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Experimental Laboratory Measurements of Thermophysical Properties of Selected Coal Types

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Work performed under
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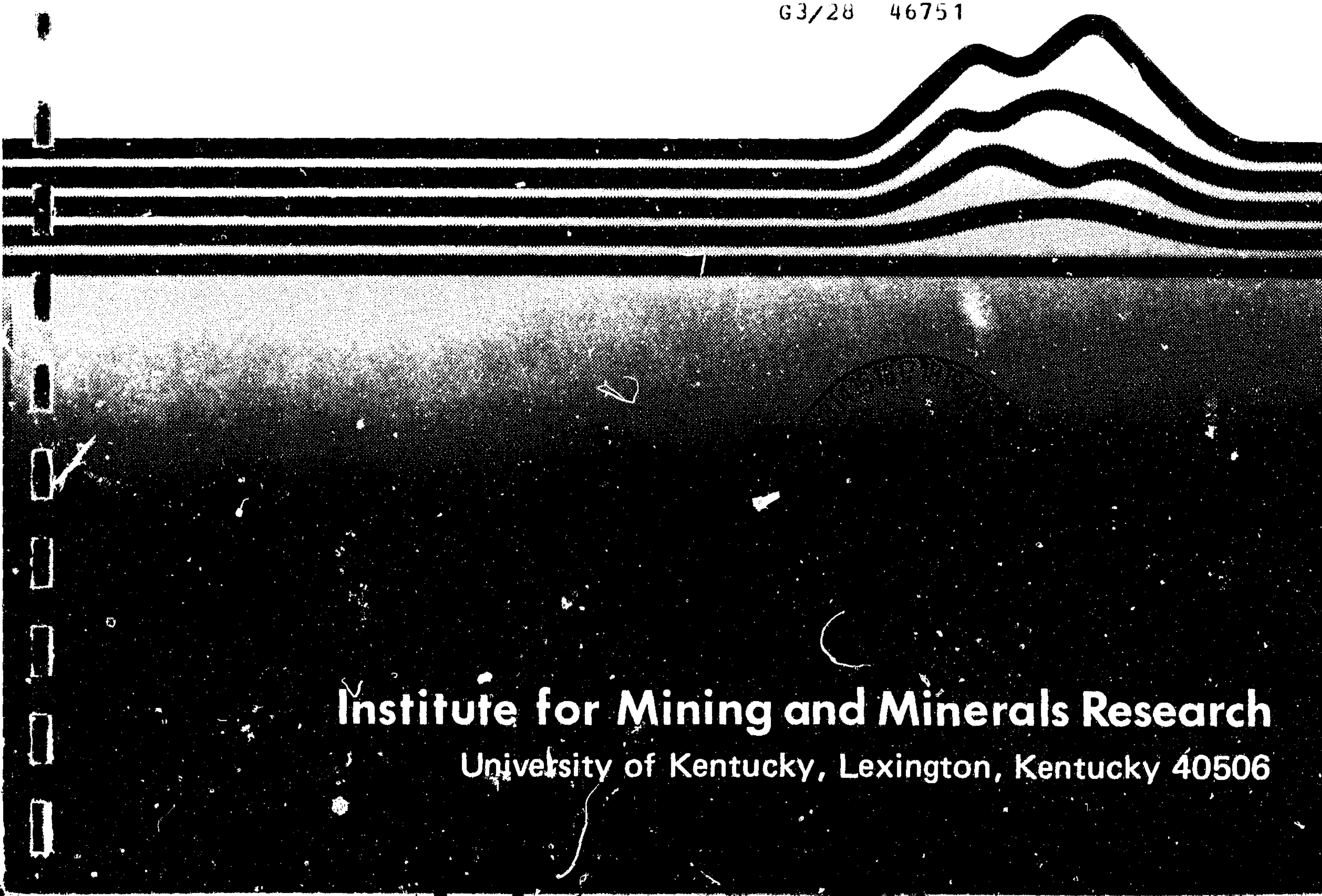

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EXPERIMENTAL LABORATORY MEASUREMENTS OF THERMOPHYSICAL PROPERTIES OF SELECTED COAL TYPES

Final Report

William G. Lloyd
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November 13, 1979

work performed under
California Institute of Technology Contract No. 955381
Subcontract under NASA Contract NAS7-100
Technical Monitor: Dr. Raymond O. Kushida, Jet Propulsion Laboratory

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Table of Contents

Index of Tables

Index of Figures

1. SUMMARY

A number of bituminous coals of moderate to high plasticity have been examined, along with portions of their extrudates from the JPL 1.5-inch 850°F screw extruder. Portions of the condensed pyrolysis liquids released during extrusion, and of the gaseous products formed during extrusion, have also been analyzed. In addition to the traditional determinations, the coals and extrudates have been examined in terms of microstructure (especially extractable fractions), thermal analysis (especially that associated with the plastic state), and reactivity towards thermal and catalyzed hydroliquefaction.

The process of extrusion increases the fixed carbon content of coals by about 5% and tends to increase the surface area. Coals containing 25% or more DMF-extractable material show an increase in extractables as a result of extrusion; those initially containing less than 20% extractables show a decrease as a result of extrusion.

Both the raw and extruded samples of Kentucky #9 coal are highly reactive towards hydroliquefaction, undergoing conversions of 75-80% in 15 min and 85-94% in 60 min in a stirred clave. The extrudate is consistently slightly less reactive than the parent coal, the difference appearing to correspond to the difference in fixed carbon contents.

The enthalpic changes associated with the plastic state have been re-examined. The 'melting' process is endothermic, with a magnitude of 10.7 ± 0.7 cal/g.

2. INTRODUCTION

This study is a continuation of previous work focussing upon the plastic state of bituminous coals with particular reference to extrusion (1). The present study is supported by the Jet Propulsion Laboratory under California Institute of Technology Contract No. 955381 (Subcontract under NASA Contract NAS7-100), dated March 13, 1979.

This laboratory has conducted a number of analyses of coals and coal extrudates, and several analyses of condensed pyrolysis liquids and head gas samples obtained during extrusion runs, in support of JPL's Coal Pump Project. In addition and at the request of the Technical Monitor we have conducted several autoclave runs to provide a basis for gauging the effect of the extrusion process (using JPL's 1.5-inch tapered screw extruder) (2,3) upon coal reactivity towards hydroliquefaction. These results are detailed in Part 3 of this report.

In the course of this work and of numerous conversations with Drs. R. O. Kushida and V. D. Sankur of JPL, we have also drawn some tentative inferences concerning the relationship between coal melting and extrusion on the one hand and coal properties and reactivity on the other. These are outlined in Part 4 of this report.

The samples of coal and coal products used in the present study were received from JPL and are identified in Table 1.

Table 1

Identification of Samples

IMMR No.	JPL Reference	Material
9324	#1 (Letter, VDS to WGL, 9 Jan 79)	Coal, Pittsburgh #8 seam
9325	#2 (Letter, VDS to WGL, 9 Jan 79)	Coal, Pittsburgh #8 seam
9326	#3 (Letter, VDS to WGL, 9 Jan 79)	Coal, Pittsburgh #8 seam
9327	#4 (Letter, VDS to WGL, 9 Jan 79)	Coal, Kentucky #11 seam
9328	#5 (Letter, VDS to WGL, 9 Jan 79)	Coal, Elkhorn #1 seam
9329	G (Letter, VDS to WGL, 9 Jan 79)	Coal, Pittsburgh #8 seam
9330	#1 Extrudate	Extrudate (coal 9324, at 20 lbs/hr)
9331	#2 Extrudate	Extrudate (coal 9325, at 30 lbs/hr)
9332	#3 Extrudate	Extrudate (coal 9326, at 35 lbs/hr)
9333	#4 Extrudate	Extrudate (coal 9327, at 16.6 lbs/hr)
9334	#5 Extrudate	Extrudate (coal 9328, at 18.3 lbs/hr)
9335	A Extrudate	Extrudate (coal 9324/329, die T = 600°F)
9336	B Extrudate	Extrudate (coal 9324/329, die T = 700°F)
9337	C Extrudate	Extrudate (coal 9324/329, die T = 800°F)
9338	D Extrudate	Extrudate (coal 9324/329, die T = 890-900°F)
9339	E Extrudate	Extrudate (coal 9324/329, die T = 1000°F)
9340	F Extrudate	Extrudate (coal 9324/329, die T = 1100°F)
9341	2A	Gas sample from extended extrusion run
9342	2	Gas sample from extended extrusion run
9343	5A	Gas sample from extended extrusion run
9344	4	Gas sample from extended extrusion run
9345	1 (Letter, VDS to WGL, 9 Jan 79)	Liquid condensate from extended extrusion run
9346	2 (Letter, VDS to WGL, 9 Jan 79)	Liquid condensate from extended extrusion run
9347	3 (Letter, VDS to WGL, 9 Jan 79)	Liquid condensate from extended extrusion run

(Continued)

Table 1 (Continued)

IMMR No.	JPL Reference	Material
9348	4 (Letter, VDS to WGL, 9 Jan 79)	Liquid condensate from extended extrusion run
9349	5 (Letter, VDS to WGL, 9 Jan 79)	Liquid condensate from extended extrusion run
9352	Pgh 8	Coal, Pittsburgh #8 seam, bulk sample
9625	Coal 1 (VDS)	Coal used for special run (VDS) of March 1979
9626	Coal 2 (VDS)	Coal used for special run (VDS) of March 1979
9627	Extrudate of coal 1	Extrudate from coal 9625, run March 1979
9628	Extrudate of coal 2	Extrudate from coal 9626, run March 1979
9648	Extrudate, Werner & Pfleiderer	Extrudate from W & P special run of April 1979*
M421	LR1 Pitt 8 (received 15 Aug 79)	Reserve sample of extrudate 9330
M422	LR2 Pitt 8 (received 15 Aug 79)	Reserve sample of extrudate 9331
M423	LR3 Pitt 8 (received 15 Aug 79)	Reserve sample of extrudate 9332
M424	LR4 KY 11 (received 15 Aug 79)	Reserve sample of extrudate 9333
M425	LR5 Elkhorn #1 (received 15 Aug 79)	Reserve sample of extrudate 9334
M436	KY 9 (received 14 Sept 79)	Coal, Kentucky #9 seam, for extrusion
M437	Extrudate (received 14 Sept 79)	Extrudate of coal M436

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* Werner & Pfleiderer failed to retain a sample of the feed coal used for this test extrusion.

2.1 Acknowledgments

The experimental work reported herein is the product of the efforts of a number of scientists and engineers. Coal analyses were carried out by Henry E. Francis, David W. Koppenaal, Anne Maurer, Karen C. Moore and Gerald A. Thomas, under the direction of John K. Kuhn, manager of the Institute's Materials Analysis Department. Elemental analyses of condensates were carried out by Ms. Maurer and Mr. Thomas. Quantitative chromatographic analyses of head gases were conducted by Arthur W. Fort. The DMF extraction studies were carried out by Clara T. Magura and Roberta Berg, following the procedure developed by Dr. Fort (Materials Analysis). We are indebted to Larry Rice (Department of Metallurgical Engineering and Materials Science, University of Kentucky) for the scanning electron micrographs. Surface area measurements by methanol adsorption were carried out by Mrs. Moore (Materials Analysis) using the procedure developed by Burtron H. Davis, of the Institute's Catalysis Section. Thermal analysis was carried out by Mr. Francis and John P. Elder (Materials Analysis).

Microclave runs were carried out by Shuji Mori of the Process Development Division, in association with Dr. Davis. The stirred autoclave runs were conducted under Institute contract at the Department of Chemical Engineering, University of Louisville, under the supervision of Professors James Watters and Dermot Collins of that department.

Errors in the interpretation of these results are the responsibility of the author.

3. EXPERIMENTAL

3.1 Proximate, Ultimate and Related Analyses

The coal and extrudate samples listed in Table 1 may be conveniently placed in three groups: a group of five different bituminous coals and their extrudates, from extrusion runs under uniform temperature profiles conducted in January, 1979; a series of extrudates obtained from a single run in which the die temperature was raised in successive steps from 600° to 1100°F; and a later group of three coals and extrudates, from runs conducted between March and September, 1979. Added to this last group are two 'odd' samples, a bulk sample of Pittsburgh #8 seam (M352) similar to those examined in Tables 2 and 3, and an experimental extrusion product from a test run by Werner & Pfleiderer (for which no feed coal sample was retained).

Proximate analyses of the coals and extrudates from the first group of extrusions are shown in Table 2. Also included in this table are the heating values, free swelling index (FSI) determinations, and the low-temperature ash contents (LTA), as determined by ashing at approximately 60-100°C and 1 torr using an oxygen plasma. These data (and those in the following tables, unless noted otherwise) are on an as-received basis; that is, the values for volatile matter content, fixed carbon content and heating value have not been corrected to a moisture- and ash-free basis.

Ultimate analyses for this same group of samples are shown in Table 3. These data are also on an as-received basis.

Table 2

Proximate and Related Analyses of Five Coals and their Extrudates

Sample	% M[1]	% A[2]	% V.M.[3]	% F.C.[4]	Heating Value[5]	FSI[6]	LTA[7]
9324 coal	0.31	7.20	39.0_1	53.4_8	13,960	7	8.83
9330 extrudate	0.03	7.32	35.5_2	57.1_3	14,070	8	8.85
M421 extrudate	0.46	7.34	34.1	58.1	13,920		
9325 coal	0.26	5.65	38.5_2	55.5_7	14,060	7½	8.36
9331 extrudate	0.0	6.79	35.4_0	57.8_1	13,610	9	8.65
M422 extrudate	0.28	6.88	34.9	57.9	13,990		
9326 coal	0.14	6.58	39.3_2	53.9_6	14,090	7½	9.08
9332 extrudate	0.03	7.68	36.8_6	55.4_3	14,020	8	9.48
M423 extrudate	0.23	7.96	35.6	56.2	13,850		
9327 coal	0.57	12.72	37.8_1	48.9_0	12,530	6	16.68
9333 extrudate	0.0	14.81	31.3_9	53.8_0	12,330	6½	19.07
M424 extrudate	0.18	15.1	31.4	53.3	12,190		
9328 coal	0.51	17.36	33.0_1	49.1_2	11,880	2	21.39
9334 extrudate	0.08	22.78	22.6_9	54.4_5	11,120	1	26.23
M425 extrudate	0.33	23.0	21.7_1	55.0	10,990		

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[1] % moisture. [2] % ash (725°C furnace). [3] % volatile matter.

[4] % fixed carbon (by difference). [5] in Btu/lb, by adiabatic bomb calorimetry.

[6] free swelling index. [7] % ash (low-temperature oxygen plasma ashing).

Table 3

Ultimate Analyses of Five Coals and their Extrudates[1]

Sample	% M	% A	% C	% H	% N	% S	% O[2]
9324 coal	0.31	7.20	77.70	5.22	0.98	2.24	6.35
9330 extrudate	0.03	7.32	77.58	4.88	0.98	2.19	7.02
M421 extrudate	0.46	7.34	77.59	4.87	1.23	2.30	6.21
9325 coal	0.26	5.65	79.03	5.24	1.02	2.37	6.43
9331 extrudate	0.0	6.79	79.05	4.91	0.63	2.44	6.18
M422 extrudate	0.28	6.88	77.30	4.85	1.21	2.46	7.02
9326 coal	0.14	6.58	77.81	5.12	0.94	2.29	7.12
9332 extrudate	0.03	7.68	78.00	4.93	0.89	2.17	6.30
M423 extrudate	0.23	7.96	77.64	4.79	1.19	2.28	5.91
9327 coal	0.57	12.72	69.34	4.87	1.01	3.83	7.66
9333 extrudate	0.0	14.81	69.73	4.23	0.74	3.93	6.56
M424 extrudate	0.18	15.10	69.49	4.25	1.12	3.86	6.00
9328 coal	0.51	17.36	66.24	4.52	0.65	0.74	9.98
9334 extrudate	0.08	22.78	64.61	3.57	0.69	0.63	7.64
M425 extrudate	0.33	23.00	62.82	3.43	1.18	0.69	8.55

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[1] Data headings from left to right are moisture, ash, carbon, hydrogen, nitrogen, sulfur and oxygen.

[2] Oxygen is calculated by difference: % oxygen = 100 - %M - %A - %C - %H - %N - %S.

The differences indicated between the parent coals and their extrudates are in general reasonable and expected. The volatile matter content drops, as a consequence of extrusion, by roughly 5% (std. dev. ± 2%), as has been noted earlier (1); the fixed carbon content increases accordingly. The change in heating value is insignificant. Moisture is, as expected, greatly reduced, and the ash content is typically increased by 0-1%, reflecting the loss of pyrolysis gases and vapors. The free swelling index is increased, on the average, by about 1 unit. The elemental composition shows moderate changes. Carbon content is increased in most extrusion runs, typically by about 0.3%, while hydrogen content drops in all cases, typically by about 0.4%. The extrusion of coal 9327 is typical; the carbon content increases by 0.39% while the hydrogen content decreases by 0.64%. The H:C atomic ratio is thus measurably reduced, from 0.84 to 0.72. This is not surprising in view of the high H:C ratios of the pyrolyzed gases and vapors. For most extrusions the nitrogen content of the extrudate is slightly lower (about 0.1% on the average) than that of the feed coal. The sulfur content is not significantly changed by extrusion. The oxygen content appears to change erratically, probably a consequence of the fact that this is estimated by difference, so that each estimate contains the sums of errors of six other analyses; the average change is approximately zero.

Tables 4 and 5 show the results of progressive increasing of the die temperature, from 600° to 1100°F, during an extrusion run with a Pittsburgh #8 seam coal sample. The one substantial difference is that between the two samples of feed coal, taken from the feed hopper before and after the extrusion run. These tables show no other significant

Table 4

Proximate and Related Analyses of Extrudates at Various Die Temperatures[1]

Sample	% M	% A	% V.M.	% F.C.	Heating value	FSI	LTA
9324 coal (initial)	0.31	7.20	39.0_1	53.4_8	13,960	7	8.83
9329 coal (final)	0.43	5.79	39.3_6	54.4_2	14,060	8	8.43
9335 extrudate (600°)	0.0	7.04	35.8_7	57.0_9	14,030	9	8.53
9336 extrudate (700°)	0.0	7.06	34.9_8	57.9_6	14,020	9	8.69
9337 extrudate (800°)	0.0	7.05	35.6_6	57.2_9	13,980	9	8.82
9338 extrudate (900°)	0.16	7.88	35.5_0	56.4_6	13,850	9	9.22
9339 extrudate (1000°)	0.0	7.38	34.3_8	58.2_4	13,980	9	*
9340 extrudate (1100°)	0.0	6.40[2]	35.2_7	58.3_3	13,890	9	9.19

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[1] Data headings and units defined in footnotes to Table 2.

[2] Datum is suspect (compare LTA data).

* Insufficient sample for determination.

Table 5

Ultimate Analyses of Extrudates at Various Die Temperatures[1]

Sample	% M	% A	% C	% H	% N	% S	% O
9324 coal (initial)	0.31	7.20	77.70	5.22	0.98	2.24	6.35
9329 coal (final)	0.43	5.79	77.75	4.97	0.85	2.42	7.79
9335 extrudate with 600°F die	0.0	7.04	78.19	4.96	0.76	2.23	6.82
9336 extrudate with 700°F die	0.0	7.06	78.47	4.89	0.89	2.29	6.40
9337 extrudate with 800°F die	0.0	7.05	78.57	4.92	0.64	2.48	6.34
9338 extrudate with 900°F die	0.16	7.88	77.49	4.75	0.65	2.66	6.41
9339 extrudate with 1000°F die	0.0	7.38	78.23	4.76	0.77	2.48	6.38
9340 extrudate with 1100°F die	0.0	6.40[2]	77.92	4.80	0.84	2.47	7.57[2]

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[1] Data headings and units defined in footnotes to Table 3 - oxygen is estimated by difference.

[2] See Table 4, note 2.

difference. Since residence time in the die is less than 2 sec, while residence time in the heated zone of the screw is of the order of 10^2 sec, it appears from these data that the die temperature is not a significant variable (within this temperature range) in determining the properties of the extrudate.

The data of Table 2, particularly comparison of the ash contents before and after extrusion, indicate apparent increases in ash content somewhat larger than expected on the basis of volatile matter losses during extrusion. To recheck these data, the JPL hold samples of these extrudates (samples M421 through M425) were analyzed. The 15-30% increase in ash content in extrudates 9333 and 9334 were duplicated in the analyses of the hold samples. No more than about 5% of this difference is attributable to volatile matter losses; the balance is believed to arise from the great difficulty of obtaining homogeneous samples of the feed coal. [Another illustration of sampling homogeneity problems is seen in Table 5, where the greatest differences are between a hopper sample of feed coal at the beginning of an extrusion run and a second sample of "the same" coal at the end of the run; the former contains 24% more ash than the latter.]

3.2 Condensate and Gas Analyses

We have received for analysis five samples of room-temperature condensates from vented products from the JPL 1.5-inch extruder (samples 9345 through 9349). These samples were visually heterogeneous, consisting of immiscible aqueous and oil phases. There is considerable compositional uncertainty in the analysis of such macroheterogeneous systems. The procedure followed to minimize this uncertainty is to agitate the sample

Table 6

Proximate and Related Analyses of Later Extrusion Runs[1]

Sample	% M	% A	% V.M.	% F.C.	Heating value	FSI	LTA
9352 coal	0.25	8.08	39.6_1	52.0_6	13,960	7½	10.14
9625 coal	0.60	6.93	39.1_8	53.3_0	14,030	7½	
9627 extrudate	0.22	7.37	34.2_4	58.1_8	14,000	9	
9626 coal	0.59	6.92	39.1_5	53.3_4	14,050	8	
9628 extrudate	0.19	7.60	32.9_0	59.3_2	13,950	9	
M436 coal	1.74	10.94	42.0_5	45.2_7	12,230		
M437 extrudate	0.55	12.73	34.0	52.7_2	12,310		
9648 W&P extrudate	0.42	9.15	28.1_0	62.3_4	13,410	1½	

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[1] Data headings and units defined in footnotes to Table 2.

Table 7

Ultimate Analyses of Later Extrusion Runs[1]

Sample	% M	% A	% C	% H	% N	% S	% O
9352 coal	0.25	8.08	77.17	5.16	0.97	2.36	6.01
9625 coal	0.60	6.93	77.56	5.18	1.04	2.12	6.57
9627 extrudate	0.22	7.37	76.23	4.82	1.08	2.11	8.17
9626 coal	0.59	6.92	77.66	5.11	0.71	2.26	6.75
9628 extrudate	0.19	7.60	75.80	4.85	0.84	2.05	8.67
M436 coal	1.74	10.94	66.54	4.88	1.17	4.33	10.40
M437 extrudate	0.55	12.73	68.60	4.24	1.15	4.21	8.52
9648 extrudate (W&P)	0.42	9.15	76.13	4.30	1.31	2.39	6.30

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[1] Data headings and units defined in footnotes to Table 3 - oxygen is estimated by difference.

vigorously, then sample quickly for elemental analysis; then, separately, to agitate the sample vigorously, sample quickly, and make an estimate of the moisture content by thermogravimetric analysis (material rapidly volatilizing at 110°C). The data obtained are shown in Table 8.

Sample quantities received by IMMR are in the range 0.8-6.9 g., and contain 10-27% moisture. The moisture-free elemental compositions -- except for the low hydrogen content of 9345 -- are not dramatically different from coal compositions, except for high oxygen content.

Four gas samples were also received by IMMR, in steel sample vessels containing head gas from extrusion runs (samples 9341 through 9344). Sample size estimation is rough, involving as it does the small difference between two large weights; in all four cases the gas mass is estimated to be between 0.2 and 0.5 g. Compositional analysis was carried out using a dedicated refinery gas-analyzing gas chromatograph in conjunction with a number of standardization runs with appropriate reference gas mixtures. Results of these analyses are given in Table 9.

The major components in all cases were CO_2 and nitrogen. In addition, all samples contained significant amounts of CO (2-5%), oxygen (3-9%), methane (2-11%), and C_2 hydrocarbons (1.3 to 7.2%). Small amounts of higher hydrocarbons were also found, as shown in Table 8. Propylene and acetylene are not distinguished from one another in this analytical procedure; on the basis of other alkane/alkene ratios and the trends among the homologous series, we believe that most or all of the propylene/acetylene signals are due to propylene.

3.3 Mineral Analyses

Low temperature ash values are always higher than conventional furnace

Table 8

Analysis of Room Temperature Condensates*

Sample	Net Mass, grams	% Carbon	% Hydrogen	% Nitrogen	% Sulfur	% Moisture**
M9345	2.13	62.17 (84.93)	5.19 (2.99)	0.45 (0.61)	1.00 (1.37)	26.8
M9346	1.15	68.88 (85.35)	6.63 (5.54)	0.51 (0.63)	1.01 (1.25)	19.3
M9347	0.75	66.84 (74.10)	6.87 (6.40)	0.20 (0.22)	1.13 (1.25)	9.8
M9348	4.44	69.84 (84.01)	6.83 (5.92)	0.16 (0.19)	1.31 (1.58)	17.3
M9349	6.87	57.29 (66.62)	5.98 (5.13)	0.20 (0.23)	0.48 (0.56)	14.0

* Data in parentheses on moisture-free basis.

** Approximate moisture content data taken from thermogravimetric weight loss at 110°C.

Table 9

Analysis of Extruder Head Gas Samples

Sample	M9341	M9342	M9343	M9344
Wt., g	0.25 ± .05	0.24 ± .05	0.40 ± .05	0.25 ± .05
Component	%m	%m	%m	%m
CO_2	59.2	55.8	61.8	33.4
O_2	2.8	6.4	9.1	5.7
N_2	21.0	26.7	18.6	28.1
CO	5.1	2.7	1.7	4.8
nonhydrocarbons	88.1	91.6	91.2	72.0
CH_4	3.7	2.0	6.6	10.9
C_2H_6	5.4	2.3	1.1	5.9
C_2H_4	1.4	0.5	0.2	1.3
C_3H_8	1.4	-*	0.16	3.0
C_3H_6 and CHCH	0.71	-	0.10	1.62
i-C_4H_{10}	0.16	-	0.11	0.74
n-C_4H_{10}	0.07	-	0.02	0.91
1-C_4H_8	0.03	-	0.01	0.35
i-C_4H_8	0.04	-	0.01	0.43
Trans-C_4H_8	0.02	-	0.01	0.26
cis-C_4H_8	0.01	-	0.004	0.18
i-C_5H_{12}	0.19	-	0.09	0.49
C_4H_6	-	-	-	0.04
n-C_5H_{12}	0.02	-	0.004	0.22
pentenes, C_6's and C_7's	0.14	- -	0.02	0.74
all hydrocarbons	13.3		8.4	27.1
Closure	101.4	-	99.6	99.1

* C_3 and higher hydrocarbons were not determined on this sample owing to an electrometer malfunction.

(high temperature ash) values, since the LTA retains thermally labile groups such as carbonates. For the parent coals, the ratio LTA/HTA is in the range 1.23 - 1.48, median value about 1.3. For the extrudates (omitting 9340) the LTA/HTA ratio is found within the range 1.15 - 1.29, median 1.23. These ratios, and the indication that the LTA/HTA ratio decreases slightly (as expected) in the heat-treated coal extrudates, is in good accord with earlier data (ref. 1, pp 12-13).

A comparison (Table 2) of coal 9326 with its extrudate (9332) shows a relatively large jump in the ash content, from 6.6% to 7.7%, although there is no concomitant increase in the total sulfur. This led to additional analyses of ashes prepared from these two coals. Results are shown in Table 10. These data indicate no significant change in the iron content of the ash as a result of extrusion, and probably no significant difference in the sulfur content of the ash as a result of extrusion. The marginally lower values for sulfur in the extrudate ash parallel a very slight drop in total sulfur found in the extrudate itself (Table 3).

It has been determined at JPL that the material loss from the screw after these extrusion runs was found to be extremely small, far too slight to account for the increased ash contents of several extrudates (4). To further check the above coal-extrudate pair, however, the whole unashed coal and extrudate were examined with specific reference to the Fe Kα intensity. Results are shown in Table 11. These analyses confirm those of Table 10: the iron content of the extrudate is essentially proportional to its total ash content. No detectable iron pickup is observed as a consequence of extrusion.

Table 10

Analyses of Ashes of a Coal and its Extrudate

Analysis of Ash	Coal 9326 (Pittsburgh #8)	Extrudate 9332 (from same coal extruded at 35 lb/hr)
Total iron (X-ray fluorescence)	8.05%	8.03%
Sulfur as SO_3 (Fisher 270 Analyzer)	3.35%	3.14%
Sulfur as SO_3 (Modified British method)	3.18%	3.05%

- -

Table 11

Fluorescence Analysis of Iron Kα in Whole Coal

	Coal 9326 (Pittsburgh #8)	Extrudate 9332 (same coal extruded at 35 lb/hr)
Intensity of Fe Kα, cpm	17,676	18,339
Total ash (Table 2)	6.58%	7.68%
Intensity per % ash	2,690	2,390

As a part of the particular analytical attention given to the effect of extrusion upon reactivity (see Part 3.7), ash samples from a Kentucky #9 seam coal and its recent extrudate (samples M436 and M437, cf. Tables 6 and 7) were sent to a commercial laboratory (5) for determination of ash fusion characteristics under reducing and oxidizing environments (ASTM D 1857). Results are shown in Table 12.

For this test the repeatability is ± 50°F and the reproducibility is ± 100-150°F. These data indicate that under oxidizing conditions there is no significant difference in the fusion curves for the ash obtained from the raw coal and that obtained from the extrudate. Under reducing conditions there appears to be a significant reduction in the fusion curve of the extrudate-derived ash. More data would be needed to verify this. The reduction in temperature of the fusion curve, if real, is small (95°F on the average), and leaves the initial fusion temperature a good 1000°F above the extruder operating temperature.

3.4 New Sample of Pittsburgh #8 Seam Coal

Coal 9352, a new supply of Pittsburgh #8 seam obtained by JPL, was submitted for a general characterization. The determinations for this coal are given in Table 13.

The as-received proximate and ultimate analyses of this coal show no major differences from those of the earlier sample examined last year.[1] The greatest observed change is in the volatile matter content, down about 1½%, a difference of marginal significance. The ash analysis shows higher alumina content (by about 10% relative), lower Fe_2O_3 (by about 10% relative), and

Table 12

Ash Fusion Analyses of a Coal and its Extrudate

	Coal 9326 (Pittsburgh #8)	Extrudate 9332 (from same coal extruded at 35 lb/hr)
OXIDIZING ATMOSPHERE		
Initial deformation	2340°F	2340°F
Softening temperature	2480	2460
Hemispherical temperature	2520	2550
Fluid temperature	2560	2580
REDUCING ATMOSPHERE		
Initial deformation	2000	1900
Softening temperature	2120	2000
Hemispherical temperature	2180	2100
Fluid temperature	2220	2140

Table 13

Characterization of Pittsburgh #8 Seam Coal (#9352)

Property	As-received	Dry basis
Moisture	0.25%	-
Ash	8.08	8.10
Volatile Matter	39.61	39.71
Fixed Carbon	52.06	52.19
% Carbon	77.17	77.36
% Hydrogen	5.16	5.14
% Nitrogen	0.97	0.97
% Sulfur	2.36	2.37
% Oxygen (by difference)	6.26	6.06
Forms of Sulfur		
% pyritic	0.81	0.81
% sulfate	0.02	0.02
% organic	1.53	1.53
Gieseler plastometry		
softening temperature	403°C	
max. fluid temperature	423°C	
solidification temperature	483°C	
maximum fluidity	15,576 ddpm	
Ash Analysis	% HTA	8.08%
	% LTA	10.14%
SiO_2		51.8 %
Al_2O_3		25.9 %
Fe_2O_3		14.4 %
TiO_2		2.59%
P_2O_5		0.49%
CaO		3.16%
MgO		0.82%
Na_2O		1.19%
K_2O		1.28%
SO_3		4.17%

markedly more TiO_2 (from 1.5% to 2.6%). The most dramatic difference is seen in the Gieseler plastometric data:

	Old Pgh #8	New Pgh #8
Softening temperature	372°C	403°C
Maximum fluidity	>>25000 ddpm	15600 ddpm
Solidification temperature	483°C	485°C .
Plastic range	111°C	82°C

The new Pittsburgh #8 more closely resembles the previously reported Kentucky #11 seam sample,[1] that is, it is a highly plastic coal with a plastic range of 80-85° under standard Gieseler conditions, but it does not have the "super-plastic" properties of the earlier sample of Pittsburgh #8.

[It has been suggested earlier[1] that plasticity might be correlated with ash composition, more specifically with the Fe_2O_3/Al_2O_3 ratio. There is still no sufficient body of internal data to test this notion. It may be noted, however, that the value of this ratio drops from the old Pittsburgh #8 (0.75, in the 'highly plastic' range) to the new Pittsburgh #8 (0.56, moving towards the 'moderately plastic' range)].

3.5 Microstructure

3.5.1 Extractable Fractions. The amount of organic material that can be extracted from powdered coals by refluxing N,N-dimethylformamide (DMF) in an atmospheric-pressure Soxhlet extractor varies according to the coal from less than 1% to as much as 30% or more. In previous work we have noted that the extrudates of two plastic coals (from Pittsburgh #8 and Kentucky #11 seams) had higher DMF-extractable fractions than did their parent coals (1). DMF is a neutral polar aprotic solvent. At its reflux temperature (153°C) it is unlikely to bring about significant thermal degradation of coal structure. If coal is viewed structurally as a crosslinked macromolecular network structure containing a fraction of interstitially distributed "sol fraction" molecules, then the DMF-extractable fraction is a measure of the sol fraction in a coal.

Most of the coal samples in this study have been subjected to DMF extraction, following the method developed in this laboratory by A. W. Fort (Appendix Part 6.1). The results of extractions of six coals and of their extrudates are shown in Table 14.

The highly plastic Pittsburgh #8 and Kentucky #11 seam coals show extractables in the range 28-31%, similar to values obtained previously with coals from these seams (1). The Elkhorn #1 and Kentucky #9 seam coals yielded 15-17% extractables. The effect of the extrusion process on the first four coals is to <u>increase</u> the DMF-extractable fraction to 38-47%. The effect of extrusion upon the last two coals is to <u>decrease</u> the DMF-extractable fraction to about 10%. [In previous work a coal with 19% extractables yielded an extrudate with 15% extractables (1).]

If no microstructural changes occur as a consequence of extrusion, the null-case assumption would be that some of the sol fraction molecules are lost to the coal by volatilization during the hot extrusion process, and that therefore extrudate sol fractions would be expected to be less than those of the parent coals. At 850°F, however, pyrolytic bond-breaking and bond-forming reactions are occurring. The most plastic coals are, almost by definition, those in which bond-breaking reactions predominate in the early stages of

Table 14

DMF-Extractable Fractions of Five Coals and their Extrudates[1]

Sample and Description	% Extracted by hot DMF	
9324 Pgh #8 coal	28.3% 28.5%	28.4%
9330 Extrudate from above coal	46.9 47.3	47.1
9325 Pgh #8 coal	30.9 30.7	30.8
9331 Extrudate from above coal	37.5 39.6	38.6
9326 Pgh #8 coal	29.3 29.9	29.6
9332 Extrudate from above coal	37.7 38.7	38.2
9327 Ky #11 coal	27.7 28.5	28.1
9333 Extrudate from above coal	42.0 41.7	41.9
9328 Elkhorn #1 coal	15.0 14.5	14.8
9334 Extrudate from above coal	8.8 11.4	10.1
M436 Ky #9 coal	17.2 15.6	16.4
M437 Extrudate from above coal	10.5 8.6	9.6

pyrolysis. If extrusion is viewed, from the viewpoint of thermal history and ignoring the mechanical aspects, as a brief excursion into the plastic zone, then the data of Table 14 can be rationalized: the most plastic coals are initially increasing their sol fractions, while the least plastic coals are decreasing their sol fractions.

The effect of progressively increasing the extrusion die temperature from 600° to 1100°F upon extractable fraction is shown in Table 15. The first two samples are of unheated feed coal, sampled from the hopper at the beginning and at the end of the extrusion run. As noted earlier (Tables 4 and 5), there are significant differences between these coal samples; but for the purposes of Table 15 these differences are fairly small.

Excepting the data at 700°F, the pattern of the data in Table 15 is fairly consistent. Figure 1 shows percent DMF-extractables as a function of die temperature. There appears to be a slight decrease in extractables as die temperature is increased from 600° to 1000°F, sharpening as the die temperature increases to 1100°F (593°C). This suggests that at the high end of this temperature range, even with the short contact times at die temperature, there is probably a significant conversion to semicoke.

The experimental Werner & Pfleiderer extrudate (sample 9648) was also subjected to DMF extraction, yielding 19.2%, 22.4% and 19.2% (average 20.3%) extractables. This cannot be interpreted in the absence of a sample of feed coal.

Tables 14 and 15 contain 20 pairs of duplicate analyses. The average difference between duplicates is 1.07% and the standard deviation 0.94%. This indicates the 95% probability range for a single datum is about ± 2%.

Table 15

DMF-Extractable Fractions of Extrudates at Various Die Temperatures

Sample and description	Die temp., °F	% Extracted by hot DMF	
9324 Coal	untreated	28.3% 28.5%	28.4%
9329 Coal	untreated	32.8 32.3	32.6
9335 Extrudate	600°	44.7 44.8	44.8
9336 Extrudate	700°	32.4 34.1	33.3
9337 Extrudate	800°	38.2 40.9	39.6
9338 Extrudate	900°	41.0 38.1	39.6
9339 Extrudate	1000°	37.2 37.8	37.5
9340 Extrudate	1100°	31.9* 26.9*	29.4

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* Sample thimbles probably reversed. If so, duplicate values are 29.2% and 29.6%.

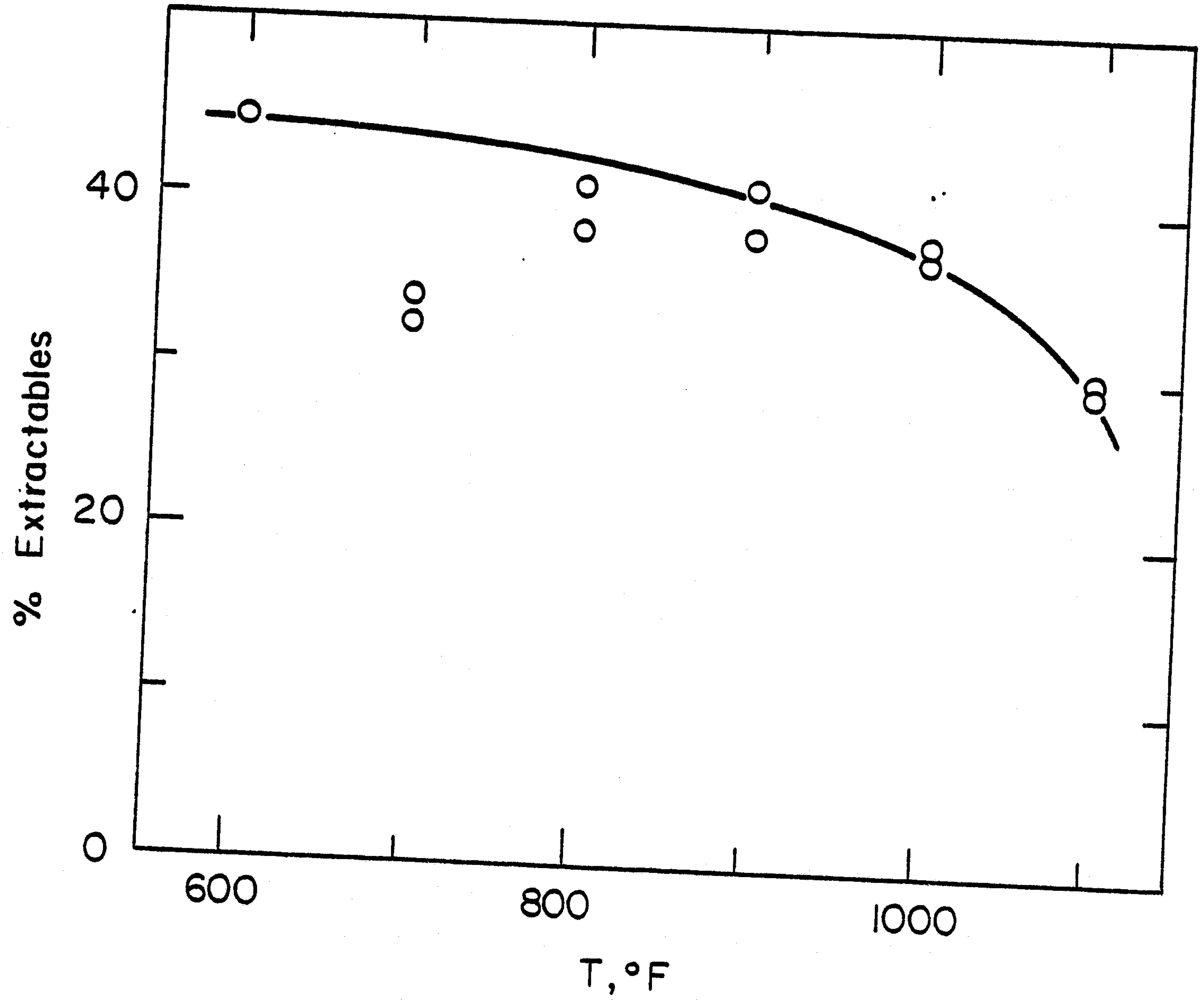

Figure l Effect of Die Temperature Upon Percent Extractables.

3.5.2 Micrography

Microscopic examinations of the parent coal from Pittsburgh #8 and Ohio #9 seams, and of the extrudates of these coals from the JPL 1.5-inch reactor, showed substantial differences in appearance (1). The coals, as seen by scanning electron microscopy under low magnification, are sharp-edged and often rough-surfaced solids. The extrudates are smoother, and some particles show cavities and blowholes, attesting to the physical changes (especially outgassing) which have taken place when the coals were heated to their plastic states.

Additional micrographs have been taken in the course of the present study, to compare the microscopic appearances of a Western Kentucky #9 seam coal (M436) and its extrudate (M437) which have been used in the reactivity tests reported in Part 3.7 of this report. These micrographs were made using the Institute's microscope (ETEC Omniscan) at 500X. Plate 1 shows two representative micrographs.

The parent coal, as seen in Plate 1A, appears as a collection of hard, sharp-edged solid chunks, much like the coals examined earlier (1). The extrudate (Plate 1B) is similarly solid, for this coal does not show the blowholes characteristic of the extrudates from the more highly plastic coals. The edges of the extrudate are softer and more rounded than those of the parent coal, however. It is suggestive that these particles have been brought to a softening point but not to a state of high fluidity.

Plate 1

Micrographs of Fresh and Extruded Coal

1A. Kentucky #9 seam coal (500X)

1B. Extrudate from above coal (500X)

3.5.3 Surface Area by Methanol Adsorption. Methanol adsorption surface areas have been reported previously (1); for six bituminous coals these were found to fall in the range 44 to 67 m^2/g. For six additional coals in the present study the range of values is 46 to 132 m^2/g, or 46 to 90 m^2/g if we exclude a single high-area Pittsburgh seam coal.

On the basis of preliminary data on four extrudates, it was felt that extrusion had little marked effect upon surface area. Table 16 shows the effects of extrusion upon five coals in the present study. Four of the five coals show increases in surface area as a consequence of extrusion.

The effect of varying die temperature upon surface area of the extrudate is indicated by the data of Table 17. These data suggest a possible sensitivity of area to die conditions. One rationale for these data is the following: the first effect at moderate (600°F) temperatures is volatilization of small molecules, opening pore structure and increasing the effective area. As the coal is brought into the plastic region (around 800°F) it truly melts -- as can be seen in photomicrographs in Part 3.5.2 and ref. 1 -- and the overall surface area decreases as fine pore structure is destroyed by melting. At still higher temperatures the pyrolytic process becomes increasingly important, gases and volatile vapors are blown out from the cooling melt, and the resulting fine structure shows up as increasing overall surface area.

3.6 Thermal Analysis

It has been noted earlier (1) that the thermogravimetric analysis (TGA) curves, showing weight loss of coal heated under an inert atmosphere, are not

Table 16

Surface Areas by Methanol Adsorption of Five Coals and their Extrudates

Sample and description	Surface area (MeOH at 25°C), m^2/g
9324 Pgh #8 coal	46.
9330 Extrudate of 9324	71.
9325 Pgh #8 coal	86.
9331 Extrudate of 9325	153.
9326 Pgh #8 coal	132.
9332 Extrudate of 9326	64.
9327 Ky #11 coal	90.
9333 Extrudate of 9327	228.
9328 Elkhorn #1 coal	68.
9334 Extrudate of 9328	128.

Table 17

Effect of Die Temperature upon Surface Area by Methanol Adsorption

Sample and description	Surface area (MeOH at 25°C)
9324 Pgh #8 feed coal	46. m^2/g
9329 Pgh #8 feed coal	46.
9335 Extrudate - die at 600°F	96.
9336 Extrudate - die at 700°F	79.
9337 Extrudate - die at 800°F	43.
9338 Extrudate - die at 900°F	79.
9339 Extrudate - die at 1000°F	99.
9340 Extrudate - die at 1100°F	119.

very sensitive to heating rate. This at least is true for finely powdered small samples and for heating rates as high as 160°C/min. In the present study TGA curves have been generated with a Perkin-Elmer TGS-2 analysis system, with a nitrogen purge rate of 60 cc/min and a temperature ramp at 20°C/min, a ramp commonly used for quantitative measurements. The raw curves as well as the differential (DTGA) curves are shown in Appendix Part 6.2. A summary of these data, for five coals and their extrudates, is given in Table 18.

Some variation is evident among these coals. The range of maximum rate of weight loss for these coals is 2.4 to 7.7 %/min, with an average of about 5%/min. The temperature at which maximum loss rate occurs ranges from 450° to 500°C, with the average close to 490°C. On the other hand, the maximum rate loss rate for the extrudates is 1.4%/min to 5.1%/min, with an average of 3.3%/min. The temperature at which maximum loss rate occurs is above 500° (504-532°C) for the extrudates. These differences between coals and extrudates are thus fairly well defined.

The effect of the extruder die temperature upon the thermogravimetric behavior of the extrudates is shown in Table 19. The reference coal samples show a maximum loss rate of 7.3-7.7%/min, with a maximum loss rate temperature of 450-508°C. Extrudate samples show maximum loss rates of 2-4% at maximum loss rate temperatures of 510-520°C. No systematic dependency upon die temperature is evident.

In addition to the above, a TGA was conducted on the bulk sample of Pittsburgh #8 seam coal (sample 9352). The maximum rate loss rate was found to be 7.0%/min at about 496°C, and occurred at 14.5% weight loss. This coal is thus similar to samples 9324 and 9329.

Table 18

Thermogravimetric Analyses of Five Coals and their Extrudates

Sample and description	Wgt., mg	Temp. at maximum rate of wgt. loss	% wgt. loss at maximum rate	Maximum wgt. loss rate	Maximum wgt. loss rate
9324 Pgh #8 coal	13.0	450°C*	15.	1.0 mg/min	7.7%/min
9330 Extrudate of 9324	12.0	510	6.	0.26	2.2
9325 Pgh #8 coal	12.9	485 **	8.	0.31	2.4
9331 Extrudate of 9325	13.7	516	15.	0.70	5.1
9326 Pgh #8 coal	16.9	500	9.	0.57	3.4
9332 Extrudate of 9326	12.2	504	13.	0.54	4.4
9327 Ky #11 coal	14.9	492	13.	0.60	4.0
9333 Extrudate of 9327	13.7	532 **	7.	0.19	1.4
9328 Elkhorn #1 coal	11.0	500	13.	0.52	4.8
9334 Extrudate of 9328	15.1	506	13.	0.50	3.3

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* Inflection point poorly defined: T(max) is ± 20°C.

** Inflection point badly defined: T(max) is ± 40°C.

Table 19

Effect of Die Temperature Upon Thermogravimetric Analyses of Coal Extrudates

Sample and description	Wgt., mg	Temp. at maximum rate of wgt. loss	% wgt. loss at maximum rate	Maximum wgt. loss rate	Maximum wgt. loss rate
9324 Coal feed	13.0	450°C*	15.	1.0 mg/min	7.7%/min
9329 Coal feed	12.8	508	17.	0.94	7.3
9335 Extrudate - die 600°F	11.7	510	8.	0.30	2.6
9336 Extrudate - die 700°F	11.0	520	15.	0.46	4.2
9337 Extrudate - die 800°F	12.9	510	13.	0.48	3.7
9338 Extrudate - die 900°F	10.8	514	14.	0.42	3.9
9339 Extrudate - die 1000°F	11.1	512 *	6.	0.20	1.8
9340 Extrudate - die 1100°F	11.9	516	14.	0.53	3.2

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* Inflection point poorly defined: T(max) is ± 20°C.

From the curves in Part 6.2 it is possible to estimate total weight loss at any desired temperature. At 600°C the fresh coals show weight losses in the range 19-32%, average 25.4%, while the extrudates show weight losses in the range 11-25%, average 20.2%. At 700°C the fresh coals show weight losses of 23-34%, average 29.7%, and the extrudates show weight losses of 15.28%, average 24.3%. Thus the total pyrolyzable volatiles are reduced (on the average) by about 5% as a consequence of extrusion. This conforms well to the observation in Part 3.1 that the volatile matter content drops on the average by about 5% as a consequence of extrusion.

Enthalpy changes associated with the plastic state are discussed in Part 4.4.

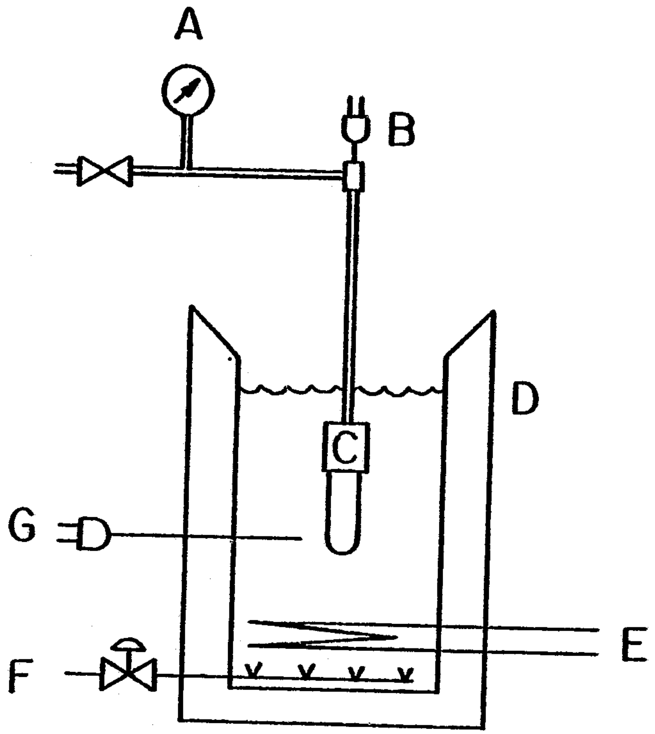
3.7 Reactivity Towards Liquefaction

3.7.1 Microclave Runs. Microclave runs are particularly convenient for the comparison of relative reactivities of two or more coals towards thermal hydroliquefaction. One advantage of microclave runs is the speed with which a run can be carried out: several runs may be completed per day, although the product analysis takes somewhat longer. Another advantage is excellent reproducibility, at least for the Institute's Mori microclave reactor (6). Still another advantage, of special importance for time-conversion data, is that warmup and cool-down times are short compared to reaction times (unlike the situation with large stirred reactors). A limitation of the microclave run is that, since it is a 'static' technique, it does not ordinarily provide useful kinetic data.

The microclave system makes use of a tubular steel microreactor of approximately 20 cc capacity, into which is placed before each run a disposable glass liner (Kimble 45060). The reactor assembly is fitted with pressure and temperature devices, as shown in Figure 2. For a standard liquefaction run the coal or extrudate is reduced to -60 mesh and a charge of 1.50 g is added, along with an additional 1.50 g of inert ceramic (16/36 mesh) which prevents agglomeration of the coal. Tetralin (6.0 g) is added, and the reactor closed and purged several times with nitrogen. The system is then pressurized to 1500 psig with hydrogen. After a 30-min pressure test the system is depressurized to 500 psig hydrogen and placed in position in the fluid bed reactor which has been preheated to 435°C (815°F).

During a run the bath temperature, reactor temperature and reactor pressure are monitored at 60-sec intervals. Bath temperature is maintained to within ± 2°C by heater adjustments. At the conclusion of a run the unit is removed and placed in a cold sand bath for an initial (60-sec) cooldown, and is then quenched in cold running water. In this manner total reaction time is closely defined.

Conversions are determined by hot pyridine extraction, using nitrogen-padded atmospheric pressure Soxhlet extractors. In the procedure used in this laboratory the residual material is subjected to a 42-hour reflux extraction with pyridine, allowed to cool, then subjected to a six-hour reflux extraction with methanol to wash out the pyridine, then dried at room temperature and finally at 60°C under vacuum (less than 1 torr) for six hours. The thimble and contents are then cooled, weighed, heated again under vacuum, cooled and reweighed. If the second weight differs from the first by more than 10 mg the drying cycle is repeated.



A Pressure Gauge
B Thermocouple to Reactor
C Microclave Reactor
D Fluid Bed and Bath
E Heater
F Air Regulator to Sand Bath
G Thermocouple and Bath

Figure 2 The Mori Microclave Reactor

The microclave reactor has been used in this study to compare the reactivities of a plastic coal (Kentucky #9 seam, sample M436) with its extrudate from the JPL 1.5-inch screw extruder (sample M437). Runs with the coal and with the extrudate were conducted at 435°C (815°F) for periods of 10, 20, 30 and 60 min. To provide an estimate of repeatability, all runs were carried out in duplicate. The pyridine extraction method provides a measure of total liquids (maltene, asphaltene and pre-asphaltene fractions, combined). Since most coals, and all plastic coals, contain pyridine-soluble fractions, "zero-minute" dummy runs were also made, in which coal and extrudate were contacted with tetralin, allowed to stand without heating, and then subjected to the extraction analysis.

Table 20 presents the results of these runs. Conversions of both coal and extrudate are in the range 60-90% in all cases. The repeatability is quite good: the standard deviation for all nine pairs of duplicate data is ± 1.8%, and for the best eight pairs is ± 1.4%.

These data provide three bits of information, most easily seen in Figure 3. First, it is clear that both coal and extrudate react rapidly, and under these conditions afford maximum conversions of 85-90% in approximately 15 min at 435°C. Second, the extrudate is nearly as reactive -- but is not quite as reactive -- as the parent coal. At any given time the extrudate conversion is running 4-9% below that of the coal; or, the extrudate requires about one minute of additional reaction time to attain a given conversion. Third, these data imply the existence of a coking reaction which progressively reduces the overall yield of pyridine solubles as the reaction time is continued beyond about 20 min. [Caution should be used in interpreting this coking reaction, as it may likely be an artifact of the static nature of this method.]

Table 20

Conversions of a Coal and an Extrudate in a Microclave at 435°C[1]

Time at 435°C	% Coal Converted to Pyridine Soluble Material		% Extrudate Converted to Pyridine Soluble Material	
	as-received basis	maf basis	as-received basis	maf basis
None	21.6%	22.7%	27.4%	31.0%
	22.3	23.5	25.0	28.2
10 min	78.7	88.1	73.2	83.8
			72.7	83.2
20 min	79.5	89.1	74.0	84.7
	78.3	87.7	73.9	84.6
30 min	72.0	80.5	61.8	70.6
	72.6	81.1	63.7	72.8
60 min	60.3	67.1	52.0	59.3
	62.6	69.7	57.2	65.3

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[1] Kentucky #9 seam coal (sample M436), and the extrudate from this coal (sample M437), received September 1979, and reacted with tetralin and 500 psig initial hydrogen at 435°C (815°F) for the indicated periods.

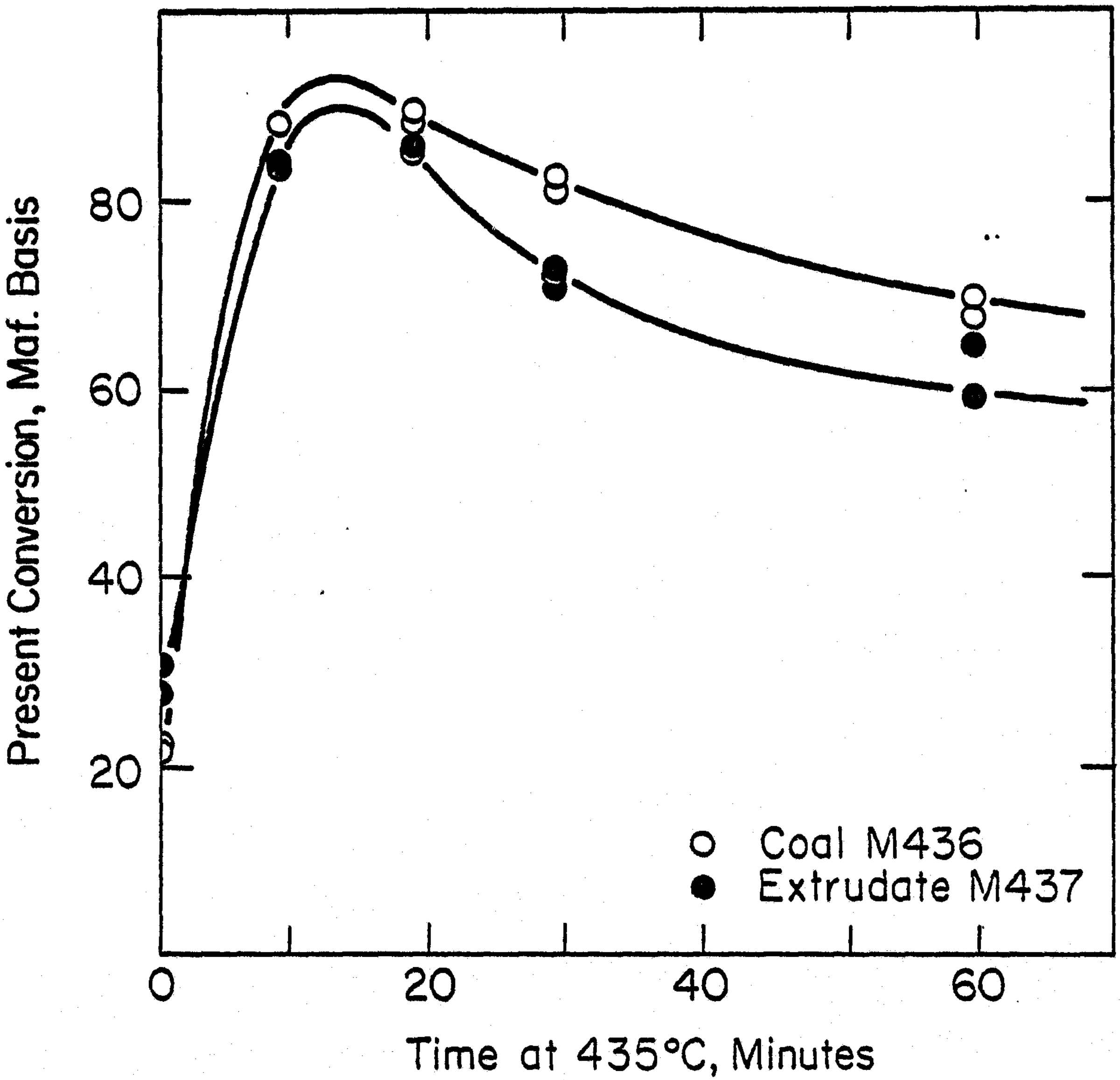

Figure 3 Liquefaction Conversion of Kentucky #9 Seam Coal and its Extrudate.

3.7.2 Stirred Clave Runs. In experiments conducted concurrently with the microclave runs described above, a set of batch liquefaction runs was conducted on the same Kentucky #9 seam coal (M436) and its extrudate (M437), using the Institute's stirred autoclave facilities located at Speed Scientific School (University of Louisville). Two runs were conducted with the parent coal, one with and one without the standard Co/Mo H-Coal catalyst. Two parallel runs were conducted using the extrudate from that coal.

The apparatus and procedure are described in Part 6.4. In summary, the 300-cc stirred autoclave is charged with 33-35 g of pulverized coal or extrudate and approximately 70 g (2:1 by weight) of tetralin. For runs with catalyst a 20-g catalyst charge is used. The autoclave is closed, purged, pressure-tested, and charged with hydrogen to 560 psig at ambient temperature. The clave is then heated with vigorous stirring to 454°C (850°F), then cooled, vented and opened. The contents are first analyzed for conversion to maltenes and asphaltenes, using a hot toluene extraction procedure. A portion of the residue is then subjected to a hot pyridine extraction, to provide an estimate of total conversion (to maltene, asphaltene and pre-asphaltenes, as was done in the microclave runs). Reaction time is calculated from the point at which the warming reactor temperature reaches 399°C (750°F). All runs are for 60 min.

Table 21 shows the results of these runs. Conversions are higher in the stirred clave than in the microclave -- not surprisingly, since the temperature is 16°C higher, the hydrogen pressure is slightly higher, and, perhaps most importantly, the contents are vigorously mixed in these runs.

The data of Table 21 can be looked at with respect to three variables. The effect of extrusion of Kentucky #9 seam coal upon its reactivity is moderate but consistent, the extrudate giving 7-8% lower conversion to pyridine-solubles (cf. 4-9% lower in the microclave runs). The pre-asphaltene fraction in both noncatalyzed runs is 10-13%, indicating a high quality product, roughly similar to that obtained by Maekawa after three hours at 400°C (7). The effect of the massive charges of commercial Co/Mo H-Coal catalyst appears to be negligible, for both coal and extrudate, with regard to the maltene-asphaltene conversion (toluene-soluble fractions), and to be negative for the pre-asphaltene fraction (toluene-insoluble but pyridine-soluble). The pre-asphaltene fraction is virtually eliminated in the presence of this catalyst.

Table 21

Conversions of Coal and Extrudate in a Stirred Autoclave Reactor*

Catalyst	Feed	Conversion to toluene-solubles	Conversion to pyridine-solubles
None	M436 - Ky #9 seam coal	83.9% maf	93.6% maf
None	M437 - Extrudate of M436	72.2	85.3
Co/Mo	M436 - Ky #9 seam coal	82.4	82.4
Co/Mo	M437 - Extrudate of M436	74.9	75.8

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* Using a 300-cc Autoclave Engineers stirred clave reactor, charged with (typically) 35 g coal, 70 g tetralin, and 20 g commercial H-Coal Co/Mo catalyst (if catalyst used), pressured to 560 psig with hydrogen and reacted for 60 min at 850°F. System pressure at 850° is 1850-1900 psig.

4. DISCUSSION

4.1 Effect of Extrusion upon Coal Properties

In the 1.5 inch JPL extruder residence time in the screw is on the order of one minute. For roughly half of this period the dry powder is being brought up to about 800°F (427°C); for the balance of the time the coal is 'at temperature', is melting, and ultimately is extruded in its plastic state. The temperature of the die itself may be varied from about 600°F (316°C) to about 1200°F (649°C). Contact time in the die itself is only of the order of two sec (8), however; the effects of die temperature (noted in Tables 4, 5, 15, 17 and 19) are -- with the possible exception of surface area -- minimal.

It has been noted previously (1) that extrusion has little effect upon apparent rank or heating value. The most noticeable consequence of extrusion is the increase in fixed carbon by several percentage points. In the present study these observations are confirmed: the fixed carbon content increases by an average of about 5%. Ash contents are slightly increased (up to about 1%), as a consequence of losses of gases and organic vapors.

Plasticity is in general retained, the period of exposure being far too brief to accomplish much coking (1).

Ultimate analysis values are changed by extrusion, with carbon content typically increased by a few tenths of a percent and hydrogen content diminished by a like amount. This reflects the loss of hydrogen-rich products (e.g., methane, water vapor) during the hot extrusion.

The ratio of low temperature ash (LTA) to high temperature ash (HTA) is always greater than unity, reflecting the fact that oxygen plasma ashing at temperatures in the vicinity of 100°C leaves species such as labile carbonates which are not stable under the conditions of the standard ashing procedure at 700-750°C (1292-1382°F) (9). This ratio varies among coals; in the present study the ratio is found to have a median value of 1.30. The median value of the LTA/HTA ratio of the corresponding extrudates is 1.23, indicating that -- as expected -- there has been some decomposition of labile material as a result of the heating history during extrusion. There is not, however, any indication by photomicrographic or petrographic examination that any widespread or general structural changes have taken place (1). Closely related to this point is the comparison of ash fusion data (Table 12). Under oxidizing conditions the ash fusion temperatures of a Pittsburgh #8 seam coal and its extrudate are identical. Under reducing conditions there is a small drop -- of marginal significance in comparison with the precision of the analysis (10) -- in the fusion temperatures of the extrudate ash.

Thermogravimetric analyses show substantial variations among coals and among extrudates. The maximum rate of weight loss at a heating ramp of 20°C/min is on the average about 5%/min for fresh coals in this study, and about 3.3%/min for their corresponding extrudates. This appears to be a real effect, and is not surprising when one recalls that during extrusion at 800°F the processed coal has already lost a fraction of its most thermally labile 'volatile matter'.

Earlier work (1) confirmed that nitrogen adsorption gives a poor estimate of surface area; adsorption measurements with CO_2 and with methanol vapor give more meaningful results, and compare reasonably well with one another (1, 11). The surface areas of five plastic coals average about 65 m^2/g (Table 16). The average area of five extrudates of these coals was found to be 129 m^2/g. For four out of five pairs, the extruded coal shows a significantly higher surface area. This may indicate a potential kinetic advantage, e.g., for gasification. As Table 17 indicates, surface area may be one physical characteristic that is really sensitive to extruder die temperature. When screw extrusion is used to feed a coal conversion process, there may be a significant advantage to be obtained in optimizing this temperature.

Extractions with N,N-dimethylformamide (DMF) have been used before (1) and again in the present study (Tables 14, 15, Figure 1) to probe structural changes associated with the extrusion process. Of the nine coals which have been subjected to standard extrusions [three in a previous report (1)], six contain more than 25% DMF-extractables and three contain less than 20% DMF-extractables. All six of the coals with high DMF-extractables yield extrudates with considerably increased levels of DMF-extractables. The increase in extractables ranges from 8% to 19% and averages 12% for these coals. All three of the coals with low DMF-extractables yield extrudates with significantly reduced levels of DMF-extractables. The decrease ranges from 4% to 7%, average 5%.

The molecular events causing this pattern are not clear. The following is offered as a speculative explanation. The thermal homolysis which initiates the 'melting' process sets up a competition between hydrogen transfer (which requires the kind of small interstitial molecules that are assayed in a DMF extraction) and a coking-like condensation. The hydrogen transfer processes generally will produce more small molecules and hence an extrudate with a larger DMF-extractable fraction, while condensation will produce products which are less soluble or are insoluble. This competition occurs in the internal structures of all coals as they enter the plastic state. The DMF extraction (if this explanation is correct) may therefore be a useful predictor both of plastic behavior and of extrudate properties.

4.2 Effect of Extrusion upon Coal Reactivity

The data reported in Parts 3.7.1 and 3.7.2 are in remarkable agreement, considering the marked differences both in liquefaction conditions and in analytical procedures. The Kentucky #9 seam coal is readily reacted at 435-450°C to 90-94% conversion (maf basis) to pyridine-solubles. The extrudate of this coal under the same sets of conditions reacts similarly, but not quite as far or as fast. At the same periods of reaction its conversion may be 4-9% lower. Another way of indicating this difference in reactivity (cf. Figure 3) is that, during the first ten minutes or so of reaction (when most of the liquefaction takes place), the fresh coal reaches a given level of conversion about one minute ahead of the extrudate.

It has been noted earlier that the fixed carbon content of coal is increased typically by about 5% as a consequence of extrusion. For this coal (M436) the increase is from $45.2_7\%$ to $52.7_2\%$ as received, or by about 7.5%. On a maf basis the fixed carbon increases from $51.8_4\%$ to $60.7_9\%$, or by about 9.0%.

One way of comparing conversions of coals in thermal hydroliquefaction processes is to take it for granted that any material which is capable of escaping the heated coal as volatile matter, in the absence of hydrogen or external hydrogen-donor solvent, is assuredly going to escape the solid matrix and make up a part of the liquefaction product when that same coal is heated in the presence of excess H-transfer solvent and molecular hydrogen. [This argument is not without fault. Most of the pyrolysis weight loss occurs in the 500-650°C range, well above that of liquefaction processes.] On this basis, liquefaction begins to count for something as a process only when conversions are well in excess of the volatile matter content of the coal. Conversion can then be viewed in terms of the amount of fixed carbon which has been converted:

$$\text{Conversion(AFC)} = \text{Conversion(maf)} - \text{Vol Matter(maf)} \qquad (1)$$

or in terms of the percentage of fixed carbon which has been converted:

$$\text{Conversion(PFC)} = \frac{\text{Conversion(AFC)}}{\text{Fixed Carbon(maf)}} \qquad (2)$$

If the incremental amount of fixed carbon resulting from the extrusion process is viewed as an inert coke-like material, then Eqn. (1) is the appropriate form for comparing conversions in terms of fixed carbon contents. On the other hand, if that incremental amount of fixed carbon is considered to be comparable with the fixed carbon present in the original coal, then Eqn. (2) is indicated. Plots of the microclave conversion data, converted to AFC and PFC bases by Eqns. 1 and 2, are shown in Figure 4. On the AFC basis the extrudate appears to be marginally more reactive than the parent coal; on the PFC basis the reverse is true.

Figure 3 shows that on a straight conversion basis the parent coal is measurably more reactive than its extrudate. When conversion is calculated on the basis of fixed carbon contents, Figure 4 shows that the conversion curves become very close. If it were possible to include in these calculations the volatile material escaping the screw during extrusion, the differences between conversions of parent coal and extrudate might well become too small to call.

No gasification conversion runs have been made in this study. Under most conditions, however, the rate of gasification with steam or CO_2 is expected to vary monotonically with surface area. Most of the surface area data in Tables 16 and 17 (10 out of 12 cases) show significantly increased surface area as a result of extrusion. This may indicate that the extrusion process produces a form of coal which is more reactive with respect to gasification than the parent coal.

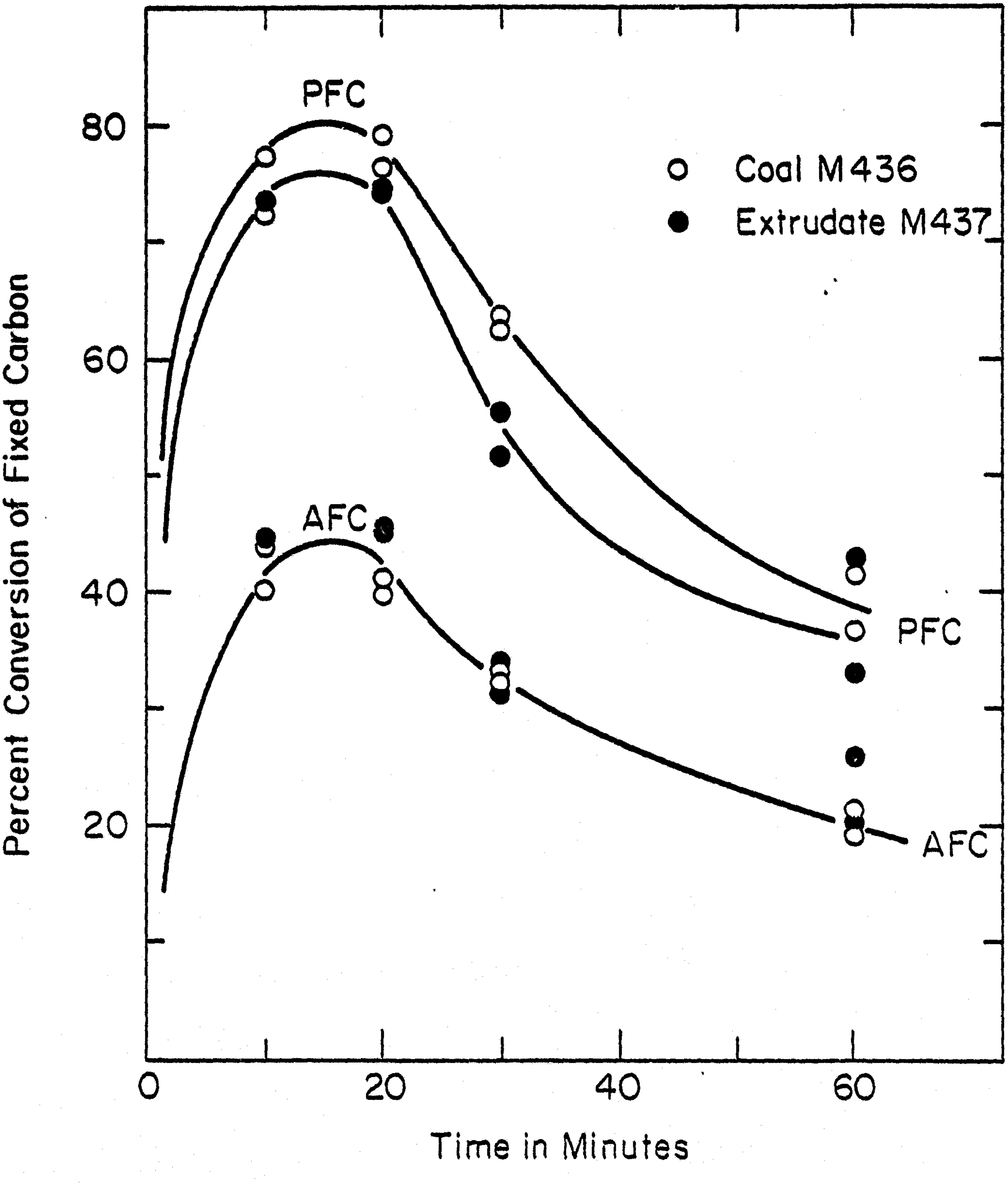

Figure 4 Microclave Conversions as Functions of Fixed Carbon

4.3 Plasticity and Extrusion: a Preliminary Analysis

In trying to understand the bases and implications of the plastic phenomenon in bituminous coals, we need to be concerned with three interacting aspects: extrudability, which is of prime practical importance to the parent program; fluidity (or viscosity), for which we have developed a working model with melting and coking pseudo-rate constants from plastometry curves (1, 12); and the extractable fraction, which from a structural viewpoint seems likely to be a critically important factor in predicting/explaining the variability of fluidities among coals.

Each of these three factors is interrelated with the other two: in a sense they are three faces of a single structural-kinetic complex. The relationship between extrudability and fluidity is mechanically obvious. The varying effects of the extrusion process upon extractables have been discussed in Part 4.1.

A direct relationship between extractables and fluidity has been demonstrated by Pierron and his associates (13, 14). When the extractable fraction is removed from a plastic coal, the residue is found to have lost its plastic properties. When this fraction is partially returned to the coal residue, fluidity is partially returned; and when this fraction is fully returned, the coal again becomes fully plastic. [We have repeated and verified Pierron's work, and have found that a synthetic hydrocarbon mixture also confers plasticity on a nonplastic extraction residue.] It has also been noted that, among different coals of similar rank, maximum fluidities are reasonably well correlated with the fractions extractable by hot pyridine (14).

Another kind of relationship between extractables and fluidity has been reported by Dryden and Joy (15). When coals are examined by Gieseler plastometry and are interrupted at various stages in their fluidity, quenched, and the Gieseler solids extracted with chloroform, a systematic change in extractable fraction is found to relate to the fluidity at the moment of quenching. Highly fluid coals have chloroform-extractables exceeding 10%, while 8% extractables are close to the minimum possible for significant fluidity on both the melting and coking portions of the plastic curves (15).

The plasticity phenomenon in another sense is based upon a series of sequential and parallel processes which, in the 'melting' stages, result in an increase in the fluid fraction of the coal mass. When enough fluid is present, the coal mass becomes a 'melt' which is in fact a very heterogeneous solid suspension (mineral matter, unmelted coal, an unmeltable fraction of inert macerals, and an increasing amount of melt-produced semicoke) in a liquid continuum (the metaplast, or metastable plastic phase). The viscous behavior of solid-in-liquid suspensions can be examined in terms of standard relationships such as the Nicodemo-Nicolais equation (16):

$$\eta = \eta^{\circ} \exp(a\phi) \qquad (3)$$

where η and η° denote the viscosities of the melt and of the pure solvent, respectively, ϕ is the solid fraction, and a is a constant reflecting the eccentricity of the average solid particle. In terms of coal fluidity, this can be rewritten as:

$$f = f^{\circ} \exp(-\alpha\phi) \qquad (4)$$

where f and f° are the fluidities of the coal and of the pure metaplast, respectively, α is a constant, and ϕ is the volume fraction of solids as in Eqn. (3).

There is independent evidence for this relationship in the Gieseler fluidities of various coal-coal and coal-char blends. When a fluid coal is blended with a nonplastic coal, a char, or an oxidized (and hence nonplastic) coal, the fluidity characteristically falls off exponentially as the fraction of the nonplastic component is increased. Figure 5 illustrates this relationship (17). The linearity of these data over nearly three orders of magnitude provides strong support for the speculation (12) that coal melts conform to the relationship of Eqn. (4).

Work now under way in this laboratory is testing the general applicability of Eqn. (4) to the behavior of coal-char, coal-coal, and coal-plasticizer mixtures. The fluidity of molten coal can, it is hoped, be more rigorously and hence more usefully expressed in terms of the parameters f° and ϕ.

A parallel study now under way is examining the variations in non-Newtonian behavior of selected coals and mixtures, using an adjustable-torque plastometer (18). A third target area is the quantification, in terms of the isothermal plastic model (12), of the large effects of pressure upon coal fluidity (19, 20).

It is hoped that these studies will lead to the development of an explicit model for plastic behavior of coal melts, that will accommodate both shear and pressure variations.

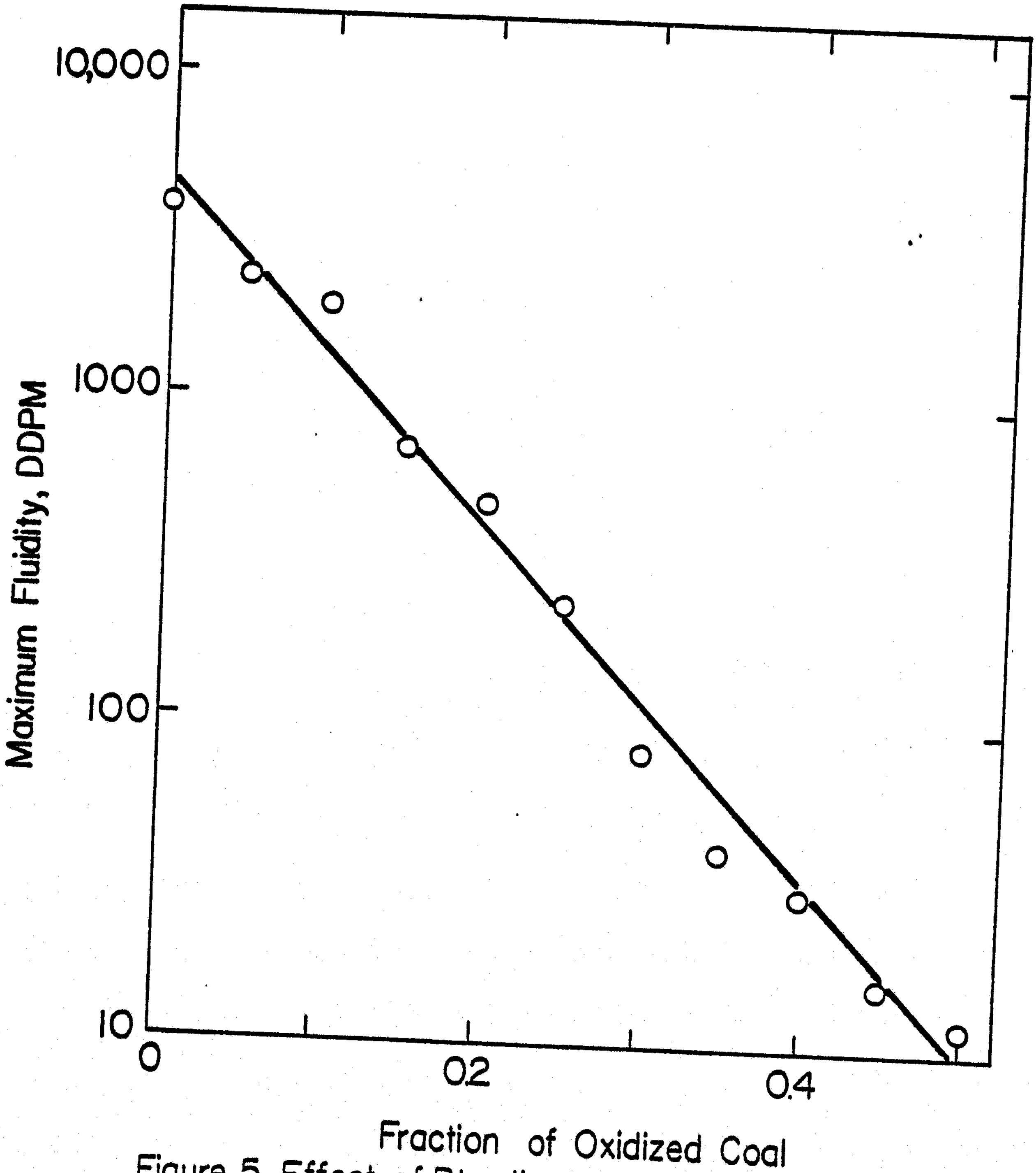

Figure 5 Effect of Blending upon Maximum Gieseler Fluidity

4.4 The Melting Endotherm

In a previous report (1) we reviewed data obtained in this laboratory and elsewhere on the question of the enthalpic changes associated with the passage of coal through the plastic state. We have since then conducted additional work and have continued examination of the thermochemical literature. Following is a brief recapitulation and update of this question.

Earlier studies led to conflicting results. Both Whitehead (21) and Berkowitz (22) found prominent exotherms upon heating coal through the plastic state and under an inert atmosphere, while Glass (23) and Roga (24) found these processes to be endothermic, a conclusion supported by the results of Kroger and Pohl (25) on pure macerals.

Recently there have been several reports of an important exotherm associated with the plastic state of bituminous coals. Hathi and Sliepcevich (26) found a substantial, although poorly reproducible, exotherm in coals taken above 500°C, by differential scanning calorimetry. A similar observation is reported in a JPL progress report (27), namely an exotherm at about 490° from a medium rank (hvBb) coal, the magnitude of which was found to be highly dependent upon heating rate. A most systematic and thorough study of this phenomenon has been made by Gold (28,29), who has concluded that "there is ample evidence of the existence of substantial exothermic processes above 400°C during coal pyrolysis" (29). We have found it easy to obtain an erratic but large "exotherm" on heating plastic coals in a differential scanning calorimeter (1). For reasons noted below, however, we believe that this effect observed by us and by others (26-29) is a system artifact.

All of the studies reporting an important exotherm associated with the plastic state rely upon the same thermal tool, namely, differential scanning calorimetry. Our contention that this exotherm is artifact is based upon three arguments: that in the hands of several careful workers the exotherm is erratic and nonreproducible; that experiments run with coal-char mixtures demonstrate the phenomenon to be non-colligative; and that a consensus of other workers' findings shows the process to be endothermic and even provides a good estimate of its magnitude of the endotherm for plastic coals.

The peculiar character of the "exotherm" has been described in detail by Gold (28, 29). This exothermic excursion, appearing in the range 415-475°C, is sharply dependent upon heating rate: in going from 80° to 40° to 20°/min the magnitude of the exotherm is reduced by approximately a factor of five at each step; at 10°/min it is completely absent. It is abnormally dependent upon the mesh size of the coal: coal of 80-100 mesh yields only about one quarter the exotherm of a parallel sample of 60-80 mesh, and the same coal at -100 mesh yields no detectable exotherm. It is abnormally dependent upon sample size: at 80°/min with 20-30 mesh coal the exotherm from a 20-mg sample is more than twentyfold greater than that obtained with a 10-mg sample. [A similar effect is found at a ramp of 20°/min.] Gold notes that with decreasing sample mass he encounters "an abrupt disappearance of the exotherm" (29). These are not characteristics of a measured colligative property.

The explanation which we favor (1) is that this "exotherm" is a heat transfer artifact associated with the flowing together and foaming of the coal mass into a low-density cellular structure on the DSC pan. Temporarily the sensor records a loss in heat capacity (i.e., an "exothermic" event). As soon as a new equilibrium temperature gradient is established between the sample pan mass and the center of mass of the "foamed" coal, the pen returns to or near to the baseline, thus completing the artifact "exothermic peak".

DSC curves were obtained in this laboratory with Pittsburgh #8 seam coal and with mixtures of this coal and a sample of 950° char prepared from this coal (1). With 100% coal after two small endotherms a large "exotherm" at 500° takes the pen off scale. With a 75:25 coal:char mix, a slight exotherm is obtained, less than one tenth that found with the original coal. With 50:50 coal:char there is no trace of exotherm. The small endotherms are attenuated rationally, i.e., they are approximately in the ratio 4:3:2 for these three runs. The elimination of the exotherm parallels the elimination of the flowing/foaming phenomenon as a result of admixture with the inert char.

Other DSC work conducted at elevated pressure (5.6 MPa) has found the coking process to be endothermic for coals from hvCb through anthracite (30). At these pressures the small molecules formed by pyrolysis can be seen to be substantially retained by the coal mass (19); hence in the absence of foaming the DSC exotherm is not observed.

Heilpern has examined a group of Polish coals of varying rank by differential thermal analysis (DTA, not subject to the "artifact" effect of DSC) and has found over the entire coking range (to 900°C) a spread of endotherms which vary with rank, largest endotherm reported being 157 cal/g (31). The study by Mahajan et al. at elevated pressures (30) reports an overall endotherm of 50 cal/g for a plastic coal. Looking specifically at the enthalpy changes associated with the plastic state (roughly, 400-475°C), estimates are available from five different sets of workers. Kirov and Stephens determined by DTA that the melting process has associated with it an endotherm of approximately 10 cal/g (32). Agroskin and his associates have published several papers reporting melting endotherms in the range 6.6 to 17.5 cal/g (33), 1.4 to 43.1 cal/g over a broader range of ranks (34), from zero to 40 cal/g over a similarly broad range of coals (35), and for three plastic Russian coals a narrow endotherm range of 10.2 to 12.2 cal/g (36). Lee and his associates have made an estimate by following heat flux in laser-heated cylinders of powdered coal; they estimate the process to be endothermic by approximately 18 cal/g (37). Henry Francis of this laboratory conducted a quantitative DSC thermogram at 20°C/min on Pittsburgh #8 seam coal, and by area integration (ignoring the exothermic excursion discussed above) has made the estimate of an endotherm of 11.3 cal/g (38). More recently John Elder of this laboratory conducted a TGA study, also at 20°C/min but on a Mettler Model TA-2000B, using the same Pittsburgh #8 seam coal; his estimate of the endotherm is 10.5 cal/g (39).

Taking the best values from these sources, namely, 10 (32), 10.7 (33), 11.2 (36), 18 (37), 11.3 (38), and 10.5 (30) cal/g, the geometric average of these is 11.7 cal/g. The five best values for the plastic state endotherm of plastic coals are in the range 10-11.3 cal/g, average 10.7 cal/g. [It should be recalled that, as Heilpern and Agroskin have shown, a considerable variation is likely among coals of substantially different rank. Application of the above consensus should therefore be limited to plastic coals of hvAb or hvBb rank.]

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6. APPENDIX

6.1 Notes on Extractions with N,N-Dimethylformamide and Pyridine

Soxhlet extractions with N,N-dimethylformamide (DMF) are used to determine extractable fractions (Part 3.5.1). Similar extractions using pyridine are used to assay total conversion in the microclave liquefaction runs (Part 3.7.1). This portion of the Appendix includes two documents.

The detailed procedure employed for quantitative DMF extractions is presented in the memorandum by Dr. A. W. Fort of January 16, 1980 (following pages). In this memorandum is described the evidence of significant nitrogen retention by the coal residue, even after drying to constant weight at 60°C under vacuum.

A second memorandum by Dr. Fort, dated January 21, 1980, discusses the pyridine extraction procedure -- virtually identical to the DMF procedure -- and similar evidence that some of the polar solvent is tightly held by the residual coal. This retention is evident also from the data of other workers (13, 14).

In both instances the quantitative extraction results are substantially improved by a final drying in vacuo at 150°C. This would be especially important if subsequent surface-sensitive measurements were to be made. When these techniques are used (as they are in the present study) to make bulk determinations of total extractables, however, solvent retention at 60° appears to introduce only a moderate systematic error which does not alter the comparative relationships among coals and extrudates.

January 16, 1980

MEMORANDUM

TO: W. G. Lloyd

FROM: A. W. Fort

SUBJECT: Some Observations on the Procedure Employed for Dimethylformamide Extractions of Coals and Extrudates, JPL Project

Dimethylformamide (DMF) extractability of the bituminous coals employed in this program has been correlated with thermoplasticity of the coals. DMF extractability of these coals has been correlated also with extractability and thermoplasticity of the corresponding extrudates.

Results obtained in a control experiment, performed at an early date in this program, indicated that extraction of powdered coal with hot DMF goes to completion, and does so within a few hours when the extraction is performed with rapid reflux of the solvent. Results obtained subsequently have all tended to confirm the belief that the extraction time employed in our procedure is more than adequate for completeness of extraction.

The extraction procedure used in this work is described in detail below. The mild conditions (60°C, vac.) used for removing solvents from extracted coals and extrudates were sufficient for bringing the extraction residues to nearly constant weight in two or three drying periods, and replication was usually satisfactory. However, in the course of the present work a coal (W. KY No. 11) and two extrudates (from Elkhorn No. 1 and W. KY No. 11 coals) were encountered for which extraction results were not satisfactorily reproducible. This complication led us to doubt the effectiveness of methanol extraction for complete removal of DMF from the extraction residues. Consequently, we examined some of the extraction residues for retention of DMF. We also considered the possibility that more or less dimethylamine (which arises from DMF by hydrolysis or decomposition in the course of extraction) might be retained at acidic sites in the extraction residues.

Nitrogen determinations on the extraction residues from W. KY No. 9 coal and its extrudate revealed that these residues had much higher nitrogen contents than the original, unextracted samples. These results clearly indicated retention of nitrogen-rich material, DMF and/or dimethylamine.

Coal (Extrudate)			Residue from DMF Extraction	
No.	description		60° drying	150° drying
789325	Pitts. No. 8	1.02% N	1.98% N	1.04% N
M436	W KY No. 9	1.17% N	2.83% N	1.25% N
M437	Extrudate from M436	1.15% N	3.03% N	1.33% N

Another residue (from Pitts. No. 8 coal), one that had come to constant weight easily and reproducibly at 60°C, was also found to have a high nitrogen content. When these residues were heated for a period of six hours at 150°C (vac.) small weight losses were observed and nitrogen levels were reduced almost to levels expected for no retention of DMF (or dimethylamine.) Another heating period at 150° resulted in no significant further loss of weight from these residues.

A part of the nitrogen-rich material that was removed from these residues at 150° was dimethylamine. This conclusion follows from the observation that brief leaching of the residues with cold dilute hydrochloric acid resulted in significant lowering of the nitrogen content in each case.

	Nitrogen content	
Residue from	residue dried at 60°	leached, neutralized, redried
789325	1.98%	1.49%
M436	2.83%	2.26%
M437	3.03%	1.90%

When the hydrochloric washings were made alkaline a distinct odor of dimethylamine was noted (very faint in the case of Pitts. No. 8 residue).

The results obtained in the 150° drying experiment indicate that our extraction work would have been tidier if extraction residues had been brought to constant weight at a temperature higher than 60°C: the residues would have been brought to constant weight more readily; overall reproducibility would probably have been improved; and extractabilities of the coals and their extrudates would have been observed to be somewhat larger than those reported.

Coal (extrudate)		Result of DMF extraction	
No.	description	drying at 60°	drying at 150°
789325	Pitts. No. 8	31% extracted	35% extracted
M436	W KY No. 9	16% extracted	21% extracted
M437	extrudate from M436	8% extracted	15% extracted

However, it does not appear that conclusions drawn in the report would need to be changed in any significant way.

Dimethylformamide Extraction Procedure

Four Soxhlet extraction assemblies were employed, normally. Two powdered coals or extrudates were extracted in duplicate, with a turn-around time for the extraction assemblies of three days. Dryings and weighings also required three days, usually. One operator, keeping the vacuum oven and Soxhlet assemblies in operation, started two samples (in duplicate) through the extraction procedure at three-workday intervals.

Materials:

four beakers;
four cellulose extraction thimbles, 33 x 99mm;
vacuum oven;
large desiccator with calcium chloride lumps;
large vacuum desiccator with calcium chloride lumps;
four Soxhlet extraction assemblies, complete, with 250-ml round-bottom flasks, heating mantles, magnetic stirrers, stirring bars, and calcium chloride drying tubes;
dimethylformamide (DMF), reagent grade;
methanol, reagent grade

Procedure:

1. Dry the beakers for one hour or more at 100-110°C, cool (desiccator) and weigh to nearest mg. Add ten g. of powdered sample to each beaker and weigh again to nearest mg, working rapidly. All subsequent weighings will be to the nearest mg.

2. Dry the samples in a vacuum oven at 60°C for a period of six hours. Dry four marked extraction thimbles in the oven with the samples. Allow the samples and the thimbles to cool under vacuum*. Transfer thimbles and beakers containing samples to a desiccator. Weigh samples to obtain moisture loss. Weigh thimbles, transfer samples to thimbles and weigh again to obtain weight of dried sample to be extracted.

3. Place 150 ml of DMF and a magnetic stirring bar in the pot of each extraction assembly. Insulate the Soxhlet assemblies so that condensation of solvent vapor occurs mainly in the condensers. Protect with a calcium chloride drying tube. Maintain vigorous stirring and heating for a period of 22±2 hours. Inspect each assembly periodically to insure that DMF drips rapidly from the condenser drip tip and that DMF siphons normally from the extraction compartment.

4. Interrupt heating and stirring* and introduce approximately 100 ml of methanol through the top of the condenser to rinse the bulk of DMF from the extraction compartment. Replace the pot containing DMF and methanol with a pot containing 150 ml of fresh methanol. Resume heating and stirring, extracting DMF from the extraction thimble contents with methanol for a period of five to six hours. Allow to cool

5. Remove the thimble from each extraction assembly and allow the methanol to drain from the thimble. Place thimbles in a vacuum desiccator and evacuate, using an aspirator, for at least one-half hour. Seal desiccator and allow thimbles to remain under vacuum over calcium chloride overnight*.

6. Transfer thimbles to a vacuum oven and dry for a period of six hours, at 60°C (vac.) Allow the oven to cool* to below 40°C before breaking the vacuum. Transfer thimbles to a desiccator for weighing.

7. Repeat drying procedure for a period of two hours (four thimbles) to four hours (eight thimbles). Two drying periods are usually sufficient for

extracted coal samples, and three drying periods are usually sufficient for coal extrudate extraction residues.

8. Transfer sample to a labeled and tared vial for storage.

Data:

moisture loss, %;
weight of dry coal or extrudate to be extracted;
weight loss on extraction with DMF, %.

(*) A convenient point at which to interrupt work.

January 21, 1980

MEMORANDUM

TO: W. G. Lloyd

FROM: A. W. Fort

SUBJECT: The procedure used for pyridine extraction of coal liquefaction product mixtures, JPL Project

Pyridine extractions following very closely the dimethylformamide extraction procedure (Memorandum, A.W.F. to W.G.L., 1/16/80) have been performed in the Organic Analysis Laboratory on coal-derived products with satisfactory results. However, it became necessary to modify that procedure somewhat when pyridine extraction was applied to the contents of the Mori microclave:

1) weights of materials charged to the reactor were obtained by personnel of the Process Development Division and were supplied to Organic Analysis along with the sealed reactor containing the liquefaction product mixture;
2) the contents of the reactor were transferred to a weighed extraction thimble (previously dried in a vacuum oven) with the aid of some pyridine;
3) the flow of liquid through the thimble wall was very slow at first, and it was necessary to carry out extraction slowly in order to avoid spilling over the top of the thimble;
4) extraction time was increased to 42 hours to compensate for the decreased rate of extraction;
5) and, extraction assemblies were blanketed with nitrogen during extraction.

Solvents were removed from extraction residues at 60°C (vac.) as described for DMF extractions. The residues came to constant weight readily under the drying conditions employed, and results were satisfactorily reproducible. However, our work on DMF extractions has raised the possibility that the basic solvent, pyridine, might be strongly retained at acidic sites in the extraction residues. Indeed, E.D. Pierron and D.W. Rees (Illinois State Geol. Survey Circular 288-1960) found that a small amount of pyridine had been retained by a pyridine-extracted coal after two hours at 116°C (vac.)

We have obtained some preliminary results indicating that such residues of pyridine extractions can be dried safely and efficiently at 150°C (vac.):

1) a sample of W. KY No. 11 coal, dried at 60° (vac.) was found to be stable toward further weight loss at 150°C (vac.);
2) cellulose extraction thimbles are sufficiently stable at 150° (vac.) for such drying to be feasible, providing the sample is large, preferably 1.0g or larger;

(3) two residues of pyridine extraction, dried to constant weight at 60° (vac.), gave up residual pyridine readily at 150° (vac.)

		Pyridine-insoluble residue	
No.	Identification	dried at 60°C	dried at 150°C
M653	W. KY No. 11 coal, dried	68% (2.17% N)	63% (1.32% N)
M630	same, heated at 450°C in tetralin under H_2	31% (1.07% N)	30% (0.83% N)

(4) results of analysis of the residues for nitrogen indicate that the residue from M653 contained no more than about 2% pyridine and that the residue from M630 contained no appreciable amount of pyridine after these had been heated at 150° (vac.)

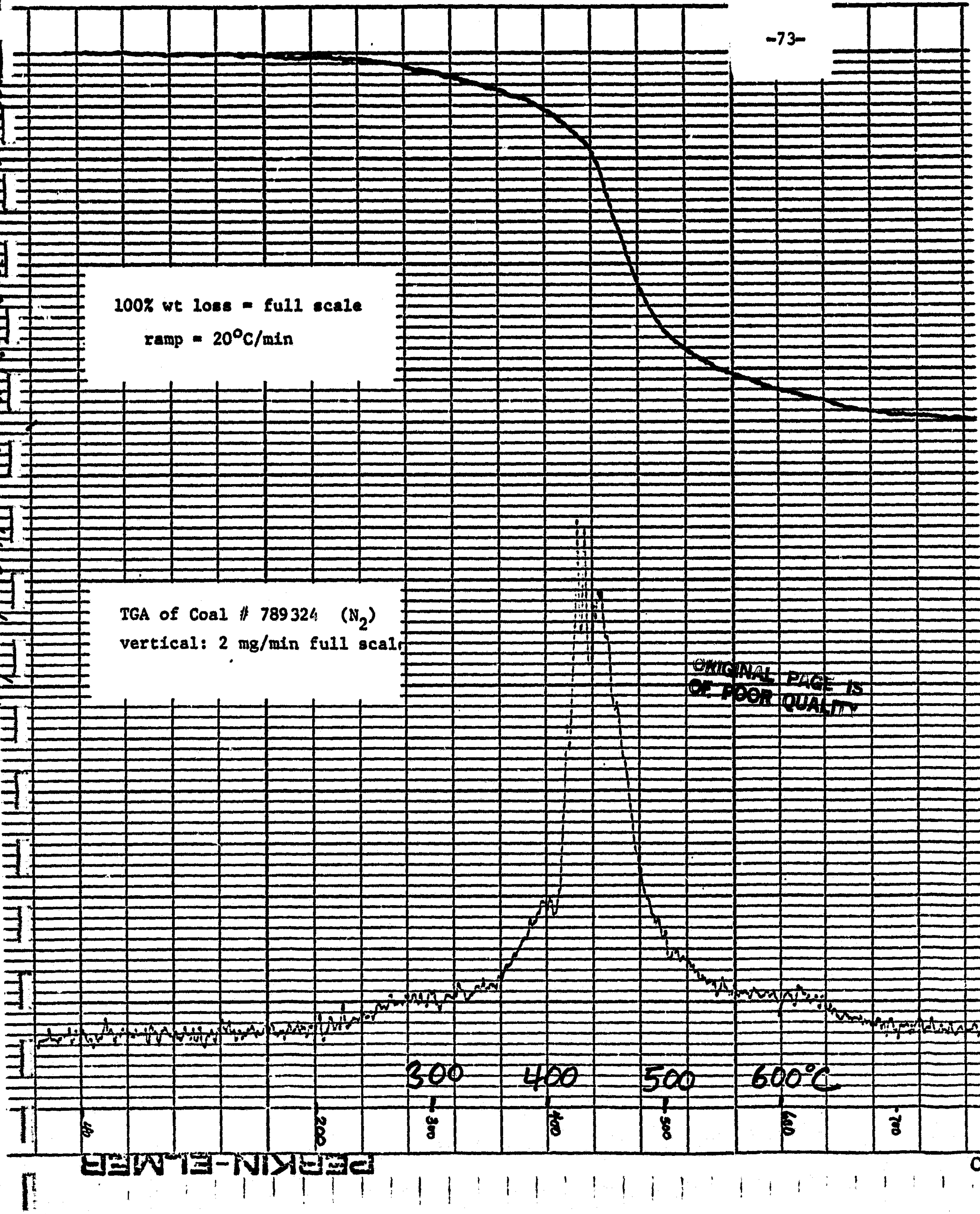
It appears that there are some advantages in using drying conditions of 150°C (vac.) rather than 60° (vac.) and we are considering a change in the pyridine extraction procedure accordingly. However, the results that have been obtained with drying conditions of 60°C (vac.) would not be very different if conditions of 150° (vac.) had been used instead, and there is no reason to doubt the validity of conclusions drawn therefrom.

kh

6.2 Thermogravimetric Curves of Coals and Extrudates

The data of Table 18 (Part 3.6) is based upon analysis of a series of thermogravimetric curves, in which coals and extrudates are heated under a nitrogen purge and their weight losses are continuously measured. The raw curves upon which these data are derived are shown (following pages). For each plot the upper curve is a plot of mass (abscissa) vs. temperature. The lower curve is a first derivative plot, d[mass]/d[T] vs. temperature. Since these are linearly programmed, these are also mass/time plots.

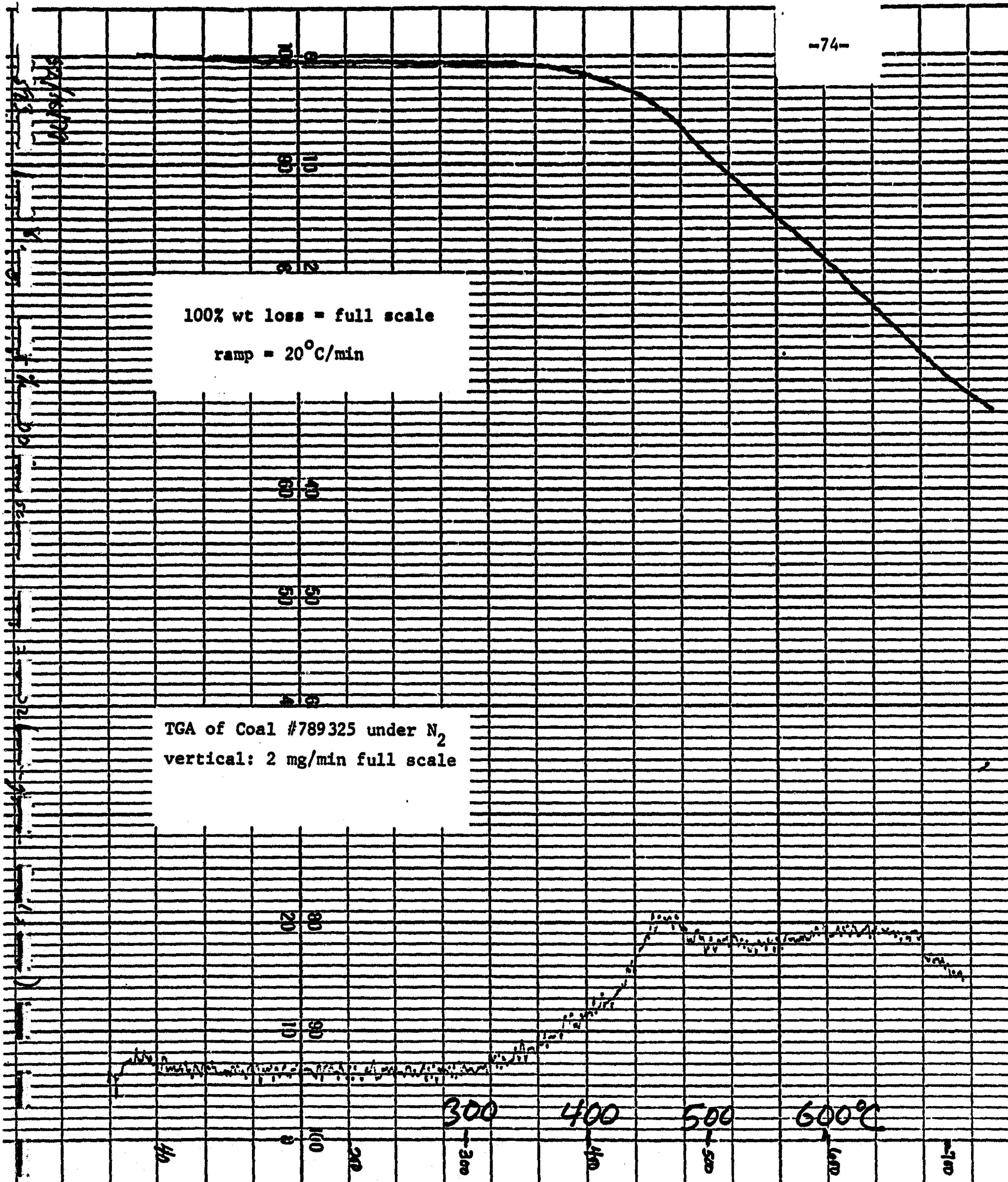
These data were obtained using a Perkin-Elmer TGS-2 vertical furnace unit, with approximately 10-mg samples, under a nitrogen purge of 60 cc/min and at a constant temperature ramp of 20°C/min.


100% wt loss = full scale

ramp = 20°C/min

TGA of Coal # 789324 (N_2)

vertical: 2 mg/min full scal

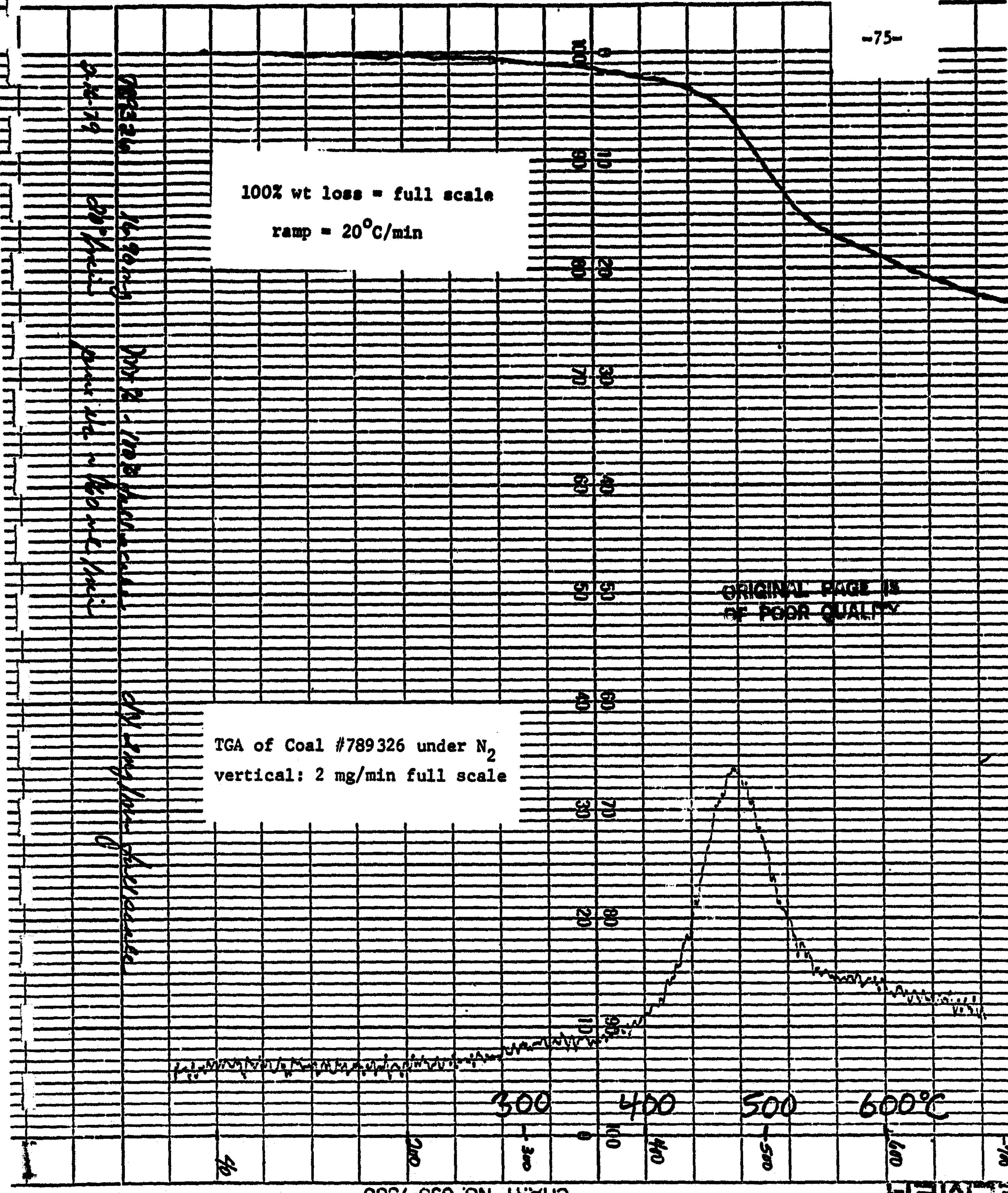


100% wt loss = full scale

ramp = 20°C/min

TGA of Coal #789325 under N_2

vertical: 2 mg/min full scale

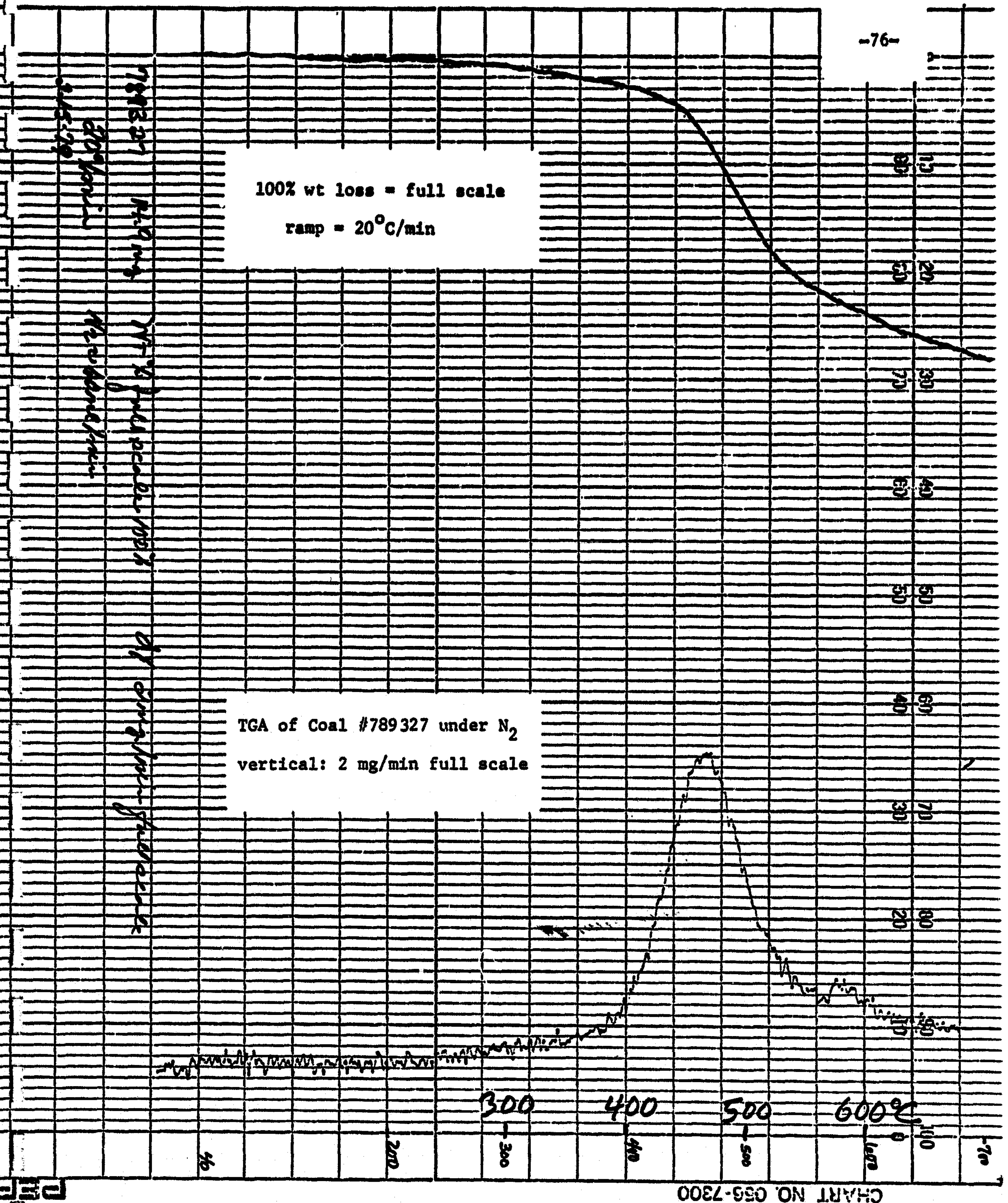


100% wt loss = full scale

ramp = 20°C/min

TGA of Coal #789326 under N_2

vertical: 2 mg/min full scale

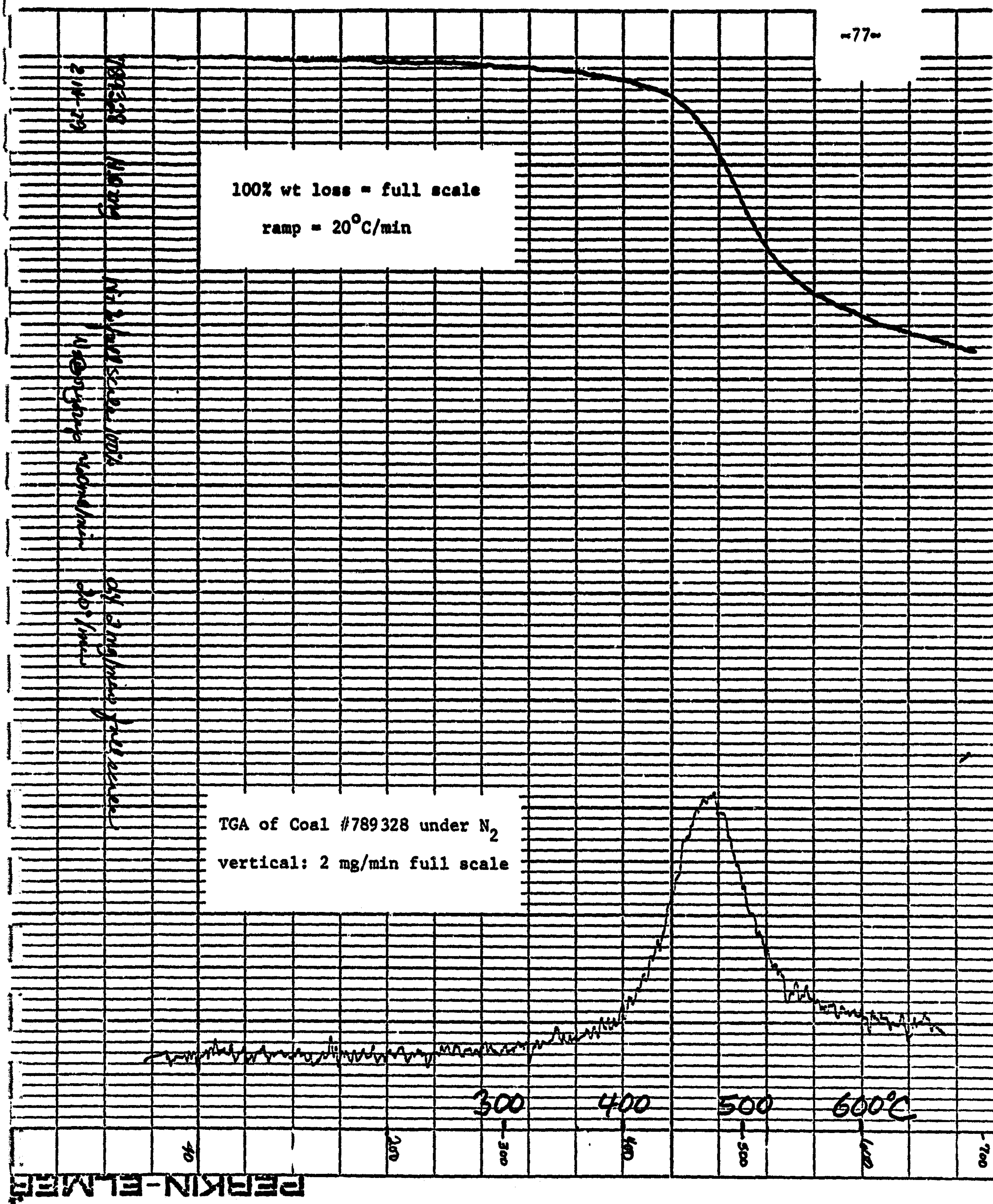


100% wt loss = full scale

ramp = 20°C/min

TGA of Coal #789327 under N_2

vertical: 2 mg/min full scale

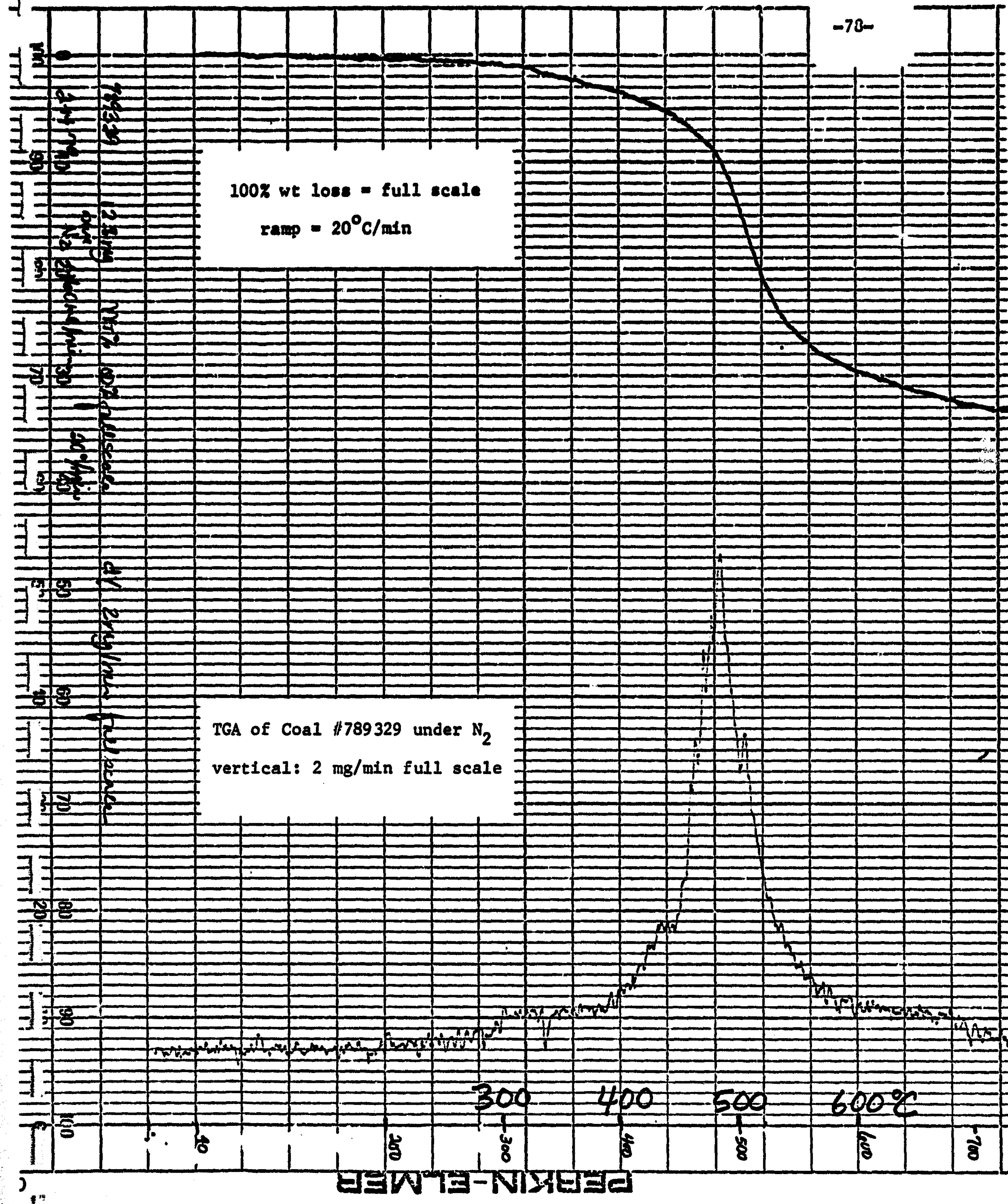


100% wt loss = full scale

ramp = 20°C/min

TGA of Coal #789328 under N_2

vertical: 2 mg/min full scale

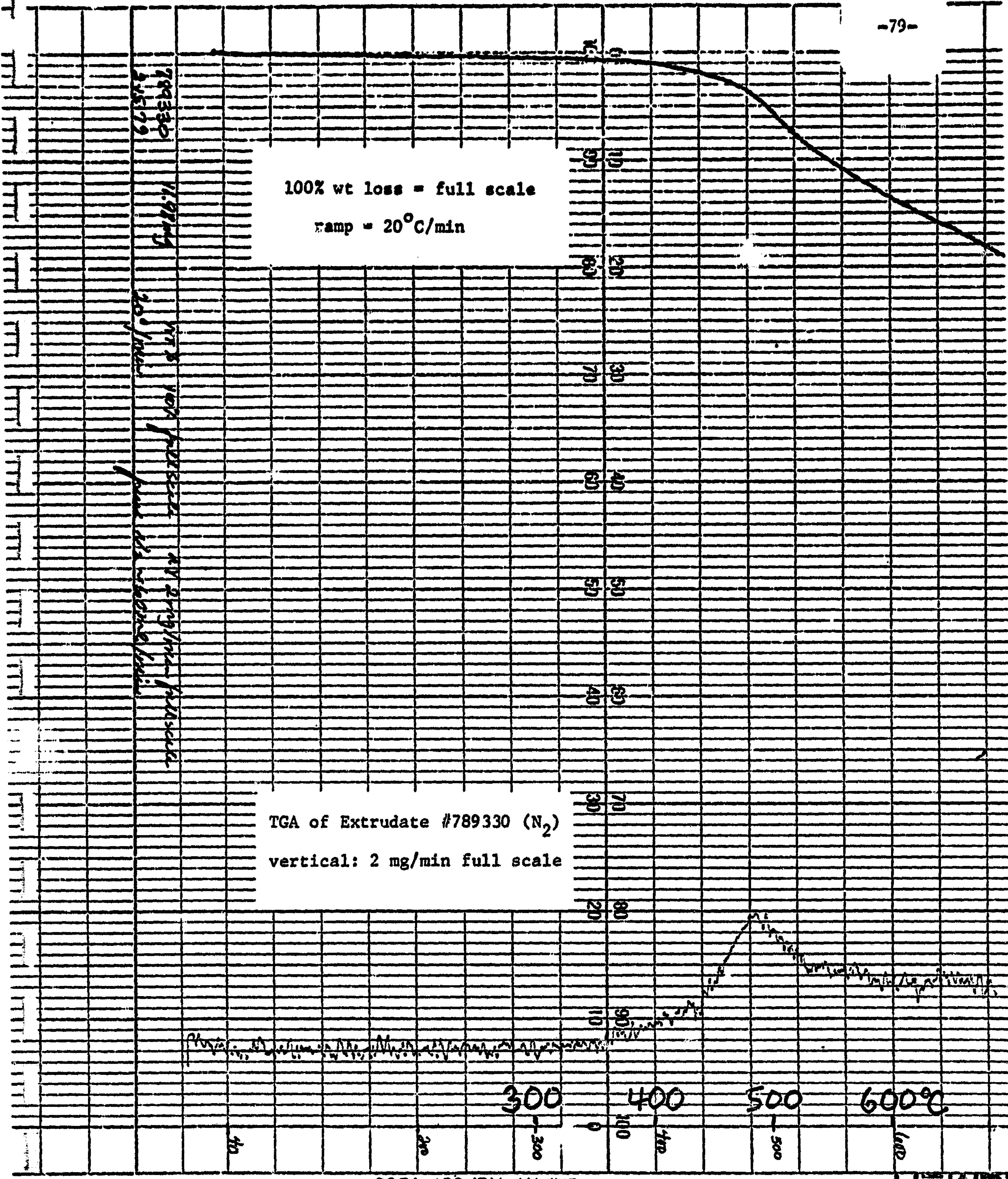


100% wt loss = full scale

ramp = 20°C/min

TGA of Coal #789329 under N_2

vertical: 2 mg/min full scale

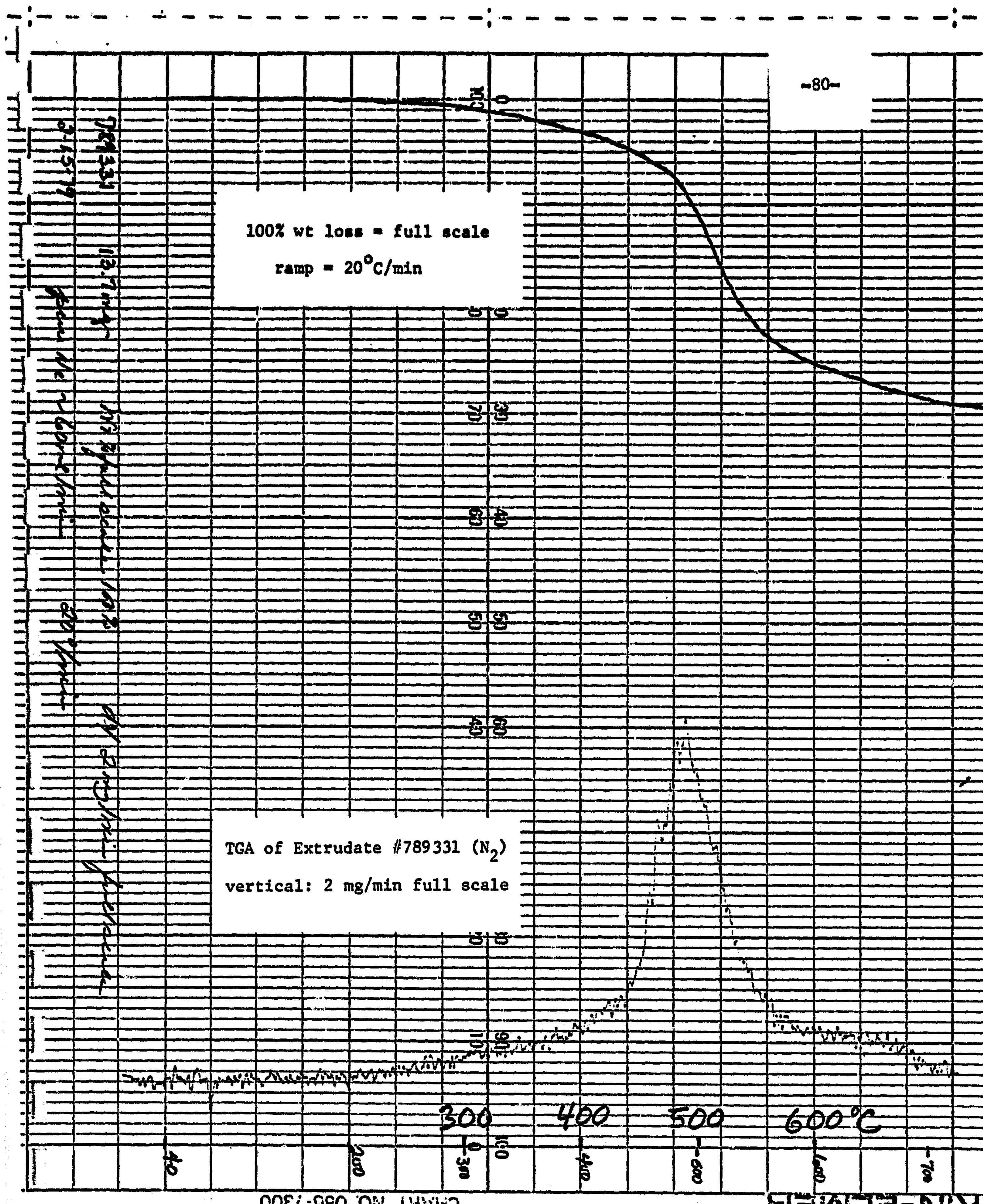


100% wt loss = full scale

ramp = 20°C/min

TGA of Extrudate #789330 (N_2)

vertical: 2 mg/min full scale

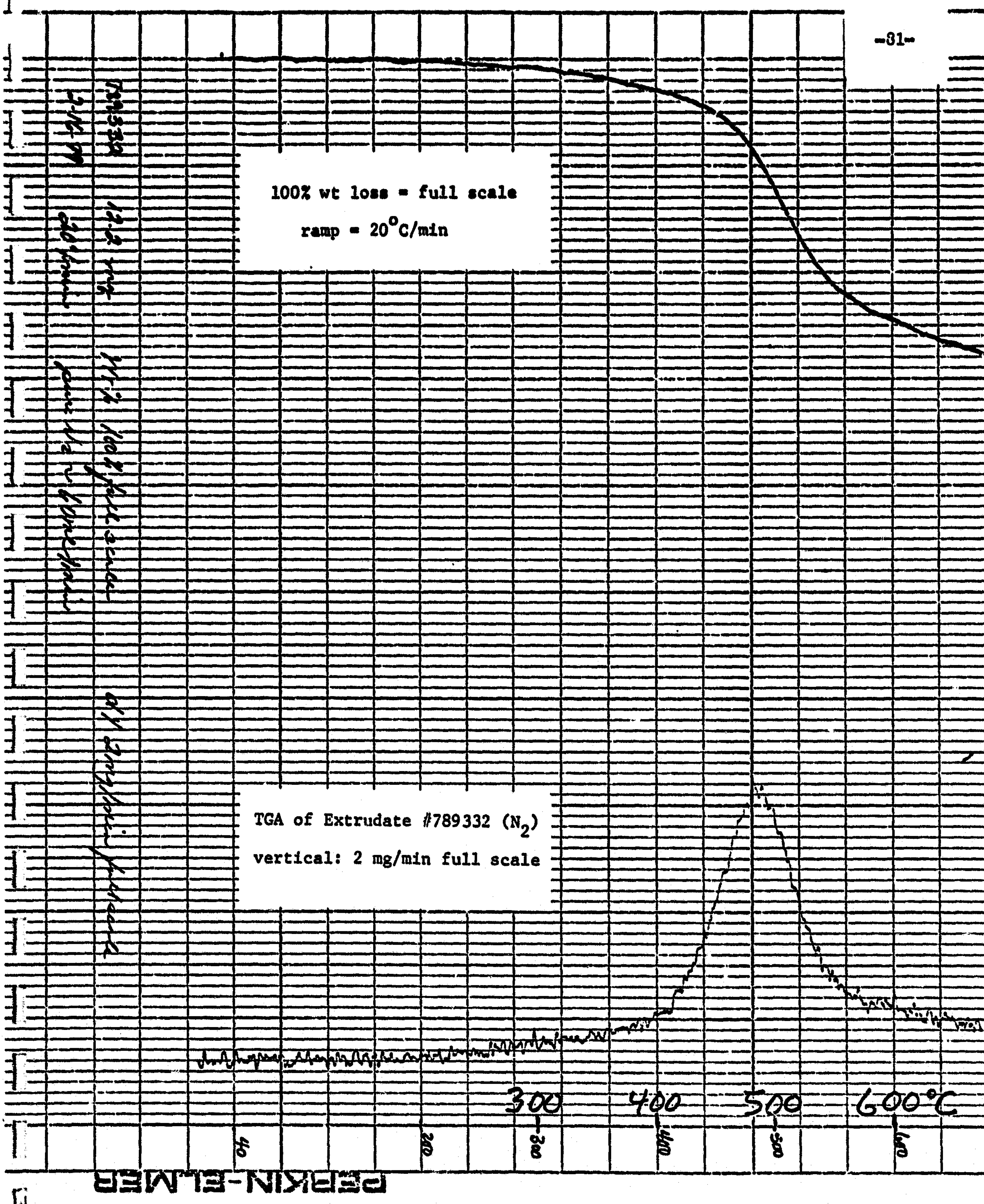


100% wt loss = full scale

ramp = 20°C/min

TGA of Extrudate #789331 (N_2)

vertical: 2 mg/min full scale

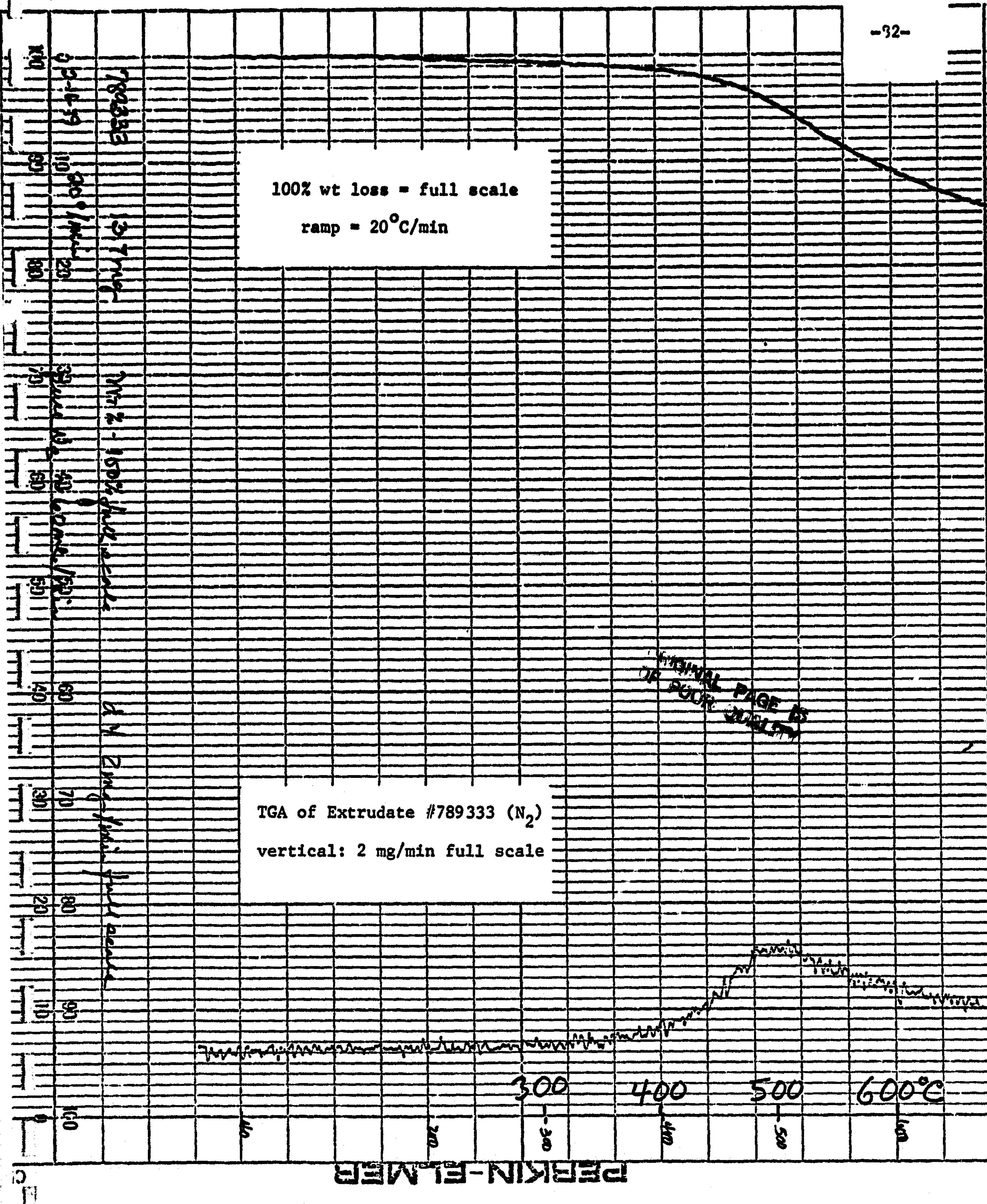


100% wt loss = full scale

ramp = 20°C/min

TGA of Extrudate #789332 (N_2)

vertical: 2 mg/min full scale

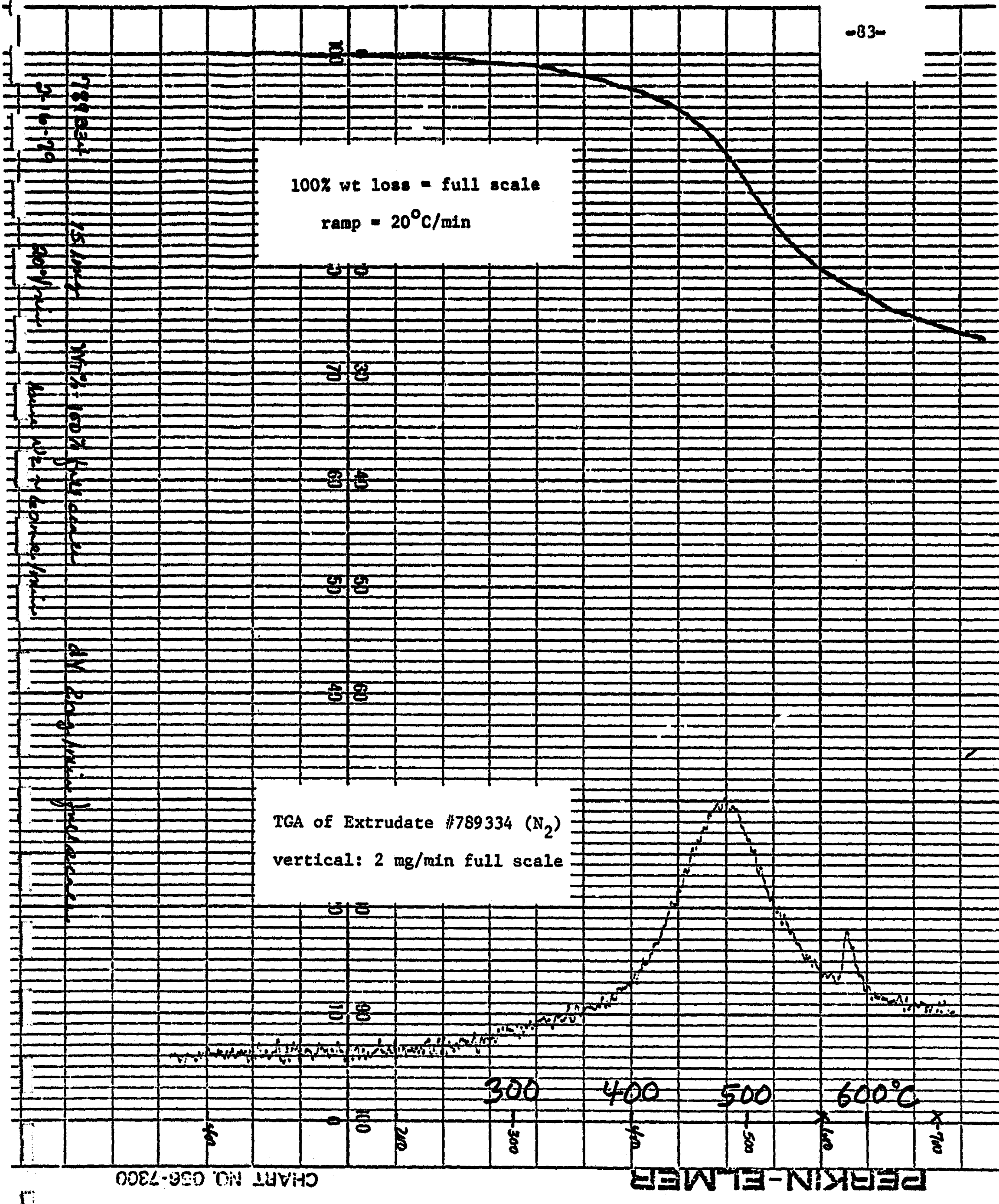


100% wt loss = full scale

ramp = 20°C/min

TGA of Extrudate #789333 (N_2)

vertical: 2 mg/min full scale

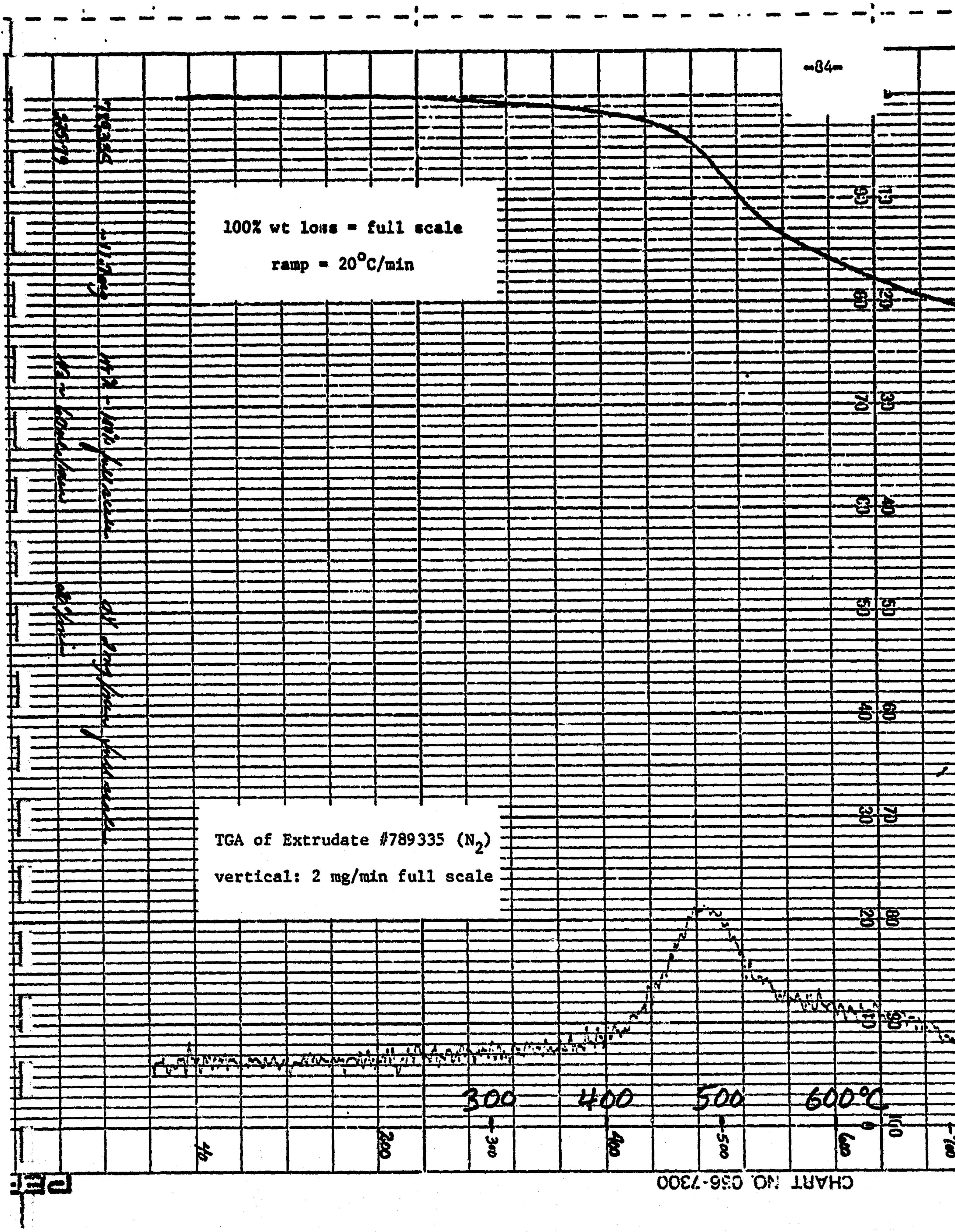


100% wt loss = full scale

ramp = 20°C/min

TGA of Extrudate #789334 (N_2)

vertical: 2 mg/min full scale

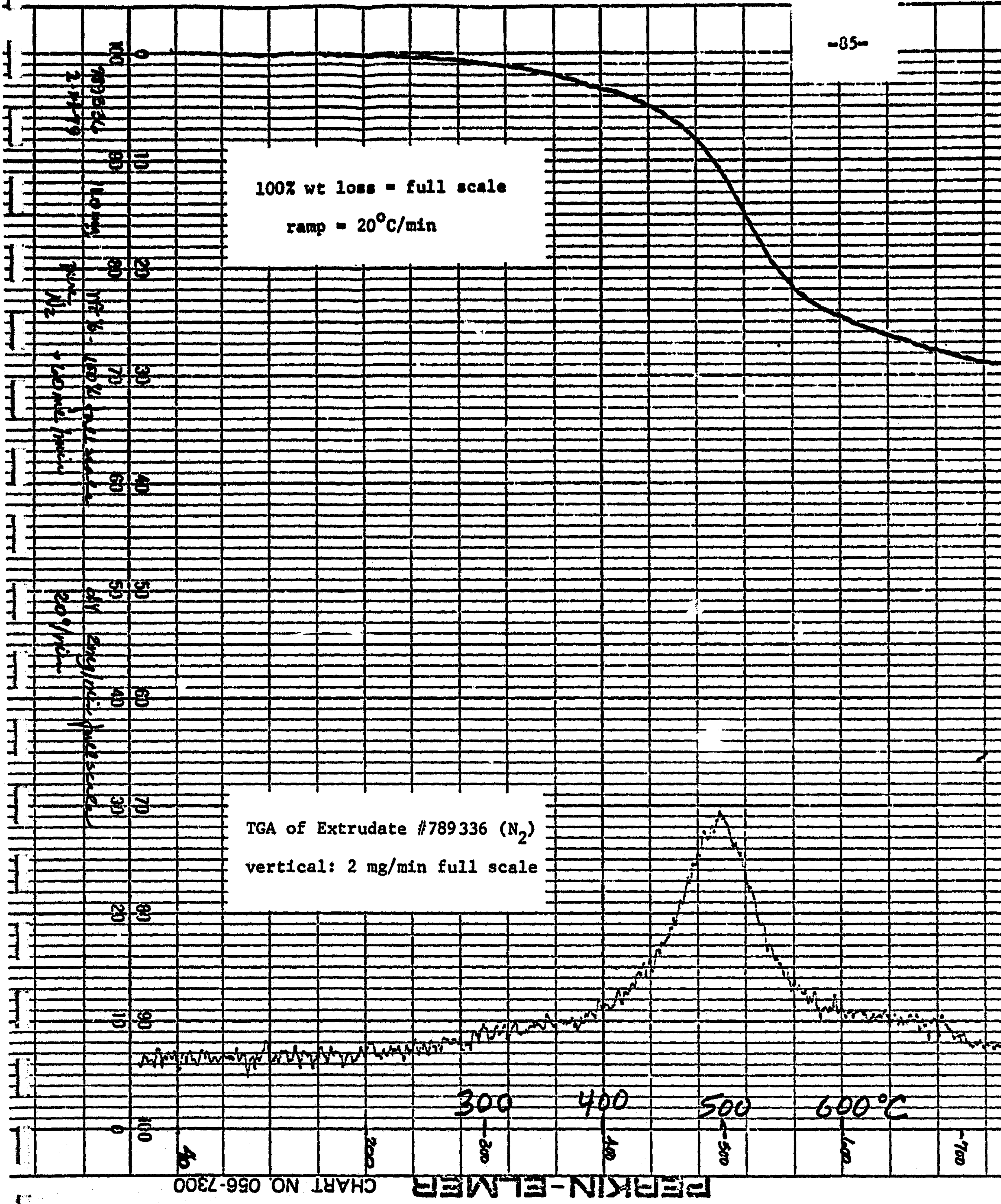


100% wt loss = full scale

ramp = 20°C/min

TGA of Extrudate #789335 (N_2)

vertical: 2 mg/min full scale

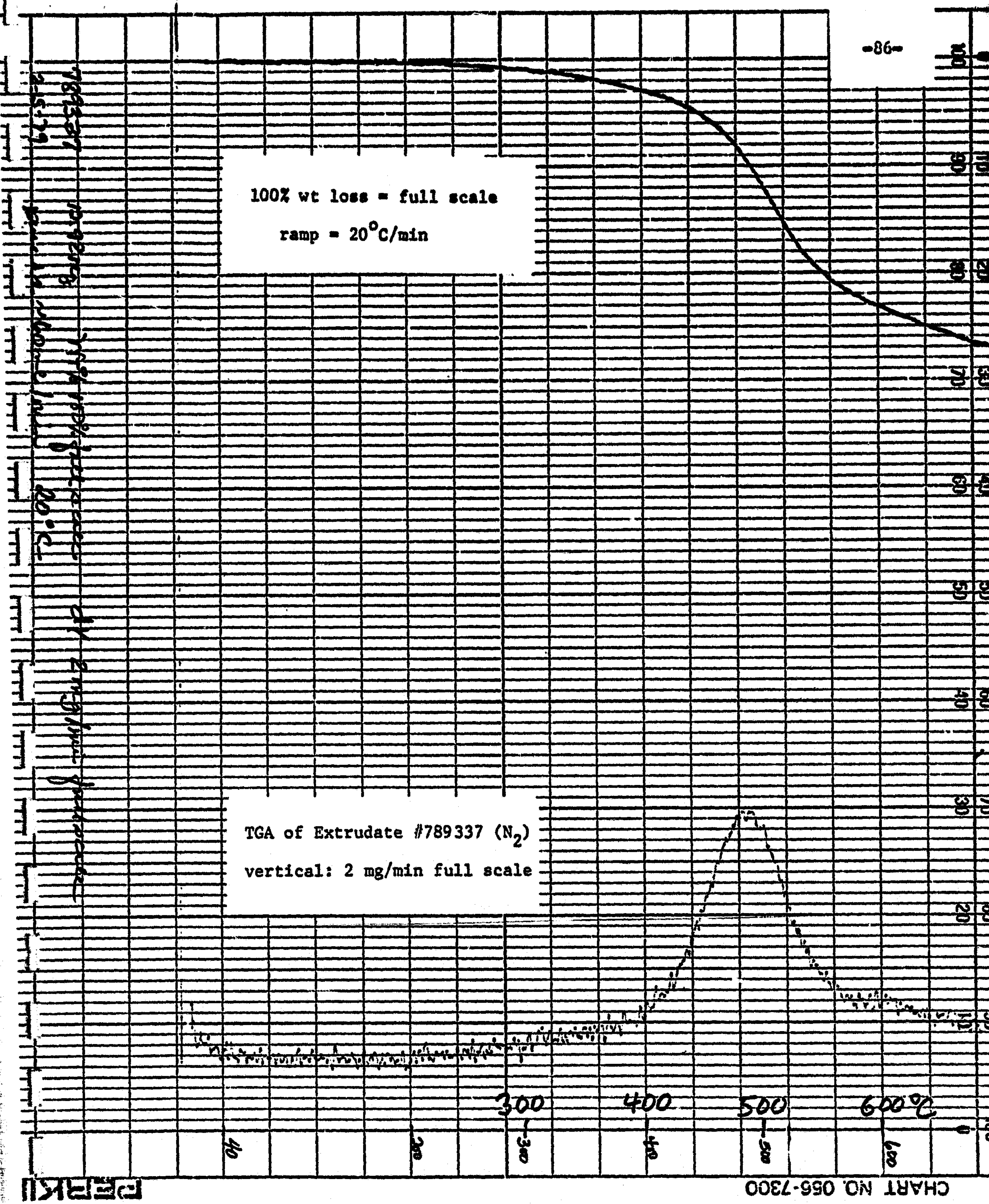


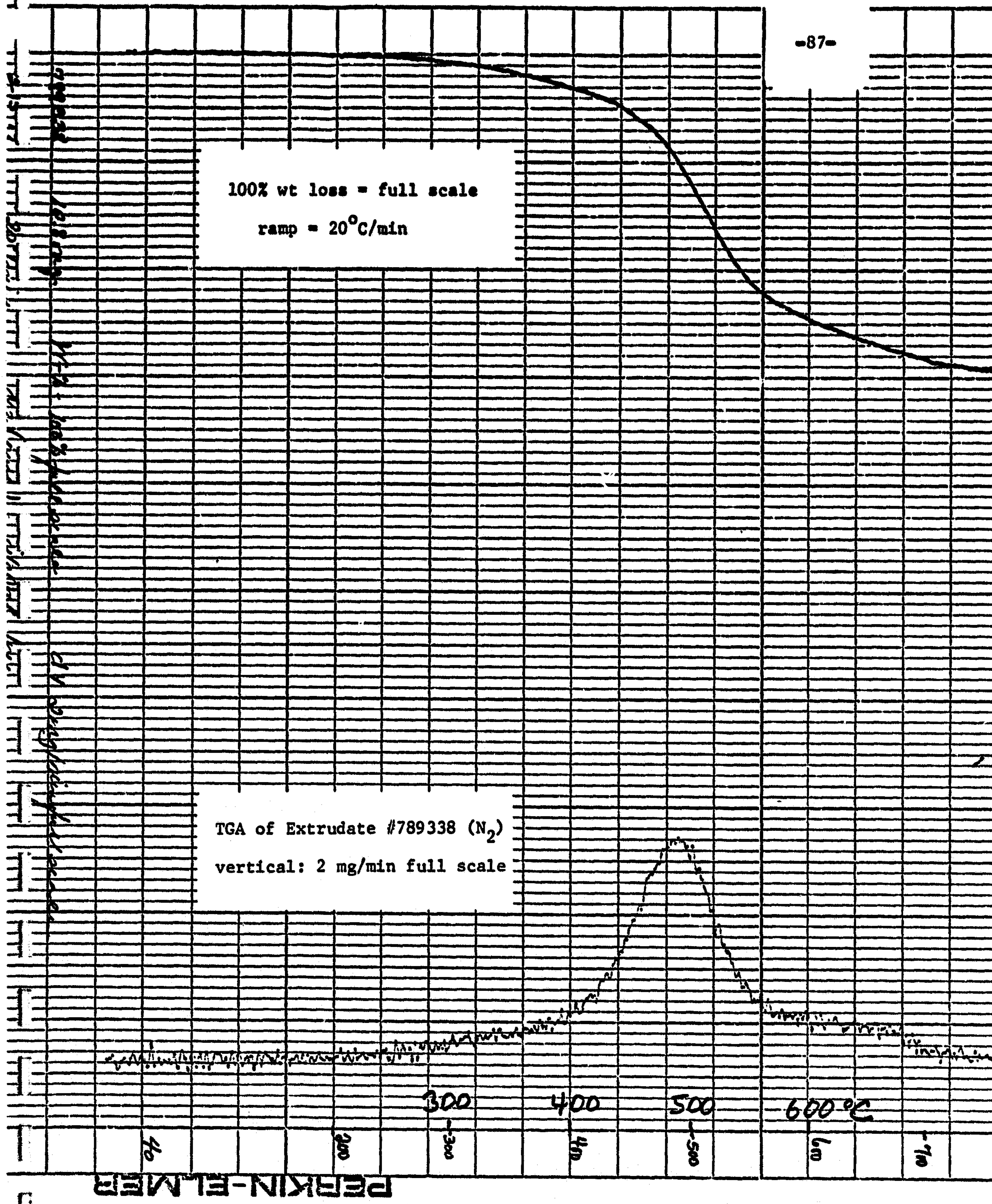
100% wt loss = full scale

ramp = 20°C/min

TGA of Extrudate #789336 (N_2)

vertical: 2 mg/min full scale


100% wt loss = full scale
ramp = 20°C/min
TGA of Extrudate #789337 (N_2)
vertical: 2 mg/min full scale
300
400
500
600°C
40
200
300
400
500
600
100
90
80
70
60
50
40
30
20
10
0
789337
2-5-79
20°C
CHART NO. 056-7300

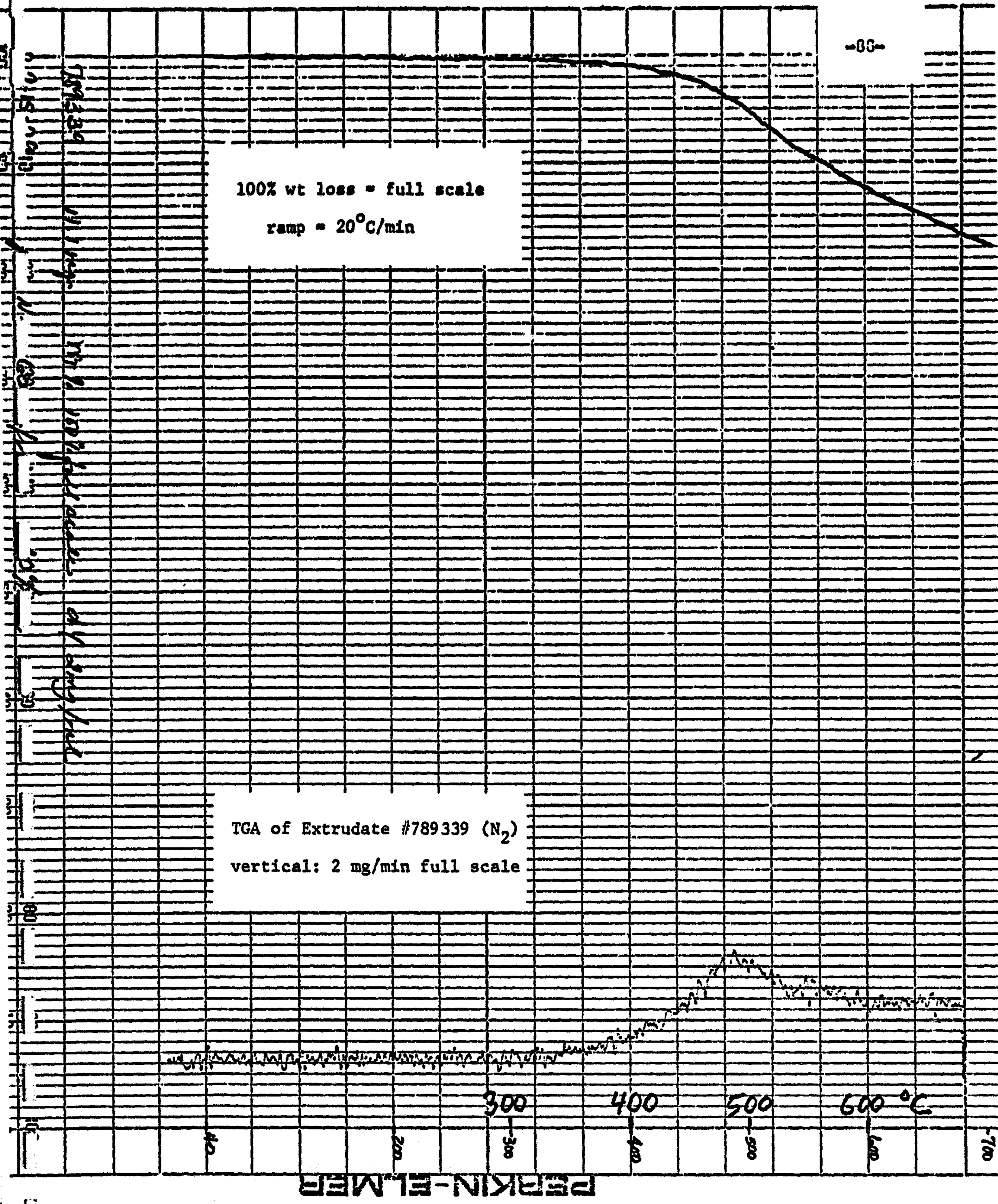


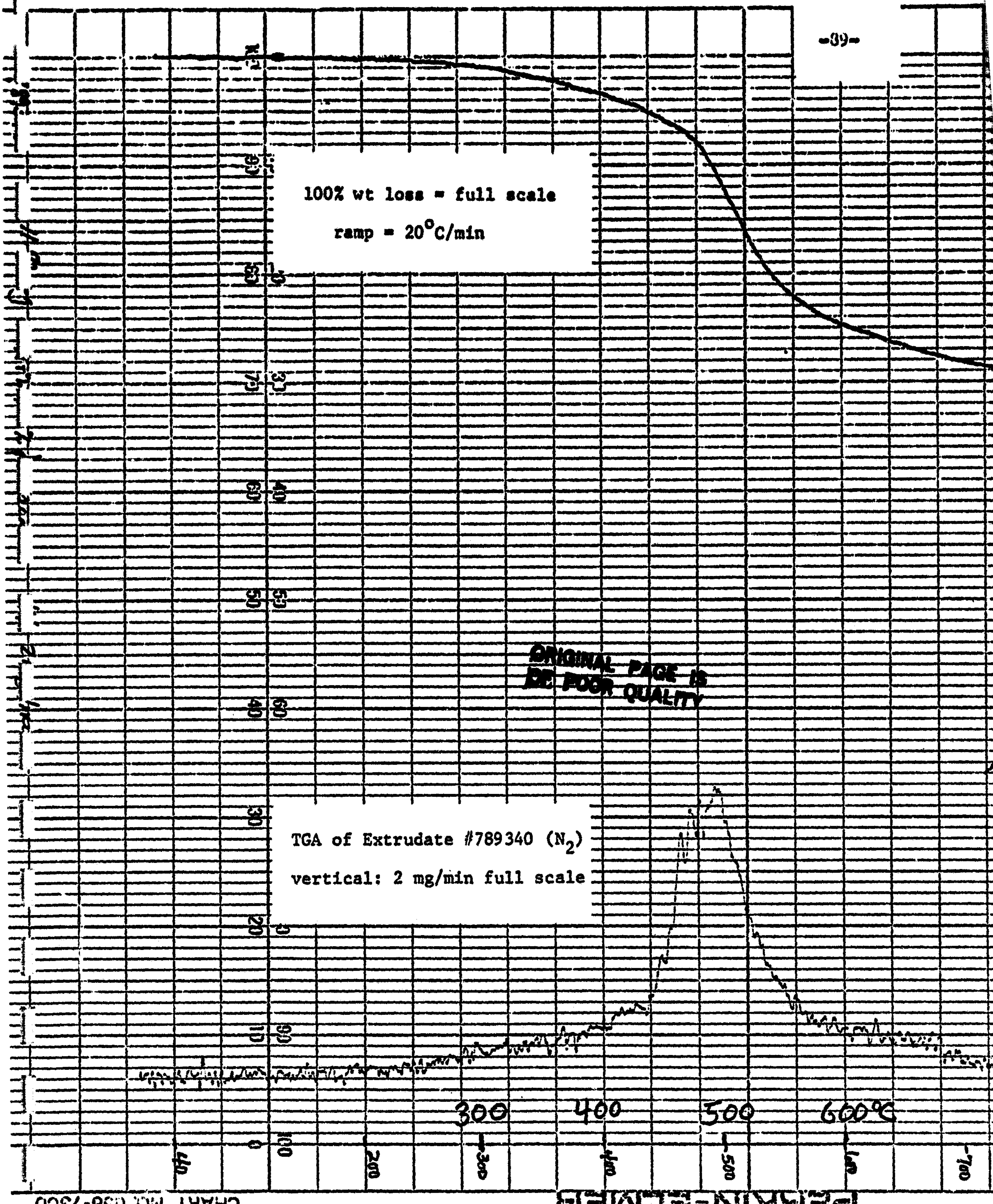
100% wt loss = full scale

ramp = 20°C/min

TGA of Extrudate #789338 (N_2)

vertical: 2 mg/min full scale


100% wt loss = full scale
ramp = 20°C/min
TGA of Extrudate #789339 (N_2)
vertical: 2 mg/min full scale
789339 wt loss 100% full scale
dy/dt 2 mg/min
14.15 mg
N_2
20°/min
300
400
500
600 °C
100
200
300
400
500
600
700
PERKIN-ELMER

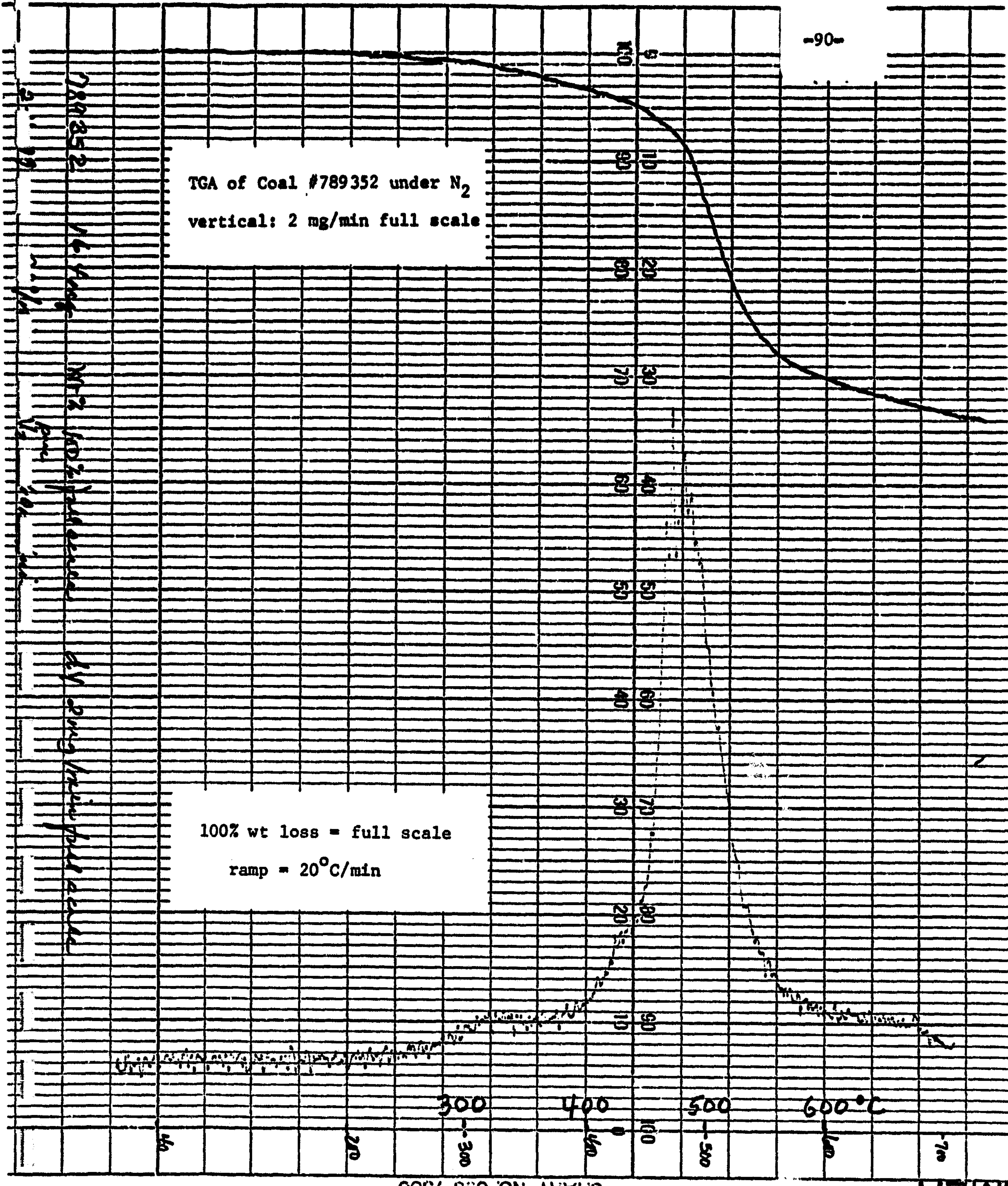


100% wt loss = full scale

ramp = 20°C/min

TGA of Extrudate #789340 (N_2)

vertical: 2 mg/min full scale



TGA of Coal #789352 under N_2

vertical: 2 mg/min full scale

100% wt loss = full scale

ramp = 20°C/min

6.3 The Microclave Procedure

The Mori microclave reactor is described in general terms in Part 3.7.1 and shown schematically in Figure 2. The reactor is an upright steel tube capped to encase the coal/tetralin slurry, lined with a disposable glass tube 13 x 100 mm, and fitted with a 2 in. (diam) pressure gauge, a 1/4 in. stainless steel Swagelok valve, and a 1/16 in. type J thermocouple (Omega ICSS-116G-12).

After charging (as described in Part 3.7.1) the reactor is flushed by pressurizing with nitrogen and venting for at least three cycles, is pressurized to 1500 psi with hydrogen, and is then held at this pressure for 30 min. (leak test). Hydrogen pressure is then vented down to 500 psig at ambient temperature, and the unit placed in the fluidized sandbath furnace (Tecam SBL-2) which has been preset at 435°C. The initial hydrogen partial pressure at reaction temperature is 1190 psi.

During a run, both bath temperature and reactor temperature were monitored regularly. Maintenance of the bath temperature at the desired set point is easy; however in our experience the furnace temperature may on occasion drift away from the set point if operator adjustments are not made at fairly short intervals. By checking temperature each minute during a run, a highly uniform temperature is maintained.

For nine pairs of duplicate runs on the microclave the standard deviation of percent conversion is ± 1.8%, which drops to ± 1.4% when the 'worst' pair is excluded. [Raw data are shown in Table 20.] This standard error is the square root of the sum of variances associated with sample inhomogeneity, the microclave run itself, and the Soxhlet analytical procedure used for the conversion analysis. This is an unusually small standard error for operations of this type.

6.4 The Stirred Clave Procedure

The stirred autoclave liquefaction runs (Part 3.7.2) use a standard Autoclave Engineers 300-cc stirred clave fitted with thermocouples, pressure gauge, and the facilities for gas input, rupture disc, vent line, trap for condensibles, and head gas sampling (Figure A-1). Valves attached to the reactor are 1/4 in. stainless steel; other valves are 1/8 in. stainless steel. To the autoclave is charged typically 35 g pulverized coal and 70 cc tetralin. The clave is then purged with helium, and charged to 560 psig hydrogen at ambient temperature.

Clave warm-up takes about 20 min. (Figure A-2). For a 60-min. autoclave run at 454°C (850°F) the time of reaction starts when the clave contents reach 399°C (750°F). Temperature is maintained at 454° with a high degree of uniformity (within ± 5°). The initial hydrogen partial pressure is calculated to be about 1390 psig; total pressure typically continues to increase at 454°C for the first half hour of reaction, eventually lining out at 1800-50 psig, and showing a very slight decrease in the second half-hour of reaction (Figure A-2).

The attached memorandum and figures includes observations by Professors Watters and Collins. Their comments concerning potential error sources in the estimation of pyridine-solubles are of particular interest.

The results of these stirred clave runs are reported in Table 21. In addition to these data, head gases from all four stirred clave runs were analyzed by quantitative gas chromatography and were found to be of similar composition:

Hydrogen	72 - 77%
Methane	13 - 14%
Ethane	3.3 - 4.6%
Propane	1.0 - 1.4%
Propene	0.0 - 0.08%
C_4's	0.2 - 0.3%
C_5's	0.03 - 0.15%
CO	0.0 - 0.7%
CO_2	0.6 - 1.6%
N_2	0.2 - 0.4%
Closure	93 - 97%

C-2

University of Kentucky
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(606) 252-5535

December 11, 1979

MEMORANDUM

TO: W. G. Lloyd

FROM: Jim Watters and Dermot Collins

SUBJECT: Clave Conversions of JPL Samples

The following are the results of hydrogenation tests run on Western Kentucky #9 coal and its extrudate. The tests were run to determine the effect of extruding the coal on its reactivity. The tests were performed at the University of Louisville in a 300c.c. autoclave under approximate H-coal conditions (see Figure 1 and Table 1). All runs were conducted under approximately the same conditions of temperature and pressure (see Figure 2). In each run, the reactor was initially charged with about 560 p.s.i. hydrogen.

From the results, it has been concluded that extruding the coal lowers its reactivity by approximately 10%, based on toluene extraction data. Data based on pyridine extractions are inconclusive due to the variation in conversion. Calculations involving pyridine extraction data are often inaccurate due to the fact that small amounts of material are being used. Small errors in measurement usually produce large percentage errors in conversion. These runs can be duplicated with more attention to pyridine extraction data if necessary.

Encls.

/jso

Table A-1

Reaction Conditions

Temperature: 850°F (455°C)

Donor Solvent: Tetralin

Solvent-To-Coal Ratio: 2/1 (weight basis)

Catalyst: H-coal or none

Organics-To-Catalyst Ratio: 5/1 (weight basis)

Initial Gas Pressure: 560 psig (± 4%)

Reaction Time: 60 minutes

Heat-up Time: 22 minutes (from ambient to 750°F)

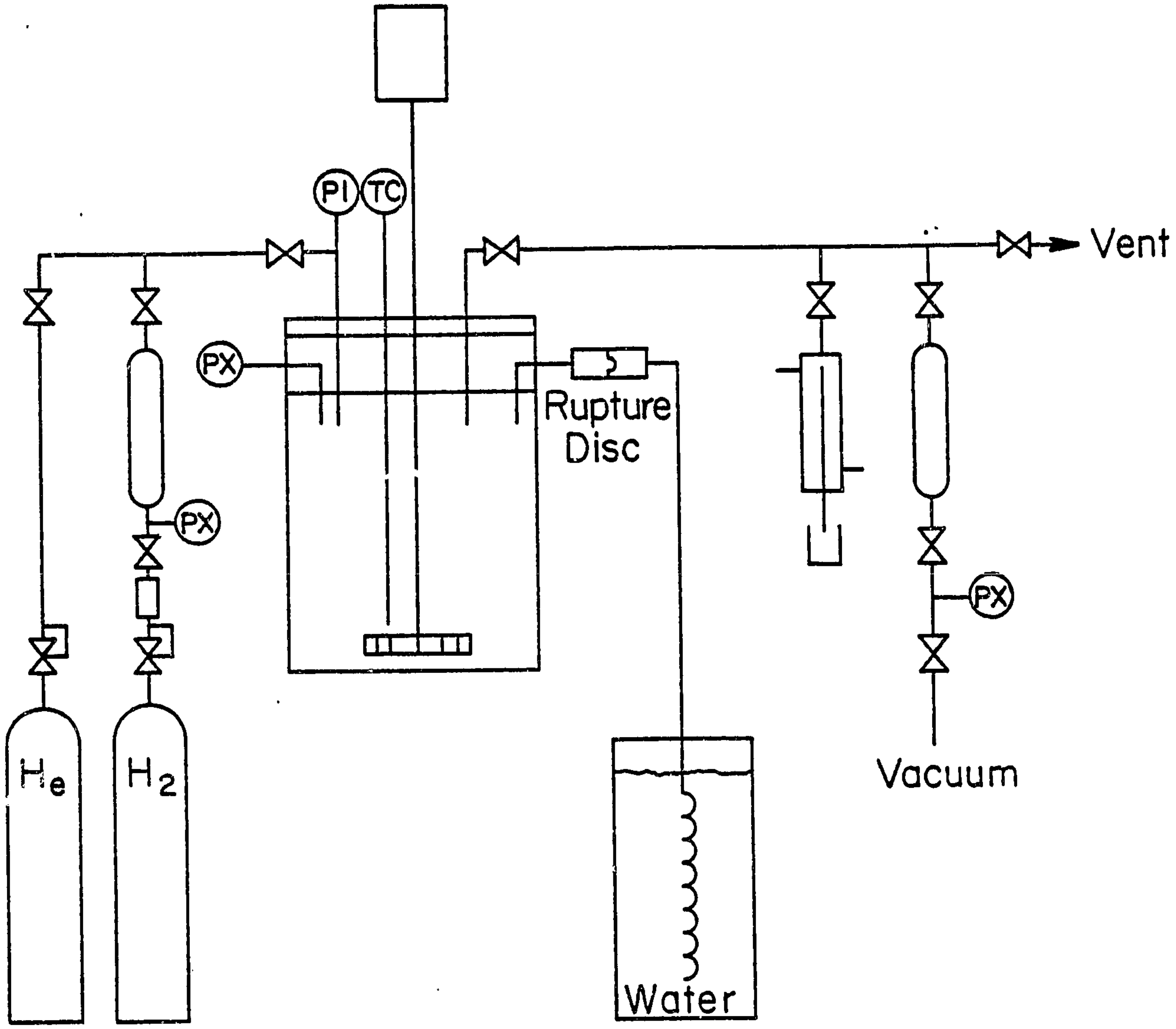

Figure A-1 Schematic of Experimental Apparatus.

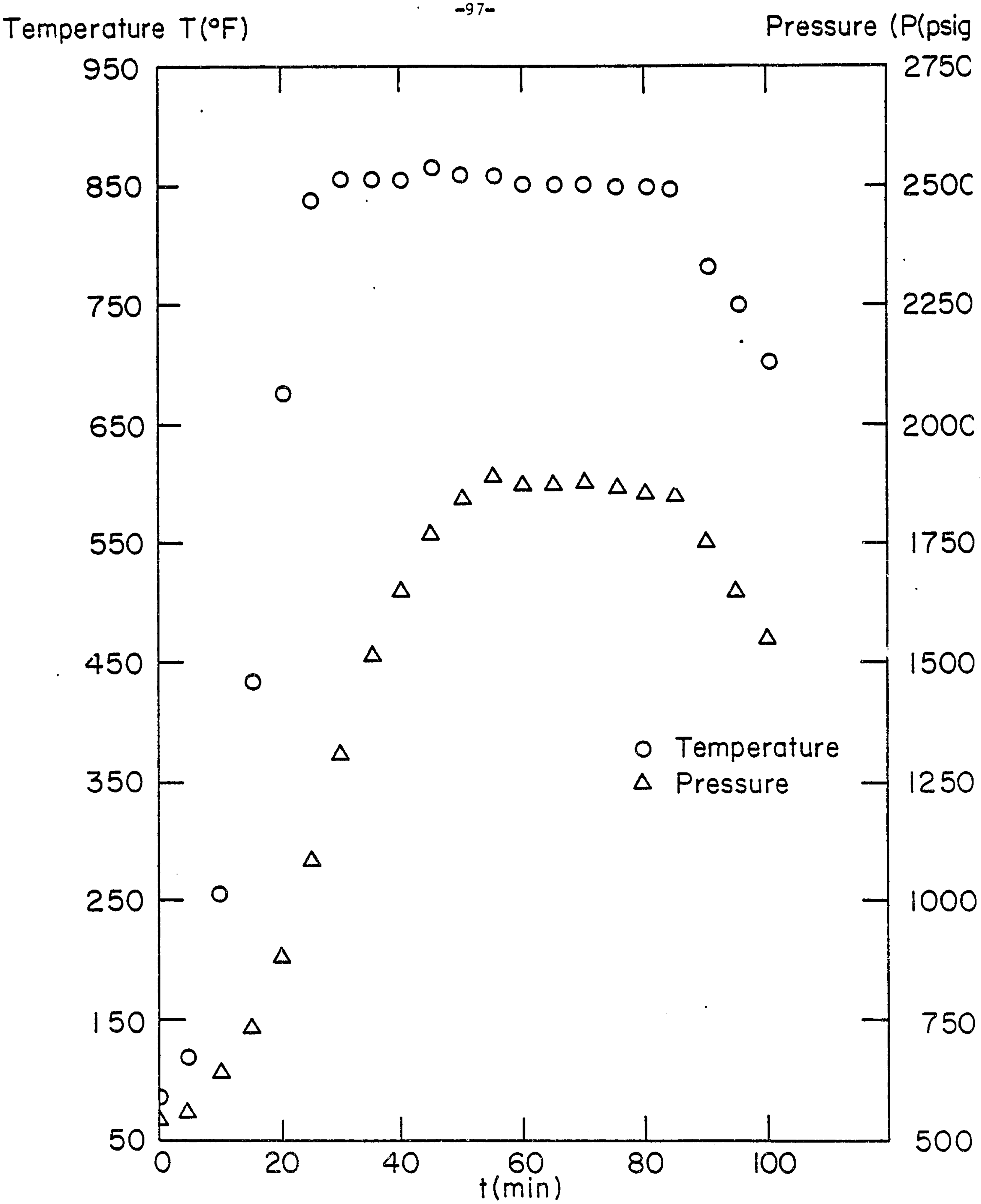

Figure A-2 Typical Temperature and Pressure Profiles.

6.5 A Model for Isothermal Plasticity of Coals

As a spinoff from the previous (1) and present study, members of the Institute staff and of the Coal Pump Project team at JPL have become interested in the interpretation of the plasticity-time curves observed when coals are tested under isothermal conditions in a Gieseler plastometer. This has led to a draft paper to be presented before the Division of Fuel Chemistry, American Chemical Society, at the Houston meeting, March 1980.

A draft of this paper is attached.

A MODEL FOR THE ISOTHERMAL PLASTOMETRIC BEHAVIOR OF COALS

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Pasadena, CA 91103

Introduction

The plasticity of bituminous coals in the range 350-500°C is of critical importance in thermomechanical fluidization such as is required for coal pumping by heated screws (1-3) and in hydrogenolysis in the absence of added solvent (4,5). The fact that the optimum reaction temperatures for three major current liquefaction technologies are nearly identical (6) and are close to the fluidity maxima for many plastic coals suggests that the processes comprising coal "melting" are critically important to hydroliquefaction. More generally, coal plasticity is obviously involved in caking problems (7-10).

The most widely used method of measuring coal plasticity was developed by Gieseler (11). With minor modifications this remains a standard procedure (12); its relationship to other measurements has been discussed elsewhere (13). This method measures the resistance of a mass of well-packed pulverized coal to the rotation of a rabble-arm stirrer which is driven through a constant-torque clutch. At low temperatures the solid mass completely immobilizes the stirrer shaft. In the standard Gieseler procedure the coal is heated at a uniform rate of 3°C/min. As the coal begins to soften -- typically at about 390°C -- the stirrer shaft commences to turn slowly. As temperature increases the coal becomes more fluid and the shaft turns more rapidly, eventually achieving a maximum rate. The coal melt -- actually a heterogeneous mixture of solids, molten phase and gaseous pyrolyzate -- then undergoes a thickening or "coking"; the stirrer shaft turns progressively more slowly, and eventually stops. Gieseler data are recorded in units of dial divisions per min (ddpm), where 100 ddpm = 1 shaft rotation per min. For three bituminous coals of varying plasticity the standard Gieseler data are shown in Table 1.

The Isothermal Model

It is often useful to study phenomena under isothermal conditions. Gieseler plastometry lends itself to such studies, since sample warmup time in the standard crucible (2-3 min.) is short in comparison with the usual melting/coking time scale (20-120 min.). Isothermal Gieseler plastometry has been explored by Fitzgerald (14,15) and by Van Krevelen and coworkers (16,17). A plot of log(ddpm) against time shows a long linear coking region (14,15).

Figure 1 (open circles) shows the isothermal plastometric curves at 410-2°C obtained with the three coals described in Table 1. Both the maximum fluidities and the periods of fluidity are seen to vary substantially among these coals.

The linearity of the coking slopes has been interpreted to imply a sequence of first-order reactions (14-17):

$$C \rightarrow M \qquad k(\text{init}) \qquad (\text{first-order melting}) \tag{1}$$

$$M \rightarrow S \qquad k(\text{coke}) \qquad (\text{first-order coking}) \tag{2}$$

where C, M and S represent the meltable portion of the original coal, the fraction which is molten (metaplast), and the fraction which is resolidified (coked). This scheme gives rise to the rate law:

$$d[M]/dt = k_i[C] - k_c[M] \tag{3}$$

There are two problems with this scheme. First, it does not generate model curves which resemble observed curves. Specifically, it predicts the rate of increase of fluidity during the softening process to decelerate progressively, while in fact this increase is exponential with time over most of the melting period. Second, this scheme specifically assumes that Gieseler fluidity is a linear measure of the molten fraction or metaplast; but that assumption is mistaken, as we will show.

For the purpose of more closely modeling the actual isothermal curves we propose a second melting process, such that the rate of increase of fluidity is dependent upon the concentrations of both metaplast and unmelted fraction:

$$C + M \rightarrow 2\,M \qquad k(\text{melt}) \tag{4}$$

The rate law now acquires a third term:

$$dF/dt = k_i[C] + k_m[C][M] - k_c[M] \tag{5}$$

(We use F for fluidity, rather than [M] for metaplast, on the left-hand side). The virtue of Equation 5 is that, for most isothermal runs, it can provide a fairly good fit to the experimental data, and therefore can define the experimental curves in terms of numerical constants associated with the melting and coking processes. The solid points in Figure 1 are values generated by the Equation 5 model, using the values given in Table 2. It is a characteristic of this model that the experimental points in the vicinity of maximum fluidity tend to be higher than those generated by the model. This may reflect formation of gas bubbles, which lead to anomalously high experimental readings.

In applying this model, the least-squares melting and coking slopes are calculated from the experimental data; we use all data between 1 ddpm and one fourth the maximum observed fluidity. The extrapolated maximum fluidity (emf) and the time of maximum fluidity are taken from the intersection of these slopes.

From these determinations, approximate values for the model constants can be estimated empirically from the cubic equations:

$$\frac{m(\text{melt})}{k(\text{melt})} = -0.3179 + .71507 \times R - .15991 \times R^2 + .012348 \times R^3 \qquad (6)$$

$$\frac{m(\text{coke})}{k(\text{coke})} = -0.6934 + 1.1504 \times R - .26779 \times R^2 + .020826 \times R^3 \qquad (7)$$

$$\ell n[k(\text{init})] = -16.127 + 2.8478 \times P - .25098 \times P^2 + .005726 \times P^3 \qquad (8)$$

where m(melt) and m(coke) denote the melting and coking slopes, R = m(melt)/m(coke), and P = [(m(melt) + m(coke)) x t(max flu)]. These equations give fairly good fits when k(melt) is in the range 0.5 to 4 min.^{-1} and k(coke) is in the range 0.2 to 1.5 min.^{-1}. To relate the conceptual molten fraction [M] to the observed ddpm, the emf from a model curve is compared with that from the experimental curve. For example, Ohio #9 seam coal at 411° has an experimental emf of 81.3 ddpm, and a calculated emf (using the k values of Table 2) of [M] = 0.683. When each datum in the model curve is multiplied by the factor 81.3/0.683, the model fluidities are converted to units of ddpm. [Detailed procedures and programs for these estimates are available from the authors.]

Effect of Temperature

Isothermal curves were obtained upon Kentucky #11 seam coal at five additional temperatures, in the range 400-460°C. Values of the model constants are given in Table 3. An Arrhenius plot of the model constants k(melt) and k(coke) is shown in Figure 2. For this coal the value of the apparent E_a for k(melt) (best 5 of 6 data) is 173 ± 13 kJ; that for k(coke) (also best 5 of 6) is 228 ± 6 kJ. Viscosities commonly show an analogous "activation energy of viscosity" (18,19). The apparent E_a of maximum fluidity is approximately 600 kJ, high when compared with those for asphalt (120-150 kJ) and glass (390-400 kJ) (20,21).

When the temperature dependencies for the parameters of this model have been estimated from the data of Table 3, isothermal curves may be calculated for any interpolated temperature, or for any extrapolated temperature close to the range of experimental data. Figure 3 shows a family of fluidity envelopes for the Kentucky #11 seam coal, based upon data calculated for the range 392-468°C. Each curve is an "isofluidity" envelope, open at the top. Figure 3 is read along horizontal (isothermal) lines. At 430° this coal exhibits a plastic period (fluidity greater than 1 ddpm) from 2 to 30 min., and has a fluidity exceeding 100 ddpm from 5 to 20 min. This projection, which will afford markedly different envelopes for different coals, may find use in applications in which the plastic properties of bituminous coals are important.

Discussion

The organic structures of coals are numerous and varied. Bonds which thermally cleave at useful rates at 390-400°C (dissociation energies of 210-230 kJ) are not the same as those cleaved at 460° (240-260 kJ). A major reason for isothermal measurements is to control this variable.

Gieseler fluidity can be related to viscosity units by calibrating with standard fluids. Measurements with the plastometer used in this study and with appropriate standards (22) in the range 500 - 10,000 poise yield a linear calibration:

$$\ell n(\text{poise}) = 16.2789 - 0.96787\ \ell n\ (\text{ddpm}) \qquad (9)$$

with a correlation coefficient of .9997. Actual coal melts are heterogeneous (7,16), pseudoplastic (23), and viscoelastic in their later coking stages (24). It is nevertheless useful to interpret Gieseler fluidities as estimates of true viscosities.

Nicodemo and Nicolais (25) and Fedors (26) have shown the viscosity of Newtonian suspensions of solids to conform to the expression:

$$\eta/\eta_o = \exp(a\phi) \qquad (10)$$

where η, η_o, and ϕ are the suspension viscosity, solvent viscosity, and solids fraction. Data obtained by Lee (27) show the logarithm of the maximum fluidity of coal blends to vary linearly with composition. These observations are telling us the same thing: that the logarithm of fluidity, not fluidity itself, is a direct measure of the molten fraction. If we assume that a fluidity of 1 ddpm corresponds to the maximum solid fraction ϕ_{max}, we can project the relationship:

$$\ell n(F) = \ell n(F°)\cdot[1 - \frac{\phi}{\phi_{max}}] \qquad (11)$$

To use Equation 11 we need estimates of ϕ_{max} and of the fluidity of pure metaplast, F°. The maximum solid fraction in a random dispersion of monodisperse spheres is 0.63 (28,29). This fraction is higher for polydisperse spheres (30) and for some size distributions may be as high as 0.9 (31). For coal melts we will assume a value of ϕ_{max} of 0.80. If the extrapolated maximum fluidity of the Pittsburgh #8 seam sample at 412° (1.0×10^6 ddpm) is taken as a rough estimate of F°, we can estimate solid fractions in other coals from fluidities at this temperature. Fluidities of 10, 100, 1,000 and 10,000 ddpm indicate solid fractions of approximately .67, .53, .40 and .27. The minimum values of ϕ for Ohio #9 and Kentucky #11 samples in Table 2 are approximately 0.55 and 0.41.

The linearity of log(F) with ϕ has mechanistic implications as well. The left-hand of Equation 3 is more accurately expressed as d $\ell n[M]/dt$. The curves of Figure 1 show linear increases of metaplast with time in the early stages, and linear decreases of metaplast with time (zeroth order kinetics) in the later coking stages.

Extrusion pumping of coals in the plastic state entails substantially isothermal operations for residence times of a few minutes in the screw (1-3). Several coals, including those of the present study, have been extruded with no difficulty in JPL's 1.5-in. coal pump. Two coals which showed very little plasticity (less than 2 ddpm) were not extrudable (3). The isothermal plastometry profiles may prove to be a useful tool in predicting behavior in coal pumps. Recent evidence of the substantial effect of pressure upon observed plasticity (10) indicates that this variable should be considered in future work.

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Table 1

Properties of Three Bituminous Coals

Seam	Ohio #9	Kentucky #11	Pittsburgh #8
source	Noble Co.	Webster Co.	(from METC)
Proximate:[1]			
moisture	2.15%	1.97%	0.79%
ash	18.87	8.34	8.65
vol. matter	39.40	41.19	40.85
fixed carbon	39.58	48.50	49.71
Ultimate:[2]			
carbon	79.41	82.21	84.83
hydrogen	5.30	5.43	5.49
nitrogen	1.13	1.36	1.44
sulfur	5.38	3.52	2.92
oxygen[3]	8.78	7.48	5.33
Heating value[2]	14,010 Btu/lb	14,770 Btu/lb	15,290 Btu/lb
Free swelling index	3	7	7½
Petrographic analysis[1]			
exinoids	2.1%	5.1%	4.0%
vitrinoids	70.1	76.3	75.3
other reactives	1.9	1.2	0.9
inert macerals	12.9	11.0	13.7
ASTM Gieseler plastometry			
softening T	398°C	392°C	372°C
coking T	462°	474°	485°
max flu T	435°	435°	(414-459°)
max fluidity	114 ddpm	6240 ddpm	>>25000 ddpm

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[1] As received.

[2] Moisture- and ash-free basis.

[3] By difference.

Table 2

Characteristics of Three Isothermal Plastic Curves at 410-412°C

	Ohio #9 411°C	Kentucky #11 410°C	Pittsburgh #8 412°C
Melting slope	0.425	0.621	1.084
Coking slope	-0.216	-0.151	-0.125
Maximum fluidity, ddpm[1]	81	896	1.0×10^6
Time of maximum fluidity[1]	14.3_4	15.4_2	15.7_5
Calculated values:[2]			
k(init)	6.0×10^{-4}	4.3×10^{-5}	3.4×10^{-8}
k(melt)	0.77	0.79	1.24
k(coke)	0.35	0.16	0.125

[1] By extrapolation of melting and coking slopes.

[2] Using the three-parameter model described in text. Dimensions of k(init) and k(coke) are min^{-1}; k(melt) is min^{-1} mass fraction^{-1}.

Table 3

Effect of Temperature upon the Isothermal Plastic Curves of Kentucky #11 Seam Coal (400-460°C)

Temperature, °C	400.	410.	425.5	440.	449.9	460.
Melting slope	0.172	0.621	1.35	1.60	2.57	$5._3$
Coking slope	-0.069	-0.151	-0.325	-0.67_9	-1.11	-1.5_6
Maximum fluidity, ddpm[1]	44	896	2.58E4	3.34E4	8.89E4	2.21E6
Time of maximum fluidity[1], min.	25.8_2	15.4_2	11.1_4	8.1_2	6.3_0	4.1_3
Calculated values:[2]						
k(init)	1.2E-3	4.3E-5	1.9E-6	3.0E-6	6.5E-7	4.3E-7
k(melt)	0.26	0.79	1.74	2.49	4.05	$7._1$
k(coke)	0.083	0.158	0.339	0.84_8	1.40	1.6_6

[1] By extrapolation of melting and coking slopes.

[2] See Table 2, footnote 2.

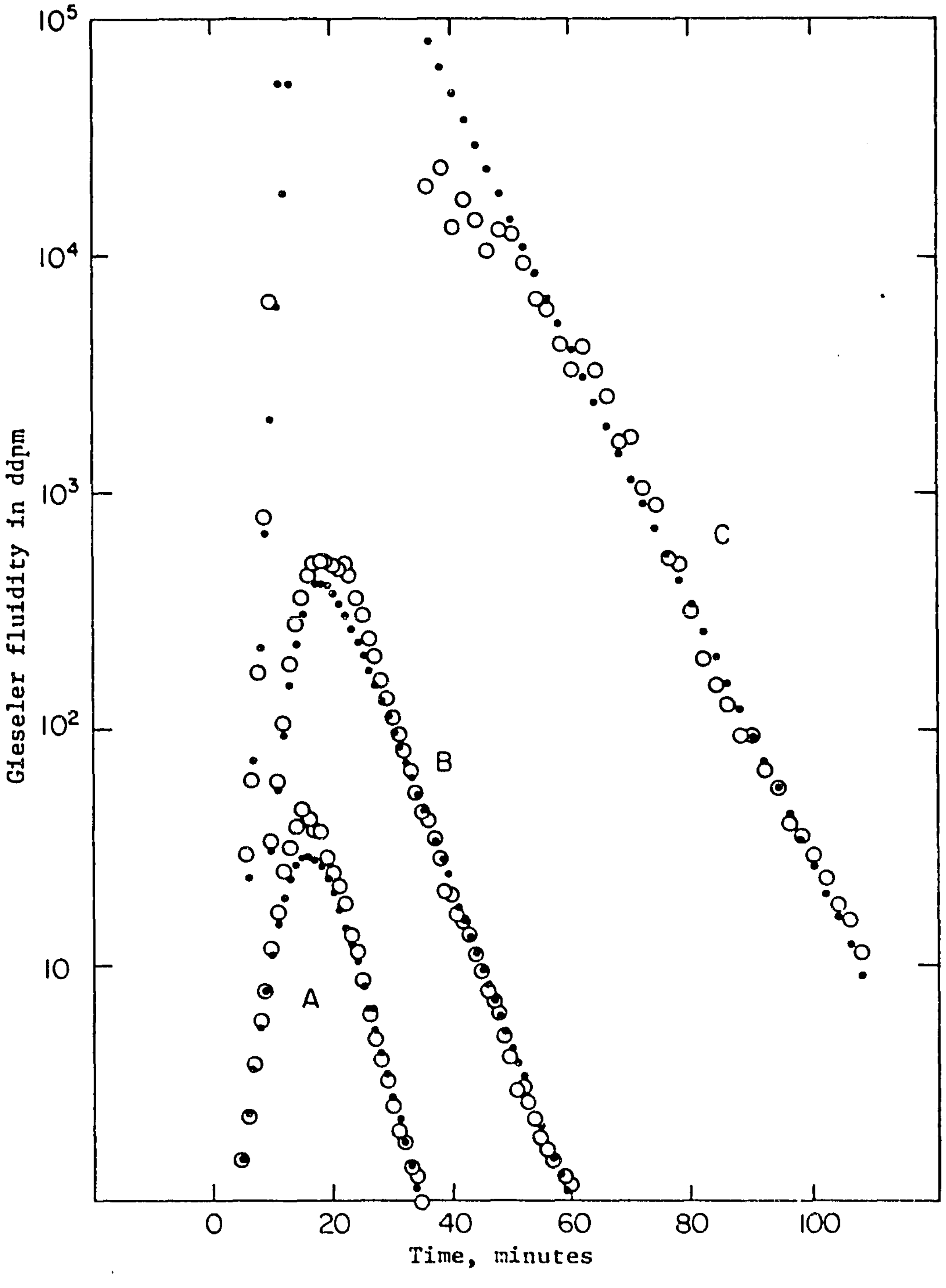

Figure 1. Isothermal plastometric curves of three bituminous coals. A - Ohio #9 seam (Noble Co.) at 411°C. B - Kentucky #11 seam (Webster Co.) at 410°C. C - Pittsburgh #8 seam (from METC) at 412°C. Open circles are experimental data; solid points are calculated by the three-parameter model (values given in Table 2).

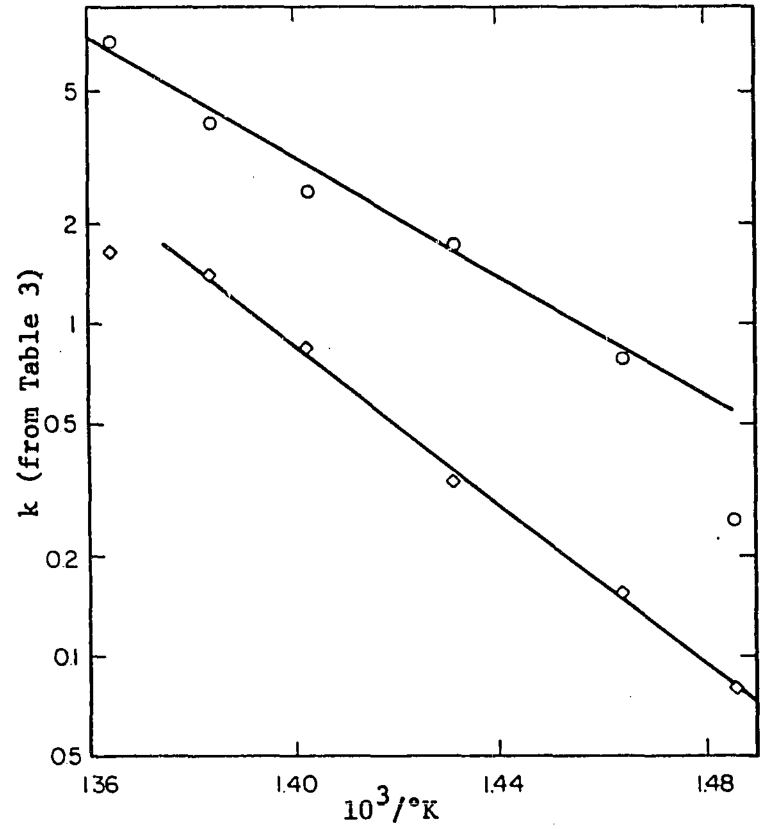

Figure 2. Arrhenius dependency of the model constants k(melt) (circles) and k(coke) (diamonds) for Kentucky #11 seam coal

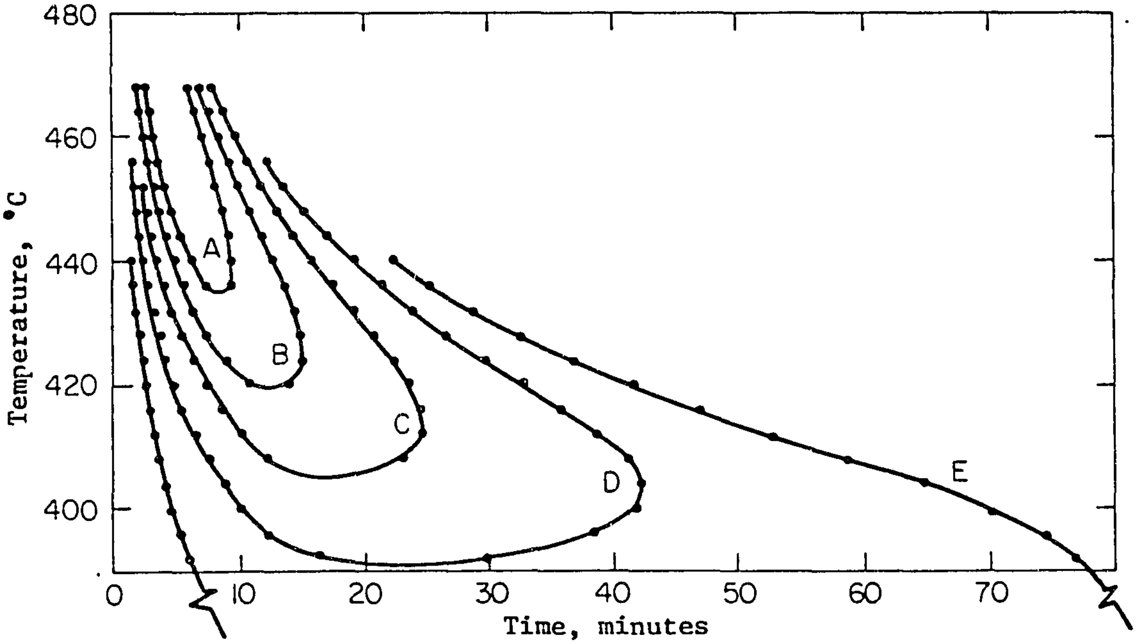

Figure 3. Isothermal fluidity envelopes for Kentucky #11 seam coal A - 10^4 ddpm. B - 10^3 ddpm. C - 10^2 ddpm. D - 10 ddpm. E - 1 ddpm