The Fractionation of Crude Petroleum by Capillary Filtration.

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY WITH THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY.

BY

MARSHALL PERLEY CRAM.

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EASTON, PA.:
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The author takes pleasure in expressing his gratitude to President Remsen, Professor Morse, and Professor Jones for instruction in the lecture room and laboratory. Especial thanks are due to Dr. Gilpin, under whose personal direction this investigation has been pursued, and to Dr. D. T. Day, of the U. S. G. S., who has contributed valuable suggestions and apparatus.

The Fractionation of Crude Petroleum by Capillary Filtration.

When in process of refinement, black vaseline is filtered through warm dry fuller's earth the first product is an oil perfectly liquid at ordinary temperatures, while the succeeding portions are progressively more viscous until quite hard vaseline is obtained. This observation, that a fractional separation of oils in vaseline had been effected, suggested to D. T. Day that a like result might be obtained with crude petroleum. He applied this method to a sample of the green crude petroleum from the "third sand," Venango County, Pennsylvania, and found that light products, chiefly gasoline, first appeared when such crude oil was allowed to filter down through a long glass tube filled with granulated or powdered fuller's earth.[1]

Following this a more elaborate system of specially constructed funnels similar to those used by the refiners of vaseline in testing the comparative value of various fuller's earths was used. The results from this were briefly summarized in a paper upon the ability of petroleum to migrate in the earth.[2] Engler later verified these results and showed that the separation was mechanical and that no oxidation was effected in the process. Day next used a large closed funnel of galvanized iron holding about one hundred pounds of fuller's earth. When crude petroleum was dropped slowly and regularly into this, quite light oils at first, followed by the usual succession of heavier oils, were obtained. As it was evident from this work that much of the oil passed through crevices without any change he tried the effect of reversing the route of the oil and of allowing it to diffuse

[1] Philadelphia Acad. of Sci., 1897.

[2] Trans. Petroleum Congress (Paris), 1900.

upward through a tube packed tightly with fuller's earth. In such a tube the lighter constituents rose much more rapidly than the more viscous oils so that by separating the fuller's earth from different sections of the tube and displacing the oil by water, quite different oils were obtained from the upper and lower parts of the tube.

By using several tubes and uniting oils of the same specific gravity, oil of different grades could be collected in sufficient quantity to be fractionated again, and the process continued until oils result which are not altered by further passage through tubes filled with fuller's earth. At the suggestion and with the coöperation of Day, we have taken up this problem with the results here stated.

The tubes used first were three feet long and one and one-eighth inches in diameter. They were closed at the lower end with corks, along the sides of which grooves had been cut, the top of the cork being covered with a bit of cotton cloth to prevent the earth from sifting out of the grooves. Such tubes filled with fuller's earth[1] were placed with their lower ends in an open dish of petroleum and the oil was allowed to rise.

At room temperatures (18°–22° C.) and atmospheric pressure, the rate of rise of crude petroleum in a tube filled with fuller's earth was very slow. In seven days the oil ascended but 73 cm. in one tube, while ten days in one case and seven in another were required for it to rise 59 cm. To study the effect of heat, a glass tube about three feet long and $1\,{}^1/_8$ inches in diameter, was filled with earth and placed in a bottle holding about two liters of oil, and the whole heated by an electric stove with which temperatures considerably above those of the room could be maintained day and night. The temperature of the tube was kept between 40° and 70° for three days, in which time the oil rose 54.7 cm. in the tube; in another tube packed in all ways like the former but held at room temperature (about 20°), the oil rose 46 cm. in the same length of time. With two tubes in which the earth was packed much less compactly, the time required for the oil to rise 54 cm. was four days for the tube at room

[1] The fuller's earth used in this work was kindly furnished by the Atlantic Refining Co., of Philadelphia.

temperature and two days for the one at 50° to 80°. The rate of rise evidently was but little effected by heat, at least within this range of temperature, and higher temperatures could not be used without loss of the more volatile constituents of the oil.

The next attempt at increasing the rate of rise of the oil consisted in applying diminished pressure to the top of the tube which reduced the time required for the oil to reach the top of a tube five feet long from several weeks to seventeen hours. If diminished pressure is continued after the oil has reached the top, provided the oil is not exhausted in the reservoir at the bottom, oil will be drawn over from the top of the tube. The specific gravity of the oil thus collected steadily rises as it comes over. The samples so obtained, however, stand under very low pressures for some time, which may cause a loss of their more volatile constituents. This suggested applying increased pressure to the oil in the reservoir rather than diminished pressure to the top of the tube, and an iron bomb, like those used for the transportation of mercury, was fitted with an iron pipe seven feet long to contain earth and a side arm at the bottom of the bomb to which a water column might be attached.

The bomb which held about two liters could be partly filled with petroleum and the pipe containing the earth screwed into the top. The side arm which opened into the bottom of the bomb could then be connected with the water pressure so that the lower part of the bomb was filled with water which drove the petroleum upwards. The oil obtained at the top, however, was fractionated no further nor in any larger amounts than when the oil was not allowed to emerge from the top of the tube. The difficulty of setting up such a pressure apparatus with tight connections, as well as the range of pressure required—a column of water seven feet high being too great when the oil was just started up the tube while a column thirty feet high was insufficient when it was near the top—made its use impracticable.

To use diminished pressure, the earth in the tubes must not be packed so hard that the air just above the oil cannot be drawn through the earth above, nor must the earth be packed so loosely that the oil will rise as in a vacuum. The right degree of hardness is obtained by filling about a foot of the tube at a time and packing that much earth as hard as possible with a wooden rod tipped with a rubber stopper. If the tube when pounded upon the floor, rings in the hand, the earth is apt to be packed too closely. Packing tubes may be much facilitated by filling several at once with a separate ramrod for each. By allowing a few minutes to elapse between successive liftings of the ramrod, much labor is avoided.

The fuller's earth was first heated in shallow iron pans until it ceased to form geysers when stirred. The earth must be thoroughly cold before it is packed into tubes or the contraction is sufficient to allow the oil to run up the tube immediately when the air is exhausted.

The lower end of the tube is best closed with a cork with six or seven grooves cut along the side, and the inner end covered with a bit of cloth to keep the earth from sifting out of the grooves. At the top of the tube a bit of cotton waste below a rubber stopper will prevent any earth from being drawn up when the air is exhausted.

The tubes used first were three feet long and one and one-eighth inches in diameter and of glass. Much trouble was experienced on account of their breaking, not when in service, but soon after they had been used. This was thought to be due to the age of the tubing, but the same happened with new tubes five feet long and one and one-fourth inches in diameter. With the idea that the iron scraper used to remove the earth from the tubes might be the cause, a scraper entirely of wood was tried, but this did not decrease the breakage, it being nothing unusual on going to the laboratory in the morning to find half of the tubes which had been emptied the day before cracked.

It had been considered necessary to use tubes of glass in order that the height to which the oil had risen could be seen and that in removing the oil from the middle of the tube it might be scraped out to a sharp dividing line, since the level to which the oil has risen is the point from which all measurements should be made of sections into which the tube is to be divided. Tin tubes were used later to avoid the trouble experienced with glass tubes. These tin tubes were emptied by shaking the earth from the bottom into four thirty centimeter cylinders of the same diameter as the tube, these cylinders being made of two curved pieces of tin held together by a cap at one end and a ring at the other. The cylinders containing the contents of the tube could be opened lengthwise and the earth divided into any desired lengths. Two glass tubes five feet long and one and one-fourth inches in diameter were set up in the same dish of petroleum with ten or twenty tin tubes five and one-half feet long and of the same diameter, and when the oil stood at the top of the glass tubes the tin ones were also opened. Glass tubes, of course, can be emptied as well as tin ones by shaking the contents from the bottom, and no more tubes broke after this method was adopted.

The level to which the oil will rise can be regulated by the amount of oil in which the tube is placed, and in the later work the adoption of this method did away with the use of glass tubes entirely. 950 cc. of oil in a tube one and one-fourth inches in diameter and five and one-half feet long will rise to within 20 to 35 cm. of the top.

When the oily earth has been removed from the tube, the oil may be separated by adding water. As first practised, enough water was added to form a very thin mud which was thoroughly stirred by a small propeller driven by a water motor. The mixed earth, oil, and water were then poured into a large separating funnel and allowed to stand several minutes until the oil had collected at the top. The earth and water could then be drawn off and the pure oil left.

It was found later, however, that if less water is added to the earth as removed from the tubes, after standing a few minutes all the water will pass into the earth and this will be accompanied by the liberation of oil. Oil so liberated can then be poured off directly from the earth without the labor of churning. When water first begins to liberate oil, the earth is granular while when more water has been added and the last of the oil recovered the earth has the consistency of a thin paste which will flow when the dish is inclined, which it will not do when the oil begins to come off.

All the oil from the same section of a tube is of the same color irrespective of whether it is the first oil to come off when water is added or whether it does not come until the last. It was assumed at first that all such oil which came from the same section of earth had the same specific gravity irrespective of whether it was the first or last replaced when water was added, but this was found later not to be the case.

The first oil to be collected, if taken in sufficiently small volume, is slightly heavier than the next portion. If too much is included in the first sample this will not be the case. Beginning with the second sample the successive portions of oil steadily increase in specific gravity, this gradual addition of water affording another means of fractionation in addition to the separating power of the earth. Both of these methods of separation have been combined in this investigation. The earth must be thoroughly mixed after each addition of water to prevent a layer of water wet earth from isolating earth, which contains oil, from the water added.

The petroleum used was a dark green oil from Venango County, Pennsylvania, of specific gravity 0.810. When 950 cc. of this were drawn upwards in a tin tube five and one-half feet long the following separation was obtained as shown in Table I.

TABLE I.—SINGLE TUBES IN THE CRUDE PETROLEUM.

	(1)		(2)		(3)	
Time required	23.5 hrs.		17.5 hrs.		17.5 hrs.	
Distance from top of tube to oil when opened	31 cm.		28 cm.		28 cm.	
	Sp. gr.	cc.	Sp. gr.	cc.	Sp. gr.	cc.
A, 8 cm. at top	0.796	42	0.8012	30	0.8022	18
B, next 8 cm.	0.808	45	0.804	37	0.803	35
C, next 18 cm.	0.8125	75	0.807	47	0.8075	66
	0.8137	24	0.809	22	0.810	25
D, next 30 cm.	0.815	130	0.8125	148	0.812	140
E, next 35 cm.	0.818	170	0.8185	190	0.8175	145
F, rest	0.8205	125	0.823	100	0.821	105
		611		574		534

The oil from section C was collected in two portions, the second being obtained by the addition of more water after the first lot of oil was poured off. Although 950 cc. of crude petroleum were used in each case, it will be noticed that the oil recovered measures much less than that. When several tubes were worked up together in one case 9070 cc. of crude petroleum yielded 5951 cc. of oil, and in another case 8915 cc. gave 5415 cc.

To collect a sufficient quantity of oil several tubes were placed in the same container of petroleum, two of the tubes being of glass and the rest of tin. When the oil had reached the top of the glass tubes they and the tin ones were opened, and the earth from the same level in all the tubes mixed in tin pails. The oil was then liberated in several successive fractions by the addition of successive amounts of water. If the earth had been thoroughly mixed after each addition of water the various oils from the same lot of earth would increase regularly in specific gravity, instead of showing the variations which in many cases they do, *e. g.*, the first oil to be displaced by water in D and E of (4), in Table II, with so large volume, would not have been heavier than the succeeding oils if the water and earth had been thoroughly mixed before the oil was poured off. If we were to repeat the work instead of using one common reservoir for all the tubes, we would use a separate reservoir for each tube, and open the tube when the oil in the reservoir was exhausted. This would do away with the use of glass tubes entirely, besides insuring that the level of the oil in each tube when opened would be practically the same. If a common reservoir is to be used the tubes should all be packed with practically the same degree of hardness if the oil is to ascend in all with equal rapidity since the ascent in all tubes is checked at the same time, *i. e.*, when the oil in the reservoir is exhausted.

Diminished pressure was obtained by use of a Chapman water pump which reduced the pressure to from five to twelve cm. Hg when connected with a system of tubes. In the earlier work the pump was not run through the night, which is the reason for the much longer time required for these lots of tubes.

The earth from a tube was divided into six sections, the level to which the oil had ascended in the tube being taken as the point to be measured from. A, the top section, includes the eight cm. next the top; B, the next eight cm.; C, the next eighteen; D, the next thirty; E, the next thirty-five; while F includes what earth is left. F varies of course depending upon the height to which the oil has risen. In fractionating the crude petroleum in bulk, F was usually discarded since it was so viscous that it was deemed impossible to pass it through earth again. Records from several lots of tubes are given in Table II. The specific gravity was measured with a Westphal balance, the oil being in every case at exactly 20° C. While the fourth decimal place is not to be taken as strictly accurate, yet it is considered worth while to record it as giving a nearer approach to the truth than would result from the use of only three decimal places.

TABLE II.—FIRST FRACTIONATION OF CRUDE PETROLEUM.

	(4)		(5)		(6)	
Tubes	2 glass, 8 tin.		2 glass, 7 tin.		2 glass, 8 tin.	
Distance from level of oil to top of tube in cm.[1]	Glass. 0, 15. Tin, 40, 15, 24, 22, 28, 19, 24, 32.		Glass, 0,6. 5. Tin, 26, 28, 18, 15, 28, 12, 24.		Glass, 0, 12. Tin, 30, 28, 22, 30, 13, 12.	
Hrs. required	54		24		54	
	Sp. gr.	cc.	Sp. gr.	cc.	Sp. gr.	cc.
A	0.8015	50	0.804	100	0.805	65
	0.8005	350	0.8055	190	0.805	200
B	0.807	260	0.8085	220	0.807	140
	0.810	190	0.811	120	0.8097	125
C	0.809	100	0.8097	430	0.810	390
	0.809	400	0.8122	300	0.8135	380
	0.810	225				
	0.8115	260				
D	0.815	425	0.813	530	0.8133	610
	0.8145	625	0.8135	600	0.816	325
	0.8175	460	0.816	200	0.8175	435
					0.825	125
E	0.816	440	0.8162	480	0.816	850
	0.815	400	0.8162	725	0.8195	260
	0.821	830	0.819	390	0.821	330
					0.827	325

[1] The glass tubes are five feet long, the tin tubes five and one-half feet. Both are one and one-quarter inches in diameter.

TABLE II. (*Continued*).

	(7) 2 glass, 7 tin. Glass, 0, 7. Tin 25. 26. 23, 26, 28, 20, 28, 84		(8) 2 glass, 7 tin. Glass, 0, 5. Tin, 16. 34, 28, 15, 18, 23, 10. 48		(9) 2 glass, 7 tin. Glass, 8, 5, 15. Tin 58, 31, 60, 40, 16, 53, 16. 117		(10) 2 glass, 9 tin. Glass, 0, 8. 5. Tin, 40, 32, 36, 26, 27, 27, 20, 25, 18, 84	
A	0.800	200	0.798	130	0.8025	175	0.7995	200
	0.802	115	0.801	130	0.8037	120	0.8037	160
							0.806	23
B	0.8042	200	0.803	155	0.8042	180	0.8085	125
	0.8048	200	0.8045	230	0.8078	215	0.810	275
							0.8112	23
C	0.808	330	0.8072	430	0.809	300	0.810	350
	0.8078	430	0.808	275	0.8095	440	0.812	525
	0.811	95	0.808	225	0.8127	100	0.8135	150
D	0.812	425	0.8117	420	0.812	390	0.8148	440
	0.812	625	0.812	580	0.8137	400	0.8175	700
	0.814	360	0.822	250[1]	0.8145	300	0.817	370
			0.8145	300	0.8155	200	0.817	200
			0.8177	42				
E	0.8172	240	0.8135	390	0.818	340	0.8197	315
	0.816	650	0.814	560	0.8197	240	0.8215	720
	0.8162	660	0.8248	390[1]	0.818	290	0.8223	570
	0.8195	300	0.817	230	0.818	350	0.821	215
			0.821	42				

[1] These fractions stood uncovered on top of the earth over night and consequently were exposed to considerable evaporation.

TABLE II. (*Continued*).

	(11) 2 glass, 8 tin. Glass, 0, 4. Tin, 0, 0, 0, 0, 20, 17, 7, 5. 39		(12) 2 glass, 6 tin. Glass, 7, 13. Tin, 32, 19, 32, 35, 48, 29. 60		(13) 2 glass, 9 tin. Glass, 2, 2, 5, Tin, 17, 10, 11, 22, 16, 29, 8, 5, 5, 5, 14. 20		(14) 2 glass, 9 tin. Glass, 0, 0. Tin, 20, 20, 5, 13, 5, 15, 14, 5, 19, 8, 12, 14. 16.5	
A	0.799	80	0.798	150	0.8015	110	0.798	225
	0.802	180	0.801	140	0.8055	40	0.8005	110
					0.8028	125	0.8015	80
					0.8033	100		
B	0.807	200	0.8022	160	0.802	230	0.8015	210
	0.8115	140	0.806	105	0.8072	60	0.804	150
			0.8072	20	0.8085	50	0.8058	120
					0.8075	75		
C	0.810	300	0.807	400	0.806	340	0.8048	500
	0.811	490	0.809	200	0.808	220	0.8065	385
	0.8145	175	0.8115	60	0.8072	320	0.8075	225
					0.8097	150		
D	0.8133	450	0.811	400	0.809	400	0.810	500
	0.8133	530	0.8097	420	0.8135	250	0.810	660
	0.816	290	0.811	290	0.8115	680	0.810	650
	0.8142	250	0.815	60	0.812	650	0.812	260
E	0.8172	400	0.815	260	0.813	400	0.8135	470
	0.818	520	0.8148	510	0.818	285	0.8155	530
	0.819	405	0.815	400	0.8167	700	0.8155	700
	0.8175	370	0.817	100	0.8167	805	0.8162	680

(11) During the night oil was drawn entirely through and out at the top of five tubes which were lost.

(12) Three other tubes were set up with these but when opened the oil in these was 81, 81, and 90 cm. respectively from the top, so they were discarded. This unevenness between the tubes was probably caused by using earth in some of them which was not entirely cold.

(13) Beginning with lot (13) the pump was run continuously day and night.

TABLE II. (*Continued*).

	(15)		(16)		(17)	
	2 glass, 9 tin. Glass, 0, 10. Tin, 32, 31, 23, 23, 24, 26, 9, 16, 14. 16.75		2 glass, 9 tin. Glass, 0, 5. Tin, 24, 19, 16, 15, 17, 23, 17, 4, 2. 16.5		1 glass, 9 tin. Glass, 14. Tin, 8, 27, 13, 6, 8, 0, 0, 0, 0. 17	
A	0.800	300	0.800	125	0.804	240
	0.805	95	0.8025	200	0.8055	120
			0.8028	80	0.8085	23
B	0.802	300	0.8042	245	0.812	220
	0.808	90	0.8065	100	0.812	155
	0.8055	120	0.810	110	0.8127	45
C	0.8065	800	0.8085	230	0.814	500
	0.810	350	0.8085	600	0.8125	450
			0.8115	210	0.815	40
D	0.8112	600	0.8117	435	0.814	540
	0.8142	525	0.8135	650	0.814	670
	0.8122	680	0.8137	370	0.8145	350
	0.8155	200	0.8148	350		
E	0.8145	740			0.817	740
	0.820	400	see		0.8172	750
	0.818	400	below			
	0.817	820				

TABLE II. (*Continued*).

	(18)				(19)			
	2 glass, 9 tin. Glass, 8, 5. Tin, 17, 2, 15, 19, 12, 22, 21, 0, 0.		2 glass, 9 tin. Glass, 14, 17. Tin, 30, 42, 39, 28, 35, 33, 42, 30, 42.		2 glass, 9 tin. Glass, 0, 0. Tin, 17, 11, 18, 12, 15, 13, 18, 11.		2 glass, 8 tin Glass, 0, 9. 5, Tin, 13, 12, 23, 15, 19, 11, 13, 26.	
	21.5				23			
A	0.8005	425			0.806	200		
	0.8005	225			0.804	300		
	0.8015	190			0.8085	180		
B	0.803	320			0.8055	290		
	0.803	320			0.8072	175		
	0.8042	200			0.809	175		
	0.8055	75			0.807	200		
C	0.8078	475			0.809	570		
	0.8078	680			0.8097	930		
	0.808	500			0.8135	140		
	0.8085	200			0.813	100		
	0.8095	170						
	0.8105	150						
D	0.8117	420	0.8122	500	0.8128	560	0.8128	475
	0.8117	680	0.8125	500	0.813	725	0.813	740
	0.813	660	0.814	350	0.815	400	0.8185	180
	0.8155	90	0.817	40				
E	0.8158	1450			0.816	930		
	0.8158	1000			0.816	930		
	0.8165	420			0.8165	460		
	0.8175	350			0.8185	400		
	0.8187	500			0.8185	520		
					0.820	200		

(18) and (19) Two reservoirs of crude oil were used but the earth from all 22 tubes was worked up together. Grade D from all 22 tubes was first united and then for convenience in working divided into two portions.

To study further the fractionation on addition of water, E from lot 16 was collected in fourteen fractions. The weight of the earth impregnated with oil before any water had been added was 13.5 pounds, while the weight of the earth containing all the water added, but minus the oil, was 17.5 pounds. The earth was placed in a galvanized iron garbage pail and the water stirred in with an iron paddle. When the first portion of oil was liberated the mass was of the consistency of bran, but as more water was added it turned to a fluid paste. When water was added and the pail inclined, oil would continue to drain for half an hour or longer before the addition of more water became necessary. The oil which was liberated by one lot of water, therefore, could be collected in several portions, and this was done to see whether the oil which comes off immediately after the addition of water is the same as that which drains later. The brackets indicate that the fractions included were liberated by one addition of water.

	0.821	25 cc.
{	0.818	70
	0.818	70
	0.8193	250
{	0.818	395
	0.818	350
	0.818	460
	0.820	60
{	0.8208	575
	0.8222	55
{	0.824	170
	0.828	16
	0.827	95
	0.830	45

This occurrence of a first fraction of higher specific gravity than the ones immediately following occurs regularly if the right amount of water is added to liberate a first fraction of small enough volume. As the volume of the fraction first obtained becomes larger it approaches nearer to the second fraction in specific gravity, and will fall below it if its volume is made too large.

The range of specific gravity covered by this first fractionation of the crude petroleum of sp. gr. 0.810 was from 0.800 to 0.830. Oils of the same specific gravity and of the same grade were united and the products chilled and filtered to remove all the dissolved paraffine possible. The oils were chilled and filtered out of doors during the last of December when the thermometer stood at about 4° to 8° C. Lower temperatures as well as throwing paraffine out of solution would cause the whole oil to thicken. The oils were filtered through large plaited filters of drying paper, 24 hours or more often being required for a filter to empty completely. The lighter oils in grades A and B deposited no paraffine. The heavier grades deposited sometimes as much as 10 per cent. of their weight accompanied often by a slight change in specific gravity.

When these oils were filtered through earth again they behaved as shown in Table III. 950 cc. were used in each case and the tube divided into five sections. A, as before, is the top 8 cm., B the next 8, C the next 18, D the next 30, and EF the rest.

TABLE III.—THE SECOND FRACTIONATION.

	(20)		(21)		(22)*		(23)	
	A 0.8015		A 0.806		B 0.805		B 0.8055	
	Sp. gr.	cc.	Sp. gr.	cc.	Sp. gr.	cc.	Sp. gr.	cc.
A	0.8012	36	0.8038	45	0.7997	50	0.8005	45
B	0.800	44	0.8035	48	0.802	50	0.8033	48
C	0.8012	68	0.8035	78	0.8055	108	0.805	115
	0.8027	35	0.8052	28				
D	0.8022	170	0.805	160	0.8063	175	0.8063	180
EF	0.8047	330	0.807	320	0.808	260	0.8085	260
		683		679		643		648

	(24)		(25)		(26)*		(27)*	
	B 0.8065		B 0.809		B 0.8105		B 0.812	
A	0.8077	38	0.8013	45	0.8075	38	0.8105	42
B	0.807	50	0.805	50	0.8085	50	0.8105	42
C	0.808	80	0.807	75	0.8105	100	0.8085	73
			0.810	30			0.810	22
D	0.8092	160	0.8095	180	0.8125	160	0.8115	140
EF	0.8115	300	0.8115	350	0.8135	275	0.8145	250
		628		730		523		569

TABLE III. (*Continued*).

	(28) C 0.8095		(29) C 0.810		(30) C 0.811		(31)* C 0.811	
A	0.805	52	0.8035	40	0.8005	50	0.803	50
B	0.8065	52	0.808	40	0.809	38	0.808	55
C	0.8085	70	0.810	75	0.812	115	0.813	105
	0.811	28	0.8115	30				
D	0.811	160	0.8115	140	0.813	175	0.8135	180
			0.8135	40				
EF	0.813	350	0.813	350	0.8145	310	0.8155	300
		712		715		688		690

	(32) C 0.8115		(33) C 0.813		(34)* C 0.8135		(35)* C 0.8135	
A	0.806	45	0.8072	20	0.803	42	0.8025	35
B	0.807	35	0.811	35	0.810	53	0.8077	35
C	0.810	60	0.812	70	0.813	100	0.8135	100
	0.812	33	0.813	25				
D	0.812	70	0.8145	90	0.815	150	0.8145	160
	0.813	97	0.815	80				
EF	0.813	103	0.8155	200	0.817	300	0.817	325
	0.8135	105	0.8155	125		645		655
	0.813	50	0.818	35				
	0.813	47		680				
	Unused,	63						
		708						

	(36) C 0.815		(37)* C 0.8155		(38)* C 0.8155		(39)* C 0.8165	
A	0.805	43	0.8053	50	0.808	40	0.808	50
B	0.8105	40	0.812	45	0.8095	50	0.8145	50
C	0.814	98	0.816	103	0.8135	100	0.816	82
D	0.815	155	0.8175	160	0.817	165	0.8175	125
EF	0.817	280	0.819	310	0.819	290	0.820	310
		616		668		645		617

TABLE III. (*Continued*).

	(40)*		(41)		(42)		(43)	
	D 0.8135		D 0.814		D 0.814		D 0.814	
A	0.8095	45	0.8045	30	0.806	32	0.806	25
B	0.8085	45	0.8115	45	0.811	45	0.8097	30
C	0.811	95	0.8135	75	0.813	92	0.814	50
			0.8165	28				
D	0.8155	165	0.818	140	0.8175	140	0.8157	145
EF	0.817	320	0.821	300	0.8195	310	0.8175	400
		670		618		619		650

	(44)		(45)		(46)		(47)	
	D 0.814		D 0.814		D 0.8145		D 0.815	
A	0.8008	45	0.800	50	0.808	45	0.800	42
B	0.8077	50	0.8065	55	0.8115	40	0.807	47
C	0.814	103	0.8125	100	0.8135	65	0.814	110
					0.8155	30		
D	0.8175	160	0.816	160	0.817	105	0.816	150
					0.818	58		
EF	0.819	310	0.817	300	0.8195	180	0.819	330
		668		665	0.8202	120		679
					0.821	53		
						696		

	(48)		(49)		(50)		(51)	
	D 0.815		D 0.8155		D 0.8155		D 0.8155	
A	0.810	37	0.8045	40	0.8105	45	0.8058	40
B	0.805	47	0.811	48	0.8148	47	0.810	40
C	0.812	105	0.815	98	0.810	100	0.8132	60
							0.8145	50
D	0.817	160	0.8185	160	0.815	140	0.8172	75
							0.8188	55
							0.8188	38
EF	0.819	300	0.820	310	0.819	400	0.820	38
		649		656		732	0.819	100
							0.8208	30
							0.8208	45
							0.8208	30
							0.8208	95
							Unused,	40
								736

TABLE III. (*Continued*).

	(52) D 0.816		(53)* D 0.816		(54) D 0.8165		(55) D 0.8165	
A	0.806	38	0.803	43	0.806	47	0.8095	42
B	0.8115	42	0.8105	30	0.811	48	0.8135	40
C	0.814	70	0.815	100	0.815	98	0.8145	77
	0.8175	25						
D	0.8185	125	0.8185	175	0.8188	150	0.8188	150
EF	0.821	300	0.820	290	0.8208	300	0.821	295
		700		638		643		604

	(56)* D 0.8165		(57)* D 0.817		(58)* D 0.818		(59) D 0.8187	
A	0.806	45	0.8075	40	0.808	45	0.811	40
B	0.810	45	0.8115	40	0.8135	45	0.812	45
C	0.8145	95	0.815	100	0.817	105	0.814	92
D	0.8185	160	0.818	130	0.820	150	0.819	150
EF	0.821	295	0.821	330	0.822	300	0.823	305
		640		640		645		632

	(60)* D 0.8205		(61) E 0.814		(62)* E 0.8163		(63)* E 0.817	
A	0.8045	45	0.8075	33	0.8155	42	0.804	45
B	0.813	45	0.810	35	0.808	50	0.8075	50
C	0.8175	90	0.8125	80	0.8095	70	0.8145	102
					0.812	25		
D	0.822	170	0.818	125	0.8175	105	0.8205	150
					0.8182	32		
EF	0.823	270	0.8245	300	0.823	250	0.8245	300
	Unused,	70			0.8255	41		
				573				647
		692				615		

TABLE III. (*Continued*).

	(64)*		(65)*		(66)*		(67)	
	E 0.817		E 0.818		E 0.818		E 0.818	
A	0.805	42	0.8065	90	0.805	38	0.805	40
			0.809	20				
B	0.810	42	0.810	110	0.811	38	0.811	45
C	0.8145	75	0.8155	186	0.8135	104	0.8145	85
			0.817	50				
D	0.820	135	0.8205	385	0.819	175	0.8185	125
			0.8205	75				
EF	0.8255	235	0.8255	650	0.8235	240	0.824	325
			0.8255	260				
		529		1826		695		620
			3 tubes.					

	(68)*		(69)		(70)		(71)*	
	E 0.8185		E 0.819		E 0.819		E 0.819	
A	0.8205	15	0.804	24	0.8115	21	0.8095	23
B	0.8043	35	0.808	40	0.814	31	0.8085	34
C	0.810	60	0.8145	85	0.815	90	0.814	80
	0.812	30						
D	0.817	160	0.8195	140	0.8165	120	0.820	160
EF	0.8225	300	0.824	300	0.824	330	0.824	280
		590		589		592		577

	(72)*		(73)*		(74)		(75)	
	E 0.8195		E 0.8195		E 0.8195		E 0.8197	
A	0.8145	30	0.8055	34	0.816	40	0.8025	40
B	0.8105	42	0.811	45	0.8135	42	0.8105	38
C	0.8135	103	0.8155	80	0.809	65	0.816	90
					0.814	34		
D	0.8195	160	0.820	120	0.8185	160	0.822	150
EF	0.824	285	0.824	290	0.824	260	0.8255	300
					0.827	30		
		620		569		631		618

TABLE III. (*Continued*).

	(76)*– E 0.820		(77)* E 0.8205		(78) E 0.8215		(79)* E 0.822	
A	0.8045	48	0.806	32	0.8045	28	0.8105	32
B	0.812	40	0.8125	45	0.8135	36	0.8145	42
C	0.817	91	0.8175	90	0.8185	78	0.819	77
D	0.822	155	0.823	100	0.823	150	0.8225	155
EF	0.826	260	0.8245	330	0.8275	300	0.827	280
		594		597		592		586

	(80) E 0.822		(81) E 0.822		(82) E 0.824		(83)* A–B 0.804	
A	0.817	30	0.8083	26	0.8125	48	0.803	32
B	0.810	40	0.814	40	0.8127	48	0.8035	25
C	0.8153	46	0.8185	92	0.818	53	0.8035	63
	0.8163	42			0.819	50		
D	0.8225	160	0.824	140	0.8245	175	0.804	140
EF	0.8265	295	0.8265	270	0.828	200	0.806	275
					0.830	90		
		613		568	left,	50		535
						714		

	(84)* A–B 0.8065		(85)* A–B 0.808		(86)* B–C–D 0.8125		(87)* B–C–D 0.8125	
A	0.8035	40	0.8085	30	0.805	32	0.805	80
B	0.8055	40	0.807	30	0.808	42	0.8085	73
C	0.809	80	0.8065	92	0.813	85	0.812	118
							0.813	75
D	0.8085	155	0.8085	115	0.815	175	0.815	285
EF	0.811	300	0.8115	330	0.820	280	0.8175	520
		615		597		614		1151
							2 tubes.	

TABLE III. (*Continued*).

	(88)*		(89)*		(90)*		(91)*	
	C–D–E 0.813		C–D–E 0.813		B–C–D 0.8145		D–E 0.815	
A	0.8035	40	0.8035	130	0.8065	130	0.801	165
			0.807	20	0.808	27	0.8025	176
B	0.808	40	0.8077	160	0.809	137	0.8075	206
					0.8115	20	0.8085	156
C	0.8115	73	0.8125	330	0.813	305	0.812	330
	0.813	30	0.813	60	0.815	40	0.812	512
D	0.8155	160	0.815	550	0.815	560	0.817	340
			0.8175	90	0.8175	75	0.817	800
							0.817	150
EF	0.8195	290	0.8175	830	0.8175	775	0.8215 etc.	
			0.818	425	0.818	410		
		633		2595		2479		5568
			4 tubes.		4 tubes.		9 tubes.	

	(92)*		(93)		(94)	
	D–E 0.8163		F 0.822		F0.822	
A	0.805	84	0.8107	35	0.804	28
	0.8075	20				
B	0.807	100	0.810	43	0.808	37
	0.8115	20				
C	0.815	205	0.814	70	0.8165	63
	0.816	45	0.816	25	0.817	30
D	0.820	350	0.8215	156	0.8218	146
	0.820	102				
EF	0.8225	500	0.8285	250	0.831	255
	0.8225	480	0.831	60		
		1906		639		559
	3 tubes.					

* 950 cc. were needed for each tube and for many tubes this amount was available of the same grade (A, B, C, etc.), and of the same specific gravity. In some cases, though, it was necessary to unite oils of the same grade which differed slightly in specific gravity. Such samples differed in no case by more than 0.0015 and are all marked.*

To chill and filter these products of two fractionations would have entailed too much loss. As it was, much uniting of samples which differed but silghtly from one another was necessary to obtain sufficient oil for further fractionation. The unions which were made are given in Table IV.

TABLE IV.—PRODUCTS OF TWO FRACTIONATIONS UNITED FOR THE THIRD FRACTIONATION.

Lot.	Sp. gr.												
95	0.805	B	0.8033	48	A	0.8035	240	B	0.8035	25			
		C	0.8035	63	A	0.804	65	D	0.804	140			
		A	0.8045	150	A	0.805	360	B	0.805	95			
		C	0.805	115									
96	0.807	A	0.8058	40	A	0.806	235	EF	0.806	275			
		A	0.8065	240	B	0.8065	100	D	0.8063	180			
		A	0.807	53	C	0.807	75	C	0.8065	92			
97	0.8085	B	0.808	767	C	0.808	80	A	0.8083	26			
		A	0.809	20	C	0.809	210	A	0.8085	118			
98	0.8085	A	0.8072	20	A	0.8075	290	B	0.8075	480	D	0.8075	270
		A	0.8077	38									
99	0.8105	A	0.8105	70	C	0.8105	270	A	0.811	40	B	0.811	580
		C	0.811	115	A	0.8115	21	B	0.8115	308	C	0.8115	73
100	0.8115	EF	0.811	300	EF	0.8115	920						
101	0.8125	C	0.8123	520	D	0.8125	160	EF	0.8125	820			
102	0.813	C	No uniting necessary.										
103	0.8135	B	0.8125	180	B	0.813	45	C	0.8132	60			
		B	0.8135	106	C	0.8135	925						
104	0.814	D	0.8135	370	EF	0.8135	715						
105	0.814	C	No uniting necessary.										
106	0.8145	D	0.814	500	C	0.8145	910						
107	0.815	D	No uniting necessary.										
108	0.8155	EF	" " "										
109	0.8163	D	" " "										

TABLE IV. (*Continued*).

Lot.	Sp. gr.									
110	0.817	D	No uniting necessary.							
111	0.817	EF	" " "							
112	0.8175	C	0.8165	258	D	0.817	425	D	0.8172	75
		C	0.8175	200						
113	0.8175	EF	No uniting necessary.							
114	0.8187	EF	" " "							
115	0.819	D	0.8175	305	D	0.818	990			
116	0.819	EF	0.8185	845	EF	0.819	683			
117	0.819	D	No uniting necessary.							
118	0.819	EF	" " "							
119	0.8195	EF	" " "							
120	0.820	D	0.8195	475	D	0.820	600			
121	0.821	EF	No uniting necessary.							
122	0.8215	EF	" " "							
123	0.822	EF	0.8215	700	D	0.8218	460	EF	0.822	300
124	0.8225	EF	No uniting necessary.							
125	0.8235	EF	" " "							
126	0.824	D	0.823	250	EF	0.8235	860	D	0.824	140
127	0.8255	EF	No uniting necessary.							

950 cc. of each of these were fractionated by earth again, with the results as given in Table V.

TABLE V.—THE THIRD FRACTIONATION.

	(95) A–D 0.805		(96) A–EF 0.807		(97) A–C 0.8085		(98) A–D 0.8085	
A	0.8065	33	0.8045	37	0.806	40	0.8047	38
B	0.805	33	0.806	38	0.8068	40	0.8052	38
C	0.804	62	0.8065	65	0.807	58	0.808	70
	0.805	40	0.8083	25	0.8095	18	0.8093	30
D	0.8055	150	0.808	142	0.8093	154	0.8095	132
EF	0.808	315	0.8095	250	0.812	295	0.811	335
		633		557		605		643

	(99) A–C 0.8105		(100) EF 0.8115		(101) C–EF 0.8125		(102) C 0.813	
A	0.8105	33	0.8065	30	0.808	33	0.806	26
B	0.810	36	0.809	36	0.8085	34	0.8105	33
C	0.8075	71	0.810	60	0.811	54	0.8105	50
	0.8085	17	0.812	20	0.8145	22	0.813	17
D	0.811	115	0.812	136	0.8145	162	0.813	136
EF	0.814	300	0.815	315	0.817	295	0.8157	365
		572		597		600		627

	(103) B–C 0.8135		(104) D–EF 0.814		(105) C 0.814		(106) C–D 0.8145	
A	0.8065	28	0.8042	35	0.804	40	0.803	33
B	0.810	33	0.8115	36	0.810	40	0.810	40
C	0.8135	60	0.8125	60	0.8142	58	0.8145	54
	0.8165	18	0.8147	28	0.816	25	0.816	22
D	0.815	150	0.815	175	0.8163	270	0.816	150
EF	0.817	325	0.819	230	0.8185	280	0.8185	260
		614		564		713		559

TABLE V. (*Continued*).

	(107) D 0.815		(108) EF 0.8155		(109) D 0.8163		(110) D 0.817	
A	0.8035	45	0.809	52	0.810	33	0.8065	35
B	0.8115	47	0.811	47	0.8105	45	0.8125	40
C	0.815	85	0.815	55	0.8132	55	0.817	68
	0.8177	30	0.815	40	0.8145	33	0.818	30
D	0.8175	156	0.8165	170	0.8185	140	0.8195	145
EF	0.8195	300	0.8185	255	0.8215	275	0.821	290
		663		619		581		608

	(111) EF 0.817		(112) C–D 0.8175		(113) EF 0.8175		(114) EF 0.8187	
A	0.8043	30	0.8145	35	0.8065	35	0.817	30
B	0.8105	32	0.811	32	0.812	48	0.8065	25
C	0.8152	65	0.8165	60	0.8155	75	0.8122	30
	0.816	43	0.818	30	0.8175	18	0.813	15
D	0.8182	160	0.819	150	0.8185	150	0.8175	150
EF	0.8205	290	0.822	245	0.8225	283	0.822	340
		620		552		609		590

	(115) D 0.819		(116) EF 0.819		(117) D 0.819		(118) EF 0.819	
A	0.8055	16	0.8032	30	0.8045	33	0.805	30
B	0.807	lost	0.8115	36	0.813	38	0.813	30
C	0.816	43	0.816	52	0.8175	60	0.8165	60
	0.817	30	0.820	21	0.8175	34		10
D	0.820	130	0.8205	160	0.8215	150	0.821	154
EF	0.8235	300	0.8235	240	0.8235	325	0.8243	295
		lost		539		640		579

	(119) EF 0.8195		(120) D 0.820		(121) EF 0.821		(122) EF 0.8215	
A	0.805	23	0.805	33	0.8075	33	0.803	41
B	0.814	35	0.811	35	0.814	41	0.811	43
C	0.8165	58	0.817	53	0.8182	63	0.8165	60
	0.8175	32	0.8175	35	0.819	18	0.818	23
D	0.8205	152	0.822	165	0.822	150	0.8225	182
EF	0.823	300	0.825	310	0.8245	273	0.828	270
		600		633		578		629

TABLE V. (*Continued*).

	(123) D–EF 0.822		(124) EF 0.8225		(125) EF 0.8235		(126) D–EF 0.824	
A	0.808	34	0.807	31	0.804	35	0.805	35
B	0.813	35	0.8095	27	0.813	40	0.814	35
C	0.8178	52	0.8175	65	0.8185	70	0.820	60
	0.8192	42	0.8185	17	0.8195	21	0.821	20
D	0.8233	155	0.8232	150	0.8252	144	0.8253	170
EF	0.8265	260	0.8275	300	0.829	280	0.828	300
		578		590		590		620

	(127) EF 0.8255	
A	0.8055	45
B	0.8155	40
C	0.821	75
	0.823	25
D	0.8275	170
EF	0.830	280
		635

From the products of the third fractionation, oil in sufficient quantity and of five grades was obtained by uniting fractions as given in Table VI., the results of the fourth fractionation being given in Table VII.

TALBE VI.—PRODUCTS OF THREE FRACTIONATIONS UNITED FOR THE FOURTH FRACTIONATION.

Lot.	Sp. gr.	Composed of:				Composed of:			
128	0.815	(99)	EF	0.814	300 cc.	(100)	EF	0.815	315 cc.
		(101)	C	0.8145	22 "	(101)	D	0.8145	162 "
		(103)	D	0.815	150 "	(104)	C	0.8147	28 "
		(104)	D	0.815	175 "	(105)	C	0.8142	58 "
		(106)	C	0.8145	54 "	(107)	C	0.815	85 "
		(108)	C	0.815	55 "	(108)	C	0.815	40 "
		(109)	C	0.8145	33 "	(111)	C	0.8152	65 "
									1542
129	0.8168	(101)	EF	0.817	295 cc.	(105)	D	0.8163	270 cc.
		(102)	EF	0.8157	365 "	(106)	D	0.816	150 "
		(103)	EF	0.817	325 "	(108)	D	0.8165	170 "
									1575
130	0.819	(104)	EF	0.819	230 cc.	(108)	EF	0.8185	255 cc.
		(105)	EF	0.8185	280 "	(113)	D	0.8185	150 "
		(106)	EF	0.8185	260 "	(109)	D	0.8185	140 "
									1315

TABLE VI. (*Continued*).

Lot.	Sp. gr.	Composed of:					Composed of:		
131	0.8205	(107)	EF	0.8195	300 cc.	(115)	D	0.820	130 cc.
		(110)	D	0.8195	145 "	(116)	D	0.8205	160 "
		(111)	EF	0.8205	290 "	(118)	D	0.821	154 "
		(119)	EF	0.8205	152 "				
									1467
132	0.823	(113)	EF	0.8225	283 cc.	(120)	D	0.822	165 cc.
		(115)	EF	0.8225	300 "	(121)	D	0.822	150 "
		(119)	EF	0.823	300 "	(122)	D	0.8225	182 "
									1380

TABLE VII.—THE FOURTH FRACTIONATION.

	(128) C-EF 0.815		(129) D-EF 0.8168		(130) D-EF 0.819		(131) D-EF 0.8205	
A	0.8135	19	0.812	30	0.8115	24	0.8095	18
B	0.815	27	0.8122	42	0.8127	35	0.813	26
C	0.8118	50	0.8165	55	0.8173	60	0.819	45
	0.813	15	0.818	25	0.8185	22	0.8195	17
D	0.8147	140	0.818	160	0.820	160	0.8215	130
EF	0.8175	360	0.8195	305	0.8215	310	0.824	340
		611		617		611		576

	(132) D-EF 0.823	
A	0.8092	35
B	lost	35
C	0.8195	60
	0.8213	25
D	0.8235	150
EF	0.826	280
		585

To better compare the oils of different specific gravities which were obtained by the process just described five samples of 300 cc. each were separated by distillation into ten fractions. Each was distilled in the same 500 cc. distilling bulb which was heated by an electric stove which entirely surrounded the bulb. Each was first heated to 200° under atmospheric pressure and then to 360° under 50 mm. pressure. The diminished pressure was obtained with a large Chapman water pump and kept constant at 50 mm. by the use of a valve which automatically admitted air to the evacuated system whenever the pressure fell below 50 mm.

This valve was constructed from a piece of iron pipe one inch in diameter and five feet long. The lower end was closed with a cap and the pipe filled with mercury to a depth of 76 cm. The upper end of the pipe was closed with a two-hole rubber stopper. In one hole was a long glass tube with the lower end beveled, which reached to the bottom of the mercury and which could be raised or lowered as the barometer varied from day to day. In the other hole of the stopper was a tube which passed just through the stopper and which was connected on the outside with the apparatus to be exhausted. To prevent mercury from being drawn up and over into the apparatus by the air admitted, the end of the tube inside the stopper was drawn out and bent at a right angle and over this was slipped a cap made of larger tubing which was closed at the bottom but which had a fine opening in the side for air. This cap was about six cm. long and extended about three cm. below the end of the tube inside. If any mercury passed through this first fine opening into the cap, it would fall to the bottom without being drawn over into the apparatus or clogging the fine opening in the tube leading thereto. With this valve there was no difficulty in keeping a pressure of 50 mm. constant to within one mm.

Each distillate of sufficient volume, which was not too viscous or partly solid, was tested as to specific gravity, viscosity, and per cent. absorbed when treated with concentrated sulphuric acid (sp. gr. 1.84).

Viscosity was measured by taking the time of flow of a measured volume of oil through a capillary, the viscometer used being the one described by Ostwald and Luther as modified by Jones and Veazey.[1] The capacity of the small bulb was 4.5 cc. and the diameter of the capillary such as to require for from five to eight minutes for that amount of oil to flow through it, and one minute 2.6 seconds for the same amount of water. The viscosity as well as specific gravity was always measured at 20°.

Viscosities have been calculated from the following formula: $\eta = \eta_0 \frac{TS}{T_0 S_0}$ in which η_0 is the coefficient of viscosity for water, S_0 is the sp. gr. of water, and T_0 the time of flow of water through any given capillary at a given temperature; η is the viscosity coefficient of the solution investigated, S is its specific gravity as compared with water as unity at any given temperature, and T is the time of flow of the given solution

[1] Z. physik. Chem., 61, 651.

at that temperature. The value for pure water at 20° was taken from the work of Thorpe and Rodger.[1]

Thirty cc. of each of these distillates, where that much oil was available, all the oil there was where the volume was less than 30 cc., were mixed with an equal volume of concentrated sulphuric acid (sp. gr. 1.84) and shaken half an hour or longer in a shaking machine. The oil and acid were then poured into a separating funnel and the acid drawn off. The oil was then washed twice with water, once with aqueous NaOH, again with water, and then with this last wash water poured into a burette and allowed to settle. After standing over night the volume was read.

The oils boiling below 200° (50 mm.) separated clear, but the heavy distillates were milky from water. The volume of these milky oils was read, their specific gravity taken, and then the milkiness was removed by shaking and heating to 60° or so with $CaCl_2$. The specific gravity of the clear oil was then taken and the proper correction made to the milky volume. In no case, however, was this correction at all large, and only for the three or four heaviest oils did it exceed one-half of 1 per cent., the largest correction of all being 2.6 per cent. for the distillate between 230°–260° of the oil of sp. gr. 0.824. An attempt to treat with acid the oils selected to be distilled, resulted in so much loss from the formation of emulsions that the loss in volume and change in specific gravity could not be determined with any degree of accuracy.

[1] Phil. Trans., 185A, 397 (1894).

TABLE VIII.—DEGREE OF FRACTIONATION OBTAINED.

		(1)	(2)	(3)	(4)	(5)	(6)
	Sp. gr.	0.801	0.808	0.815	0.8195	0.824	0.810
	Viscosity	0.0404	0.0555	0.0589		0.0657	0.0441
	Tubes passed through	1	3	3	4	4	crude oil
Normal pressure below 150°	cc.	36	1	13	5	2	45
	Sp. gr.	0.720		0.737			0.714
	Vis.	0.0052		0.0059			0.0047
	Acid	4.4%		...			8.6%
	Sp. gr. after acid	0.722		0.7365			0.712
150°–200°	cc.	47	61	52	60	60	43
	Sp. gr.	0.749	0.7465	0.756	0.757	0.759	0.759
	Vis.	0.0075	0.0073	0.0075	0.0073	0.0072	0.0076
	Acid	3.4%	4.4%	8.2%	11.3%	12.0%	9.3%
	Sp. gr. after acid	0.749	0.7469	0.750	0.749	0.750	0.752
50 mm. pressure below 140°	cc.	10	9	3	6	10	19
	Sp. gr.						0.7805
	Vis.						0.0112
	Acid						11.9%
	Sp. gr. after acid						0.7735

TABLE VIII. (*Continued*).

		(1)	(2)	(3)	(4)	(5)	(6)
140°–200°	cc.	69	75	80	80	73	48
	Sp. gr.	0.790	0.790	0.797	0.800	0.8015	0.804
	Vis.	0.0212	0.0185	0.0211	0.0216	0.0196	0.0254
	Acid	3.4%	4.4%	8.9%	9.6%	14.8%	11.0%
	Sp. gr. after acid	0.790	0.7885	0.7915	0.795	0.7915	0.799
200°–230°	cc.	25	30	23	25	30	21
	Sp. gr.	0.813	0.8135	0.818	0.8225	0.822	0.823
	Vis.	0.0556	0.0594	0.0573	0.0661	0.0505	0.0593
	Acid		4.3%	11.0%	8.4%	10.5%	8.7%
	Sp. gr. after acid	0.813	0.8125	0.816	0.8217	0.818	0.8175
230°–260°	cc.	23	27	23	20	24	22
	Sp. gr.	0.8255	0.826	0.830	0.833	0.838	0.8355
	Vis.	0.1106	0.1150	0.1116	0.1168	0.1259	0.1284
	Acid	3.4%	8.5%	7.0%	8.9%	7.6%	12.6%
	Sp. gr. after acid	0.8255	0.8255	0.828	0.832	0.833	0.830
260°–300°	cc.	20	22	23	24	20	17
	Sp. gr.	0.8395	0.838				
	Vis.	0.2520		fluid	fluid	fluid	fluid

TABLE VIII. (*Continued*).

		(1)	(2)	(3)	(4)	(5)	(6)
300°–340°	cc.	25	30	27	30	26	25
	Sp. gr.	0.847	0.849				
340°–360°	cc.	21 fluid	26 (below 355°) fluid	solid 22 fluid	solid	solid 19 fluid	solid 20 fluid
Residue	cc.	22 fluid	17 fluid	30 fluid	45 fluid	35 fluid	32 fluid
Total vol.		298	298	296	295	299	292

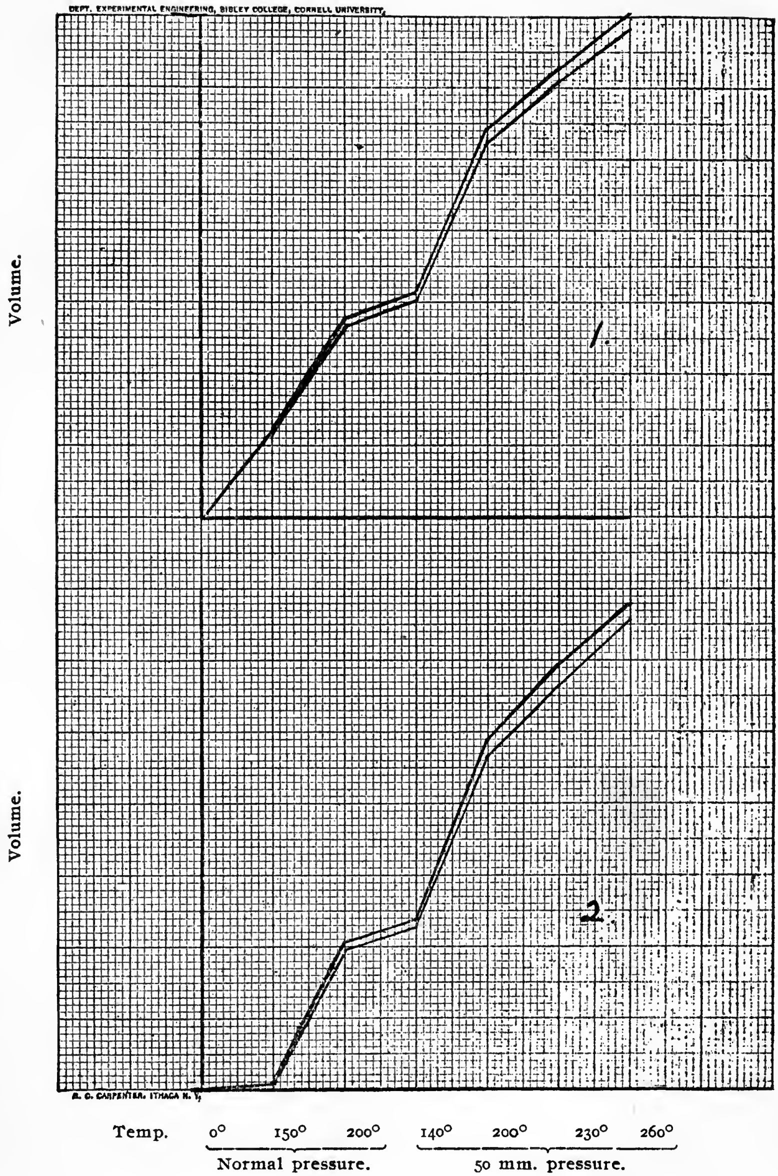
"Fluid" means that the oil at 20° was partly solid but would flow when the bottle was inclined; "solid," that the bottle could be turned upside down without the oil changing shape.

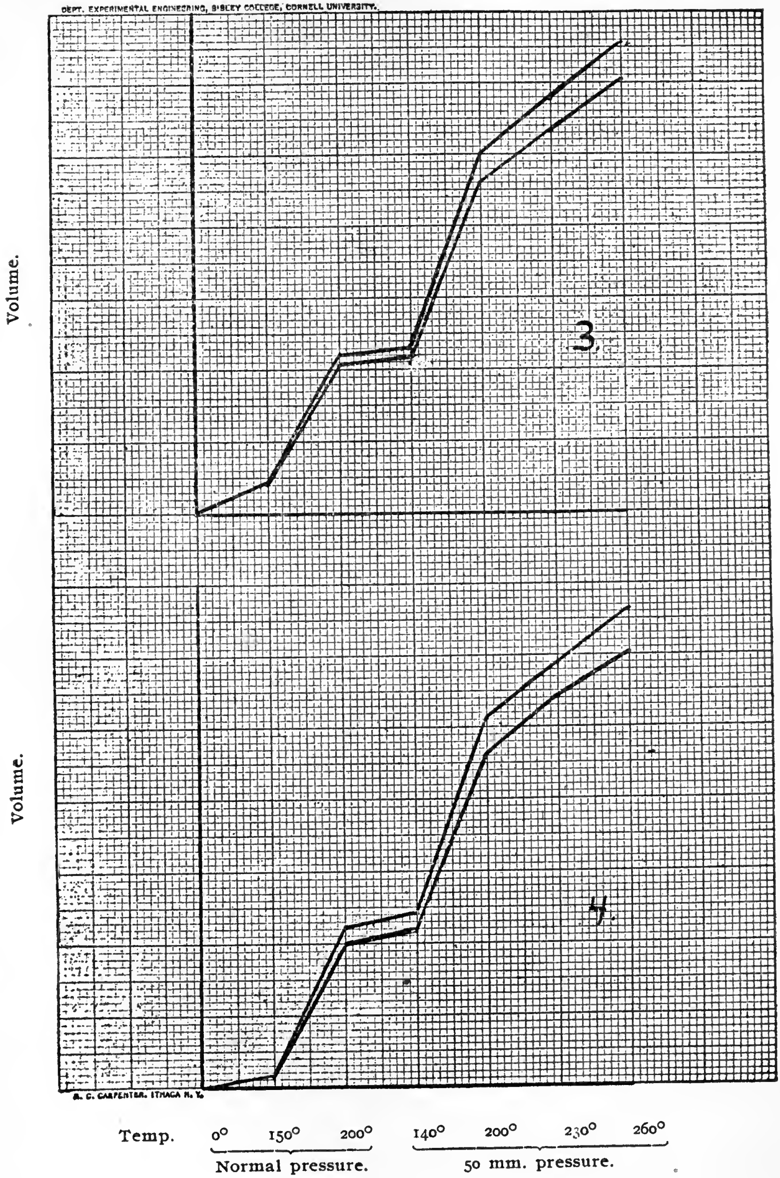
It was hoped that sulphuric acid of the strength used (sp. gr. 1.84) would dissolve only unsaturated hydrocarbons and leave untouched the paraffines and benzene. By long-continued shaking at ordinary temperature, however, with acid of this strength, benzene is dissolved, provided that the acid is in large excess. One hundred cc. of benzene were completely dissolved in 434 cc. of acid on being shaken four hours.

Three of the distillates which had been shaken with acid, however, gave no action when treated with a mixture of equal parts concentrated sulphuric acid and fuming nitric acid, while distillates which had not been previously shaken with sulphuric acid were acted upon by this nitrating mixture. The action of the sulphuric acid, therefore, appears to have been complete.

The action of sulphuric acid shows that over 90 per cent. of the oil dealt with consists of paraffine hydrocarbons, and that in the filtration through earth the paraffine hydrocarbons tend to collect at the top of the tube and the unsaturated hydrocarbons at the bottom.

The increasing amount dissolved by sulphuric acid in the heavier oils may be seen in the following curves: The abscissas represent temperatures and the ordinates volumes. The same distance upon the X axis is taken to represent a distillate, whatever be the number of degrees over which it may have been collected. The upper curve represents the per cent. of the total volume which distilled between given temperatures; the lower curve, the per cent. of the total volume recovered which was not absorbed by sulphuric acid (*i. e.*, the paraffine hydrocarbons). For the upper curve the ordinates were obtained by dividing the number of cubic centimeters in the distillate by the total volume of oil recovered. For the lower curve the ordinates were obtained by dividing the number of cubic centimeters in the distillate


DEPT. EXPERIMENTAL ENGINEERING, SIBLEY COLLEGE, CORNELL UNIVERSITY.
Volume.
1.
Volume.
2.
B. C. CARPENTER, ITHACA N. Y.
Temp.
0°
150°
200°
140°
200°
230°
260°
Normal pressure.
50 mm. pressure.


DEPT. EXPERIMENTAL ENGINEERING, SIBLEY COLLEGE, CORNELL UNIVERSITY.
Volume.
3
Volume.
4.
B. C. CARPENTER, ITHACA N. Y.
Temp.
0°
150°
200°
140°
200°
230°
260°
Normal pressure.
50 mm. pressure.


EXPERIMENTAL ENGINEERING, SIBLEY COLLEGE, CORNELL UNIVERSITY.
Volume.
5
Volume.
6
G. C. CARPENTER, ITHACA N. Y.
Temp.
0°
150°
200°
140°
200°
230°
260°
Normal pressure.
50 mm. pressure.

not absorbed by sulphuric acid, by the total volume of oil recovered.

The area between the two curves represents the proportion of hydrocarbons soluble in sulphuric acid, which it will be seen is greatest for the oils of highest specific gravity.

On referring to Tables III. and V. it will be noticed that there are several tubes given where the specific gravity of the oil of grade A is heavier than grade B and sometimes than grade C. Tubes where this irregularity is marked are 48, 62, 68, 72, 74, and 80 of Table III., and 112 and 114 of Table V. A slight irregularity appears in 20, 21, 24, 27, 40, 71, and 85 of Table III. and in 99 of Table V. If the oils in these cases are not colorless, the color is strongest where the specific gravity is greatest, so that although oil of the grade A has passed through the most earth it is yet more strongly colored than oil of grade B or C.

No reason for this variation has been established. It should be remembered, however, that the different oils rise in the earth with differing velocities, not because they differ from one another in specific gravity but because they differ in surface tension. A rough attempt was made to measure relative surface tensions by measuring the height to which different oils rise in the same capillary tube, but although a kathotometer was used and the level of the oil in the capillary brought to the same spot each time, the work sufficed only to show that the difference between the surface tension of the oils obtained was so slight as to require very careful measurement for the results to be of any value.

That viscosity shows the same irregularity in these oils as color and specific gravity, appears from the following measurements.

	(62)		(68)	
	Sp. gr.	Vis.	Sp. gr.	Vis.
A.......	0.8155	0.0539	0.8205	0.0626
B.......	0.808	0.0469	0.8043	0.0469
C.......	0.8095	0.0509	0.810	0.0520
	0.812	0.0555	0.812	0.0554
D.......	0.8175	0.0525	0.817	0.0524
	0.8182	0.0535	..	..
EF......	0.823	0.0612	0.8225	0.0606

In (50) of Table III. an irregularity appears in grade B which is also found in the viscosity.

(50)

	Sp. gr.	Vis.
A..........	0.8105	0.0532
B..........	0.8148	0.0559
C..........	0.810	0.0526
D..........	0.815	0.0526
EF..........	0.819	0.0552

The oils obtained by one fractionation of the crude petroleum have the following viscosities, the fractions measured being those previously given in Table I.

	(1)		(2)		(3)	
	Sp. gr.	Vis.	Sp. gr.	Vis.	Sp. gr.	Vis.
A	0.796	0.0376	0.8012	0.0408	0.8022	0.0401
B	0.808	0.0529	0.804	0.0485	0.803	0.0470
C	0.8125	0.0501	0.807	0.0443	0.8075	0.0453
	0.8137	0.0529	0.809	0.0476	0.810	0.0471
D	0.815	0.0504	0.8125	0.0460	0.812	0.0472
E	0.818	0.0521	0.8185	0.0537	0.8175	0.0529
F	0.8205	..	0.823	..	0.821	..

That the viscosity does not increase with the specific gravity, particularly with the higher fractions, is apparent in two of the three series just given. The same is also shown in the following four tubes taken from Table III.

	(21)		(22)	
	Sp. gr.	Vis.	Sp. gr.	Vis.
A	0.8038	0.0465	0.7997	0.0421
B	0.8035	0.0456	0.802	0.0485
C	0.8035	0.0456	0.8055	0.0502
	0.8052	0.0485		
D	0.805	0.0479	0.8063	0.0496
EF	0.807	0.0480	0.808	0.0510

	(47)		(53)	
	Sp. gr.	Vis.	Sp. gr.	Vis.
A	0.800	0.0453	0.803	0.0515
B	0.807	0.0538	0.8105	0.0563
C	0.814	0.0542	0.815	0.0684
D	0.816	0.0528	0.8185	0.0570
EF	0.819	0.0556	0.820	0.0559

This drop in viscosity in the oils which occurs at the bottom of the tube, appears to be a regular occurrence in the dozen or so oils which have been tested. Further investigation of this point is intended.

Water Fractionation.

To test the effectiveness of water fractionation alone, 1000 cc. of crude petroleum, previously chilled and filtered, of specific gravity 0.807, were mixed with 1000 gms. of earth and allowed to stand 24 hours. Water was then added in small amounts and the oil collected.

	Sp. gr.	Volume of oil. cc.	Total water present. cc.
A......	0.8148	44	500
B.......	0.8139	278	650
C.......	0.816	211	800
D.......	0.820	84	950
E.......	0.8225	28	1400
F.......	0.8245	28	2750
		673	

The fractions of large enough volume were then mixed with earth again and the oil replaced with water. One gram of earth was used for each cc. of oil, the earth having been heated first and allowed to cool.

B. 0 8139 278 cc. stood 1.5 hours.			C. 0.816 211 cc. stood 6 hours.			D. 0.820 84 cc. stood 2.5 hours.		
Sp. gr.	Oil.	Water. cc.	Sp. gr.	Oil.	Water. cc.	Sp. gr.	Oil.	Water. cc.
0.8185	10	70	0.820	10	80	0.822	32	76
0.818	10	110	0.820	20	125	0.823	20	207
0.818	21	164	0.8195	72	250		52	
0.818	20	..	0.820	30	410			
0.817	42	..	0.820	10	588			
0.819	10	216		142				
0.820	44	277						
0.820	16	428						
0.8215	20	686						
	193							

It is apparent that while petroleum is fractionated by simply mixing the oil with fuller's earth and then displacing the oil from the earth with water, the fractionation is much less complete than when tubes are used as previously described.

It will be noticed that although fractions C and D in the table last given are separated hardly at all by further treatment with earth and water, yet the specific gravity of all the oil recovered is higher than that of the oil used, *e. g.*, from C of sp. gr. 0.816 is obtained nothing lighter than 0.8195, and from D of sp. gr. 0.820 is obtained nothing lighter than 0.822.

To determine whether the specific gravity of the oil recovered will continue to rise after the oil is fractionated no further by repeated treatment, 330 cc. of sp. gr. .819, obtained by uniting several products of one fractionation of the crude petroleum, were mixed with 330 grams of earth and water was added.

	Sp. gr.	Vol. oil.	Total water present. cc.
A.............	..	6	64
B.............	0.8215	50	...
C.............	..	12	214
D.............	0.821	60	270
E.............	0.821	82	413
F.............	0.8225	26	613
		236	

Seventy-five cc. of E of sp. gr. 0.821 were next mixed with 75 grams of earth and 150 cc. of water were added. Fifty-one cc. of oil whose specific gravity was unchanged, but whose color was reduced, were obtained. Fifty cc. of this when treated with earth and water returned 34 cc. of oil with the color considerably lighter, but the specific gravity still 0.821.

Although only two-thirds of the oil used are recovered whenever oil is mixed with earth and then displaced with water, yet this loss does not seem to affect the specific gravity of the oil obtained for longer than one or two treatments after the oil ceases to be fractionated. After this the oil recovered has the same specific gravity as the oil used.

The Oil Lost in the Earth.

The sum of the fractions of oil displaced from the earth is usually about two-thirds of the volume of the oil used.

A pressure of approximately 200 tons per square inch upon the earth from which water has displaced all oil that it will, results in the liberation of considerable water but very little oil. When earth which has been pressed is heated to 165° for three hours, considerable water distills over but much less oil than would be expected, *e. g.*, from 75 grams of earth which should contain 25 cc. of oil, but 4 cc. of oil were obtained. The earth was removed once from the flask and pulverized, and when the heat was discontinued the earth was thoroughly dry. On extraction with ether the earth gave a solution having the color of the original petroleum. The extraction was made with a Soxhlet extractor and continued until the extract was colorless. On evaporation of the ether there remained about 8 cc. of a heavy oil with the color of the natural petroleum. Pressure, heat, and extraction with ether together gave about half the amount of oil which the earth must have contained.

Earth which had been used once was allowed to dry for several weeks at room temperatures until it had lost all appearance of containing moisture. It was then pulverized, sifted, and used in a tube with the crude petroleum of sp. gr. 0.810 with the following results.

		cc.
8 cm. at top	..	0
Next 8 cm	0.8284	10
Next 18 cm	0.8225	45
Next 30 cm	0.8143	60
	0.8155	80
Rest	0.8175	83
	0.819	114
		392 cc.

Earth used, 720 gms.
Crude petroleum used, 740 cc.

The first oil up the tube evidently is absorbed by heavy material in the earth, while the first oil recovered dissolves material from the earth which increases its specific gravity beyond that of the next fraction.

To see how much of the weight of the earth just used was due to material which it had retained from its first use, 300 grams of earth were mixed with 300 cc. of crude petroleum and the oil displaced by water. The oil recovered measured 205 cc., and the weight of the earth after drying for several weeks at room temperature was 347.5 grams. Fully 15 per cent., therefore, of the weight of the earth used in the tube just mentioned was solid matter which it had retained from its first use.

In all cases the earth was heated before it was used because it was believed that heating decreased the amount of oil lost in the earth. The earth was heated usually in iron pans on a gas stove until it ceased to form geysers when stirred. A tube packed with earth which had not been heated gave results as follows with crude petroleum of sp. gr. 0.810.

	Sp. gr.	Vol. cc.
Top 8 cm.	0.803	30
Next 8 cm.	0.8045	38
Next 18 cm.	0.8103	85
Rest	..	440
		593
Crude oil used		930

Earth used, 948 gms.
Tube 5 feet long, 1 1/4 inches diameter.
20 hours required at diminished pressure.

In a case of water fractionation alone with unheated earth but 242 cc. of oil were recovered from 500 cc. of crude petroleum.

Results obtained toward the close of our work indicate that the loss of oil when unheated earth is used is much less than we had supposed it to be. The gain from heating the earth may not pay for the trouble of heating it, and this point should be investigated before any very extensive investigation is again undertaken.

Earth after heating must become thoroughly cold before it is used to pack tubes. The earth holds its heat for several hours, and if it is used the same day upon which it is heated, there is apt to be contraction in a tube so packed sufficient to allow the oil to run up the side of the tube as it would in a vacuum.

The length of the tubes used was five and one-half feet. A tube nine feet long was held for two days with a constant diminished pressure of about 10 cm. Hg, and connected to the same vacuum pump with several five and one-half foot tubes. The oil was drawn to the top of the latter, and these removed and a second lot substituted which were likewise fully impregnated with oil before the long tube was opened. When it was opened the oil had ascended but 45 cm., showing that the diminished pressure had not penetrated that length of earth and reached the bottom of the tube.

A shorter tube in which the earth was packed very much harder, so that the tube filled with earth rang like an iron rod when pounded upon the floor, when connected with a vacuum pump at one end and a manometer at the other, showed diminished pressure on the manometer when the column of earth was two feet long but not when two feet, four inches.

The Fractionating Power of Substances Other Than Fuller's Earth.

A clay from Topsham, Maine, was found which in tubes showed a power of fractionating as well as decolorizing the higher fractions. Compared with fuller's earth, the action was:

	Sp. gr.	
	Clay.	Fuller's earth.
8 cm. at top	0.799	0.793
Next 8 cm	0.804	0.800
Next 8 cm	0.810	0.806
Next 10 cm	0.810	0.807
Next 30 cm	0.812	0.8092
Next 45 cm	0.812	0.8112
Time required	69 hours,	76 hours.

Sp. gr. petroleum used, 0.806.
Tubes 5 feet long, $1^{1}/_{4}$ inches in diameter.

Neither powdered brick made from the same clay nor powdered feldspar showed any power of fractionation.

Another similar clay (from Mere Point, Brunswick, Maine) showed a power of water fractionation, but its behavior in a tube was not tested. 400 grams of this clay, previously sifted and heated, were mixed with 170 cc. of crude petroleum of sp. gr. 0.806 and allowed to stand 14 hours. Water was then added and the following fractions obtained:

Sp. gr.	Vol. in cc.	Total water present.
0.8165	24	104
0.817	60	133
0.8188	20	234
..	6	374
	110	

The color was scarcely changed at all.

Summary.

(1) When petroleum is allowed to rise in a tube packed with fuller's earth, there is a decided fractionation of the oil, the fraction at the top of the tube being of lower specific gravity than that at the bottom.

(2) When water is added to fuller's earth which contains petroleum, the oil which is displaced first differs in specific gravity from that which is displaced afterwards when more water is added.

(3) When petroleum is allowed to rise in a tube packed with fuller's earth, the paraffine hydrocarbons tend to collect in the lightest fraction at the top of the tube and the unsaturated hydrocarbons at the bottom.

(4) Whenever oil is mixed with fuller's earth and then displaced with water, about one-third of the oil remains in the earth.

BIOGRAPHY.

Marshall Perley Cram was born in Brunswick, Maine, on January 1, 1882. He was prepared for college at the Brunswick High School, and entered Bowdoin College in 1900, from which he was graduated in 1904 with the degree of A.B. He was assistant in chemistry in the same college for the year 1904–5 and received the degree of A.M. in 1905. Since October, 1905, he has been a graduate student in chemistry in the Johns Hopkins University, his subordinate subjects being physical chemistry and geology.