ATTACHMENT 1

Evaluation of GTL #1 and Crude Oil Blends
For Yield Stress Values

A REPORT BY WESTPORT TEHCNOLOGY CENTER

WESTPORT
TECHNOLOGY CENTER INTERNATIONAL

RT-01-005 January 2001

Evaluation of GTL and Crude Oil Blends For Yield Point Values

Final Report

Work By:
S. Brown, N. Magri, R. Collins

Westport Technology Center International
6700 Portwest Drive
Houston, Texas 77024
(713) 479-8400
(713) 864-9357 (Fax)
www.westport1.com

Prepared for Department of Petroleum Engineering, University of Alaska W.O.# M10327

Table of Contents

Introduction

The gel strength of various GTL (gas to liquid samples) and North Slope crude oil blends were determined by the rotating vane method. The tests for determining the yield stress, or yield point, of the cooled crude oil blends, were performed following Westport's Standard Laboratory Procedure (SLP) 307, "Crude Oil Yield Point Determination by Vane Viscometry". This determination was made with Brookfield rotary viscometers and vane spindles, which extend horizontally through a sample, minimizing the impact of slippage at the spindle wall. This method determines the minimum amount of torque necessary to initiate oil movement at low shear, and subsequent gel breakdown after initiation of flow. These data can be directly used in modeling of crude oil behavior in pipelines, during start-up conditions.

Additionally, extended gas chromatography was performed to define the quantitative composition from C2 through C30+ on samples (a) and (b) listed below and on GTL plus crude oil blends (i) through (iv).

Test Results

Twenty-four test samples were prepared by weight for testing, four each at the six ratios listed below:

Initially, 2 samples of Wax Distillate:GTL mixes were prepared as follows:

(a). 25% wax distillate + 75% Light Hydrocarbon GTL
(b). 50% wax distillate + 50% Light Hydrocarbon GTL

Blended samples of (a) and (b) with crude oil in the following ratios, respectively:

(i). Sample (a) + crude oil in the ratio of 1:4
(ii). Sample (a) + crude oil in the ratio of 1:3
(iii). Sample (b) + crude oil in the ratio of 1:4
(iv). Sample (b) + crude oil in the ratio of 1:3

Blended Light Hydrocarbon GTL sample with crude oil in the following ratios:

(v). LH sample + Crude oil in the ratio of 1:4
(vi). LH sample + crude oil in the ratio of 1:3

The client supplied the wax and light hydrocarbon GTL samples. The crude oil sample was supplied by the Alyeska Pipeline Service Company taken from the flowing TAPS mixed stream at Pump Station 1. The paraffin wax was separated from Shellwax® 200 by a modified ASTM-1160 Vacuum Distillation process to produce only a 20% overhead fraction. This wax fraction was then mixed with the light hydrocarbon GTL liquid as outlined above for samples (a) and (b). All blend mixes were carried out by weight to weight measurements.

Samples were tested at selected temperatures as the crude oil blends were cold ramped from 90°F to -20°F over a twenty-one day period. The maximum recorded torque obtained during vane rotation at a constant speed of 0.01 rpm was converted into a yield stress value. The summary of vane test results is presented in Table 1 and Figures 1 and 2. Table 2 presents the C2 to C30+

data from quantitative gas chromatography of samples (i) through (iv). The GC data is also presented in graphical format on pages 36 – 41 of Section 2.

Initially, test temperatures were set at 9°, 0° and –20°F. However, testing at 9°F (Tests 1-8) indicated gel strengths beyond the measurable limits of the viscometers for samples (i) through (iv), and relatively high strengths with the GTL/Crude oil blends (v) and (vi) containing no wax distillate material. The cold ramp was continued and testing resumed (Tests 9 and 10) at 0°F for only samples (v) and (vi).

Due to the high yield stress values encountered it was decided to drop testing at –20°F and test the remaining samples at higher temperatures in an attempt to determine gelation onset and buildup. Therefore, all remaining samples, sealed in their closed cups were re-heated to 150°F in the environmental chambers for several hours, slowly decreased in temperature to 90°F, then cold ramping re-established on the 21-day ramp cycle.

Tests 11 and 12 were performed at 60°F on the higher content wax/GTL samples (iii) and (iv) resulting in 0.07 and 0.0 dynes/sqcm, respectively. The other samples were not tested in an effort to conserve sample quantity.

Tests 13 through 18 were performed at 40°F on samples (i), (ii), (iii) and (iv). Tests 13 and 15 resulted in maximum torque readings beyond the selected viscometer limits. Repeats were performed after changing the viscometer to one with a higher spring rating. The measured yield stresses were 20.7, 63.7, 539 and 1192 dynes/sqcm with respect to sample number.

Test 19 through 23 were performed at 20°F on samples (i), (ii), (iv), (v) and (vi). Test 23 on sample (v) was beyond the strongest viscometer's limit, and the yield stress can only be reported as greater than 1589 dyne/sqcm. The trend of higher yield stresses with higher wax content was again observed. Samples (i) and (ii) had yield stresses of 739 and 1384 dyne/sqcm. The blends of GTL and crude oil showed gel onset with yield stresses of 71 and 92 dyne/sqcm for samples (v) and (vi), respectively.

There was some variability seen with sample (vi) on Tests 3 and 8 at 9°F, (229 versus 438 dyne/sqcm) that could not be attributed to procedural variation. This is not uncommon when weak gel structures have formed. If sample quantity had been higher, a third repeat test would have been warranted. Test 8 results fall within the data trend having a higher yield value in comparison with Test 2 (364 dyne/sqcm), which had a lower wax/GTL ratio; therefore a high degree of confidence can be associated with the Test 8 yield stress value even without a backup test result.

TABLE 1

Yield Stress Data for GTL & Crude Oil Blendes

Test Sample (mixture reference)	Test Number (Sequence)	Brookfield Viscometer Model	Temperature Temperature (°F)	Yield Point Maximum Torque (dyne-cm)	Yield Stress (dynes/sqcm)
(i)	14	RV	40	747	20.7
(i)	21	HB	20	26736	739
(i)	7	HB	9	>57496	>1589
(ii)	13	LV	40	>674	>18.6
(ii)	18	RV	40	2307	63.7
(ii)	22	HB	20	50079	1384
(ii)	6	HB	9	>57496	>1589
(iii)	12	LV	60	2.69	0.07
(iii)	15	RV	40	>7187	>199
(iii)	16	HB	40	19491	539
(iii)	5	HB	9	>57496	>1589
(iv)	11	HB	60	0.0	0
(iv)	17	HB	40	43122	1192
(iv)	23	HB	20	>57496	>1589
(iv)	4	HB	9	>57496	>1589
(v)	20	HB	20	2587	71
(v)	1	RV	9	>7187	>199
(v)	2	HB	9	13167	364
(v)	10	HB	0	24206	669
(vi)	19	HB	20	3335	92
(vi)	3	HB	9	8279*	229*
(vi)	8	HB	9	15869	438
(vi)	9	HB	0	22366	618

* Test results appears to be anomalous in comparison to data trends.

(i) (25% wax distillate + 75% GTL) + Crude Oil in the ratio of 1:4
(ii) (25% wax distillate + 75% GTL) + Crude Oil in the ratio of 1:3
(iii) (50% wax distillate + 50% GTL) + Crude Oil in the ratio of 1:4
(iv) (50% wax distillate + 50% GTL) + Crude Oil in the ratio of 1:3
(v) GTL + Crude Oil in the ratio of 1:4
(vi) GTL + Crude Oil in the ratio of 1:3

The precision of the Vane test method and results, based on running multiple samples can be stated as;

Repeatability (r) - The difference between successive results obtained by the same operator in the same laboratory with the same apparatus under constant operating conditions on identical test material would, in the normal and correct operation of this method, have a relative standard deviation at or below 15%.

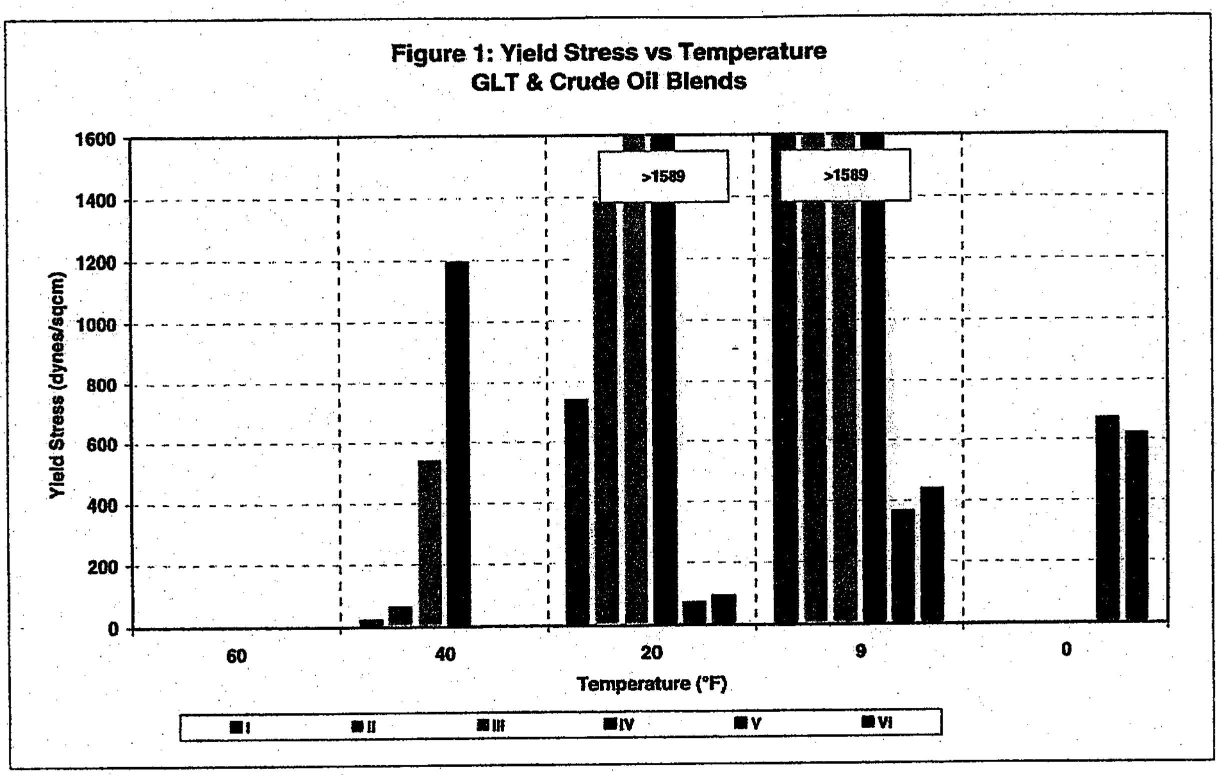


Figure 1: Yield Stress vs Temperature
GLT & Crude Oil Blends
Yield Stress (dynes/sqcm)
1600
1400
1200
1000
800
600
400
200
0
>1589
>1589
60
40
20
9
0
Temperature (°F)
I
II
III
IV
V
VI

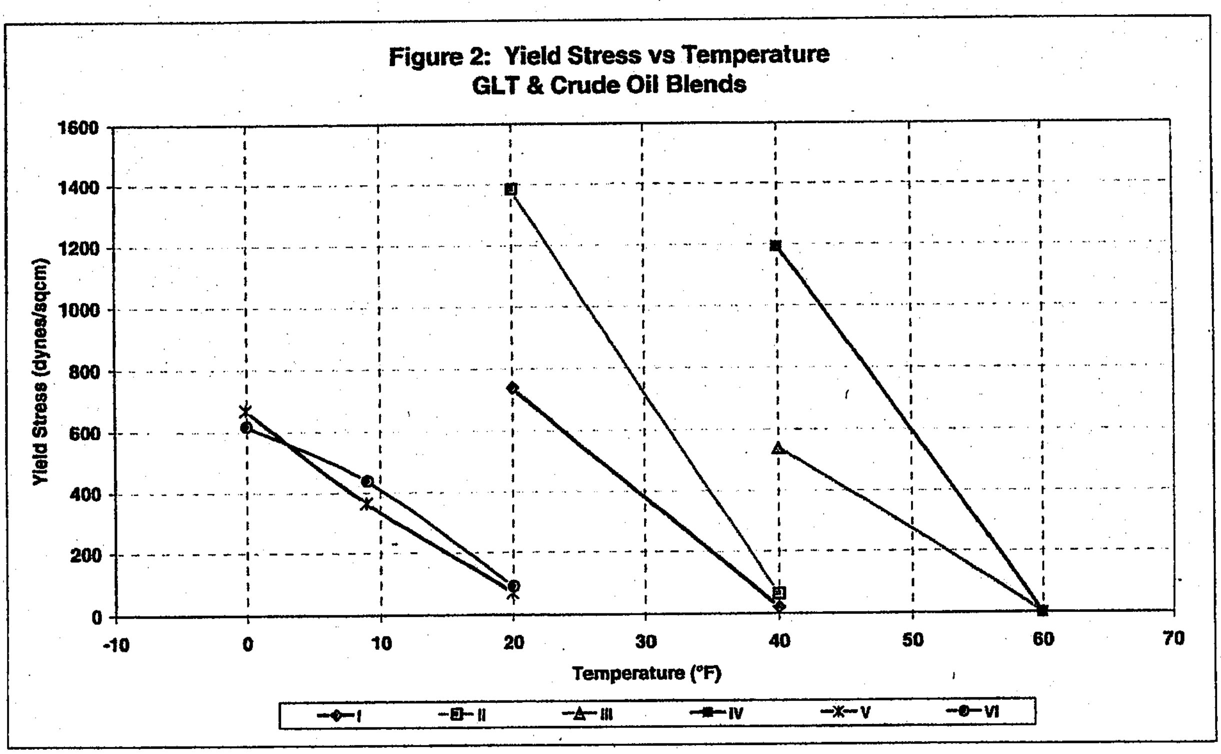


Figure 2: Yield Stress vs Temperature
GLT & Crude Oil Blends
Yield Stress (dynes/sqcm)
1600
1400
1200
1000
800
600
400
200
0
-10
0
10
20
30
40
50
60
70
Temperature (°F)
I
II
III
IV
V
VI

Table 2: Quantitative Composition of Blends by Capillary Gas Chromatography

Sample	Gas to liquids product (GTL)	25% Wax / 75% GTL	50% Wax/ 50% GTL	TAPS Mix Crude Oil @ PS-1	25:75 Wax/GTL 80g @ 320g oil	25:75 Wax/GTL 100g @ 300g oil	50:50 Wax/GTL 80g @ 320g oil	50:50 Wax/GTL 100g @ 300g oil
ChemStation File	J261N.D	I365N.D	I366N.D	J260REG.D	I861ISO.D	I862ISO.D	I864ISO.D	I863ISO.D
Components	Wt%	Wt%	Wt%	Wt%	Wt%	Wt%	Wt%	Wt%
C2	0.002	0.003	0.003	0.009	0.000	0.001	0.002	0.001
C3	0.145	0.107	0.066	0.167	0.033	0.050	0.088	0.069
IC4	0.003	0.011	0.007	0.259	0.128	0.149	0.210	0.160
NC4	1.215	0.904	0.245	0.954	0.734	0.852	0.951	0.797
IC5	0.146	0.110	0.069	0.630	0.502	0.508	0.568	0.484
NC5	2.972	2.212	1.367	0.967	1.098	1.195	1.074	1.015
C6	7.826	5.800	3.901	1.836	2.758	3.050	2.443	2.463
BENZENE	0.003	0.002	0.001	0.340	0.270	0.255	0.271	0.244
C7	8.889	6.633	4.167	3.358	3.904	4.060	3.509	3.476
TOLUENE	0.029	0.022	0.016	0.792	0.623	0.588	0.621	0.565
C8	8.764	6.570	4.147	4.078	4.572	4.662	4.111	4.092
C9	8.539	6.384	4.071	4.115	4.506	4.579	4.042	4.048
C10	7.940	6.230	3.972	3.715	4.121	4.202	3.696	3.737
C11	7.290	5.607	3.989	3.174	3.663	3.760	3.291	3.367
C12	6.446	5.241	3.827	2.989	3.403	3.490	3.112	3.208
C13	5.748	4.908	3.854	3.308	3.584	3.640	3.360	3.413
C14	5.065	4.610	3.942	3.160	3.421	3.492	3.293	3.367
C15	4.414	4.367	4.101	3.108	3.312	3.359	3.266	3.342
C16	3.811	4.189	4.348	2.757	3.042	3.105	3.083	3.194
C17	3.273	4.096	4.693	2.636	2.914	2.985	3.047	3.184
C18	2.799	4.071	5.119	2.590	2.919	2.991	3.145	3.292
C19	2.389	4.070	5.522	2.543	2.847	2.923	3.154	3.329
C20	2.026	4.001	5.753	2.296	2.653	2.747	3.050	3.230
C21	1.705	3.795	5.674	2.134	2.493	2.571	2.876	3.079
C22	1.421	3.422	5.236	2.037	2.324	2.409	2.711	2.894
C23	1.165	2.914	4.511	1.898	2.122	2.169	2.456	2.600
C24	0.939	2.353	3.650	1.781	1.909	1.948	2.180	2.286
C25	0.747	1.816	2.804	1.669	1.723	1.744	1.929	1.984
C26	0.607	1.369	2.086	1.624	1.572	1.592	1.718	1.757
C27	0.583	1.094	1.584	1.557	1.470	1.478	1.563	1.570
C28	0.433	0.764	1.104	1.532	1.375	1.378	1.437	1.422
C29	0.247	0.458	0.710	1.482	1.249	1.274	1.301	1.270
C30+	2.418	1.866	5.457	34.506	28.757	26.796	28.444	27.061
Total	100.000	100.000	100.000	100.000	100.000	100.000	100.000	100.000

Wt% Wax	0.00	50.00	25.00	0.00	5.00	6.25	10.00	12.50
Wt% GTL	100.00	50.00	75.00	0.00	15.00	18.75	10.00	12.50
Wt% Crude	0.00	0.00	0.00	100.00	80.00	75.00	80.00	75.00

SECTION 1

Yield Stress versus Elapsed Time For GTL & Crude Oil Blends

Summary of Test Method

Westport's SLP-307 consists of determining the yield point of a crude oil by measuring the torque on a spindle, using a Brookfield viscometer, rotating at 0.01 rpm in the material. The spindle to be used consists of four rectangular vanes dimensioned (0.75"w x 2.25"h) and oriented at 90 degree increments around the central axis. The sample cup is dimensioned (1.5" id x 4.0"h). Vertical orientation of vanes within the sample cup is dimensioned (1.00" from top and 0.75" from bottom).

The crude oil blends were initially heated to 150°F to destroy all temperature and shear histories and then cooled to 100°F at which point they were loaded into the vane closed-cup apparatus. The closed-cup apparatus holds the vanes rigidly during cooling and aging and prevents loss of light ends through evaporation. After loading into the cup apparatus the samples were cooled in an environmental chamber at a controlled rate to below 0°F. The cooling rate mimics the expected rate of cooling of the Trans-Alaska pipeline oil in the case of shut-in.

Samples were withdrawn from the environmental chamber at five test temperatures (approximately 60, 40, 20, 9 and 0°F) and transferred to a refrigerated circulator that maintains the sample at test temperature. The spindle was attached to the Brookfield viscometer (LV, RV or HB) before the spindle clamping mechanism was released. The clamping mechanism was released and the viscometer was started at 0.01 rpm and torque as a function of time was measured, until a maximum reading was obtained. The maximum torque (dyne/cm) obtained is divided by a vane parameter constant K to obtain the yield stress (dynes/sqcm). The constant K is calculated based on the dimensions of the vanes. ($K=36.19\ cm^3$, for a Vane with D=0.75 inch (1.905 cm) and H=2.25 inch (5.715 cm). For further detailed information Westport's SLP-307 is attached in Appendix B, page 79.

Temperature Ramping Profile

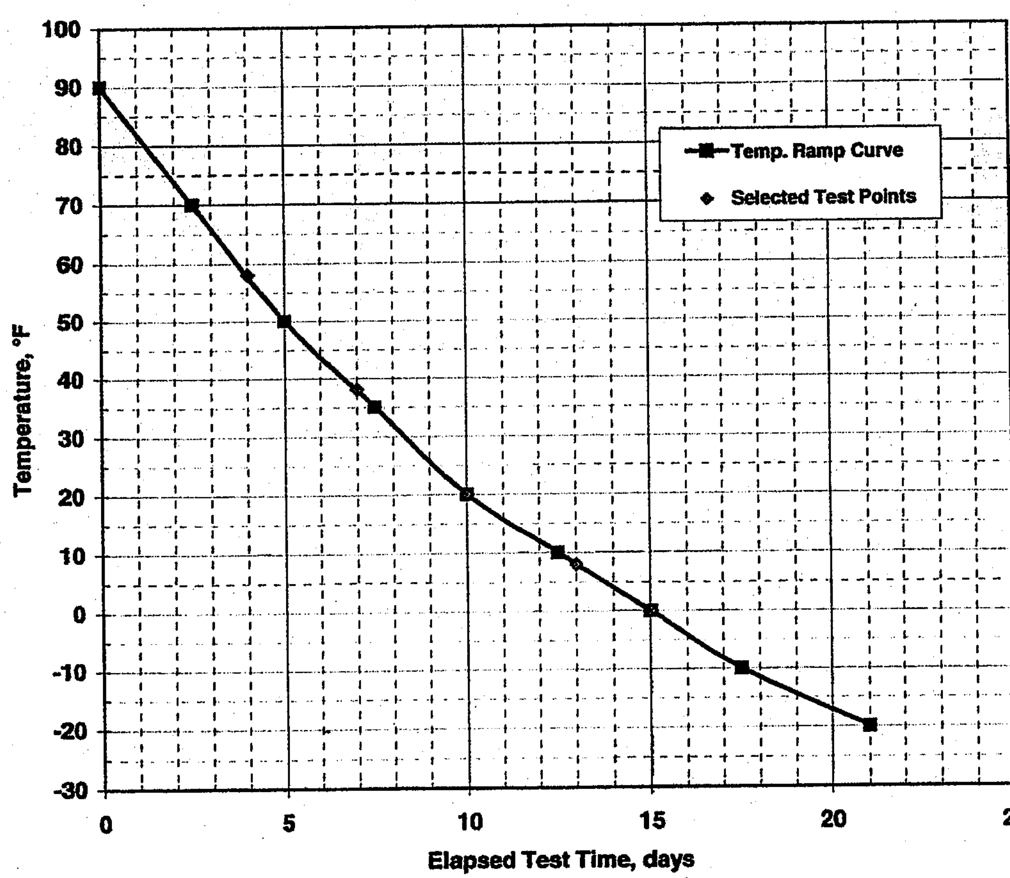
The temperature decay curve used for test sample preparation was taken from Trans-Alaska Pipeline cold restart data supplied by the Alyeska Pipeline Service Company. Based on this curve, selective temperatures were entered into the program menu of the environmental cooling chamber, a cryogenic chamber cooled by liquid Nitrogen vapor. Temperatures are recorded on strip chart display with digital inscriptions at 12-hour intervals. The programmed temperature ramp is presented in Table 3 and Figure 3, along with the selected test points.

Table 3: Test Temperature Profile
VANE VISCOMETRY

Environmental Chamber Temperature Ramp Program				
Step #	Days	Hours	Temp °F	Temp °C
0	0	0	90	32.2
1	2.5	60	70	21.1
2	5.0	120	50	10.0
3	7.5	180	35	1.7
4	10.0	240	20	-6.7
5	12.5	300	10	-12.2
6	15.0	360	0	-17.8
7	17.5	420	-10	-23.3
8	21.0	504	-20	-28.9
9	Hold	576	-20	-28.9

App. Test Temp.	60	40	20	9	0	-20
Samples Tested	(iii, iv)	(i, ii, iii, iv)	(i, ii, iv, v, vi)	(i, ii, iii, iv, v, vi)	(v, vi)	none

Figure 3: Test Temperature Profile



Determination of Yield Point

Figures 4 through 26 on the following pages present torque buildup versus elapsed test time. The yield point is determined from the maximum torque response, usually followed by a decline indicating any gel structure present was broken by the applied stress and degrades under continued shearing. In most tests, several minutes of "no torque" response at test initiation are recorded; this response is associated with the time for the 'S'-hook connections to "tighten" before movement, or stress, is applied to the vane shaft. One test sample was lost during aging. Numerical data for the remaining twenty-three tests are presented in Appendix A, pages 42 - 78.

Sample (i): (25%wax distillate + 75% GTL) + Crude Oil in a ratio of 1:4

Figure 4: Test 14

Figure 4 presents torque response (dyne/cm) versus elapsed test time at a test temperature of 40°F. The test was performed with Sample (i) on the Brookfield RV viscometer. A maximum torque of 747 dyne/cm was recorded giving a yield point of 20.7 dynes/sqcm.

Figure 5: Test 21

Figure 5 presents torque (dyne/cm) versus elapsed test time at a test temperature of 20°F. The test was performed with Sample (i) on the Brookfield HB viscometer. A maximum torque of 26736 dyne/cm was recorded giving a yield point of 739 dynes/sqcm.

Figure 6: Test 7

Figure 6 presents torque (dyne/cm) versus elapsed test time at a test temperature of 9°F. The test was performed with Sample (i) on the Brookfield HB viscometer. A maximum torque limit of the HB viscometer was reached (57496 dyne/cm); therefore the yield point was greater than 1589 dynes/sqcm. The HB viscometer has the highest rated spring torque available for this testing.

Sample (ii): (25%wax distillate + 75% GTL) + Crude Oil in a ratio of 1:3

Figure 7: Test 13

Figure 7 presents torque response (dyne/cm) versus elapsed test time at a test temperature of 40°F. The test was performed with Sample (ii) on the Brookfield LV viscometer. A maximum torque limit of the LV viscometer was reached (674 dyne/cm); therefore the yield point was greater than 18.6 dynes/sqcm. The LV viscometer has the lowest rated spring torque available for this testing. The data acquisition program failed to initialize during the first seven minutes of this test, as can be seen by the gap in data points at the test start. A second sample was tested on the RV viscometer in Test 18.

Figure 8: Test 18

Figure 8 presents torque (dyne/cm) versus elapsed test time at a test temperature of 40°F. The test was performed with Sample (ii) on the Brookfield RV viscometer. A maximum torque of 2307 dyne/cm was recorded giving a yield point of 63.7 dynes/sqcm.

Figure 9: Test 22

Figure 9 presents torque (dyne/cm) versus elapsed test time at a test temperature of 20°F. The test was performed with Sample (ii) on the Brookfield HB viscometer. A maximum torque of 50079 dyne/cm was recorded giving a yield point of 1384 dynes/sqcm.

Figure 10: Test 6

Figure 10 presents torque (dyne/cm) versus elapsed test time at a test temperature of 9°F. The test was performed with Sample (ii) on the Brookfield HB viscometer. A maximum torque limit of the HB viscometer was reached (57496 dyne/cm); therefore the yield point was greater than 1589 dynes/sqcm. The HB viscometer has the highest rated spring torque available for this testing.

Sample (iii): (50%wax distillate + 50% GTL) + Crude Oil in a ratio of 1:4

Figure 11: Test 12

Figure 11 presents torque response (dyne/cm) versus elapsed test time at a test temperature of 60°F. The test was performed with Sample (iii) on the Brookfield LV viscometer. A maximum torque of 2.69 dyne/cm was recorded giving a yield point of 0.07 dynes/sqcm. At this temperature there was very little, if any, gel structure present.

Figure 12: Test 15

Figure 12 presents torque (dyne/cm) versus elapsed test time at a test temperature of 40°F. The test was performed with Sample (iii) on the Brookfield RV viscometer. A maximum torque limit of the RV viscometer was reached (7187 dyne/cm); therefore the yield point was greater than 199 dynes/sqcm. A second sample was tested on the HB viscometer in Test 16.

Figure 13: Test 16

Figure 13 presents torque (dyne/cm) versus elapsed test time at a test temperature of 40°F. The test was performed with Sample (iii) on the Brookfield HB viscometer. A maximum torque of 19491 dyne/cm was recorded giving a yield point of 539 dynes/sqcm.

Figure 14: Test 5

Figure 14 presents torque (dyne/cm) versus elapsed test time at a test temperature of 9°F. The test was performed with Sample (iii) on the Brookfield HB viscometer. A maximum torque limit of the HB viscometer was reached (57496 dyne/cm); therefore the yield point was greater than 1589 dynes/sqcm. The HB viscometer has the highest rated spring torque available for this testing.

Sample (iv): (50%wax distillate + 50% GTL) + Crude Oil in a ratio of 1:3

Figure 15: Test 11

Figure 15 presents torque response (dyne/cm) versus elapsed test time at a test temperature of 60°F. The test was performed with Sample (iv) on the Brookfield HB viscometer. The selection of the HB viscometer for this test was not appropriate and no torque response was recorded. At this temperature there was very little, if any, gel structure present. With the limited number of samples no repeat test was performed at this temperature.

Figure 16: Test 17

Figure 16 presents torque (dyne/cm) versus elapsed test time at a test temperature of 40°F. The test was performed with Sample (iv) on the Brookfield HB viscometer. A maximum torque of 43122 dyne/cm was recorded giving a yield point of 1192 dynes/sqcm.

Figure 17: Test 23

Figure 17 presents torque (dyne/cm) versus elapsed test time at a test temperature of 20°F. The test was performed with Sample (iv) on the Brookfield HB viscometer. A maximum torque limit of the HB viscometer was reached (57496 dyne/cm); therefore the yield point was greater than 1589 dynes/sqcm. The HB viscometer has the highest rated spring torque available for this testing.

Figure 18: Test 4

Figure 18 presents torque (dyne/cm) versus elapsed test time at a test temperature of 9°F. The test was performed with Sample (iv) on the Brookfield HB viscometer. A maximum torque limit of the HB viscometer was reached (57496 dyne/cm); therefore the yield point was greater than 1589 dynes/sqcm. The HB viscometer has the highest rated spring torque available for this testing.

Sample (v): GTL + Crude Oil in a ratio of 1:4

Figure 19: Test 20

Figure 19 presents torque response (dyne/cm) versus elapsed test time at a test temperature of 20°F. The test was performed with Sample (v) on the Brookfield HB viscometer. A maximum torque of 2587 dyne/cm was recorded giving a yield point of 71 dynes/sqcm.

Figure 20: Test 1

Figure 16 presents torque (dyne/cm) versus elapsed test time at a test temperature of 9°F. The test was performed with Sample (v) on the Brookfield RV viscometer. A maximum torque limit of the RV viscometer was reached (7187 dyne/cm); therefore the yield point was greater than 199 dynes/sqcm. A second sample was tested on the HB viscometer in Test 2.

Figure 21: Test 2

Figure 17 presents torque (dyne/cm) versus elapsed test time at a test temperature of 9°F. The test was performed with Sample (v) on the Brookfield HB viscometer. A maximum torque of 13167 dyne/cm was recorded giving a yield point of 364 dynes/sqcm.

Figure 22: Test 10

Figure 18 presents torque (dyne/cm) versus elapsed test time at a test temperature of 0°F. The test was performed with Sample (v) on the Brookfield HB viscometer. A maximum torque of 24206 dyne/cm was recorded giving a yield point of 669 dynes/sqcm.

Sample (vi): GTL + Crude Oil in a ratio of 1:3

Figure 23: Test 19

Figure 23 presents torque response (dyne/cm) versus elapsed test time at a test temperature of 20°F. The test was performed with Sample (vi) on the Brookfield HB viscometer. A maximum torque of 3335 dyne/cm was recorded giving a yield point of 92 dynes/sqcm.

Figure 24: Test 3

Figure 24 presents torque (dyne/cm) versus elapsed test time at a test temperature of 9°F. The test was performed with Sample (vi) on the Brookfield HB viscometer. A maximum torque of 8279 dyne/cm was recorded giving a yield point of 229 dynes/sqcm. This result was unexpectedly lower than Test 2 (364 dynes/sqcm), which had a lower GTL ratio. Therefore, for quality purposes a second sample was tested at this temperature in Test 8.

Figure 25: Test 8

Figure 25 presents torque (dyne/cm) versus elapsed test time at a test temperature of 9°F. The test was performed with Sample (vi) on the Brookfield HB viscometer. A maximum torque of 15869 dyne/cm was recorded giving a yield point of 438 dynes/sqcm. This result followed the data trend of having a higher yield point as GTL ratios increased.

Figure 26: Test 9

Figure 26 presents torque (dyne/cm) versus elapsed test time at a test temperature of 0°F. The test was performed with Sample (vi) on the Brookfield HB viscometer. A maximum torque of 22366 dyne/cm was recorded giving a yield point of 618 dynes/sqcm. This result was lower than Test 10 with Sample (v), but without repeat tests for data assurance Test 9 results are well within the 10-15% variability range for the Vane test.

Figure 4: Sample (i) at 40°F

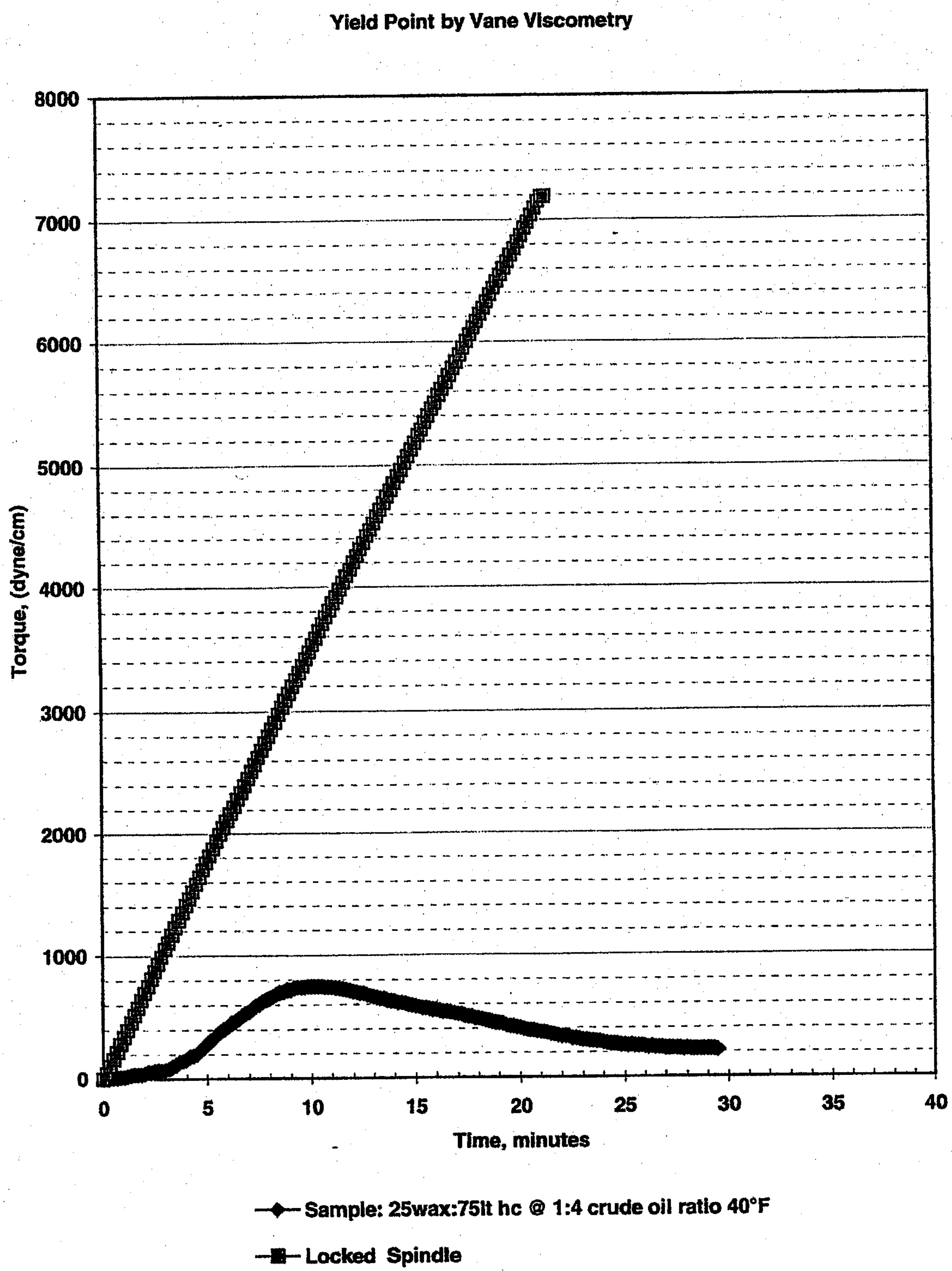


Figure 5: Sample (i) at 20°F

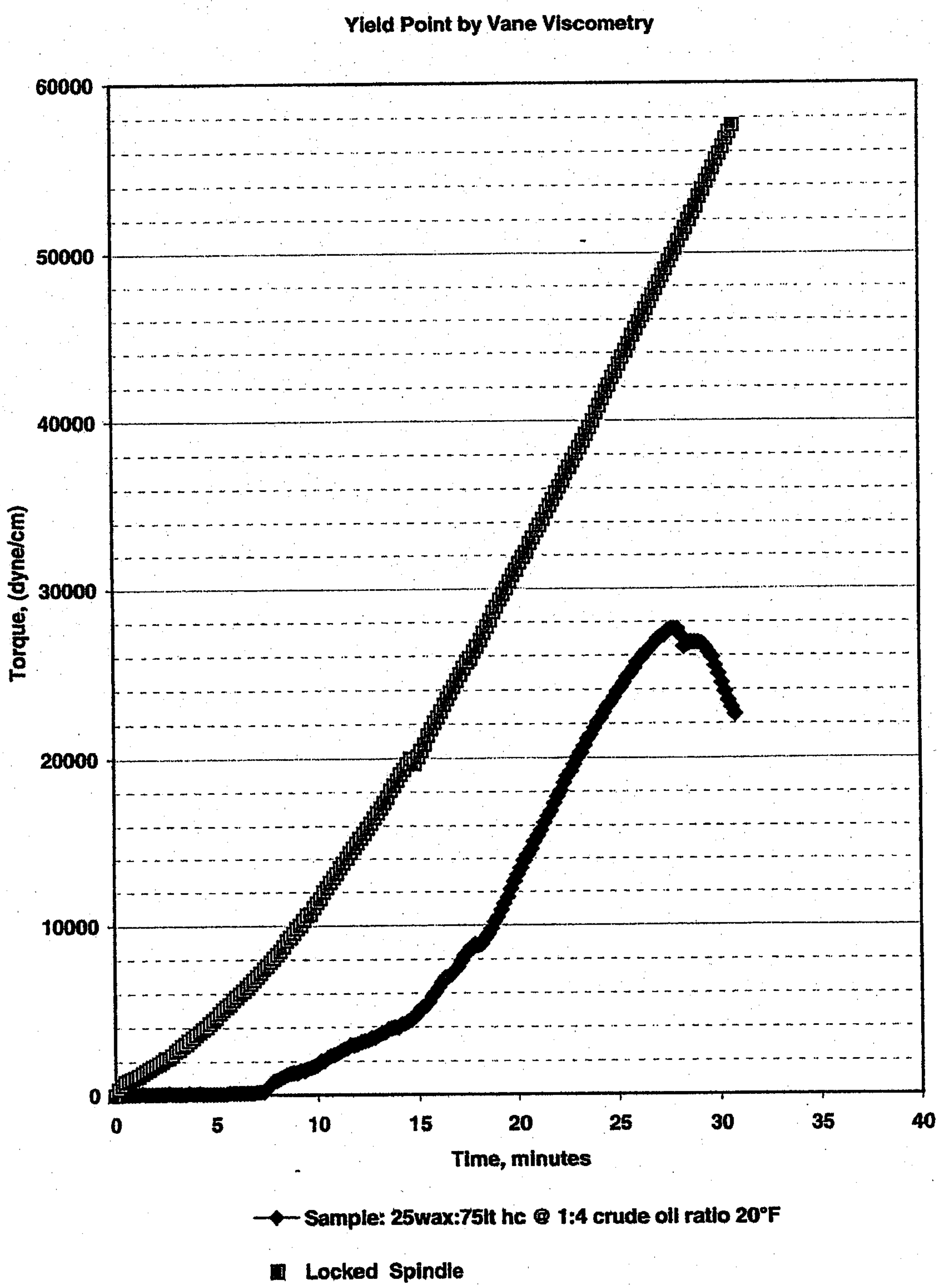


Figure 6: Sample (i) at 9°F

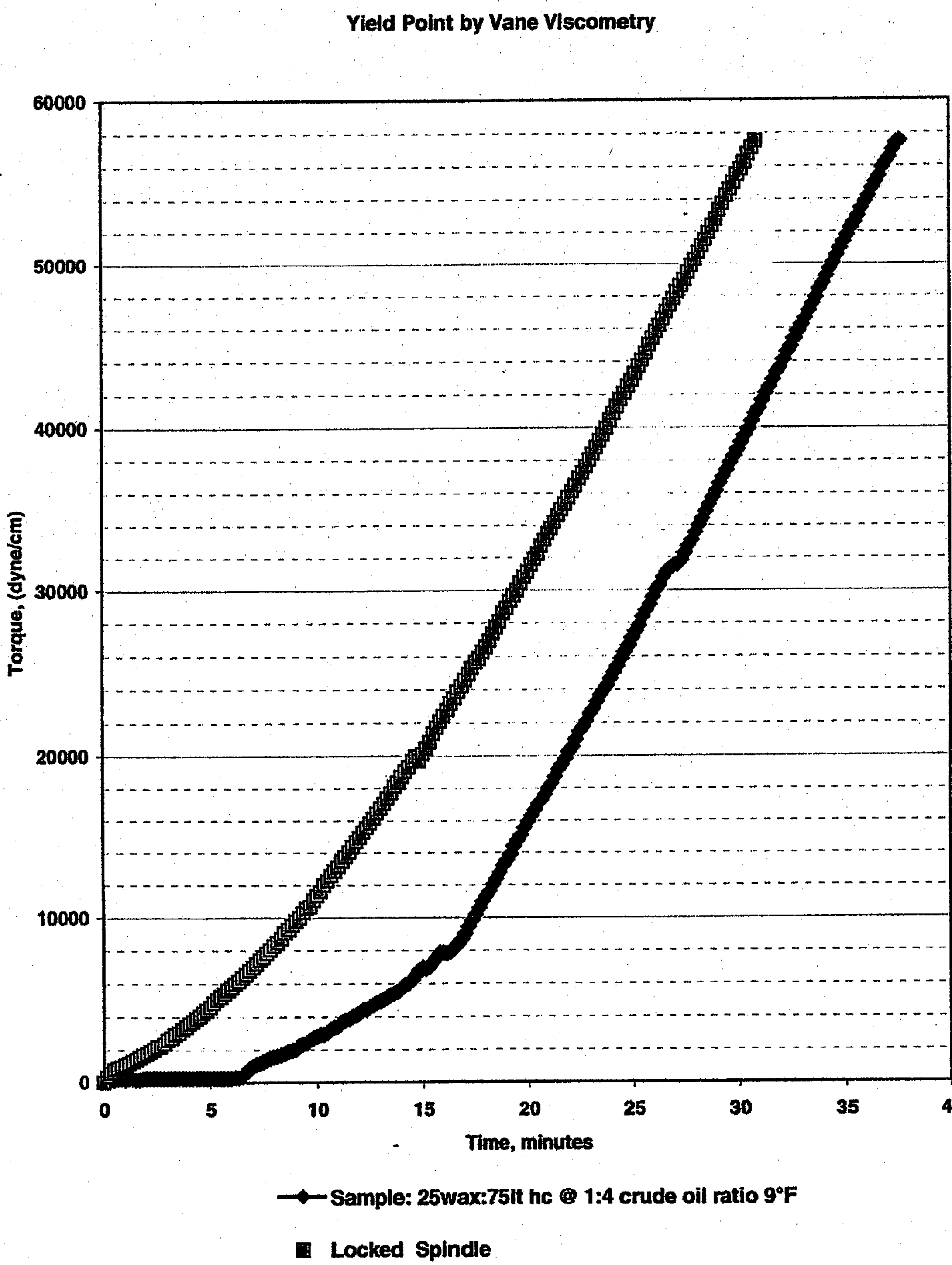


Figure 7: Sample (ii) at 40°F

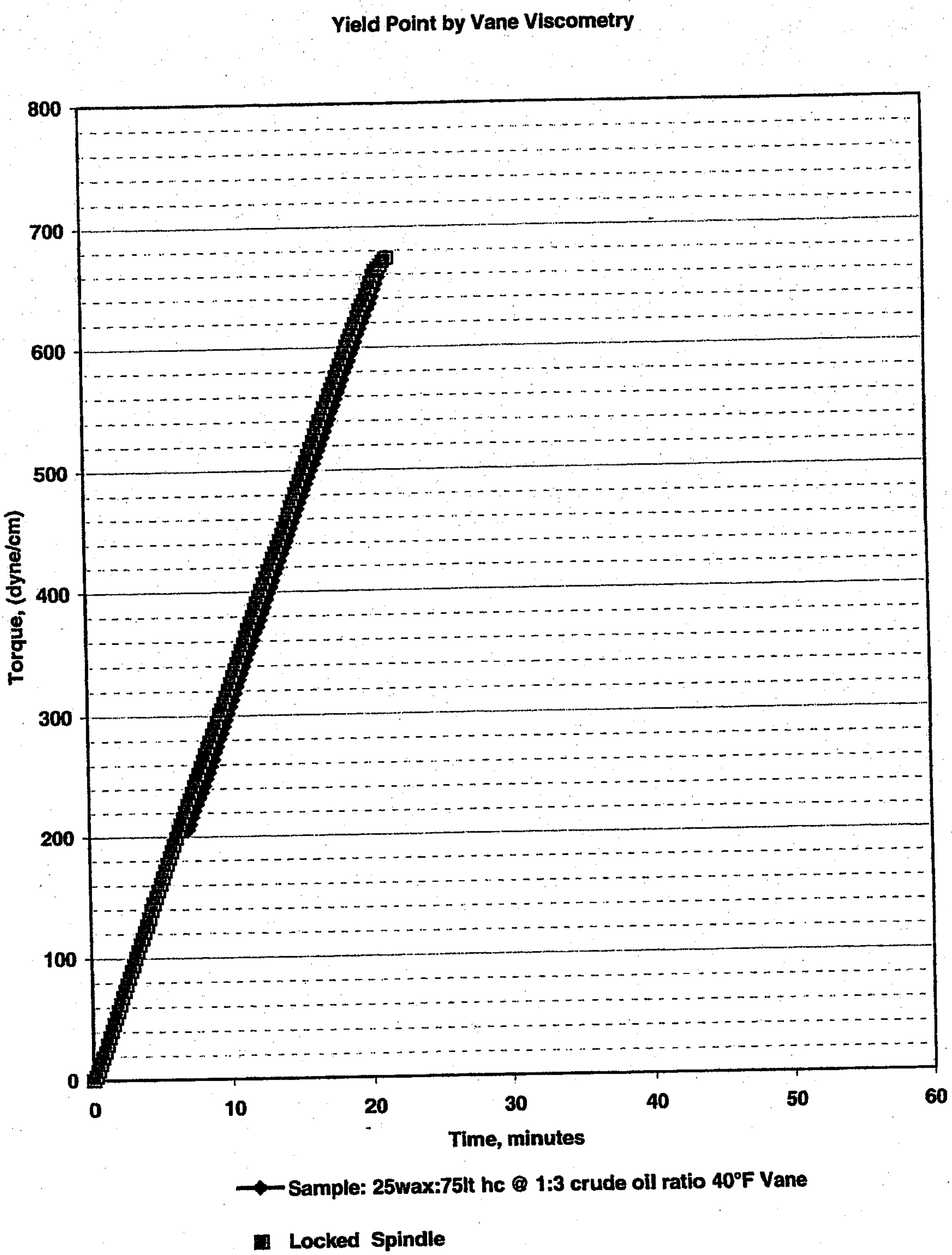


Figure 8: Sample (ii) at 40°F

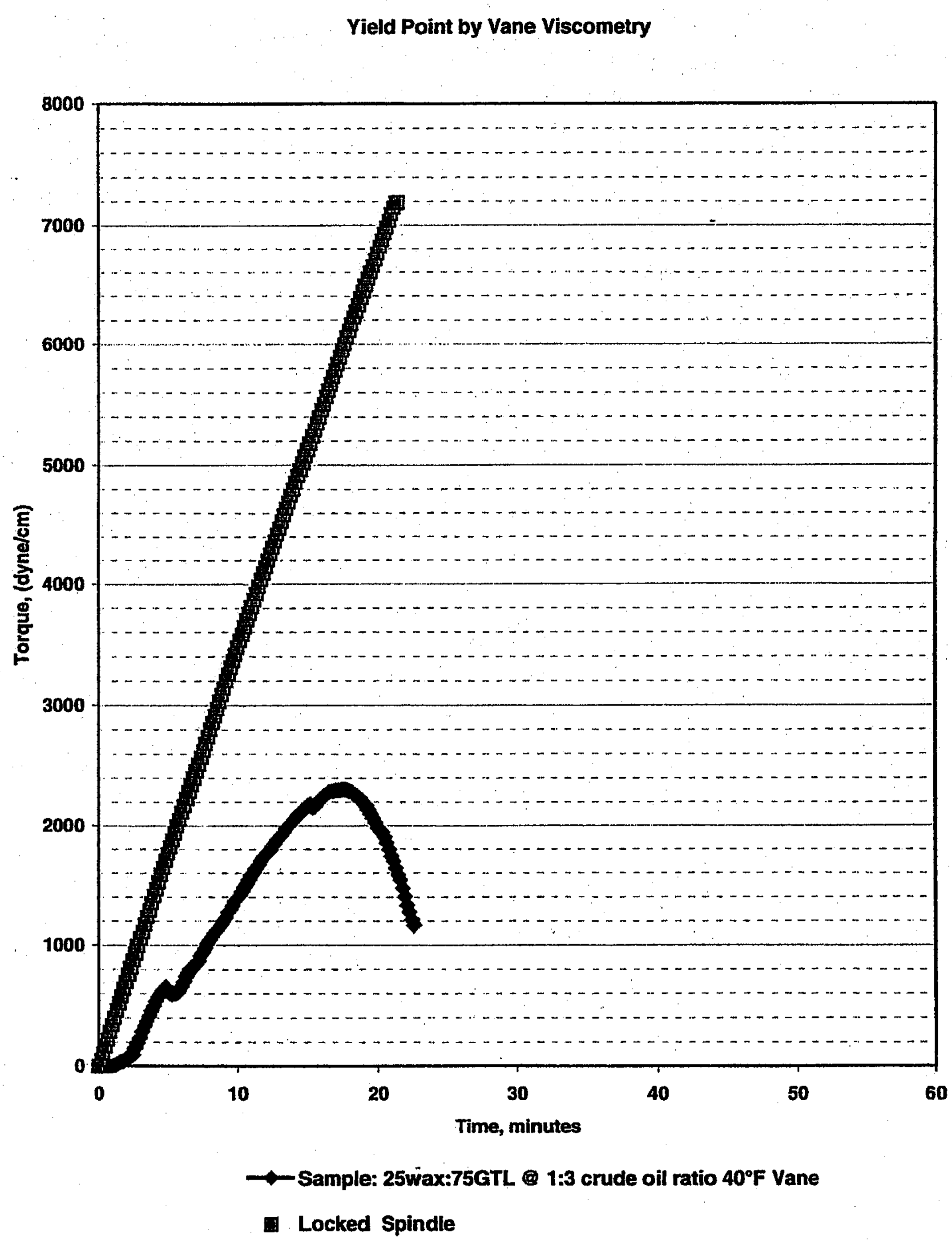


Figure 9: Sample (ii) at 20°F

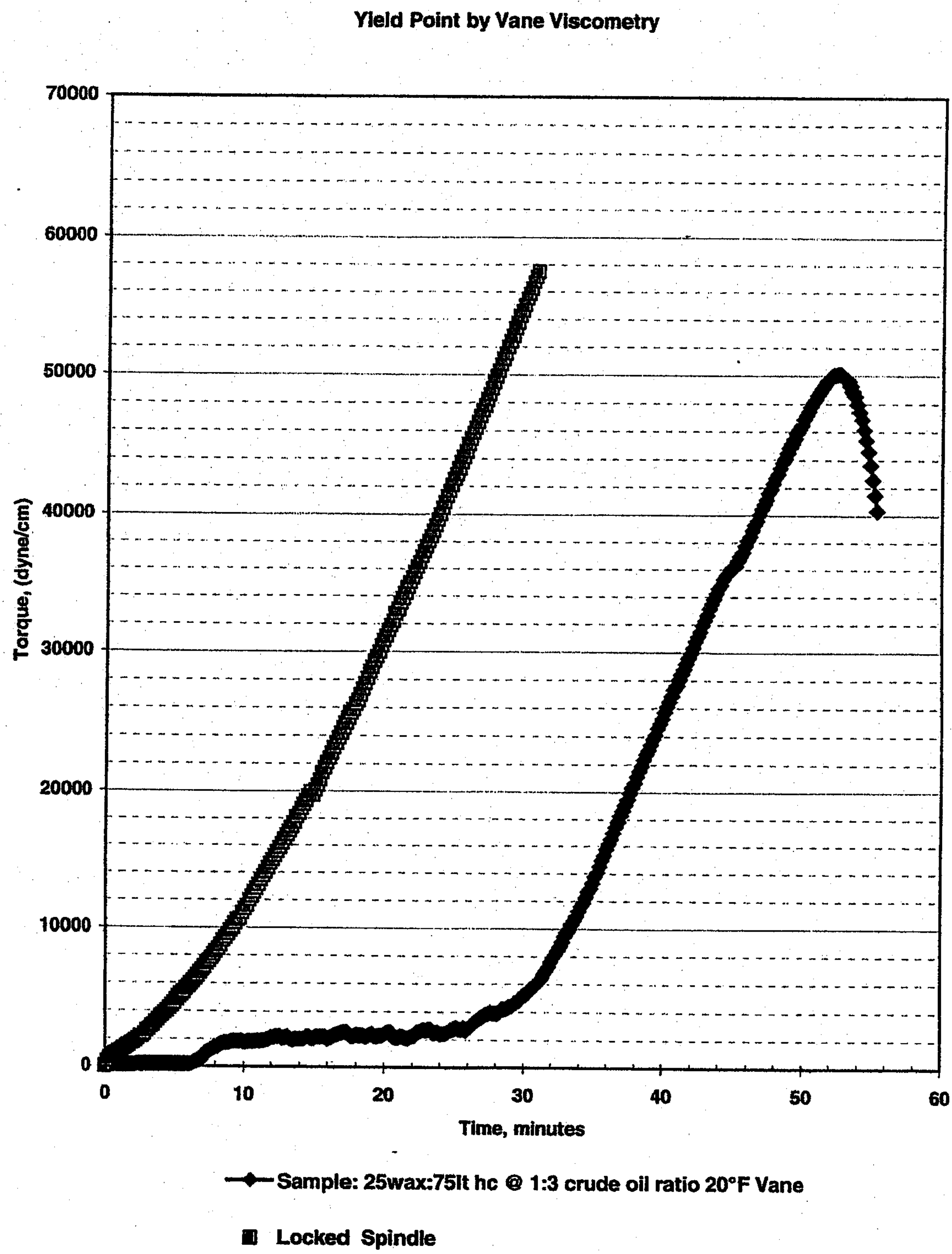


Figure 10: Sample (ii) at 9°F

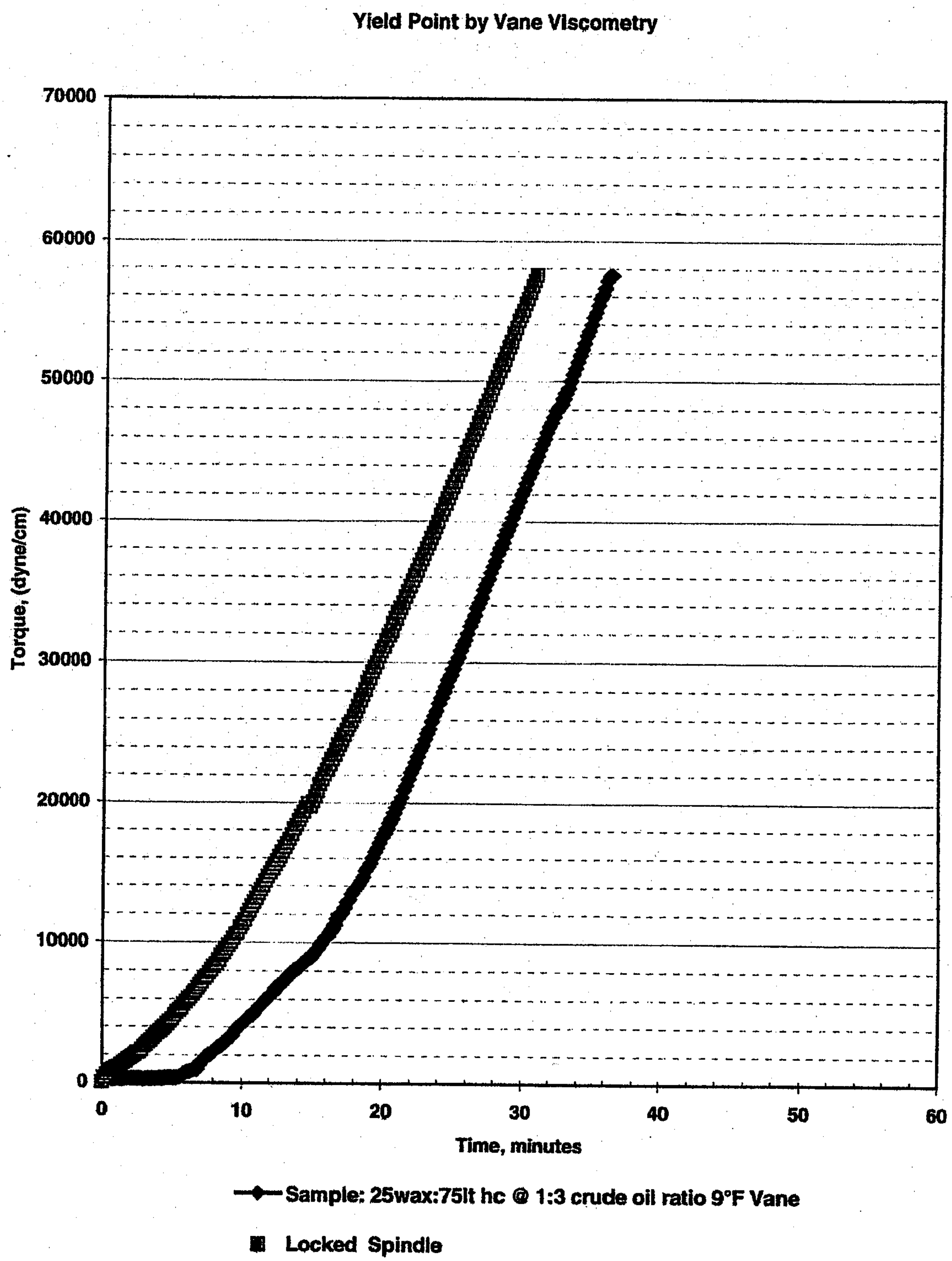


Figure 11: Sample (iii) at 60°F

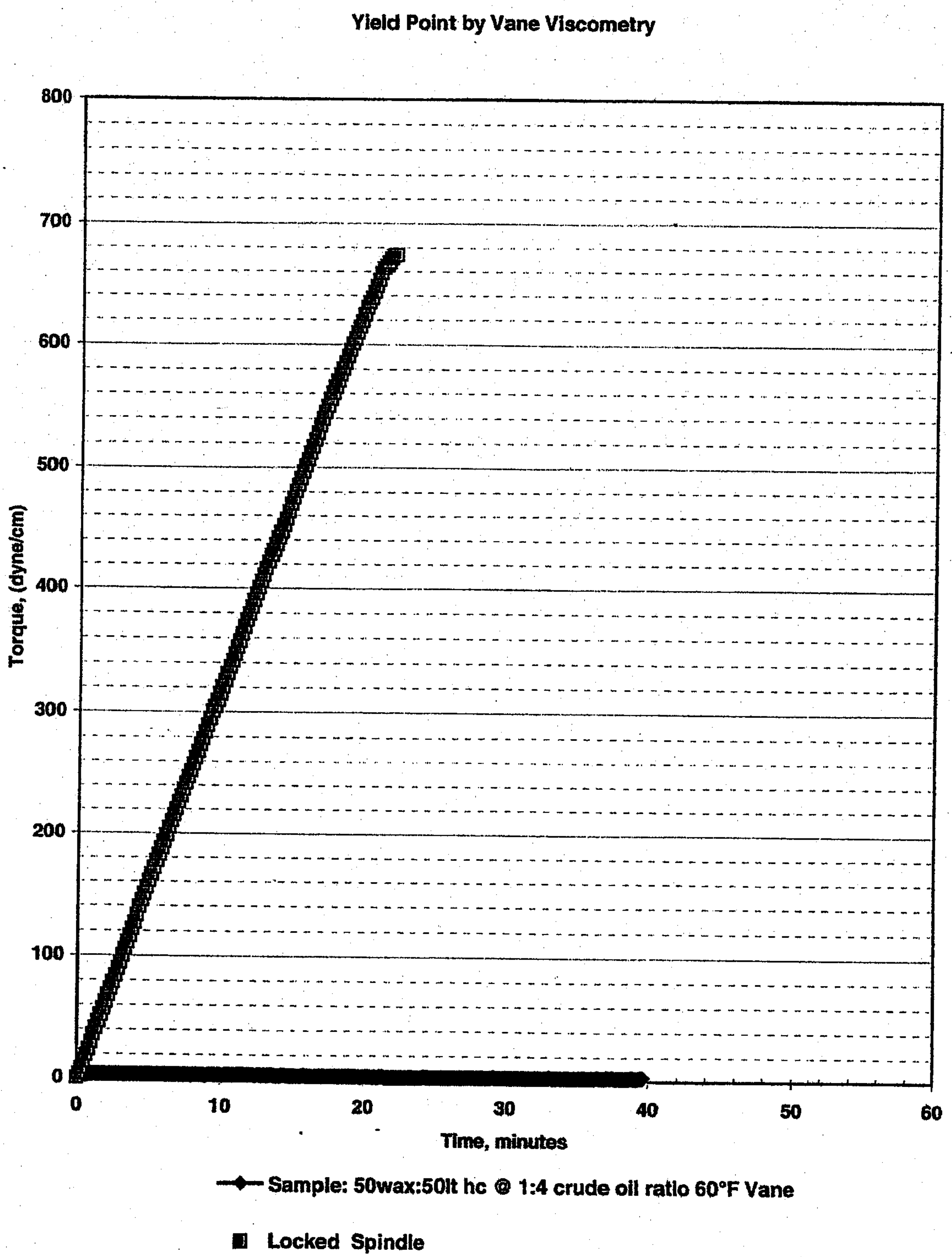


Figure 12: Sample (iii) at 40°F

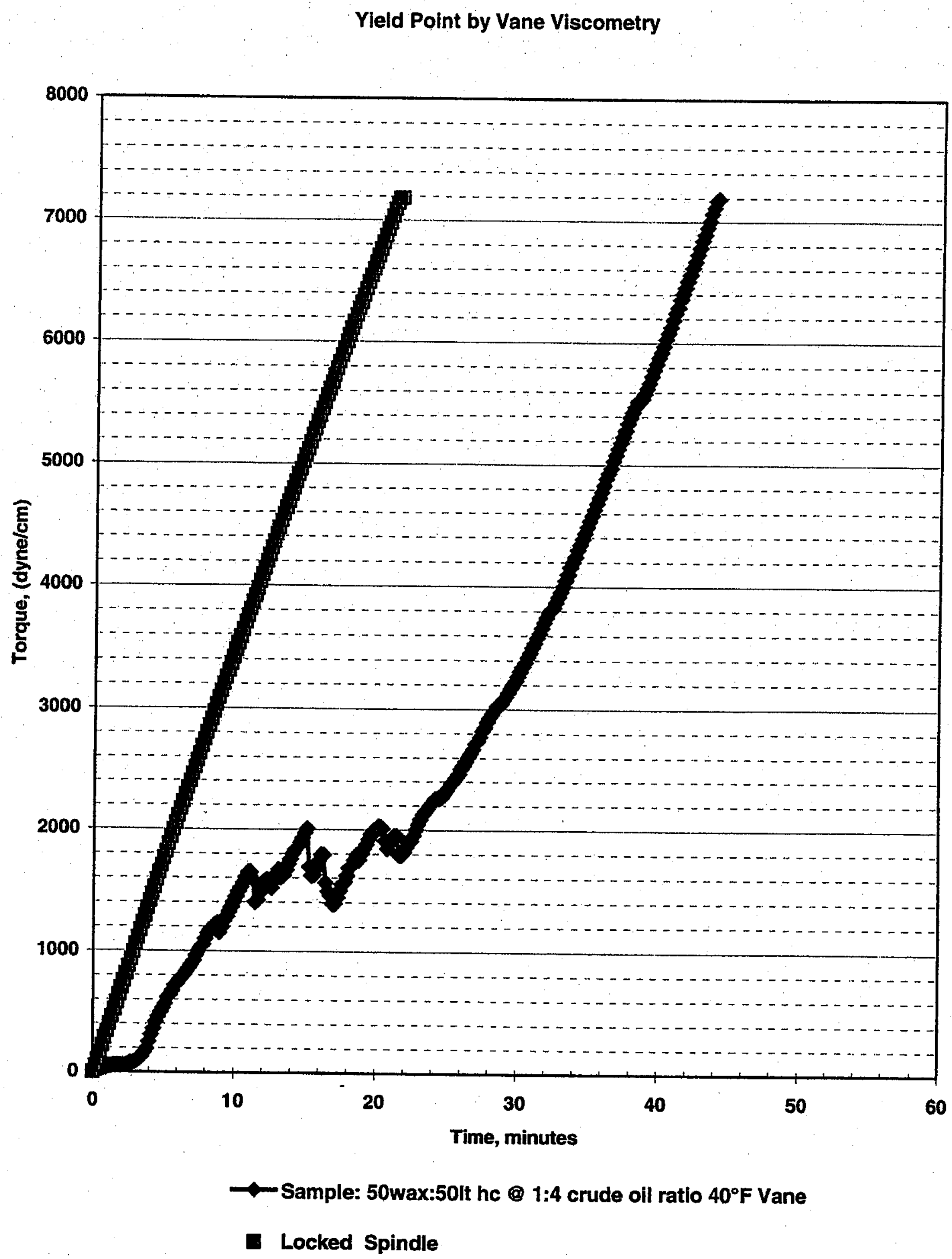


Figure 13: Sample (iii) at 40°F