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BUREAU OF ENGINEERING

Report on

# Atmospheric Distillation of the "A" Series of Fuel Oils and the Analysis of the Fractions.

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# ABSTRACT

(1) In this report are given the temperature at which the "A" series first begin to distill and the temperatures at which each 5% fraction comes over up to 40%, employing the Engler apparatus ordinarily used for the distillation of light petroleum products at atmospheric pressure.

(2) In this report will be found the carbon and hydrogen content of the first and the second twenty per cent distilled over as described by the specification for the Engler distillation. The residue remaining in the flask after this distillation was also analyzed for its hydrogen and carbon composition.

(3) In this report will be found the average molecular weight as found by the cryoscopic method using naphthalene as a solvent on the fractions described above.

(4) The findings in this report, while interesting and valuable for research, do not give any information that can be used by the Navy at this time as an aid in writing specifications.

# ATMOSPHERIC DISTILLATION AND ANALYSIS OF FRACTIONS OF "A" SERIES

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## INTRODUCTION

### (a) Authorization

This problem was authorized by Bureau of Engineering Project Order 36/31 of 2 June 1931.

### (b) Statement of Problem

The original problem given in the above reference dealt with the characteristics and supply of fuel oil for the Navy. This Laboratory, the Engineering Experiment Station and the Naval Boiler Laboratory have studied 18 cracked fuel oils with the desire of finding out why certain fuels cause trouble and other fuels do not. The Naval Boiler Laboratory Report No. 2084 gives the scoring of these fuel oils and their value to the Navy as judged by their tests. In this report will be found the carbon and hydrogen content as well as the molecular weight, as determined by the cryoscopic methods using naphthalene as a solvent, for the fractions distilled from these cracked fuels. Three fractions have been studied: (1) first 20 per cent, (2) second 20 per cent, and (3) the residue.

### (c) Facts Bearing on the Problem

In the study of petroleum products, distillation is used for lighter products such as gasoline and burning oils. Some distillation tests are made with lubricating oils but these tests, especially on heavier oils, are made at reduced pressures. Any fuel oil that is made by blending a heavy residuum with a lighter fraction will have its viscosity changed very much by the addition of this small percentage of lighter product. In the study of the fuel oils it would be advantageous to know, if possible, the percentage of this lighter material that has been added to blend the heavy base and also to know its composition. In any distillation of fuels, especially at atmospheric pressures, a point soon comes where hydrogen sulfide is given off. This point occurs at a fairly definite temperature but the volume distilled over varies with the fuel studied. The point where the hydrogen sulfide appears in quantity is noted as the beginning of the cracking of the oils studied. The fuels can be distilled under reduced pressure and this cracking may not appear, probably because the temperature is kept below 300°C and an atmosphere of carbon dioxide is blown in in the preliminary heating. It is well known that when the pressure is reduced to less than 1 mm, the distillation is rather easy and any number of fractions can be obtained for study. At this Laboratory, A-9 was distilled at a vapor pressure such that 65% was recovered with a maximum temperature of around 260°C for the overhead (see Appendix II).

## (d) Theoretical Considerations

In the distillation of fuel oils two questions arise: (1) method to use, and (2) the number of fractions. For distillation two set-ups can be used: (1) the ordinary Engler distillation outfit that is used for the distillation of gasoline, or (2) reduced pressure.

The Engler method of atmospheric distillation is described in detail in Federal Specifications VV-L-791 on pages 25 to 33, and can be used for the distillation of fuel oils up to a certain point. A heavy fuel can usually be distilled fairly well up to 40% without excessive cracking, while a fuel oil such as A-1, which has a high specific gravity and a low molecular weight, can be distilled up to 80% without appreciable decomposition. Cracking is used in this report to mean that point at which large quantities of hydrogen sulfide come off and simultaneously "smoke" often appears in the flask and condenser. With ordinary fuels this point does not become excessive until 40% has been distilled over.

Vacuum distillation causes much less damage to the organic compounds making up the fuel oil than does atmospheric distillation. But there is one disadvantage and that is that the vacuum distillation is slow in comparison to the atmospheric set-up and as the information given in this report is primarily of the "prospecting" nature, it was not deemed of sufficient value to warrant the vacuum distillation at this time. If this work should be repeated in vacuo, the pressure should be less than one millimeter, if possible.

The question of the number of fractions was determined by the fact that most of the fuels used by the Navy usually do not contain over 20% of a light oil used as diluent and the fact that beyond 40% some of the fuels show excessive cracking. Therefore, the first fraction was set at 20%, the second at 20 to 40% plus the drainage of the condenser, and the "residue" is the remainder.

In a theoretical study, it is well known that any number of fractions can be taken -- the more fractions, the greater the chance of separating the fuel into its component parts. The American Petroleum Institute has had a research project at the National Bureau of Standards for years, the main object of which has been to isolate and identify the fractions that are present in petroleum distillates. Their work, until the last year or more, has been concentrated on the lighter fractions, that is, the gasoline fraction. At the present time, they are doing some work on the lighter lubricating oil fraction. No systematic attempt, as far as this Laboratory knows, has been made by them to isolate or identify the compounds that may be present in the fractions obtained in distillation of a fuel oil. To isolate and identify the compounds present in any oil, especially when it is a heavy fuel such as found in this "A" series, is almost an impossible task.

The fractions themselves were analyzed for hydrogen and carbon and are discussed in this report primarily as the "hydrogen-carbon" ratio. The molecular weight of each fraction was determined by the freezing point depression using naphthalene as a solvent (see NRL Report P-25-7 of 12 May 1933). The temperature at which this is done is 80°C or 176°F near the atomizing temperature of the fuels. At the present time it is questionable whether this freezing point depression method using naphthalene as a solvent gives a true picture of the molecular aggregates found in a fuel oil at lower temperatures, such as 77°F. In NRL Report No. P-1127 of 4 March 1935 on the reproducibility of viscosity measurements, it is shown that an oil remaining unstirred for a period of two or three months and its viscosity determined, has a viscosity that is very different from that which has been heated to 160°F and then cooled to 77° for the measurement. If this information is any criterion, it shows that the aggregates or particle size may be very different at lower temperatures. Attempts were made at this Laboratory to determine molecular weights at the freezing point of benzene, but some of the oils that were tried were not soluble except in very dilute solutions in benzol at the temperature of its freezing point (5-1/2°C).

### (e) Original Work at this Laboratory

No previous work has been reported from this Laboratory on the distillation of heavy fuels. The Engler distillation of Diesel fuel oils was reported by the Report P-25-10 of 1 August 1933. In this report Diesel fuel oils were distilled and the temperatures found were given. The analysis of heavy fuels, that is, the determination of the hydrogen and carbon, is found in NRL Report No. P-1019 of 23 January 1934. The molecular weight of fuel oil samples is found by the cryoscopic method using naphthalene as a solvent and is reported in NRL Report No. P-25-7 of 12 May 1933.

## METHODS

### (a) Preparation of Materials

The distillation method used is the ASTM method given in Federal Specifications VV-L-791 on pages 25 to 33, except that the sample was distilled with a free flame to get greater flexibility. In the distillation of heavy products that may have a small percentage of water, there is apt to be what is known as "bumping". When heating with a free flame this bumping can be reduced to the minimum. The first drop that comes into the receiver is taken as the initial boiling point. Readings were taken at the end of each 5 cc. as they were caught in the graduated cylinder. The first fraction was cut at the end of 20%, when a new graduated cylinder was put in to receive the distillate. When 20% more had come over, or in all 40%, the temperature was read and heating discontinued. The apparatus was then allowed to cool and usually there were about 2 cc. of drainage from the condenser system and this was collected in the second fraction. The condenser, after the distillation, was thoroughly cleaned and another flask was used for the next run. During the distillation there comes a point which is noted in this tabulated data as the cracking temperature. By that, it is meant that there is vigorous evolution of hydrogen sulfide and other volatile sulfur compounds. These sulfur compounds may be mercaptans or they may be hydrogen sulfide with an added mixture of low boiling hydrocarbons. This does not mean that no hydrogen sulfide has been given off previous to the point marked, for anyone distilling heavy fuel oils will know that there is a slight amount of hydrogen sulfide being given off even though the percentage of sulfur in the oil is low. Samples A-9 and A-11 were distilled until 35% or more was over before an appreciable amount of hydrogen sulfide appeared.

The fractions obtained were analyzed for carbon and hydrogen as described in NRL Report No. P-1019 of 23 January 1934. The molecular weights of these oils were also determined at the freezing point of naphthalene as described in NRL Report No. P-25-7 of 12 May 1933. The log of the distillation temperatures as well as the analysis and molecular weights are given in detail in Appendix I. It will be noted that any temperature reading with straight atmospheric distillation will vary with the amount of super-heat, may vary slightly due to the barometer reading, and will vary due to the rate of distillation, and as a result of these factors the temperature readings may vary 10°F and maybe more after the first 5% are over. The first point known as I.B.P. will vary much more, probably due somewhat to the temperature of the water that surrounds the condenser tube and the water content of the fuel oil itself. In Appendix I will be given the time it takes from the first application of heat to the different fractions as they are read. With this information available, one can estimate the rate of distillation and note if there has been any excessive heat applied. When the point is reached at which hydrogen sulfide is given off in quantities, the temperature may remain fairly constant and yet distillation occurs steadily. This may be due in part to the fact that cracking is occurring, and when cracking occurs the temperature often drops. Oils A-9 and A-11 distilled readily, no odor of hydrogen sulfide was appreciable until 35% to 40% was over and even then there was no visible smoking in the distillation flask or receiver. A-1 is another oil that distilled very nicely, as would be expected due to lower molecular weights. In the first tabulated data no mention was made for A-11, A-15 and A-17 where cracking first appeared. These oils were re-run and the temperature noted, but with A-11 there was no appreciable cracking even at 40% over.

## CONCLUSIONS AND RECOMMENDATIONS

### (a) Facts Established

This report discusses the composition of the fractions obtained by the Engler distillation of the fuel oils known as the "A" series. This distillation was carried out at atmospheric pressure. Two 20 cc fractions were distilled over and the remainder was called the residue. The actual temperature readings are of interest if one plans to obtain some knowledge of the actual carbon compounds that may be present in the fuel oil fractions. To do this, it is first necessary to know the carbon and hydrogen content and the approximate molecular weight of the fractions studied. In many discussions of fuel oils, the percentage composition in terms of per cent carbon or per cent hydrogen is discussed, but it is difficult to know the ratio of carbon to hydrogen in terms of the atoms present when the percentage composition only is given. In this report the hydrogen-carbon ratio is used. This hydrogen-carbon ratio is determined as follows: Divide the per cent of hydrogen by 1.008 and the per cent of carbon by 12. The value found for hydrogen by this method is then divided by the value found for carbon and this gives the hydrogen-carbon ratio. Benzene, on analysis, gives 92.3% carbon and 7.7% hydrogen. This 92.3% carbon divided by 12 gives 7.7 The hydrogen divided by 1.008 gives roughly 7.7. Then 7.7 divided by 7.7 gives 1, the hydrogen-carbon ratio for benzene. The formula for benzene is $C_6H_6$. For the heavier aromatic compound, this hydrogen-carbon ratio may be less than one if there are condensed rings such as naphthalene ($C_{10}H_8$) which has a hydrogen-carbon ratio of 0.8. The ordinary saturated aliphatic hydrocarbons have a hydrogen-carbon ratio of two or greater, dependent upon the length of the carbon chain present. Take for instance decane, having a formula $C_{10}H_{22}$, which has a hydrogen-carbon ratio of 2.2. If part of this is replaced by a benzene group so that you have butyl benzene, the hydrogen-carbon ratio will be 1.4. What the effect is on solvent properties due to the presence of one or two aromatic nuclei is not clearly known, though it is well known in the oil industry that when a cracked residue is cut back with a straight run gas oil, there is greater difficulty in getting a stable oil than if it were cut back with a cracked gas oil. The hydrogen-carbon ratio of a straight run gas oil may be roughly 2.0, while the hydrogen-carbon ratio of a cracked gas oil may be as low as 1.5. In this report, A-2 has a hydrogen-carbon ratio of 1.37 for the first 20% and 1.57 for the second 20%, while A-8 has a hydrogen-carbon ratio of 1.67 for both the first and second fractions. A-9, which gave the most stable viscosity readings other than A-1, has a hydrogen-carbon ratio of 1.45 for the first 20% and 1.39 for the second 20%, showing that the lighter fractions are decidedly aromatic in nature and therefore could give a stable fuel. A-1 in comparison has a hydrogen-carbon ratio of 1.47 for the first 20% over and 1.38 for the second 20%, not far from the values for A-9.

In the discussion of the hydrogen-carbon ratio, the sizes of the molecules one has to deal with are also of interest. The molecular weights given in this report are only the average as determined by the freezing point method, using naphthalene as a solvent. The value thus established for the average molecular weights is that found at 80°C or 176°F. This value gives a good idea of the nature of the average molecular weights close to the atomizing temperature of the fuels, but gives no idea of the average molecular weights at the pumping temperature at approximately 80°F.

If possible, a solvent should be found for the study of the molecular weights at a temperature of approximately 80°F to get some information as to the nature of the molecules present in the oil at the lower temperatures.

With the molecular weight and the hydrogen carbon ratio, an approximate formula can be determined for the original as well as all the fractions obtained. In checking over the composition of the first 20%, it is found that the average formula will contain approximately 12 to 17 carbons in the first 20% over; for the second 20% it will vary from 15 to 18 carbons, while the residue will go from 24 to 37 carbons. This information, while interesting, is not exceedingly helpful due to the fact that no knowledge is available as to the per cent of sulfur and nitrogen present in the fractions and as to what relationship they have to the compounds present. Thus, one sample may have 1% sulfur and this sulfur may be bound up in a compound that is difficultly soluble in the other compounds present, or it may be very reactive and the effect of this small per cent sulfur will show up in the reactions of the fuel oil studied. In NRL Report No. P-1019 it was shown that the sulfur and nitrogen compounds may account for as much as 40% of the oil present when one assumes the presence of only one sulfur or one nitrogen atom in the molecule. Of course, if there is more than one sulfur or nitrogen atom in the molecule, the percentage of the oil made up by these compounds is smaller.

In the atmospheric distillation of fuel oils, the presence of sulfur compounds will cause generation of hydrogen sulfide in quantities. The temperature at which this appeared and the per cent over have been tabulated against the per cent sulfur in the fuel oil. These data are given in the following table:

| | % over | Temp. °F | % S |
|---|---|---|---|
| A-1 | over 40 | above 644 | 0.30 |
| 2 | 20 | 639 | 0.87 |
| 3 | 35 | 642 | 1.16 |
| 4 | 25 | 602 | 1.25 |
| 5 | 25 | 668 | 1.73 |
| 6 | 20 | 648 | 1.13 |
| 7 | 25 | 640 | 1.83 |
| 8 | 15 | 640 | 1.35 |
| 9 | 40 | 682 | 0.33 |
| 10 | 35 | 680 | 1.61 |
| 11 | 40 | 680 | 1.31 |
| 12 | 35 | 668 | 0.81 |
| 13 | 30 | 664 | 1.39 |
| 14 | 35 | 658 | 1.37 |
| 15 | 25 | 666 | 2.56 |
| 16 | 25 | 676 | 0.53 |
| 17 | 40 | 710 | 0.77 |
| 18 | 30 | 682 | 1.95 |

This information is exceedingly interesting. The decomposition of the sulfur compounds as indicated by the generation of hydrogen sulfide does not occur much below 600°F or 316°C. With samples that have a small percentage of sulfur such as A-1 and A-9, 40% can be distilled of A-1 without appreciable cracking and no noting of hydrogen sulfide, while with A-9, 40% is distilled before this occurs. It is well known that the nature of the sulfur compound present in the oil will have a large effect upon this cracking temperature. Thus, one oil may have free sulfur in it, and as a result hydrogen sulfide will be liberated very quickly at the low temperatures, while other compounds may have a large amount of sulfur in the form of thiophenes and substituted thiophenes and there will be a small amount of hydrogen sulfide given off. Thus, A-8 and A-11 show some interesting figures. For comparison, the following data are given:

| | A-8 | A-11 |
|---|---|---|
| % sulfur | 1.35 | 1.31 |
| Cracking | | |
| % distilled over | 15 | 40 |
| °F for distillate | 640 | 680 |
| H/C radio | | |
| 1st fraction | 1.669 | 1.644 |
| 2nd fraction | 1.666 | 1.559 |
| residue | 1.408 | 1.348 |
| Molecular weight | | |
| 1st fraction | 209 | 185 |
| 2nd fraction | 242 | 215 |
| residue | 474 | 429 |

Both have nearly the same percentage sulfur and yet one shows decomposition much earlier in the distillation than the other. The one showing decomposition earlier has the greater hydrogen carbon ratio as well as the higher molecular weights for the fractions distilled. This earlier cracking may be accounted for if A-8 happens to have the sulfur compounds present as sulfides or disulfides of the aliphatic type, while with A-11 the sulfur compounds would be aromatic in nature. It would be of interest to find out the nature of the sulfur compounds present in the fuels, but that is not part of this research.

The Conradson carbon residue as determined by the A.S.T.M. method and described in Federal Specifications VV-L-791, pages 83 to 85, was determined on the "A" series. This carbon residue is used to denote if the heavy carbon compounds that make up a fuel oil are stable on distillation. It is not in the province of this report to discuss the cause of the carbon residue and what tends to increase or decrease the per cent of carbon residue found. It is interesting to note that A-1 and A-4 have practically the same hydrogen-carbon ratio of the residue, but the molecular weight of A-1 is 322 and A-4 is 413, and the carbon residue for A-1 is 6.6% and for A-4, 17.6%. A-12 has a hydrogen-carbon ratio of the residue of 1.14 and has a carbon residue of 13.3, approximately half-way between A-1 and A-4; the molecular weight of the residue of A-12 is very close to that of A-4. The factors that influence the carbon residue will be discussed in a future report from this Laboratory with a hope of trying to find some of the factors that influence the per cent carbon residue. The carbon residue, hydrogen-carbon ratio, and molecular weight of the residue on distillation follow:

| | Conradson Carbon Residue | $\frac{H}{C}$ Ratio of Residue | M.W. of Residue |
|---|---|---|---|
| A-1 | 6.6 | 1.150 | 322 |
| 2 | 8.8 | 1.343 | 438 |
| 3 | 17.3 | 1.020 | 409 |
| 4 | 17.6 | 1.143 | 413 |
| 5 | 10.4 | 1.284 | 439 |
| 6 | 9.3 | 1.339 | 504 |
| 7 | 11.0 | 1.280 | 424 |
| 8 | 9.4 | 1.408 | 474 |
| 9 | 9.3 | 1.236 | 379 |
| 10 | 10.5 | 1.278 | 447 |
| 11 | 8.4 | 1.348 | 429 |
| 12 | 13.3 | 1.142 | 409 |
| 13 | 13.6 | 1.233 | 457 |
| 14 | 11.9 | 1.268 | 436 |
| 15 | 12.0 | 1.330 | 526 |
| 16 | 7.1 | 1.375 | 449 |
| 17 | 8.7 | 1.278 | 416 |
| 18 | 12.4 | 1.333 | 479 |

In studying the fuel oils one should not lose sight of the fact that the fuels are to be burned. Many samples are of much interest theoretically, but in practical use they will be rarely encountered. It has been very interesting to note the results that the Naval Boiler Laboratory has had in burning these fuels. The Naval Boiler Laboratory Report No. 2084 of 22 August 1934 gives the scoring of these oils as obtained by them under actual burning conditions. In scoring these oils, the percentage weight given to each item is given below:*

| | |
|---|---|
| Tank deposits | 15% |
| Heater deposits | 10% |
| Atomizer deposits | 5% |
| Stack solids | 6% |
| Pumping viscosity | 20% |
| Firing viscosity | 12% |
| Overall efficiency | 20% |
| Fire room air pressure | 5% |
| Hydrocarbon loss | 5% |
| Slagging of furnace brickwork | 2% |

*The detailed scoring using this method is found on Plate 26, Figure 3, of the above report.

Using the above method of scoring, the Naval Boiler Laboratory suggests that any oil rating below 60% would be unacceptable in operation, that between 60% and 70% undesirable, and that above 70% acceptable. The oils were tabulated according to this scoring system and opposite each percentage rating are given the molecular weights, the hydrogen-carbon ratio, the deposits as determined by tank, heater and atomizer, the hydrocarbon losses, the per cent stack solids as determined by the Naval Boiler Laboratory findings, the per cent sulfur and nitrogen, the viscosity at 77°F, the variation in viscosity at 77° as given in NRL Report No. P-1127, the density at 60°F, and the source of the crude making up the oil.

| Sample | NBL Rating % | Molecular Weights |  |  |  | $\frac{H}{C}$ Ratio |  |  |  | Avg. B.P. °F |  | Deposits* |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  | Orig. | 1st | 2nd | Res. | Orig. | 1st | 2nd | Res. | 1st Cut | 2nd Cut | Tank | Heater | Atomizer |
| A-8 | 45.2 | 443 | 209 | 242 | 474 | 1.518 | 1.669 | 1.666 | 1.408 | 625 | 676 | 1 | 3 | 3 |
| A-18 | 49.1 | 410 | 201 | 253 | 479 | 1.435 | 1.608 | 1.558 | 1.333 | 608 | 681 | 1 | 1 | 1 |
| A-15 | 51.2 | 415 | 221 | 228 | 526 | 1.437 | 1.550 | 1.601 | 1.330 | 627 | 666 | 1 | 1 | 1 |
| A-2 | 53.0 | 365 | 197 | 227 | 438 | 1.404 | 1.365 | 1.572 | 1.343 | 602 | 653 | 1 | 2 | 3 |
| A-12 | 53.7 | 306 | 174 | 223 | 409 | 1.254 | 1.440 | 1.364 | 1.142 | 545 | 661 | 1 | 1 | 3 |
| A-3 | 60.8 | 310 | 163 | 213 | 409 | 1.278 | 1.629 | 1.473 | 1.020 | 475 | 621 | 0 | 1 | 3 |
| A-4 | 64.8 | 320 | 174 | 224 | 413 | 1.317 | 1.675 | 1.500 | 1.143 | 499 | 630 | 0 | 0 | 2 |
| A-13 | 66.6 | 346 | 192 | 224 | 457 | 1.351 | 1.569 | 1.508 | 1.233 | 563 | 670 | 0 | 0 | 2 |
| A-6 | 70.4 | 361 | 209 | 243 | 504 | 1.418 | 1.532 | 1.517 | 1.339 | 609 | 675 | 0 | 0 | 2 |
| A-17 | 74.3 | 374 | 232 | 234 | 416 | 1.401 | 1.532 | 1.514 | 1.278 | 677 | 719 | 0 | 0 | 0 |
| A-14 | 74.4 | 321 | 177 | 219 | 436 | 1.406 | 1.656 | 1.512 | 1.268 | 497 | 640 | 0 | 0 | 1 |
| A-5 | 76.9 | 365 | 215 | 242 | 439 | 1.398 | 1.580 | 1.524 | 1.284 | 612 | 683 | 0 | 0 | 0 |
| A-7 | 77.3 | 341 | 204 | 235 | 424 | 1.391 | 1.567 | 1.549 | 1.280 | 581 | 655 | 0 | 0 | 1 |
| A-16 | 77.6 | 355 | 209 | 235 | 449 | 1.477 | 1.574 | 1.547 | 1.375 | 618 | 688 | 0 | 0 | 0 |
| A-9 | 78.6 | 297 | 192 | 225 | 379 | 1.292 | 1.447 | 1.392 | 1.236 | 561 | 651 | 0 | 0 | 0 |
| A-10 | 80.4 | 334 | 183 | 232 | 447 | 1.385 | 1.619 | 1.532 | 1.278 | 549 | 671 | 0 | 0 | 0 |
| A-11 | 84.5 | 332 | 185 | 215 | 429 | 1.476 | 1.644 | 1.559 | 1.348 | 541 | 659 | 0 | 0 | 0 |
| A-1 | 90.9 | 261 | 182 | 220 | 322 | 1.253 | 1.469 | 1.375 | 1.150 | 545 | 623 | 0 | 0 | 0 |

* 0 = None
1 = Trace
2 = Moderate amount
3 = Heavy

| Sample | $\frac{H}{C}$ Losses | % Stack Solids | % Carbon Residue | % Hexane Insol. #4 Filter |  | Vis. 122° F SSF | Vis. Var. @77°F | % S | % N | Source of Crude | Density at 60°F ° A.P.I. |
|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  | Orig. | After Heating |  |  |  |  |  |  |
| A-8 | 10.86 | 0.147 | 9.4 | 6.4 | 6.4 | 141.4 | 108.3 | 1.35 | 0.43 | East Texas | 15.3 |
| A-18 | 9.84 | 0.550 | 12.4 | 9.5 | 9.8 | 148.9 | 31.8 | 1.95 | 0.33 | Van Zandt Texas | 11.8 |
| A-15 | 10.35 | 0.097 | 12.0 | 10.8 | 11.5 | 233.0 | 6.6 | 2.56 | 0.50 | Venezuela | 11.1 |
| A-2 | 12.22 | 0.113 | 8.8 | 5.9 | 6.4 | 80.2 | 91.0 | 0.87 | 0.53 | East Texas | 12.1 |
| A-12 | 10.92 | 0.267 | 13.3 | 9.6 | 9.8 | 77.2 | 31.9 | 0.81 | 0.38 | Okla. and Texas | 6.9 |
| A-3 | 11.93 | 0.160 | 17.3 | 16.0 | 17.7 | 115.6 | 6.7 | 1.16 | 0.71 | California | 6.7 |
| A-4 | 10.45 | 0.153 | 17.6 | 16.9 | 17.5 | 136.1 | 6.4 | 1.25 | 1.12 | California | 7.7 |
| A-13 | 9.92 | 0.120 | 13.6 | 11.8 | 14.1 | 151.9 | 16.8 | 1.39 | 1.00 | California | 9.0 |
| A-6 | 8.09 | 0.207 | 9.3 | 6.2 | 5.9 | 80.8 | 52.6 | 1.13 | 0.19 | West Texas | 12.3 |
| A-17 | 10.14 | 0.073 | 8.7 | 4.8 | 5.6 | 86.5 | 18.5 | 0.77 | 0.42 | East Texas | 11.5 |
| A-14 | 10.56 | 0.067 | 11.9 | 10.5 | 11.9 | 56.2 | 11.1 | 1.37 | 0.87 | California | 11.2 |
| A-5 | 8.82 | 0.020 | 10.4 | 6.9 | 7.3 | 81.2 | 19.6 | 1.73 | 0.45 | Mixed Tex.&Venezuela | 10.3 |
| A-7 | 11.39 | 0.117 | 11.0 | 7.2 | 7.9 | 52.7 | 77.7 | 1.86 | 0.48 | East & West Texas | 11.5 |
| A-16 | 9.55 | 0.033 | 7.1 | 4.5 | 5.2 | 60.9 | 21.9 | 0.53 | 0.41 | East Texas | 13.4 |
| A-9 | 9.40 | Lost | 9.3 | 6.2 | 6.7 | 37.7 | 1.4 | 0.33 | 0.30 | Coastal | 8.8 |
| A-10 | 9.70 | 0.055 | 10.5 | 6.8 | 6.8 | 48.7 | 64.4 | 1.61 | 0.44 | East & West Texas | 11.9 |
| A-11 | 10.70 | 0.033 | 8.4 | 6.0 | 5.9 | 28.2 | 72.1 | 1.31 | 0.34 | Louisiana & Texas | 15.2 |
| A-1 | 12.42 | 0.023 | 6.6 | 1.8 | 3.0 | 21.7 | 0.8 | 0.30 | 0.27 | Gulf Coast & East Texas | 8.3 |

The source of the fuels shows that only four are from California. Of the four oils from California, A-3, A-4, A-13 and A-14, three are undesirable, and one is acceptable according to the Naval Boiler Laboratory rating. The hydrogen-carbon ratio of these four oils shows that they are highly aromatic in nature and that A-3 and A-4 are cut back from a heavy cracked residuum. The hydrogen-carbon ratio of the first 20% of the four oils is very similar in nature, that is, 1.57 to 1.68, the molecular weight of the first cut bearing from 163 to 192.

Samples A-1 and A-9, which in the NRL report have shown the greatest stability in viscosity at 77°F, are supplied by two different refineries and it is very interesting to note that the source of the crude for both refineries was probably the same. The per cent sulfur in both oils is low. The nitrogen is low for A-9 and 0.7% for A-1. The hydrogen-carbon ratio for both is very similar in characteristics for the first and second 20% distilled. The hydrogen-carbon ratio of the residue for A-1 is more aromatic in nature than that for A-9. The molecular weights as well as the boiling points show that A-9 is made up of molecules having the higher molecular weight, but that its density is not far from that of A-1.

A-2, a fuel made up from an East Texas crude of the 12.1 A.P.I. gravity, given an unacceptable rating by the Naval Boiler Laboratory, is, nevertheless, very interesting from the chemical aspect. The first 20% over shows that the lighter fraction is aromatic in nature (hydrogen-carbon ratio, 1.37), more so than the second fraction that comes over (hydrogen-carbon ratio, 1.57). This first fraction that comes over in many of the fuels may be present in the fuel as made and may be the result of cracking of a refractory portion of the oil or it may be a lighter cut that is used to blend the fuel oil to a lower viscosity. The molecular weight of this first cut, 197, does not vary appreciably from the other fuels studied. The second 20% over has a hydrogen-carbon ratio of 1.57, which is higher than most of the other oils of this group.

The molecular weight of the first 20% over of all the fuels given in this report shows that the California material has the smallest molecular weight. Thus, A-3, A-4, A-13 and A-14 have molecular weights of 163, 174, 192 and 177, respectively. For the first 20% over, 163 is the lowest value found. The molecular weights of the other fuels for the first 20% will vary up to 232.

The second fraction from 20% to 40% over shows the variation in the molecular weight from 213 to 253. The residue varied from 322 for A-1 to 526 for A-15. It is not surprising that A-15 shows a high molecular weight because it is a Venezuelan crude with high sulfur, 2.56%, and on distillation, cracking, as indicated by the presence of hydrogen sulfide, showed up very early, in fact with only 20% over. With this hydrogren sulfide liberation there can be one of two things occurring: first, the removal of hydrogen when free sulfur is present to form hydrogen sulfide, or secondly, a compound carrying sulfur in the make-up that decomposes readily to split out $H_2S$. If the cracking is due to the decomposition of sulfur compounds, then the elimination of hydrogen sulfide may occur with polymerization, and especially the formation of highly aromatic rings carrying sulfur as one member of the ring. The two oils showing the lowest molecular weight of the residue are A-1 and A-9, and these two oils have the smallest per cent sulfur. One should note here that the presence of sulfur does not always indicate excess cracking when distillation occurs, for certain sulfur compounds of the thiophene grouping are entirely stable in distillation.

### (b) Recommendations

The facts given in this report show that the distillation of cracked fuels can give some interesting information as to the composition of the lighter fractions present. It is doubtful if distillation will ever be useful by the Navy in specifications. For research both atmospheric and vacuum distillation should be very useful. If a study is to be made on the composition of the heavy residues after the first 40% or 50% have been distilled over, the distillation should be made with a pressure of 0.1 mm or less, that is, a mercury diffusion pump should be used.

## SUMMARY

In this report is given the distillation of the "A" series of fuel oils using the Engler method. Temperatures are recorded for the initial boiling point and each 5% over as high as the distillation was carried. Three fractions were taken as follows: 0-20%, 20-40%, and the remainder known as the residue.

In this report is given the carbon and hydrogen percentage for each of the above fractions.

In this report is given the average molecular weight of each fraction as found by the freezing point method using naphthalene as a solvent.

In this report it is shown that some fuel oils can be distilled up to 80% with no appreciable cracking, while others begin when 15% has been distilled over.

In Appendix II of this report is given the vacuum distillation of certain of these fuel oils.

# APPENDIX I

## Distillation of the "A" Samples at Atmospheric Pressure

The distillations reported in the first table of this appendix were made during the months of May and June 1934. In this table will be found the length of time that was necessary to heat the oil before the initial boiling point arrived and the length of time necessary to distill 5% fractions. With all these samples 100 cc was taken, that is, the sample was weighed out with the density of 80° being used as a basis. In this same table is given the temperature at which the I.B.P. occurred and the temperature for each 5 cc up to 40 cc. The temperature for the first 20% over is averaged and put in this table in degrees Fahrenheit as well as Centigrade. The same is done for the second 20%. The volume of the fractions taken for No. 1 is 20 cc throughout; the second fraction contains the volume from 20 to 40 cc and the distillate that drains from the condenser and therefore varies from 20 to 24 cc. The heating stopped in all cases when the second 20% had been distilled into the receiver. The next table gives the per cent carbon and hydrogen that is found in the original sample and reported previously by this Laboratory, and in the first and second fractions and the residue. No sulfur or nitrogen determinations were made. Following the analysis will be given the molecular weight of the original as well as the three fractions. This molecular weight is the value that is found by the freezing point method using naphthalene as a solvent. The distillation of some of these samples was repeated several times and is given in the next table that follows the molecular weight determinations. A-1 was distilled four times. Run No. 1 shows the results using electric heat part of the way and after that gas heat. It was found in operating with this oil, and others as well, that the distillation was handled easier with a gas flame. Runs No. 2 and No. 3 of A-1 were determined about the same time as Run No. 1 — about January 1934. Run No. 4 under A-1 is that given in Table 1 of this appendix and was used to obtain the necessary fractions for analysis. Under A-2, Run No. 1 was an experimental run to find out something concerning the cracking of the fuel oil. Only 30% was distilled over. Run No. 2 was the one reported previously and Run No. 3 was determined in February 1935; the first fraction, 20 cc, as well as the second cut, was taken for check analysis of carbon and hydrogen. Under A-3, Run No. 1 was made during January 1934, and Run No. 2 from May to June 1934. The same occurs for A-4, A-5, A-6 and A-7. The first run of A-9 was determined from May to June 1934 and Run No. 2 in February 1935. The same time relations hold for the distillations of A-11, A-15 and A-17. A-11, A-15 and A-17 were re-run to note at which temperature the presence of hydrogen sulfide became very noticeable. As has been said before in this report, the accuracy of the temperature readings for each fraction is not the highest. In other words, there may be a variation in the temperature of the distillate without appreciable cracking as much as 10°F. With samples

A-11, A-15 and A-17, there is a large variation with initial boiling point. The cause of this variation, while not definitely known, seems to accompany the presence of water as in sample A-11, and further study should be made at this point if the distillation of fuels and the study of the fractions is to be continued. The differential in temperatures for the other fractions from 5% on to 40% is fairly large for A-17, while for A-11 it is well within the experimental differences that would be found.

# LOG OF DISTILLATIONS, time, temperature and volume

| | A-1 | A-2 | A-3 | A-4 | A-5 | A-6 | A-7 | A-8 | A-9 | A-10 | A-11 | A-12 | A-13 | A-14 | A-15 | A-16 | A-17 | A-18 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Minutes Heating | | | | | | | | | | | | | | | | | | |
| I.B.P. | 7 | 8 | 7 | 7 | 9 | 8 | 6 | 8 | 7 | 6 | 4.5 | 7 | 5 | 5 | 6 | 9 | 6 | 5 |
| % over 5 | 8 | 9 | 8 | 8 | 10 | 9 | 7 | 9 | 8 | 9 | 6 | 8 | 5.5 | 6 | 7 | 10 | 7 | 6 |
| 15 | 10 | 11 | 10 | 10 | 12 | 11 | 9 | 11 | 10 | 12 | 8 | 10 | 8.5 | 8 | 8.5 | 12.5 | 8.5 | 8 |
| 25 | 12 | 13 | 12 | 12 | 14 | -- | 11 | 13 | 12 | 14 | 10 | 12.5 | 10 | 10 | 10 | 14 | 10 | 9 |
| 35 | 14 | 15 | 14 | 14 | --- | --- | 13 | 15 | 14 | 16 | 12 | 15 | 12 | 11 | 13 | 16 | 11.5 | -- |
| Temperatures | | | | | | | | | | | | | | | | | | |
| I.B.P. | 436 | 462 | 346 | 356 | 440 | 466 | 441 | 440 | 468 | 380 | 390 | 412 | 430 | 410 | 504 | 470 | 546 | 410 |
| % over 5 | 508 | 561 | 416 | 435 | 558 | 564 | 528 | 576 | 522 | 485 | 478 | 494 | 498 | 448 | 576 | 563 | 640 | 540 |
| 10 | 534 | 596 | 450 | 472 | 604 | 603 | 565 | 626 | 549 | 532 | 524 | 525 | 540 | 476 | 620 | 614 | 670 | 594 |
| 15 | 556 | 613 | 492 | 526 | 630 | 620 | 605 | 641* | 576 | 573 | 564 | 556 | 588 | 510 | 648 | 634 | 684 | 636 |
| 20 | 582 | 639* | 540 | 563 | 655 | 648* | 626 | 655 | 596 | 604 | 596 | 604 | 626 | 554 | 664 | 660 | 692 | 662 |
| 25 | 598 | 646 | 580 | 602* | 668* | 664 | 640* | 663 | 622 | 648 | 630 | 640 | 652 | 588 | 672 | 676* | 711 | 680 |
| 30 | 616 | 698 | 615 | 625 | 682 | 677 | 651 | 672 | 640 | 668 | 656 | 658 | 664* | 634 | 648 | 686 | 718 | --* |
| 35 | 633 | 636 | 642* | 640 | 688 | 680 | 658 | 681 | 660 | 680* | 666 | 668* | 680 | 658* | 660 | 692 | 721 | 684 |
| 40 | 644 | 632 | 648 | 653 | 693 | 680 | 672 | 687 | 682* | 688 | 682 | 678 | 684 | 678 | 682 | 698 | 724 | 680 |
| Avg. boiling points | | | | | | | | | | | | | | | | | | |
| 0-20% °F | 545 | 602 | 475 | 499 | 612 | 609 | 581 | 625 | 561 | 549 | 541 | 545 | 563 | 497 | 627 | 618 | 677 | 608 |
| °C | 285 | 317 | 246 | 259 | 322 | 321 | 305 | 330 | 294 | 287 | 283 | 285 | 295 | 258 | 331 | 326 | 358 | 320 |
| 20-40% °F | 623 | 653 | 621 | 630 | 683 | 675 | 655 | 676 | 651 | 671 | 659 | 661 | 670 | 640 | 666 | 688 | 719 | 681 |
| °C | 328 | 345 | 327 | 332 | 362 | 357 | 346 | 358 | 344 | 355 | 348 | 350 | 354 | 338 | 352 | 364 | 382 | 361 |
| Volume fractions in cc. | | | | | | | | | | | | | | | | | | |
| #1 | 20 | 20 | 20 | 20 | 20 | 20 | 20 | 20 | 20 | 20 | 20 | 20 | 20.5 | 20 | 20 | 20.5 | 20 | 20 |
| #2 | 21.5 | 22 | 22 | 22 | 22 | 22 | 22 | 23 | 23 | 23 | 22 | 22.5 | 22.5 | 21.5 | 24 | 22 | 22 | 23 |

* Cracking begins.

## PER CENT CARBONS AND HYDROGEN AND MOLECULAR WEIGHTS OF "A" SAMPLES AND FRACTIONS

| | Original | | 1st fraction | | 2nd fraction | | Residue | | Molecular Weights | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | %C | %H | %C | %H | %C | %H | %C | %H | Orig. | 1st | 2nd | Residue |
| A-1 | 89.81 | 9.46 | 89.12 | 11.00 | 89.20 | 10.30 | 90.17 | 8.71 | 261 | 182 | 220 | 322 |
| 2 | 88.09 | 10.38 | 88.30 | 10.15 | 87.08 | 11.49 | 88.44 | 9.99 | 365 | 197 | 227 | 438 |
| 3 | 87.80 | 9.42 | 87.06 | 11.90 | 87.71 | 10.86 | 88.29 | 7.55 | 310 | 163 | 213 | 409 |
| 4 | 87.39 | 9.67 | 86.13 | 12.12 | 87.05 | 10.96 | 87.47 | 8.40 | 320 | 174 | 224 | 413 |
| 5 | 87.09 | 10.23 | 87.66 | 11.63 | 86.46 | 11.09 | 86.91 | 9.36 | 365 | 215 | 242 | 439 |
| 6 | 87.84 | 10.46 | 87.74 | 11.29 | 87.44 | 11.15 | 87.78 | 9.87 | 361 | 209 | 243 | 504 |
| 7 | 87.36 | 10.21 | 86.69 | 11.41 | 86.73 | 11.29 | 86.31 | 9.28 | 341 | 204 | 235 | 424 |
| 8 | 86.83 | 11.08 | 86.95 | 12.20 | 86.75 | 12.15 | 87.44 | 10.35 | 443 | 209 | 242 | 474 |
| 9 | 89.18 | 9.67 | 88.91 | 10.80 | 88.82 | 10.38 | 89.62 | 9.32 | 297 | 192 | 225 | 379 |
| 10 | 87.46 | 10.18 | 86.89 | 11.81 | 87.11 | 11.20 | 87.56 | 9.40 | 334 | 183 | 232 | 447 |
| 11 | 87.57 | 10.85 | 86.90 | 12.00 | 87.05 | 11.39 | 86.16 | 9.76 | 332 | 185 | 215 | 429 |
| 12 | 89.28 | 9.40 | 88.13 | 10.66 | 88.62 | 10.15 | 89.61 | 8.61 | 306 | 174 | 223 | 409 |
| 13 | 86.79 | 9.85 | 86.11 | 11.36 | 86.91 | 11.01 | 87.17 | 9.02 | 346 | 192 | 224 | 457 |
| 14 | 86.63 | 10.23 | 86.23 | 12.01 | 86.57 | 10.99 | 87.17 | 9.28 | 321 | 177 | 219 | 436 |
| 15 | 86.28 | 10.41 | 86.75 | 11.30 | 85.74 | 11.54 | 85.03 | 9.52 | 415 | 221 | 228 | 526 |
| 16 | 86.98 | 10.80 | 87.88 | 11.60 | 87.50 | 11.37 | 88.25 | 10.18 | 355 | 209 | 235 | 449 |
| 17 | 88.17 | 10.38 | 87.66 | 11.29 | 87.67 | 11.16 | 88.72 | 9.53 | 374 | 232 | 234 | 416 |
| 18 | 87.12 | 10.50 | 86.94 | 11.75 | 86.67 | 11.44 | 87.11 | 9.76 | 410 | 201 | 253 | 479 |

| | A-1 | | | | A-2 | | | A-3 | | A-4 | | A-5 | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Run #1 | Run #2 | Run #3 | Run #4** | Run #1 | Run #2** | Run #3 | Run #1 | Run #2** | Run #1 | Run #2** | Run #1 | Run #2** |
| Temperatures, °F | | | | | | | | | | | | | |
| I.B.P. | 436 | 441 | 438 | 436 | 442 | 462 | 478 | 342 | 346 | 362 | 356 | 440 | 440 |
| % over 5 | 496 | 504 | 505 | 508 | 550 | 561 | 548 | 422 | 416 | 434 | 435 | 556 | 558 |
| 10 | 523 | 528 | 528 | 534 | 602 | 596 | 608 | 452 | 450 | 468 | 472 | 597 | 604 |
| 15 | 546 | 554 | 552 | 556 | 637 | 613 | 644 | 490 | 492 | 509 | 526 | 627 | 630 |
| 20 | 568 | 576 | 575 | 582 | 660 | 639* | 676 | 532 | 540 | 554 | 563 | 652* | 655 |
| 25 | 583 | 595 | 596 | 598 | 676* | 646 | 684* | 581 | 580 | 593* | 602* | 666 | 688* |
| 30 | 600 | 614 | 613 | 616 | 684 | 698 | 693 | 626 | 615 | 626 | 625 | 677 | 682 |
| 35 | 616 | 632 | 630 | 633 | -- | 636 | 697 | 640 | 642* | 642 | 640 | 684 | 688 |
| 40 | 628 | 647 | 644 | 644 | -- | 632 | 705 | 656* | 648 | 660 | 653 | 688 | 693 |
| 45 | 635 | 660 | 658 | -- | -- | -- | -- | 662 | -- | 672 | -- | 693 | -- |
| 50 | 636 | 674 | 672 | -- | -- | -- | -- | 667 | -- | 680 | -- | 695 | -- |
| 55 | 675 | 690 | 682 | | | | | | | | | | |
| 60 | 689 | 700 | 690 | | | | | | | | | | |
| 65 | 702 | 710 | 697 | | | | | | | | | | |
| 70 | 705 | 715 | 702 | | | | | | | | | | |
| 75 | 702# | 718 | -- | | | | | | | | | | |
| 80 | -- | 722 | -- | | | | | | | | | | |

# This run was made with electric heat up to 50% over. The remainder was made with gas heat.

* Cracking begins.

** This run was previously reported in this report.

|  | A-6 |  | A-7 |  | A-9 |  | A-11 |  |  | A-15 |  | A-17 |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  | Run #1 | Run #2** | Run #1 | Run #2 | Run #1** | Run #2 | Run #1** | Run #2 | Run #3 | Run #1** | Run #2 | Run #1** | Run #2 |
| Temperatures °F |  |  |  |  |  |  |  |  |  |  |  |  |  |
| I.B.P. | 444 | 466 | 437 | 441 | 468 | 476 | 390# | 302 | 360# | 504 | 508 | 546 | 468 |
| % over 5 | 560 | 564 | 551 | 528 | 522 | 534 | 478 | 484 | 492 | 576 | 562 | 640 | 621 |
| 10 | 598 | 603 | 570 | 565 | 549 | 554 | 524 | 532 | 530 | 620 | 618 | 670 | 638 |
| 15 | 625* | 620 | 605 | 605 | 576 | 585 | 564 | 564 | 560 | 648 | 632 | 684 | 664 |
| 20 | 656 | 648* | 634* | 626 | 596 | 606 | 596 | 598 | 588 | 664 | 655 | 692 | 675 |
| 25 | 558 | 664 | 652 | 640* | 622 | 629 | 630 | 628 | 624 | 672 | 666* | 711 | 682 |
| 30 | -- | 677 | 665 | 651 | 640 | 653 | 656 | 654 | 648 | 648 | 680 | 718 | 685 |
| 35 | -- | 680 | 672 | 658 | 660 | 658* | 666 | 662 | 666 | 660 | 688 | 721 | 700 |
| 40 | -- | 680 | -- | 672 | 682* | 685 | 682 | 686 | 684* | 682 | 674 | 724 | 710* |

# A-11 on distillation showed a few drops of water. The first drop over or I.B.P. gave a large variation due to water. No appreciable $H_2S$ was evident during the entire distillation.

* Cracking begins.

** This run was previously reported in this report.

# APPENDIX II

## Distillation of Fuel Oil Under Reduced Pressure

The main part of this report has to do with the distillation of fuel oils at atmospheric pressures, or approximately 760 mm. With atmospheric distillation it has been shown that it is usually not wise to go beyond 40% in the distillation because beyond this excessive cracking occurs. One oil, A-1, could be distilled up to 80% with minimum damage. Several of the "A" series were distilled under reduced pressure to note if these oils could be distilled without trouble. The vacuum set-up used was one where the pressure could be regulated readily to any desired value as shown in the accompanying drawing. Thus, some oils are best distilled at one pressure, while others at a different pressure due to the boiling ranges of the compounds making up the oil. A-1 could be distilled at 10 mm with success, while with A-9 it was necessary to run to 1.9 mm to get a large percentage of the oil over. In distilling a heavy oil such as A-9, the fractions coming over after 50% has been distilled are usually very viscous and have a tendency to congeal to a jelly-like mass. Thus, in distillation of A-9 with a 172-gram charge, when 108 cc have been distilled off, the overhead was very viscous with a dark red color. In these distillations there was a stream of carbon dioxide going through the oil at all times to reduce the cracking to a minimum. If vacuum distillation is to be used in the study of heavy fuels, and it seems it would be worthwhile to do so, one definite pressure should be used at which to study the various oils, and cuts should be made at fairly narrow temperature differences and the volume of these cuts should be sufficient for further study.

Some of the characteristics of these three oils as well as the summarized data for the atmospheric and vacuum distillation follows:

| | | A-1 | A-2 | A-9 |
|---|---|---|---|---|
| Gravity, ° API.................. | | 8.3 | 12.1 | 8.8 |
| Viscosity, 122°F................. | | 20.7 SSF | 80.2 SSF | 37.7 SSF |
| Ultimate Analysis, | %C........... | 89.81 | 88.09 | 89.18 |
| | H........... | 9.46 | 10.38 | 9.67 |
| | S........... | 0.30 | 0.87 | 0.33 |
| | N........... | 0.71 | 0.53 | 0.30 |
| Conradson Carbon %............... | | 6.6 | 8.8 | 9.3 |
| Rating by N.B.L. %............... | | 90.9 | 53.0 | 78.6 |
| Avg. molecular weight............ | | 261 | 365 | 297 |
| Atmospheric distillation: | | | | |
| Avg. B.P. °F | 1st 20%......... | 545 | 602 | 561 |
| | 2nd 20%......... | 623 | 653 | 651 |
| H/C Ratio | 1st 20%......... | 1.469 | 1.365 | 1.447 |
| | 2nd 20%......... | 1.375 | 1.572 | 1.392 |

|  | A-1 | A-2 | A-9<br>1st | A-9<br>2nd |
|---|---|---|---|---|
| Vacuum Dist. |  |  |  |  |
| Charge.................. | 202 | 175 | 174 | 171 |
| Pressure, mm............ | 10 | 5 | 5 | 5 to 1.7 |
| Recovered gr............ | 112.4 | 31.8 | 92.1 | 111.5 |
| %.................. | 55.6 | 18.2 | 52.9 | 64.9 |
| I.B.P. °F.............. | 142 | 140 | 104 | 109 |
| Final °F................ | 448 | 397 | 473 | 507 |

It is interesting to note that the maximum temperature reached with these vacuum distillations was lower than the temperature reached for atmospheric distillation for the first five percent over. At no time was the temperature reached at which cracking was noted in the atmospheric distillations. It would be interesting to learn at what temperature cracking would occur during vacuum distillation, for the temperature in the flask may be as much as 90°F above the temperature of the overhead and the overhead temperatures did not go over 507°F.

A-1 202 gram charge, pressure 10 mm

| Vol. cc | Temp. °C | Vol. cc | Temp. °C |
|---|---|---|---|
| I.B.P. | 61 | 54 | 177 |
| 2 | 86 | 60 | 184 |
| 4 | 95 | 64 | 188 |
| 6 | 102 | 68 | 190 |
| 8 | 105 | 72 | 193 |
| 10 | 110 | 76 | 200 |
| 12 | 118 | 80 | 203 |
| 18 | 129 | 84 | 205 |
| 24 | 133 | 86 | 208 |
| 28 | 139 | 92 | 214 |
| 32 | 146 | 95 | 217 |
| 36 | 150.5 | 99 | 220 |
| 38 | 152 | 103 | 226 |
| 46 | 168 | 105 | 231 |
| 50 | 172 |  |  |

|  | cc | gr. | sp.gr. |
|---|---|---|---|
| 1st fraction | 40 | 36.9 | 0.923 |
| 2nd fraction | 53 | 51.1 | 0.964 |
| 3rd and drainage of condenser | 24 | 24.4 | 1.017 |
|  |  | 112.4 |  |

$$\frac{112.4}{202} \times 100 = 55.6\%$$

A-2, 175 gram charge, pressure 5 mm

| | Temp. °C | Distillate |
|---|---|---|
| I.B.P. | 60 | |
| 2 cc | 85 | |
| 4 cc | 104 | yellow |
| 6 cc | 108 | |
| 8 cc | 113 | |
| 12 | 128 | |
| 14 | 135 | |
| 16 | 143 | yellow |
| 18 | 153 | |
| 20 | 160 | |
| 22 | 167 | |
| 24 | 175 | |
| 26 | 180 | |
| 28 | 183 | |
| 33 | 203 | |

weight of distillate, 31.8 grams or 18.2%

A-9, Charge run #1, 174 gr. Run #2, 171.2 gr.

| | Run #1 | | Run #2 | |
|---|---|---|---|---|
| | Pressure | Temp. °C | Pressure | Temp. °C |
| I.B.P. | 5 mm | 40 | 5 mm | 43 |
| 2 | | 91 | | 90 |
| 4 | | 98 | | 98 |
| 6 | | 103 | | 104 |
| 8 | | 108 | | 109 |
| 10 | | 111 | | 115 |
| 12 | | 114 | | 118 |
| 14 | | 117 | | 122 |
| 16 | | 120.5 | | 125 |
| 18 | | 124 | | 128 |
| 20 | | 128 | | 131 |
| 22 | | 131 | | 134.5 |
| 24 | | 133 | | 137.5 |
| 26 | | 137 | | 140.5 |
| 28 | | 140 | | 143 |
| 30 | | 142 | | 147.5 |
| 32 | | 145 | | |
| 34 | | 154 | | |
| 36 | | 158 | | 155 |
| 38 | | 161 | | 156.5 |
| 40 | | 162 | | 158.5 |
| 42 | | | | 161.5 |

A-9 cont'd

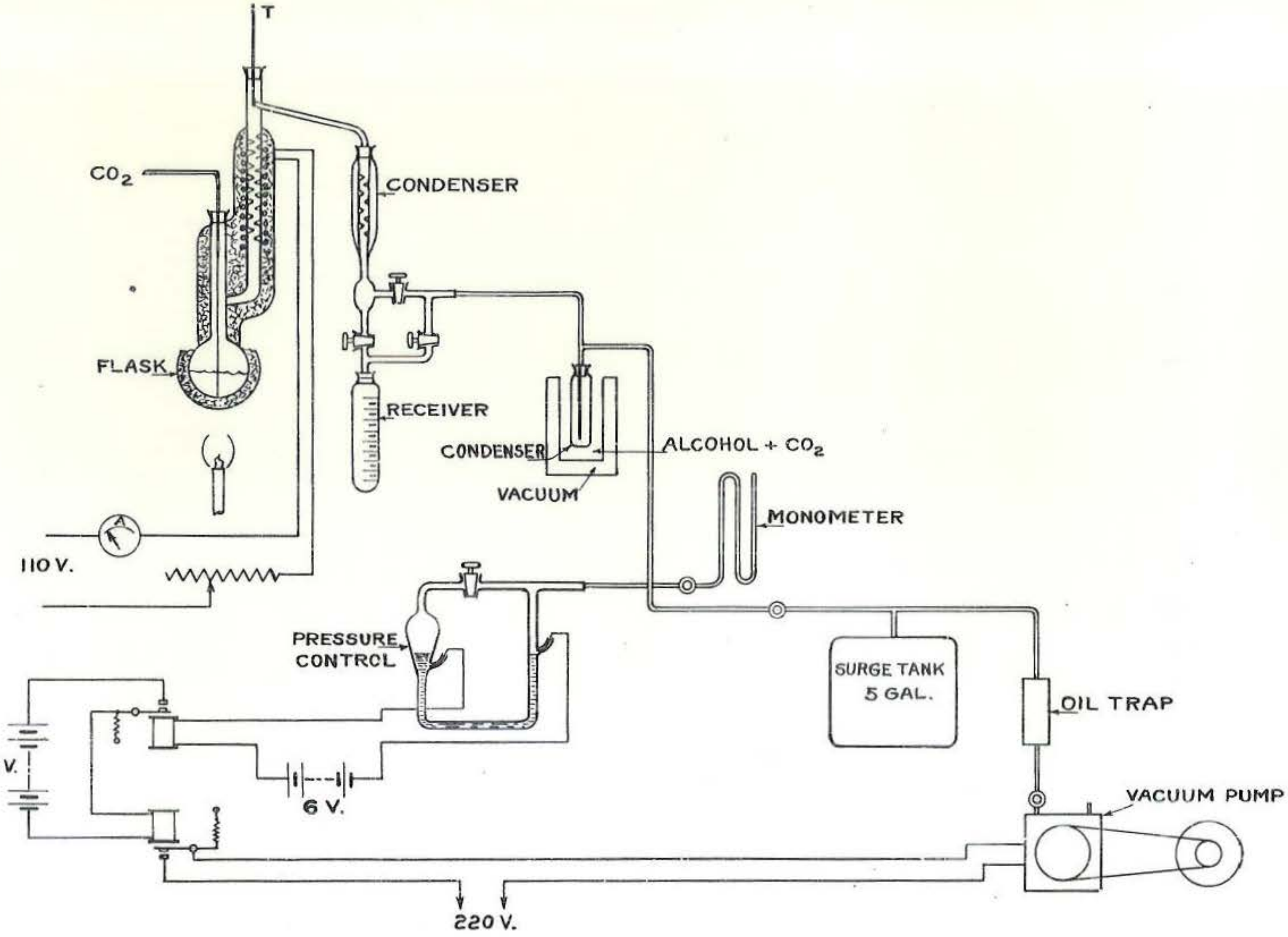
| | Run #1 | | Run #2 | |
|---|---|---|---|---|
| | Pressure | Temp. °C | Pressure | Temp. °C |
| 44 | 5 mm | | 5 mm | 167 |
| 46 | | 173 | | 170 |
| 48 | | 177 | | 175 |
| 50 | | 179 | | 183.5 |
| 52 | | 182 | | 187 |
| 54 | | 184.5 | | 192 |
| 56 | | 186 | | 195 |
| 58 | | 191.5 | | 198 |
| 60 | | 196 | | 200.5 |
| 62 | | 199 | | 202.5 |
| 64 | | 201 | | 204 |
| 66 | | 204 | | 211 |
| 68 | | 207 | | 214.5 |
| 70 | | 209 | | 218 |
| 72 | | 215 | 1.9 mm | 190 |
| 74 | | 220.5 | | 198 |
| 76 | | 225 | | |
| 78 | | 228 | | |
| 80 | | 231 | | 207 |
| 82 | | 233 | | 211 |
| 84 | | 235.5 | | 217 |
| 86 | | | | 222.5 |
| 88 | | 240 | | 225 |
| 90 | | 245 | | |
| 95 | | | | 232 - 3 |
| 98 | | | | 235 |
| 100 | | | | 244 |
| 103 | | | | 248 |
| 105 | | | | 252 |
| 108 | | | 1.9 | 255 |
| 112 | | | 1.7 | 259 |
| 115 | | | 1.7 | 264 max.temp. |

| | cc. | gr. | cc. | gr. |
|---|---|---|---|---|
| 1st fraction | 40.0 | 37.0 | 30 | 27.4 |
| 2nd | 56.0 | 54.7 | 41 | 40 |
| 3rd | | | 19 | 18.6 |
| 4th | | | 25 | 25.1 |
| $CO_2$ trap | | 0.4 | | 0.4 |
| | | 92.1 | | 111.5 |

$$\frac{92.1}{174} \times 100 = 52.9\%$$

$$\frac{111.5}{171.2} \times 100 = 64.9\%$$

PLATE I



VACUUM DISTILLATION OF FUEL OILS