

CATALYTIC DESULFURIZATION OF HEAVY GAS OILS
WITHOUT USE OF A HYDROGEN SUPPLY OR GAS RECYCLE

BY

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A thesis submitted to the faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Science in Petroleum Refining Engineering.

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ABSTRACT

The main objective of this investigation is the development of a continuous desulfurization process for high-sulfur heavy gas oils, which would be within the capacity and facilities of small refineries. The process attempted makes use of the catalytic action of chemical materials in absence of a hydrogen supply or gas recycle. However, the highly nonreactive form in which the sulfur compounds of heavy petroleum distillates exist necessitates the use of highly active materials, along with an optimum for the appropriate set of operating conditions.

Among the materials studied, anhydrous aluminum chloride showed its long-time-proved capability for refining and upgrading petroleum and its products. A fair degree of sulfur removal was attained in the bulk product, ranging from 41 to 63 per cent according to the type of feed stock treated. For a centrifuged clear cut of the treated gas oils, the percentage of sulfur reduction ranged from 72.5 to 85; in each case, little molecular breakdown took place. Furthermore, the

ratio of aluminum chloride consumed to feed stock treated is only 1 to 10 by weight for about 55 per cent sulfur removal from the 2.78 weight per cent-sulfur-feed in the bulk product. At this rate of consumption, the cost of aluminum chloride per gallon of gas oil treated is 3¢.

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INTRODUCTION

The increased consumption of petroleum products brings large quantities of high-sulfur crude oils to the world market. Distillates obtained from the processing of such crude oils carry sulfur in different proportions and forms. The spread of sulfur compounds, as non-hydrocarbon constituents in the various petroleum distillates, follows the same pattern of increasing molecular weight and complexity of structure as that of the hydrocarbon constituents with increasing boiling range. Investigations dealing with individual components of heavier petroleum products have proved practically hopeless, ever since petroleum chemistry was recognized, owing to the enormous number of constituents present in those fractions. Consequently, what is always best hoped for is a determination and identification of the chemical constituents' classes. The ring analysis affords an excellent means in this respect. Heavy distillates, from almost all kinds of crude oils, have been found to consist predominantly of naphthenes and aromatics, in highly condensed forms. Furthermore, the aromatics of

these high boiling fractions include aromatic hydrocarbons as well as non-hydrocarbon constituents. The condensation products between the polycyclic naphthenes and aromatics, and non-hydrocarbon constituents of sulfur, nitrogen, and oxygen, form the asphaltenes and resins which concentrate to the major extent in the high boiling distillates. Those asphaltic and resinous materials which are then the principal carriers of sulfur in heavy petroleum products, being expectedly quite nonreactive, impose the difficulty of desulfurizing such products.

The expression "you can always hide what you don't want in heavy fuel oils" held true for a long time after the beginning of the refining industry; however, with the tremendous advancements and refinements continually introduced into the various industries utilizing fuel oils, the necessity of desulfurization became apparent. In the glass and ceramic industries, low sulfur content is a requisite, usually requiring a maximum of 0.25 per cent sulfur. The greatest users of heavy petroleum products are the metallurgical industries, and particularly, the open hearth furnaces of steel mills; a low sulfur oil, with a maximum ranging from 0.75 per cent to 1.00 per cent, is of critical importance. For power boilers, the combustion of high sulfur oils yields an unnecessarily low heat value. This is because 4000 Btu are liberated when one pound of sulfur is burned, as compared with 14,600 and 62,000 Btu per pound of carbon and hydrogen, respectively. Moreover, the combustion of high sulfur oils causes excessive corrosion of burners and steel smoke stacks, as well as a much faster deterioration of the fire-brick structures.

Blending with other low-sulfur oils is customarily practiced in order to reduce the sulfur content of heavy distillates. However, it should be remembered that the other low-sulfur blending component is usually a lighter distillate with greater value elsewhere. Desulfurization by solvent extraction is another popular process for straight-run diesel fuels as kerosene, No. 1 and No. 2 distillates, but with heavier products, most of the solvents recommended lose their selectivity and solvating power. The continually improved catalytic hydrodesulfurization process can only be economically justified for lighter diesel fuels with moderate sulfur contents; but when high-sulfur heavy distillates are to be handled, high pressures and excessive consumption of hydrogen are required. The process then becomes, in the extreme, a total hydrogenation with considerable molecular breakdown. The consumption of hydrogen gets as high as 1200 SCF per bbl. This great demand of hydrogen along with equipment construction considerations can hardly be within the capacity of small refineries.

The main objective of this investigation is an attempt to develop a continuous catalytic process for the desulfurization of high-sulfur heavy gas oils, without the use of an outside source of hydrogen or gas recycle. Treatment with highly active, readily available chemical materials, along with the search for an optimum of operating conditions, constitutes the development work of this thesis.

Of the chemical materials studied, anhydrous aluminum chloride

proved most effective for attaining a fair degree of sulfur removal in the bulk product, ranging from 41 to 63 per cent according to the type of feed stock treated. For a centrifuged clear cut of the treated gas oils, the percentage of sulfur reduction ranged from 72.5 to 85 per cent. In each case, little molecular breakdown took place, as revealed by the ASTM distillation and the API gravity. In addition, the ratio of aluminum chloride consumed to feed stock treated is only 1 to 10 by weight, for about 55 per cent sulfur removal in the bulk product.

The use of anhydrous aluminum chloride as a refining and an upgrading agent for petroleum and its products is as old as the refining industry itself. In 1878, Friedel and Crafts communicated to Abel a description of the first aluminum chloride process wherein low-quality whole crude oils could be upgraded with simultaneous removal of sulfur. Since then, a new field of research was opened up in attempting to determine the course of the reaction and the nature of the products.

The essentials of the development work conducted were considered to be:

1. The process should be capable of handling a wide range of feed stocks so as to provide flexibility in refinery operations.
2. The product, except for sulfur reduction, should have properties and boiling range not substantially different from those of the feed stock.
3. Consumption of the treating material should be kept to a minimum.

CHEMICAL CONSTITUENTS OF GAS OILS

The composition of petroleum and its products, even of gasoline fractions, is extremely complex. At present, more than 100 hydrocarbons have been identified in the gasoline range (up to 200°C end point). The number of hydrocarbons present in gas oils would undoubtedly be much greater than in gasolines, owing to the greater number of possible isomers, a number which grows rapidly with increasing molecular weight of hydrocarbons. Consequently, owing to an enormous number of constituents, heavier fractions cannot be readily resolved into individual components, and the separation and determination of hydrocarbon classes is as important as the separation and identification of individual hydrocarbons.

The ring analysis for gas oils (Sachanen, 1945, p. 218) gives figures which differ widely for paraffinic and naphthenic or asphaltic products. For the highly naphthenic gas oil under investigation (V. I. = - 109), the percentage of paraffinic side chains may be as low as 40. The ring content is correspondingly high. The proportion of naphthenic rings in the hydrocarbon cluster is usually much greater

than that of aromatic rings, with an average number of rings per molecule from 2 to 3.

Olefins and other unsaturates have also been reported to be practically absent in virgin heavy naphthenic distillates. It would also seem appropriate to state that such distillates may consist almost exclusively of naphthenes and aromatics, and furthermore, the content of paraffins is small (Sachanen, 1945, p. 219).

The most effective present method of determining and separating aromatic hydrocarbons by absorption has a serious shortcoming when applied to high boiling petroleum products. Oxygen, sulfur, and nitrogen compounds present in heavy fractions are desorbed with polycyclic aromatic hydrocarbon molecules. The ultimate quantitative separation of those polycyclic aromatics from the non-hydrocarbons is not feasible by any known physical or chemical methods (Brooks and others, 1954, p. 22). For this reason "the aromatics of gas oils" include hydrocarbons as well as non-hydrocarbon constituents. It is beyond doubt that the non-hydrocarbon components present in high-boiling petroleum products are essentially of ring structure, that is, sulfur, oxygen, and nitrogen atoms of these compounds are connected in some way with aromatic polycyclic rings. The content of the non-hydrocarbon components in heavy fractions would therefore depend upon two factors:

1. Boiling range and specific gravity of the product.
2. Origin of the crude oil.

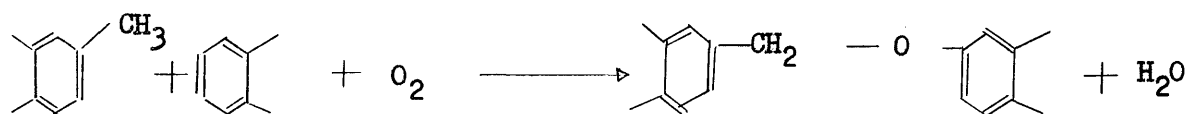
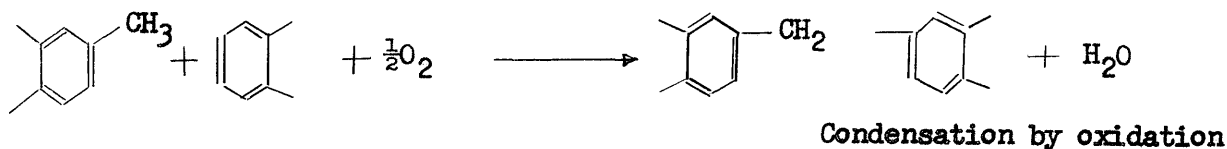
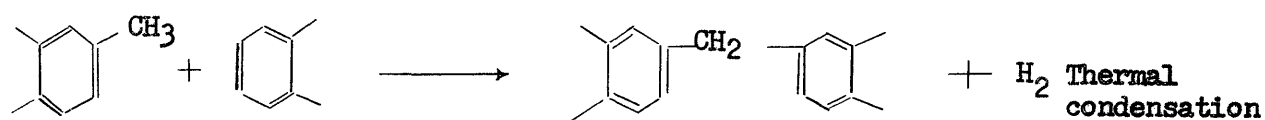
So that, for a given crude oil, the non-hydrocarbon content of aromatics increases with increasing boiling range of fractions.

Brooks and others (1954, p. 25) stated that densities and refractive indices of aromatic hydrocarbons separated from heavy petroleum distillates, as well as those of cycloparaffins dewaxed and freed from aromatics, are in general high, and much higher than the densities and refractive indices of derivatives of benzene and monocyclic cycloparaffins boiling in the range of the distillate. Moreover, the densities and refractive indices increase rapidly with increasing boiling range of heavy petroleum fractions. These facts lead to the conclusion that the cycloparaffin and aromatic hydrocarbons of heavy petroleum stocks are predominantly polycyclic and that the polycyclic character of these hydrocarbons increases with increasing boiling range of the fractions. Equivalently, the chemical composition of gas oils, in general would follow the pattern of a gradual decrease in the content of paraffins and an increase in the content of polycyclic naphthenes and aromatics with increasing boiling range.

The ring structure of polycyclic naphthenes and aromatic hydrocarbons in heavy petroleum distillates has not been definitely established. The predominance of fused (or condensed by joining through two ring-carbon atoms) ring structures, such as naphthalene, 1,2,3,4-tetrahydronaphthalene, among the polycyclic hydrocarbons in kerosene and light gas oils leads to the hypothesis that the fused

cyclic structures may predominate in heavy petroleum stocks too. This theory is supported by the plentiful formation of naphthalene and its derivatives on cracking of heavy cracking stocks, undoubtedly as a result of degradation of high-molecular-weight fused polycyclic structures preexisting in the stocks.

Those high-molecular-weight fused polycyclic naphthenes and aromatics, together with the nonhydrocarbon components, atoms of oxygen, sulfur, and nitrogen, would constitute the asphaltenes and resins present and concentrating in heavy distillates. Sachanen (1945, p. 406) discusses the methods by which asphaltenes and resins are formed during crude oils processing. The condensation processes which form the asphaltic compounds can be brought about by purely thermal reactions at high temperatures or by oxidation at moderate temperatures. The three types of reaction are:



Thus, the condensation product formed by oxidation may or may not contain oxygen. The sulfur content of these condensation products can be explained by the fact that sulfur can replace the oxygen in the latter reaction.

Based on solubility in n-pentane at ambient temperature, the "asphalt" of crude oils and heavy distillates is arbitrarily divided into two fractions; the soluble fraction being known as the maltene, and the insoluble fraction as the asphaltenes. The maltene can be further segregated into a water-white oil, a dark oil, and an asphaltic resin through a stepwise elution from a fuller's earth column with n-pentane, methylene chloride, and methyl ethyl ketone. More recently (Yen and Erdman, 1962, p. 5), much has been learned about the extent of condensation and the number of naphthenic and aromatic clusters per unit of the asphaltic structure. The structure of the asphaltic fractions has been found to be that of a two-dimensional fabric consisting of clusters of naphthenic and aromatic rings linked by short aliphatic chains. While certain structural differences depending on source are evidenced by variation in elemental composition, studies utilizing resin and asphaltene fractions of crude oils from different geographic localities suggest closely related basic structural formations. Naphthenes are present in the asphaltenes in a condensed form identical to that of the aromatics; furthermore, upon dehydrogenation of an asphaltene fraction, the naphthenes would yield aromatic clusters of about the size of those naturally present.

This can be evidenced by the low proportion of naphthenes usually found in heat treated refinery asphalt, where dehydrogenation of naphthenic structure to aromatic structure is likely to occur due to mild cracking or pyrolysis. The aliphatic portion of the asphaltene structure is believed to consist primarily of short, unbranched alkyl chains. Maltene, on the other hand, is low in respect to aromaticity and the aromatic clusters probably are substituted to a high degree by aliphatic or naphthenic groups. Yen and Erdman also concluded that the asphaltic fractions of petroleum distillates consist, to the major extent, of high-molecular weight nonhydrocarbon compounds, where the heteroatoms are principally sulfur, oxygen, and nitrogen. Furthermore, studies of rates of oxidation with permanganates have indicated that the heteroatoms are present in chemically stable configurations, namely, the asphaltenes and maltene-ring structures. The content of asphaltic fraction in crude oils may represent less than the limit of detection or as much as 50 per cent of the total.

Those asphaltic and resinous complex compounds are believed also to decompose to some extent during the various processings of the crude oil, liberating simpler substances as hydrogen sulfide, mercaptans, sulfides, which could then be distributed along the various products streams.

Free sulfur can only be present in distillates which contain hydrogen sulfide, as upon exposure to air, hydrogen sulfide oxidizes

to form sulfur crystals. This fact reduces the possibility of the existence of free sulfur in heavy fractions.

According to the preceding discussion, the content of sulfur in petroleum distillates increases with increasing boiling range and gravity; thus high-molecular-weight sulfur compounds predominate and are concentrated in the heavy fractions, in contrast to a smaller content of lower molecular-weight sulfides and mercaptans; those latter are mostly concentrated in lighter distillates.

DESULFURIZATION OF HEAVY PETROLEUM DISTILLATES

A considerable number of alternative processes for desulfurizing heavy products are already available to the industry. A brief account on the presently known processes might prove useful.

Desulfurization of heavy petroleum distillates can be effected in either of two major ways; solvent extraction or catalytic hydrodesulfurization.

The solvent extraction process is based on the principle of separating the sulfur bearing molecule from pure hydrocarbons by extraction with a suitable solvent. An ideal solvent would remove all sulfur compounds and none of the hydrocarbons. Needless to say, however, such a perfectly selective solvent is not known. The best solvents recommended are sulfur dioxide, hydrogen fluoride, and furfural.

Sulfur dioxide extracts principally aromatic sulfur compounds. Therefore, it is best suited to those distillates where a major part of the sulfur content is present in aromatic form, for example, cycle

oils. As sulfur dioxide is an excellent solvent for aromatic hydrocarbons, these compounds are removed together with the sulfur compounds, and consequently the raffinate yield is unnecessarily low.

Hydrogen fluoride removes aliphatic, naphthenic, and aromatic sulfur compounds, but its solvent effect decreases with increasing molecular weight of the sulfur compound. It is worth noting also that these aromatic disulfides where both carbon atoms which are linked by the sulfur atom form part of an aromatic ring, are only slightly extracted, if at all.

The selectivity of furfural for extraction of sulfur compounds is better than that of sulfur dioxide, but not quite so good as that of hydrogen fluoride. It extracts aromatic and naphthenic sulfur compounds as well as hydrocarbons. The degree of sulfur removal is moderate and so is the raffinate yield.

Catalytic hydrodesulfurization processes split the sulfur atom from the hydrocarbon molecule and reduce it in a hydrogen atmosphere to hydrogen sulfide. Because of the combined action of high temperature and catalyst, the carbon-sulfur bonds are ruptured and the free valences are saturated with hydrogen. The resulting hydrogen sulfide leaves the system with the by-product gases, and the sulfur-free hydrocarbons become part of the product. The boiling point of the product hydrocarbon may be lower than that of the mother sulfur compound because of a break in the hydrocarbon chain. In the alkyl-S-alkyl type of compounds the drop in boiling point may be considerable because

of the large decrease in molecular weight.

Typically, the hydrodesulfurization catalyst has almost always been cobalt oxide-molybdenum oxide on alumina activated in various ways. In these processes, the desulfurization is actually a mild selective hydrogenation, so mild that aromatics are not usually hydrogenated to naphthenes. However, high-boiling distillates require a pressure of 700 - 1000 psig, with a temperature ranging from 600 to 800°F, although carbon deposition on catalyst becomes excessive at temperatures exceeding 750°F. The amount of hydrogen recycling could also be as high as 10,000 SCF per bbl when residue feed stocks are handled; and hydrogen disappearance is mainly a function of the amount of sulfur that is eliminated (up to 1200 SCF per bbl). The vigorous treatment required for high sulfur content heavy distillate necessitates a space velocity from 3 down to as low as 0.5 wt per wt per hr. As mentioned above, coke deposition may represent 2 to 6 per cent by weight of the feed stock when heavy distillates are desulfurized, so that regeneration of the catalyst may be required as frequently as 1 to 4 times a day. Yields are close to 100 liquid volume per cent, and the efficiency of desulfurization depends upon the charge stock and the severity of treatment, ranging from as low as 50 to 60 per cent for mild operations to almost complete desulfurization.

Still another version of hydrodesulfurization is a relatively new process called auto-hydrofining or simply, autofining. The main

feature of this process (Porter and Lorne, 1953, p. 58) is that the hydrogen necessary for the hydrodesulfurization is provided by simultaneous dehydrogenation of part of the feed stock, and the desulfurization process could then become self supporting with respect to hydrogen. It is obvious that the success of such a process depends on a critical degree of dehydrogenation of the naphthenes present in the feed stock under mild conditions to ensure long on-stream hours. Again, such a process is adequate for only moderate degrees of sulfur removal where the consumption of hydrogen can be confined within reasonable limits. Distillates with end points around 600°F could only be 50 per cent desulfurized at 780°F, 100 psig, space velocity of 2 vol per vol per hr, and 2000 SCF per bbl recycle gas rate.

By way of pointing out the disadvantages of solvent extraction and catalytic hydrodesulfurization processes when applied to heavy petroleum distillates, we readily find out that the former has a serious shortcoming, namely, that it removes the entire sulfur-bearing molecule as well as some sulfurless hydrocarbons; and that with almost all of the solvents recommended, their selectivity and solvating power decreases with increasing boiling range of the petroleum distillate.

The high pressure used in the catalytic hydrodesulfurization does not seem desirable both from economic considerations of equipment construction and from the fact that the process becomes, in the

extreme, a total hydrogenation of the feed stock with considerable breakdown in molecular structure. The main disadvantage of this process is its high consumption of hydrogen, the amount required being proportional to the sulfur removed and the nature of the sulfur compound. The process requires about 70 SCF per bbl (Porter and Hyde, 1955, p. 193) for as little as 1 per cent by weight sulfur removal from the feed stock; so that future development of this process will depend upon the provision of cheap hydrogen.

Catalytic desulfurization without hydrogen or gas recycle - for example, the Perco process (Brooner and Conn, 1946, p. 96), and the Gray process (Martin and Carlson, 1942, p. 138) - is known to desulfurize successfully the light distillates with end points up to 200°C. However, with higher boiling distillates such as kerosene and gas oils, these processes are less successful, and only with very frequent regenerations of the catalyst when the process could be possible. The high temperatures, 750 - 800°F, which have to be employed with heavier distillates, tend to produce unstable products.

The work carried out in this investigation is an attempt to develop a continuous catalytic process for desulfurizing high-sulfur-content heavy petroleum distillates dispensing with the use of an outside source of hydrogen or gas recycle. The essentials of the process were considered to be:

1. Conditions of operation should be such that little or no molecular breakdown occur, and the product, except for sulfur

reduction, should have properties and a boiling range not substantially different from the feed stock.

2. The process should be capable of handling a wide range of feed stocks so as to provide flexibility in refinery operations.

3. On-stream time should be reasonably long to avoid excessive consumption of treating material.

Sodium Hydroxide Desulfurization

As outlined in the section on gas oils composition, sulfur can be present in heavy distillates in the form of mercaptans. One of the general reactions of mercaptans is the formation of the sodium salt of the mercaptan through its reaction with sodium hydroxide. It was thought then that this kind of reaction could take place, and if part of the sulfur content of the feed stock is present in the form of mercaptans with mobile hydrogen atom, it could be removed in this manner. However, as indicated in the experimental work, little or no sulfur was removed from the gas oil. Sodium hydroxide in various states were tried such as 20 per cent aqueous solution in a batch-wise treatment, and in a solid form as a bed of pellets and of commercial flakes, with or without additives to the continuously flowing gas oil stream. Evidently, the sulfur is not present in the form of mercaptans.

Anhydrous Aluminum Chloride Desulfurization

The use of aluminum chloride as a refining agent for petroleum

distillates is based on its polymerizing and desulfurizing effect (Thomas, 1941, p. 830). The desulfurizing action of aluminum chloride at ordinary temperatures is thought to be due to the formation of addition compounds; at higher temperatures, however, cracking occurs.

The advent of aluminum chloride cracking process stems back to the 1870's when Friedel and Crafts found that hydrocarbons heated at 100 - 160°C in the presence of aluminum chloride were converted to lighter hydrocarbons. Naphthalene produced benzene, toluene, and other products; low grade petroleum gave both light and heavy oils with simultaneous removal of sulfur.

A new field of research was then opened up in attempting to determine the course of the reaction and the nature of the products.

A. M. McAfee (1915, p. 737-741) of the Gulf Refining Company describes a process for the production of gasoline from topped crude. The process briefly consists of distilling crude oil to remove any water and straight run gasoline. From 3 to 10 per cent of anhydrous aluminum chloride is then added to the residue and heated to 500 - 550°F for 24 hours while being thoroughly agitated. The distilled product of the reaction is a mixture of gasoline and kerosene in varying percentages depending upon the type of crude used. The crude oil had to be low in sulfur and thoroughly dried since both sulfur and water contribute toward the consumption of aluminum chloride.

The desulfurizing action of aluminum chloride was then first studied by Wood and others (1924, p. 1116-1120). Pure sulfur organic compounds dissolved in naphtha to give a 0.71 wt-per cent sulfur content were treated with aluminum chloride in varying percentages, in batch agitated vessels, for equal time intervals at room temperature. Sulfur removal increased from 35 to 95 per cent when the amount of aluminum chloride added was increased four times. The effect of temperature was studied by conducting the treatment in a distilling flask. When 50 per cent of the total volume was distilled off, the collected naphtha distillates were desulfurized from 0.71 wt-per cent to 0.11 wt-per cent, that is, 84 per cent sulfur removal as compared to 35 per cent at room temperature. Evolution of hydrogen sulfide was observed throughout the distillation. Furthermore, the 0.11 wt-per cent sulfur in the collected naphtha distillates was predominantly hydrogen sulfide and mercaptans.

It is important to note that the original sulfur compound dissolved in the naphtha was iso-amyl disulfide. The study also covered the change in the desulfurizing effect of aluminum chloride with changes in the nature of the organic sulfur compounds. They concluded that the desulfurization action of aluminum chloride at ordinary temperature is due to formation of an addition complex compound (except with thiophenes) and at higher temperatures is due to cracking; most of the sulfur being eliminated as hydrogen sulfide, with the formation of simpler mercaptans.

Youtz and Perkins (1927, p. 1247-1250) did very much the same kind

of investigation as that of Wood, with some more emphasis on the variation of the kind of sulfur organic compounds treated. They concluded that secondary heptyl sulfide, allyl sulfide, and benzyl sulfide react with aluminum chloride almost completely on simple refluxing; and that on distillation most of the sulfur compounds, sulfides, disulfides, and thiophenes, react further with aluminum chloride because of the higher temperature involved. They also put forth another important conclusion that if aluminum chloride formed an addition complex with a sulfur-bearing molecule, and largely or partly removed it from solution, the complex might be decomposed again by the higher temperature toward the end of the distillation, liberating simpler sulfur compounds. Those simple sulfur compounds, unless removed by some kind of a mild alkali after-wash, would remain in the treated material. They also concluded that increased amounts of aluminum chloride could have decomposed all of the sulfur compounds investigated almost completely.

Meadow and White (1950, p. 925) used n-heptane as a solvent for synthetic mixtures with a series of sulfur organic compounds including aliphatic and aromatic mercaptans, sulfides, disulfides, and thiophenes. The sulfurization effect of aluminum chloride in agitated batches at room temperature was similar to what has been found out in the earlier investigations.

Goldstein and Semenova (1939, p. 8238) reported that the extent of desulfurization of gasoline with aluminum chloride depends on the amount

of reagent employed, the temperature, and an optimum of the duration of treating (space velocity in flow processes). In their laboratory experimentation, they treated gasoline with aluminum chloride, in batches, at atmospheric pressure and a series of temperatures between 20 and 50°C. The optimum duration of treating was 1 hour, and by prolonging the length of treatment practically no effect on the desulfurization resulted. In order to decrease the consumption of aluminum chloride the gasoline was first treated with a 2.5 per cent caustic soda solution. The authors also reported the formation of a fluid complex between the sulfur-bearing molecules and aluminum chloride which was readily destroyed by an alkali solution with the formation of hydrogen chloride, hydrogen sulfide and an oily layer (48 - 50 per cent) consisting of the hydrocarbon and part of the sulfur compounds.

According to Englin and Brazhnikov (1939, p. 5339), aluminum chloride reacts at room temperature with the sulfur compounds of the gasoline forming liquid complexes that can be easily destroyed, and removed from the gasoline, with water or alkali solution. In order to improve the desulfurizing effect of aluminum chloride, they found it desirable to subject the gasoline to an alkali treatment before contact with aluminum chloride. The authors also pointed out that aluminum chloride decomposes the sulfur-bearing molecules forming low-boiling fractions of mercaptans. These should be removed with an alkali after-wash. In their investigation, they were able to

reduce the sulfur content of gasoline from 0.33 to 0.2 wt-per cent with a consumption of 0.5 per cent of aluminum chloride at room temperature.

It is obviously difficult to obtain a true insight into the mechanism of decomposition of any substance as complex as petroleum oils. Practically all types of oils will yield paraffinic, aromatic, and naphthenic hydrocarbons in an aluminum chloride cracked distillate; the ratio of those constituents will vary with the original composition of the feed stock.

Pictet and Lerczynska (1916, p. 182) cracked a variety of heavy distillates and found the resultant low-boiling products to consist of 35 per cent paraffins and 65 per cent "cyclic compounds of the formula C_nH_{2n} " cycloparaffins. They assumed that these products were formed by splitting the naphthenes with a long side chain, present in the oil, into paraffins and cycloparaffins. The latter products were polymerized partly to asphalt-like substances.

Borisov and others (1935, p. 4926) decomposed kerosene and heavier distillates in the presence of aluminum chloride. The mechanism of the reactions was found to be dependent upon the source and composition of the oil and the temperature of treatment. At 150°C (302°F), acyclic saturated hydrocarbons break easily into light, gaseous or liquid paraffins and unsaturated derivatives which may polymerize to build up higher saturated hydrocarbons. Aromatic hydrocarbons may decompose or may be alkylated in presence of olefins. Naphthenes are the most

resistant to reaction at 150°C; however, they also undergo conversion to paraffins, aromatics, and residual asphaltenes.

Some general conclusions can, therefore, be drawn to account for the influence of aluminum chloride as a cracking and a desulfurizing agent for petroleum distillates:

The desulfurizing action of aluminum chloride at ordinary temperatures is probably due to the formation of addition complex compounds. At higher temperature, however, such an addition complex is formed but then finally partly undergoes cracking to simpler sulfur compounds. Hydrogenation of unsaturated residue formed in the decomposition of aluminum chloride-hydrocarbon-sulfur complexes can occur fairly readily. The shortage of hydrogen to complete this process, where no hydrogen is supplied from outside, permits polymerization and carbonization, limiting maximum conversion to clear products to about 70 per cent (as will be seen later in the experimental work of this investigation). Most of the mercaptan sulfur is eliminated as hydrogen sulfide, but alkyl sulfides, alkyl disulfides, and thiophenes are converted to hydrogen sulfide and mercaptans. A mild alkali after-wash proves useful.

A maximum of 10 per cent aluminum chloride, based on feed stock, gives the optimum conversion to useful products. If temperatures above the sublimation temperature of aluminum chloride, 185 - 195°C (365 - 383°F) at atmospheric pressure, are employed, pressure should be used to prevent sublimation of the catalyst. The complex formed between aluminum chloride and the sulfur-bearing hydrocarbons is a satisfactory

catalyst and simplifies handling of the aluminum chloride; however, such materials thicken and are difficult to use in a continuous manner.

EXPERIMENTAL PROCEDURE

The desulfurization process attempted is a continuous contacting catalytic process adapted to high sulfur heavy petroleum distillates, without the use of hydrogen or gas recycle. The work carried out in this investigation is a development-type research, with the main objectives being the location of the optimum operating conditions with materials that show an adequate desulfurizing effect.

Several materials were tried at the beginning of the research in an exploratory manner. Fuller's earth and calcium oxide were found not promising; hence, further investigation with them was dropped. Treatments carried out with solid sodium hydroxide and anhydrous aluminum chloride form the subject matter of this thesis.

A simplified flow diagram of the process is shown in figure 1. The flow path can also be traced in figure 2. The apparatus consists of a reservoir, pump, an oil-bath preheater, the contacting column, air cooler, and a receiver. The pump used is a Zenith gear-pump of 60 ml per min maximum capacity, driven through a Graham variable-

speed transmission so that the flow can be varied through a range of 3 to 60 ml per min. All flow lines are 1/4-in. copper tubing. The contacting column is a 1-in.-I.D., 12-in.-long copper pipe, with threaded caps on both ends. A heating coil is wound along the column, with a voltage regulator to provide variable heat inputs with a maximum temperature attainable of 700°F. Temperature is measured by an iron-constantan thermocouple embedded in a thermowell extending 4 in. into the contacting bed and connected to a Micromax (Leeds and Northrop) single-channel temperature recorder.

The desired temperature of the bed was maintained remarkably constant by manipulating the powerstats on the oil-bath preheater and the heating coil while maintaining a steady flow of gas oil. Strainers of copper gauze were used on both ends of the contacting column to assist in supporting the bed as well as to minimize the carry-over of the catalyst fines out of the bed by the flow stream.

The 1/4-in. copper tubing air cooling coil was capable of bringing down the temperature of the product stream to room temperature.

Briefly, the gas oil is pumped at the prescribed rate through the oil-bath preheating coil, from which it flows upwards through the treating bed in the contacting column. The flow stream then acquires the final required temperature, undergoes any desulfurizing action, and emerges through the overhead line to the air cooling coil to be finally collected in the receiver.

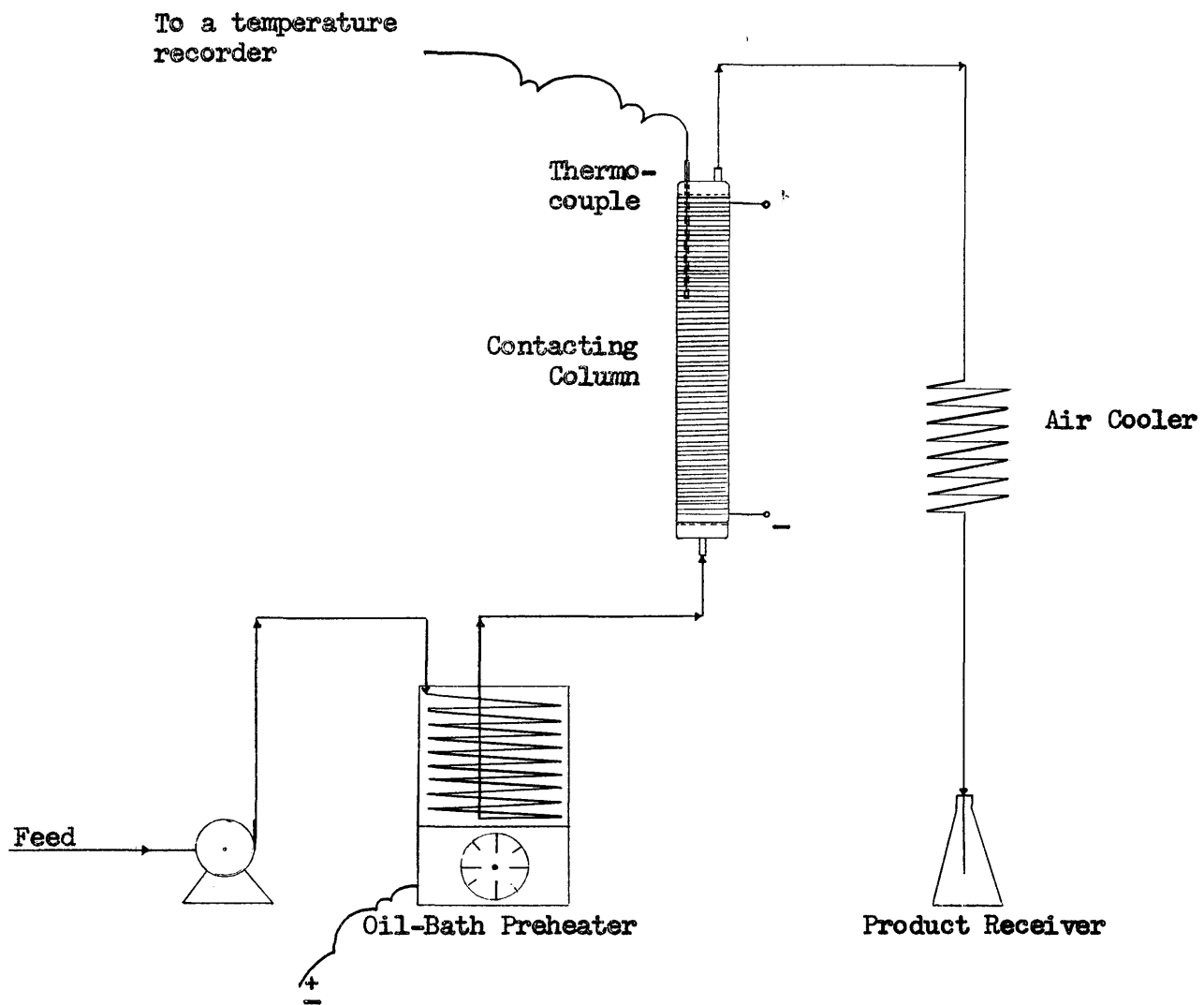


Figure 1. Desulfurization Flow Diagram

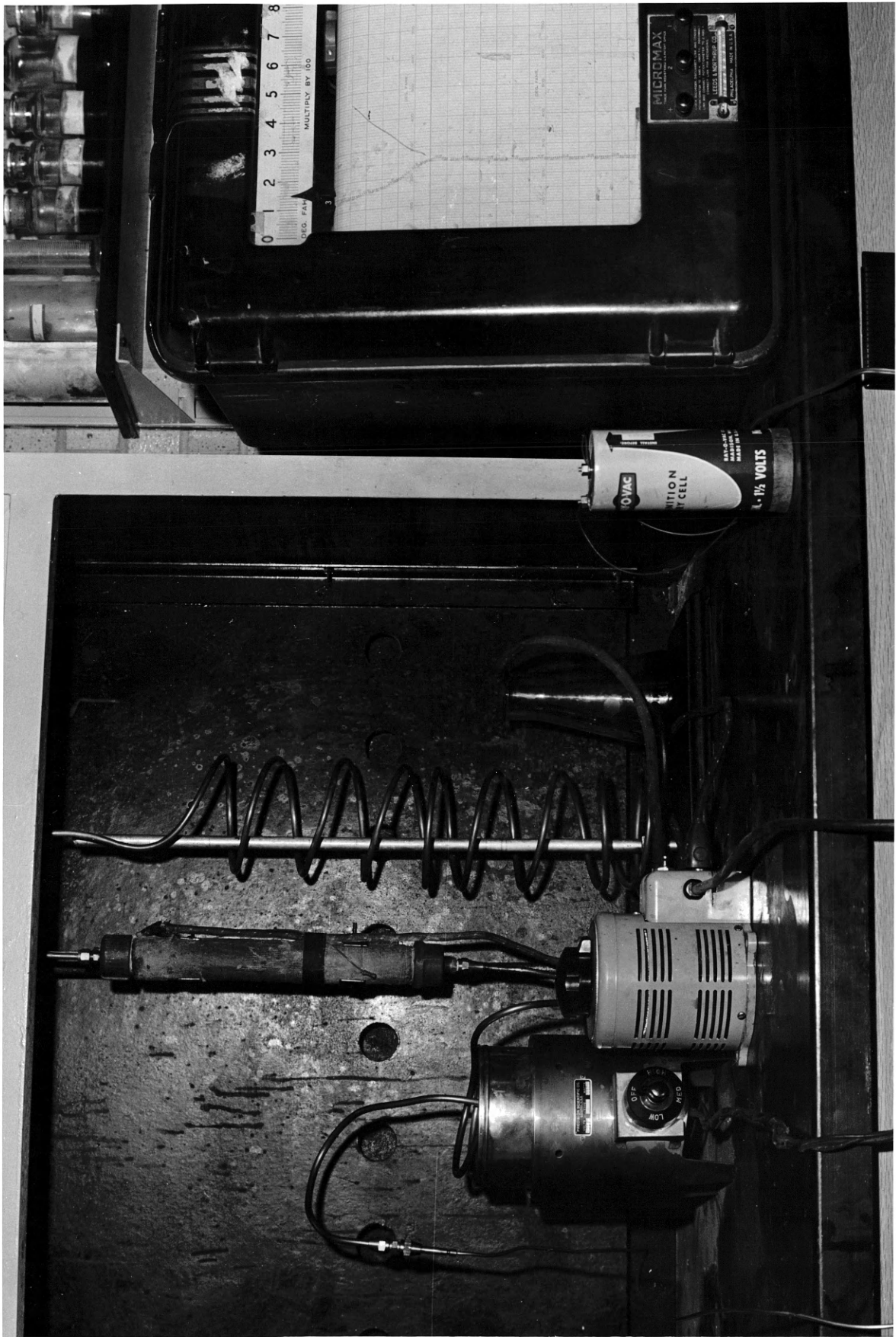


FIGURE 2. DESULFURIZATION APPARATUS

The Process Variables

The desulfurization process was conducted primarily in the liquid phase due to two factors: first, the thermal cracking temperature of the feed stock is around 608°F, at 40 per cent volume distilled, which sets an upper limit as to the temperature that can be used with this kind of feed stock, and second, the sublimation temperature of anhydrous aluminum chloride is 185 - 195°C (365 - 383°F), which sets another limit as to the temperature that might be used with this kind of catalyst if it is to be investigated in its solid state.

Therefore, pressure as a process variable was not of interest in this study, except to the extent that the charging pump should have a delivery pressure sufficient to overcome friction and hydrostatic pressure losses throughout the contacting set-up. Furthermore, different gas-oil flow rates set for the different treatments did not involve so wide a change as to cause any appreciable change in pressure from one run to the other.

The effect of temperature on desulfurization, at constant pressure, as outlined in earlier discussions, has been attributed to the formation of addition-type complexes, of the form aluminum chloride - sulfur - hydrocarbon, at lower temperatures, and to the cracking of sulfur-bearing molecules to hydrogen sulfide and simpler sulfur compounds at elevated temperatures.

With such high-sulfur-content feed stock, where desulfurization proves really difficult and can only be improved upon rather than go

to completion, space velocity is an important process variable.

Experimental Data and Results

The experimental results presented in table 1 clearly indicate a rather poor effect for sodium hydroxide as an agent for desulfurizing high-sulfur heavy petroleum products.

The data presented in table 2 for treatments with anhydrous aluminum chloride can be divided into two more or less constant space-velocity groups, with a set of temperature-different runs in each. Examination of this set of data and by reference to figures 3 and 4 clearly indicates a definite influence of temperature on desulfurization; an optimum range of approximately 300 - 325°F can be set for temperature. By comparing results of the two sets of desulfurization runs, presented in table 2 and figures 3 and 4, it can readily be seen that percentage sulfur removal is inversely proportional to space velocity.

Additives were tried with solid sodium hydroxide treatments. Water and isopropyl alcohol were maintained emulsified in the feed stock in amounts equivalent to 2 mol per cent of the sodium hydroxide charged in the column. It was thought that such additives would provide for better ionization of the mercaptans, if there was any, and possibly activate the surface of sodium hydroxide by bringing clean surface into the reaction medium.

The treating bed in the aluminum chloride process contained,

as its lowermost and its uppermost sections, pellets of sodium hydroxide in amounts equivalent to 10 per cent of the anhydrous aluminum chloride charged. This was because the desulfurizing action of aluminum chloride was found to improve by first treating the distillate with an alkali.

It is important to mention that hydrogen sulfide was distinctly liberated from the aluminum chloride-treated oil by shaking.

The product from runs 4, 5, 6, and 7 with aluminum chloride was centrifuged at 1700 rpm, giving a clear yellow with some reddish-tint cut and a black sludge in varying proportions; the ratio of light to heavy phase decreased as the temperature of the treatment increased.

The bulk product and the centrifuged oil from each run were always given a mild alkali after-wash, 20 per cent caustic soda solution, then washed with water and finally dried by filtration through anhydrous calcium chloride.

This mild alkali after-wash gave little effect, with the improvement in the percentage sulfur removal ranging from as little as 0.5 per cent to almost 7 per cent, increasing as the temperature of the treatment increases. Water washing of the sludge fraction from the centrifuge was found necessary in order to remove the fine particles of aluminum chloride that were carried over from the contacting apparatus. Removal of the last traces of water from the sludge was performed by an Oil Shale Research and Development procedure using a column of rock salt

at 160°F, followed by high-speed centrifugation. On the various fractions, tables 3 and 4 show some of the miscellaneous data that might prove useful to the discussion. Tables 5, 6, and 7 show, respectively, the ASTM distillations (D-158) for the feed stock, bulk product, and the centrifuged oil of runs 5 and 7.

The aluminum chloride desulfurization process was tested for applicability to other kinds of feed stocks. The original feed stock was blended in equal parts by volume with a highly waxy lighter distillate (36.5° API) with a sulfur content of 0.412 wt-per cent. The resultant blend was 30.2° API gravity and 175 wt-per cent sulfur. Operating conditions of run number 5 were used; experimental results are as presented in table 8. It might be observed that the desulfurization action of anhydrous aluminum chloride is greatly enhanced by changing the content and form of sulfur in the treated distillate.

Table 1. Data and experimental results of solid sodium hydroxide treatments

Run	Space Velocity w/w/hr	Temperature OF	Additives	Sulfur Content of Product wt-% (±0.041)	Sulfur Removal % (±0.92)
1	5	330	-	2.665	6
2	5	480	-	2.618	7.5
3	10	330	-	2.699	4.8
4	2.5	460	-	2.614*	7.8
5	5	430	2 mol-% H ₂ O	2.633	7.1
6	5	420	2 mol-% i-propanol	2.721	4
7	2.5	425	2 mol-% H ₂ O	2.618	7.5

Feed: 2.835 wt-% sulfur*

*average of two determinations

Table 2. Data and experimental results of anhydrous aluminum chloride treatments - bulk product

Run	Space Velocity w/w/hr	Temperature °F	Sulfur Content of Product wt-% (± 0.034)	Sulfur Removal %, (± 0.67)	g-AlCl ₃ consumed per 650 g gas oil treated
1	5.5	325	1.793	35.5	-
2	5	250	1.85*	33.5	-
3	5.5	190	2.38	14.5	-
4	3.5	265	1.64	41	-
5	2.5	300	1.27*	54.5	82.5
6	2.5	350	2.04*	26.8	-
7	2.5	315	1.5	46.2	-

Feed sulfur content = 2.78 wt-%*

*average of two determinations

Table 3. Miscellaneous data with aluminum chloride treatments -
bulk product

Run	Sp. Gr. °API	Viscosity Saybolt Universal Seconds		Viscosity Index
		100°F	210°F	
1	27.3	149.4	45	17.65
2	27.7	161.8	42.1	44.6
3	25	157.3	42	50
5	30	144.1	43.2	116
7	27.8	147	42.5	86.5

Feed: Sp. Gr. = 23.8°API

Viscosity, Saybolt Universal Seconds = 225 at 100°F
42.5 at 210°F

Viscosity Index = -109

Table 4. Sulfur content and miscellaneous data on centrifuged fractions from aluminum chloride treatments

CENTRIFUGED FRACTION		RUN			
		4	5	6	7
Light Phase	Sulfur Content, wt-%, (+ 0.02)	0.76	0.665	0.417*	0.647
	Sulfur Removal, %, (+ 2.35)	72.5	76.2	85	77
	Sp. Gr., °API	31	31.5	33	31.5
	@ 100°F	115.4	114	110	116
	Viscosity, S.U. sec				
	@ 210°F	40	40	39.5	40
	Viscosity Index	73	77.5	65	71
Vol-% in Bulk Product	75	72	35	55	
Sludge	Sulfur Content, wt-%	5	5	-	-
	Vol-% in Bulk Product	25	28	65	45

*average of two determinations

Table 5. ASTM distillation of feed stock for the aluminum chloride treatments

Temperature °F	Percent Volume Distilled
482	IBP
508	2
516	3
525	4
534	5
543	7.5
553	10
574	15
588.5	20
602	30
608	40
606	50
599	60
588	70
580	80
-	discontinued

Table 6. ASTM distillation of bulk product from aluminum chloride treatments, runs 5 and 7

Temperature °F	Percent Volume Distilled
251	IBP
427	2
462	3
481	4
498	5
516	7.5
531	10
541	15
542	20
542	25
574	30
560	35
560	40
494	50
452	60
-	discontinued

Table 7. ASTM distillation of centrifuged clear oil from aluminum chloride treatments, runs 5 and 7

Temperature °F	Percent Volume Distilled
246	IBP
390	2
430	3
470	4
488	5
518	7.5
532	10
552	15
564	20
568	30
568	40
558	50
524	60
520	70
518	80
-	discontinued

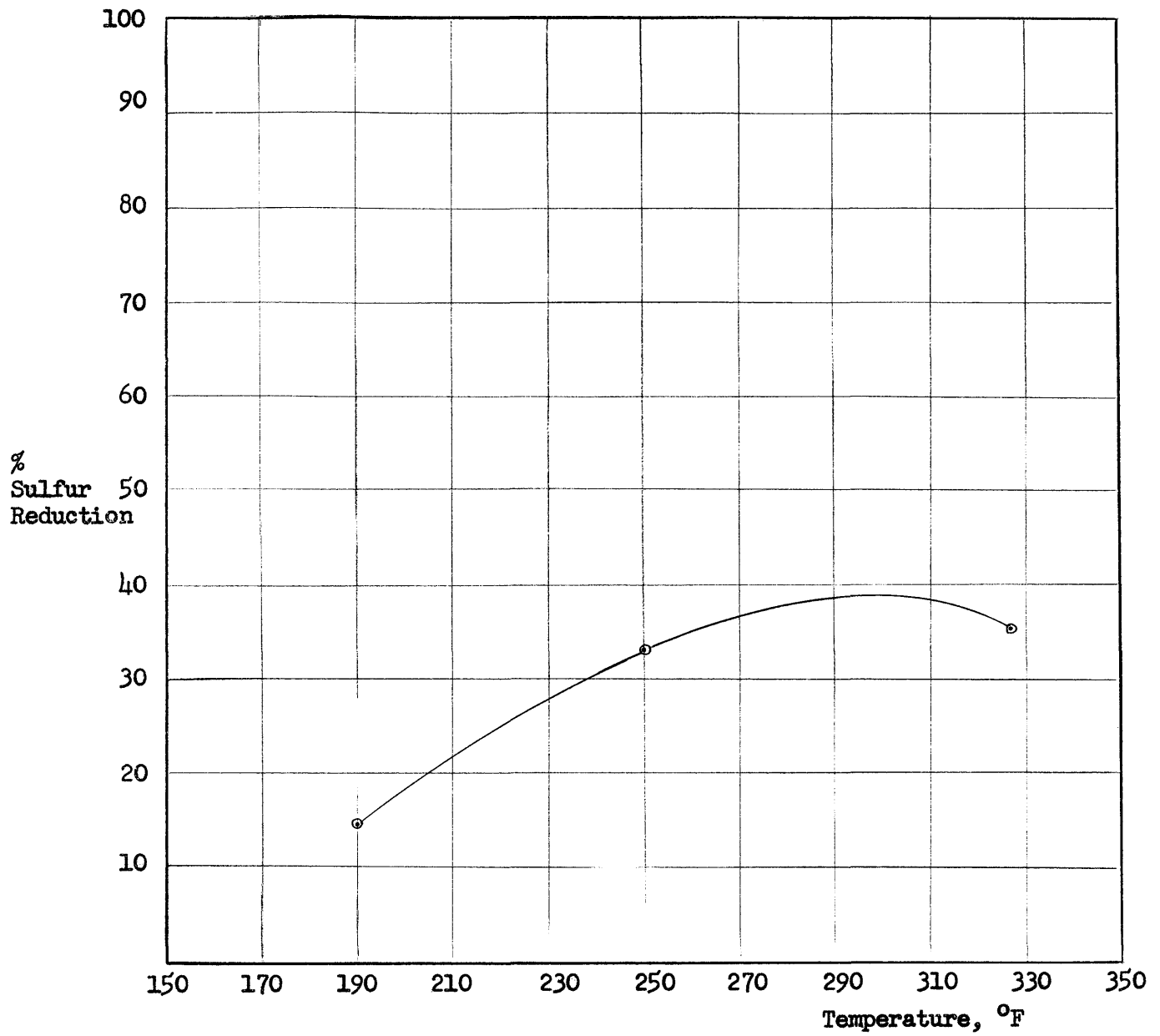


Figure 3. Percentage sulfur removal vs temperature, aluminum chloride treatment runs 1, 2, and 3 - bulk product

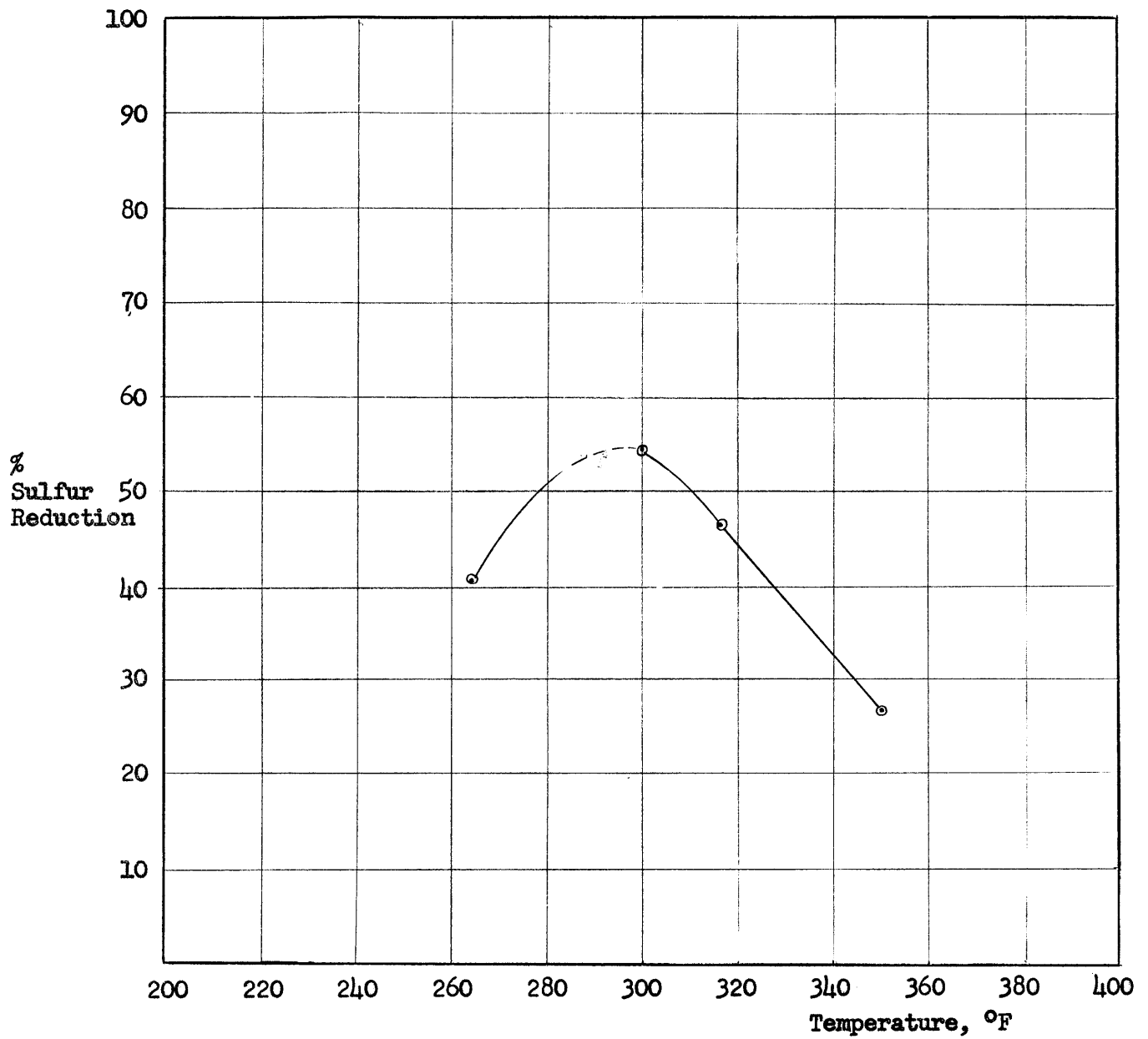


Figure 4. Percentage sulfur reduction vs temperature, aluminum chloride treatment runs 4, 5, 6, and 7 - bulk product.

ANALYTICAL PROCEDURES

The analytical work involved in this investigation comprises two quantitative determinations, namely, the determination of sulfur contents and the determination of the consumption of anhydrous aluminum chloride.

Sulfur Content Determination

The Institute of Petroleum quartz tube method, designated as IP 63/55 tentative, was chosen for the determination of sulfur content. It is a simple, relatively fast method adapted to less volatile petroleum products. The apparatus assembly, essentially as shown in figures 5 and 6, consists of:

I. Combustion unit:

i) Combustion tube: of clear fused quartz, 18 mm O.D. and 540 mm long. A section of the tube, 110 mm long, is packed with quartz particles which are held in place by two fused-in perforated quartz plates.

ii) Combustion boat: of unglazed porcelain, 10-ml capacity, Coors No. 6.

iii) Furnace: A Hevi Duty Electric Co. furnace type 123-2, serial No. 45632, capable of maintaining the quartz filled section of the combustion tube at 1742 - 1832°F (950 - 1000°C).

iv) A chromel-alumel thermocouple, in a porcelain socket lying along the combustion tube in the packed portion, measures the temperature and is connected to a Brown Temperature indicator calibrated from 0 to 2000°F.

II. Absorption system consisting of two Pyrex vessels with sintered glass partitions.

III. Water-aspirator connected to a splash head in the absorption system, capable of drawing air through the set-up at a rate consistent with the proper rate of volatilization of the sample in the combustion boat; air rate is mostly in the order of 2.5 - 3 liters per minute.

IV. Air purification trains: consisting of six vessels in the following order:

- i) Absorption tower; packed with silica gel.
- ii) Wash bottle; containing 200 ml of 50 wt-% sulfuric acid solution.
- iii) Wash bottle; empty.
- iv) Wash bottle; containing 200 ml of 30 wt-% sodium hydroxide solution.
- v) Wash bottle; containing 200 ml of distilled water.

vi) Wash bottle; empty.

V. Miscellaneous items, as:

1. Bunsen burner
2. 25-ml burette graduated in 0.05-ml divisions
3. Volumetric flasks and pipets

Materials:

1. Hydrogen peroxide, 30% w/v
2. Sulfuric acid, 1.84 sp. gr.
3. Sodium hydroxide, A. R.
4. Fresh silica gel, gas adsorption quality
5. Methyl purple indicator in an aqueous solution
6. Sodium carbonate, A. R.

Sample: materials containing over 2 wt-% sulfur, use 0.2 to 0.3 grams.

Outline of Method:

The sample, carefully vaporized by gentle heating in the combustion boat, is carried by a stream of purified air through the quartz-particle filled portion of the combustion tube. The latter is maintained at 1760°F. The products of complete combustion are absorbed in a freshly prepared 3% w/v hydrogen peroxide solution. The sulfuric acid thereby formed is determined volumetrically by titration with a standard solution of sodium hydroxide.

The method originally recommends duplication of the combustion and absorption units in the set up for simultaneous blank determination. This requirement, however, was satisfied by occasional determination

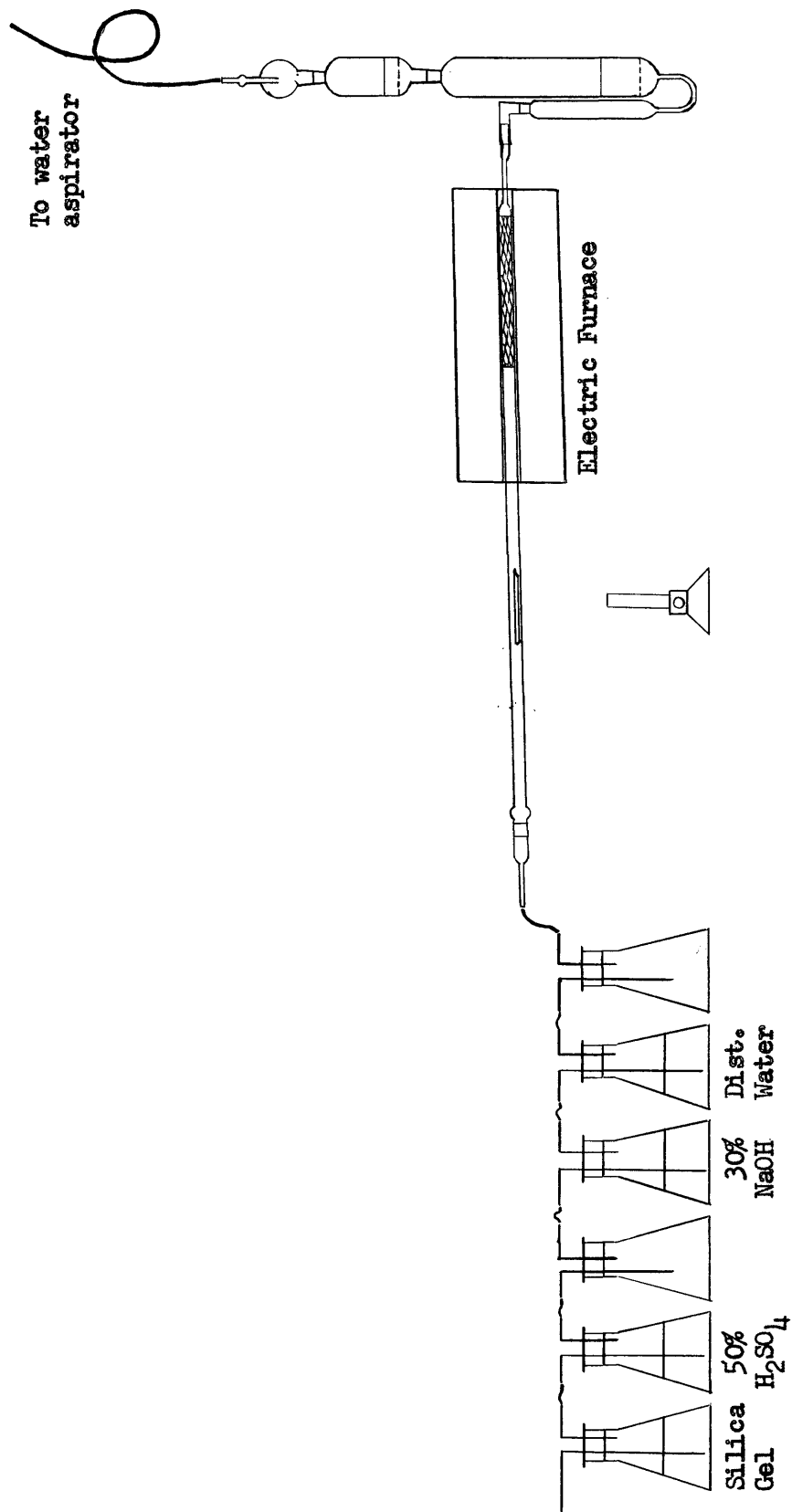


Figure 5. Sulfur Content Determination Flow Diagram

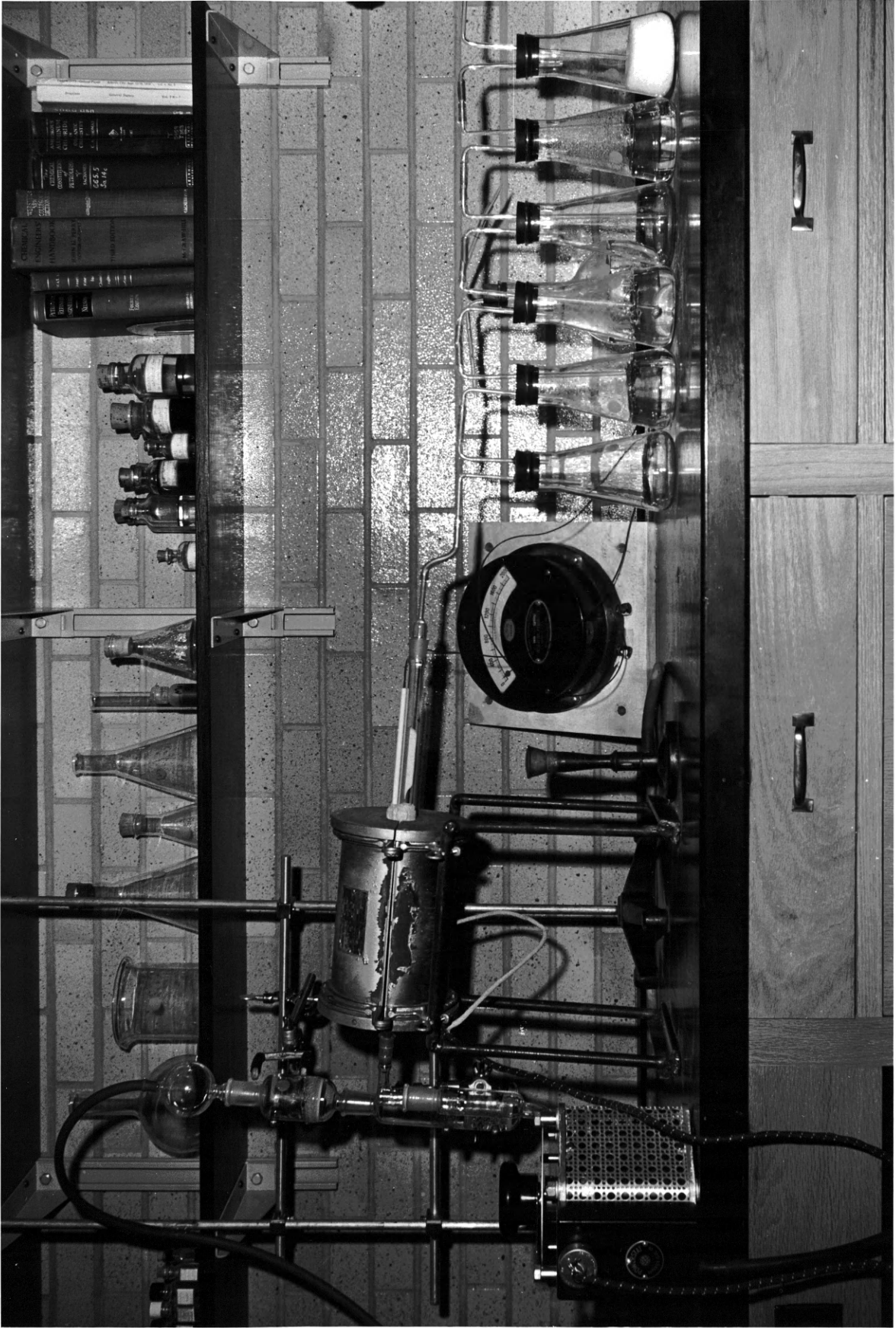


FIGURE 6. SULFUR CONTENT DETERMINATION APPARATUS

of the blank separately under identical conditions. Duplicate determinations were made for feed stocks and occasionally, when the need arose for other determinations, and they were found to be well within the repeatability limits of the method. For a sample calculation and precision of the method, refer to the appendix.

Determination of Aluminum Chloride Consumption

Material remaining in the contacting bed in run number 5, after the treatment of 650 g gas oil desulfurized to 54.5 per cent, was obtained in solution using 6N hydrochloric acid. The volume of the solution, after the elimination of the last traces of oil, was made up to 1430 ml.

Aluminum chloride was determined through the ammonia precipitation of aluminum as the hydrated oxide, and the subsequent determination of aluminum as Al_2O_3 (Vogel, 1951, p. 411).

Procedure

A 10-ml sample of the acidic aluminum chloride solution is mixed with 200 ml of water and 5 g of pure ammonium chloride with a few drops of methyl red indicator and heated just to boiling. Pure dilute ammonia solution (1:1) is added dropwise until the color of the solution changes to distinct yellow. The solution is then boiled for 1 to 2 minutes, and immediately filtered through a quantitative filter paper. The precipitate is then washed with hot 2 per cent ammonium chloride solution. In a previously ignited silica crucible, the precipitate is dried,

charred, and ignited. Crucible and content are allowed to cool in a desiccator and finally weighed.

Calculation:

$$\text{Sample} = 10 \text{ ml}$$

$$\text{Weight of Al}_2\text{O}_3 = 0.18 \text{ g}$$

$$\text{Weight of Aluminum} = (0.18) (54/102) = 0.0952 \text{ g}$$

$$\text{Total Aluminum} = (0.0952) (143) = 13.62 \text{ g}$$

$$\text{Aluminum Chloride in solution} = (13.62) (133.5/27) = 67.5 \text{ g}$$

So that, aluminum chloride consumed per 650 g oil, 54.5% desulfurized:

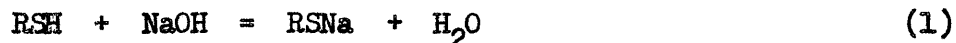
$$150 - 67.5 = 82.5 \text{ g}$$

Where 150 g anhydrous aluminum chloride were originally charted in the contacting column.

DISCUSSION OF RESULTS AND CONCLUSIONS

It may well seem appropriate to state at the beginning that the sulfur content of heavy petroleum distillates can successfully be reduced through catalytic action, in the absence of a hydrogen supply or gas recycle. However, highly active materials are required to overcome the inertness of the kind of sulfur compounds present in these fractions.

The use of sodium hydroxide in this investigation was based upon the premise that part of the sulfur content of the gas oil could be present in the form of mercaptans. Results presented in table 1 may be considered to account for the fact that it is only just a small part of the sulfur content of the oil that is in the form of mercaptans. With equal validity, however, sodium hydroxide could have reacted with those mercaptans to form mercaptides in accordance with the equation



With the hot water after-wash and in presence of air those mercaptides

would readily oxidize to disulfides according to



The disulfides liberated would normally remain in the oil phase.

Anhydrous aluminum chloride can readily be shown, through the data of tables 2, 4, and 8, to have proved its influence as a desulfurizing agent for high-boiling petroleum products. It should be emphasized that a 50 per cent sulfur reduction in the bulk product with an oil of 2.78 wt-per cent sulfur content means a removal of 1.39 wt-per cent sulfur. The last figure can best be appraised when it is remembered that drastic operating conditions along with an excessive consumption of hydrogen are required for the catalytic hydrodesulfurization to attain the same effect. Furthermore, a considerable degree of molecular breakdown through hydrogenation usually occurs in the catalytic hydrodesulfurization process, whereas the extent of cracking with the aluminum chloride desulfurization was not more than 5 vol-per cent distilled below the initial boiling point of the feed stock, as can clearly be seen in tables 5, 6, and 7. The API gravity is still another consideration in this respect, the change being only about 5 degrees between the feed stock and the bulk product, which could even be due mostly to the reduction in sulfur content. However, the ASTM distillations in tables 5, 6, and 7 also indicate that the aluminum chloride desulfurization process yields a product which is more susceptible to cracking than the feed stock. The cracking vapor temperature has been lowered from 608°F for the feed stock to 542 and 568°F for the bulk product and the

centrifuged clear oil, respectively. The difference in the cracking temperatures for the two cuts of product is due to the fact that heavier distillates require lower cracking temperatures.

The mechanism of aluminum chloride desulfurization reactions has been attributed in earlier discussions to the formation of an addition complex between the aluminum chloride and the sulfur-bearing hydrocarbon molecules at low temperatures, and to a degree of cracking at higher temperatures. The formation of the addition complex can readily be evidenced through the sharp change in viscosity index from a highly naphthenic negative for the feed stock, -109, to an intermediate-base positive for the product. The sulfur content of the gas oil, being predominantly associated with polycyclic naphthenes and aromatics, has been reduced through the formation of a polymerized addition complex which was subsequently separated, in its greater part, as a heavy asphaltic sludge for the centrifuged product, and to a lesser extent, decomposed and removed by water washing for the bulk product. If the formation of the addition complex would account for the sulfur removal, it would certainly also account for the reduction in the naphthene and aromatic content, and hence, for the resultant change in viscosity index.

The mild alkali after-wash given to the aluminum chloride-treated oil gave but little effect; that effect becomes fairly pronounced as the temperature of the desulfurization run increases. This experimental observation indicates that sodium hydroxide solution is no better than

water for decomposing the addition complex and carrying out the newly formed simpler sulfur compounds. Equations 1 and 2 may furnish the grounds upon which such an observation could be explained. However, with higher temperature desulfurization treatments, the mild alkali after-wash did have some effect; an improvement in the desulfurization of almost 7 per cent over that of the water-washed product was obtained in run no. 1. This is because hydrogen sulfide constitutes most of the newly formed simpler sulfur compounds because an enhanced degree of cracking takes place at higher temperatures.

The effect of temperature on the aluminum chloride desulfurization process has already been shown to be due to the creation of regions where anhydrous aluminum chloride would exercise its desulfurizing action differently. The extent of sulfur removal through the addition complex formation, or through cracking would then be taken as a measure to the effect of the different temperature levels. There is, necessarily, an optimum at which the extent of desulfurization due to both kinds of reaction mechanism would be most pronounced. Figures 3 and 4 show that at too low a temperature, neither one of the two reaction mechanisms can start, and at too high a temperature, the percentage sulfur removal drops. At higher temperatures, cracking takes place to a considerable extent, and resultant polymerization and carbonization not only make it difficult to decompose and remove the liberating sulfur compounds, but also limit the yield of clear oil to a low proportion. An optimum temperature of 300°F at a consistent space velocity for the aluminum

chloride desulfurization process seems proper.

The data and results presented in table 2 can be divided into two, more or less constant space velocity groups. Examination of this set of data and by reference to figures 3 and 4 would clearly indicate a definite influence for the space velocity. The percentage of sulfur removal can readily be seen to be inversely proportional to space velocity.

The aluminum chloride desulfurization process proved quite capable of handling different types of feed stocks at different levels of sulfur content. The results in table 8 indicate that a 63 per cent sulfur removal in the bulk product could be attained. It is interesting to point out that the blending component, used with the original feed stock in equal parts by volume, is a highly waxy residue, and yields a blend which is markedly paraffinic with a viscosity index of 193. The ease with which the desulfurization of this kind of feed stock took place could very well then be understood to be due to the ease with which acyclic saturated hydrocarbons break into lighter paraffinic compounds and unsaturated derivatives which can readily form the aluminum chloride addition complex. Conversely, it might also be understood that the aluminum chloride process would have its most promising success with feed stocks of a paraffinic base.

As indicated in table 2, 82.5 g of anhydrous aluminum chloride disappeared upon the treatment of 650 g of oil desulfurized to 54.5 per cent in the bulk product. All efforts were made in order to

minimize the carryover of fines from the contacting bed, but in spite of this, the presence of aluminum chloride particles in the recovered product was quite noticeable when the caustic soda and water wash was given to the material. Therefore, in closely controlled operations, the consumption of aluminum chloride would, perhaps, never be more than 10 per cent of the feed stock, for the same level of sulfur reduction.

For a consumption of 10 wt-per cent, the cost of desulfurizing a barrel of the 23.8-API- gravity feed stock to 54.5 per cent, is \$1.26 at the current price of technical-grade aluminum chloride of \$3.95 per 100 pounds.

Various means have been devised for the recovery of aluminum chloride from the centrifuged sludge (Thomas, 1941, p. 861). Treatment of the preheated sludge with a stream of hot chlorine or hydrogen chloride leads to the reformation and volatilization of the aluminum chloride. Another method consists of washing the centrifuged sludge with gasoline to remove the oil which it carries, and the subsequent treating with sufficient water to hydrate the aluminum chloride and form a concentrated solution. The solution obtained is then heated until decomposed into alumina and hydrogen chloride at a low red heat. Other methods deal with the volatilization of aluminum chloride by heating the sludge to about 750°F in a rotating furnace. Still another approach to recover aluminum chloride consists of roasting the sludge with a limited access of air to form aluminum oxide which is electrolyzed to yield aluminum. Still a different approach to the recovery is through the production of

zinc chloride; by heating a mixture of zinc oxide and the aluminum chloride-containing sludge sufficiently, zinc chloride is formed and vaporized.

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APPENDIX

The sulfur content determined by the quartz tube method is calculated through the following formula:

$$\text{Sulfur Content, wt-\%} = \frac{16}{1000} \frac{N(V-C)}{W} \times 100$$

where: N = normality of the sodium hydroxide solution

V = milliliters of standard sodium hydroxide solution required for titration of absorbent containing combustion products

C = milliliters of standard sodium hydroxide solution required for titration of the hydrogen peroxide reagent in the same volume as used in the absorption vessels

W = weight of oil sample in grams

$$\frac{16}{1000} = \left(\frac{S}{H_2SO_4} \right) \left(\frac{H_2SO_4 \text{ equivalent-wt}}{1} \right) = \left(\frac{32}{98} \right) \left(\frac{49}{1000} \right)$$

Precision: Duplicate determinations should not differ by more than the following:

Sulfur Content	Repeatability	Reproducibility
0 - 1.0%	0.1	0.1
over 1.0%	0.10 0.04A	0.10 0.08A

where A is the arithmetic mean.

Sample calculation:

The determination of sulfur content of the bulk product from run no. 2 will be considered.

First determination:

$$\begin{aligned} W &= 0.28 \text{ g} \\ V &= 3.15 \text{ ml} \\ C &= 0.07 \text{ ml} \\ N &= 0.104 \end{aligned}$$

$$\text{Sulfur content, wt-\%} = \frac{(1.6) (0.104) (3.15 - 0.07)}{(0.28)} = 1.832$$

Second determination:

$$\begin{aligned} W &= 0.245 \text{ g} \\ V &= 2.812 \text{ ml} \\ C &= 0.071 \text{ ml} \\ N &= 0.104 \end{aligned}$$

$$\text{Sulfur content, wt-\%} = \frac{(1.6) (0.104) (2.812 - 0.071)}{(0.245)} = 1.867$$

Precision analysis:

$$\text{Arithmetic average} = \frac{1.832 + 1.867}{2} = 1.849$$

$$\begin{aligned} \text{maximum allowable repeatability difference} &= \\ 0.10 + (0.04) (1.8495) &= 0.17398 \end{aligned}$$

$$\begin{aligned} \text{actual difference between duplicate determinations} \\ 1.867 - 1.832 &= 0.035 \end{aligned}$$

$$\text{actual difference to maximum allowable difference, \%} = 20$$

Along similar lines, and on basis of the last scale, the precision limits appearing in tables 1, 2, 4, and 8, were estimated.