CANADA

VAPOUR-PHASE STRIPPING OF LLOYDMINSTER CRUDE OIL IN A SLOPING-PLATE DISTILLATION TOWER

by

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DEPARTMENT OF MINES AND TECHNICAL SURVEYS, OTTAWA

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F. L. Booth [1], R. E. Carson [2] and D. S. Montgomery [3]

SUMMARY

This experimental investigation was undertaken to examine the process of vapour-phase stripping of Lloydminster crude oil to yield a high-softening-point pitch, employing a sloping-plate distillation tower. The experiments and calculations described in this report demonstrate that, under the present operating conditions, the mechanism of pitch formation is almost entirely due to the distillation of the volatile components from the crude oil. The extent of thermal cracking of the pitch may, for all practical purposes, be considered negligible. Under these conditions it is possible to produce a pitch with a softening point in the order of 200°F (Ring and Ball), amounting to approximately 25% by weight of the crude oil feed. It is believed that the mechanism of the pitch formation is sufficiently well defined that operating conditions can be selected which will yield a 250°F-softening-point pitch with no coke formation.

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Direction des mines

Rapport de recherches R 84

SÉPARATION EN PHASE VAPEUR DU PÉTROLE BRUT DE LLOYDMINSTER DANS UNE TOUR DE DISTILLATION À PLAQUES INCLINÉES

par

F. L. Booth[1], R. E. Carson[2] et D. S. Montgomery[3]

RÉSUMÉ

La présente étude expérimentale a été entreprise en vue d'examiner le procédé de séparation en phase vapeur du pétrole brut de Lloydminster dans une tour de distillation à plaques inclinées afin d'obtenir un brai à point de ramollissement élevé. Les expériences et les calculs décrits dans le présent rapport démontrent que, dans les conditions actuelles de fonctionnement, le processus de formation du brai est attribuable presque exclusivement à la distillation des constituants volatils libérés par le brut. Le degré de craquage thermique du brai peut être considéré comme négligeable à toutes fins pratiques. Dans de telles conditions, il est possible de produire un brai à point de ramollissement de l'ordre de 200°F (anneau et bille), dans une proportion d'environ 25 p. 100 en poids du brut soumis au traitement. Les auteurs du présent rapport croient que le processus de formation du brai est suffisamment bien défini pour qu'on puisse choisir des conditions de fonctionnement capables de fournir un brai à point de ramollissement de 250°F sans formation de coke.

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INTRODUCTION

In the year 1949, the Mines Branch of the Federal Department of Mines and Technical Surveys at Ottawa undertook a pilot-plant investigation of the cold-water separation of bitumen from the bituminous sands of Alberta. In conjunction with this program, the Fuels Division of the Mines Branch developed a novel process, on a pilot-plant scale, for dehydrating, topping and coking the separated bitumen, which still contained considerable quantities of water, fine mineral matter, and diluent oil. The essential element in these latter processes was a vapour-phase stripping operation employing sloping-plate distillation towers.

A time limit was imposed on the entire project by the decision of the Department to erect, in 1951, the present Mines Branch machine shop on the site of the then-existing pilot plant. Consequently the vapour-phase stripping equipment, one of the components of the pilot plant, had to be dismantled after only an abbreviated experimental program that provided very little operational data on the performance of the distillation apparatus.

In 1953 it was decided to investigate further the vapour-phase stripping operation to secure information on the performance of this type of tower. This decision coincided with an expression of interest in the process by Excelsior Refineries Limited, Edmonton, Alberta. This company was seeking a method that would produce

a hard pitch from Lloydminster crude oil and, at the same time, increase the yield of gas oil over that obtained by conventional vacuum-steam distillation.

Consequently, the sloping-plate distillation unit that had been used for dehydrating and topping Athabasca bitumen was reassembled in 1954, with a few modifications. These modifications were incorporated to broaden the scope of the original investigation, i.e. from dehydration and diluent recovery to the production of a large overhead fraction leaving a hard pitch with a softening point in excess of 250°F (Ring and Ball). It was felt that information on the performance of the flash-distillation tower under these extreme conditions would be helpful in evaluating this technique as a potential method of making both a distillate that would be at least as suitable as coker distillate for hydrogen treating and a residue that would be more valuable than coke.

DESCRIPTION OF THE EXPERIMENTAL APPARATUS

A simplified schematic diagram of the arrangement of the apparatus used in these experiments is shown in Figure 1. Modifications made to the column bottom are shown in Figure 2. This equipment is more completely described in an earlier Fuels Division report.[1]* The main modification to the tower was the incorporation of a system of valves to permit a portion of the recirculating gas to be passed through two perforated pipes below the level of the

* References are listed at the end of this report in the order in which they are numbered in the text.

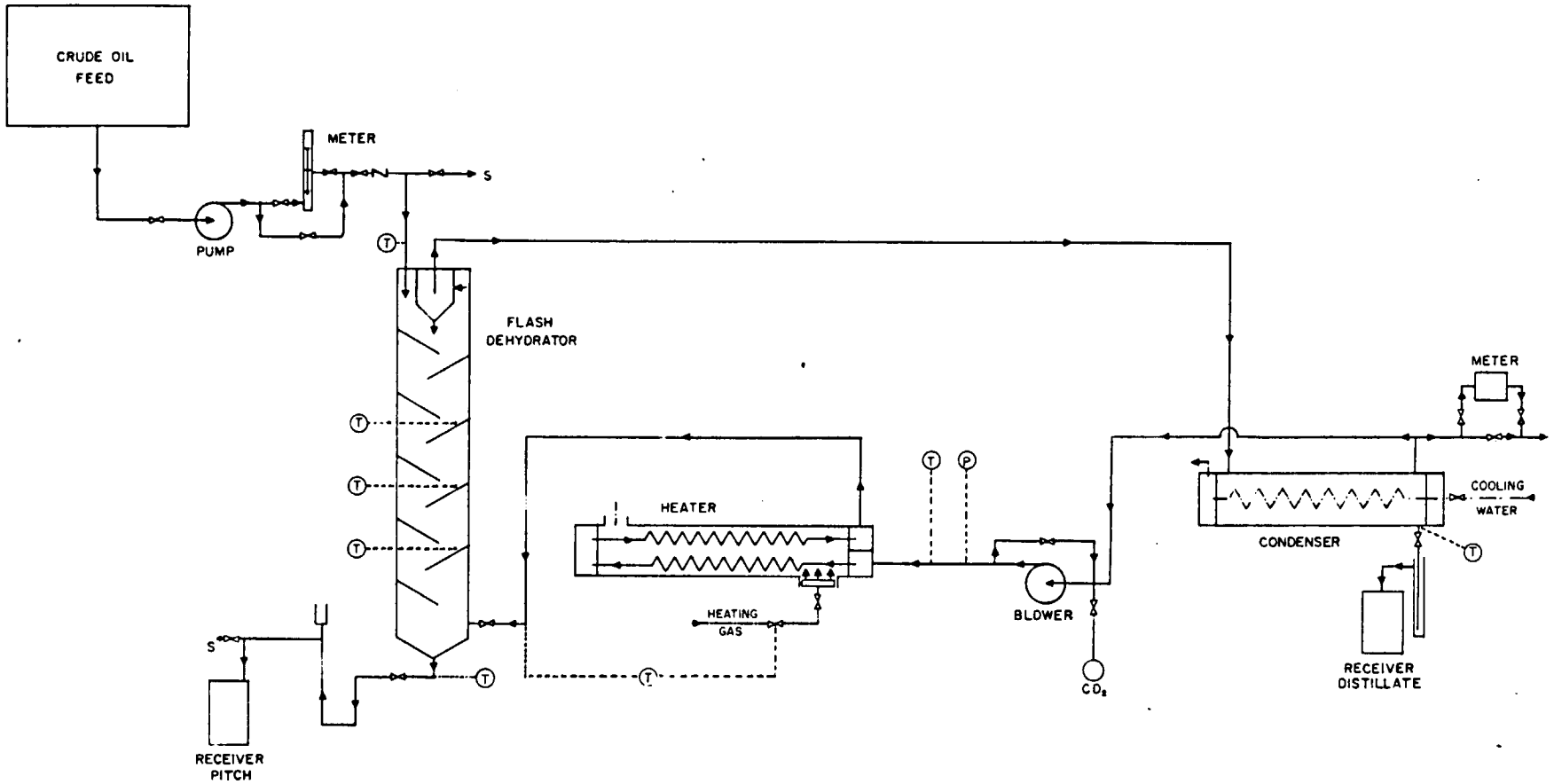


Figure 1. Simplified schematic diagram showing the arrangement of the apparatus.

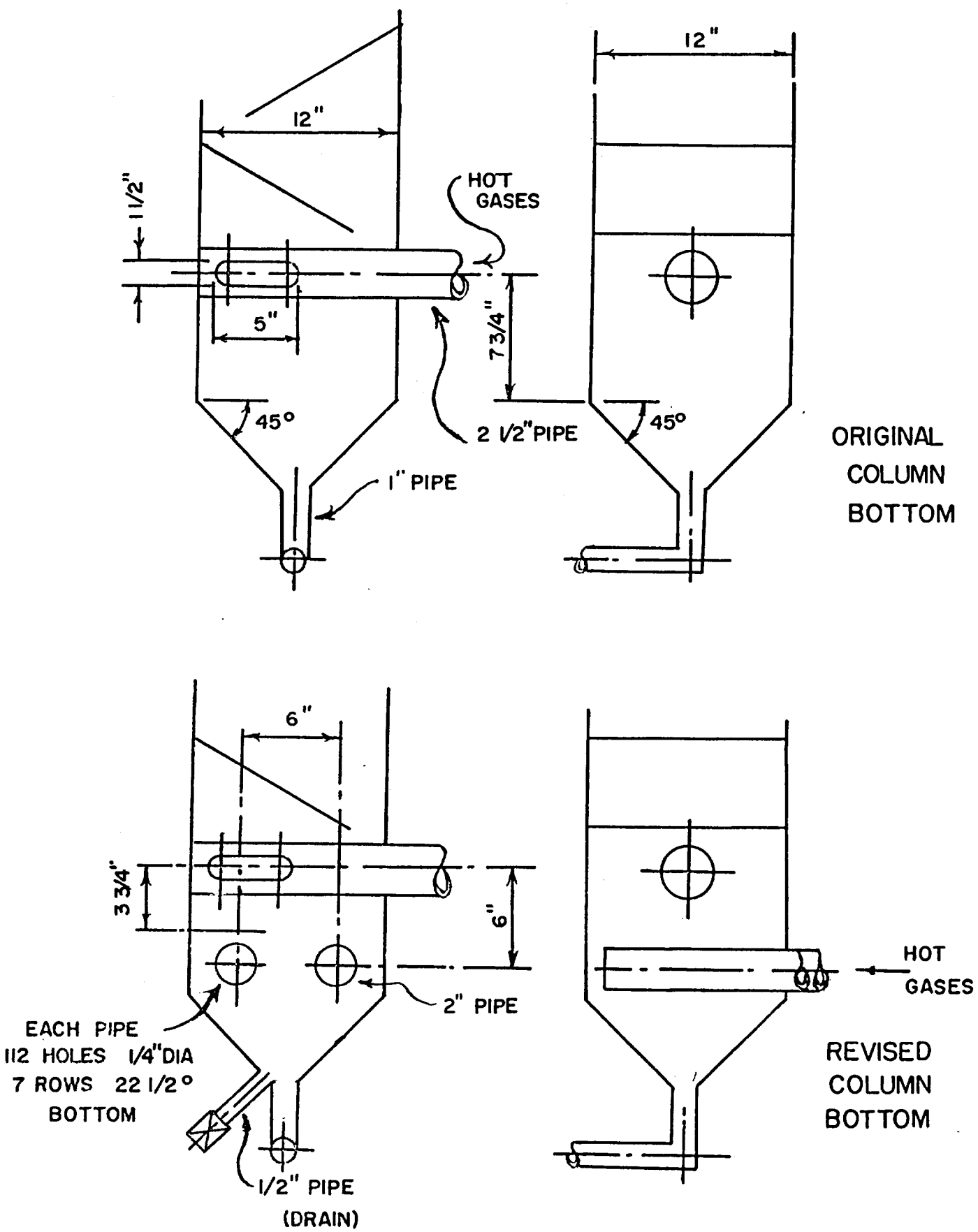


Figure 2. Diagram showing modifications to existing flash tower.

liquid pitch at the bottom of the tower. The perforations were directed downward to scour the bottom of the column and maintain the pitch in a state of violent agitation, in order to prevent localized overheating which would lead to coke formation.

DESCRIPTION OF THE FEED

The feed used in these experiments was crude oil received in 45-gallon drums from the Excelsior Refineries Limited at Lloydminster, Sask., and designated as "Clean Lloydminster Crude". An analysis of the feed is given in Tables 1 and 2.

GENERAL PROCEDURE OF EXPERIMENTS

The general procedure employed is described in the following paragraphs.

With the gas blower circulating inert purge gas through the system at a set rate, the gas-fired tube-and-shell heater was turned on and the temperature control set to maintain the gas leaving the heater at the temperature required.

When the temperatures throughout the apparatus became steady, the cold feed was introduced at the top of the distillation column. The feed rate was determined by timing two-pound increments on the feed drum scales. An instantaneous check was provided by a flowmeter of the rotameter type.

The distillation residue flowed through the gooseneck seal

TABLE 1

Analysis of the Oil Feed

CHARACTERISTICS

Water	0.05 per cent by volume
Sulphur	2.9 per cent by weight
Ash	0.028 per cent by weight
Specific Gravity	0.966 at 60°F/60°F
A.P.I. Gravity	15.0° at 60°F

DISTILLATION, HEMPEL METHOD

Distillation performed at atmospheric pressure of 750 mm Hg.

Fraction No.	Cut at °C	Cut at °F	Cut at °C	Cut at °F	Per Cent by Volume	Sum Per Cent by Volume	Per Cent by Weight	Sum Per Cent by Weight	Specific Gravity at 60°F	A.P.I. Gravity at 60°F	Saybolt Universal Viscosity at 100°F, sec
First drop #			95	203			(Calculated)				
4			125	257	0.8	0.8)					
5			150	302	1.0	1.8)					
6			175	347	1.8	3.6)					
7			200	392	2.7	6.3)	4.8	4.8	0.795	46.5	-
8			225	437	3.5	9.8	2.8	7.6	0.834	38.2	-
9			250	482	4.9	14.7	4.0	11.6	0.852	34.6	33
10			275	527	8.9	23.6	7.4	19.0	0.871	31.0	36

Distillation was then continued at 5 mm Hg pressure

	at 5 mm Hg		Converted to 760 mm Hg								
First drop	147	297	304	580							
11	175	347	338	640	4.1	27.7	3.8	22.8	0.899	25.9	45
12	200	392	367	692	5.4	33.1	5.0	27.8	0.913	23.5	63
13	225	437	394	742	6.4	39.5	6.0	33.8	0.928	21.0	105
14	250	482	426	798	5.4	44.9	5.2	39.0	0.940	19.0	243
15	275	527	454	850	5.8	50.7	5.6	44.6	0.949	17.6	617
16	300	572	484	903	5.8	56.5	5.7	50.3	0.957	16.4	1458
17	320*	608*	507*	945*	11.2	67.7	11.1	61.4	0.963	15.4	1429
Residuum					32.3	100.0	36.1	97.5	1.080	-	
Distillation loss					0.0	100.0	2.5	100.0			

Water was present. * Cracking.

TABLE 2

Molecular Weight Table for Hempel Fractions of the Oil Feed

Cut No.	Cut Temperature, °F	Sum % by wt of Overhead	Specific Gravity, 60/60°F	Kinematic Viscosity		Molecular Weight[2]
				Centistokes at 100°F	Centistokes at 210°F	
4-7	392	4.8	0.795	1.000	0.550	
8	437	7.6	0.834	1.570	0.757	
9	482	11.6	0.852	2.175	0.944	
10	527	19.0	0.871	3.105	1.186	
11	640	22.8	0.899	5.967	1.780	
12	692	27.8	0.913	11.04	2.470	268
13	742	33.8	0.928	21.67	3.578	307
14	798	39.0	0.940	52.31	5.651	338
15	850	44.6	0.949	133.2	9.201	382
16	903	50.3	0.957	314.6	14.32	412
17	945	61.4	0.963	308.3	14.32	414*

* The low molecular weight of this cut is due to cracking in the laboratory distillation (see distillation curve, page 28).

at the bottom of the tower into one-gallon sample receivers on a weigh scale where the pitch rate was determined by increments of weight over 15-minute intervals. The vapourized portion of the feed that condensed in the condenser was continuously collected in a 45-gallon drum and the rate was similarly determined over 15-minute intervals.

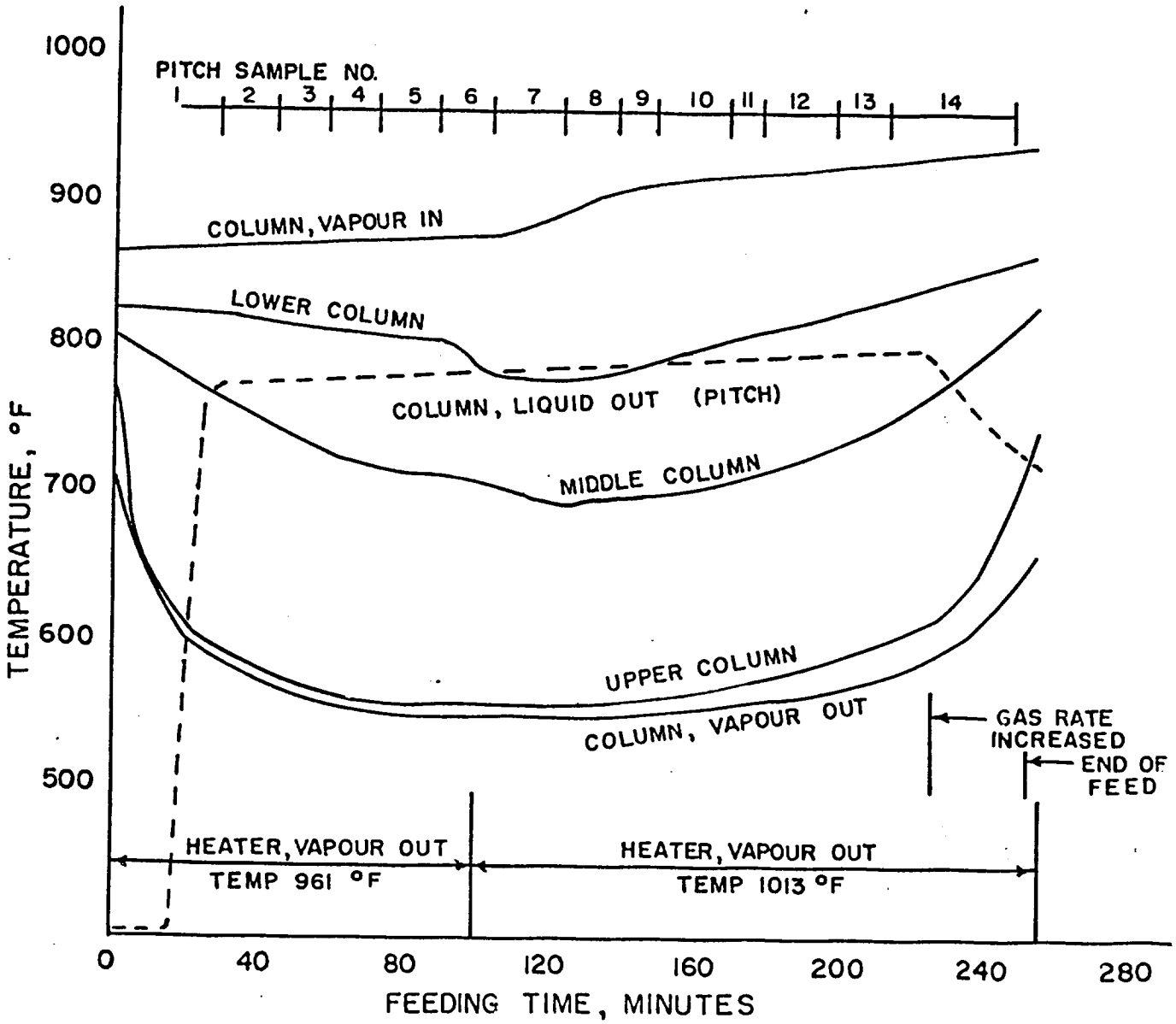
Column temperature readings were taken every 15 minutes, and when these readings had reached a constant value and the distillation residue and distillate rates were also constant, samples of feed, recirculation gas and distillate were taken.

EXPERIMENTAL

Experiment 1

In Experiment 1, prior to the introduction of cold feed, steady conditions were obtained after three hours, and at this point the apparent recirculation rate of the inert gas (CO_2) was 2300 cubic feet per hour. The temperature of the gas was 960°F when leaving the heater and 869°F when entering the column. The bottom, middle and top baffle plate temperatures were respectively 830, 812 and 788°F, and the temperature of the exit gas from the column was 722°F.

After the introduction of the feed, temperature readings throughout the column were taken at 15-minute intervals and plotted in Figure 3. Fifteen minutes after the liquid feed pump was started,



LIQUID FEED TEMPERATURE, 67 °F
LIQUID FEED RATE, 98 LB/HR
GAS FLOWMETER READING, 3200 CFH

Figure 3. Column temperatures, Experiment 1.

hot liquid reached the product outlet line at the bottom of the column, as indicated by an abrupt rise in the temperature at this point from 405°F to 770°F. This hot liquid filled the outlet seal and passed through the outlet valve to the product receiver. The operating conditions were held constant for 100 minutes until thermal equilibrium was approached within the column, as shown in Figure 3. During this time, approximately eight pounds of pitch product were withdrawn every 15 minutes into one-gallon containers. The apparent gas recirculation rate was now 3200 cubic feet per hour.

The temperature controller was now adjusted to increase the temperature of the vapour leaving the heater from 961°F to 1013°F. This increased the temperature of the vapour entering the column by 42°F--that is, from 878°F to 920°F. This temperature rise took place over a time interval of 50 minutes. Then there followed a somewhat slower temperature rise of 12°F during the subsequent 65 minutes. Coincident with increasing the temperature control point, the temperature of the thermocouple at the bottom plate unaccountably fell abruptly from 810°F to 786°F. This was accompanied by a more gradual drop in temperature at the middle plate, from 720°F to 698°F. The plate temperatures then increased steadily for the next 120 minutes, as may be seen by referring to Figure 3.

During this total feeding period of 220 minutes, the pitch product had been flowing steadily from the outlet valve at a gradually increasing temperature, as can be noted from the plot of product

temperatures in Figure 3. The total increase amounted to 22°F (from 780°F to 802°F).

The gas recirculation rate was now increased from an apparent rate of 3200 cubic feet per hour to 3400 cubic feet per hour. The flow of pitch from the outlet valve slowed immediately to a mere trickle. All column temperatures increased at a more rapid rate, but the product outlet temperature fell off abruptly, indicating that the hot liquid pitch was not reaching the bottom of the column. After 15 minutes the gas rate was returned to 3200 cubic feet per hour, with no noticeable change in the trend of column temperatures. The product outlet temperature continued to fall. The experiment, however, was continued for an additional 20 minutes before being terminated.

In this experiment 410 pounds of crude oil had been fed to the column and 265 3/4 pounds of distillate, 120 1/2 pounds of pitch and 80 cubic feet of gas were produced. These products as percentages of the crude oil fed, and assuming a gas density of 0.08 pound per cubic foot, were as follows:

Distillate	64.8%
Pitch	29.4%
Gas	1.5%

After the column cooled, the front cover plates were removed. A very thin layer of pitch covered all the plates except the bottom

three. On and between these bottom plates was an accumulation of very light, lacy coke that had the appearance of having been formed from a liquid while being tossed about in a vapour stream. This coke was removed and its weight amounted to 3 1/4 pounds, or 0.8% of the liquid feed.

Preliminary results from Experiment 1 (see page 23) indicated the possible existence of a critical temperature in the relationship between pitch product temperature and pitch hardness. Below this critical temperature point, an increase in temperature would be accompanied by an increase in pitch hardness because of insufficient distillation. Above the critical point, the pitch hardness would decrease with increasing temperature as a result of thermal cracking of high molecular weight components yielding a lower-softening-point material that was, however, still too high in molecular weight to distil. This interpretation of the results influenced the selection of the conditions under which the next experiment, Experiment 2, was made.

Experiment 2

In Experiment 2 it was intended to operate at slightly lower recirculating gas temperatures in order to reduce the tendency to thermal cracking of the pitch. It was also proposed to gradually decrease the feed rate during the experiment, starting at an initial value of 125 pounds per hour, and note the effect of this change

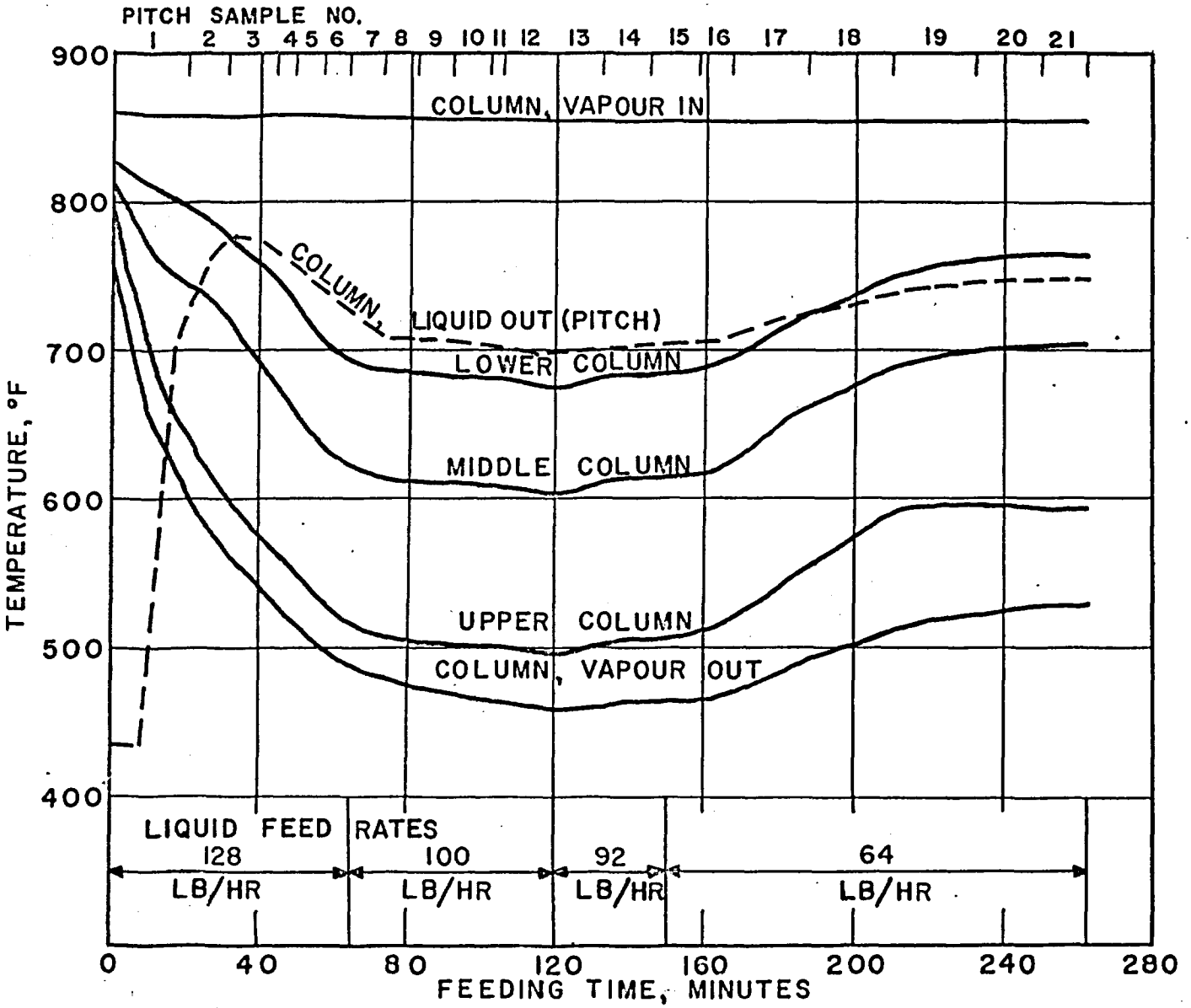
upon the pitch produced.

Accordingly, in Experiment 2 the recirculating gas temperatures throughout the system were allowed to reach the following stable values:

Heater outlet.....	950°F (control)
Column, vapour in	860°F
Column, bottom section	826°F
Column, middle section	813°F
Column, top section	798°F
Column, vapour out	754°F

The recirculating gas rate as read at the rotameter was 3200 cubic feet per hour.

Feed, at 128 pounds per hour, was introduced into the top of the column. Temperature readings throughout the column were then taken at 15-minute intervals and plotted (see Figure 4), together with the corresponding pitch product outlet temperatures. Eight minutes after feeding commenced, hot pitch reached the outlet valve and flowed steadily through the outlet seal to the product receiver. Throughout 65 minutes feeding time the column temperatures decreased continuously, giving no indication of approaching a steady state. Consequently, the feed rate was decreased to 100 pounds per hour. This rate was maintained for 55 minutes, during which time the column temperatures became stable (as can be observed in Figure 4). The feed rate was then decreased to 92 pounds per hour. The column temperatures increased slightly and became stable after 30



TEMPERATURE, HEATER VAPOUR OUT, 950 °F
TEMPERATURE, LIQUID FEED, 60 °F
GAS FLOWMETER READING, 2800 C F H.

Figure 4. Column temperatures, Experiment 2.

minutes. Finally, the feed rate was reduced to 64 pounds per hour and, in response to this change, the column temperatures increased again and ultimately reached a steady value after 112 minutes. At this point the experiment was concluded. The apparent recirculating gas rate, during the first 45 minutes after the feed was introduced, fell from 3200 to 2800 cubic feet per hour and then remained at this rate until the conclusion of the experiment.

In this experiment the column was charged with 399 pounds of crude oil, and yielded 222 1/4 pounds of distillate, 163 pounds of pitch and 77 cubic feet of gas. Assuming a gas density of 0.08 pound per cubic foot, these products, expressed as percentages by weight of the crude oil fed, were as follows:

Distillate	55.7%
Pitch	40.9
Gas	1.5

The pitch product was collected in 21 separate containers during the experiment. The period during which each portion was collected is shown in Figure 4.

Experiment 3

The softness of the pitch produced in Experiment 2 (see page 29) indicated that higher recirculating gas temperatures or lower liquid feed rates were required to produce a satisfactory pitch. Consequently, for Experiment 3 the temperature controller was set to

supply recirculating gas at the heater outlet at 1015°F. It was then planned to attain thermally stable conditions in the column at liquid feed rates of 100, 75, 50 and 25 pounds per hour, respectively.

Prior to Experiment 3, alterations were made to the apparatus to allow the pitch product to pass directly from the outlet seal to a 45-gallon drum on a weigh scale. This drum was vented to the outside atmosphere. Provision was also made for sampling the pitch being produced at any time during the experiment.

In Experiment 3, steady thermal conditions were established four hours after the recirculating gas blower and heater were turned on. Under these conditions the apparent recirculating gas rate was 3100 cubic feet per hour and the gas temperatures throughout the system were as follows:

Heater outlet.....	1015°F
Column, vapour in	899°F
Column, bottom section	871°F
Column, middle section	861°F
Column, top section	846°F
Column, vapour out	786°F

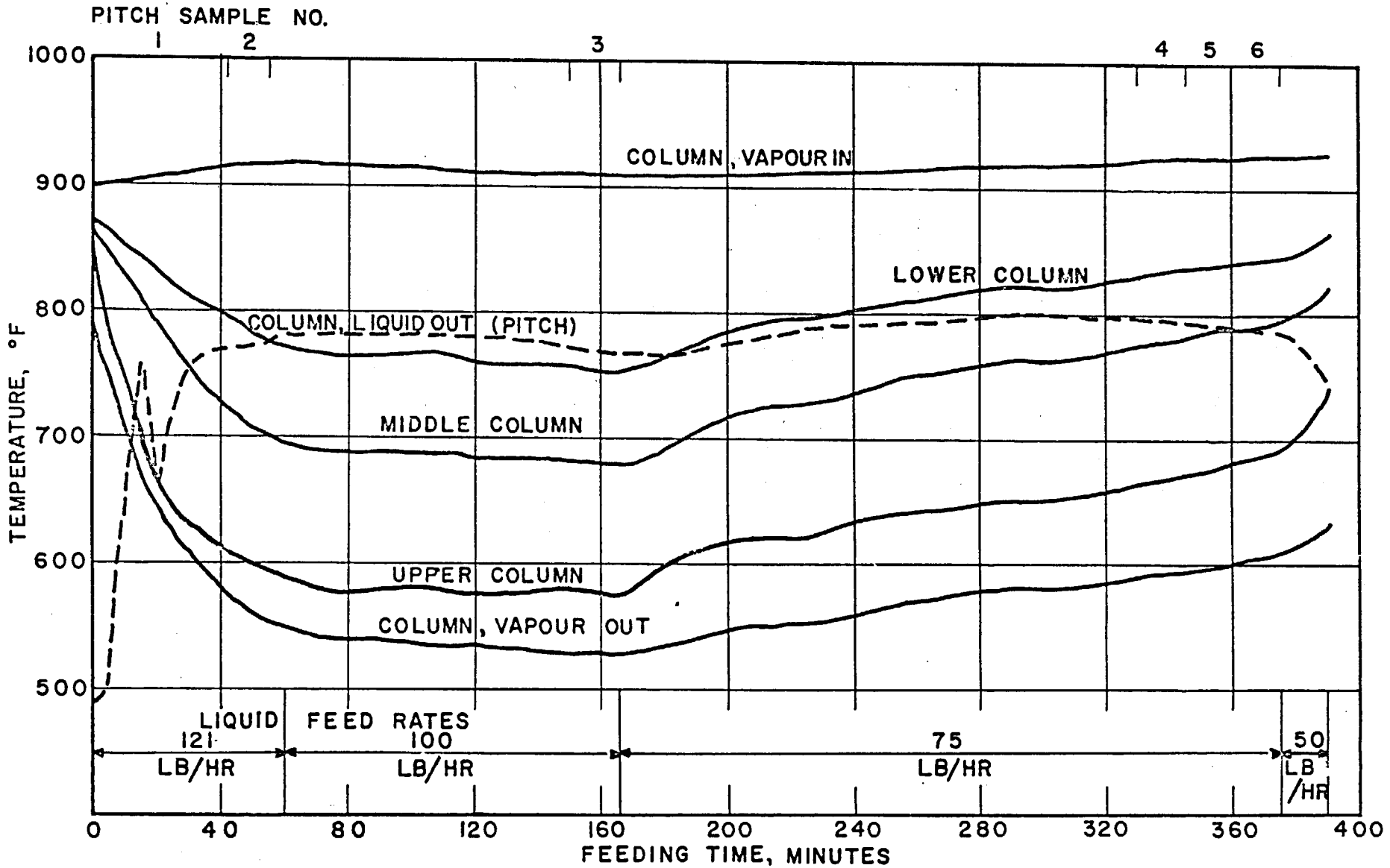
The oil feed was then introduced at a rate of 121 pounds per hour. This feed rate was intentionally somewhat higher than the 100 pounds per hour which it was proposed to maintain. From the previous experiments it had been observed that the pitch produced at any given feed rate was much harder at the beginning of the feeding period, at which time the entire column was heated to its maximum

temperature by the hot recirculating gas. When the column was cooled by the influx of cold oil, the pitch produced was softer. Consequently, by employing a rapid initial feed rate the possibility of coking on the plates or blocking the outlet lines was reduced and the time required to cool the baffle plates to the level attained under steady conditions at 100 pounds per hour was shortened.

After the introduction of the feed, temperature readings throughout the column were taken at 15-minute intervals and plotted (see Figure 5). Three minutes after the liquid feed pump was started, hot liquid reached the product outlet line at the bottom of the column. From Figure 5 it can be seen that the temperature at the product outlet line increased rapidly to 758°F, decreased rapidly to 662°F, and increased again to 758°F, where it began to reach a steady value. The fall in temperature was due to solidification of pitch in the outlet line where it entered the product receiver. The clearing of this line was reflected by the rapid return to temperature.

The total amount of pitch produced in the first 40 minutes was collected in a sample receiver and designated Pitch Sample 1. Similarly, Pitch Sample 2 consisted of all the pitch produced in the following 15 minutes.

After feeding for 60 minutes at 121 pounds per hour, the feed rate was adjusted to 100 pounds per hour. At this point the column temperatures were as follows:



TEMPERATURE, HEATER VAPOUR OUT, 1015 °F
TEMPERATURE, LIQUID FEED, 71 °F
GAS FLOWMETER READING, 2900 C F H

Figure 5. Column temperatures, Experiment 3.

Vapour in	918°F
Bottom section	775°F
Middle section	697°F
Top section	590°F
Vapour out	551°F
Pitch out	784°F

The apparent gas recirculation rate under these conditions was 2900 cubic feet per hour.

Shortly after reduction of the feed rate, thermal conditions in the column became relatively stable. After oil was fed for 90 minutes at a rate of 100 pounds per hour, the pitch produced in the following 15-minute period was collected in a sample receiver and designated Pitch Sample 3. The average column temperatures during the period when this sample was being collected were as follows:

Vapour in	912°F
Bottom section	764°F
Middle section	682°F
Top section	578°F
Vapour out	530°F
Pitch out	771°F

The apparent gas recirculating rate was again 2900 cubic feet per hour.

The feed rate was then reduced to 75 pounds per hour. This immediately caused all column temperatures to undergo a steady rise, which continued for 120 minutes, reaching the following values:

Vapour in .....921°F
Bottom section .....822°F
Middle section .....762°F
Top section .....652°F
Vapour out .....580°F
Pitch out .....800°F

These temperatures remained relatively constant for approximately 25 minutes, after which all the column temperatures started to rise again accompanied by a gradual drop in pitch outlet temperature. After 20 minutes, Pitch Samples 4, 5 and 6 were taken over successive periods of 15 minutes each. During the same periods that Pitch Samples 4 and 5 were being taken, samples were taken of the distillate product recovered from the condenser. Table 3 shows the average column temperatures and the apparent recirculating gas rates during the three sampling periods.

TABLE 3

Column Conditions During Sampling Periods, Experiment 3

	Pitch Sample 4	Pitch Sample 5	Pitch Sample 6
Vapour in, °F	925	926	928
Bottom section, °F	834	840	844
Middle section, °F	780	787	793
Top section, °F	669	677	687
Vapour out, °F	593	599	606
Pitch out, °F	795	792	790
Apparent recirculating gas rate, cfh	2900	2850	2800

The feed rate was then decreased to 50 pounds per hour. Immediately the pitch outlet temperature began to fall rapidly, and all column temperatures began to rise rapidly except for the vapour inlet temperature, which remained steady at 928°F. The flow of pitch from the outlet seal slowed to a mere trickle, and finally stopped 15 minutes after the reduction of feed to 50 pounds per hour. Twelve minutes later the experiment was terminated.

When the front plates were removed from the column, two pounds of coke were recovered from between and below the bottom three baffle plates. The remaining six plates contained no noticeable coke deposit. Figure 6 is a photograph showing the interior of the column following Experiment 3.

The total length of feeding time during Experiment 3 was 6 hours and 42 minutes. During this time, 593 pounds of crude oil had been pumped to the column and 166 pounds of pitch and 405 pounds of distillate were recovered. A total of 115 cubic feet of gas passed through the excess-gas meter, and, assuming a gas density of 0.08 pound per cubic foot, this amounted to 9 pounds of gas. Calculating these products as per cent by weight of liquid feed, the following was obtained:

Pitch	28.0%
Distillate	68.3
Gas	1.5
Coke	0.3
Loss	1.9
	100.0

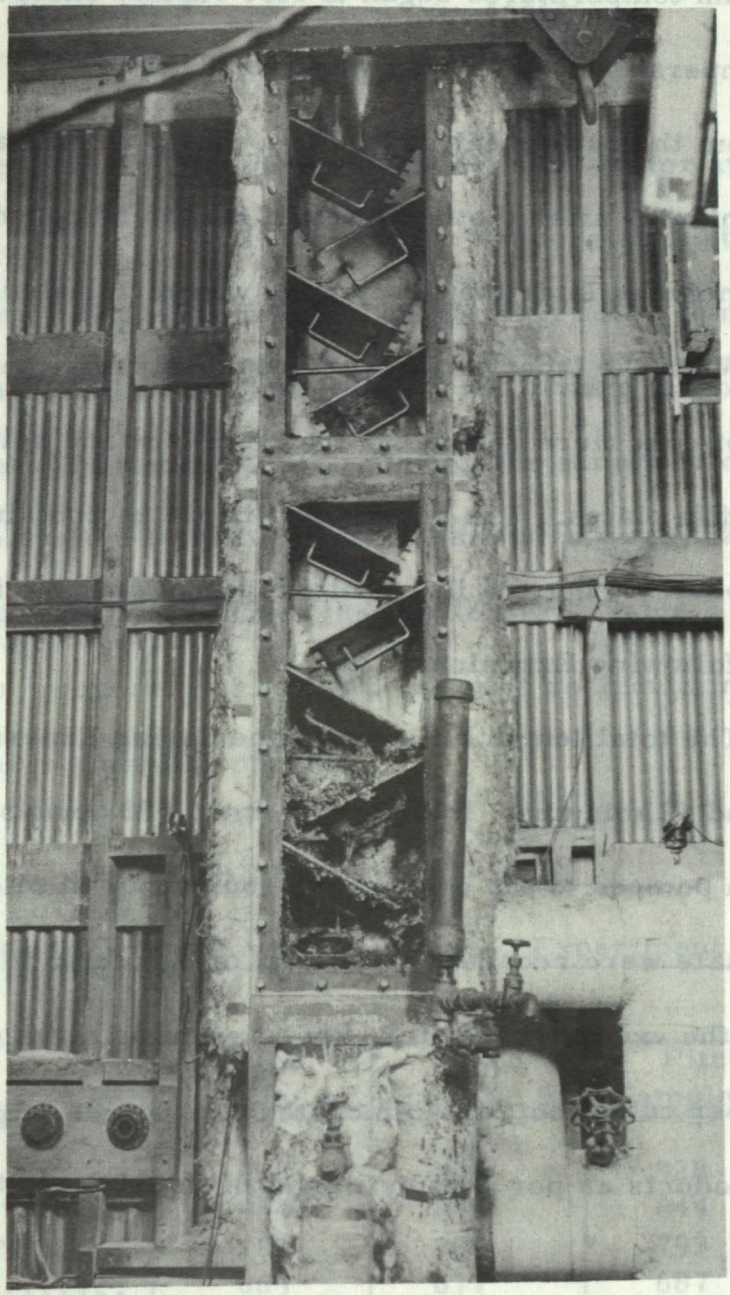


Figure 6. Interior of column following Experiment 3.

RESULTS

Experiment 1

Table 4 shows the results of analyses of the pitch samples taken during Experiment 1. Softening points are plotted in Figure 7. The sample numbers listed correspond to the numbers shown with the column temperature curves in Figure 3, where the interval in which each sample was collected is indicated.

The total overhead liquid product recovered had a specific gravity at 60°F of 0.914, corresponding to an A.P.I. gravity at 60°F of 23.3°. Results of a Hempel distillation are shown in Tables 5 and 6 and Figure 8. The results of a Hempel distillation on the feed (see Table 1) are also plotted in Figure 8.

In order to determine the relative amount of cracking which had taken place during the experiment, the Hempel distillation curve for the overhead liquid product, with the Hempel fraction recovered calculated as a percentage of the liquid feed, was also plotted in Figure 8.

TABLE 4

Analyses of Pitch Samples, Experiment 1

Sample No.	Softening Point (Ring and Ball in Glycerine), °F	Softening Point (Ring and Ball in Water), °F	Penetration, 100 g in 5 sec		Penetration, 200 g at 100°F		Per Cent by Wt Soluble in Carbon Tetra-chloride	Per Cent Loss on Heating (50 g in 5 hours at 325°F)
			77°F	100°F	In 5 sec	In 10 sec		
1	222				7	7		
2	216				8	9		
3	208				9	10		
4	197				10	14		
5	198		1.5	5.5			99.9	0.04
6	176				27	34		
7	168				38	49		
8	167				42	53		
9	160				49	51		
10	159				53	67		
11	162				49	66		
12	162				44	50		
13		165	7.1	17.7			99.9	0.07
14	189		5.0	9.9			99.9	0.08

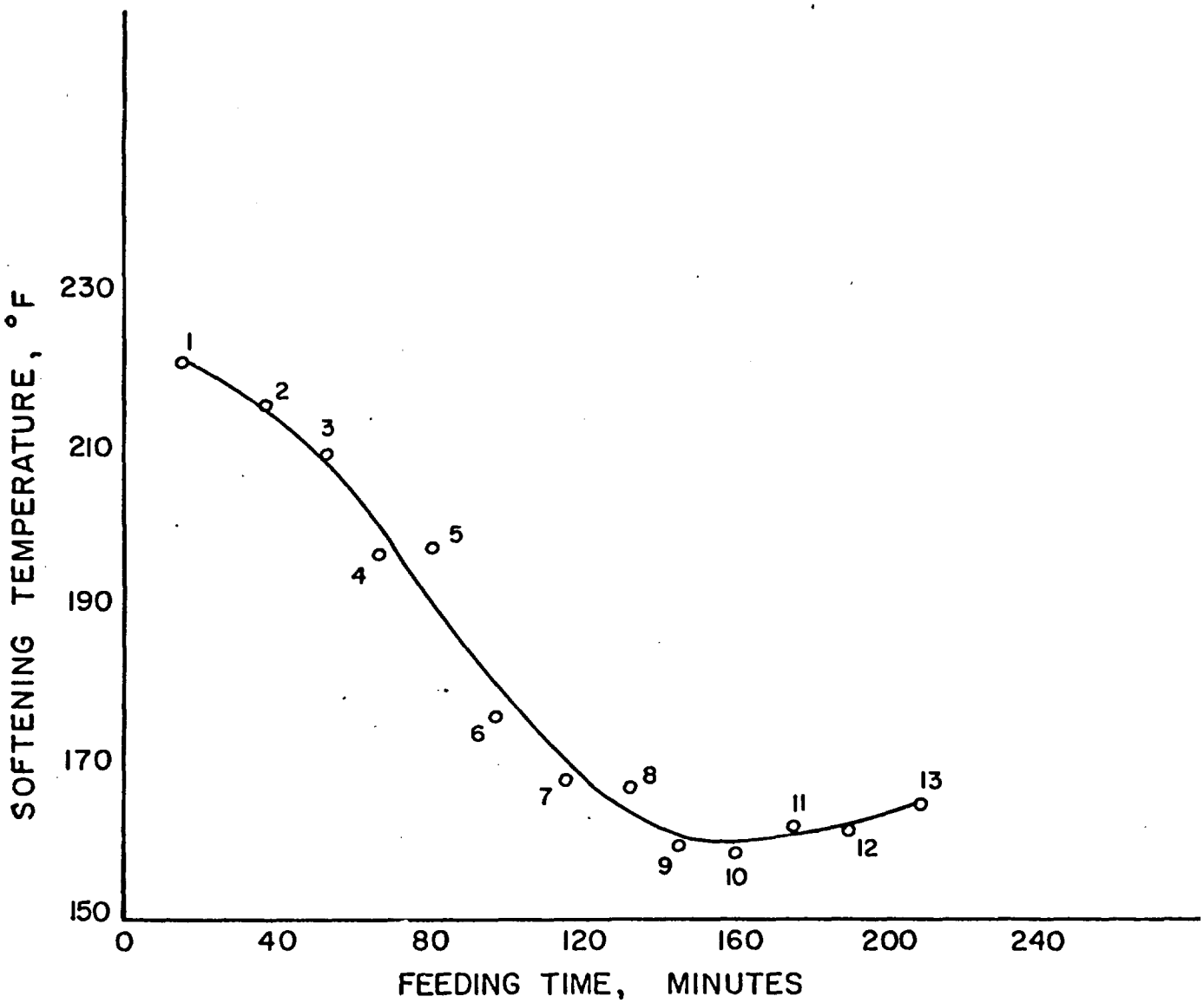


Figure 7. Softening points of pitch samples, Experiment 1.

TABLE 5

Hempel Distillation of Overhead Liquid Product, Experiment 1

Distillation performed at atmospheric pressure of 750 mm Hg.

Fraction No.	Cut at °C	Cut at °F	Cut at °C	Cut at °F	Per Cent by Volume	Sum Per Cent by Volume	Per Cent by Weight	Sum Per Cent by Weight	Specific Gravity at 60°F	Degrees A. P. I. at 60°F
First drop			101	214	-	-	(calculated)			
4			125	257	1.1	1.1		)		
5			150	302	1.7	2.8		)		
6			175	347	2.7	5.5		)		
7			200	392	3.6	9.1	7.5	7.5)	0.793	46.9
8			225	437	4.8	13.9	4.2	11.7	0.834	38.2
9			250	482	6.0	19.9	5.4	17.1	0.852	34.6
10			275	527	9.0	28.9	8.2	25.3	0.870	31.1

Distillation was then continued at 5 mm Hg pressure.

	at 5 mm		Converted to 760 mm Hg							
First drop	131	268	268	546						
11	150	302	308	586	3.7	32.6	3.5	28.8	0.890	27.5
12	175	347	338	640	6.3	38.9	6.1	34.9	0.900	25.7
13	200	392	367	692	8.3	47.2	8.2	43.1	0.913	23.5
14	225	437	394	742	8.3	55.5	8.2	51.3	0.928	21.0
15	250	482	426	798	7.8	63.3	7.9	59.2	0.940	19.0
16	275	527	454	850	10.2	73.5	10.4	69.6	0.949	17.6
17	300	572	484	903	7.5	81.0	7.8	77.4	0.958	16.2
18	325	617	513	955	7.0	88.0	7.3	84.7	0.965	15.1
19	350	662	541	1005	7.0	95.0	7.3	92.0	0.971	14.2
20	365*	689*	557*	1035*	3.7	98.7	3.9	95.9	0.976	13.5
Residuum					1.3)		2.5	98.4	-	-
Distillation loss					)	100.0	1.6	100.0		

* Cracking.

TABLE 6

Molecular Weight Table for Hempel Fractions,
Overhead Liquid Product, Experiment 1

Cut No.	Cut Temperature, °F	Sum % by wt of Overhead	Specific Gravity, 60/60°F	Kinematic Viscosity, Centistokes at 100°F	Kinematic Viscosity, Centistokes at 210°F	Molecular Weight (2)
4-7	392	7.5	0.793	0.917	0.521	
8	437	11.7	0.834	1.519	0.743	
9	482	17.1	0.852	2.071	0.914	
10	527	25.3	0.870	3.101	1.180	
11	586	28.8	0.890	4.182	1.430	
12	640	34.9	0.900	6.237	1.788	
13	692	43.1	0.913	10.87	2.444	266
14	742	51.3	0.928	22.15	3.592	302
15	798	59.2	0.940	49.42	5.481	339
16	850	69.6	0.949	134.4	9.391	388
17	903	77.4	0.958	374.3	15.37	414
18	955	84.7	0.965	798.5	23.50	453
				Centistokes at 130°F		
19	1005	92.0	0.971	454.9	39.22	540
20	1035	95.9	0.976	-	-	-

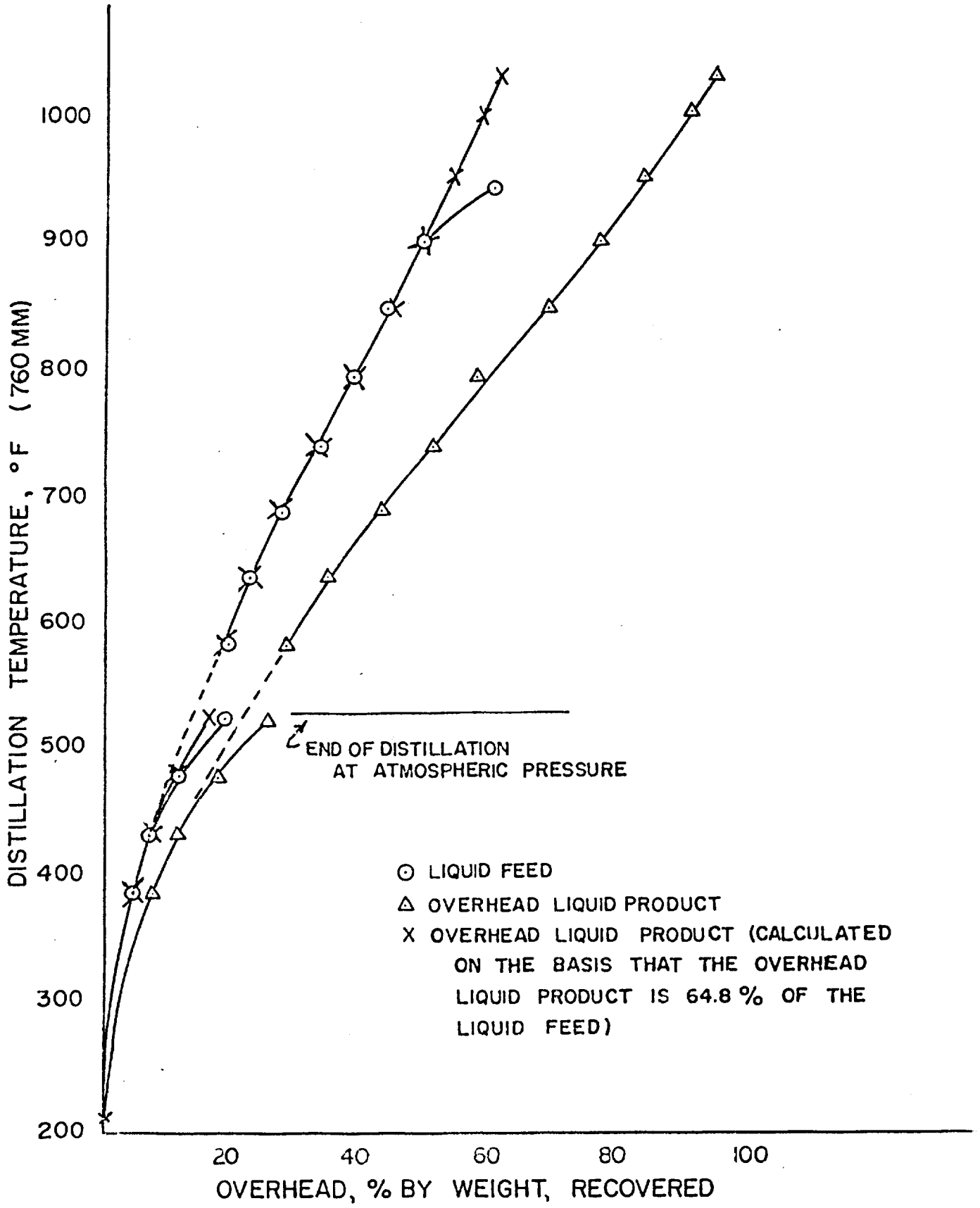


Figure 8. Hempel distillation curves, feed and overhead liquid product, Experiment 1.

Experiment 2

Table 7 shows the penetrations and the softening points of the pitch samples taken during Experiment 2. The softening points are plotted in Figure 9. The period during which each sample was collected is shown with the column temperature curves in Figure 4.

TABLE 7

Penetration and Softening Points of Pitch Samples, Experiment 2

Sample No.	Penetration, 200 g at 100°F in 5 sec	Softening Point (Ring and Ball in Glycerine), °F
1	10.5	197
2	19.0	180
3	32.0	167
4	128.0	142
5		127
6		122
7		119
8		120
9		117
10		118
11		114
12		116
13		120
14		121
15		118
16		124
17	90.0	145
18	45.0	159
19	27.0	170
20	29.0	170
21	26.5	170

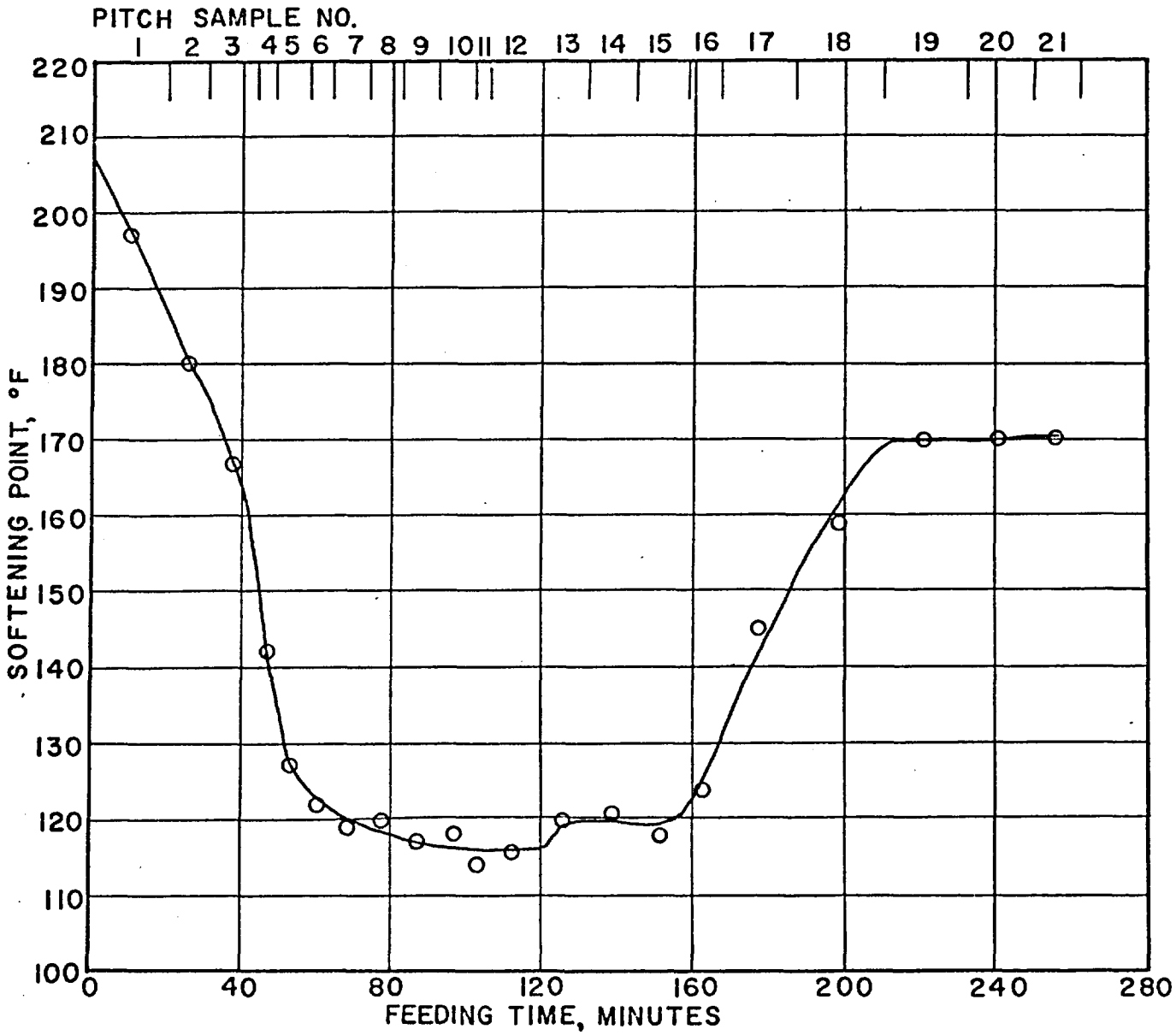


Figure 9. Softening points of pitch samples, Experiment 2.

Experiment 3

Properties of the six samples of pitch are shown in Table 8. The period during which each sample was collected is indicated on the time-temperature graph, Figure 5. Samples were withdrawn from the top and bottom of Pitch Sample 1 to assess homogeneity of the sample

TABLE 8

Analyses of Pitch Samples, Experiment 3

Pitch Sample No.	Penetration, 200 g in 5 sec, 77°F	Penetration, 200 g in 5 sec, 100°F	Softening Point (Ring and Ball in Glycerine), °F	Bitumen Soluble in Carbon Tetrachloride, % by Wt
1	Top 4.0 Btm 3.5	Top 5.5 Btm 4.5	Top 243 Btm 251	99.82
2	18.0	27.0	175	99.91
3	95.0	159.0	135	99.99
4	11.5	14.0	187	99.93
5	8.5	10.5	202	99.94
6	5.5	6.5	223	99.87

Analyses of the overhead liquid product are shown in Table 9. Distillate Sample 1 was taken during the period when Pitch Sample 4 was being collected, and Distillate Sample 2 was taken while Pitch Sample 5 was being collected.

TABLE 9

Analyses of Distillate Samples, Experiment 3

	Distillate Sample 1	Distillate Sample 2
Specific gravity at 60°/ 60°F	0.916	0.917
Viscosity at 100°F, centistokes	17.57	18.74
Viscosity at 210°F, centistokes	3.464	3.598
Molecular weight[2]	326.6	329.3
Refractive Index N_d^{20}	1.5082	1.5094
Dispersion $(N_f - N_c) \times 10^4$	125.6	129.8

DISCUSSION OF RESULTS

The process of making pitch from Lloydminster crude oil in a sloping-plate distillation tower, under the conditions employed, has been shown to be one of simple distillation with a minimum of attendant cracking. The use of recirculating hot inert gases as the source of heat for distillation effectively decreases the partial pressure of the vapourized oil, creating a condition similar to that of steam distillation.

This interpretation of the mechanism of the process was strongly indicated from the results of Experiment 1 by the coincidence of the Hempel distillation curves of the crude oil and the distillation curves of the overhead distillate from the sloping-plate tower. Additional support for this interpretation was obtained from the results of Experiment 3, in which a comparison of Distillate Samples 1

and 2 (Table 9) and the associated Pitch Samples 4 and 5 (Table 8) showed that increased column temperatures cause a simultaneous increase in the molecular weights of the distillate and the pitch. The increase in molecular weight of the pitch may be inferred from the increase in the softening point and the decrease in the penetration value. On the other hand, the high solubility of the pitch in carbon tetrachloride showed that no appreciable coke formation or polymerization by cross-linking was taking place in the pitch.

From the point of view of engineering design, it would be desirable to be able to calculate the proportion of crude oil that would be vapourized on each sloping plate. At the present time, insufficient experimental data and theoretical information are available to undertake this task. However, it is possible to make an estimate of the efficiency of the distillation column if it is assumed that no thermal cracking is taking place, and that the process is one of distillation in an inert gas stream.

The following calculations were undertaken to develop a liquid-vapour phase diagram for Lloydminster crude oil to enable such efficiency calculations to be made. The method described by Edmister and Pollock[3] was employed, which was based upon their equilibrium flash vapourization data.

If the pitch-making operation may be considered to be an equilibrium flashing operation, as it appears reasonable to assume, then the phase diagram will provide valuable assistance in any analysis

of the process.

The only distillation data available on the crude oil were the results of a Hempel distillation carried out by the Fuels and Mining Practice Division. This distillation was conducted at two pressures, with Stage I at atmospheric pressure and Stage II at 5 mm Hg. The method of converting these data to equilibrium flash vapourization data will be described in detail. Briefly, it was necessary to undertake the following steps:-

(1) Convert Stage II data to 40 mm Hg pressure to conform to U.S. Bureau of Mines Hempel distillation.

(2) Convert the U.S. Bureau of Mines Hempel distillation to the A.S.T.M. distillation.

(3) Convert the A.S.T.M. distillation to the Equilibrium Flash Vapourization distillation.

It should be emphasized that in the course of this conversion it was found that extensive extrapolation was necessary. This reduced the reliability of the final diagram. Also, the Edmister correlation is not as reliable for oils of wide boiling range as for narrow cuts, nor is it too accurate at extremely low pressures. However, to the authors' knowledge there is no better correlation method available, and, while its accuracy is debatable, at least it affords a rough approximation of the yield of distillate at a given combination of temperature and pressure.

Table 10 shows the results of a Hempel distillation of the

TABLE 10

Hempel Distillation of Oil Feed

Fraction No.	Cut Temperature, °F	Volume Per Cent Distilled
	STAGE I	
	Distillation at 750 mm Hg pressure Gravity - 15.0° A.P.I. I.B.P. - 203°F	
4	257	0.8
5	302	1.8
6	347	3.6
7	392	6.3
8	437	9.8
9	482	14.7
10	527	23.6
	STAGE II	
	Observed at 5 mm Hg pressure / Corrected to 40 mm Hg pressure	
1st drop	297 / 392	
11	347 / 446	27.7
12	392 / 504	33.1
13	437 / 545	39.5
14	482 / 597	44.9
15	527 / 634	50.7
16	572 / 690	56.5
17 (cracking)	608 / 741	67.7

crude oil. The distillation data at both atmospheric and 5 mm Hg are presented. Table 10 also shows the data at 5 mm Hg corrected to 40 mm Hg, to conform with the U.S. Bureau of Mines Hempel distillation. Correction was made by the Cox vapour chart, Figure 10.[4] Information given in Table 10 is plotted in Figure 11.

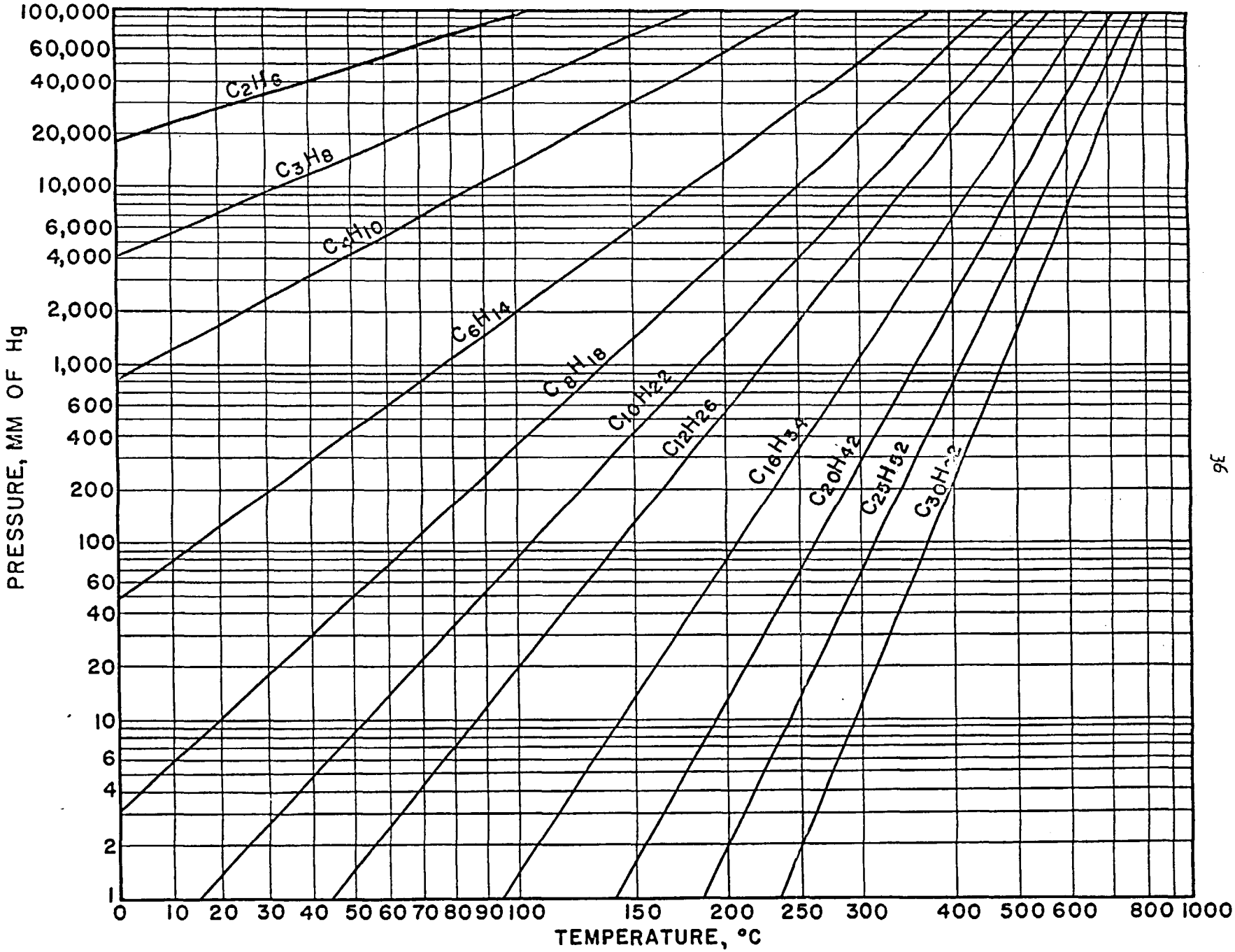


Figure 10. Cox vapour pressure chart.

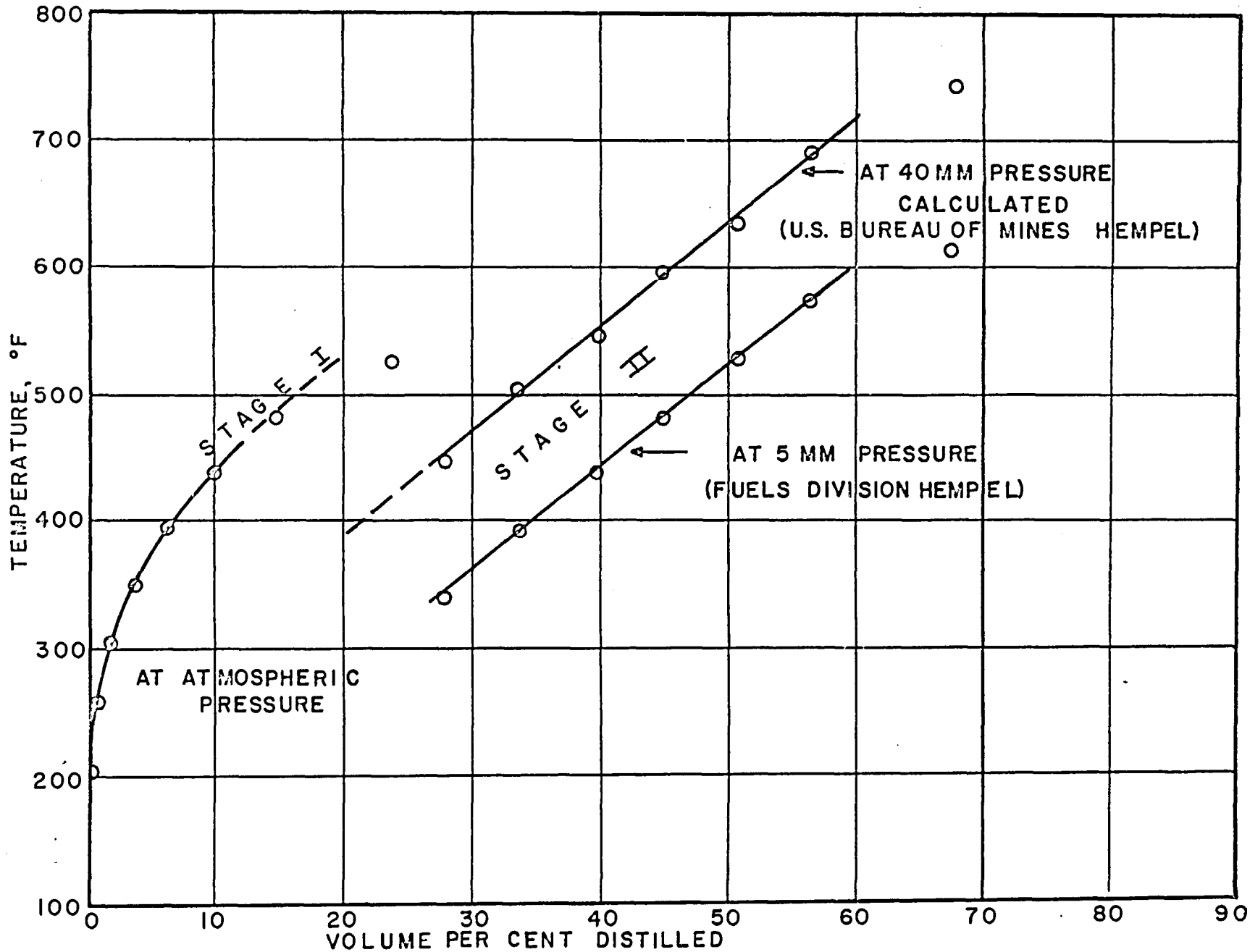


Figure 11. Hempel distillation curves, Lloydminster crude oil.

The Bureau of Mines Hempel distillation was then converted to the A.S.T.M. distillation, using the method described by Francis and Van Winkle.[5] The Bureau of Mines 50% point was determined to be 633°F, from Figure 11. The A.S.T.M. 50% point was reckoned at 852°F, from Figure 12.[5]

Table 11 shows the derivation of the A.S.T.M. distillation data from the Bureau of Mines distillation data, using Figure 11 to obtain the Bureau of Mines Hempel slopes, and Figures 13[5] and 14[5] to obtain the A.S.T.M. slopes. The A.S.T.M. temperatures were derived using the temperature differences starting from the 50% point.

These calculated A.S.T.M. distillation data are plotted in Figure 15.

From Table 11, the A.S.T.M. 10-30% slope is:

$$\frac{665 - 492}{20} = 8.7$$

From Figure 16[3] a value of -7°F was obtained for the equilibrium flash vapourization (E.F.V.) 50% point minus the A.S.T.M. 50% point. Therefore, the E.F.V. 50% point is 852 - 7 = 845°F.

Table 12 shows the calculation of data for the E.F.V. curve. The A.S.T.M. slopes were obtained, using temperatures from Figure 15, and converted to E.F.V. slopes by extrapolation on

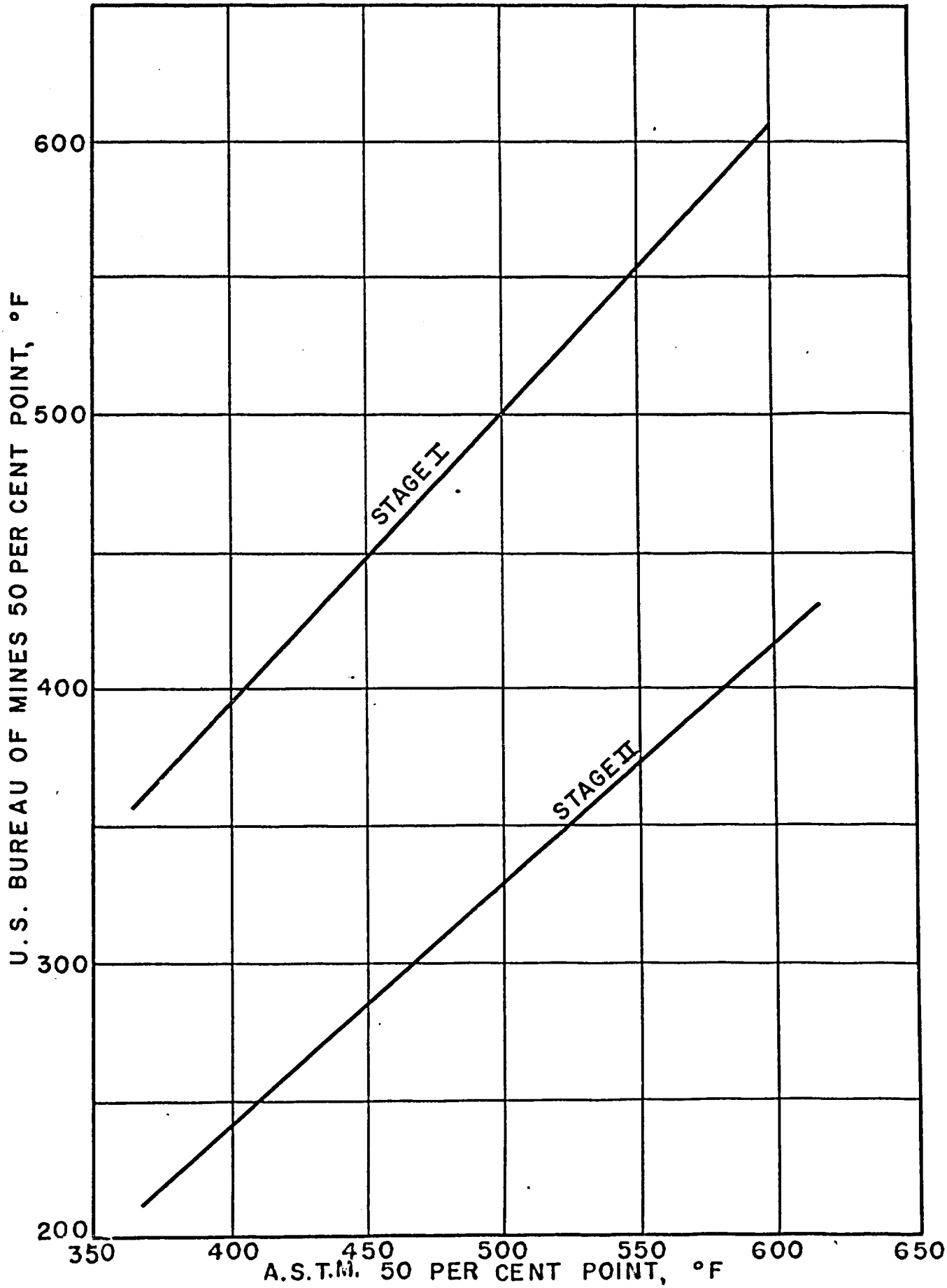


Figure 12. 50 per cent points. (Francis and Van Winkle)

TABLE 11

Conversion of U.S. Bureau of Mines Distillation Data to A.S.T.M. Basis

Volume, % Distilled	Range, %	U.S. Bureau of Mines Hempel (From Figure 11)			A.S.T.M. (From Figures 13 and 14)		
		Temp., °F	Difference, °F	Slope, °F/%	Slope, °F/%	Difference, °F	Temp., °F
		Stage I Distillation at Atmospheric Pressure			(From Figure 13)		
0		203					253
	0-10		237	23.7	23.9*	239	
10		440					492
	10-20		95	9.5	7.9	79	
20		535*					
		Stage II Distillation at 40 mm Hg Pressure			(From Figure 14)		
20		388*					571
	20-30		82	8.2	9.4	94	
30		470					665
	30-40		82	8.2	9.4	94	
40		552					759
	40-50		81	8.1	9.3	93	
50		633					852
	50-60		82	8.2	8.6	86	
60		715					938

* Extrapolated.

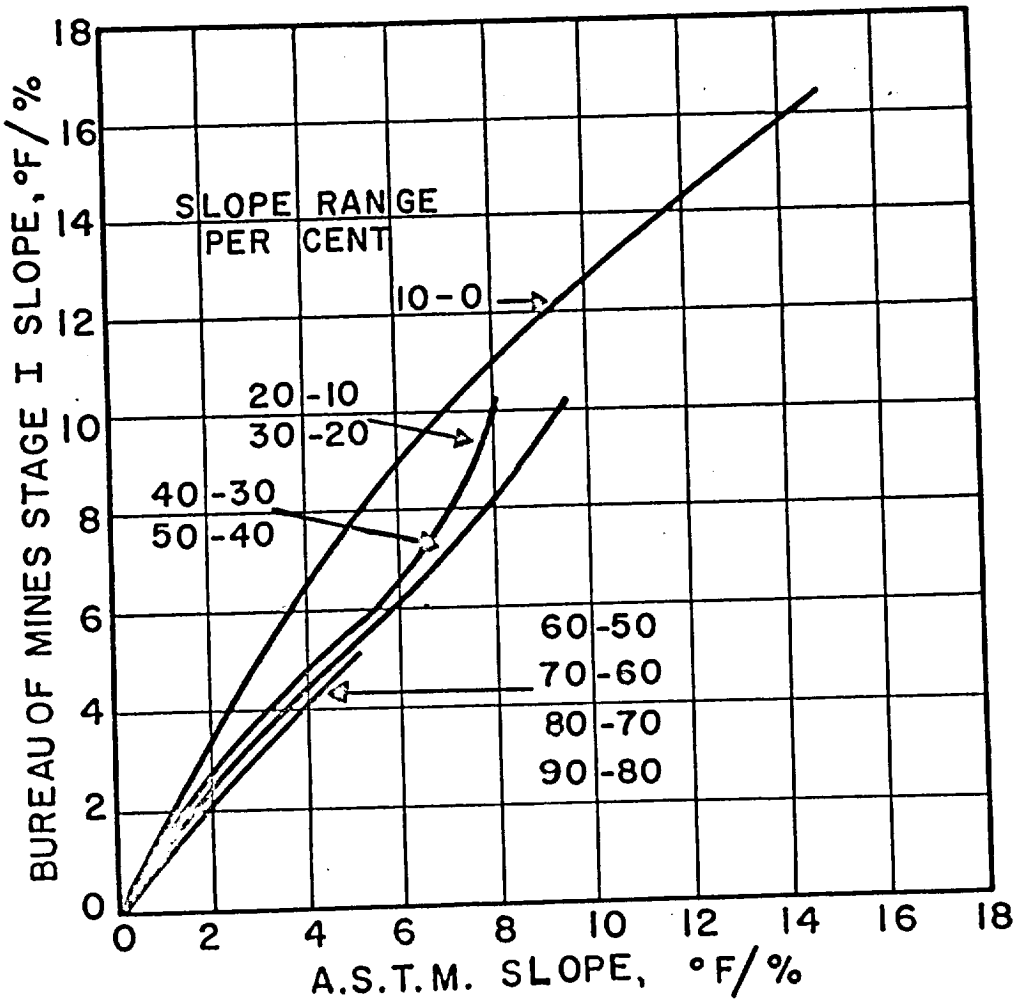


Figure 13. U.S. Bureau of Mines stage I slopes versus A.S.T.M. slopes. (Francis and Van Winkle)

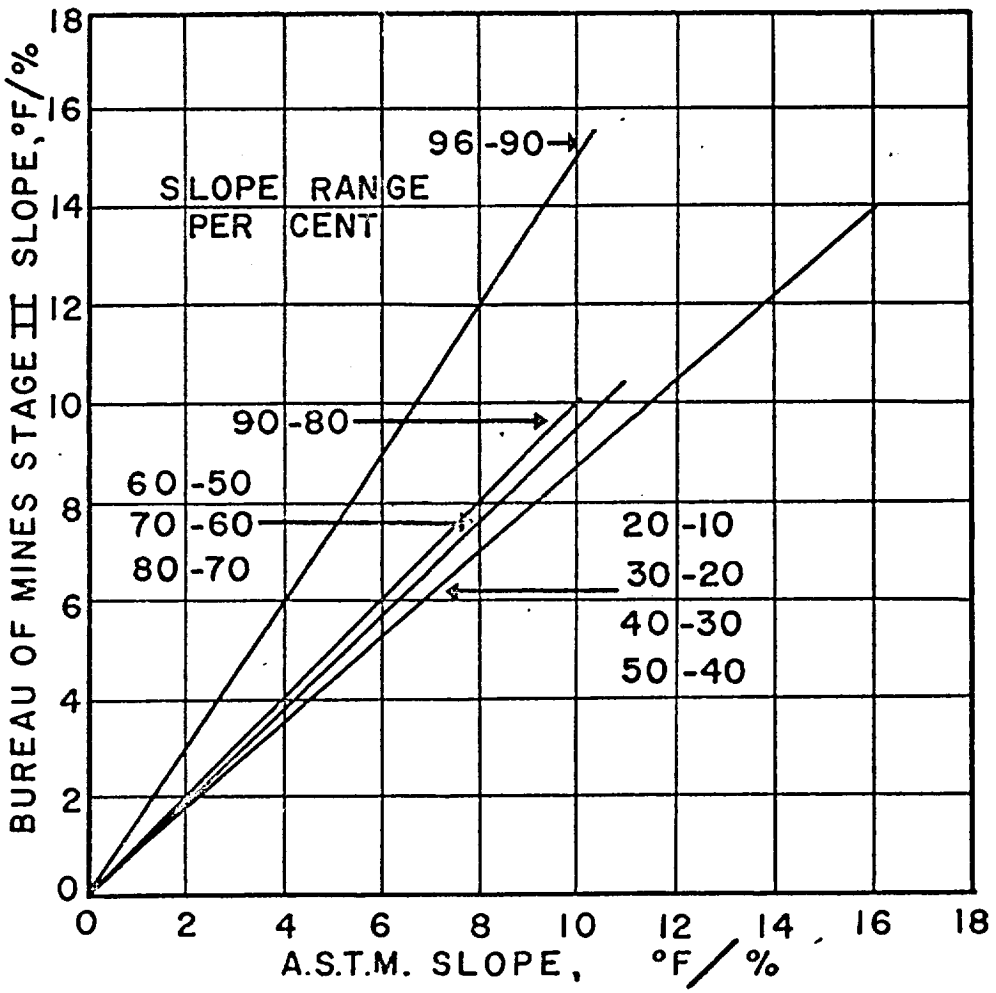


Figure 14. U.S. Bureau of Mines stage II slopes versus A.S.T.M. slopes. (Francis and Van Winkle)

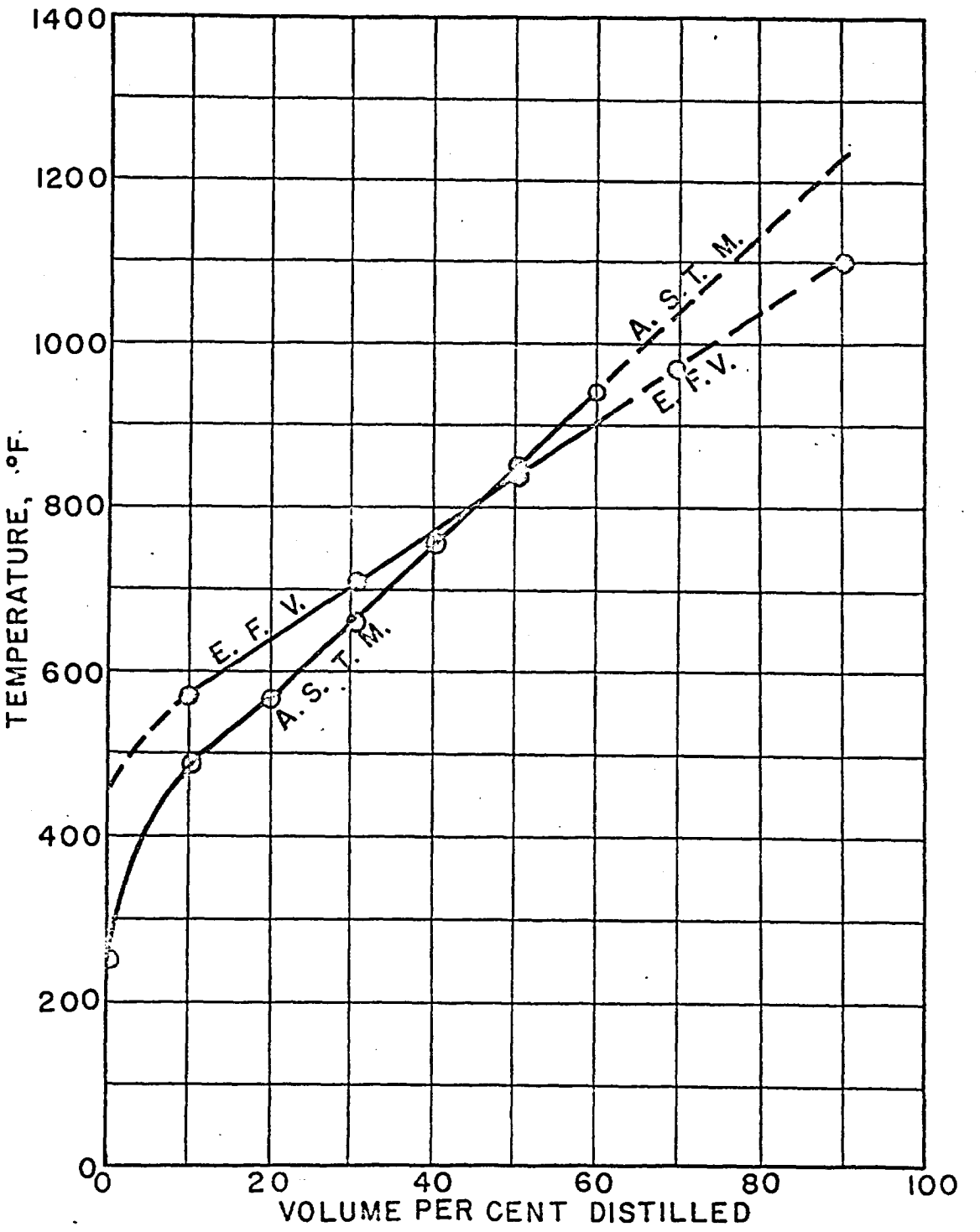


Figure 15. Distillation curves, A.S.T.M. and equilibrium flash vapourization, Lloydminster crude oil.

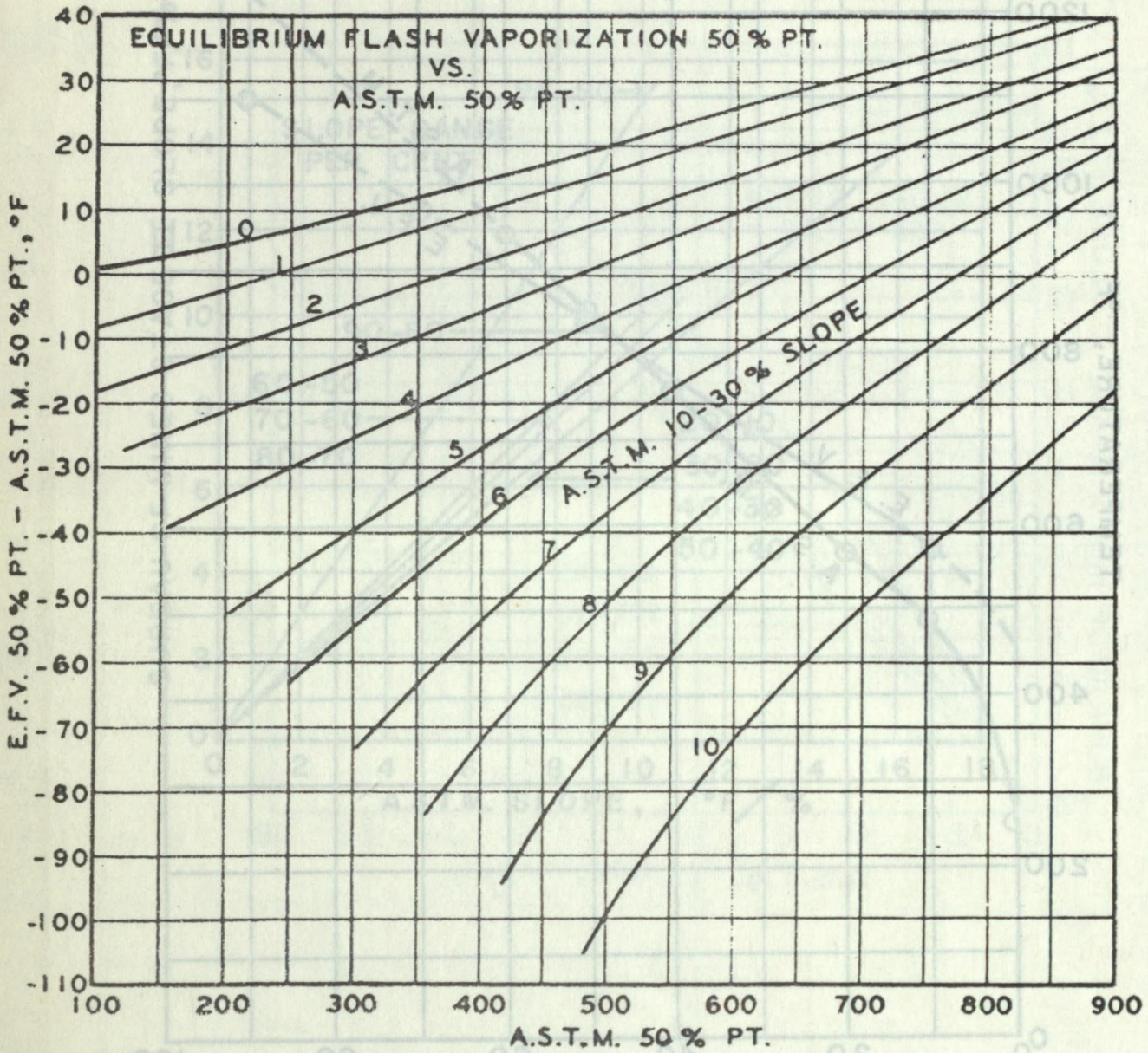


Figure 16. A.S.T.M. and E.F.V. 50 per cent points. (Edmister and Pollock)

Figure 17.[3] The E.F.V. temperatures were then determined using the temperature differences starting from the 50% point. These data are also plotted in Figure 15.

TABLE 12

Conversion of A.S.T.M. Distillation Data to E.F.V. Basis

Volume % Distilled	Range, %	A.S.T.M. (From Table 11 and Figure 15) Temp., °F	Difference, °F	Slope, °F/%	E.F.V. (From Figure 17) Slope, °F/%	Difference, °F	Temp., °F
0		253					
	0-10		239	23.9			
10		492					575
	10-30		173	8.7	6.7	134	
30		665					709
	30-50		187	9.4	6.8	136	
50		852					845
	50-70		188	9.4	6.5	130	
70		1040*					975
	70-90		189	9.4	6.3	126	
90		1229*					1101

*Extrapolated.

The A.S.T.M. volumetric average boiling point (V.A.B.P.) is the average of the 10%, 30%, 50%, 70% and 90% A.S.T.M. points, and from Table 12 this is equal to -

$$\frac{492 + 665 + 852 + 1040 + 1229}{5} = 856°F$$

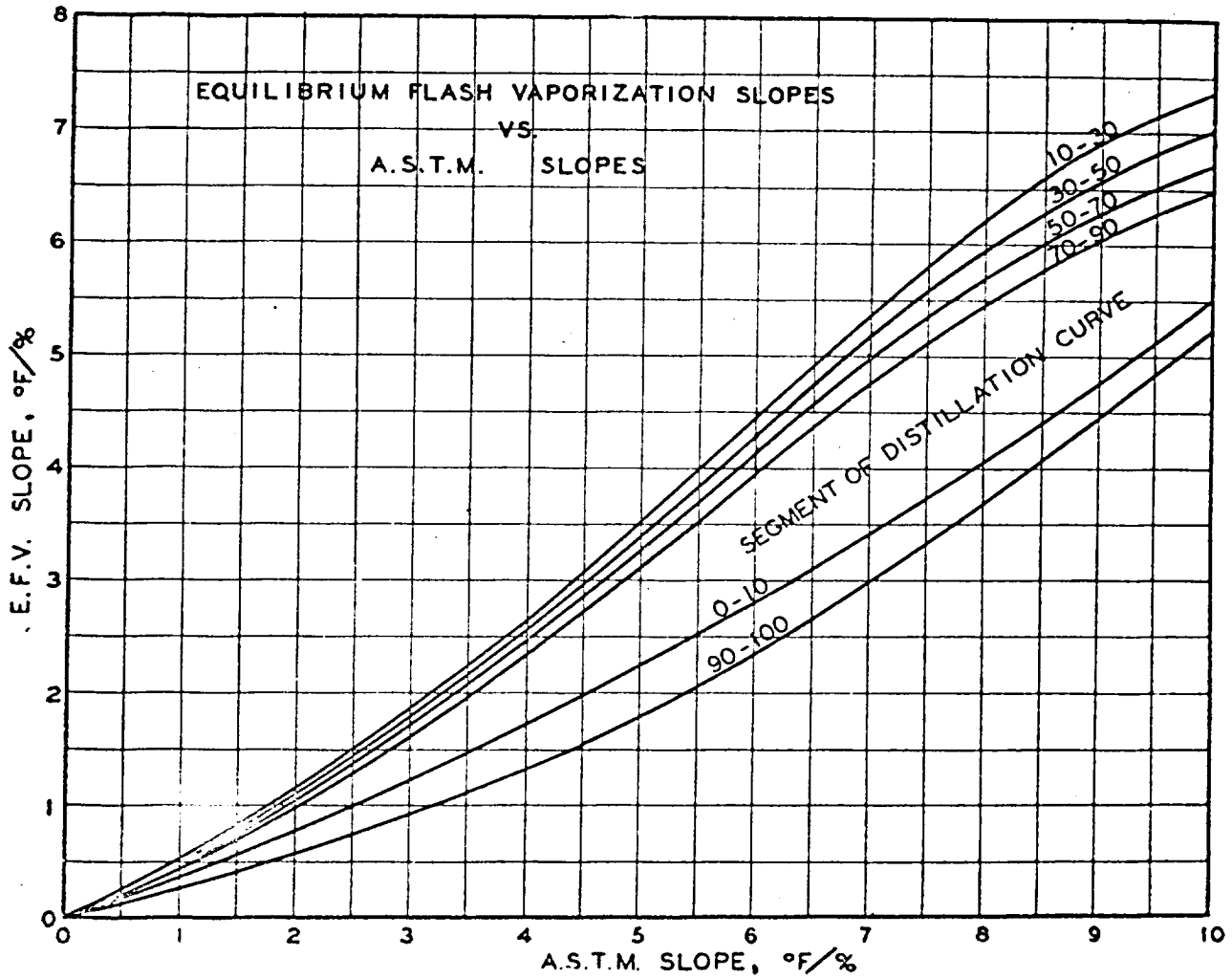


Figure 17. E.F.V. slopes versus A.S.T.M. slopes. (Edmister and Pollock)

From Figure 18,[3] the value of T critical - V.A.B.P. = 313.

Then, T critical = 313 + 856 = 1169°F.

From Table 12, the A.S.T.M. 10-90% slope = (1229-492) ÷ 80 = 9.2.

Extrapolating in Figure 19,[3] the value of P critical = 631 psia (pounds per square inch, absolute).

T focal = T critical + 57 (from Figure 20[3]) = 1169 + 57 = 1226°F.

P focal = P critical + 110 (from Figure 21[3]) = 631 + 110 = 741 psia.

The atmospheric E.F.V. curve and the critical and focal points were located on Figure 22. In constructing this figure, which is a Cox-type vapour pressure chart, the logarithm of the absolute pressure, in pounds per square inch, and the reciprocal of the absolute temperature, in degrees Rankine, were used as linear coordinates. For ease of usage, the units of the ordinate have been marked off in pounds per square inch absolute and the units of the abscissa in degrees Fahrenheit. Straight lines were drawn connecting the various points of the atmospheric E.F.V. curve with the focal point. These straight lines are lines of constant quality. The straight line through the critical and focal points at 14.7 pounds per square inch gives the boiling point. This line is the bubble point line.

In analyzing the pitch-making process, it was considered as an equilibrium flash operation with the flash temperature taken as the temperature of the pitch as it passed from the bottom of the

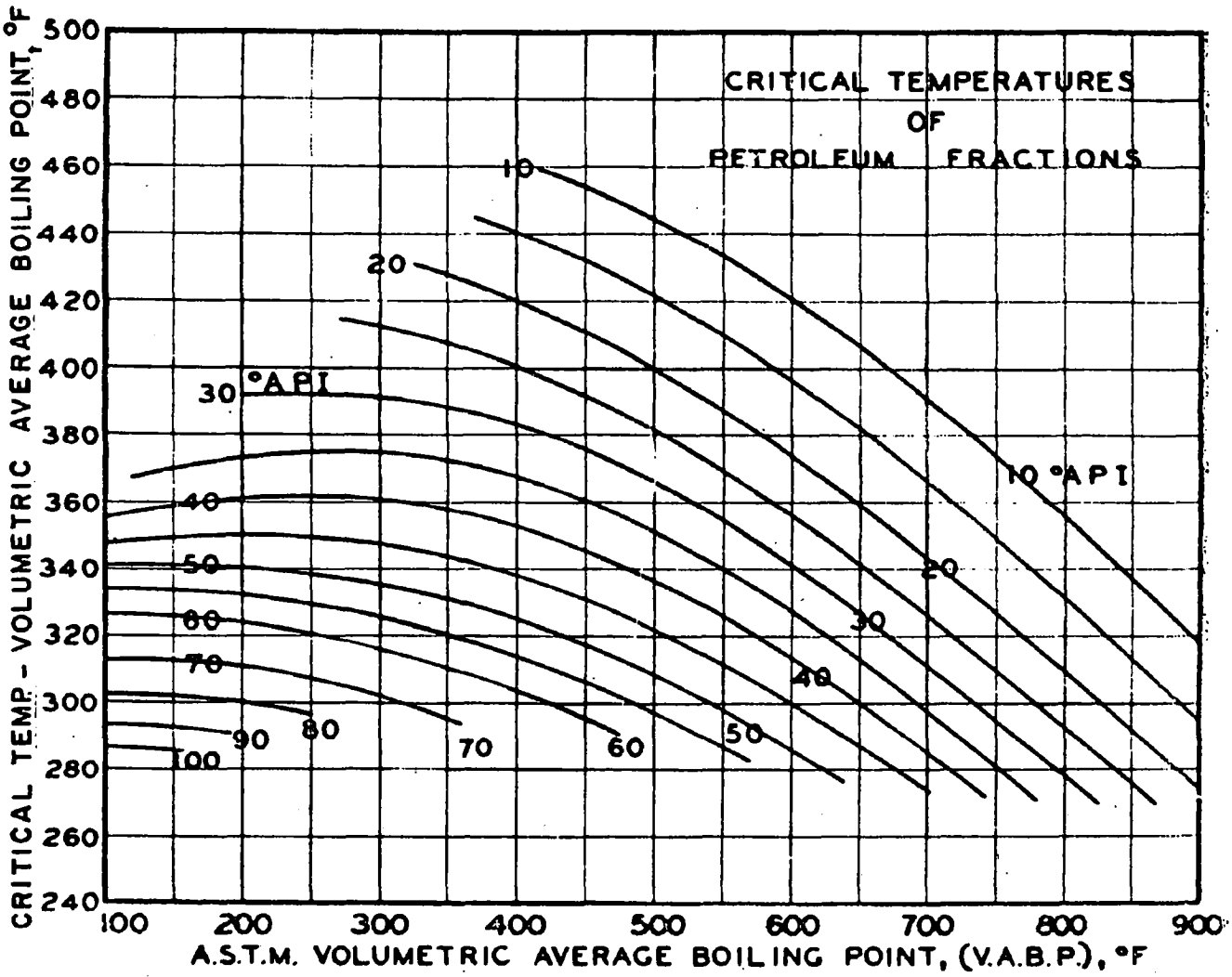


Figure 18. Critical temperatures of petroleum fractions. (Edmister and Pollock)

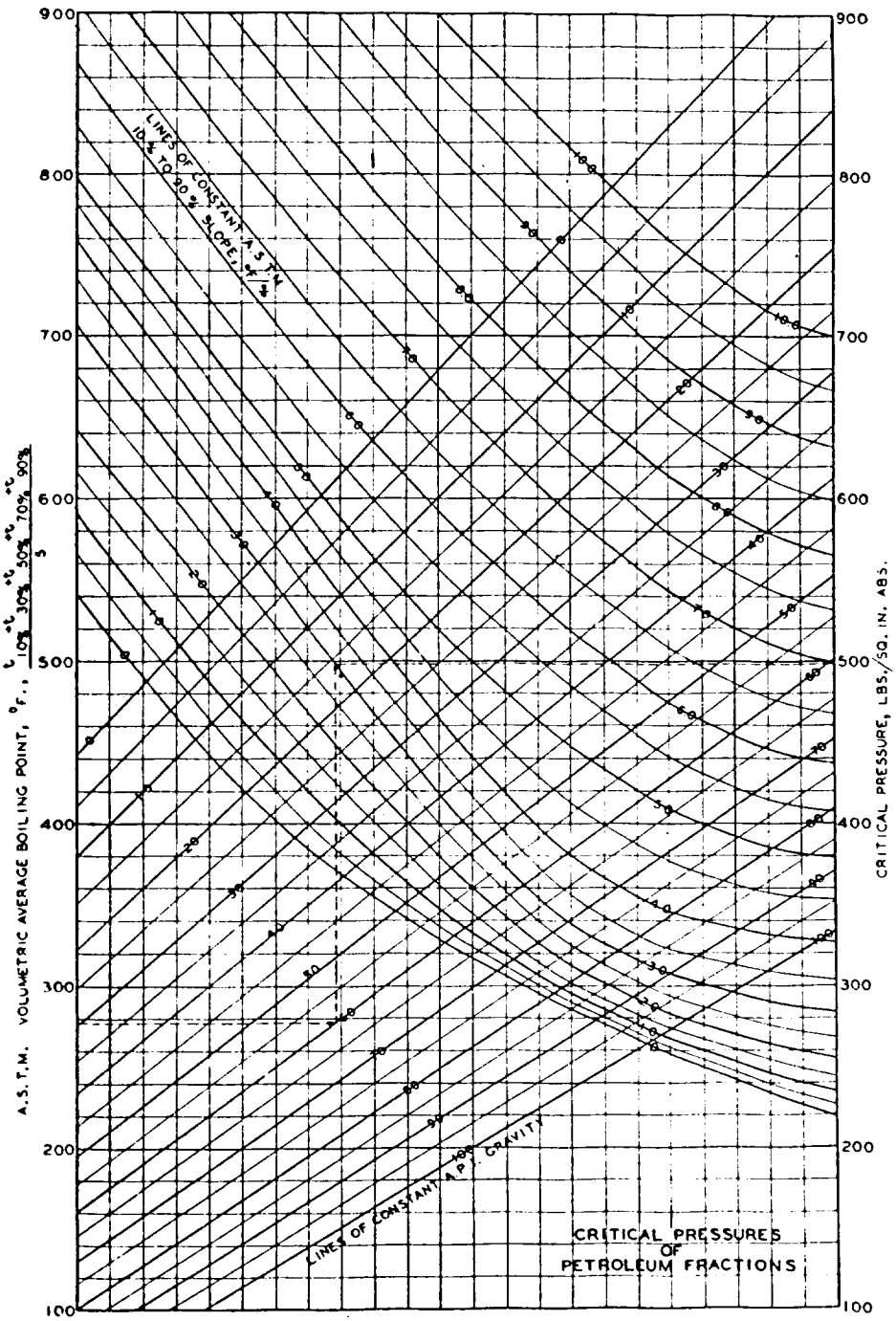


Figure 19. Critical pressures of petroleum fractions. (Edmister and Pollock)

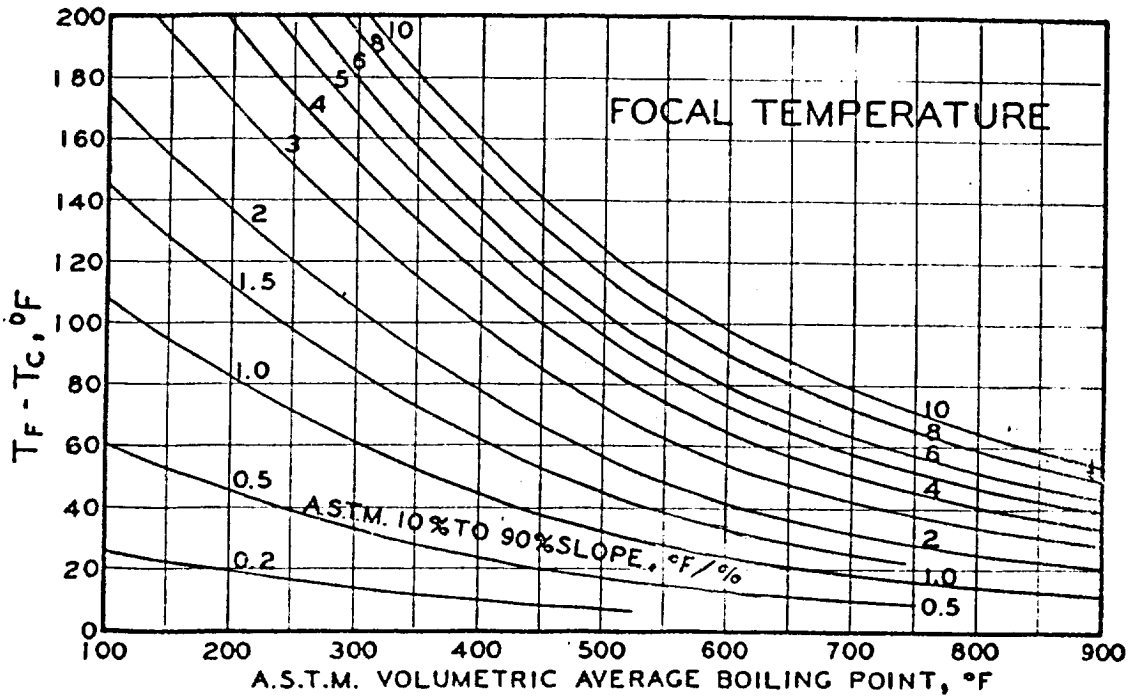


Figure 20. Focal temperature. (Edmister and Pollock)

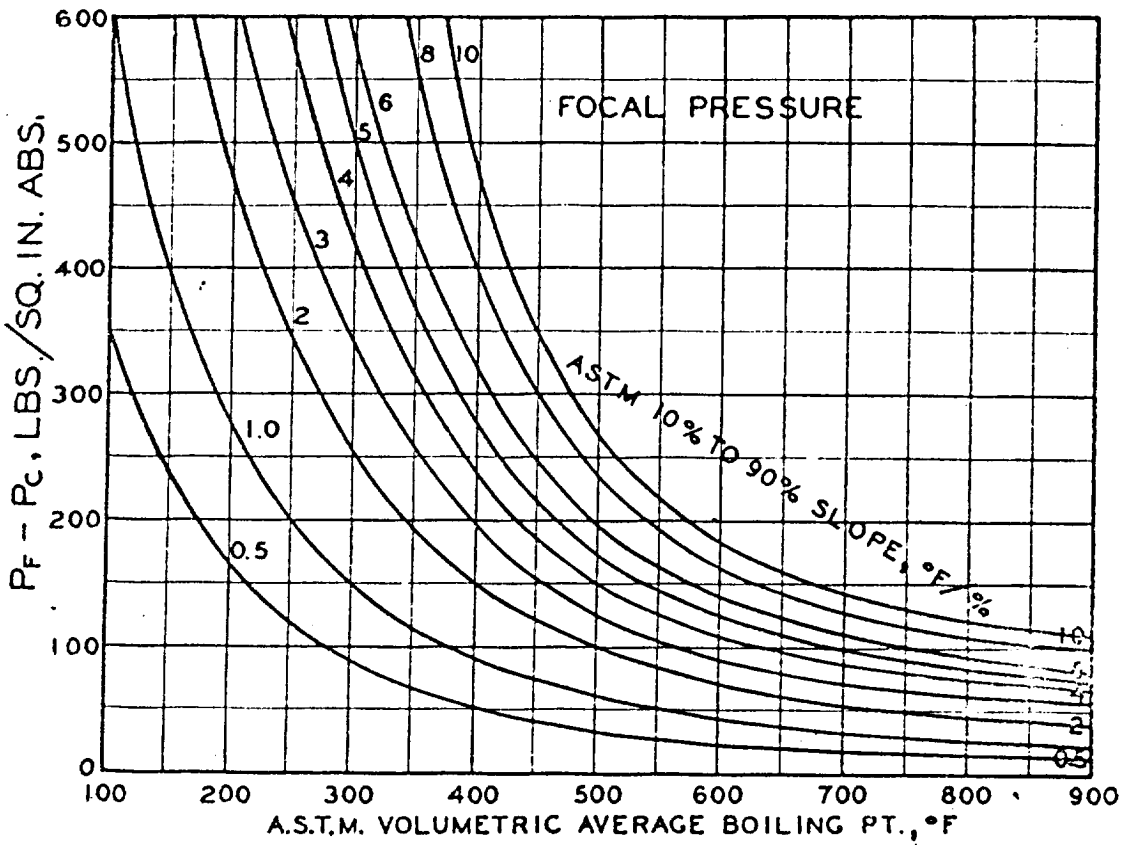


Figure 21. Focal pressure. (Edmister and Pollock)

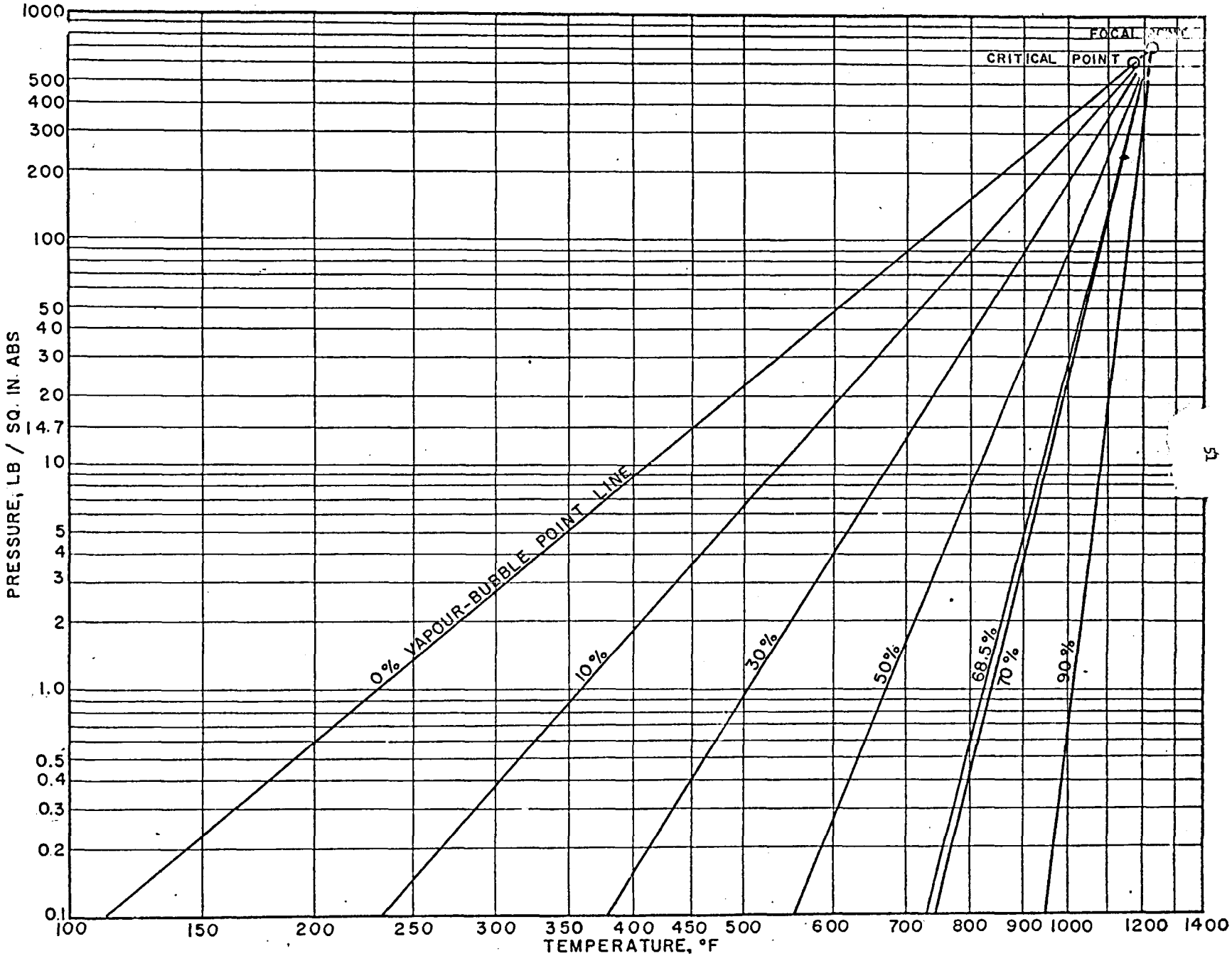


Figure 22. Phase diagram for Lloydminster crude oil.

tower. In Experiment 1, the average pitch temperature was approximately 791°F, or 1251°R. The product recoveries, as per cent by weight of feed, were as follows:

Distillate	64.8
Pitch	29.4
Gas	1.5
Coke	0.8

The losses, amounting to 3.5%, were assumed to be predominantly gas and pitch, so that the actual distillate produced was not significantly different from the distillate recovered.

The specific gravities of the distillate and feed were 0.914 and 0.966, respectively, so that the percentage by volume of distillate produced was $\frac{64.8}{0.914} \times \frac{0.966}{100} \times 100 = 68.5$.

From the E.F.V. curve (Figure 15), the 68.5% overhead point is 965°F or 1425°R. From Figure 22, the pressure corresponding to a flash vapourization temperature of 791°F (1251°R) is 0.426 pounds per square inch or 0.426 x 51.77 = 22.1 mm Hg.

The apparent gas rate during the feeding period in Experiment 1 was 3200 cubic feet per hour. This rotameter reading was based on a gas with specific gravity of 1.39 at 14.7 psia and 150°F.

The actual gas being recirculated had an approximate specific gravity of 1.142 at 14.7 psia and 70°F. Passing through the meter, this gas was at 15.0 psia and 170°F. From this information the actual gas rate was calculated (Fischer and Porter

Bulletin No. 60) to be 3540 cubic feet per hour. At normal temperature and pressure this gas rate would be 2830 cubic feet per hour. Therefore, the pound mols of gas recirculating per hour was

$$\frac{2830}{359} = 7.9.$$

The total pressure at the bottom of the column was 780 mm Hg. The partial pressure of the gas was therefore 780 - 22.1 = 757.9 mm.

The mols of vapour per mol of vapour-free gas was then

$$\frac{22.1}{757.9} = 0.029.$$

Therefore, the mols of oil evaporated per hour equals

$$7.9 \times 0.029 = 0.231.$$

The molecular weight of the overhead liquid product recovered was estimated to be 314 pounds per mol.[2] Therefore, pounds of oil evaporated per hour = $0.231 \times 314 = 72.4$. As the feed rate was 98 pounds per hour, the actual pounds of oil evaporated per hour was $\frac{64.8}{100} \times 98 = 63.5$.

The efficiency of the sloping plate column under these operating conditions, as compared with the theoretical maximum, was estimated to be $\frac{63.5}{72.4} = 88\%$.

The above graphical and computational scheme permits an estimate to be made of the fraction of the crude oil which will be vapourized if the pitch temperature and the ratio of the mols of vapour to mols of circulating gas are known. It was important,

therefore, to secure a relation between the amount of distillate removed from a given quantity of crude oil and the physical properties of the resulting pitch. This would enable the properties of the pitch to be directly related to the outlet pitch temperature and the gas circulation rate. The desired relation was secured through the material and ash balances in the following manner: for convenience, let O represent 100 pounds of crude oil fed to the cracking tower and V the weight of material vapourized, including both liquid distillate and cracked gas. The weight or per cent of pitch produced from this crude oil may be denoted by P. From the material balance we have,

$$O = V + P = 100$$

If it is assumed that the ash content of the vapourized oil is negligible, while that of the crude oil is 'a' and that of the pitch is 'x', we obtain from the ash balance,

$$Oa = Px$$

$$\text{or, } \frac{Oa}{x} = P = 100-V$$

Figure 23 is a nomogram obtained from a plot of P against $\frac{1}{x}$ for various values of 'a'. Knowing the ash contents of a particular oil feed and pitch product, the amount of distillate removed may be determined from this figure. The ash content of the Lloydminster crude employed in these experiments was 0.028%.

Figure 24 shows the relation between the hardness of the

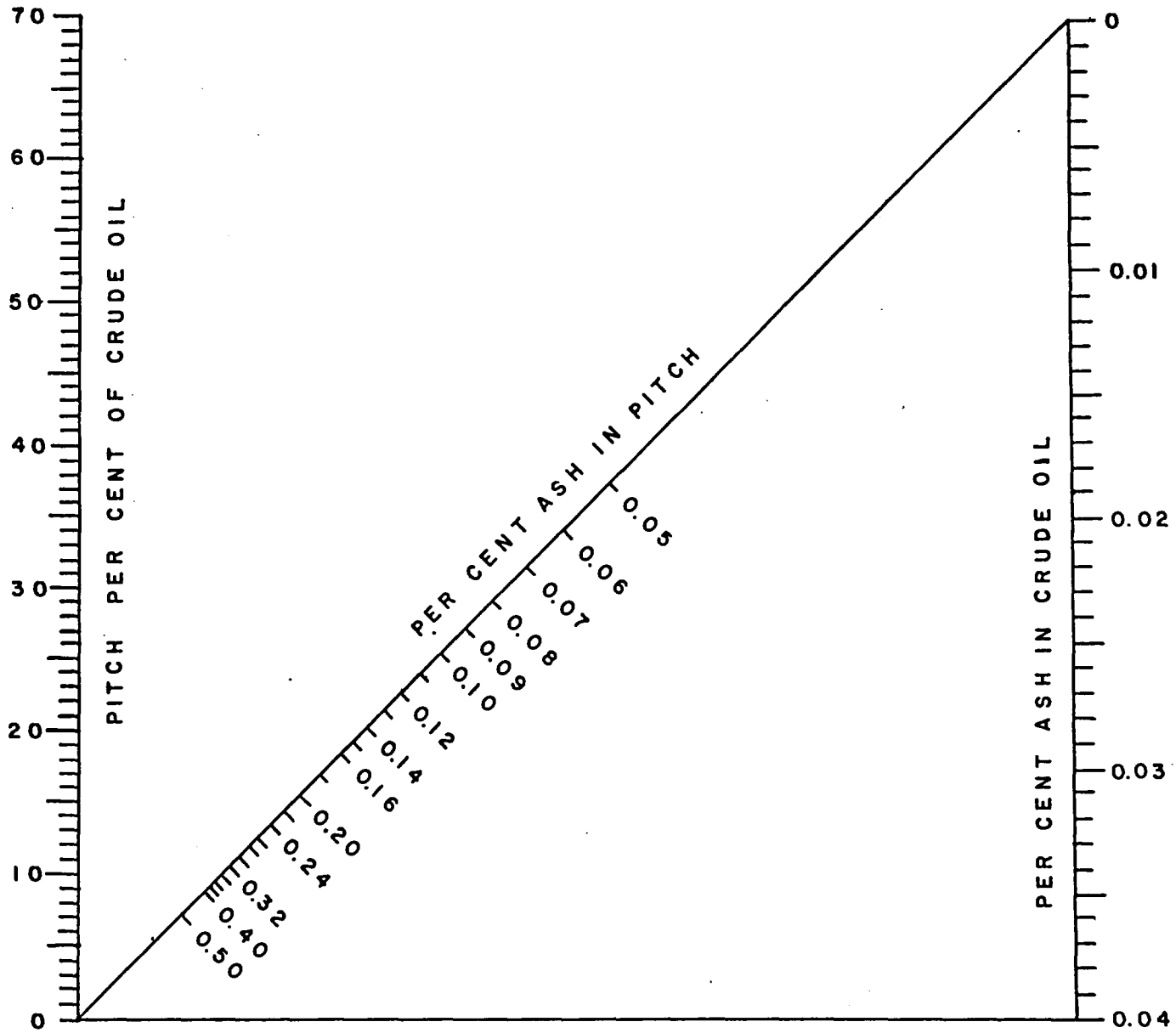


Figure 23. Conversion of crude oil to pitch and distillate, based on the ash content of the pitch.

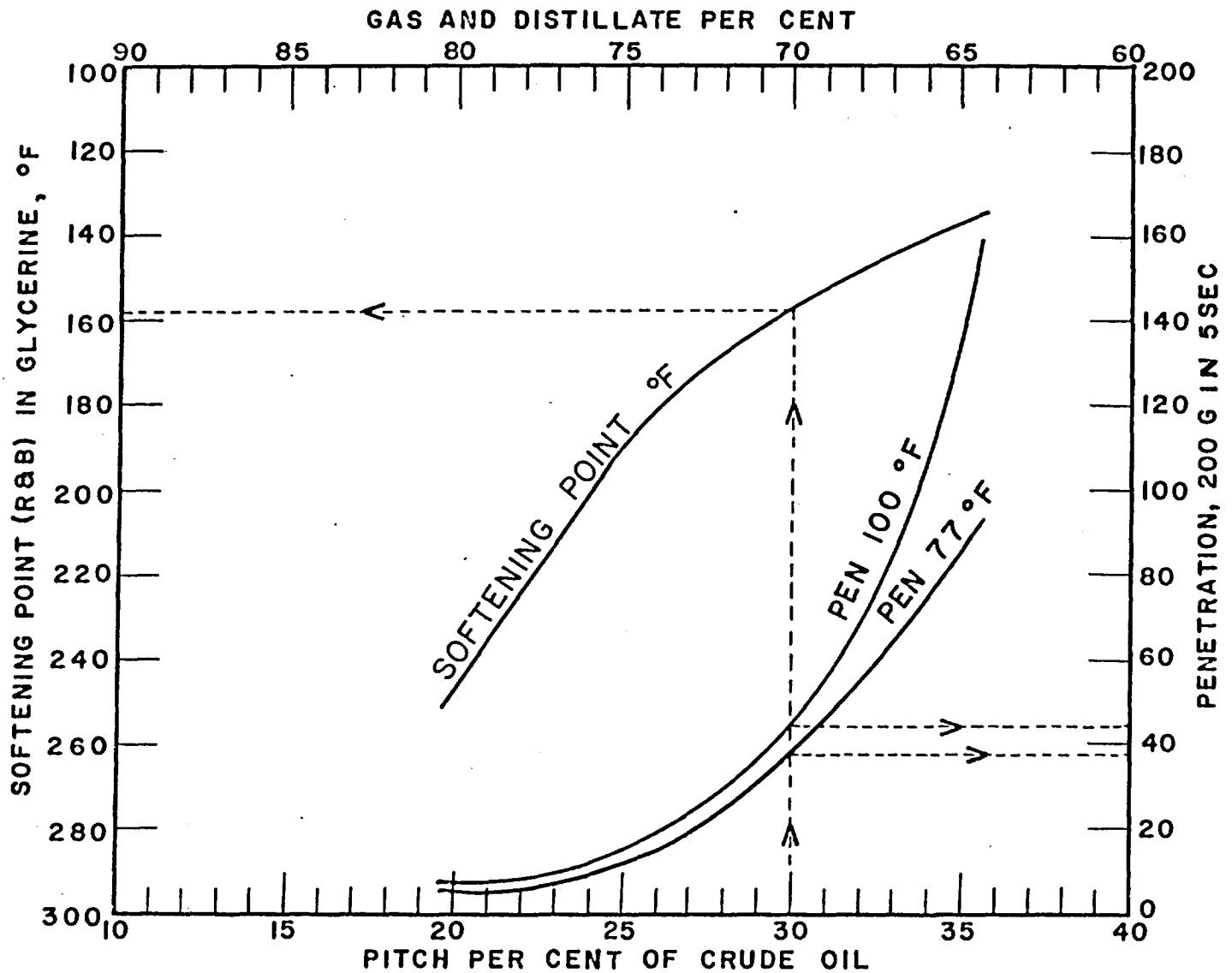


Figure 24. Relation of pitch hardness to percentage of distillate removed from the crude oil.

pitch (measured by the Ring and Ball test) and the penetration of the pitch, as a function of both the percentage of the crude oil vapourized and the remaining fraction of pitch.

As the quantity of cracked gas amounts to only 1.5% of the crude oil, V may be taken without appreciable error to represent the quantity of liquid distillate.

From Figures 23 and 24 it was estimated that, at a liquid feed rate of 100 pounds per hour, to achieve a pitch hardness of the order of 250°F (Ring and Ball), an outlet pitch temperature of the order of 880°F would be required at the present gas recirculation rates. This high temperature level suggested that coke formation might be difficult to avoid.

CONCLUSIONS

The initial assumption made following Experiment 1 was that the mechanism of pitch formation involved extensive thermal cracking and distillation. This interpretation led to the deduction that a critical pitch temperature existed in the relationship between pitch product temperature and pitch hardness.

However, this prediction was not supported by the subsequent experimental data. The only remaining possibility was that thermal degradation of the pitch was negligible. This alternative interpretation was consistent with all the observations.

It was further concluded that the close agreement between the

calculated quantity of liquid distillate and that actually obtained supported the view that little thermal cracking took place. Also, it was inferred that the operation might be regarded, from a computational point of view, as one similar to steam distillation.

The experiments showed that a relation existed between pitch hardness and the fraction of the crude oil which had been vapourized. This relation clarified the interpretation of the general observation that at the beginning of an experiment the pitch was always hard but decreased in hardness as time progressed. This observation could be entirely ascribed to the increased amount of distillate removed by the hot plates. In the course of time the column plates cooled as a result of the introduction of cold oil feed.

Experiences with blocking of the pipe lines by froth-like coke and ignition of the pitch in preliminary experiments, emphasized some of the difficulties which may be encountered in pitch manufacture and confirmed the need for fire-fighting equipment, and for shields to prevent the operators from being splashed with hot pitch.

The results from Experiments 2 and 3 indicated that without substantial reduction in the feed rate it would be impossible to achieve a pitch hardness of the order of 250°F (Ring and Ball). Alternatively, at the present gas recirculating rates, if the feed rate were maintained at 100 pounds per hour, the inlet gas temperatures would have to be raised until the outlet pitch temperature was of the order of 880°F.

Apart from the configuration and size of the sloping-plate tower, the variables which govern the pitch hardness are: the liquid feed rate, the residence time of the liquid in the tower, and the recirculating-gas rate and temperature. To bring about harder pitch, some change must be made in these quantities. As it had been shown that increasing the gas flow prevented the descent of the oil in the tower, and that raising the temperature produced froth coke, it was concluded that the most promising field for future experiments lay in increasing the residence time of the liquid by installing a stand pipe at the foot of the column. This measure would not only increase the residence time of the pitch but would provide an opportunity for intimate contact between the inlet gas stream and the pitch. The greater residence time would also provide more opportunity for thermal cracking to take place.

If increasing the residence time still did not give satisfactory results, the recirculating gas temperature would have to be raised. This would involve replacing the mild steel tubes in the gas heater with stainless steel tubing(preferably type 446). The temperature controller would have to be replaced with one permitting temperatures up to 1200°F to be maintained and controlled.

The behaviour of the sloping-plate tower in Experiment 1 showed that when the recirculating gas rate was increased from 3200 to 3400 cubic feet per hour the flow of pitch was greatly reduced, so that there seemed little possibility of increasing this rate without

reducing the length of the plates to permit a wider passage for the gas around the ends. Such a change would involve a reduction in the surface available for evaporation on the plates.

As far as the quality of the pitch was concerned it was concluded that a pitch with a hardness of the order of 200°F (Ring and Ball) could be continuously produced with the present tower and operating conditions. While this degree of hardness was considerably less than the specified value of 250°F (Ring and Ball), the operation was sufficiently well understood to permit the selection of the conditions necessary to achieve the desired product.

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FLB:REC:DSM:(PES) LC