The deodorization of a heavy petroleum gas oil
by Alistair S Couper

A THESIS Submitted to the Graduate Faculty In partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering
Montana State University
© Copyright by Alistair S Couper (1953)

Abstract:
The primary purpose of this investigation was to find a commercially suitable method of reducing the odor intensity of a heavy petroleum gas oil obtained from an Oregon Basin, Wyoming crude.

The theories of odor which have been postulated were reviewed and it was found that there is little understanding of the nature of an odor. An attempt was made to isolate the odorous constituents of the heavy gas oil by rectification but proved unsuccessful. Since neither of these investigations gave any objective approach to the problem, the attempts to deodorize the oil consisted of methods reported to have been successful in the deodorization of substances similar to the gas oil.

The methods of deodorization investigated were the treatment of the oil with various gases (air, ammonia, sulfur dioxide, and oxygen), steam distillation, and liquid extraction with a formaldehyde-sodium metasilicate solution, sulfuric acid, or acetone. Other methods investigated were the addition to the oil of the liquids benzaldehyde or alkaline potassium mercuric iodide, the use of adsorbents charcoal and silica gel, and the passing of hot oil over catalysts of cyclocel and cobalt molybdate in a high temperature reactor, A fair-Wells osmoscope was used to measure odor intensity, which gave a comparative reading of odor intensity. By comparing the odor of treated samples with the odor of a commercial deodorized oil, treatment of the oil with air, sulfur dioxide or steam was found to give a sufficient reduction in odor intensity. Silica gel and cobalt molybdate showed promise but require further investigation.

The secondary purpose of this investigation was to survey the literature for possible new fields of application for this gas oil. The fields of application investigated were coal spray oils, herbicides and insecticides and cutting oils. The conditions of applicability are reported but no conclusions drawn since many of the variables have not been investigated.

THE DEODORIZATION OF A HEAVY PETROLEUM GAS OIL

by

ALISTAIR S. COUPER

A THESIS

Submitted to the Graduate Faculty

in

partial fulfillment of the requirements

for the degree of

Master of Science in Chemical Engineering

at

Montana State College

Approved:

Lloyd Berg
Head, Major Department

Lloyd Berg
Chairman, Examining Committee

Dean, Graduate Division

Bozeman, Montana
August, 1953

N378
C828d
cop. 2

TABLE OF CONTENTS

page

ABSTRACT. 3

INTRODUCTION. 4

THEORIES OF ODOR PERCEPTION 11

MATERIALS, EQUIPMENT AND METHODS. 17

RESULTS 29

SUMMARY 33

POSSIBLE COMMERCIAL USES FOR A HEAVY GAS OIL. 34

ACKNOWLEDGEMENT 41

LITERATURE CITED. 42

APPENDIX. 45

108561

ABSTRACT

The primary purpose of this investigation was to find a commercially suitable method of reducing the odor intensity of a heavy petroleum gas oil obtained from an Oregon Basin, Wyoming crude.

The theories of odor which have been postulated were reviewed and it was found that there is little understanding of the nature of an odor. An attempt was made to isolate the odorous constituents of the heavy gas oil by rectification but proved unsuccessful. Since neither of these investigations gave any objective approach to the problem, the attempts to deodorize the oil consisted of methods reported to have been successful in the deodorization of substances similar to the gas oil.

The methods of deodorization investigated were the treatment of the oil with various gases (air, ammonia, sulfur dioxide, and oxygen), steam distillation, and liquid extraction with a formaldehyde-sodium metasilicate solution, sulfuric acid, or acetone. Other methods investigated were the addition to the oil of the liquids benzaldehyde or alkaline potassium mercuric iodide, the use of adsorbents charcoal and silica gel, and the passing of hot oil over catalysts of cyclocel and cobalt molybdate in a high temperature reactor.

A fair-Wells osmoscope was used to measure odor intensity, which gave a comparative reading of odor intensity. By comparing the odor of treated samples with the odor of a commercial deodorized oil, treatment of the oil with air, sulfur dioxide or steam was found to give a sufficient reduction in odor intensity. Silica gel and cobalt molybdate showed promise but require further investigation.

The secondary purpose of this investigation was to survey the literature for possible new fields of application for this gas oil. The fields of application investigated were coal spray oils, herbicides and insecticides and cutting oils. The conditions of applicability are reported but no conclusions drawn since many of the variables have not been investigated.

INTRODUCTION

The fact that nobody knows exactly what causes an odor has not stopped man from using or eliminating odors when he feels that such action would be a benefit to his society. To most people odors may be expressed in two ways, good and bad. For the good odors man has developed many uses and thereby large industries, of which the cosmetics and perfumery are the most typical. The bad odors, however, have only limited applicability (such as in natural gas to give warning of leakages) and in most instances are considered undesirable, and therefore attempts are made to eliminate or hide such malodors.

What constitutes the line of demarcation between a good and a bad odor is unknown and seems to be completely arbitrary and dependent solely on the whims of a particular society. In our present society we seem to have come to the completion of an historical cycle and attained an odor consciousness similar to that of ancient Greece and Rome. In the intervening period of time the sense of smell seems to have been neglected and, while the romantic poets eulogized the scent of a rose, they still lived with and accepted open sewers in their streets with an equally noticeable odor. The relative speed with which our odor evaluation has changed can be seen by the fact that in 1770 an English law was passed to the effect that any woman obtaining marriage by the use of perfume, false hair, or high heels would be considered a sorceress and her marriage declared null and void (6).

At the present time the acute public evaluation of good and bad odors has caused the growth of a definite odor consciousness in industry, and all

possible attempts are being made to satisfy and utilize the public's wish to have, not only the desired product, but to have the desired product with the desired odor.

The heavy petroleum gas oil which is produced from the Oregon Basin, Wyoming crude is quite a desirable product, but its utilization is limited by the fact that it has an undesirable odor. The work described in this thesis was therefore aimed at eliminating or modifying the malodor and thereby expanding the commercial utilization of the oil.

In attempting to eliminate odors, considerable difficulty is encountered in that the problem cannot be attacked objectively since there is no universal method of evaluating and recognizing an odor other than by the human sense of smell. The lack of a positive understanding of odor can be seen from its definition as "that property of a substance which affects or excites the sense of smell." Where the stimulants of the senses of sight and hearing can be stated as a wavelength and a vibration frequency respectively, there is for smell no accepted, reliable and reproducible terminology.

The classification of odors has been attempted by various workers in the field but with limited success, and in all cases the classification was ultimately dependent on the acuteness of the individual sense of smell. The main methods of classification have been listed and examined by Crocker (12), who considers the first suitable classification to be that of Zwaardenmaker (57). Zwaardenmaker classified odors under nine general headings with certain subsections.

1. Etherial or Fruity
2. Aromatic
   a. Camforaceous
   b. Spicy
   c. Anise-lavender
   d. Lemon-rose
   e. Amygdalin
3. Fragrant or Balsamic
   a. Floral
   b. Lilly
   c. Balsamic
4. Ambrosial
5. Alliaceous or Garlic
   a. Alliaceous
   b. Cacodyl-fish
   c. Bromine
6. Burnt
7. Hircine or Goat
8. Repulsive
9. Nauseating

All odors could then be estimated as being of a certain type or a mixture of types. The method, however, was extremely clumsy and so was further modified by Henning (30) to six distinct classes. Henning imagined a hexagonal figure in which any odor could be given a point position based on its relative amounts of the following classes of odor:

1. Spicy
2. Flowery
3. Fruity
4. Resinous
5. Foul
6. Burnt

The method used by Henning was still very complex and considerable difficulty was encountered in reaching agreement by estimators as to the amounts of each type of odor present.

The final method of classification of odors considered by Crocker was that of Crocker and Henderson (14) which has been used with reasonable

success for over twenty-five years. In this method odors are considered to have four coordinates:

1. Fragrant or sweet
2. Acid or sour
3. Burnt or empyreumatic
4. Caprylic or oenanthic

The intensity of each odor coordinate is arbitrarily listed numerically from zero to eight. Thus the odor of acetic acid is listed as having coordinates 3803 and benzyl acetate as 8445.

This method is still dependent on the perception of the investigator and, to have any meaning, must be backed by considerable experience of varied odors by the investigator. Because of its complexity, and the fact that, in the work of this thesis, quality of odor was not a consideration, no attempt was made to apply any classification to the odors of the oil or the products obtained on treatments designed to modify the odor of the heavy petroleum gas oil.

In estimating the effectiveness of the methods of deodorization attempted on the heavy gas oil, only changes in odor intensity were utilized. The unit of measurement used to determine odor quantitatively is the amount of odorous material that will contaminate one cubic foot of air to the threshold point (25).

The concept of a threshold point is that all normal individuals if subjected to pure odorless air to which is slowly added an odor in increasing amounts, will first perceive the odor at approximately the same concentration of odorous material in the pure air. The threshold point could therefore be defined as that mixture of odorless air and the odor vapor

which can just be detected by the human sense of smell.

Again difficulty is encountered by the fact that the ultimate measurement is by the investigator's sense of smell. In determining threshold values the fact that odor quality may give complications must be ignored. The reliability and reproducibility of threshold odor tests have been investigated by Hulbert and Feben (32), who reported that the results obtained from a series of operators doing odor analyses on water were extremely random. They even found that over a period of time a single operator would obtain results varying ±35 percent from the arithmetic mean of the series of readings. By applying a time limit this variation could be reduced to ±15 percent.

One of the reasons suggested by Hulbert and Feben for the large discrepancies is the existence of a "twilight zone" just before the threshold point is reached. In this "twilight zone" the odor is indistinct and may be classified as present or absent by the operator due to the effect of outside influences on his keeness of odor perception. In a series of panel tests made by the author, with the help of his associates, some of the odors measured were found to have this uncertainty of definition. In subsequent measurements the author, therefore, ignored any reading he felt was doubtful and carried on his measurements until the perception of the odor was distinct and certain.

The series of tests carried out by Hulbert and Feben (33) were made by simply sniffing samples of the malodorous water diluted to different ratios with odorless water. In the estimation of odors there have, however,

been several devices constructed which mix air and odorous vapor in varying ratios to give comparative readings of odor intensity.

The more useful devices used were described by Crocker (13) to be those attributed to (a) Zwaardenmaker (57) - a construction of two concentric tubes with the odorous material smeared on the inside of the outer tube. The inner tube was fitted with a nostril piece and could be slid back and forth inside the larger tube. To measure the threshold value of the odor the operator sniffed through the nostril piece and moved the inner tube up from the bottom of the outer tube until the odor was just perceived. The position of the inner tube gave a measure of the odor intensity.
(b) Elsberg (21) - a wide mouthed bottle was fitted with a rubber stopper through which passed glass inlet and outlet tubes. The outlet tube was connected by a piece of rubber hose to a Y-shaped nosepiece. The nosepiece was made in such a way that the end of the branches of the Y could be inserted into the nostrils. By fitting a calibrated syringe to the inlet tube, measured amounts of air were passed over the odorous material placed in the bottle and injected into the nose with no sniffing by the analyzer. The volume of air required to produce an odor threshold value was the measure of odor intensity.

A new mechanical device for mixing odorous material vapors and air in known proportions to measure the threshold value is described by Gex and Snyder (25). The apparatus used in the work described in this thesis is that of Fair and Wells (22), which is of the air-odor mixture type and is shown in Figure 1.

These instruments are, however, ultimately dependent on the human sense of smell and can, therefore, only be comparative and not objective. An attempt at making an objective device was reported by the Franklin Institute (24) in which they determined the quantity of odor in an odorous air by passing the air through a liquid nitrogen condenser at -300°F and finding the quantity of odorous constituents obtained in the condensate. This, however, would only be applicable if the chemical causing the odor was known and could be recognized in the condensate.

The science of odor is, as yet, not fully understood, and there is still no accepted procedure or nomenclature for qualitative or quantitative odor determinations or for methods of modifying any odors present in a particular substance. The modification of odors is done extensively in industry by many methods, each of which may or may not apply to more than one substance.

In this work the author has, therefore, proceeded on the basis of trying methods of deodorization known to be successful for materials of a similar chemical and physical nature to a heavy gas oil, in the hope that some of these methods would prove satisfactory and economically feasible in the deodorization of the heavy petroleum gas oil obtained from an Oregon Basin, Wyoming crude.

THEORIES OF ODOR PERCEPTION

The human nose is probably the most sensitive of man's senses. It is capable of detecting one millionth of a milligram of an odorous material and can distinguish between and recognize many distinct odors in a fraction of a second. The nose also has a memory, and often if the thoughts are centered on a happening of the past associated with an odor, that odor can be smelled even though there is no possible physical source of the particular odor.

Physiologically the nose is constructed for two purposes, respiration and the perception of odor by the sense of smell. The nose consists of two channels or nostrils separated from each other by a bony-cartilaginous wall, the septum. The lateral walls of each nasal channel consist of practically horizontal folds - the conchae of which there are generally three, but in some humans there may be as many as four, five or six.

Between the septum and the uppermost concha in each nostril is the olfactory cleft, which acts as the receiver for the sense of smell. The olfactory cleft is formed of a yellow colored mucous whereas the normal respiratory mucous is red. Each olfactory cleft has an area of six hundred and twenty-five square centimeters.

In the olfactory cleft there are three types of cells, the epithelium, the basal and the bipolar or olfactory. The epithelium and basal cells act as supports for the olfactory cells, which are the true odor perceptors, although the basal cells also seem to be capable of odor perception when the olfactory cells are damaged. The olfactory cells are long and thin

with one end attached to the nervous system and the other, which is slightly enlarged, exposed to the air. Protruding from this enlarged end are from six to eight olfactory hairs or filaments immersed in an aqueous mucuous. The olfactory endings are lipoid in character, and although lipoid soluble substances produce the strongest odors, it is not known how the olfactory cells are stimulated or how they transmit the sensation of an odor to the olfactory bulb of the brain (5).

In attempts to explain why the olfactory system recognizes an odor, numerous theories have been proposed, of which the most common is the chemical theory. The explanation of an odor in this case was that the odorous material gave off a vapor which was absorbed on the olfactory plate and there reacted with the mucous or lipoid matter to give a chemical reaction. The effect of this chemical reaction was transferred to the nerves and thence to the brain (12).

To identify materials capable of producing odors, various authors have proposed certain physical and chemical properties necessary for odor production. Jones (34) proposed that all odorous material has a density greater than fifteen times that of hydrogen gas, and Dyson (18) stated that an odorous material must have three properties: it must have a perceptible vapor pressure, be soluble in lipoid matter, and exhibit a shift in the Raman Spectra frequencies of 1400 to 3500. Certain chemical groupings such as double and triple bonds, halides, hydroxy groups, and several other groupings, were held by Hornbostel (31) to cause odor. A list of 53 such groupings or osmophores is published by McCord and Witheridge (43).

The chemical theory of odors seems to have become more concentrated now on the shape and electrochemical structure of molecules as the criterion of odor characteristics. The Raman shift frequency relationship of Dyson (18) may be a manifestation of the fact that certain shapes and electron distributions are the causes of odor. If this postulation is correct, it would explain the similarity in odors of different chemicals of similar stereometry found by Haagen-Smit (27) and also Moncrieff's (45) findings of different odors for stereoisomers of the same chemical. In fact, it is now felt by Pauling (47) that the physiological action of chemicals is probably due more to the shapes and sizes of molecules than to their chemical properties.

Another theory reported by Crocker (12) is one in which the olfactory sensory cells were believed to be masses of protoplasm extending into the air space of the nose. Each cell was enclosed by a semipermeable membrane. Sugar and other nutrients were able to permeate the membrane and once inside were oxidized to form acids denoted as H^+A^-. The H^+ ions then diffused out through the membrane at a quicker rate than the A^- ions, and so left a negative charge in the cell. This charge produced an orientation of the membrane's proteins with their positive ends inwards and the negative ends outwards. The odorous material on contacting the cell disturbed the protein orientation and so gave points of leakage in the cell which allowed A^- ions to diffuse and reduce the charge in the cell. This charge in the cell was then transmitted as an "action current" up the nerves to the brain where it stimulated the olfactory lobe of the brain and gave the sensation of smell.

Hainer (28) proposed that the mechanism of odor detection by the sense of smell was similar to the mechanism of an electronic computor. The olfactory cleft was considered to contain 1900 active points or glomeruli which were each capable of sending up to twenty-four impulses to the brain on activation. The numbers of impulses sent to the brain formed a code, which corresponded to the particular odor causing the activation. It was calculated that sixteen million different codes could be produced corresponding to sixteen million distinct odors. The strength of an odor was held to be due to the number of glomeruli activated, and by calculation it was shown that there should be thirty perceivable levels of odor intensity. This is believed to be the number of levels perceivable by experienced odor analyzers.

A theory which has aroused much controversy is that proposed by Beck and Miles (3) based on some experiments carried out on insects (periplaneta americana). These insects have external olfactory receptors and so are very suitable for odor experimentation. In the theory it was proposed that the olfactory cells in the nose gave off a continuous stream of infra-red rays of 7.5 to 14 micron wave lengths. An odorous material absorbed these rays in certain wave lengths, thereby producing a coolness in certain localities of the olfactory cells. This coolness was then transmitted to the brain as a specific odor.

Young, Pletcher and Wright (56), however, formed the deuteroxyl counterpart of n-butyl alcohol and found no difference in odor although there is a difference in infra-red absorption spectra. The theory is also

unable to explain the difference in odor of dextro and levo forms of certain optically active isomers which have the same infra-red absorption spectra.

Kistiakowsky (37), believing that one more theory would cause no harm among so many, gave an hypothesis that smell was due to the inhibition of certain enzymes, an hypothesis for which he had no experimental evidence. He supposed that in the olfactory cells there were certain chemical reactions taking place which he represented by A $\longrightarrow$ A' $\longrightarrow$ A", B $\longrightarrow$ B' $\longrightarrow$ B" etc. Each reaction step was catalyzed by a separate enzyme, and each step casually related to the olfactory nerve signals. The relative amounts of the compounds A, A', A", B, etc. were related to a number of basic odors and any change in concentration of any compound gave a signal to a certain nerve. Thus on the contact of the olfactory cells with an odorous material certain enzymes were inhibited by a definite amount. These inhibitions produced changes in the relative concentrations of A, A", B, etc. causing corresponding nerve signals to be sent to the brain. The sensation of a specific odor was thus produced. On removal of the odorous material the enzymes were no longer inhibited and the concentrations of A, A', A", B, etc. returned to normal. In this way Kistiakowsky felt he accounted for (1) high odor sensitivity due to the minute quantities of enzymes necessary for catalyses, (2) wide range of odorous compounds due to the enzymes being frequently inhibited by a variety of compounds and yet being selective in the amounts of inhibition and the enzymes inhibited, (3) complex odors as being the result of several inhibitions, and (4) reversability of reactions and the non-reversability

due to the persistance of certain odors.

The publication of this hypothesis, however, brought forth a report by El-Baradi and Bourne (20) of some experiments conducted on the taste buds of rabbits. They found that the histiochemical reactions of certain rabbit taste bud enzymes were inhibited by some substances that have a well defined taste and were not inhibited by other substances. They emphasized that they were not ready to state their results as conclusive, but felt that in the light of Kistiakowsky's hypothesis and the similarity and relationships between the senses of taste and smell, that their results may show the feasibility of the enzymatic inhibition mechanism for odor perception.

From the foregoing review of the major theories of odor perception, the author feels it can clearly be seen just how little the very complex and active sense of smell is understood. There are many workers in the field attempting to solve this problem, but until it is solved, and the nature of odor perception's mechanism understood, the problems of deodorization can only be tackled on the basis of past experiences in that field of endeavor.

MATERIALS, EQUIPMENT AND METHODS

Materials

The oil used in this investigation was a straight run malodorous, heavy gas oil obtained as the bottom gas oil cut from the primary fractionator of the Husky Oil Company in Cody, Wyoming. The specific gravity of the oil was about 21° A.P.I. and the sulfur content approximately 3.28% by weight. Further physical data for the oil was obtained by the author from a close fractionation and is presented in Table III and graphically in Figure 4.

The chemicals used in the various deodorization methods were all of commercial grade. The catalysts used in the catalytic methods were cyclocel and cobalt molybdate. The cobalt molybdate was produced by the Harshaw Chemical Company and had the composition

MoO_3	9.5 %
CoO	3.0
SiO_2	5.0
Graphite	2.0
Al_2O_3	Balance

Equipment

Odor Measurement: The apparatus used to detect any change in odor intensity of the heavy gas oil after treatment is shown in Figure 1. It consisted of a Fair-Wells Type B osmoscope and an Anderson-Prichard osmoscope flask.

The osmoscope is an instrument, devised by Fair and Wells (22), to measure the odor intensity of a material on the basis of the threshold value. It is constructed of stainless steel and consists of two concentric

cylinders and two nostril pieces, through which a variable mixture of odorless air and the odorous vapors are sniffed. The outer cylinder is split into two sections. The lower section slides over the inner cylinder to control the amount of odorous vapors drawn through the inner cylinder into the upper section of the outer cylinder, which acts as a mixing chamber and contains the odorless air inlet. The mixture then goes to the nostril pieces and thence to the operator's nose.

The position of the lower section of the outer cylinder is controlled by a series of grooves on the inner cylinder. These grooves are numbered from one to six and are such that each reading numerically above one indicates double the odor intensity for the previous reading. That is, a material with an odor reading of six has thirty-two times the odor intensity of a material giving a reading of one. The apparatus, therefore, gives a method of obtaining comparative values for odor intensity, but does not give any indication of changes in odor quality or type.

The Anderson-Prichard flask is a device, originated by the Anderson-Prichard Oil Company, for odor intensity measurement reproducibility. The pyrex flask is round and shallow and has a large cross sectional area. Two funnel shape openings are constructed at either end, and a thermowell in the middle. The odorous liquid is placed in the flask and the lower end of the osmoscope inserted in the longer of the two funnels. On applying suction to the osmoscope, air is drawn through the smaller funnel, over the liquid and into the osmoscope, thus carrying the odorous vapors towards the mixing chamber from which it passes to the nose for identification.

Rectification: To carry out the rectification of the heavy gas oil a vacuum distillation column was set up. This consisted of a three-liter, round-bottomed flask connected to a three foot, glass helice packed column of about twenty-five theoretical plates. A condenser-reflux system was fitted to the top of the column. The whole apparatus was connected to a vacuum pump fitted with two storage tanks connected by a pressure controlled relay switch so that the vacuum could be controlled to $\pm$ 1 mm of mercury. An insulated heating jacket was put on the flask and a current carrying nichrome wire wrapped around the rectification column to give additional heat to the oil during distillation. Both heaters were controlled by powerstats and were operated on 110 volts, although 220 volts were used on the column during the final stages of the rectification.

Gaseous Treatment: The oil was held in a one-liter Erlenmeyer flask and could be heated to the desired temperature by a powerstat controlled 110 volt electric heater. The flask was fitted with a rubber stopper through which passed two glass tubes, a gas inlet and outlet. The inlet tube was connected to the gas supply at one end and had the other end immersed in the oil so that the gas would bubble through the oil before escaping from the flask by the outlet tube. The gas passed through the outlet tube to a water trap before exhausting to the atmosphere. A calibrated manometer tube was attached to the inlet tube to measure the gas flow rate and a thermometer immersed in the oil to measure the temperature of the oil being treated.

Steam Distillation: A special apparatus shown in Figure 2 was used

in bubbling steam through the oil. The steam from the laboratory steam supply line was first of all passed through a superheater. The superheater consisted of a long steel tube packed with steel balls and heated electrically by three nichrome resistance wires wound around the steel tube. The wires were connected to 110 volt supply and their heating capacity controlled by Powerstats. The superheater was insulated with layers of asbestos tape and magnesia mud.

The steam from the superheater passed through a water trap before being bubbled through the hot oil in the same way as the gases above. Two outlets were fitted to the flask. The first acted as an exhaust line and was fitted with a condenser while the second acted as a sampling tube. This tube had one end immersed in the oil and the other fitted to a small Erlenmeyer flask into which oil samples could be sucked without stopping the steam bubbling.

Catalytic Treatments: The apparatus used is shown in Figure 3. It consisted of an oil reservoir constructed of steel pipe and fitted with an outlet tube through which the oil passed either to a drainage line or to an adjustable bellows pump. The pump forced the oil into the top of the catalyst chamber, which was similar in construction to the steam superheater except for a thermowell inserted down the middle of the reactor. The reactor was filled with alundum balls and 100 mls. of catalyst. From the foot of the reactor the oil passed to a steel condenser, the lower end of which was open to the atmosphere. The oil from the condenser was collected in a receiver.

A compressed air line was attached to the top of the reactor and was used in the regeneration of the catalyst. The air was passed over the catalyst held at a sufficiently high temperature to burn off any carbon or oil deposited in the reaction chamber, and the smoke and gases obtained were exhausted to the atmosphere by a special line fitted to the foot of the reactor.

Methods

Odor Measurement: A sample of the oil of sufficient volume to give a complete coverage of the foot of the Anderson-Prichard flask was put in the flask and the osmoscope fitted through a rubber stopper to the longer outlet funnel of the flask. The osmoscope was first of all set so that no odor was being drawn through the nostril pieces on sniffing. The lower section of the outer cylinder was then slid upwards from one setting to the next with considerable sniffing at each position. This operation was continued until a definite odor was perceived. The operation was then stopped and the cylinder position number noted. The nose was refreshed by a good strong inhalation of fresh air and the complete operation repeated two or more times until two equal readings were obtained. The flask was then emptied, carefully washed, and dried before another sample was analyzed for odor intensity. To ensure that this method was giving reproducible results, occasional samples were analyzed by several persons, and in almost all cases the author's readings were verified.

Rectification: A charge of 2500 ml. of the heavy gas oil was put in the flask, and with an initial automatically controlled pressure of 10 mm.

of mercury, heat was slowly applied to the flask and the column. The column was flooded at total reflux and the heat supply adjusted until steady operating conditions were obtained, with liquid condensation being apparent in the column almost to the top of the glass helice packing. The reflux ratio was then adjusted to approximately 25 to 1 and rectification begun.

Readings of pressure, flask, column and product vapor temperatures were made every 15 minutes and necessary adjustments made to control the variables of flask and column temperatures and pressure. The distillate obtained was collected in 25 ml. fractions, bottled, and retained for analyses. Ninety-three samples and a residue were obtained.

Two shut-downs were experienced during the run, and in both cases the apparatus was restarted as described above for the initial start. In both cases the column reverted to approximately the same conditions which prevailed before the stoppage.

After fifty-two fractions had been obtained, the pressure was reduced to 4 mm. of mercury to reduce the temperature of the rectification. The pressure was further reduced after the sixty-second fraction to 3 mm. of mercury and sampling continued at this pressure until it became too difficult to take samples due to the solidification of wax in the sampling system. The deposition of wax was reduced as much as possible by lagging the sampling system with asbestos tape and by heating the system with an electric heater. After eighty samples had been obtained, the column was operated with no reflux.

The fractions obtained were analyzed for specific gravity by the Westphal balance method and for refractive index by the Abbé Refractometer. Odor analyses were made by the author on the first ten fractions obtained, but since no variation in odor intensity was apparent, only every tenth subsequent fraction and the last fraction were analyzed thereafter. Most of the fractions analyzed for odor intensity were also tested for sulfur content by the Braum-Shell Combustion Sulfur Apparatus at the Husky Oil Company refinery in Cody, Wyoming. The analytical results are shown in Table III and represented graphically in Figure 4.

Gaseous Treatment: A charge of 500 ml. of the heavy gas oil was placed in the Erlenmeyer flask and the heater below the flask adjusted to give desired temperature for the test. The temperatures used were 20°C, 50°C, 100°C and 150°C. Once the oil had attained the desired temperature, the control valve attached to the gas cylinder (or in the case of air - the laboratory compressed air supply tap) was opened and adjusted to give the desired flow rate. The flow rate was measured by a mercury or water manometer which had previously been calibrated with a wet test gas meter, using compressed air as the supply.

The flow rates actually used in the experiments were generally those used by other investigators and reported in the literature. The flow rates were as follows:

TABLE I
GAS FLOW RATES

	Gas	Av. Flow Rate	Source
A	Air	5.0 liters per minute	Carleton (10)
B	Ammonia	0.5 " " "	Graves (26)
C	Sulfur Dioxide	0.25 " " "	Daigle (15)
D	Oxygen	0.25 " " "	Kipper (36)
	Oxygen(10%, 50° BeNaOH added to oil)	0.25 " " "	Browder & Smith (7)

The temperature of the oil and the flow rate of the gas were checked at half-hourly intervals and adjusted to keep conditions as nearly constant as possible. During the treatments samples were taken for odor analyses. For all gases the samples were taken by stopping the gas flow, removing the rubber stopper from the oil flask, and pouring out about 25 ml. of the treated oil. The apparatus was then reassembled and the bubbling continued under the same conditions as before.

Before odor analyses could be carried out on the samples taken from the ammonia and sulfur dioxide treatments, the samples were blown free of ammonia and sulfur dioxide gases respectively, by bubbling compressed air through the sample. This method was recommended by the patentees of those processes and proved satisfactory. The experimental data are listed in Table IV.

Steam Distillation: In the case of steam bubbling, a special technique was necessary since at oil temperatures above 100° C any water condensing in the oil bubbler became superheated and caused violent eruption of the oil. The rate of flow of 5 liters per minute was used as suggested by Phelps (49).

Two tests were carried out. The first, with the oil at 100°C, used the wet supply steam at 98°C and was carried out in the same manner as for the gases above, except that occasionally the water condensate formed in the flask and had to be separated from the oil. All the samples taken were also subjected to separation of oil and water.

The second test was carried out using the apparatus shown in Figure 3. In this case, the supply steam was passed through the superheater and a steam trap before being bubbled into the oil, which was maintained at 150°C. The steam was heated to about 110°C and was passed at the same flow rate as before. The flask in this case was fitted with two outlets, one of which carried the effluent steam to a condenser and receiver and the other used as a sampler and safety valve. The outlet of the sampler came from below the oil level and led out to a 200 ml. Erlenmeyer flask which had a mouthpiece attached, thereby permitting samples to be sucked out of the oil bubbler without stopping the steam flow. This prevented possible settling of any moisture in the oil and so reduced the possibility of oil eruption.

The sampler outlet was left open at all times so that if there should be any eruption of the oil and a corresponding increase in pressure inside the flask, the pressure would dissipate itself by merely blowing oil into the sampling flask. The danger of explosion and possible fire was thus reduced.

Samples were taken periodically as before and the results of analyses are shown in Table V. An attempt was also made to isolate any odorous

material from the distillate by benzene extraction, but the small amount of oil isolated was not malodorous and so was not further investigated.

Liquid Extraction: Fifty ml. of the heavy gas oil were put in a separating funnel and thoroughly shaken with an equal volume of the extraction medium. The resulting mixture was left to settle and the oil layer separated from the solvent layer. The oil was then prepared for odor intensity measurements.

The solvents used in these tests were (a) acetone, (b) a mixture of two parts 40% formaldehyde solution to one part of a solution of 0.5 gm. sodium meta silicate in 100 ml. water giving an alkaline mixture of pH about 10.2 (55), (c) concentrated sulfuric acid at varying strengths of 25%, 50%, 75% and 100% (9).

In (a) and (b), the recovered oil was heated to drive off any residual acetone and formaldehyde, respectively, from the sample before odor intensity measurements were made. The oil separated from the acid in (c) was given a caustic wash followed by a water wash. The oil was then dried over solid anhydrous calcium chloride before the sample was analyzed for odor intensity. The results of the liquid extraction tests are shown in Table VI.

Liquid Addition: A 50 ml. sample of the heavy oil was treated by adding measured quantities of certain recommended deodorizers, and after sufficient time for any reaction to have taken place, odor intensity measurements made. The reactants used were (1) Benzaldehyde in quantities of 0.01%, 0.05%, 0.1%, 0.5% and 1.0% by volume of the heavy gas oil (50),

(2) a solution of one part of an aqueous solution of 14% potassium mercuric iodide and 18% sodium hydroxide to seven parts of water added in quantities of 2.5 and 5.0 ml. to 50 ml. of heavy gas oil as recommended for a sour gas oil (38).

The results of these tests are shown in Table VII.

Adsorption: Fifty mls. of the gas oil were treated with varying weights of activated charcoal and silica gel under varying conditions of temperature. Two methods of treatment were used: (1) the oil was heated to the desired temperature and passed through the adsorbent held on a filter paper, (2) the oil was heated to the desired temperature in contact with the adsorbent and the oil then decanted from the solid. The conditions used were as follows with tests in each case made by both methods (1) and (2): Activated Charcoal: (a) 5 gm. charcoal with 50 ml. oil at 85°C as recommended for petroleum wax by Maier and Green (39), (b) 10 gm charcoal with 50 ml. oil at 100°C, 150°C and 200°C. Silica Gel: (a) 5 gm silica gel with 50 ml. oil at 130°C as suggested by Ostenberg (46), (b) 10 gm silica gel with 50 ml. oil at 100°C, 150°C and 200°C. The results of these treatments are shown in Table VIII.

Catalytic Treatment: One hundred ml. of the catalyst, cyclocel or cobalt molybdate, were put in the reactor along with alundum balls as shown in Figure 3. The reactor was then slowly heated to the temperature of the treatment which in this series was 250°C, 300°C, 350°C or 400°C. When the temperature registered by thermocouples inserted in the thermowell was constant at the desired value, the bellows pump was started and adjusted

to give a flow rate of approximately 50 ml/hr as suggested by Rooch (51) for alumina treatment at the above temperatures and atmospheric pressure. The conditions of the experiment were kept as nearly constant as possible by taking temperature and sample volume readings every 30 minutes and at the same time making any necessary adjustment in the heating or pumping controls.

After passing down through the catalyst chamber, the products were cooled in a steel condenser and the resulting oil collected in 60 ml. samples. These samples were collected throughout the tests and analyzed for odor intensity.

Some of the tests were made using catalyst regenerated from a previous test by passing air through the reactor at a temperature above 300°C. This treatment removed the carbon and oil deposited in the catalyst chamber, thus returning the catalyst to virtually its original condition. The weights of the oil passed through the reactor and the oil collected from the reactor were found and noted. The catalyst was also weighed before treatment, after treatment, and after regeneration. All results are shown in Table IX.

RESULTS

As previously stated, the purpose of this investigation was to find a commercially feasible method of deodorizing a heavy petroleum gas oil. Because odor strength is purely relative, an odor intensity value had to be decided upon which would designate a satisfactorily deodorized oil. Anderson-Prichard Corporation markets a deodorized oil (Deodorized Apco 125) which on the Fair-Wells osmoscope has a reading of two. An odor intensity reading of two was therfore considered to show a deodorized gas oil.

Reliability of Results: In the measurement of odor intensity by the Fair-Wells osmoscope, the ultimate measurement depends on the perception of the nose. As the author has pointed out, however, the human nose is not reliable and can be affected physiologically and psychologically by influences outside of the odor being measured. The results could therefore vary slightly due to many outside influences.

In attempting to produce reliable and reproducible results, the author occasionally had his measurements repeated and verified either by his associates or by himself. In most cases the author's original readings of odor intensity were verified, but in some cases they were found to vary from further measurements. The results of such an analysis are shown in Table II and quite a wide range of odor intensity values are given by different investigators.

This variance in some instances may be due to the "twilight zone" discussed previously, but in other cases, such as in sample (2) in Table II, a four-fold difference in odor concentration is indicated between the

readings of testers A and C, which could be due only to personal differences or the confusion due to the burning sensation. Both of these reasons are outside influences and, therefore, give considerable doubt as to the reproducibility of the results. A solution of this problem, suggested by Anderson-Prichard, is the use of three experienced odor analyzers for each analysis. This method, however, could not be applied in this investigation.

Rectification: The close rectification, of which the results are tabulated in Table III and shown graphically in Figure 4, was carried out in an attempt to isolate the odorous constituent. The attempt, however, was unsuccessful and the odor found to be fairly evenly distributed over the whole boiling range. The possibility of a correlation between the percentage of sulfur and odor was also considered since many sulfur compounds are known to be malodorous. There was, however, no apparent correlation. The rectification was therefore of no avail in aiding the deodorization, but it is hoped that the physical data obtained in the analysis will prove useful in any future alteration in the cuts to be taken from the primary fractionator at Cody, Wyoming.

Gaseous Treatments: Of the treatments attempted as shown in Table IV, only two gases seem to be satisfactory in reducing the odor to an osmoscope reading of two - air and sulfur dioxide. Deodorization of the heavy gas oil by air bubbling proves to be satisfactory at 100°C and 150°C taking a treating time of 48 hours and 24 hours respectively. Treating the oil at 150°C, however, leads to some asphalt formation, which may account for the rise in odor intensity after 24 hours.

Sulfur dioxide at 0.25 liters per minute with the oil at 150°C and a 24 hour treatment seems satisfactory in reducing the odor to an odor intensity of two.

Steam Distillation: The two experiments carried out are shown in Table V. The treatment of the oil at 100°C proved to be unsatisfactory over the period tested, whereas the results of treatment of the oil at 150°C shows very favorable results with a satisfactory product being obtained after four hours of treatment at 5 liters per minute flow rate.

Liquid Extraction: None of the methods attempted gave any decrease in odor intensity as shown in Table VI. The increase in odor intensity to a reading of six shown by the treatment of the oil with 75% and 100% sulfuric acid seems to have been caused by a chemical reaction taking place to produce an acid sludge.

Liquid Addition: The methods attempted are shown in Table VII and all proved unsatisfactory as methods of deodorization.

Adsorption Treatments: The results of the experiments on the use of activated charcoal and silica gel are shown in Table VIII. Although none of the tests carried out show a sufficient decrease in odor intensity, the heating of 50 ml. of the oil to 200°C in the presence of 10 gm. silica gel gave a product with an odor reading of three. It may, therefore, be possible to obtain the desired deodorization by increasing the temperature of the oil during treatment or the contact time of the oil with the adsorption agents. Silica gel seems more promising than activated charcoal as a deodorant.

Catalytic Treatments: The results of runs using cyclocel and cobalt molybdate are shown in Table IX. None of the runs attempted showed satisfactory results. The increase in odor intensity (reading from five to six) shown in Experiment 20, was probably due to a certain amount of cracking of the oil which took place in the reactor.

Of the two catalysts used, cobalt molybdate seems to be more effective. Low temperature treatment with cobalt molybdate gave better results than high temperatures. It was thought that the action of the catalyst in deodorization might be a slight desulfurization. The samples from Experiment 33 were therefore analyzed for sulfur, but the results did not show any correltation between sulfur and odor intensity.

SUMMARY

1. The measurement of odor intensity is subject to many outside influences and measurements made are not 100% reproducible.

2. The odor prevails throughout the boiling range of the heavy gas oil.

3. The methods attempted in this investigation were only some of the successful deodorization treatments reported in the literature, and are by no means a complete survey.

4. Treatments proving to be successful were:

   (a) Five liters per minute of air passed through oil at 100°C and 150°C for 48 and 24 hours respectively.

   (b) 0.25 liters per minute of sulfur dioxide passed through oil at 150°C for 24 hours.

   (c) Five liters per minute of superheated steam passed through oil at 150°C. for four hours.

   The economics of these methods was not studied since only the variable of oil temperature was tested and the results do not necessarily show the best conditions of the treatment.

5. Treatment of the oil with silica gel or cobalt molybdate appeared promising, but further investigation would be necessary before any conclusion could be drawn.

POSSIBLE COMMERCIAL USES FOR A HEAVY GAS OIL

To obtain a better understanding of the possibility of expanding the commercial utilization of the heavy gas oil, the author made a literature research into some of the possible outlets for an oil such as the one used in this investigation.

Coal Spray Oils

Coal spray oils are those oils used for reducing dust formation in handling coal. Waters (53) made a list of desirable properties for a good coal spray oil which are as follows:

1. Low evaporation rate
2. Tacky to give good adhesion
3. Able to penetrate the water film on the coal surface and preferentially wet the coal surface
4. Have proper viscosity for handling and application - about 200 s.s.u. at 100°F
5. High and low viscosity oils equally effective with bituminous or low or medium volatile coals
6. Flash point high enough to prevent pre-combustion
7. Have a pour point for viscous oils which facilitates handling
8. Oil should be free of odor

The property which seems to be the most critical in dust suppression is that of viscosity, and oils have been recommended as follows: Martin and Cloyd (41) were of the belief that the most viscous oil that could be handled was the most effective dedusting agent. The effect of oil viscosity on dedusting was examined by experimenters at the Battelle Memorial Institute (2) who found that the initial superiority of a 200 s.s.u. viscosity oil at 100°F over a 100 s.s.u. oil at 100°F in reducing dustiness decreased if the sprayed coal was stored outside for a period of time greater than three months.

Ambrose and Gaspari (1) felt that the ability of the oil to penetrate the pores on the coal surface was also a criterion of dedusting ability. They reported oils of 100-200 s.u.v. at 100°F to be satisfactory. The viscosity of a suitable dedusting oil was reported from the Viking Manufacturing Company (52) to depend on the quality of the coal to be sprayed. Their results were: (a) low inherent moisture, low volatile matter coals required oils of viscosity 300 s.s.u. at 100°F, a low cold test, and flash point below 300°F, (b) high inherent moisture, high volatile matter coals required oils of viscosity 600-2,500 s.s.u. at 100°F, and flash point below 300°F.

The physical properties of some oils in use are:

Sample	1	2	3	4	5	6	7
Flash Point °F	350	340	350	380	390	400	275
Pour Point °F	-15	0	0	0	0	0	0
s.s.u. viscosity at 100°F	145-155	490-510	-	-	-	-	100
s.s.u. viscosity at 212°F	-	-	80-85	52-58	57-63	62-68	-
Color	Black						
Odor Intensity	5	5	4	4	4	4	odorless

Data of samples 1 to 6 were reported by Brown (8) and that of 7 by West (54).

The odor intensity measurements on 1 to 6 were made by the author as was also done on three other commercial coal spray oils. In all cases the odor intensity was four or five which compares favorably with the reading of five for the untreated heavy gas oil being investigated.

The advantages of spraying coal with oil are:

1. Better ignition and burning characteristics
2. Decreased freezing
3. Water shedding ability improved
4. Reduced loss in transit and storage

5. Decreased segregation and arching
6. Less corrosion of metal parts contacting coal
7. Reduced tendency for spontaneous heating and combustion
8. Less disintegration by air
9. Better carbonization properties

Coal spraying can, however, be dangerous and certain safety precautions should be taken during spraying. These precautions are listed by the Kentucky Actuarial Bureau (35).

Oil-Coal Mixtures as Fuel

Oils of A.P.I. gravity 9-10° and viscosity 165 s.s.u. at 122°F to specific gravity 1.10 at 60°F and viscosity 1350 s.s.u. at 122°F, were suggested by Hendrick (29) for use with powdered coal as a locomotive fuel. Difficulties were experienced in grinding the coal and mixing the coal and oil to give a stable mixture which could be easily atomized and burned. The utilization of this mixture as a commercial fuel was economically uncertain.

Cutting Oils

The oils suitable for use as lubricants in the cutting of metals are listed by Forbes (23) to be of five types:

1. Alkaline soap solutions - for cooling, rust prevention and laying down dust in grinding
2. Water soluble oils - for cooling
3. Straight mineral oils - for lubrication and cooling of non ferrous metals
4. Fatty oils blended with mineral oil
5. Oils containing sulfur or chlorine - the sulfur and chlorine atoms react with the metallic surface to give metallic salt films which act as a lubricant during machining

The oils recommended by Forbes (23) for various metals were:

(a) for steel - viscosity 100-500 s.s.u. at 100°F and 0.5-5% Sulfur
(b) for copper - " 75-150 " " " " 0.5-1% "
(c) for magnesium & aluminum 40-60 " " " " 0.5-1% "

Oils in Printing Inks

The oils used for this purpose, according to Mattiello (42), should be clear and contain a minimum of colored bodies which have a tendency to stain and give a gray-yellowish cast to the paper. Naphthenic oils are suitable for ink vehicles but highly paraffinic oils are not so good. A good oil for printing inks is indicated by a high viscosity-gravity constant (V.G.C.) value. Paraffins have a V.G.C. of 0.8 while naphthenes approximate to 0.90.

$$V.G.C. = \frac{10\,G - 1.0752\,(\log V - 38)}{10 - \log (V - 38)}$$

where G = specific gravity at 60°F

V = viscosity in s.s.u. at 100°F

Naphthenates or linoleates of cadmium, lead, and manganese are sometimes added to the oil to increase the drying rate for newspaper inks (44).

Use of Oils for Extraction of Sulfur From Low Sulfur Ores

The use of an oil at a temperature below 140°C to extract sulfur from crushed ores containing elemental sulfur is described by Economopolous (19). The sulfur crystallized out of the oil on cooling to give 100% pure sulfur with complete removal of sulfur from a 20% sulfur ore and only a 1.3% gas oil loss. The oil used was a Romanian gas oil with the following properties:

Specific Gravity	0.865
Flash Point	100°C
Viscosity (Engler at 20°C)	1.55
A.S.T.M. Distillation	
Initial Boiling Point	215°C
35% Distillation	270°C
65% "	300°C
Color (Union Calorimeter)	2

Use of Oils in Herbicides and Insecticides

Petroleum oils have been used fairly extensively as contact herbicides. Their toxic effects were held by Crafts and Harvey (11) to be due mainly to unsaturates and aromatics. Petroleum oils have desirable properties as herbicides since they are compatible with plant cuticle, wet and spread easily, and persist without evaporation. The nature of oil films on plants has led to the belief that the plants are killed by smothering, but as plant cells have been known to stay alive in paraffin oil with the protoplasm actively streaming, Crafts and Harvey feel that mechanism is not wholly correct.

Hough and Mason (32) describe the use of diesel oil, stove oil, and fortified oil as weed killers among crops of carrots, parsley, parsnips, and other related crops. The average specifications were:

	Stove Oil	Shell Weed Killer # 10	Standard Weed Killer # 1
A.P.I. Gravity	37.2	43.3	43
s.s.u. Viscosity at 100°F	32.2	Less than 30	Less than 30
Flash Point °F	146	106	107
A.S.T.M. Distillation			
Initial Boiling Point °F	-	316	314
50% Distilled °F	443	-	342
Final Boiling Point °F	573	395	400
Unsulfonated Residue	86.6	-	-
% Aromatics	-	22	17
% Sulfur	0.29	-	-

The effect of the aromatic ring as a herbicide, according to Bell and Norem (40), is enhanced by one or more paraffinic side chains and reaches a maximum toxicity when the molecular weight of the paraffinic groups is almost equal to the molecular weight of the aromatic nucleus. They

recommend that for umbelliferous crops the oil should have 10-20% aromatics and boiling range of 300-400°F; for general contact weed killers, an oil of more than 40% aromatics and boiling range of 300-700°F; and for water submerged weeds, an oil of more than 70% aromatics.

The use of petroleum oils as carriers for insecticides was felt by de Ong (16) to be advantageous since many insects have a waxy coating and are therefore not affected by an aqueous solution of insecticides. Oil-water emulsions were found to be the most effective carriers, and oils of 50 to 345 s.s.u. viscosity were used successfully as carriers for nicotine. de Ong (17) listed the important factors in choosing a spraying oil as

(a) Color - for identification
(b) Sulfur - elemental sulfur ineffective but combined sulfur effective as insecticides and fungicides
(c) Acidity - must be neutral and resist oxidation to acid by air. Less than 1% acid
(d) Volatility - highly volatile for insects, low volatility for plants
(e) Viscosity - 50-75 s.s.u. at 100°F for most insects with 95-100 s.s.u. at 100°F for resistant insects
(f) Oxidation - oil saturated to resist acidification

Pearce, Chapman and Frear (48) stated that the two basic factors in insecticidal properties were molecular weight and chemical structure. Their ideal spray oil had the following properties:

Viscosity at 100°F	70-80 s.s.u.
Unsulfonated Residue	greater than 92%
Density at 20°C	0.840 (max.)
Refractive Index	1.464 (min.)
50% Boiling point at 1 mm. Hg	370± 5°F
Pour Point	below 30°F

Martin (41) gave a list of some petroleum products which can be used as spreaders. Spreaders are capillary active ingredients used to give

better spreading and wetting properties to the oil. The compounds suggested were: calcium gamma sulfonates, sodium beta sulfonates, alkaline naphthenates, sulfonated products of oxidized petroleum oils or shale oils, and ammonium salts of sulfonic acids prepared from the oils.

ACKNOWLEDGEMENT

The author wishes to acknowledge the courtesy of the Husky Oil Company who supplied the heavy gas oil and carried out some of the chemical analyses done on the heavy gas oil fractions. Acknowledgement is also made to the Husky Oil Company and the Montana State College Experiment Station for sponsoring this investigation.

LITERATURE CITED

(1) Ambrose, H. A. and Gasperi, H. J. R., "Oil Treatment", Coal Age, 42, 2, p. 252, (1937).

(2) Battelle Memorial Institute, "Higher Viscosity Oils More Effective in Dust Control", Coal Age, 42, 11, p. 90, (1937).

(3) Beck, L. H. and Miles, W. R., Science, 106, p. 511, (1947).

(4) Bell, J. H. and Norem, W. L., "Petroleum Weedkillers", Agricultural Chemicals, 5, 4, p. 31, (1950).

(5) Bienfang, R., "The Subtle Sense", University of Oklahoma Press, (1946).

(6) Bogert, M. T., "Perfumes - Natural and Synthetic", Ind. Eng. Chem., 14, 4, p. 359, (1922).

(7) Browder, J. C., and Smith, A. R., U. S. Patent No. 2,569,370, (1951).

(8) Brown, E. K., "Coal Spray Oil Specifications," Private Communication, (1953).

(9) Brown, R. H. and Meyerson, S., "Cyclic Sulfides in a Petroleum Distillate", Ind. Eng. Chem., 44, 11, p. 2620, (1952).

(10) Carleton, R. A., U. S. Patent No. 2,578,670, (1951).

(11) Crafts, A. S. and Harvey, W. A., "Herbicides", Agricultural Chemicals, 5, 3, p. 38, (1950).

(12) Crocker, E. C., "Seeking a Working Language for Odors and Flavors", Ind. Eng. Chem., 27, 10, p. 1225, (1935).

(13) Crocker, E. C. et al., "Odor Detection and Thresholds", Chem. Eng. News, 27, 27, p. 1922, (1949).

(14) Crocker, E. C. and Henderson, L. F., Am. Perfumer, 22, 359, (1927).

(15) Daigle, E. C., U. S. Patent No. 2,498,201, (1950).

(16) de Ong, E. R., "Petroleum Oil as a Carrier for Insecticides and as a Plant Stimulant", Ind. Eng. Chem., 20, 8, p. 826, (1928).

(17) de Ong, E. R., "Selection of a Petroleum Oil for Spraying Purposes", Ind. Eng. Chem, 22, 8, p. 836, (1930).

(18) Dyson, G. M., "The Scientific Basis of Odor", Chem and Ind., 57, 28, p. 647, (1938).

(19) Economopolous, N. P., "Use of a Gas Oil to Extract Low Sulfur Ores", Ind. Eng. Chem., 44, 1, p. 106, (1952).

(20) El-Baradi, A. F. and Bourne, G. H., "Theory of Tastes and Odors," Science, 113, 2945, p. 660, (1951).

(21) Elsberg, C. A. et al, Science 83, 2148, p. 211, (1936).

(22) Fairs, G. M. and Wells, W. F., U. S. Patent No. 2,136,844 (1935).

(23) Forbes, W. G., "Lubricants and Cutting Oils for Machine Tools," New York, John Wiley and Sons, Inc. (1943).

(24) Franklin Institute of Philadelphia, "Odors in Air Now Measured," Science N. L., 61, 5, p. 76, (1952).

(25) Gex, V. E. and Snyder, J. P., "New Device, Wider Concept, Helps to Measure Odor Quantitatively," Chem. Eng., 59, 12, p. 200, (1952).

(26) Graves, F. M., U. S. Patent No. 2,455,670, (1948).

(27) Haagen-Smit, A. J., "Smell and Taste", Sci. Am., 186, 3, p. 28, (1953).

(28) Hainer, R. H. et al., Science N. L., 63, 18, p. 276, (1953).

(29) Hendrich, J. E., "Oil-Coal Mixture," Coal Age, 45, 12, p. 65, (1940).

(30) Henning, "Der Geruch," Leipzig, 1924.

(31) Hornbostel, "Odor Theory," Chem. Zentr., II, 3014, (1931).

(32) Hough, W. S. and Mason, A. F., "Spraying, Dusting and Fumigating of Plants," New York MacMillan and Sons, (1951).

(33) Hulbert, R., and Feben, D., "Studies on the Accuracy of Threshold Odor Values," J. A. W. W. A., 33, 11, p. 1945, (1941).

(34) Jones, M. E., "Taste and Smell," Chem. and Ind., 60, 15, p. 248, (1941).

(35) Kentucky Actuarial Bureau, "Coal Sprays are Hazardous," Coal Age, 42, 8, p. 387, (1937).

(36) Kipper, H. C., U. S. Patent No. 2,221,301, (1940).

(37) Kistiakowsky, K. B., "Theory of Odors," Science, 112, 2901, p. 154 (1950).

(38) Loetel, C. E., U. S. Patent No. 2,310,099, (1943).

(39) Maier, C. E. and Green, J. D., U. S. Patent No. 2,441,202, (1948).

(40) Martin, G. A. and Cloyd, R. W., "Dustproofing with Coal," Coal Age, 56, 7, p. 87, (1951).

(41) Martin, H., "Petroleum Products as Spray Spreaders," J. Soc. Chem. Ind. T., 52, p. 429, (1933).

(42) Mattiello, J. J., "Protective and Decorative Coatings," New York, John Wiley and Sons, Inc., (1943).

(43) McCord, C. P., and Witheridge, W. N., "Odor, Physiology and Control," New York, McGraw-Hill Book Co., Inc., (1949).

(44) Mill, C. C., "Printing Inks," Chem. and Ind., 71, 8, p. 156, (1952).

(45) Moncrieff, R. W., "Olfaction and Odor," Chem. and Ind., 69, 13, p. 255, (1950).

(46) Ostenberg, Z., U. S. Patent No. 2,230,903, (1941).

(47) Pauling, L. "Analogies Between Antibodies and Simpler Chemical Substances," Chem. Eng. News, 24, 8, p. 1064, (1946).

(48) Pearce, G. W. et al., "Insecticidal Efficiency of Saturated Petroleum Fractions," Ind. Eng. Chem, 40, 2, p. 284, (1948).

(49) Phelps, G. W., U. S. Patent No. 2,407,616, (1946).

(50) Prutton, C. F., and Johnson, H. E., U. S. Patent No. 2,319,630, (1943).

(51) Rooch, A. T., U. S. Patent No. 2,574,498, (1951).

(52) Viking Manufacturing Company, "Fundamentals of Controlling Dust on Coal," Coal Age, 46, 8, p. 62, (1941).

(53) Waters, G. W., "Oil Treatment of Coal," Coal Age, 53, 11, p. 97, (1948).

(54) West, C. E., "Dustproofing Coal," Coal Age, 41, 6, p. 229, (1936).

(55) White, A. R., U. S. Patent No. 2,077,060, (1937)

(56) Young, C. W. et al., "Olfaction and Infra Red Theories," Science, 108, 2806, p. 411, (1948).

(57) Zwaardenmaker, "Die Physiologie des Geruchs," Leipzig, 1935.

APPENDIX

		page
Table II	Panel Test on Osmoscope Reproducibility.	46
Table III	Physical Data on Heavy Gas Oil Fractions	47
Table IV	Gaseous Treatments	51
Table V	Steam Distillation	52
Table VI	Liquid Extraction	53
Table VII	Liquid Addition Treatments	54
Table VIII	Adsorption Treatments.	54
Table IX	Catalytic Treatments	55
Figure 1	Odor Intensity Measurement Apparatus	59
Figure 2	Steam Distillation Unit.	60
Figure 3	Catalytic Treatment Unit	61
Figure 4	Fractional Distillation Curves	62

TABLE II
PANEL TEST ON OSMOSCOPE REPRODUCIBILITY

	Osmoscope Readings			
Tester	A	B	C	D
Sample No. (1)	4	5	5	5
Sample No. (2)*	3	4	5	-
Sample No. (3)*	5	5	5	5
Sample No. (4)	4	4	5	5
Sample No. (5)	5	5	5	5

*These readings were confused due to a strong acidity, which gave a burning sensation rather than an odor. Burning was detected as follows:

	Osmoscope Readings			
	A	B	C	D
Sample No.(2)	4	4	4	-
Sample No.(3)	6	6	6	6

TABLE III

PHYSICAL DATA ON HEAVY GAS OIL FRACTIONS

Fraction No.	Boiling Range * °C	Weight of Samp. gm	Total Wt Distilled gm	Specific Gravity $\frac{20°C}{4°C}$	Refractive Index 20°C	% Sulfur	Osmoscope Reading	Remarks
1	214-			0.922	1.5133	3.28	5	Undistilled Oil
2	214-255	20.46	20.46	0.843	1.4656		5	10 mm Hg. Press.
3	255-273	20.95	41.41	0.865	1.4781		6	
4	273-285	19.69	61.10	0.872	1.4829		5	
5	285-296	21.10	82.20	0.879	1.4865	2.36	4	
6	296-309	21.59	103.79	0.884	1.4894		5	
7	309-310	15.22	119.01	0.887	1.4918		6	
8	309-310	22.56	141.57	0.887	1.4915		5	
9	310-316	20.89	162.46	0.890	1.4926		5	
10	316-320	23.08	185.54	0.892	1.4934	2.58	5	
11	320-328	19.72	205.26	0.894	1.4948			
12	328-331	20.66	225.92	0.896	1.4966			
13	331-332	20.20	246.12	0.901	1.4989			
14	332-338	20.07	266.19	0.903	1.5004			
15	338-339	23.14	289.33	0.903	1.5007			
16	339-340	20.20	309.53	0.905	1.5018			
17	340-343	20.02	329.55	0.906	1.5029			
18	343-344	19.72	349.27	0.909	1.5044			
19	344-348	20.04	369.31	0.910	1.5055			
20	348	20.42	389.73	0.911	1.5059	3.20	4	
21	348-357	23.30	413.03	0.913	1.5064			
22	348-357	18.09	431.12	0.913	1.5064			
23	357-360	26.38	457.50	0.914	1.5071			
24	360	19.72	477.22	0.915	1.5079			
25	360-362	19.84	497.06	0.915	1.5083			
26	362-363	18.72	515.78	0.915	1.5085			
27	363-365	19.57	535.35	0.914	1.5084			
28	365-367	25.14	560.49	0.915	1.5085			
29	367-368	20.28	580.77	0.916	1.5091			

TABLE III (cont'd)
PHYSICAL DATA ON HEAVY GAS OIL FRACTIONS

Fraction No.	Boiling Range* °C	Weight of Samp. gm	Total Wt. Distilled gm	Specific Gravity 20°C/4°C	Refractive Index 20°C	% Sulfur	Osmoscope Reading	Remarks
30	368-369	21.46	602.23	0.917	1.5100	3.35	5	
31	369	20.48	622.71	0.918	1.5110			
32	369-370	19.84	642.55	0.917	1.5107			
33	370-373	24.95	667.50	0.918	1.5106			
34	373-379	26.93	694.43	0.919	1.5106			
35	379-383	35.31	729.74	0.918	1.5107			Shut Down
36	383-388	19.31	749.05	0.916	1.5096			Restart
37	388-390	24.48	773.53	0.916	1.5100			
38	390-392	20.72	794.25	0.917	1.5096			
39	392-396	23.15	817.40	0.916	1.5095			
40	396-402	31.05	848.45	0.916	1.5096	3.14	5	
41	402	23.27	871.72	0.917	1.5102			
42	402	23.50	895.22	0.918	1.5107			
43	402-403	22.54	917.76	0.919	1.5107			
44	403	23.87	941.63	0.919	1.5110			
45	403	21.90	963.53	0.920	1.5117			
46	403	22.58	986.11	0.921	1.5120			
47	403	22.51	1008.62	0.921	1.5119			
48	403	23.20	1031.82	0.921	1.5121			
49	403-407	21.50	1053.32	0.921	1.5120			
50	407	23.99	1077.31	0.921	1.5118	3.16	5	
51	407-412	22.01	1099.32	0.923	1.5123			
52	412-414	19.58	1118.90	0.922	1.5133			
53	414-416	20.66	1139.56	0.923	1.5136			10 mm Hg Press
54	416-418	27.48	1167.04	0.924	1.5151			5 mm Hg Press
55	418-423	21.76	1188.80	0.925	1.5156			4 mm Hg Press
56	423-424	21.88	1210.68	0.926	1.5158			
57	424	23.74	1234.42	0.927	1.5154			
58	424-426	23.92	1258.34	0.927	1.5160			

TABLE III (cont'd)
PHYSICAL DATA ON HEAVY GAS OIL FRACTIONS

Fraction No.	Boiling Range* °C	Weight of Samp. gm	Total Wt. Distilled gm	Specific Gravity 20°C/4°C	Refractive Index 20°C	% Sulfur	Osmoscope Reading	Remarks
59	426-427	42.90	1301.24	0.927	1.5166			
60	427	22.26	1323.50	0.928	1.5165	3.36	5	
61	427-428	22.64	1346.14	0.928	1.5171			
62	428	20.22	1366.36	0.929	1.5165			
63	428	23.06	1389.42	0.930	1.5184			4 mm Hg Press
64	428	21.68	1411.10	0.930	1.5186			3 mm Hg Press
65	428	35.99	1447.09	0.930	1.5186			
66	428-440	18.89	1465.98	0.930	1.5193			
67	440-447	19.08	1485.06	0.931	1.5189			Some Waxiness Apparent at 20°C
68	447-448	37.32	1522.38	0.931	1.5192			
69	448	23.08	1545.46	0.930	1.5200			Corrected S. G.**
70	448-450	29.29	1574.75	0.937	1.5200	3.24	5	
71	450-455	25.07	1599.82	0.937	1.5215			
72	455	21.30	1621.12	0.936	1.5215			
73	455-461	54.20	1675.32	0.934	1.5196			Corrected R.I.***
74	455-461	37.33	1712.65	0.937	1.5202			
75	461	27.95	1740.60	0.938	1.5221			
76	461-462	29.54	1770.14	0.939	1.5223			
77	462-463	22.33	1792.47	0.942	1.5223			
78	463-474	46.42	1838.89	0.941	1.5231			
79	474-479	21.17	1860.06	0.942	1.5221			
80	479	23.43	1883.49	0.942	1.5229	3.22	5	Solid at 20°C
81	479-482	20.65	1904.14	0.942	1.5242			
82	482	22.34	1926.48	0.942	1.5243			Zero Reflux
83	482-486	20.79	1947.27	0.942	1.5241			
84	486-489	22.13	1969.40	0.942	1.5227			
85	489-493	28.64	1998.04	0.942	1.5231			
86	493-494	19.04	2017.08	0.941	1.5229			
87	494	22.02	2039.10	0.941	1.5232			

TABLE III (cont'd)
PHYSICAL DATA ON HEAVY GAS OIL FRACTIONS

Fraction No.	Boiling Range* °C	Weight of Samp. gm	Total Wt. Distilled gm	Specific Gravity $\frac{20^\circ C}{4^\circ C}$	Refractive Index 20°C	% Sulfur	Osmoscope Reading	Remarks
88	494-501	21.74	2060.84	0.940	1.5239			
89	501-504	20.58	2081.42	0.942	1.5251			
90	504-508	28.18	2109.60	0.943	1.5244	3.32	5	
91	508-512	23.74	2133.34	0.945	1.5271			
92	512-514	24.75	2158.09	0.945	1.5277			
93	514-515	24.50	2182.59	0.945	1.5284			
94	515-519	23.20	2205.79	0.943	1.5260	3.32	5	
95	519-	114.40	2320.19	0.990				Bottoms

*Boiling points corrected to atmospheric pressure (760 mm) by Haas-Newton Equation p 1701, Handbook of Chemistry and Physics (25th Edn.) - C. D. Hodgman and H. N. Holmes - Chemical Rubber Publishing Co., Cleveland Ohio, (1941).

**Specific gravity measurement made at 100°C and corrected to 20°C - p. 481 Standard Methods for Testing Petroleum and its Products - The Institute of Petroleum, London, 1951.

***Refractive index measurement made at 40°C and corrected to 20°C by $\Delta n = 0.6 \Delta d$ with Δd from graph by Ward, A. L. and Kurtz, S. S., Ind. Eng. Chem. (Anal. Ed.) 10, 10, 574 (1938).

TABLE IV
GASEOUS TREATMENTS

Gas	Flow Rate Liters/min	Oil Temp. °C												
Air	5.0	20	Hrs. Treatment	0	2	4	8	16	32	67	96	120	144	
			Osmoscope Reading	5	4	4	4	3	3	3	3	3	3	
Air	5.0		Hrs. Treatment	0	2	4	8	16	24	48	72	96	120	144
		50	Osmoscope Reading	5	4	4	4	4	4	4	4	4	4	3
		100	Osmoscope Reading	5	4	4	3	3	3	2	2	1	-	-
		150	Osmoscope Reading	5	4	4	-	3	2	4	3	4	3	-
Ammonia	0.5		Hrs. Treatment	0	0.25	0.5	0.75	1	2	4	8	12	16	20	24
		50	Osmoscope Reading	5	4	4	4	4	4	4	4	-	4	-	3
		100	Osmoscope Reading	5	-	4	-	4	4	3	3	3	3	-	2
		150	Osmoscope Reading	5	-	3	-	4	4	4	3	3	3	3	-
Sulfur Dioxide	0.25		Hrs. Treatment	0	0.5	1	2	4	8	12	16	24			
		50	Osmoscope Reading	5	4	4	4	3	3	3	4	2			
		100	Osmoscope Reading	5	4	4	4	4	4	4	4	4			
		150	Osmoscope Reading	5	4	3	3	3	3	3	3	2			
Oxygen	0.25		Hrs. Treatment	0	0.5	1	2	4	8	16	20	24			
		50	Osmoscope Reading	5	4	4	4	5	4	-	4	4			
		100	Osmoscope Reading	5	4	4	4	4	4	4	-	4			
		150	Osmoscope Reading	5	4	4	5	5	5	5	-	5			
		*50	Osmoscope Reading	5	5	5	5	5	5	5	-	4			
		*100	Osmoscope Reading	5	5	5	5	5	5	5	-	5			
		*150	Osmoscope Reading	5	5	5	5	5	5	5	-	-			

*500 ml. oil has 50 ml. 50° Bé NaOH added.

TABLE V
STEAM DISTILLATION

Flow Rate	Steam Temp. °C	Oil Temp. °C	Hrs. of Treatment	Osmoscope Reading
About 5.0	98	100	0	5
			1	4
			2	4
			4	4
			9	4
			16	4
			20	4
About 5.0	110	150	0	5
			1	4
			2	3
			4	2
			8	2
			16	2
			24	3

TABLE VI
LIQUID EXTRACTION

Extractive Medium	Initial Osmoscope Reading	Resulting Osmoscope Reading	Remarks
Formaldehyde and Sodium Meta-Silicate Sol.	5	5	Sample heated to drive off excess formaldehyde
25% conc. H_2SO_4 (cold)		5	Sample washed with NaOH and water
50% conc. H_2SO_4 (cold)		5	"
75% conc. H_2SO_4 (cold)		6	"
100% conc. H_2SO_4 (cold)		6	"
Acetone		5	Sample heated to drive off excess acetone

TABLE VII
LIQUID ADDITION TREATMENTS

Reagent Added to 50 ml. Oil	Quantity Added to Oil	Initial Osmoscope Reading	Resulting Osmoscope Reading	Remarks
C_6H_5CHO	0.01 % by wt.	5	5	
	0.05 "		5	
	0.10 "		5	
	0.50 "		5	Odor of benzaldehyde
	1.00 "		6	" " "
1 pt. aqueous (14% K_2HgI_4 + 18% KOH) to 7 pts. water	5 % by vol.		6	
	10 " "		6	

TABLE VIII
ADSORPTION TREATMENTS

Adsorption Medium	Wt. Used gm/50 ml. Oil	Oil Temp °C	Initial Osmo. Read.	Osmoscope Reading after Treatment Method (1) Oil Percolation	Method (2) Contact Treatment
Activated Charcoal	5	85	5	5	5
	10	100		4	5
		150		4	4
		200		4	4
Silica Gel	5	130	5	5	5
	10	100		4	4
		150		4	4
		200		4	3

TABLE IX
CATALYTIC TREATMENTS

Expt. No.	Catalyst	Reactor Temp °C	Av. Oil Flow Rate gm/hr	Length of run hrs.	Oil Recovered gms	% Recovery	Time hrs.	Oil Passed gms	Osmoscope Reading	Remarks
20	Fresh Cyclocel	400	48.0	20	799.8	83.5	0	0	5	Increase in catalyst weight 97.7-87.8 = 9.8 gm
							1	49.4	6	
							1.5	68.5	6	
							4	214.3	6	
							8	424.3	6	
							12	531.1	6	
							16	575.3	6	
							20	799.8	6	
21	Fresh Cyclocel	300	88.0	7.5	492	74.5	0	0	5	93.2 gm catalyst in reactor
							1	55.3	4	
							1.5	95.8	4	
							2.5	136.4	4	
							4	194	5	
							4.5	250.1	4	
							6.5	363.9	5	
							7.5	492	6	
22	Cyclocel Regenerated From Expt. 21	350	43.5	8.0	268.2	77.5	0	0	5	
							2.5	46.8	5	
							4	96.2	4	
							5.5	147.5	4	
							6.5	201.5	5	
							8	268.2	5	

TABLE IX (cont'd)
CATALYTIC TREATMENTS

Expt. No.	Catalyst	Reactor Temp °C	Av. Oil Flow Rate gm/hr	Length of run hrs	Oil Recovered gms	% Recovery	Time hrs	Oil Passed gms	Osmoscope Reading	Remarks
23	Cyclocel Regenerated from Expt. 22	250	46.0	8.0	272.7	74.5	0	0	5	Wt. of Catalyst after regeneration = 92.3 gm
							3.5	56.3	5	
							5	113.1	5	
							6.5	168.3	5	
							7.5	224	4	
							8	272.7	5	
24	Fresh Cyclocel	300	45.0	8.0	239.9	66.5	0	0	5	94 gm catalyst in reactor
							4.25	52	4	
							5.75	105.2	5	
							6.75	162.4	5	
							7.75	219.5	5	
							8	239.9	5	
25	Cyclocel Regenerated From Expt. 24	300	55.7	8.0	366.1	80.7	0	0	5	Wt. of Catalyst after regeneration = 87.1 gm
							2.5	56.0	6	
							3.5	111.5	6	
							4.5	166.4	5	
							5.5	221.3	5	
							6.5	276.7	6	
							7.5	329.5	5	
							8	366.1	5	

TABLE IX (cont'd)
CATALYTIC TREATMENTS

Expt. No.	Catalyst	Reactor Temp °C	Av. Oil Flow Rate gm/hr	Length of run hrs	Oil Recovered gms	% Recovery	Time hrs	Oil Passed gms	Osmoscope Reading	Remarks
31	Fresh Cobalt Molybdate	300	62.5	8	371.2	74.5	0	0	5	93.0 gm catalyst in Reactor
							3.5	52.3	3	
							5	107.8	3	
							5.75	162.8	4	
							6.25	217.9	4	
							7	270.4	5	
							8	371.2	5	
32	Cobalt Molybdate Recovered from Expt. 31	350	58.5	8	354.4	76	0	0	5	
							3	55.2	5	
							4.25	108.5	5	
							5	163.5	5	
							6	219.9	5	
							6.75	275.6	5	
							8	354.4	6	
										% Sulfur*
33	Cobalt Molybdate Regenerated from Expt. 32	250	40	8	218	68.5	0	0	5	3.09
							3.5	46.5	2	2.95
							5	95.2	4	-
							6.7	144.9	4	3.2
							7.75	192.1	4	-
							8	218.4	5	2.94

*A.S.T.M. Lamp method for sulfur estimation.

TABLE IX (cont'd)
CATALYTIC TREATMENTS

Expt. No.	Catalyst	Reactor Temp °C	Av. Oil Flow Rate gm/hr	Length of run hrs	Oil Recovered gms	% Recovery	Time hrs	Oil Passed gms	Osmoscope Reading	Remarks
34	Cobalt Molybdate Regenerated from Expt. 33	200	74.4	8	469.4	79	0	0	5	
							2	55.1	4	
							4	223.7	4	
							5	276	5	
							6	332	5	
							7	385.3	5	
							8	469.4	5	
35	Cobalt Molybdate Regenerated from Expt. 34	300	67.5	8.33	487.7	87	0	0	5	108.8 gm catalyst removed from reactor
							2.5	112.1	6	
							4.5	226.5	5	
							6	282.9	5	
							7	340.7	5	
							7.5	398.6	5	
							8.33	487.7	5	

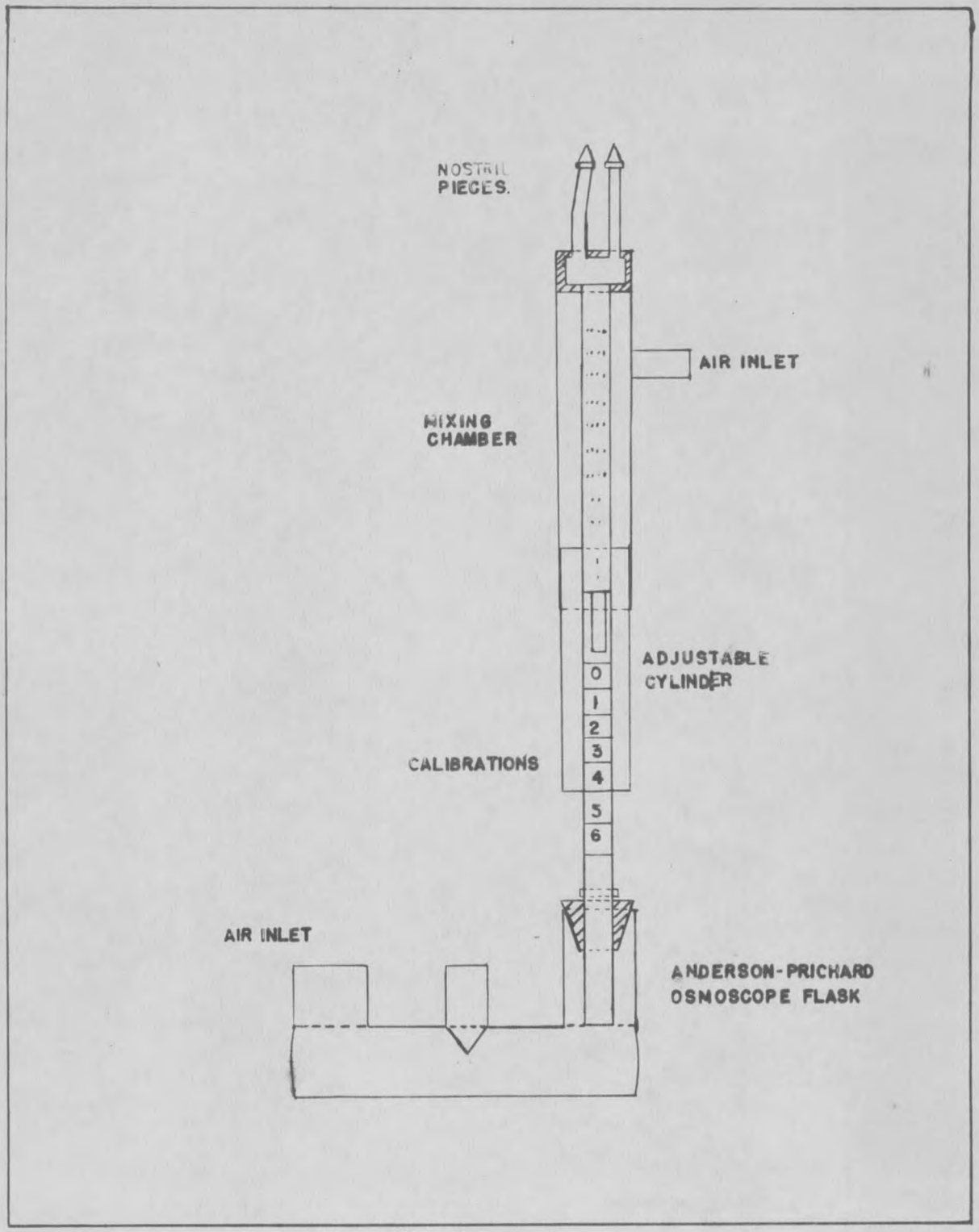


Figure 1. Odor Intensity Measurement Apparatus

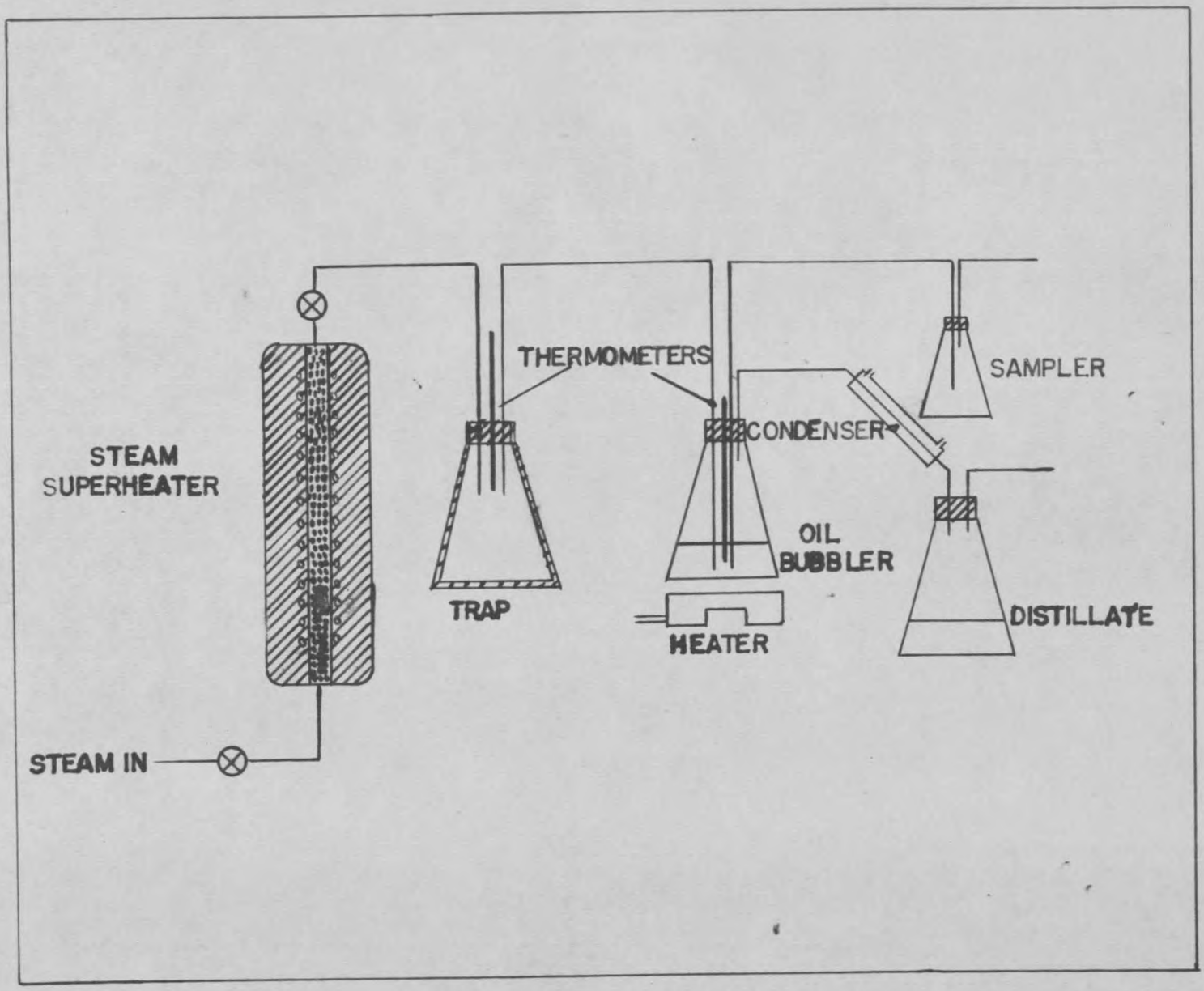


Figure 2. Steam Distillation Unit

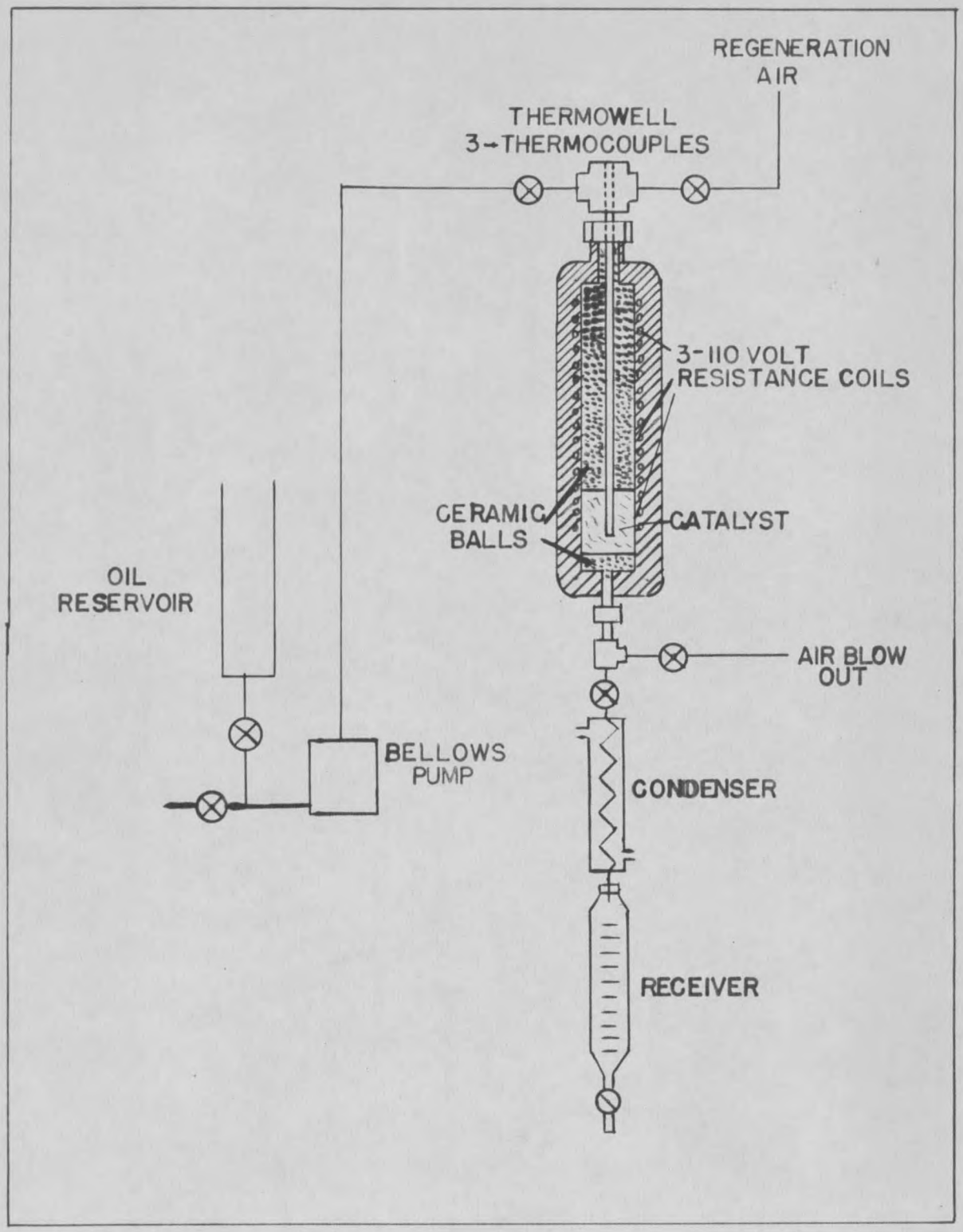


Figure 3. Catalytic Treatment Unit

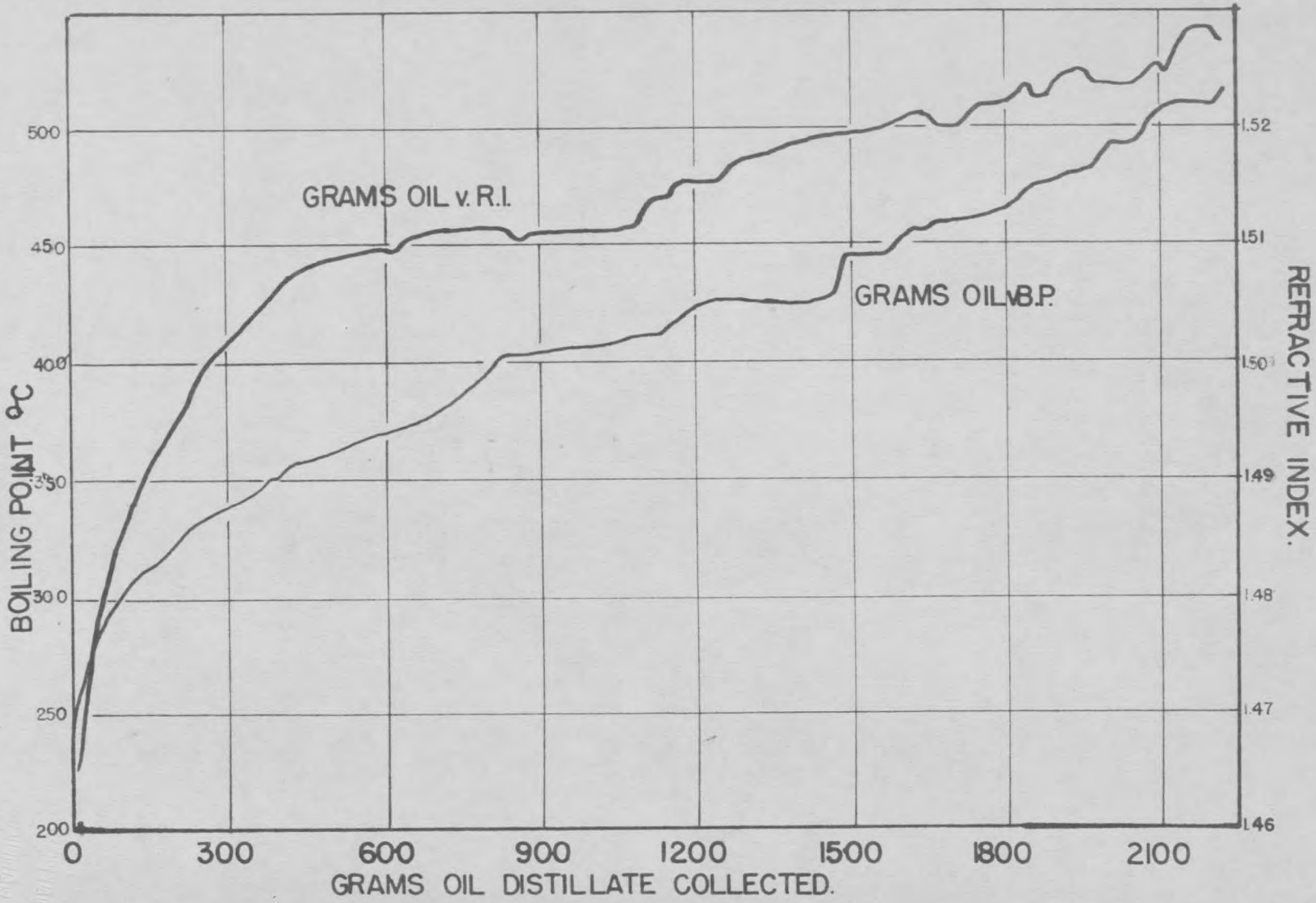
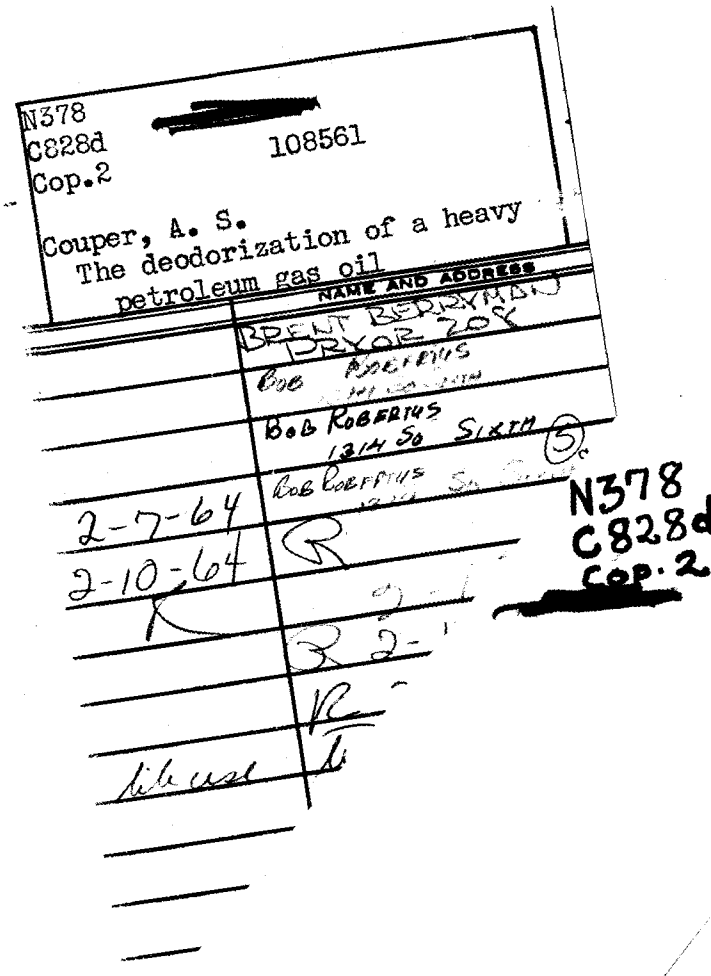


Figure 4. Fractional Distillation Curves

108561

MONTANA STATE UNIVERSITY LIBRARIES
3 1762 10013380 8



108561