the other operating factors were kept constant, (temperature = 290 °C, LHSV = 0.4 h⁻¹ and hydrogen/feedstock ratio of 800 Nm³ M⁻³). Table 1 shows that the increase of the operating pressure from 100 to 130 kg cm⁻² led to a substantial decrease in the values of the specific gravity, RI, color, VI, sulfur and nitrogen contents, pour point, VGC and the UV absorbance @ 275 nm. Therefore, increasing the applied pressure in the hydrofinishing process to 130 kg cm⁻² improved most of the specified physicochemical properties of the LDWO. This is probably through the increasing the possibility of feed and hydrogen stream contacts with the catalyst. However, increasing the pressure from 100 to 135 kg cm⁻² had slight impact on the hydrocarbon composition of the produced oils, where aromatics, naphthenic and paraffinic carbon percentages (C_A, C_N and C_P%) remained nearly constant. This also indicates that the improvement in the properties of the produced oil is mainly due to the removal of nitrogen, sulfur and oxygen containing compounds^[31].

The increase of the pressure in the hydrofinishing process gives a good improvement in color degree, viscosity and carbon residue, Table 1. The results can be attributed to the removal of the highly colored compounds such as poly-aromatics, or the change of sulfur compounds to simple ones of lower color, as well as removing other impurities. The viscosity decreased by increasing the pressure probably due to the saturation of the unsaturated hydrocarbons and the saturation reactions lead to the formation of oils with low carbon residue and higher hydrogen/carbon ratio. Table 1 shows no significant improvement in the pour point of the produced hydrofinished oil and this suggests increasing the working pressure has slightly effect on the paraffin content (C_P%) of the LDWO. Finally we can conclude, that greater conversion of impurities may be achieved by increasing hydrogen pressure and the increase in hydrogen pressure favors the hydrogenation

reactions and reduces polymerization reactions and coke formation. However, working at pressure equal to 130 kg cm⁻² compromise between the quality of the produced oil and the capital cost of the process.

Effect of reactor temperature on the hydrofinished lubricating oil properties: The effect of temperature on the hydrofinishing process of LDWO was studied at operating temperature ranging from 250 to 350°C. Other operating parameters were kept at constant values throughout all experiments, (pressure=130kg cm⁻², liquid flow rate= 0.4 h⁻¹ and hydrogen/feedstock ratio = 800 Nm³ M⁻³). The applied catalyst was a presulfided mixture of NiO and MoO₃ supported on alumina where NiO acts as a promoter.

The physicochemical properties of the hydrofinished LDWO show that the sulfur content is sharply decreased from 8800 to 460 ppm at 250°C and is remained containing 360 ppm sulfur by increasing the temperature up to 350°C, Table 1. The unchanged sulfur amount can be ascribed to the lowest hydrodesulfurization reactivity of the sterically hindered sulfur compounds such as 4,6-alkyl-dibenzothiophenes concentrated in middle distillates^[32]. On other words, as the reactor temperature increases to 330°C the sulfur content and total acidity decrease. Increasing the temperature will increase the rate of the hydrodesulfurization reactions, facilitate the removal of the sulfur from the relatively stable sulfur heterocyclic compound and probably leads to the reduction of naphthenic acids^[33]. Moreover, the decrease in the amounts of sulfur, nitrogen and acidic content is occurred with parallel increase in the average molecular weight of the produced oil, Table 1. This may suggest the removal of undesirable components that are associated with the removal of the lighter fraction.

The aromatic content (C_A%) was decreased and the naphthenic content (C_N%) was increased with increasing the operating temperature. This indicates that the temperature of the hydrofinishing process is potentially affected the hydrocarbon structures. Another related property is the viscosity index (VI) that is usually used as an indicator of the rate of viscosity change with temperature. According to the data listed in Table 1, the VI has been improved from 96 to 101 by increasing the temperature from 250 to 330°C. It is known that the increasing of paraffinic hydrocarbon gives raise to the VI values increase while the aromatics decrease this value. This observation has been noticed before and is interpreted in terms of the saturation of polycyclic aromatic hydrocarbons into the corresponding naphthenes^[33,34]. At 350°C, the VI value is slightly decreased that may be attributed to the occurrence of undesirable side reactions such as polymerization and cracking at this temperature. The viscosity gravity constant (VGC) values are usually referred to the higher aromatic contents and the greater rate of viscosity change with the change in

Table 4 : Effect of multipurpose additives Infenium and Lubrizol on the physicochemical properties of the hydrofinished LDWO.

Properties	Oil	Infenium, wt%								
		5	6	7	8	9	10	11	12	13
Specific gravity at 60/60 °F	0.8647	0.8660	0.8664	0.8670	0.8676	0.8682	0.8687	0.8694	0.8699	0.8705
Kinematic viscosity @ 40 °C,cSt	17.92	30.89	31.26	32.17	33.29	34.63	36.13	37.98	38.88	39.71
Kinematic viscosity @ 100 °C,cSt	3.78	6.30	6.49	6.75	7.05	7.36	7.70	8.08	8.30	8.49
Brookfield viscosity at -40 °C, cP	17,000	25,000	27,600	30,000	32,500	35,900	37,000	40,500	43,000	44,700
Viscosity index (VI).	98	160	168	175	181	186	190	194	197	199
Flash point, °C.	198	210	214	216	220	224	226	228	230	230
Pour point, °C.	-27	-36	-39	< -40	< -40	< -40	< -40	< -40	< -40	< -40
ASTM color.	0.0	< 1.5	1.5	< 2	2	< 2.5	2.5	3	3.5	4
Total acidity , mg KOH / gm.	0.012	0.29	0.43	0.59	0.72	0.83	0.91	1.07	1.20	1.31
Sulfur , wt%.	0.031	0.15	0.18	0.22	0.25	0.26	0.29	0.31	0.33	0.35
Oxidation test, minute	120	260	320	360	> 360	> 360	> 360	> 360	> 360	> 360
Foaming characteristics										
Sequence I, 24°C	20/ 10	15 / 5	13 / 4	11 / 3	9 / 2	7 / 1	5 / 0	5 / 0	4 / 0	3 / 0
Sequence II, 94 °C	15 / 5	10 / 2	8 / 2	6 / 1	4 / 1	2 / 0	0 / 0	0 / 0	0 / 0	0 / 0
Sequence III, 24°C	20 / 15	15 / 10	14 / 9	13 / 9	12 / 7	11 / 6	10 / 5	9 / 4	7 / 3	5 / 0

Table 4: Contd.

Properties	Lubrizol, wt%									
		5	6	7	8	9	10	11	12	13
Specific gravity at 60/60 °F										
Kinematic viscosity @ 40 °C,cSt	0.8655	0.8660	0.8664	0.8668	0.8673	0.8679	0.8682	0.8685	0.8688	
Kinematic viscosity @ 100 °C,cSt	28.40	29.30	29.71	31.26	32.07	32.86	34.23	35.82	44.26	
Brookfield viscosity at -40 °C, cP	5.79	6.04	6.20	6.53	6.77	7.01	7.32	7.65	7.88	
Viscosity index (VI).	24,700	26,600	28,000	30,800	32,500	35,000	36,500	38,200	40,300	
Flash point, °C.	152	159	165	171	177	183	187	190	192	
Pour point, °C.	206	210	212	214	216	216	218	220	220	
ASTM color.	-30	-33	-36	-39	< -40	< -40	< -40	< -40	< -40	< -40
Total acidity , mg KOH / gm.	< 1.5	< 2	< 2.5	2.5	< 3	3	< 3.5	< 4	4.5	
Sulfur , wt%.	0.23	0.31	0.43	0.50	0.64	0.70	0.79	0.84	0.91	
Oxidation test, minute	0.13	0.15	0.20	0.22	0.25	0.27	0.29	0.30	0.32	
Foaming characteristics										
Sequence I, 24°C										
Sequence II, 94 °C	17 / 7	15 / 7	12 / 6	10 / 5	8 / 4	7 / 3	6 / 2	5 / 0	4 / 0	
Sequence III, 24°C	12 / 4	11 / 4	9 / 3	7 / 3	5 / 2	4 / 2	3 / 0	0 / 0	0 / 0	
	17 / 12	16 / 11	15 / 10	14 / 8	13 / 7	12 / 6	11 / 5	10 / 5	8 / 4	

temperature^[35]. In the present study, as the temperature is increased from 250 to 330°C the VGC and C_A% values are decreased from 0.8185 to 0.8146 and from 5.50 to 1.34, respectively.

These results agree with the reported conclusion that the aromatic compounds possess poor viscosity-temperature characteristic and the removal of aromatic compounds improves the viscosity index of the hydrofinished oil^[32]. Also, increasing of hydrofinishing temperature led to an improvement in the oil color due to the reduction of the impurity content of the oil, namely, heavy aromatics sulfur, oxygenated compounds and other impurities. These impurities are relatively reactive species and readily oxidized by atmospheric oxygen during storage and application leading to the formation of dark colored compounds.

Effect of liquid hourly space velocity (LHSV) on the hydrofinished lubricating oil properties: LHSV

measures the contact time between the hydrocarbon and catalyst in the reactors and it is expressed as a liquid volumetric ratio of the hourly hydrocarbon feed rate (M³ h⁻¹) divided by the total catalyst volume (M³). It is proportional to the inverse of the residence time (h⁻¹). The effect of LHSV on the quality of the hydrofinished LDWO was studied and tabulated in Table 1. It can be deduced that the decreasing of the space velocity from 0.6 to 0.3 h⁻¹ led to a decrease in the values of specific gravity, refractive index, color, sulfur and nitrogen contents, acidity, carbon residue, UV absorbance and VGC. However further decrease of LHSV from 0.3 to 0.25h⁻¹ led to an increase of these properties^[37]. Furthermore, the viscosity temperature property of the oils expressed as VI is slightly improved from 96 to 100 by decreasing the LHSV to 0.3h⁻¹. This trend could be attributed to that, decreasing of LHSV leads to an increase of the contact time between the feed, hydrogen stream and catalyst and therefore these will increase the

reaction rate. Consequently, this will increase the removal of impurities and improve the quality of the hydrofinished oil. Further increase of LHSV more than 0.25 h^{-1} will increase the contact time between the feedstock and the catalyst may promote undesirable reactions which lowered the quality of the hydrofinished oil^[36].

Effects of temperature and space velocity on the HDS and HDN reactions: Thermodynamic treatment: The thermodynamic parameters of the influence of the hydrofinishing temperature and LHSV on the HDS and HDN reactions of the investigated oil were quantitatively measured.

Landau *et al.*^[36], indicated that the values of activation energy of HDS and HDN reactions are increased by increasing hydrofinishing temperature. As previously reported, the differences in the activation energies of HDS and HDN are as a result of the different reactivities of sulfur and nitrogen containing compounds with temperature which promotes the catalyst activity^[36].

The measurements in the present study indicate that, the LHSV range yielded an almost complete conversion of sulfur, while the decrease of HDN extent by about 77% (at 290°C and $\text{LHSV } 0.4 \text{ h}^{-1}$). At constant hydrofinishing temperature, decreasing the LHSV from 0.6 to 0.25 h^{-1} has substantial effect on the reactivity of HDS and HDN reactions. Also, this reactivity was increased with raising hydrofinishing temperature up to 350°C , Table 2.

Equation for hydrodesulfurization and hydrodenitrogenation reactions is assumed to be first order and expressed as^[25]:

$$\ln(C_{\text{in}}/C_{\text{out}}) = k/\text{LHSV}$$

Where:

C_{in} = concentration of sulfur or nitrogen (S_{in} or N_{in}) in reactor inlet

C_{out} = concentration of sulfur or nitrogen (S_{out} or N_{out}) in reactor outlet

K = apparent reaction rate constant (h^{-1})

LHSV = liquid hourly space velocity (h^{-1})

According to data in Table 2, $\log(S_{\text{in}}/S_{\text{out}})$ and $\log(N_{\text{in}}/N_{\text{out}})$ were plotted against $1/\text{LHSV}$ as in Fig. 2 a,b. The reaction rate constants (k) were determined from the slopes of curves. Figure 2c was used for the calculation of the values of apparent activation energy (E_a) for HDS and HDN reactions based on rate constants calculated from Fig. 2a,b (equation 1). The values of E_a and the intercepts of Fig. 2a, b were used for the calculation of the values of the enthalpy of activation ΔH , entropy of activation ΔS and free energy of activation ΔG .

The values of E are found to be 8.601 and $14.271 \text{ K J.mol}^{-1}$ for HDS and HDN reactions, respectively. i.e. HDS is easier to occur than HDN reaction. This could be attributed to the effect of H_2S and NH_3 on the hydrofinishing reactions. It is well established that

hydrogen sulfide and ammonia enhance desulfurization, while hydrogen sulfide inhibits denitrogenation reactions.

Table 3 indicated that, the values of ΔG for HDS and HDN are increased with increasing temperature, which indicate that HDS and HDN processes are more faster at higher temperature. Raising the temperature leads to increasing the kinetic energy of reactants and facilitates the above mentioned reactions. The values of ΔS for HDS and HDN are decreased with increasing temperature which indicate that, the two processes are less ordered at high temperature.

Formulation of ATF through the upgrading of the hydrofinished LDWO using additives: Automatic transmission fluids (ATFs) are the most important lubricating oils in many purposes, including heat dissipation, wear protection, lubrication from inhibition and shift transmission. It is usually produced through the upgrading of the hydrofinished LDWO using additives^[39, 40].

The hydrofinished LDWO of WD crude oil, that was obtained from carrying out the previously mentioned refining processes at their optimum conditions, were evaluated as a basestock for formulating the automatic transmission fluid (ATF). The solvent extraction process was achieved using NMP to feed ratio 2: 1 and extraction temperature 55°C , while the solvent dewaxing process was applied using MEK/toluene (60: 40) to raffinate ratio 4: 1 and filtration temperature -42°C . The hydrofinishing process was operated at temperature 290°C , pressure 130 kg cm^{-2} , LHSV 0.4 h^{-1} and hydrogen to feed ratio 800: 1 $\text{Nm}^3 \text{M}^{-3}$.

Formulation of ATF as a final product are enhanced by the use of different types of additives, to withstand any operating conditions. These additives are viscosity index improver, pour point depressant, anti-oxidant, anti-wear, anti-rust, anti-foam, seal swelling agents, corrosion inhibitors and detergent/dispersant^[41]. Most of these additives are included in the multi-purpose commercial additive packages. Automatic transmission fluid packages may contain up to 20 separate components which are finely tuned to provide optimum performance including delicately balanced friction characteristics^[15].

In view of these considerations, comparative studies on the compatibility and the effect of two multi-purpose commercial packages Infernum T442 and Lubrizol @ 6701 D together and with the formulated additives on the VI and pour point of the hydrofinished LDWO were found to be highly informative.

Infernum T442 is a lubricant additive containing polyolefin amide alkylene amine, poly long chain alkylmethacrylate, zinc alky dithiophosphate (Zn DTPs) and other components that are dissolved in highly refined mineral oil. Lubrizol @ 6701 D is a multi purpose package for automatic transmission fluids.

Table 5: Effect of changing the VI improver on the physicochemical properties of the hydrofinished LDWO. Anti-oxidant = 1.5, wt%, anti-wear = 1, wt%

Properties	Oil	VI, wt %								
		2	2.5	3	3.5	4	4.5	5	5.5	6
Specific gravity at 60/60 °F	0.8647	0.8656	0.8660	0.8663	0.8667	0.8669	0.8670	0.8673	0.8675	0.8676
Kinematic viscosity @40°C, cSt	17.92	28.47	29.33	29.80	30.67	31.39	32.66	33.18	34.11	34.58
Kinematic viscosity @ 100°C, cSt	3.78	5.73	5.96	6.13	6.39	6.61	6.89	7.09	7.36	7.52
Brookfield viscosity at -40 °C, cP	17,000	24,500	25,400	27,000	28,500	30,200	32,000	33,800	35,500	37,000
Viscosity index (VI)	98	148	154	160	167	173	178	184	190	194
Flash point, °C	198	204	206	208	210	212	212	216	218	220
Pour point °C	-27	-33	-36	-39	-39	< - 40	< - 40	< - 40	< - 40	< - 40
ASTM color	0.0	< 1.5	1.5	< 2	2.5	< 3	3.5	3.5	< 4	4
Total acidity, mg KOH/gm	0.012	0.32	0.46	0.63	0.77	0.84	0.93	1.11	1.24	1.35
Sulfur, wt %	0.031	0.149	0.147	0.145	0.143	0.140	0.139	0.137	0.135	0.134
Oxidation test, minute	120	> 360	> 360	> 360	> 360	> 360	> 360	> 360	> 360	> 360
<i>Foaming characteristics</i>										
Sequence I, 24°C	20 / 10	18 / 9	17 / 9	17 / 8	16 / 8	16 / 7	16 / 7	15 / 7	15 / 7	14 / 6
Sequence II, 94 °C	15 / 5	13 / 4	13 / 4	12 / 4	12 / 4	11 / 4	11 / 3	11 / 3	10 / 3	10 / 3
Sequence III, 24°C	20/15	18/13	18/12	17/ 12	17/ 11	17/ 11	17/ 10	16/ 10	15/ 10	15 / 9

Table 6: The Protection efficiency (P)obtained by impedance measurements for the hydrofinished LDWO with Infenium, Lubrizol and Formulated additives

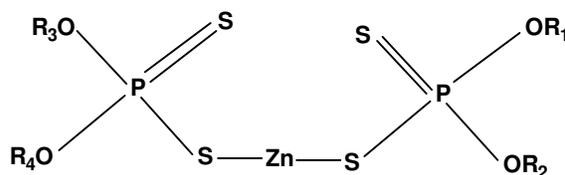
Additive (wt%)	Infenium					Lubrizol					VI (wt%)	Formulated				
	R _s x 10 ⁻⁸	(R _p) _o x 10 ⁻⁸	CPE/F x 10 ⁻¹⁴	N	P	R _s x 10 ⁻⁸	(R _p) _o x 10 ⁻⁸	CPE/F x 10 ⁻¹⁴	N	P		R _s x 10 ⁻⁸	(R _p) _o x 10 ⁻⁸	CPE/F x 10 ⁻¹⁴	N	P
Oil.	- 0.1583	0.1700	10.50	0.764	—	—	—	—	—	—	—	—	—	—	—	—
5	- 2.681	175.1	25.61	0.799	99.903	- 11.10	2139.0	50.78	0.850	99.92	2	-3.742	18.97	2.881	0.893	99.10
6	- 3.663	146.7	0.7252	0.861	99.884	- 1.757	1814.0	2503.0	0.975	99.91	2.5	- .2963	16.62	39.43	0.781	98.98
7	- 0.1127	122.3	288.6	0.904	99.861	- 2.374	1634.0	28.46	0.817	99.90	3	- 63.71	14.30	0.6817	0.901	98.81
8	- 14.18	109.9	2.635	0.767	99.850	- 8.795	1427.0	6.413	0.736	99.88	3.5	0.06543	13.12	4.719	0.834	98.70
9	0.2732	109.0	3.597	0.778	99.844	- 34.03	127.3	0.04962	0.691	99.87	4	- 2.426	9.987	3651.0	0.691	98.30
10	- 17.16	102.2	0.04616	0.673	99.834	0.04024	118.8	2140.0	0.969	99.86	4.5	-0.6182	7.634	813.7	0.815	97.77
11	- 0.3171	96.46	35.56	0.826	99.824	1.938	109.3	1934.0	0.973	99.85	5	3.721	6.831	6.183	0.768	97.51
12	- 43.41	81.36	741.5	0.729	99.791	2.664	77.83	253100.0	0.898	99.78	5.5	- 27.61	6.138	21.67	0.903	97.23
13	- 5.397	71.17	1.615	0.7511	99.760	0.4654	52.82	6517.0	0.969	99.68	6	-0.6318	5.963	61520.0	0.867	97.15

The formulated additive was prepared by adding different percentages of viscosity index improvers, 1.5wt%, anti-oxidant and 1wt% anti-wear.

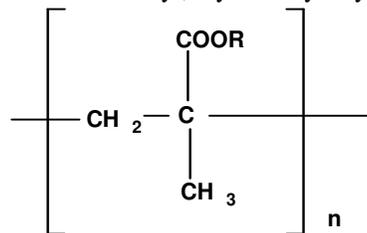
The importance of Zn DTPs (structure I) as additives for lubricating oils is due to their multifunctional performance. Not only do they act as anti-oxidants, but they also improve the wear inhibition of the lubricant and protect metals against corrosion^[42]. Several studies have explained the Zn DTP anti-wear action. They have suggested that molecules of Zn DTP are adsorbed on mechanically activated metal surface participate in the surface of polyphosphate tribofilm formation under conditions of boundary lubrication. Zinc poly thio phosphate “thermal film” have been recently recognized to be precursor reaction products in the formation of polyphosphate glasses tribofilm^[43].

The way that Zn DTP performs as an anti-oxidant is a complex interaction pattern involving hydroperoxides and the anti-oxidant mechanism peroxy radicals. It was demonstrated that is proceeded via acid catalyzed ionic decomposition of the hydroperoxide. The catalyst structure is O,O`- dialkylhydrogen dithiophosphate, (RO)₂ PS₂H, that derived from the Zn DTP^[44]. Infenium T442 also contains poly long chain alkyl methacrylate (structure II) and polyolefin amide alkylene amine in order to incorporate anti-wear, pour point depressant and dispersancy to reach the basic viscosity control properties. The multipurpose packages incorporate alkylated phenol, long chain alkyl salicylate

and sulfurized alkyl phenate. They act as detergent/dispersants and as oxidation inhibitors due to the presence of phenolic function group^[42-44].



I. Zinc Alkyl Dithiophosphates
R can be alkyl, aryl or alkyl-aryl



II. Poly Long Chain Alkyl Methacrylate

Determination of the corrosion rates by AC impedance method measurements for the automatic transmission fluids: Electrochemical impedance is the more appropriate method for many corrosion studies, particularly for corrosion rate determination,

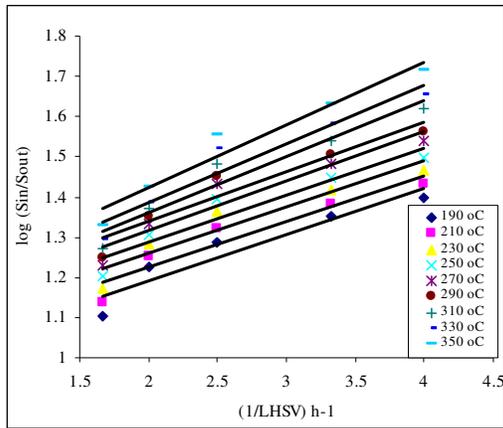


Fig. 2a: Relation between $\log (S_{in} / S_{out})$ and $1/LHSV$ for HDS reactions at different temperatures

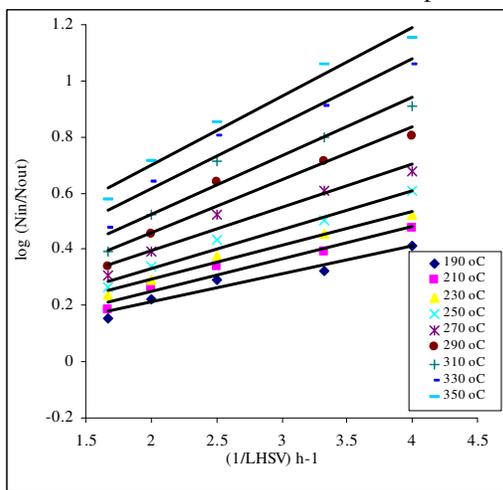


Fig. 2b: Relation between $\log (N_{in} / N_{out})$ and $1/LHSV$ for HDN reactions at different temperatures

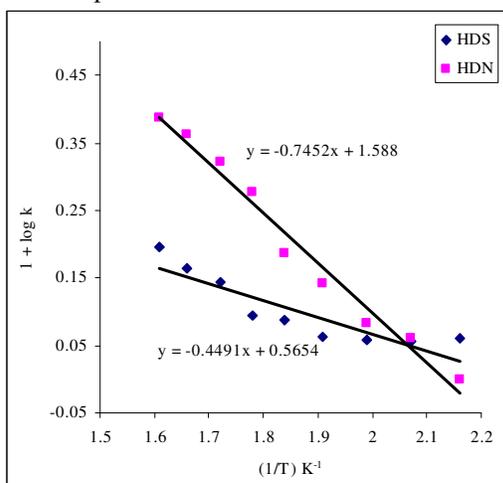
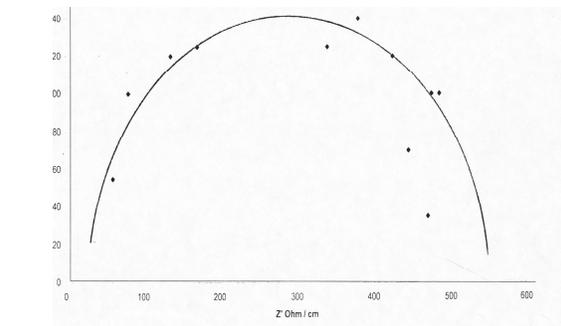
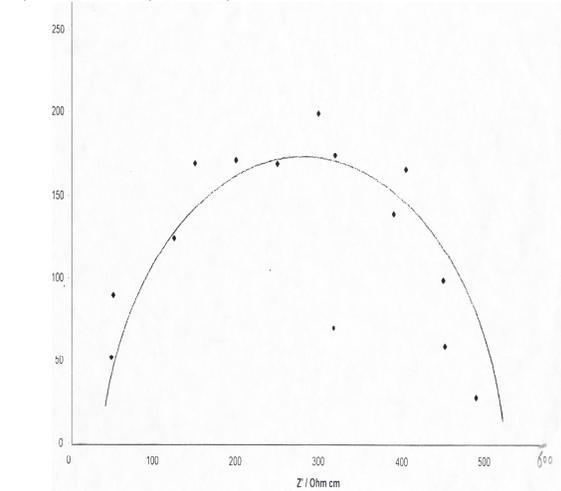


Fig. 2c: Relation between $\log k$ and $1/T$ for HDS and HDN reactions

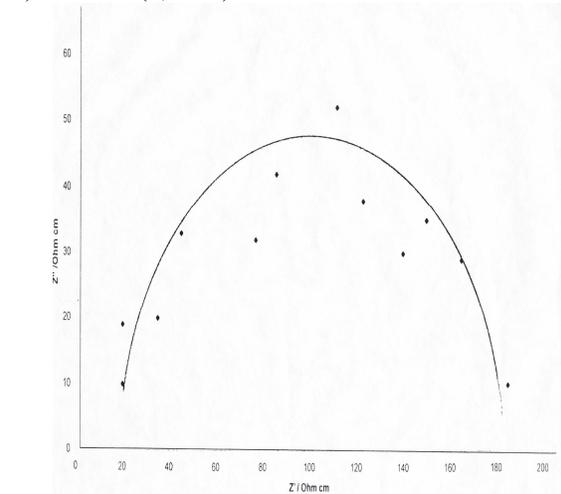
mechanistic studies and the investigation of inhibited systems. The impedance measurements typically gave a single relation or semicircle comprising the charge



a) Infernum (7, wt%)



b) Lubrizol (9, wt%)



c) Formulated (4 VI, wt%)

Fig. 3: Impedance measurements for the hydrofinished LDWO with additives

transfer resistance in parallel with the double layer capacitance^[27]. Additive efficiencies and the adsorption isotherms were calculated from the charge transfer resistance value. In addition, the capacitance-potential diagrams would provide mechanistic information on the adsorption type of compounds. AC impedance measurements were used primarily to calculate the capacity of the double layer. On the addition of an

additive, change in the double layer is expected to reflect the structural modifications of the metal solution interphase due to the adsorption of the inhibitor molecules on the metal surface^[45].

AC impedance technique was applied to study the effect of the increase sulfur and total acidity on the corrosion rates of carbon steel coupons that contact the ATF when using the lubricating oil.

Table 6 compile the impedance measurements and the protection efficiencies for the hydrofinished and non-hydrofinished LDWO of WD origin with Infenium T442, Lubrizol® 6701 D and formulated additives.

The impedance measurements of carbon steel coupons at rest potential and ambient temperature give value of $(R_p)_0 = 1.7 \times 10^{+7}$ for the hydrofinished LDWO of WD crude oil. When the coupons was immersed in the hydrofinished LDWO in the presence of T442, the values of $(R_p)_0 = 1.751 \times 10^{+10}$ and protection efficiency 99.903. The protection efficiency was decreased with increasing the additive concentrations and consequently the protection efficiency was nearly constant, 99.76. For Lubrizol R 6701 D, the protection efficiency was changed from 99.92 to 99.68 on adding 5 and 13 %wt of additive with the hydrofinished LDWO.

The protection efficiency for the formulated additive was found 99.10 corresponding to 2% VI, 1.5 anti-oxidant and 1% anti-wear and it was decreased until it was reached to 97.15 at 6% viscosity index, 1.5% anti-oxidant and 1% anti-wear.

Figure 3 shows the impedance complex diagrams of carbon steel coupons in the hydrofinished LDWO in the absence and presence of 7% Infenium, 9% Lubrizol and with formulated additive containing 4 wt% VI improver, respectively after 15 minute immersion at ambient temperature. The impedance diagrams gave a semicircle type appearance for all examined additives indicating that the corrosion process of carbon steel in the hydrofinished LDWO is controlled by a charge transfer process and the presence of abovementioned additives does not alter this mechanism.

From the above mentioned results, it is concluded that, the increase of additive percents led to slightly decrease in the protection efficiency (decrease in the values of the charge transfer resistance R_p) i.e. the effect of these additives on the corrosion of carbon steel coupons can be negligible.

CONCLUSION

The light dewaxed oil produced from Western Desert of Egypt crude oils had a relatively high VI 96 and low pour point -30 °C. Regarding to the hydrofinishing cost and the quality of the hydrofinished oil, the optimum conditions for the hydrofinishing process were at reactor temperature 290 °C, pressure 130 kg cm⁻², LHSV 0.4 h⁻¹ and H₂/HC ratio 800 Nm³ M⁻³. The ATF Dexron IID with standard specifications;

viscosity index 172 (min) and pour point - 40 (max) was produced by adding 7 wt% from Infenium T 442 or by adding 9 wt% from Lubrizol ® 6701 D. Infenium T442 was more preferable than Lubrizol ® 6701D because it is less expensive and requires less amounts to achieve ATF Dexron IID. Also, ATF Dexron IID with standard specifications was produced using a formulated additive containing 4 wt% VI, 1.5 % antioxidant and 1 wt% anti-wear.

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