CANADA

DEPARTMENT OF MINES AND TECHNICAL SURVEYS, OTTAWA

MINES BRANCH
RESEARCH REPORT

R 30

PRICE 25 CENTS

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F. L. BOOTH, R. E. CARSON, K. W. BOWLES
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FUELS DIVISION

SEPTEMBER 5, 1958

Mines Branch Research Report R 30

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ABSTRACT

The desulphurization of coker distillates from separated Athabasca bitumen was investigated by hydrogenation over a cobalt molybdate-alumina catalyst. Five process variables--temperature, pressure, liquid hourly space velocity, hydrogen-to-liquid feed ratio, and sulphur content of the liquid feed--were examined. With one particular feed, a yield of over 100% of oil product having a sulphur content of 0.2% was obtained under the following conditions: 420°C (788°F), 1000 psi, 1.8 volumes of feed per volume of catalyst per hour, and 4500 cu ft of hydrogen per barrel of feed. With the same feed at a constant hydrogen-to-liquid feed ratio and a pressure of 1000 psi, a relation was established between temperature, space velocity, and the sulphur content of the oil product.

The rate of decline of catalyst activity due to coke deposition was also studied and it was found that at a pressure of 1000 psi little coking occurred at temperatures below 430°C (806°F). Above this temperature the coke deposition increased exponentially with the temperature.

The quality of the motor gasolines produced was a little below that of commercial regular grade gasoline, the gas oils were on the borderline of acceptability as diesel fuel, and the heavier distillates were usable as numbers 4 and 5 fuel oils or cracking and recycle stocks.

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[*] Senior Scientific Officers and [**] Senior Scientist, Fuels Division, Mines Branch, Department of Mines and Technical Surveys, Ottawa, Canada.

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INTRODUCTION

This report presents a comprehensive account of the experimental investigations performed by the Mines Branch on the hydrogenation, at pressures up to 1750 psi employing a cobalt molybdate-alumina catalyst, of coker distillate derived from separated Athabasca bitumen. A small proportion of the results have been previously reported (1) and are included in this report. To simplify the presentation, the theoretical aspects of hydrodesulphurization and the research conducted at 10,000 psi will be described in two subsequent reports of this series.

To put into proper perspective the research associated with the conversion of Athabasca bitumen into marketable fuels and chemical products, it is essential to remember that this work forms an integral part of the program to ensure an adequate future supply of energy for Canada. Coal, oil, gas and uranium are the principal sources of this energy, and the relative importance of each will constantly vary, depending on economic and strategic factors.

The fundamental problem associated with the conversion of low grade oils and coal into synthetic liquid fuels is a three-part one, consisting of finding the most economical means of eliminating foreign atoms, such as oxygen, nitrogen, and sulphur; reducing the molecular weight; and adjusting the carbon-to-hydrogen ratio to values acceptable for the desired application. All these essential steps may be accomplished by high pressure hydrogenation. In

Germany during World War II the high pressure hydrogenation of coal and coal tar, which is known as the Bergius process, was developed on a large scale as an essential military measure. This process has not been economically attractive in North America, owing to the relative abundance of high quality petroleum.

Because of the shortage of petroleum which prevailed in Western Canada during the war, the Universal Oil Products Company, of Chicago, Illinois, was asked by the Dominion Government to evaluate Athabasca bitumen as a feed stock for conventional refining. This evaluation (2) indicated that the more valuable products such as gasoline and diesel oil were of poor quality and were obtained in low yields. The relatively large amount of sulphur present in the form of stable ring structures posed a serious refining problem if acceptable products were to be manufactured at competitive costs. The recognition of the inadequacy of conventional refining led the Mines Branch to study, on a pilot plant scale, various methods of improving the technique and reducing the cost of hydrogenation.

OUTLINE OF PREVIOUS RESEARCH ON THE HYDRODESULPHURIZATION OF PETROLEUM FRACTIONS

The literature relating to the desulphurization of petroleum fractions has been reviewed in the form of an annotated bibliography up to 1951 (3). This survey includes a great variety of desulphurization methods. On the other hand, the literature relating to the removal of sulphur by hydrogenation is much less voluminous, and is confined, to a considerable extent, to gasolines and low boiling products (4-16). The following review gives some of the principal papers in this field and describes the operating conditions frequently employed.

Byrns, Bradley and Lee (4) of the Union Oil Company of California catalytically desulphurized gasoline fractions of high organic sulphur content with and without hydrogen. They found that the addition of hydrogen had a marked effect upon the sulphur reduction and the catalyst life, and that hydrogen pressures of 250 psi gave better results than hydrogenation at atmospheric pressure. Of the various catalysts investigated, cobalt molybdate was found to be the most active. This catalyst was used either alone, or supported on alumina as a carrier. By this process the sulphur content of gasolines could be reduced from initial values of from 3 to 4% to less than 0.01%. Hendrics et al (17) successfully extended this process to the treatment of two Santa Maria gas oils, employing cobalt molybdate on alumina as the catalyst. One was a 33° A.P.I. virgin gas oil with 2.3% sulphur, and the other a 20° A.P.I. coker gas oil containing 3.6% sulphur. Further development of the process was reported by Berg and co-workers (18), who conducted pilot-plant studies on a coker distillate and on a heavy coker gas oil containing 3.07 and 4.15% sulphur, respectively. Both of these oils were derived from Santa Maria Valley crude oil. Berg et al stated that 650°F was the lower limit for effective desulphurization, and that above 750°F high boiling hydrocarbons underwent excessive destructive hydrogenation with a resultant increase in hydrogen consumption and coke formation and decrease in oil yield. A spectacular reduction in the sulphur content was noted with increasing pressure, a linear decrease taking place from 2.7% in the oil product at 150 psi to 0.45% at 450 psi. The optimum space velocity and hydrogen flow rate were found to be 1.0 volume of oil per volume of catalyst per hour and 3500 to 4000 cu ft of hydrogen per barrel of charge, respectively. The light products were suitable for motor gasoline blending, and the heavy products for reforming or cracking stock.

Hughes, Stine and Faris (19), of the Standard Oil Company of Ohio, also desulphurized heavy petroleum oils, using the cobalt molybdate-alumina catalyst of the Union Oil Company. They achieved a reduction of the sulphur in gas oils of high sulphur content to levels equal to those of gas oils from sweet crudes. The hydrodesulphurizations were performed under operating conditions similar to those reported by Hendrics et al and Berg and co-workers, with the exception that a relatively low hydrogen flow rate of 1000 cu ft per barrel of oil feed was found to be sufficient. The desulphurization of a 500°F reduced West Texas crude oil was also accomplished under the following operating conditions: 750°F, 400 psi, 0.5 volume of oil per volume of catalyst per hour, and 2000 cu ft of hydrogen per barrel of charge.

Hale, Simmons and Whisenhunt (20) of the United States Bureau of Mines desulphurized a crude oil containing 2% sulphur, reducing the sulphur content to 0.17 %. The catalyst used was cobalt molybdate deposited on bauxite, and the following operating conditions were employed: 750°F, 225 psi, 0.33 volume of oil per volume of catalyst per hour, and 1600 cu ft of hydrogen per barrel of feed.

Hoog (21) of the Royal Dutch Shell Company studied the kinetics of the catalytic hydrodesulphurization reaction, using a Middle East gas oil and a cobalt molybdate-alumina catalyst. The temperature was held constant at 707°F but the pressure was varied between 160 and 735 psi, the space velocity between 0.5 and 9.0 volumes of oil per volume of catalyst per hour, and the hydrogen flow rate between 4,000 and 35,000 cu ft per barrel of oil charge. In all the experimental work, no decline in the catalyst activity and no cracking of the oil were noticed. The results of this work were analyzed and correlated by computing a first order reaction rate constant.

Hoog (22) also described a procedure for continuously hydrodesulphurizing various sulphur-bearing oils, including heavy, waxy and refractory oils, using a molybdenum oxide catalyst promoted by a minor amount of chromium oxide and supported on activated alumina. Temperatures of 250° to 425°C and hydrogen recycling rates of 100 to 200 cu ft per barrel of oil were employed. Pressures of 600 to 1000 psi were found to be the most suitable.

Hoog, Klinkert and Schaafsma (23) described the Shell

"Trickle" process, which employs low hydrogen recycling rates of 250 to 1500 cu ft per barrel of oil to obtain significant savings in capital and operating costs. The feed remains mostly in the liquid phase and "trickles" downward as a thin film over the catalyst particles. Although a variety of catalysts showed satisfactory selectivity with regard to desulphurization,a cobalt-molybdenum-alumina catalyst gave the best results. The preferred temperatures and pressures for 80 to 90% sulphur removal were 690° to 720°F and 600 to 750 psi. The space velocities used were 1.1 to 3.6 volumes of oil per volume of catalyst per hour. Leaving the hydrogen sulphide in the recycling gas was found to have no appreciable effect upon the extent of the sulphur removal.

The Anglo-Iranian Oil Company (24) has patented a process for "Hydrofining" residual oils over a cobalt molybdate-alumina catalyst at 750°F, 1000 psi, 1.0 volume of oil per volume of catalyst per hour, and 4000 cu ft of hydrogen per barrel of charge. Removal of 78% of the sulphur along with 60% of the vanadium was obtained during an operating period of 400 hours. The same company (25) has patented another process, in which a petroleum fraction with or without hydrogen is passed over a catalyst in the vapour phase, employing temperatures of 650° to 800°F.

Exceptionally low pressures of 25 to 500 psi, and space velocities of less than 10 volumes of oil per volume of catalyst per hour, were employed. The catalysts were stated to be metal sulphides and oxides, preferably those of Group VI, either singly or mixed together. Cobalt molybdate on alumina was given as a specific example.

The Anglo-Iranian Oil Company (26) has also developed the "Autofining" process for desulphurizing feed stocks ranging from natural and straight run gasolines to gas oils and diesel fuels. A plant has been erected at their refinery in Llandarcy, Wales, with a daily capacity of 500,000 gallons. This process, described by Jones (27) and Sherwood (28), utilizes a cobalt molybdate catalyst because of its effectiveness in dehydrogenating naphthenes and hydrogenating organic sulphur compounds. No make-up hydrogen is required as the hydrogen from the dehydrogenation of the naphthenes is sufficient for the conversion of the organic sulphur to hydrogen sulphide. The hydrogen-rich gas is separated from the oil product and recycled at a rate sufficient to maintain the necessary partial pressure of hydrogen in the reactor. The operating conditions used are: 750 to 800°F, 50 to 200 psi, 1 to 5 volumes of oil per volume of catalyst per hour, and 2000 to 4000 cu ft of recirculating gas per barrel of feed. This process is not normally applicable to residual fuel oils containing asphaltic substances.

Clark and co-workers (29) have developed a technically feasible process for the conversion of crude shale oil into specification-grade jet and diesel fuels by a combination of recycle coking and hydrogenation of the coker distillate over a cobalt molybdate catalyst at 835°F, 1500 psi, and 0.9 to 1.1 volumes of oil per volume of catalyst per hour. The product was composed of 60% jet fuel and 40% diesel fuel.

THE ORIGIN AND CHARACTER OF THE OILS USED IN THE HYDROGENATION EXPERIMENTS

One of the conclusions of the theoretical study of the hydrodesulphurization of coker distillates over the Union Oil Company's cobalt molybdate-alumina catalyst was that the rate of the process was controlled by diffusion. The implication of this finding was that the average molecular weight, and to some extent the molecular weight distribution of the oil fed to the catalyst, would have a bearing upon the rate of sulphur removal. Another factor that was known to have a profound influence upon the performance of the catalytic refining step was the quantity of mineral matter in the oil. These considerations make it desirable to discuss the origin and nature of the processes used to separate the bitumen from the sand.

For convenience, the bituminous sand area may be arbitarily defined as lying between W. Long. 111° and 112° and between N. Lat. 56° 30' and 57° 30'. All exposures of bituminous sand in this area lie within a radius of 80 miles of McMurray, which in turn is situated approximately 250 miles north of Edmonton. The deposits extend from just above the Boiler rapids, on the Athabasca river, north to the Firebag river. The bituminous sands are extremely variable so far as the concentration of the oil in the sand is concerned, but rich deposits of economic significance consist of a depth of 100 to 150 ft of bituminous sand containing 15% bitumen under a variable overburden up to 100 ft in depth. Although the composition of the bitumen in terms of the carbon, hydrogen and sulphur contents is remarkably constant over a wide area, it has been observed that as samples are taken along the Athabasca river from the southern extremity to the northern limit, a systematic change occurs in the viscosity and specific gravity. The magnitude of the change in viscosity is illustrated by the values for samples of Abasand and Bitumount bitumens, which amount to 600,000 and 6,000 poises, respectively, at 50°F (30). The specific gravity undergoes a small but significant change from 1.027 at 77°/77°F in the south to as low as 1.002 in the northern margin of the deposit. The bitumen discussed in this report came from two sources: the Bitumount quarry located 55 miles north of McMurray on the Athabasca river, and the quarry of Abasand Oils Limited at the junction of the Horse and Athabasca rivers in the immediate vicinity of McMurray.

Though much work has been done during and since World War II by various government and industrial organizations, in an effort to develop and improve the techniques that are required to pave the way for the utilization of the Athabasca bituminous sand as a source of commercial petroleum products, much remains to be done. This past work has been concerned with three major operations, namely: the mining of the bituminous sand, the separation of the oil, and the refining of the raw oil to yield marketable products.

During World War II, Abasand Oils Limited operated a quarry, a small separation plant using the McClave hot water separation process, and a conventional distillation refinery. The Alberta government subsequently operated a pilot plant at Bitumount, where it investigated the mining of the bituminous sand by open-cut methods and the separation of the oil by the hot water process (31, 32, 33). On a laboratory pilot plant scale, the National Research Council of Canada conducted research on the separation of the bitumen from the sand, using a fluidized coking process (34) as well as the distillation of oil separated by the hot water process (35). On the other hand, the Mines Branch of the Department of Mines and Technical Surveys, in Ottawa, studied the cold water separation process, employing bituminous sand obtained from the Abasand quarry (36). This was followed by a study of the dehydration and coking of the extracted bitumen (37), and the desulphurization of the coker distillate by means of catalytic hydrogenation.

On completion of the experimental work at Bitumount, the Alberta government engaged S. M. Blair to compare the various pilot plant processes being investigated by the provincial and federal agencies, and to estimate the relative processing costs. In his report (38), Blair gave an estimate of the investment and operating costs for the hot water, cold water and fluidized bed processes, on a scale of 20,000 bbl of bitumen per day. In view of the detailed description of these refining procedures presented in the Blair report, only the briefest statement is necessary here.

The hot water process consisted of adding the bituminous sand to water just below the boiling point, allowing the sand to settle, and skimming off the oil froth. A diluent oil was added to the froth, in a subsequent step, to facilitate the separation of the water and mineral matter. This was followed by flash dehydration and distillation to recover the diluent oil.

In the cold water process, a diluent oil, water, and a wetting agent were added to the bituminous sand and this was followed by mixing, settling, and skimming of the oil. The water and diluent were then removed by combined flash dehydration and topping, in one operation.

The fluidized bed process consisted of distillation to coke from a fluidized bed of sand, heat being supplied by the combustion of the coke.

From the point of view of the subsequent catalytic desulphurization step, the two most important physical properties of the coker distillate are: specific gravity, and mineral matter content. The specific gravity increases with increasing molecular weight, and as the sulphur is much more difficult to remove from the high-molecular-weight components, this value gives a rough measure of the difficulty of sulphur removal. The mineral matter content must be kept to a minimum, as it is deposited on the catalyst, decreasing the catalytic activity. The exact mechanism of this effect is not known, but there was evidence to suggest that the clay in the mineral matter promoted coke formation under the conditions employed. A comparison of the influence of the source of the bitumen, and the influence of the subsequent treatment, on the specific gravity and mineral matter content is presented in Table 1.

As may be seen from the analyses, the separated bitumen is a heavy viscous oil with a high sulphur content. The properties of the oil produced from the hot and cold water processes, after water and diluent removal, are very similar. The oils from both of these processes contained an appreciable amount of mineral matter. It should be noted that the properties of the oil, especially the specific gravity and viscosity, are affected by the efficiency of the diluent recovery at the conclusion of the separation process. If the diluent is not removed completely, the specific gravity and the viscosity will be lower than those of the bitumen. To overcome this difficulty, the values marked with a (c) in Table 1, for the viscosity and specific gravity of the bitumen, were calculated from the measured values of these properties on a 50%-by-weight mixture of kerosene and bitumen produced from the cold water separation plant. The specific gravities were calculated from the known value for kerosene, assuming no change in volume on mixing. The viscosity of the bitumen was calculated from the measured value of the kerosene blend and the known value for kerosene, employing the method of Wright (39).

The oil from the fluidized process, being a coker distillate,

TABLE 1

Analyses of Oils from Separation Processes

Material	Separated Bitumen			Coker Distillate		
Process	Cold Water		Hot Water	Cold Water	Fluidized (a)	
Deposit	Abasand	Bitumount	Clark(b)	Abasand	Abasand	Bitumount
Sp gr, 60/60°F	1.029(c)	1.012(c)	1.027	0.936	0.967	0.960
Viscosity at 100°F, cs	2,600,000(c)	17,000(c)	-	21.4	73.8	45.7
Water, wt %	trace	-	0.3	trace	nil	nil
Ash, wt %	6.6	-	4.5	0.1	0.1	trace
Sulphur, wt %	5.0	-	5.2	3.6	3.8	4.0
Carbon, wt %	77.5	-	79.0	84.3	-	83.8
Hydrogen, wt %	9.6	-	9.8	11.3	-	11.2
C/H ratio	8.1	-	8.1	7.5	-	7.5
Molecular weight	1165	-	-	322	421	368

(a) Filtered coker distillate.

(b) Separated bitumen obtained from experimental plant of K. A. Clark on Clearwater river in the vicinity of McMurray.

(c) Calculated from measured specific gravities and viscosities of blends of bitumen and diluent taken from the cold water separation plant. No correction was made for a small amount of mineral matter contained in the blends.

was lower in specific gravity, less viscous, and contained less mineral matter, than the bitumen separated by the water processes. The mineral matter content of the unfiltered fluidized coker distillate from Abasand bituminous sand was 0.6%. This quantity of mineral matter was too much to make a suitable feed for hydrogenation over a fixed bed catalyst, and consequently the coker distillate was filtered. The proportion of mineral matter in the unfiltered distillate was dependent on the efficiency with which the solids entrained in the gas stream leaving the fluidized coker could be removed by electrostatic precipitation.

The mineral matter in the oil produced from the cold and hot water processes also greatly exceeded the allowable limit for fixed bed hydrogenation. Pyrolytic distillation was selected as the most promising method for producing an acceptable feed. The advantage of this operation is that it provides a relatively cheap method for eliminating mineral matter, carbon, and to some extent sulphur, in the form of coke. By virtue of the combined action of distillation and thermal cracking, a distillate of lower viscosity, higher volatility, and more favourable carbon-to-hydrogen ratio is produced for subsequent hydrodesulphurization. The physical properties of this distillate, which will subsequently be referred to as coker distillate, are quite similar to those of the product from the fluidized coking process.

DESCRIPTION OF EXPERIMENTAL APPARATUS

The apparatus used for the desulphurization experiments was arranged as shown in Figure 1. Its function was to pass hydrogen and oil through a vertical bed of catalyst at controlled temperature, pressure, and feed rate. The main pieces of high pressure equipment were two feed vessels, a feed pump, a vertical cylindrical reaction chamber with heater, a water-cooled condenser, and a liquid product receiver. These were arranged in vertical sequence to permit the flow of liquid through the apparatus by gravity.

In the first part of the investigation, where low liquid feed rates were used, the oil was fed to the reactor by gravity. A measured volume of oil was charged to one of the feed vessels, made of 3-in. extra strong pipe of type 18-8 chromium-nickel stainless steel. This was approximately 2-7/8 in. inside diameter and 12-1/2 in. inside length, utilizing stainless steel lens ring closures at both flanged ends. With the hydrogen pressure balanced above and below the liquid in the feed vessel, the liquid flowed downward by gravity. The liquid feed rate was controlled by regulating its passage through a needle valve, and was estimated by observing through a sight glass the number of drops per unit time issuing from a pointed dropper. To permit continuous operation, two identical feed vessels were employed; while one supplied oil to the reactor, the other was recharged with feed. Both feed vessels were filled and run alternately.

When high feed rates were used, which could no longer be measured by counting drops, a feed pump was substituted for the feed vessels and the rate was determined by measuring, in a graduated

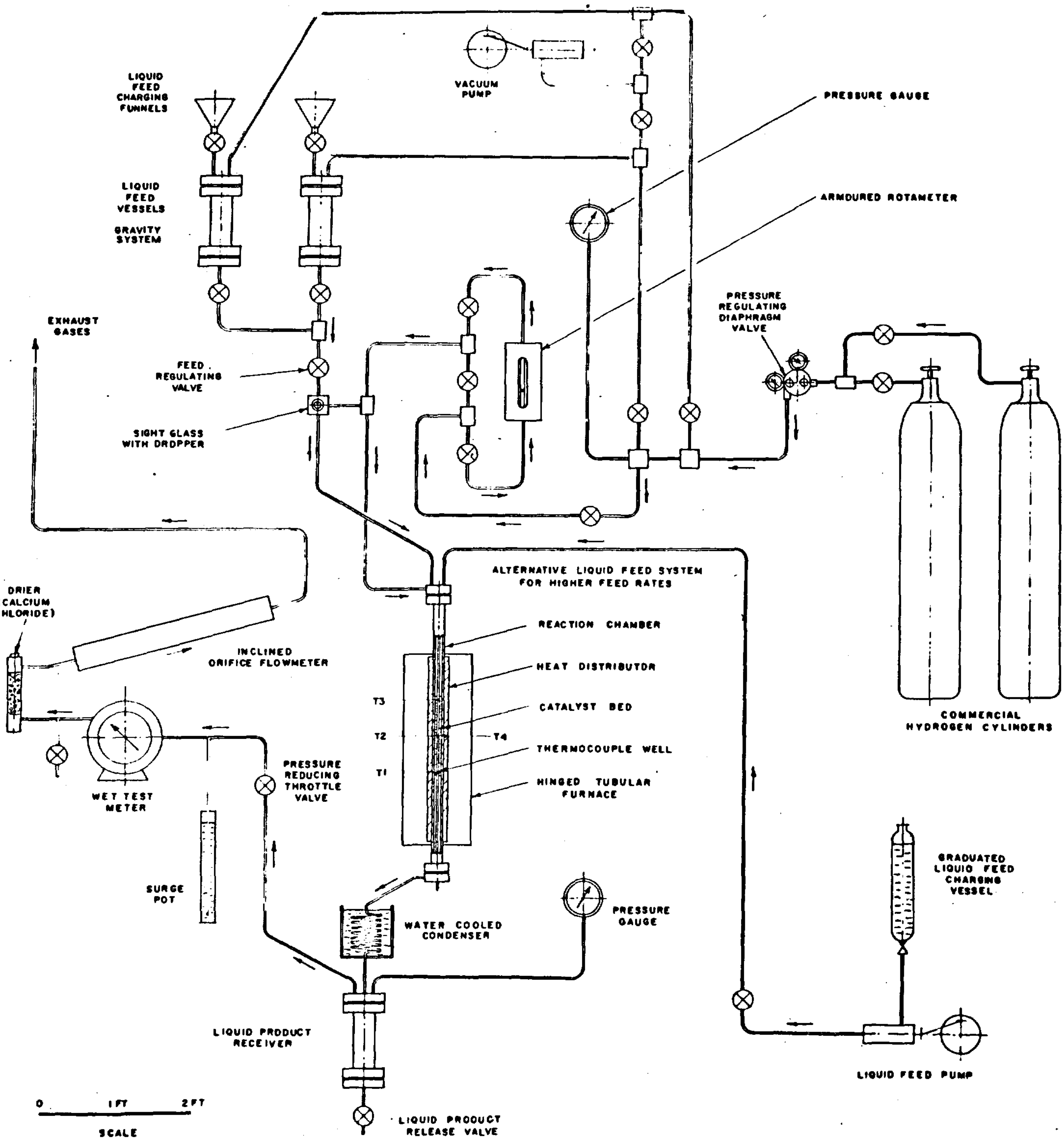

Figure 1 - Schematic diagram of hydrodesulphurization apparatus.

glass charging funnel, the volume of feed entering the suction side of the pump in a given time. The pump used was a variable stroke, positive displacement type capable of injecting the feed at pressures up to 10,000 psi, employing a piston diameter of 5/8 in. and a maximum stroke of 1-1/2 in.

The hydrogen feed was obtained in standard commercial cylinders, at a pressure of approximately 2000 psi, containing roughly 180 cu ft at atmospheric pressure and room temperature. The desired operating pressure was obtained by a pressure regulating diaphragm valve which maintained the pressure constant at a reduced value. A continuous flow of hydrogen was obtained by a piping and valve arrangement whereby a cylinder that was almost exhausted to the working pressure could be replaced instantaneously by a fully charged cylinder. The hydrogen feed rate was controlled by the rate of release of exit gases at the outlet end of the system. An instantaneous indication of the hydrogen feed rate was obtained from a high pressure flowmeter, of the rotameter type, which had been calibrated for various pressures.

The pressure on the system was measured with a Bourdon-type gauge--range, 0 to 8000 psi--which was placed in the hydrogen feed line. A similar gauge was located in the product line from the reaction chamber. Thus, any significant pressure loss in the reaction chamber due to plugging from coking or mineral matter deposition could be immediately detected.

The hydrogen and the liquid feeds passed down through vertical tubing and met at the top of the reaction chamber. This pressure tubing was of type 18-8 stainless steel, 1/4 in. outside diameter and 0.083 in. inside diameter. This tubing was used throughout the apparatus. All connections were made with union-type pressure fittings with conical seating surfaces.

The vertical reaction chamber was constructed of 1 in. double extra-strong steel pipe, type 18-8 stainless steel, approximately 19/32 in. inside diameter, and 46-1/2 in. inside length. Both flanged ends were sealed with stainless steel lens rings. For a length of 30 in. the chamber was enclosed by a split heat distributor of cast iron 3/4 in. thick, which was further enclosed by a hinged tube furnace rated at 3675 watts. The reaction chamber contained an axial stainless steel thermocouple well of 1/4 in. outside diameter tubing of 20-gauge wall thickness, which was inserted in the bottom or outlet end of the reactor and extended the entire length to the inlet end. The catalyst pellets were contained in the annular space between the thermocouple well and the inside wall of the chamber. They were supported by a stainless steel retaining ring, with drilled passages, which fitted over thermocouple well tube. The retaining ring was in turn supported by a formed piece of 1/16 in. diameter stainless steel rod extending to the bottom of the reaction space. Fifty millilitres of the pelleted catalyst occupied a length of approximately 13-1/4 in.

The desired temperature was maintained by a recording controller of the potentiometer type, operating a magnetic switch in series with the furnace heating element. The controlling iron-constantan thermocouple was inserted between the outer surface of the reaction chamber and the heat distributor, at the midpoint of the catalyst bed. The corresponding temperature, at the midpoint but within the catalyst bed, was recorded by a thermocouple in the well. Temperatures just within the bed at the top and bottom were measured by two additional thermocouples in the well.

The hydrogenated products flowed downward from the reactor through a condenser coil immersed in a cold water bath. The coil consisted of about six turns (6 in. diameter) of type 18-8 stainless steel tubing of 1/16 in. inside diameter with an equivalent length of 10 ft. From the condenser, the products entered the receiver, which was similar in construction to the feed vessels previously described. The liquid product which accumulated here was drained off through a needle valve.

The excess hydrogen and uncondensed gases passed off from the top of the product receiver continuously through another needle valve, the rate of release being used to control the hydrogen feed rate as previously mentioned. The rate of flow of these exit gases was measured by a wet test meter. With this arrangement of the apparatus, the exit gases were exhausted to the atmosphere and consequently wasted, but in actual large-scale practice they would be recirculated.

DESCRIPTION OF CATALYST

The catalyst used in this work was cobalt molybdate supported on an alumina base. It was supplied, through the courtesy of the Union Oil Company of California, in the form of 1/8 by 1/8 in. pellets and was designated as Type N. The analysis of this catalyst was reported by the Union Oil Company to be CoO 3.0%, MoO_3 8.6%, SiO_2 5.2%, and Al_2O_3 82.9%. The remaining 0.3% consisted of impurities in the alumina, primarily CaO, sulphate, Fe_2O_3, and Na_2O.

During preliminary experiments it was discovered that after regeneration the activity of the catalyst appeared to have increased slightly. Consequently, in all the experimental work described in this report, every fresh batch of catalyst was activated by heating in air for four hours at a temperature of 1000° to 1100°F.

DESCRIPTION OF FEEDS

Several liquid feeds were employed in the present experimental work. They are listed below and, for convenience in the subsequent discussion, will be distinguished by the letters A, B, C, and D.

Feed A was a filtered coker distillate from the flash cracking of the bitumen obtained by the cold water process from the Abasand bituminous sand quarry on the Horse river.

Feed B was a filtered coker distillate from the fluidized coking of bituminous sand mined in the Abasand quarry.

Feed C was a filtered coker distillate from fluidized coking of bituminous sand mined in the Bitumount area.

Feed D was a filtered 80% overhead fraction obtained from the distillation of feed C at 10 mm pressure to an endpoint of 684°F.

Feeds B, C and D were prepared and submitted by P. E. Gishler of the National Research Council. Feeds A and D were used throughout the greater proportion of the investigation, with only a relatively small proportion of the time being devoted to the study of the performance of feeds B and C as the catalyst activity declined rapidly with these feeds.

All the feeds were filtered in order to extract the mineral matter and any settled sediment. In the experiments on the variation of the process variables, glass wool on a 200-mesh screen was used. As this was not found suitable in the catalyst deterioration tests, a coarse filter paper was substituted which proved to be satisfactory.

Detailed analyses of feeds A and D and more limited analyses of feeds B and C are given in Tables 2, 3, 4 and 5.

GENERAL PROCEDURE OF EXPERIMENTS

A typical hydrogenation experiment was commenced by introducing hydrogen into the system until the pressure reached the operating level. Heat was applied from the electric furnace, and the hydrogen gas flow was started at approximately 3 cu ft per hour.

TABLE 2

Feed A - Distillate from Flash Cracked Abasand Bitumen Separated from Sand by the Cold Water Process

Specific gravity, 60°/60° F	0.936
Degrees A.P.I.	19.7
Viscosity at 100°F	
Kinematic, cs	21.35
Saybolt Universal, sec	103
Viscosity at 210°F	
Kinematic, cs	3.61
Saybolt Universal, sec	40
Pour point, °F	-30
Carbon residue (Conradson), % by weight	2.0
Water, % by volume	trace
Ash, % by weight	0.1
Sulphur, % by weight	3.6
Carbon, % by weight	84.4
Hydrogen, % by weight	11.3
Nitrogen, % by weight	0.04
Oxygen, % by weight (by difference)	0.6
Carbon/hydrogen ratio	7.47
Molecular weight	322

Distillation, Hempel method - approximate summary:

	% by Volume	Specific Gravity	Degrees A.P.I.	Viscosity, S.U., sec at 100°F
Light gasoline	0.7	0.754	56.2	-
Total gasoline and naphtha	6.4	0.795	46.5	-
Kerosene distillate	-	-	-	-
Gas oil	27.2	0.861	32.8	below 50
Nonviscous distillate	8.4	0.910-0.937	24.0-19.5	50-100
Medium distillate	7.4	0.937-0.953	19.5-17.0	100-200
Viscous distillate	14.4	0.953-0.976	17.0-13.5	above 200
Residuum	35.8	1.014	8.0	-
Distillation loss	0.4			

TABLE 3

Feed B - Distillate from Fluidized Coking of Abasand Bituminous Sand

Specific gravity, 60°/60°F		0.967
Degrees A.P.I.		14.8
Viscosity at 100°F		
Kinematic, cs		73.82
Saybolt Universal, sec		34.1
Viscosity at 210°F		
Kinematic, cs		7.86
Saybolt Universal, sec		52
Pour point, °F	below	-30
Carbon residue (Conradson), % by weight		7.0
Ash, % by weight		0.05
Sulphur, % by weight		3.8
Molecular weight		421

TABLE 4

Feed C - Distillate from Fluidized Coking of Bitumount Bituminous Sand

Specific gravity, 60°/60°F		0.960
Degrees A.P.I.		15.9
Viscosity at 100°F		
Kinematic, cs		45.7
Saybolt Universal, sec		207
Viscosity at 210°F		
Kinematic, cs		5.68
Saybolt Universal, sec		46
Pour point, °F	below	-30
Carbon residue (Conradson), % by weight		5.7
Ash, % by weight		0.02
Sulphur, % by weight		4.0
Carbon, % by weight		83.8
Hydrogen, % by weight		11.2
Nitrogen, % by weight		0.2
Oxygen, % by weight (by difference)		0.8
Carbon/ hydrogen ratio		7.48
Molecular weight		368

TABLE 5

Feed D - 80% Overhead Fraction from Distillation of Feed C

Specific gravity, 60°/60°F	0.935
Degrees A.P.I.	19.8
Viscosity at 100°F	
Kinematic, cs	15.25
Saybolt Universal, sec	78
Viscosity at 210°F	
Kinematic, cs	3.14
Saybolt Universal, sec	37
Pour point, °F	-20
Carbon residue (Conradson), % by weight	0.3
Ash, % by weight	0.03
Sulphur, % by weight	3.6
Carbon, % by weight	84.7
Hydrogen, % by weight	11.7
Nitrogen and oxygen, % by weight (by difference)	0.0
Carbon/hydrogen ratio	7.24
Molecular weight	311

Distillation, Hempel method - approximate summary:

	% by Volume	Specific Gravity	Degrees A.P.I.	Viscosity, S.U., sec at 100°F
Light gasoline	0.6	0.686	74.8	-
Total gasoline and naphtha	5.0	0.772	51.8	-
Kerosene distillate	-	-	-	-
Gas oil	29.3	0.883	28.8	below 50
Nonviscous distillate	15.0	0.924-0.949	21.6-17.6	50-100
Medium distillate	7.9	0.949-0.959	17.6-16.0	100-200
Viscous distillate	15.5	0.959-0.974	16.0-13.8	above 200
Residuum	27.1	0.990	11.4	-
Distillation loss	0.2			

When the desired steady operating temperature was reached, the hydrogen flow rate was readjusted and the flow of liquid feed was started and set at the desired rate.

Although the rotameter gave an indication of the hydrogen flow rate, the final figures recorded were those of the exit gas rate as obtained from the wet test meter at atmospheric pressure. In determining the hydrogen feed rate in cubic feet per hour, and the hydrogen-to-liquid feed ratio in cubic feet per barrel of liquid feed, it was assumed that the volume of the uncondensed gases was the same as the volume of the inlet hydrogen. Although these conditions probably did not prevail exactly, the approximation was considered sufficiently accurate, since the hydrogen consumed was only a minor fraction of the hydrogen fed and could be considered to be approximately equivalent to the hydrogen sulphide and uncondensed hydrocarbon gases resulting from the reaction and contained in the exit gases. Since the major portion of the reaction hydrogen is contained in the liquid product, the feed rate as measured by this method is less than the actual feed rate. However, it is estimated that the maximum discrepancy will be less than 10% of the measured rate. In the calculations, the average exit gas rate was obtained from the recorded total volume and the elapsed feeding time. This made possible an independent evaluation of the rates, for comparison against the average indicated rates obtained from the gas meter.

When gravity flow was employed, the liquid feed rate was indicated by the number of drops passing through a dropper visible through a sight glass. To facilitate the estimation of the desired flow rate in millilitres per hour, a relationship between drops per second and millilitres per hour was established, which was found to be non-linear and required a correction factor for pressure. To maintain the validity of this relation for feeds of different viscosity, an additional correction factor had to be determined. In the calculations, the average liquid feed rate was obtained from the total volume of feed and the elapsed time. When feeding by means of the feed pump, the length of the piston stroke was set to give the required flow rate. Again, the average feed rate was obtained from the total volume of feed withdrawn from the graduated cylinder on the suction side of the pump, and from the elapsed time.

The temperature of the controlling thermocouple and the temperature at the top, bottom and centre of the catalyst bed were recorded. The operating temperature was taken as the weighted average of the temperatures at the top, bottom and centre of the catalyst bed.

To prevent the residue from a previous experiment from contaminating the samples taken for analysis, the preliminary liquid product was withdrawn after the first half-hour of feeding. It was then measured and discarded. At the conclusion of an experiment, after the flow of liquid feed was discontinued the operating conditions were maintained for one-half hour to allow the apparatus to drain before completing the withdrawal of the liquid product. As all experiments (other than catalyst deterioration tests) were of only a few hours' duration, this liquid product was submitted in its entirety to the analytical laboratory for analysis. During catalyst deterioration tests, the liquid product was withdrawn periodically every three to six hours, depending on the feed rate. The total amount withdrawn each time was submitted for analysis.

As the reacting hydrogen was not measured directly, the hydrogen consumption was calculated by means of various mass balances. In order to simplify these calculations it was assumed that the product gases consisted of hydrogen sulphide and methane only. It was further assumed that the liquid feed contained no nitrogen or oxygen. It was considered that the error in the hydrogen consumption resulting from these assumptions was small because of the relatively low nitrogen and oxygen contents of the feed stock and because of the mild hydrogenation conditions which tend to suppress the formation of cracked hydrocarbon gases.

For the purpose of making the calculations the mass balance of the reacting substances may be stated explicity as follows:

$$\text{Oil feed and reaction } H_2 = \text{oil product} + H_2S + CH_4.$$

The amount of hydrogen sulphide was obtained from the sulphur balance, as the sulphur in the hydrogen sulphide is the difference between the total sulphur in the oil feed and the sulphur in the oil product. In a similar manner the amount of methane may be calculated from the carbon balance, as the carbon in the methane is the difference between the total carbon in the oil feed and the carbon in the oil product. The amount of reacting hydrogen was then obtained by difference from the equation of the mass balance of the reacting substances. The hydrogen consumption was expressed as the volume in standard cubic feet (60°F, 1 atmosphere) per barrel of liquid feed, as well as in terms of the weight percent of the liquid feed.

In calculating the sulphur and carbon balances, the sulphur content of the liquid feed and product was determined directly by the A.S.T.M. bomb method (40). On the other hand, the carbon and hydrogen were not determined directly by analysis, due to difficulty in obtaining sufficiently accurate values. Consequently, the hydrogen was calculated from the following relation (41):

$$\% H_2 = 26-15d,$$

where d is the specific gravity at 60°/60°F on a sulphur-free basis. The percentage of carbon was calculated as the difference between 100 and the hydrogen content. The carbon and hydrogen were then decreased proportionately to include the sulphur in the analysis. Confirmation of the reliability of the calculated values of the carbon and hydrogen was given by the good agreement with the analytical values for feeds A and B.

Regeneration of the catalyst in situ was accomplished in the following manner: Nitrogen, from a standard commercial cylinder, was throttled through a needle valve to a pressure of a few inches of water and conducted to the top of the reaction chamber through a calibrated orifice meter. Oxygen, supplied by compressed air at 90 psi, was likewise reduced in pressure, through a needle valve, to a similar value before passing to the top of the chamber. Since this operation was conducted at low pressure, rubber tubing was used for all connections. The exhaust gases from the bottom of the reaction chamber were discharged to the external atmosphere through a wet test meter.

In carrying out the regeneration, the reaction chamber was flushed with nitrogen to remove any hydrogen and then brought up to a temperature of 538°C (1000°F) with a current of nitrogen flowing through the chamber. When the operating temperature was reached and stabilized, the flow of air was started and increased and at the same time the flow of nitrogen was decreased. This operation was continued until the desired oxygen percentage was reached, all the while maintaining the temperature between 538° and 593°C (1000° and 1100°F) and the total flow rate at a constant value of approximately 5 cu ft per hour. If the temperature within the bed appeared to be rising to dangerously high values in the neighbourhood of 593°C (1100°F) which might damage the catalyst, it was reduced by decreasing the oxygen content. The nitrogen and total gas flows were recorded, the difference giving the approximate air flow. The temperatures were recorded at the same points as in the desulphurizing experiments. The operation was allowed to proceed until no products of combustion were evident at the outlet, and until the temperature difference between the external heater control point and centre of the catalyst bed was negligible.

During the experimental work the activity of the catalyst was determined periodically to ensure a constant value. This was done by using a selected feed and an arbitrary set of operating conditions for carrying out the hydrodesulphurization under what were designated as " standard conditions". The activity of the catalyst was measured by the extent of the desulphurization. When the catalyst showed a decreased activity, it was regenerated before continuing the experimental work.

STUDY OF THE VARIATION OF THE PROCESS VARIABLES

The principal variables governing the hydrodesulphurization process may be conveniently divided into two classes: those, such as liquid feed composition and catalyst characteristics, which may only be varied from one experiment to the next; and the operating variables, such as the temperature, pressure, liquid hourly space velocity, and the hydrogen feed rate, which may be varied at any instant during the experiment . The influence of variations in the operating variables upon the rate of hydrodesulphurization was first investigated with feed A, which was the filtered coker distillate from the flash cracking of bitumen obtained from Abasand bituminous sand by the cold water process.

Temperature

The first variable investigated was temperature, which was assumed to be the most influential. Experiments were made at eleven different temperatures through the range 324° to 477°C (615° to 891°F). All operating conditions, with the exception of temperature, were held constant. The results of the experiments are shown in Table 6 and Figure 2.

Variation in temperature had a marked effect upon the properties of the product. Keeping the other operating conditions constant, a small decrease in the temperature below 418°C(785°F) caused a large increase in the sulphur content of the product. However, above 425°C (797°F) a corresponding rise in the temperature produced only a slight decrease in the sulphur content. The temperature also affected the specific gravity of the product, the value decreasing steadily from the lowest to the highest temperature employed. The volume yield showed an increase with the temperature to a maximum of approximately 102% in the vicinity of 400°C(752°F), remained constant at that value to about 440°C(824°F), and then fell off rapidly above this temperature. On the other hand, the hydrogen consumption increased steadily with increasing temperature. As a temperature of approximately 420°C (788°F) gave the most satisfactory results, this temperature was used in the investigation of the other variables.

Pressure

Pressure was the next variable investigated. Experiments

TABLE 6

Effects of Temperature

Constant Operating Conditions:

Pressure, psi	1000
Liquid feed rate, ml/hr	90-92
Liquid hourly space velocity, vol feed/vol cat/hr	1.80-1.84
Exit gas rate, cfh	3.0-3.3
Hydrogen to liquid feed ratio, cu ft/bbl liq feed	5250-5760
Total volume of liquid feed, ml	359-364
Catalyst volume, ml	50
Duration of experiment, hr	3.90-3.98

Results of Temperature Variation:

Experiment No.	Average Temperature		Sulphur in Product	Sp Gr of Product	Yield of Product		Hydrogen Consumption	
	°C	°F	% by wt	60°/60°F	% by wt of liq feed	% by vol of liq feed	% by wt of liq feed	Cu ft/bbl of liq feed
29	320	608	2.42	0.920	97.1	98.7	0.7	420
26	341	646	1.79	0.912	95.6	98.3	1.0	630
27	367	692	1.19	0.905	98.1	101.3	0.7	410
28	389	733	0.70	0.895	97.4	101.7	0.9	570
31	408	766	0.35	0.886	96.1	101.4	1.3	790
23	419	787	0.19	0.876	94.7	101.2	1.7	1040
38	437	818	0.11	0.865	93.7	101.6	2.0	1270
32	446	834	0.05	0.861	93.3	101.2	2.2	1360
39	461	861	0.05	0.849	90.2	99.5	2.9	1800
40	476	889	0.04	0.840	86.2	96.0	3.7	2280

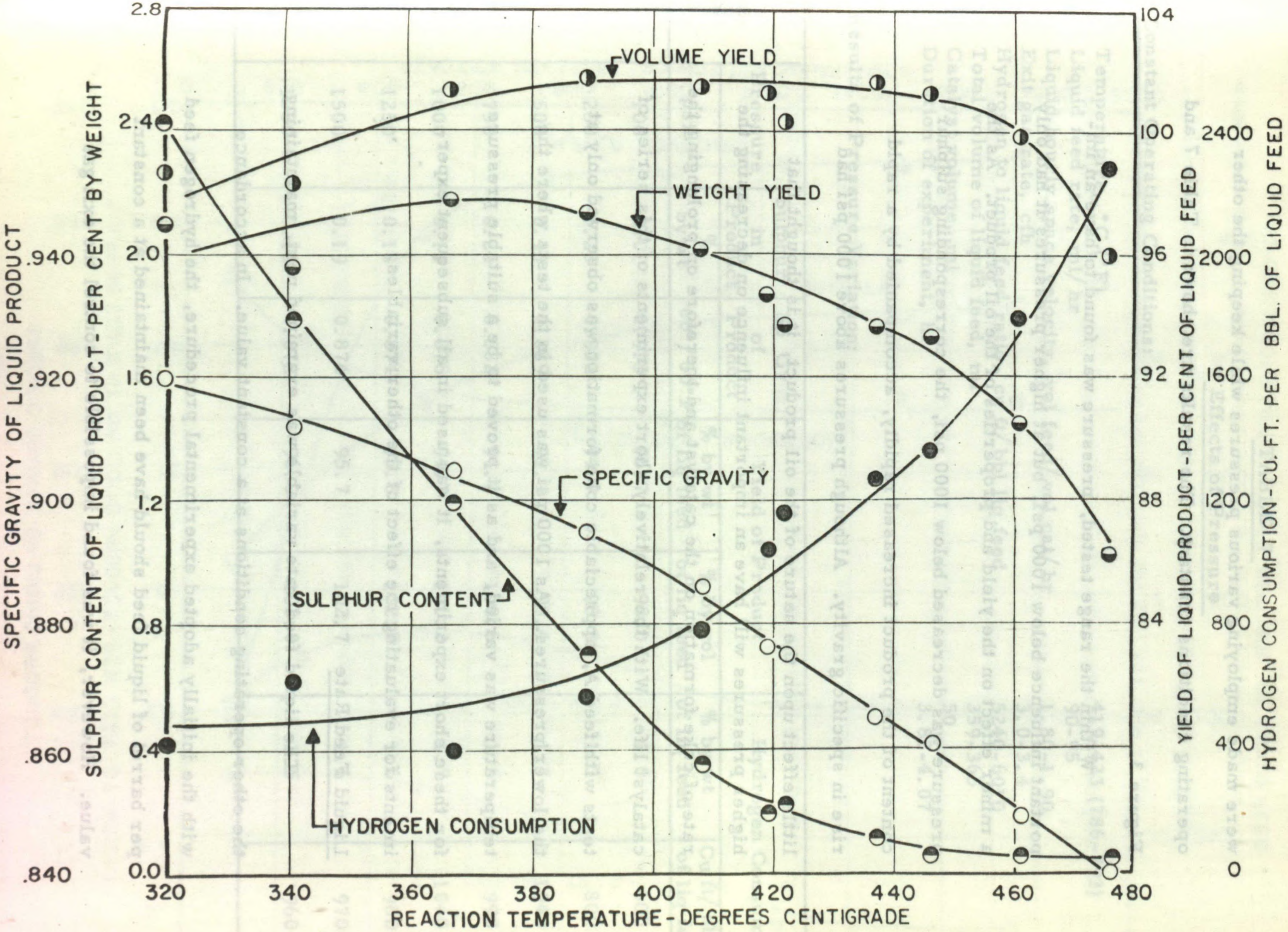

Figure 2 - Effects of temperature.

were made employing various pressures while keeping the other operating conditions constant. The results are shown in Table 7 and Figure 3.

Within the range tested, pressure was found to have an important influence below 1000 psi, but at higher pressures it had only a minor effect on the yield and properties of the oil product. As the pressure was decreased below 1000 psi, the corresponding sulphur content of the product increased rapidly, accompanied by a rapid rise in specific gravity. Although pressures above 1000 psi had little effect upon the nature of the oil product, it is thought that higher pressures will have an important influence on decreasing the rate of coke formation on the catalyst and therefore on prolonging the catalyst life. With the relatively short experiments of this series of tests with feed A, appreciable coke formation was observed only at the lower pressures. As 1000 psi was used in the tests where the temperature was varied, and as it proved to be a suitable pressure for these short experiments, it was used in all subsequent experiments for evaluating the effect of the other variables.

Liquid Feed Rate

The liquid feed rate variable was examined next, maintaining the other operating conditions at a constant value. In accordance with the initially adopted experimental procedure, the hydrogen feed per barrel of liquid feed should have been maintained at a constant value. However, it was found impossible to control the exit gas

TABLE 7

Effects of Pressure

Constant Operating Conditions:

Temperature, °C (°F)	419-423 (786-793)
Liquid feed rate, ml/ hr	90-95
Liquid hourly space velocity, vol feed/ vol cat/ hr	1.80-1.90
Exit gas rate, cfh	3.0-3.4
Hydrogen to liquid feed ratio, cu ft/ bbl liq feed	5240-6010
Total volume of liquid feed, ml	359-365
Catalyst volume, ml	50
Duration of experiment, hr	3.82-4.07

Results of Pressure Variation:

xperiment No.	Pressure	Sulphur in Product	Sp Gr of Product	Yield of Product		Hydrogen Consumption	
	psi	% by wt	60°/ 60°F	% by wt of liq feed	% by vol of liq feed	% by wt of liq feed	Cu ft/ bbl of liq feed
35	100	2.01	0.915	95.7	98.0	1.0	600
34	250	1.28	0.902	94.7	98.3	1.3	800
33	500	0.43	0.889	93.4	98.4	1.7	1040
24	750	0.24	0.882	94.6	100.5	1.6	990
23	1000	0.19	0.876	94.7	101.2	1.7	1040
22	1250	0.18	0.874	95.8	102.8	1.6	960
21	1500	0.19	0.874	95.7	102.7	1.6	970
25	1750	0.13	0.872	96.0	103.0	1.5	960

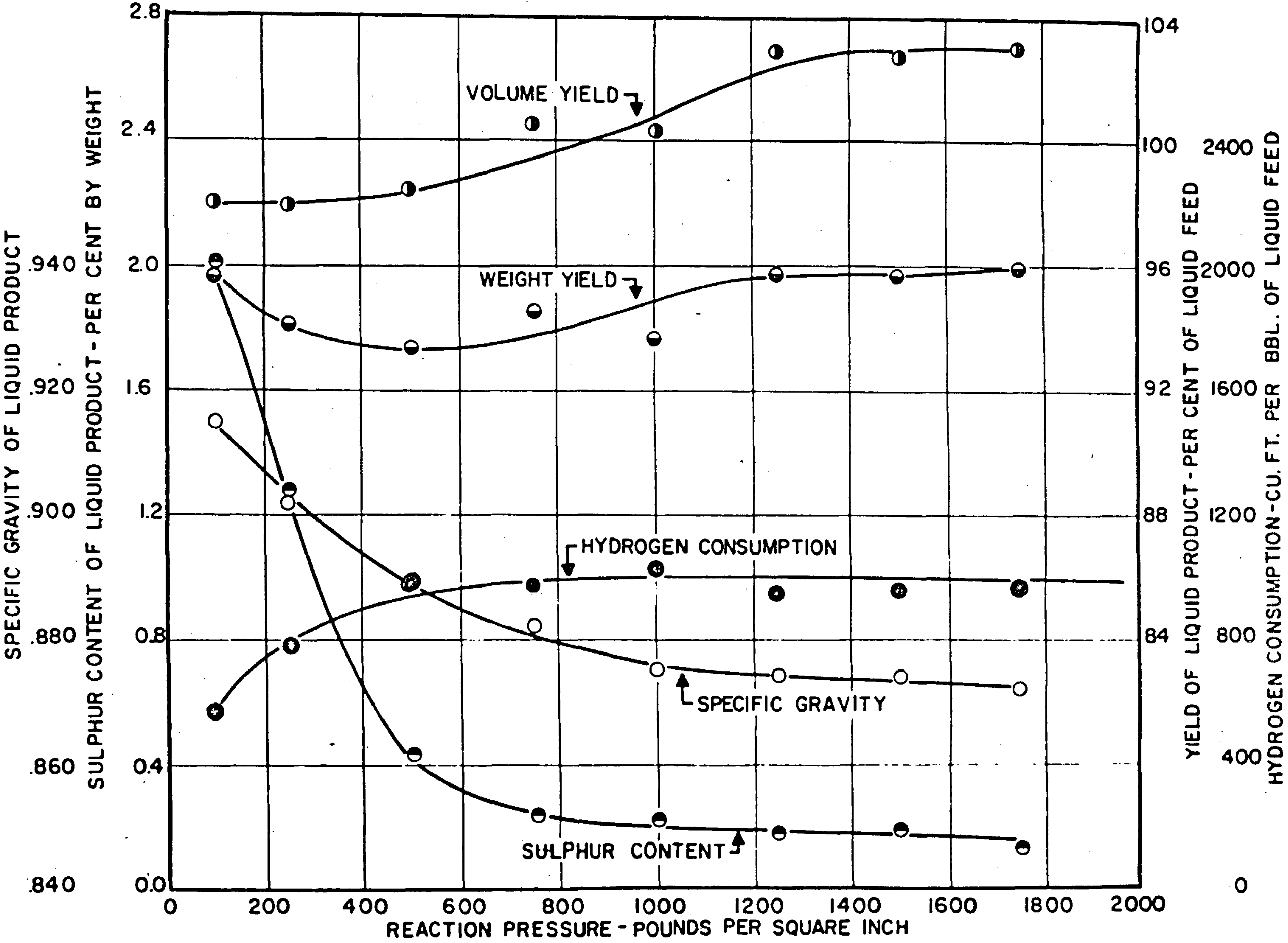

Figure 3 - Effects of pressure.

rate below the 3 cu ft/ hr necessary for the slower hydrogen flows required at the lower liquid feed rates. Consequently, in this series of experiments, it was decided to maintain the exit gas rate at the same value as in the previous series and allow the hydrogen-to-liquid feed ratio to vary accordingly. Fortunately, as will be seen in the results of the next series of experiments, the variation of the hydrogen feed per barrel of liquid feed had a negligible effect upon the extent of desulphurization.

As would be expected, the results as shown in Table 8 and Figure 4 indicate that the sulphur content and the specific gravity increase as the space velocity increases.

Hydrogen Feed Rate

The hydrogen feed rate variable was investigated with the other conditions remaining constant. As the hydrogen-to-liquid feed ratio was controlled by the exit gas rate at constant liquid feed rate, the values of both are shown with the results of the experiments in Table 9 and Figure 5. The hydrogen-to-liquid feed ratio in the range tested had little influence on the properties of the oil product. A hydrogen-to-liquid feed ratio considerably greater than the hydrogen consumption per unit volume of liquid feed was used, to enable the temperature of the reaction to be controlled.

TABLE 8

Effects of Liquid Feed Rate

Constant Operating Conditions:

Temperature, °C (°F)	416-424 (781-795)
Pressure, psi	1000
Exit gas rate, cfh	2.8-3.3
Total volume of liquid feed, ml	250-596
Catalyst volume, ml	50
Duration of experiment, hr	2.78-5.18

Results of Liquid Feed Rate Variation:

Experiment No.	Liq Feed Rate	L.H.S.V.*	H_2/ Liq Feed Ratio	Sulphur in Product	Sp Gr of Product	Yield of Product		Hydrogen Consumption	
	ml/ hr	Vol feed/ vol cat/ hr	Cu ft/ bbl liq feed	% by wt	60°/ 60°F	% by wt of liq feed	% by vol of liq feed	% by wt of liq feed	Cu ft/ bbl of liq feed
14	48	0.96	10,920	0.09	0.860	92.9	101.1	2.3	1400
23	92	1.84	5,370	0.19	0.876	94.7	101.2	1.7	1040
17	121	2.42	4,210	0.37	0.883	95.5	101.2	1.4	890
15	167	3.34	3,120	0.49	0.888	96.3	101.7	1.2	760
16	209	4.18	2,350	0.92	0.895	96.6	101.1	1.1	670

* Liquid hourly space velocity.

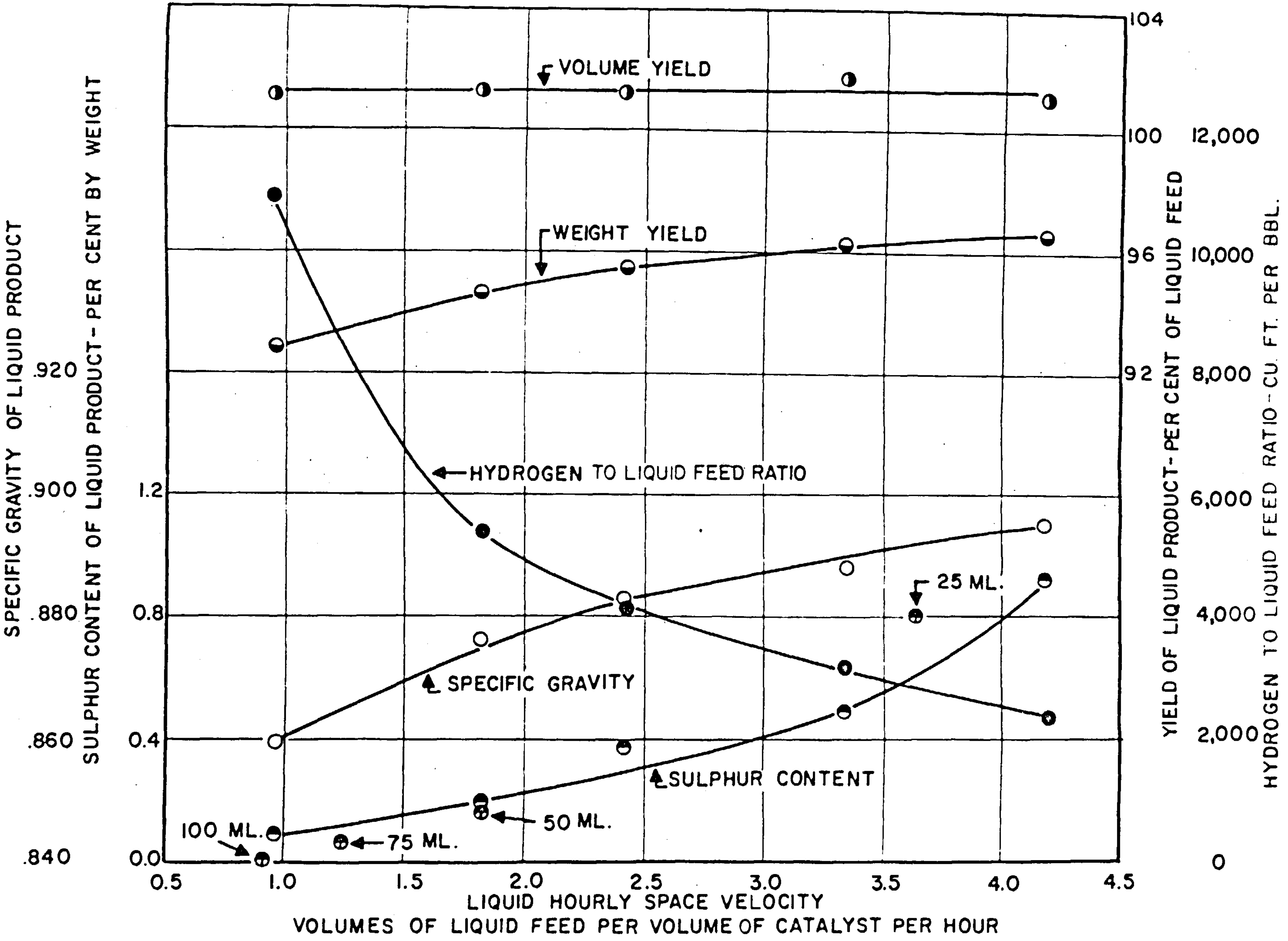

Figure 4 - Effects of liquid feed rate.

TABLE 9

Effects of Hydrogen Feed Rate

Constant Operating Conditions:

Temperature, °C (°F)	419-421 (786-790)
Pressure, psi	1000
Liquid feed rate, ml/hr	92-93
Liquid hourly space velocity, vol feed/vol cat/hr	1.84-1.86
Total volume of feed, ml	361-364
Catalyst volume, ml	50
Duration of experiment, hr	3.92-3.95

Results of Hydrogen Feed Rate Variation:

Experiment No.	H_2/Liq Feed Ratio	Exit Gas Rate	Sulphur in Product	Sp Gr of Product	Yield of Product		Hydrogen Consumption	
	Cu ft/bbl of liq feed	cfh	% by wt	60°/60°F	% by wt of liq feed	% by vol of liq feed	% by wt of liq feed	Cu ft/bbl of liq feed
19	3250	1.9	0.23	0.878	95.7	102.1	1.5	920
23	5370	3.1	0.19	0.876	94.7	101.2	1.7	1040
20	6920	4.0	0.21	0.879	94.6	100.9	1.6	1020
18	8460	4.9	0.13	0.877	95.6	102.1	1.5	940

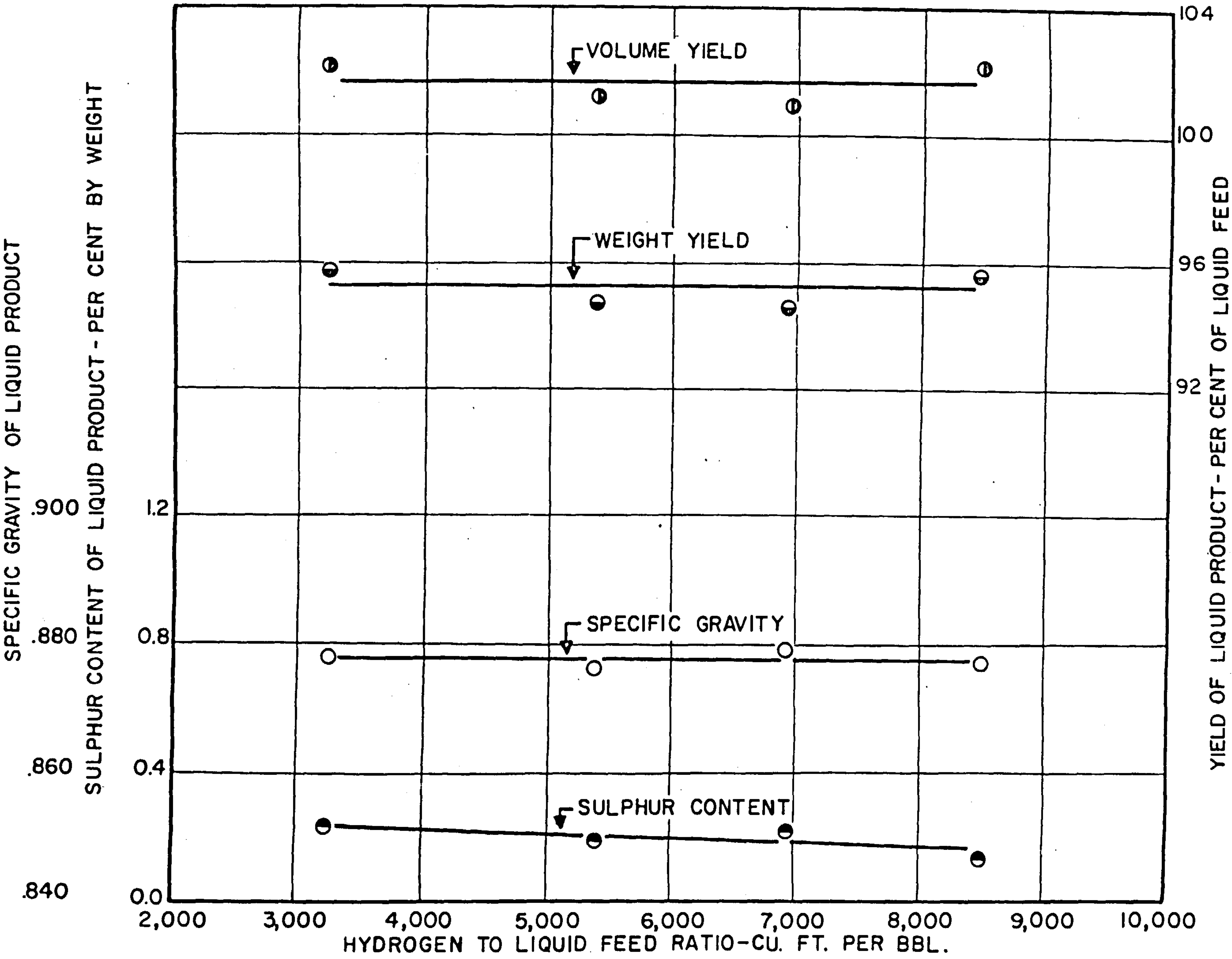

Figure 5 - Effects of hydrogen feed rate.

Catalyst Volume

In all the experiments up to this point, the catalyst volume remained constant at 50 ml and the space velocity was varied by changing the liquid feed rate. As it was considered of interest to compare the results obtained by reversing this procedure, a series of experiments was made in which the space velocity was altered by changing the catalyst volume while maintaining a constant feed rate. The other operating conditions were not changed.

Unfortunately, it was found impossible to maintain a reasonably constant temperature throughout the catalyst bed. In all previous experiments, the average temperature of the catalyst bed had been at most 4°C (7°F) below the control point temperature, which was located at the midpoint of the bed. But in this series of experiments, as the length of the catalyst bed was increased the top and bottom temperatures of the bed fell further below the control point temperature. When the volume of the catalyst bed was increased to 75 ml the average temperature was 16°C (29°F) below the control point temperature, and when the bed was increased to 100 ml the difference was 37°C (67°F). Thus, the results of the experiments as they stood could not be compared with those of the former series. However, as the Arrhenius relation describing the temperature dependence of the hydrodesulphurization reaction was known, it was possible to correct the sulphur content of the products to compensate for the temperature variations throughout the catalyst bed. The results of these experiments, with the corrected sulphur values, are shown in Table 10. The corrected sulphur values are compared with those obtained in the former series of experiments in which the space velocity was investigated, by plotting these points on the same curve in Figure 4. The results of varying the space velocity in these two different ways should be similar, provided the flow pattern in the fixed bed is not seriously altered. That the flow pattern is not seriously modified is confirmed fairly well by a comparison of the sulphur contents of the oil products in the two series of experiments.

Discussion of Operating Variables

In the foregoing experimental work, the effect of the four operating variables -- temperature, pressure, space velocity, and hydrogen feed rate -- on the hydrodesulphurization reaction, using feed A, was investigated. No extensive studies of the properties of the products were made. Evaluation of the results of the experiments was based on the sulphur content, the specific gravity, the yield of the oil product, and the hydrogen consumption. From these experimental results, a set of operating conditions may be chosen which will provide a high yield of product having a low sulphur content. These conditions are: a temperature of 420°C (788°F), a pressure of 1000 psi, a space velocity of 1.8 volumes of feed per volume of catalyst per hour, and a hydrogen-to-liquid feed ratio of 5400 cu ft per barrel of feed. Under these conditions, the oil product contained approximately 0.2% sulphur and had a specific gravity of 0.878. The

TABLE 10

Effects of Catalyst Volume

Constant Operating Conditions:

Temperature at mid-point of catalyst bed, °C (°F)	418-427 (784-801)
Pressure, psi	1000
Liquid feed rate, ml/hr	91-92
Exit gas rate, cfh	2.9-3.3
Hydrogen to liquid feed ratio, cu ft/bbl liq feed	5060-5760
Total volume of feed, ml	361-363
Duration of experiment, hr	3.95

esults of Catalyst Volume Variation:

Experiment No.	Cat Vol	L.H.S.V.*	Aver Temp of Cat Bed		Actual Sulphur in Product	Sulphur in Product, Corrected to 423°C	Sp Gr of Product
	ml	Vol feed/vol cat/hr	°C	°F	% by wt	% by wt	60°/60°F
53	25	3.64	426	799	0.75	0.80	0.891
23	50	1.84	419	786	0.19	0.16	0.876
55	75	1.23	409	768	0.11	0.06	0.874
57	100	0.91	381	718	0.11	0.01	0.871

* Liquid hourly space velocity

volume yield of the oil product was about 101 to 102% of the feed, and the hydrogen consumption was in the neighbourhood of 1000 cu ft per barrel of liquid feed.

Sulphur Content of Liquid Feed

In all previous experiments the composition of the feed was not varied and consequently the initial sulphur content remained constant. It was of interest to determine whether the sulphur in the product was directly proportional to the amount of sulphur in the feed.

In order to determine the effect of varying the sulphur content of the feed, a series of experiments was made using feeds of nine different sulphur contents, which were obtained by blending the products of former runs. A lower temperature was employed to obtain a satisfactory variation in the final sulphur quantities. This temperature was obtained from the curve in Figure 2 showing the variation of the liquid product sulphur content with temperature. The results of these experiments are shown in Table 11 and Figure 6.

Varying the sulphur content of the feed showed that the ratio of sulphur in the productto the sulphur in the feed remains constant throughout the range investigated. The divergence from the linear relationship shown by the ratios of the lower sulphur contents is due to difficulty in obtaining accurate sulphur analyses at these low values.

Different Feeds

Up to this point the effect of the operating variables had been investigated on feed A only. Now it was proposed to study the effect

Effects of Sulphur Content of Liquid Feed

Constant Operating Conditions:

Temperature, °C (°F)	383-389 (721-732)
Pressure, psi	1000
Liquid feed rate, ml/hr	87-94
Liquid hourly space velocity, vol feed/vol cat/hr	1.74-1.88
Exit gas rate, cfh	2.8-3.3
Hydrogen to liquid feed ratio, cu ft/bbl liq feed	4700-5830
Total volume of feed, ml	199-214
Catalyst volume, ml	50
Duration of experiment, hr	1.75-2.47

Results of Sulphur Content of Liquid Feed Variation:

Experiment No.	Ratio of Sulphur in Product to Sulphur in Feed	Sulphur in Feed	Sulphur in Product	Sp Gr of Feed	Sp Gr of Product	Yield of Product		Hydrogen Consumption	
		% by wt	% by wt	60°/60°F	60°/60°F	% by wt of liq feed	% by vol of liq feed	% by wt of liq feed	Cu ft/bbl of liq feed
68	0.22	3.6	0.78	0.936	0.893	95.0	99.5	1.4	850
60	0.22	2.42	0.53	0.920	0.892	97.8	100.7	0.7	430
61	0.23	1.79	0.42	0.912	0.890	99.0	100.4	0.6	380
62	0.24	1.19	0.28	0.905	0.888	97.6	99.4	0.6	390
63	0.27	0.70	0.19	0.895	0.885	98.2	100.0	0.4	260
69	0.44	0.43	0.19	0.889	0.880	99.9	100.9	0.2	100
64	0.37	0.35	0.13	0.886	0.880	98.5	99.2	0.3	200
65	0.00	0.05	0.00	0.861	0.862	100.3	100.3	-	-
66	0.50	0.04	0.02	0.842	0.848	96.9	96.0	0.4	210

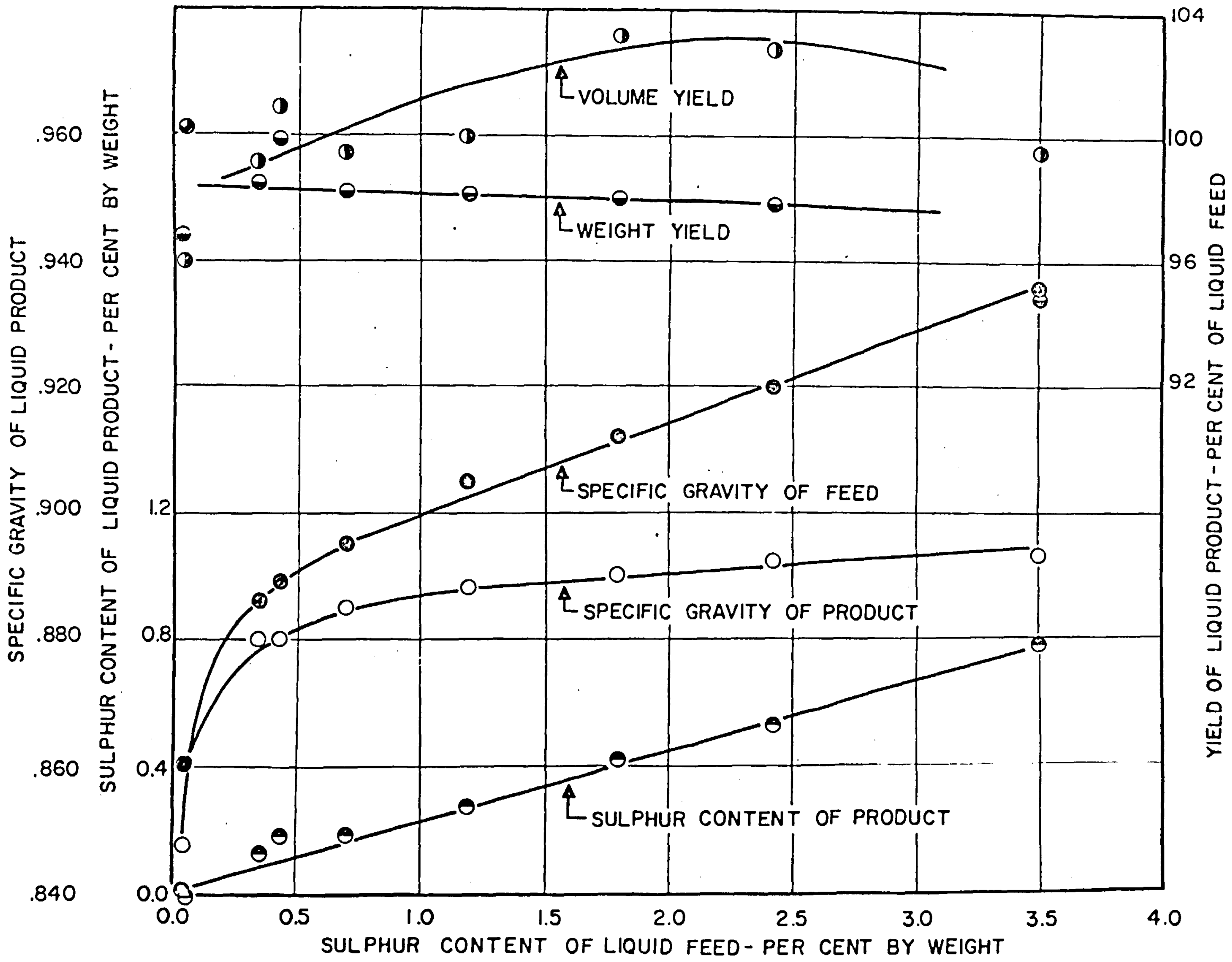

Figure 6 - Effects of sulphur content of liquid feed.

of using different feeds, namely, feeds B and C, which were filtered coker distillates from the fluidized coking of bituminous sand from the Abasand and Bitumount areas respectively. In this investigation the "standard conditions" were employed. These conditions, which were selected values of the operating variables and were also used to assess the activity of the catalyst, were as follows:

Standard Operating Conditions

Temperature, °C (°F)	420 (788)
Pressure, psi	1000
Liquid hourly space velocity, vol feed/ vol cat/ hr	1.80
Hydrogen to liquid feed ratio, cu ft/ bbl liq feed	5400
Duration of experiment, hr	4

Four experiments were made, using feed C in the first three and feed B in the last one. Table 12 shows the operating conditions and the results of these experiments, compared with those when using feed A under the same conditions. A comparison of the hydrodesulphurization behaviours of feeds B and C with feed A under "standard conditions" showed feeds B and C to be much less amenable to hydrodesulphurization than was feed A, as indicated by the high sulphur content of the products.

In all four experiments with feeds B and C, difficulty in operation was experienced, even during the first few hours, because of an accumulation of a considerable amount of sludge in the reaction chamber. This sludge, one sample of which analyzed 19.5% ash, occurred in spite of the fact that the feeds had been filtered through

TABLE 12

Effects of Different Feeds

Constant Operating Conditions:

Temperature, °C (°F)	417-420 (783-788)
Pressure, psi	1000
Liquid feed rate, ml/hr	85-94
Liquid hourly space velocity, vol feed/vol cat/hr	1.70-1.88
Exit gas rate, cfh	3.1-3.2
Hydrogen to liquid feed ratio, cu ft/bbl liq feed	5260-5800
Total volume of liquid feed, ml	340-363
Catalyst volume, ml	50
Duration of experiment, hr	3.78-4.08

Results of Liquid Feed Variations:

Experiment No.	Feed	Sulphur in Feed	Sulphur in Product	Sp Gr of Feed	Sp Gr of Product	Yield of Product		Hydrogen Consumption	
		% by wt	% by wt	60°/60°F	60°/60°F	% by wt of liq feed	% by vol of liq feed	% by wt of liq feed	Cu ft/bbl of liq feed
23	A	3.6	0.19	0.936	0.876	94.7	101.2	1.7	1040
84	B	3.8	0.85	0.967	0.901	90.6	97.2	2.5	1620
70	C	4.0	0.82	0.960	0.899	93.5	99.8	1.9	1220
75	C	4.0	0.41	0.960	0.891	94.9	102.1	1.8	1150
77	C	4.0	0.77	0.960	0.897	91.5	98.0	2.3	1460

glass wool on a 200-mesh screen. It was found that most of the sludge was deposited in the preheater section of the reaction chamber, and the remainder in the top portion of the catalyst bed. This deposit had interfered with the hydrogen and liquid feed flow through the reaction chamber and had caused a decrease in the catalyst activity.

Following each of the above experiments, a test under "standard conditions", using feed A, was made to obtain an indication of the magnitude of the decline in the activity of the catalyst. With fresh catalyst under these conditions and using feed A, the product contained 0.2% sulphur and had a specific gravity of 0.875. The results of the test under standard conditions after each of the experiments on feeds B and C showed the catalyst activity to be slightly reduced, except after the second experiment using feed C when full activity was indicated. It was not evident why this experiment should not have shown the same decrease in catalytic activity as the others. Perhaps the amount of sludge accumulation was less in this case.

Effects of Temperature at Various Space Velocities

As temperature and space velocity have a greater effect on the rate of desulphurization than do the other operating variables, it would be advantageous to obtain a relationship between these two conditions and the sulphur content of the oil product. To obtain the necessary data for calculating this relationship, experiments were made varying the temperature at selected space velocities. Feed D, a sludge-free distillate oil, was used for this work at a pressure of

1000 psi. This oil feed was obtained by topping feed C, the distillate from the fluidized coking of Bitumount bituminous sand. Feed D comprised the 80% overhead fraction from this distillation. The operating conditions and results of the experiments are shown in Table 13. Figures 7 and 8 show the effects of temperature at various space velocities on the sulphur content and specific gravity.

In establishing the relationship between the temperature, space velocity and sulphur content of the oil product, the log log of the ratio of initial and final sulphur percentages in the oil was plotted against the reciprocal of the absolute temperature for various space velocities. These plots, as shown in Figure 9, illustrate that a series of parallel straight lines may be drawn which satisfactorily fit the experimental data. The perpendicular distance between these parallel lines was plotted against space velocity, to produce the curve shown in Figure 10. From Figures 9 and 10, by selecting any two of the three quantities, temperature, space velocity, and sulphur content of product, the third quantity may be obtained. This relationship has been evaluated for only one pressure (1000 psi) and one average hydrogen-to-liquid feed ratio (5600 cu ft per barrel of liquid feed). But, as previously stated, pressure had an appreciable effect upon the properties of the oil product only at pressures below 1000 psi; between this value and 1750 psi its effect was slight. Likewise, within the range 3250 and 8460 cu ft per barrel of liquid feed, the hydrogen feed rate had little effect upon the product.

TABLE 13

Effects of Temperature at Various Space Velocities

Experiment No.	Liquid Feed Rate	L. H. S. V.	Average Temp		Press	Exit Gas Rate	Hydrogen Feed Ratio	Catalyst Volume	Duration of Experiment	S in Feed	S in Product	Sp Gr of Feed	Sp Gr of Product	Yield of Product		Hydrogen Consumption	
	ml/hr	Vol feed/vol cat/hr	°C	°F	psi	cfh	Cu ft/bbl	ml	hr	% by wt	% by wt	60°/60°F	60°/60°F	% by wt of liq feed	% by vol of liq feed	% by vol of liq feed	Cu ft/bbl of liq feed
108	88	1.76	424	795	1000	3.2	5780	50	4.1	3.6	0.06	0.935	0.872	96.2	103.2	1.5	920
109	91	1.82	401	754	1000	3.2	5600	50	4.0	3.6	0.11	0.935	0.879	95.4	101.4	1.5	920
110	91	1.82	384	723	1000	3.1	5420	50	4.0	3.6	0.32	0.935	0.886	96.3	101.6	1.2	750
111	91	1.82	358	677	1000	3.3	5750	50	4.0	3.6	0.80	0.935	0.894	96.6	101.0	1.1	660
112	92	1.84	342	648	1000	3.3	5700	50	3.9	3.6	1.19	0.935	0.902	97.5	101.0	0.8	500
192	134	3.82	449	841	1000	5.3	6290	35	4.2	3.6	0.15	0.935	0.869	93.4	100.5	2.0	1240
188	147	4.20	438	821	1000	4.7	5080	35	3.8	3.6	0.27	0.935	0.881	95.8	101.6	1.4	860
193	139	3.98	436	816	1000	5.2	5950	35	4.1	3.6	0.25	0.935	0.878	94.8	100.9	1.6	1000
213	134	3.83	433	812	1000	5.1	6060	35	6.1	3.6	0.24	0.935	0.884	95.1	100.6	1.5	900
218	129	3.68	433	811	1000	5.0	6160	35	7.0	3.6	0.24	0.935	0.881	-	-	-	-
229	128	3.66	432	810	1000	4.8	5960	35	7.1	3.6	0.25	0.935	0.883	-	-	1.3	820
194	140	4.00	421	789	1000	4.5	5110	35	4.0	3.6	0.41	0.935	0.886	96.0	101.3	1.3	790
195	139	3.97	415	779	1000	5.3	6060	35	4.0	3.6	0.47	0.935	0.887	95.9	101.1	1.3	800
196	138	3.94	403	758	1000	5.1	5860	35	4.0	3.6	0.64	0.935	0.892	96.8	101.4	1.1	660
198	137	3.92	394	742	1000	5.2	6050	35	4.1	3.6	0.88	0.935	0.897	96.7	100.8	1.0	620
235	166	4.74	466	870	1000	6.1	5840	35	5.0	3.6	0.23	0.935	0.868	-	-	1.5	930
170	165	4.72	464	868	1000	6.0	5780	35	4.2	3.6	0.17	0.935	0.868	-	-	-	-
175	170	4.86	462	364	1000	6.0	5620	35	4.1	3.6	0.21	0.935	0.869	93.7	100.8	2.0	1210
169	168	4.80	442	827	1000	5.9	5580	35	4.1	3.6	0.32	0.935	0.880	94.1	100.0	1.7	1050
167	168	4.80	441	826	1000	5.8	5500	35	4.1	3.6	0.26	0.935	0.879	94.8	100.8	1.6	990
123	247	4.94	417	783	1000	8.2	5280	50	1.5	3.6	0.50	0.935	0.890	-	-	-	-
116	244	4.88	417	783	1000	3.0	1955	50	1.5	3.6	0.50	0.935	0.887	95.5	100.6	1.4	840
168	170	4.86	407	765	1000	6.0	5600	35	4.2	3.6	0.78	0.935	0.894	96.0	100.4	1.2	720
163	284	8.12	492	917	1000	9.9	5550	35	2.6	3.6	0.28	0.935	0.862	91.8	99.6	2.4	1490
145	280	8.00	474	886	1000	9.8	5570	35	2.7	3.6	0.34	0.935	0.873	93.0	99.6	2.0	1250
199	276	7.88	454	850	1000	9.8	5640	35	4.0	3.6	0.62	0.935	0.884	95.7	101.2	1.4	860
146	284	8.11	452	846	1000	10.0	5600	35	2.7	3.6	0.56	0.935	0.887	95.1	100.2	1.4	890
204	281	8.03	448	839	1000	10.1	5720	35	2.0	3.6	0.52	0.935	0.882	96.5	102.3	1.3	790
272	279	7.95	432	809	1000	9.4	5360	35	3.6	3.6	0.89	0.935	0.894	96.9	101.3	1.0	640
160	274	7.82	418	784	1000	10.0	5790	35	2.7	3.6	1.06	0.935	0.895	97.0	101.4	1.0	630
158	278	7.95	416	780	1000	9.9	5650	35	2.7	3.6	1.20	0.935	0.897	97.6	101.7	0.9	550
138	358	10.22	483	902	1000	11.9	5280	35	1.4	3.6	0.39	0.935	0.874	90.6	96.9	2.4	1480
144	322	9.21	471	879	1000	11.4	5620	35	2.3	3.6	0.36	0.935	0.874	93.4	99.9	1.9	1200
137	358	10.22	470	878	1000	12.6	5600	35	1.4	3.6	0.51	0.935	0.881	93.4	99.1	1.8	1120
136	340	9.72	454	849	1000	11.8	5520	35	1.4	3.6	0.62	0.935	0.886	95.5	100.8	1.4	850
154	351	10.03	433	812	1000	10.7	5030	35	2.1	3.6	0.82	0.935	0.894	96.6	101.0	1.1	660
162	322	9.21	413	776	1000	12.2	6010	35	2.3	3.6	1.34	0.935	0.900	96.2	99.9	1.1	660

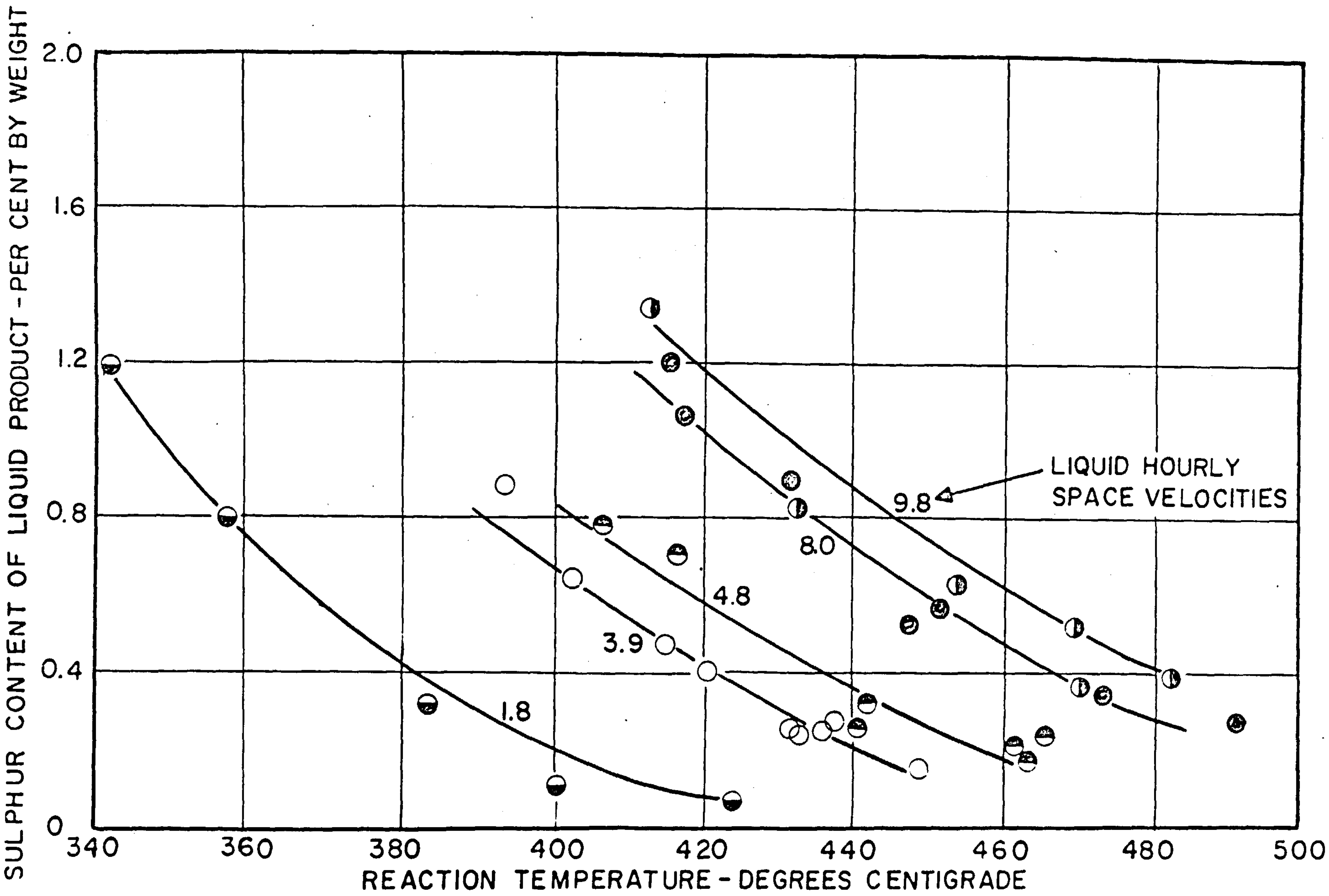

Figure 7 - Effect of temperature on sulphur content of liquid product at various space velocities.

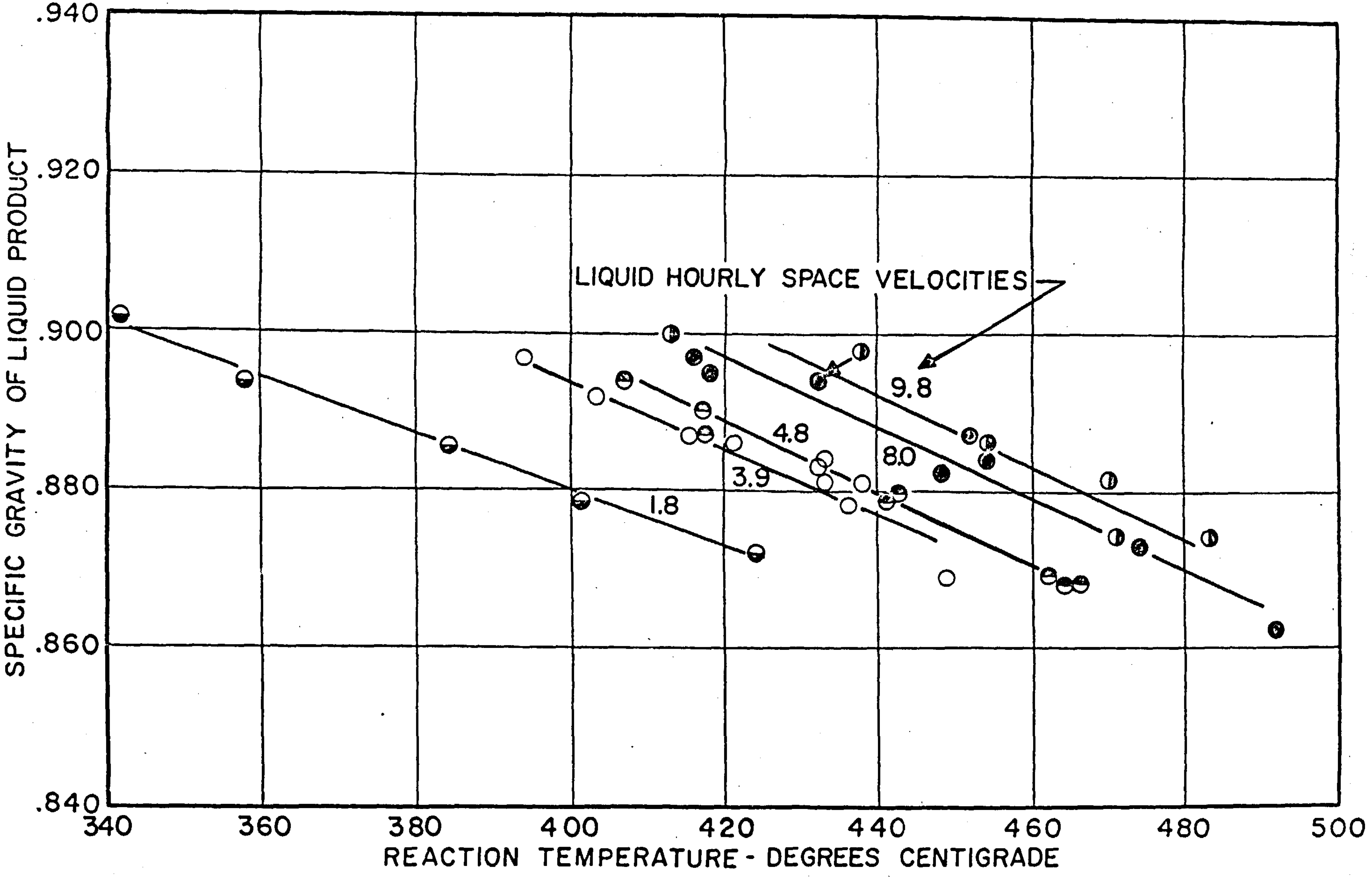

Figure 8 - Effect of temperature on specific gravity of liquid product at various space velocities.

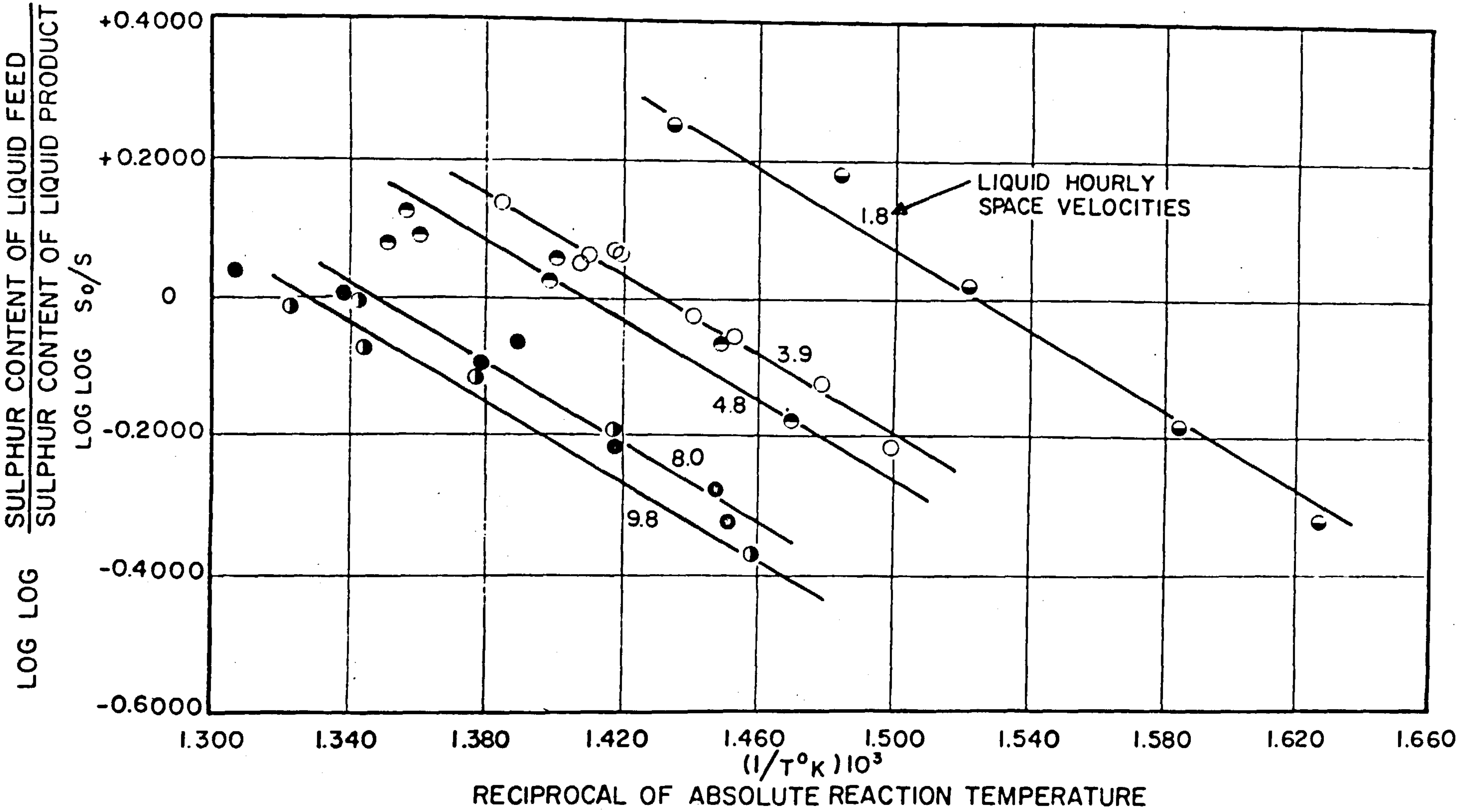

Figure 9 - Relationship between temperature and sulphur content of liquid product at various space velocities.

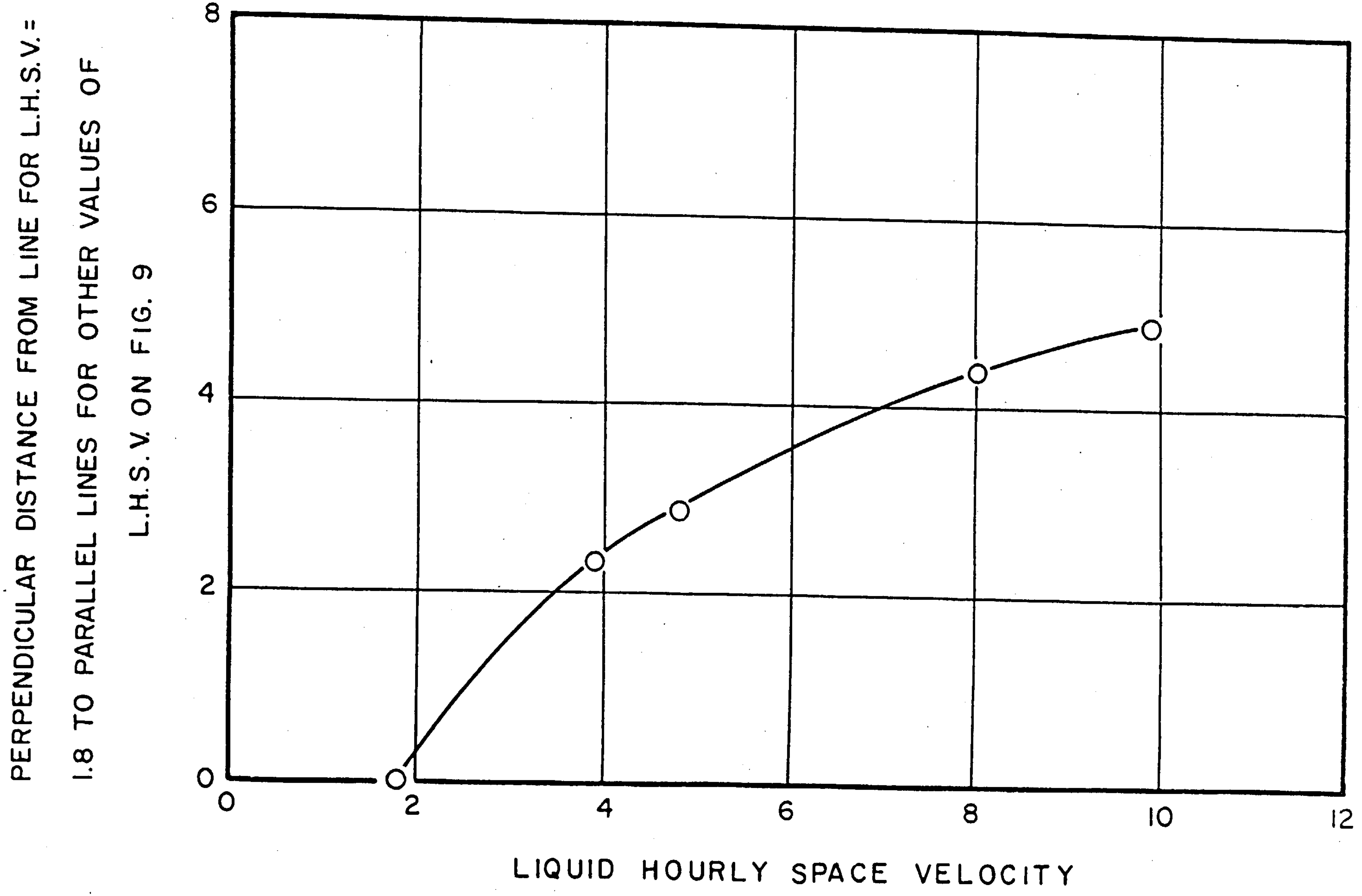

Figure 10 - Interpolation curve for space velocity lines on Figure 9.

CATALYST DETERIORATION TESTS

All experimental results up to this point had been obtained from experiments of short duration and with the catalyst presumably at maximum activity. However, it was essential to secure further information on the decline of catalytic activity with the length of the process period at various operating temperatures.

Catalyst deterioration may be classified as either temporary or permanent, depending on whether or not the initial catalytic activity can be restored by oxidation with air. The loss in catalytic activity studied in the following experiments was almost entirely due to coke deposition on the catalyst, as no significant permanent deterioration could be detected. For the purpose of this investigation, long continuous experiments were necessary to study the rate of decline of catalyst activity, as it was not known whether the rates of coke deposition on the catalyst and coke deposition on the coke would be different and would have different effects on the catalytic activity. Eight catalyst deterioration tests were made. The conditions under which these tests were conducted are shown in Table 14. The values for temperature and space velocity were so chosen that at full catalyst activity the resultant product would contain approximately 0.2% sulphur. However, the actual sulphur content of the initial product from several of the tests varied somewhat from this value.

Some operational difficulty was encountered in the first two

TABLE 14

Operating Conditions for Catalyst Deterioration Tests

Operating Data	Experiment Number							
	218	222	229	235	240	250	257	262
Feed	D	D	D	D	D	D	A	A
Average temperature, °C	432	404	432	464	477	504	498	461
°F	810	759	810	867	891	939	928	862
Pressure, psi	1000	1000	1000	1000	1000	1000	1000	1000
Liquid feed rate, ml/hr	129	68	128	166	210	284	280	168
LHSV, vol feed/vol cat/hr	3.7	1.9	3.7	4.7	6.0	8.1	8.0	4.8
Exit gas rate, cfh	5.0	2.7	4.8	6.1	7.8	10.0	10.1	6.2
Hydrogen to liquid feed ratio, cu ft/bbl	6170	6250	5960	5830	5910	5580	5720	5870
Total volume of liquid feed, ml	8,190	8,880	18,405	39,757	38,136	28,968	8,820	16,968
Catalyst volume, ml	35	35	35	35	35	35	35	35
Duration of experiment, hr	64	140	144	240	182	102	32	101

experiments. Experiment 218 was the first catalyst deterioration test made, and was conducted under what were considered to be rather mild conditions. For the first 25 hours the sulphur content and specific gravity of the product remained relatively constant at approximately 0.3% and 0.883 respectively, indicating no appreciable decrease in catalyst activity. Then, at this point the sulphur content and specific gravity of the product began to increase rapidly until, after a total of 34 hours of operation, the sulphur content of the product was 1.1% and the specific gravity was 0.899. After 37 hours of operation the apparatus became blocked in the interior of the reaction chamber, with what was believed at the time to be coke, and operations were discontinued until the blockage was removed. This was accomplished by applying hydrogen pressure at the outlet end of the reaction chamber and blowing hydrogen in reverse flow through the chamber. The experiment was then continued. The product, which was recovered immediately after resumption of operations, appeared to have a quality similar to that of the product obtained during the first part of the experiment. However, as the experiment continued the product quality deteriorated rapidly, and after three hours the sulphur content and specific gravity of the product were 0.6% and 0.891 respectively, and after nine hours these values reached 1.6% and 0.908. After eleven hours the apparatus became blocked a second time. The blockage was again removed and the experiment continued. This plugging and unplugging occurred five times, and each time the effect on the quality of the product was the same. After a total elapsed operational time of 64 hours the experiment was concluded.

The assumption was made that the temperature of 432°C (810°F) employed in Experiment 218 was too high, resulting in excessive deposition of coke on the catalyst. Consequently, in the subsequent experiment, 222, the average temperature of the catalyst bed was reduced to 404°C (759°F).

For the first 43 hours of Experiment 222, the sulphur content and specific gravity of the product remained relatively constant at approximately 0.3% and 0.886 respectively. The sulphur and specific gravity then began to increase rapidly, until after 52 hours the sulphur content was 0.6% and the specific gravity was 0.894. After 55 hours the apparatus became blocked and had to be cleared as in the previous experiment. The sulphur and specific gravity of the product then returned to a value slightly higher than that obtained during the first hours of the experiment and remained steady for about 50 hours of additional operation. The sulphur and the specific gravity then began to rise again and, after 129 hours of total elapsed time, reached values of 1.3% and 0.905 respectively. After 131 hours the apparatus again became blocked. After removal of the obstruction as before, the sulphur content and specific gravity of the product returned to approximately the same values as those of the product obtained during the first part of the experiment. After 140 hours of operation the experiment was terminated.

These first two experiments were plagued by repeated blocking of the reaction chamber, which made difficult, if not impossible, the evaluation of the process periods of the catalyst. However, the fact that the catalyst appeared to retain almost its full activity after removal of the obstruction, indicated that no appreciable coking was taking place, either on or within the catalyst pellets themselves. It was therefore considered that the obstruction was probably due to coke formation or accumulation of mineral matter within the preheater section. This preheater section consisted of 3 mm diameter glass beads which fitted closely together in bulk so that the interstitial space left for passage of fluids was small. Thus, a small accumulation of solid material here could cause a blockage. Consequently, before Experiment 229, the glass beads were removed and the preheater section was packed with protruded, Type 316 stainless steel, fractionating column packing which possessed a higher thermal conductivity and considerably greater free space than did the glass beads. The validity of this diagnosis as the cause of the blocking was confirmed by the fact that in no subsequent experiment was it observed. In particular, when the operating conditions of Experiment 218 were duplicated in Experiment 229, no blocking was encountered.

The results of all the catalyst deterioration tests are shown in Figures 11 and 12, which illustrate the effect of process time, at

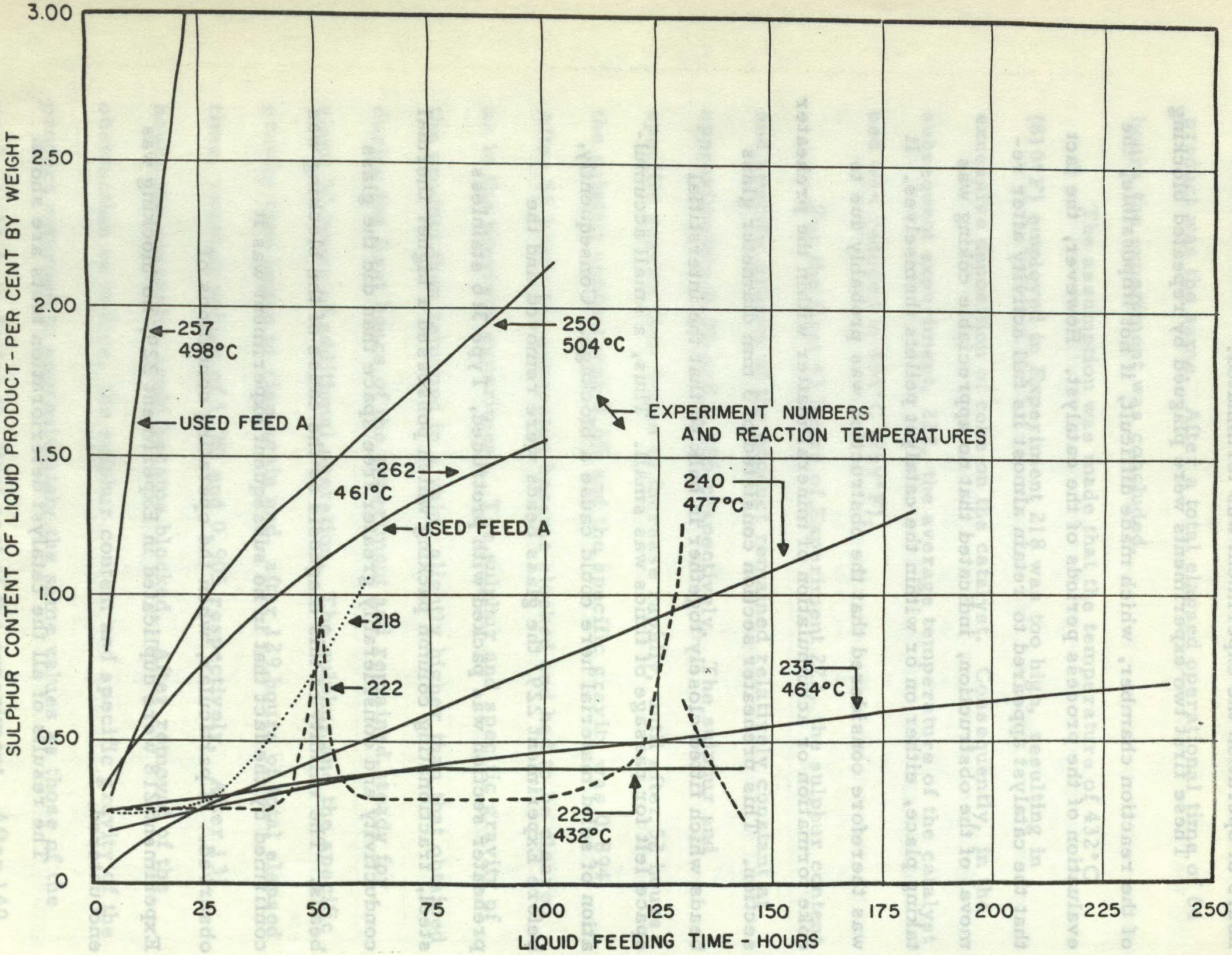

Figure 11 - **Effect of process time on sulphur content of liquid product at various temperatures.**

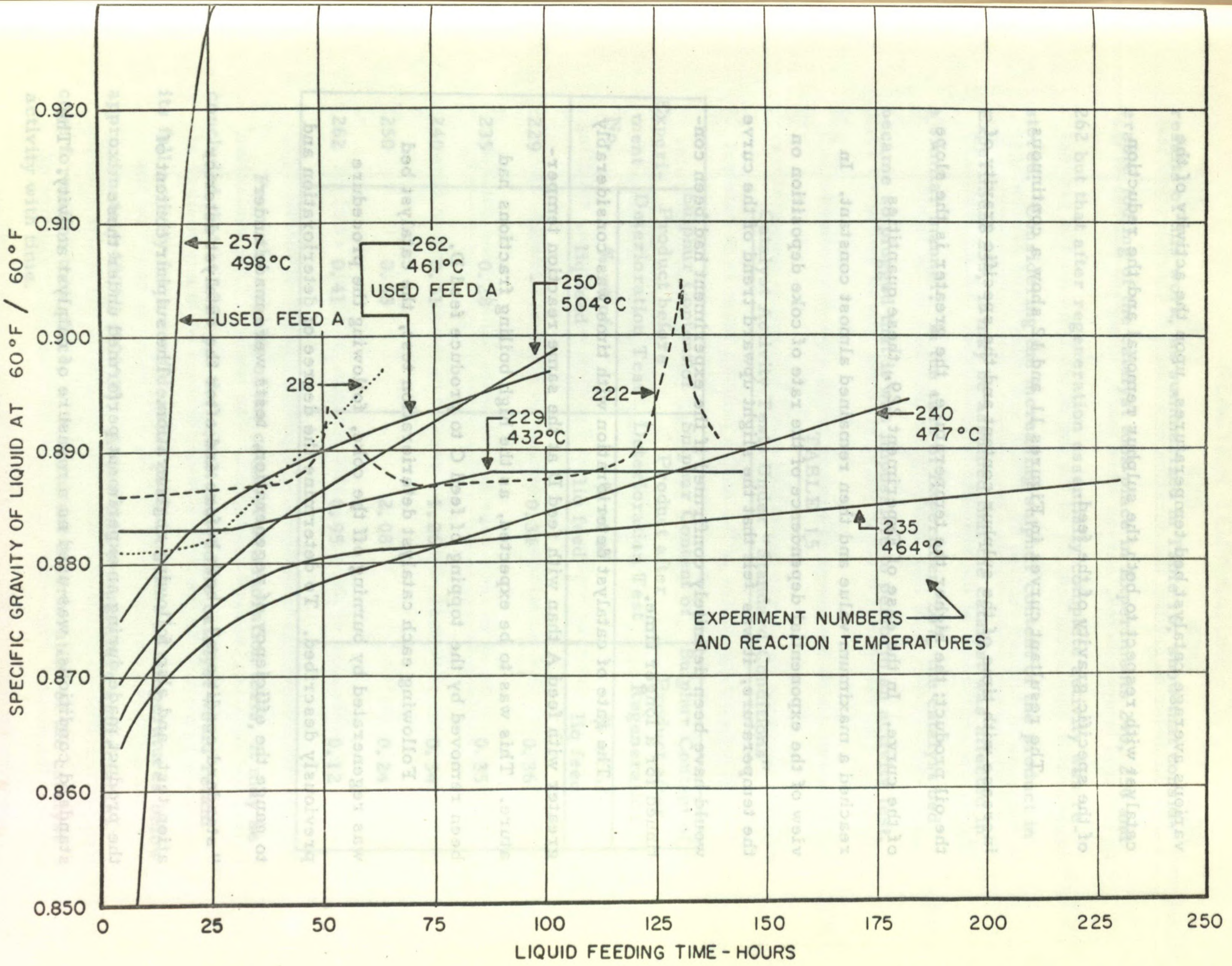

Figure 12 - Effect of process time on specific gravity of liquid

various average catalyst bed temperatures, upon the activity of the catalyst with respect to both the sulphur removal and the reduction of the specific gravity of the feed.

The resultant curves in Figures 11 and 12 show a continuous increase with time of the sulphur content and the specific gravity of the oil product; the higher the temperature, the greater is the slope of the curve. In the case of Experiment 229, these quantities reached a maximum value and then remained almost constant. In view of the exponential dependence of the rate of coke deposition on the temperature, it was felt that the slight upward trend of the curve would have been definitely confirmed if the experiment had been continued for a longer time.

The rate of catalyst deterioration with time was considerably greater with feed A than with feed D at the same reaction temperature. This was to be expected, as the high boiling fractions had been removed by the topping of feed C to produce feed D.

Following each catalyst deterioration test, the catalyst bed was regenerated by burning off the coke, following the procedure previously described. To determine the degree of deterioration and to gauge the efficiency of regeneration, tests were made under "standard conditions", both before and after the catalyst deterioration test, and also following regeneration. The sulphur content of the product made during an experiment performed under these standard conditions, was used as a measure of catalyst activity. The results of this work, as summarized in Table 15, show that considerable fouling of the catalyst took place in Experiments 240, 250 and 262 but that after regeneration essentially complete activity was restored. Considering the increasing sulphur content of the product in Experiment 235, it may be assumed that the catalyst was affected in a similar manner. In the case of Experiment 257, the catalyst bed became so plugged that it was impossible to perform an activity test.

TABLE 15

Catalyst Activity Tests Under "Standard Conditions"

Experiment No.	Sulphur Content of Product before Deterioration Test	Sulphur Content of Product after Deterioration Test	Sulphur Content of Product after Regeneration
	% wt of liq feed	% wt of liq feed	% wt of liq feed
229	-	0.34	0.36
235	0.28	-	0.35
240	0.31	1.26	0.34
250	0.33	2.08	0.24
262	0.41	0.95	0.12

From the results of the catalyst deterioration tests, it may be concluded that at 1000 psi the cobalt molybdate catalyst would retain its full activity for a considerable period of time at temperatures below approximately 430°C (806°F). Above this temperature appreciable coke formation took place, with resultant deterioration of the catalyst activity with time.

In order to predict the duration of a catalyst deterioration test at elevated temperatures, curves were made, using the results of the experiments employing feed D, of the log of the time for the product to increase in sulphur content by certain arbitrary fixed percentages versus the reciprocal of the absolute temperature. These arbitrary values varied from 0.40 to 1.20% sulphur increase in the liquid product. The result was a set of parallel lines, shown in Figure 13, by means of which the length of time to reach a predetermined sulphur increase value was estimated for any reaction temperature.

Composite samples of the entire product from each catalyst deterioration test were subjected to routine oil laboratory analysis. While no deterioration test was made under "standard conditions", a number of such experiments of short duration were made, totalling over 50 hours, with no noticeable decline in catalyst activity. A composite sample of 46 four-hour experiments under these conditions was analyzed. Table 16 shows the results of the analysis of these composite samples.

An evaluation of the composite samples of all the catalyst deterioration tests, as well as the composite sample of the 46 four-hour runs at standard conditions, was made. This evaluation was made according to the United States Bureau of Mines method of evaluating crude petroleum(42, 43, 44, 45), which is based on the Hempel distillation of the sample of the oil and on the analysis of the various fractions. Figures 14 to 21 are plots of the properties of the Hempel distillation fractions against the percent by volume

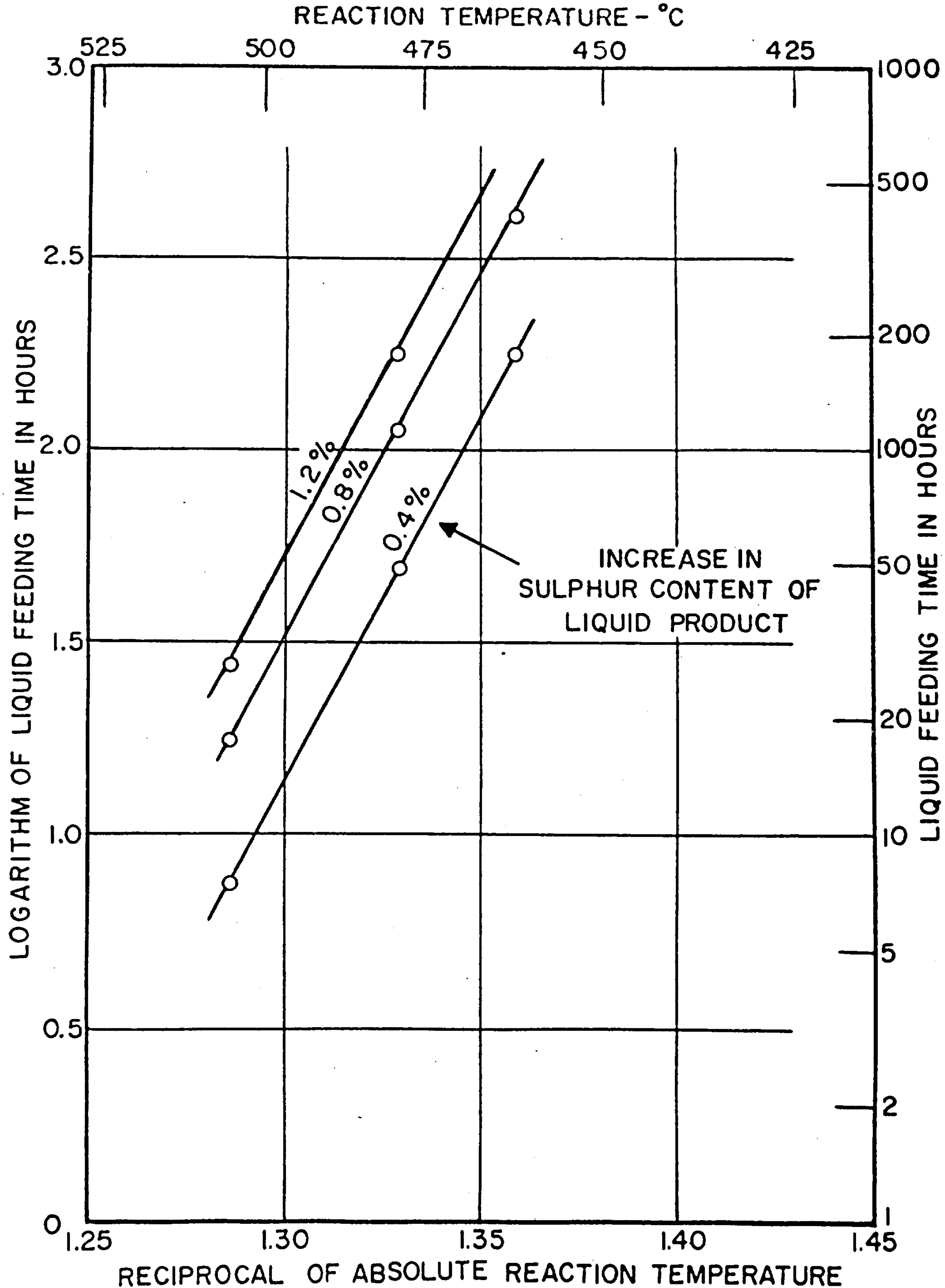

Figure 13 - Liquid feeding time for various increments of sulphur content of liquid product at various temperatures.

TABLE 16

Characteristics of Composite Samples

Experiment No.	Specific Gravity 60°/60°F	Degrees A.P.I.	Viscosity at 100°F cs	Viscosity at 210°F cs	Pour Point °F	Aniline Point °F	Carbon Residue % by wt	C % by wt	H % by wt	S % by wt	Ash % by wt	Molecular Weight	Base
229	0.887	28.0	5.65	1.78	-25	130	0.04	86.01	12.42	0.4	0.001	219	Naphthene (wax-bearing)
235	0.883	28.8	4.17	1.48	-10	121	0.04	88.76	12.07	0.5	0.005	213	" (" ")
240	0.887	28.0	4.08	1.47	-25	114	0.1	84.30	11.36	0.7	-	200	" (" ")
250	0.890	27.5	3.22	1.28	-30	97	0.2	85.32	11.39	1.4	-	187	" (" ")
Standard Conditions	0.880	29.3	5.88	1.86	-30	136	0.2	87.44	12.90	0.2	0.001	220	Intermediate
262	0.890	27.5	5.33	1.82	-40	123	0.5	85.67	12.51	1.1	0.004	215	Naphthene (wax-free)
257	0.899	25.9	4.20	1.69	-55	103	1.0	84.50	11.54	2.2	0.001	200	" (" ")

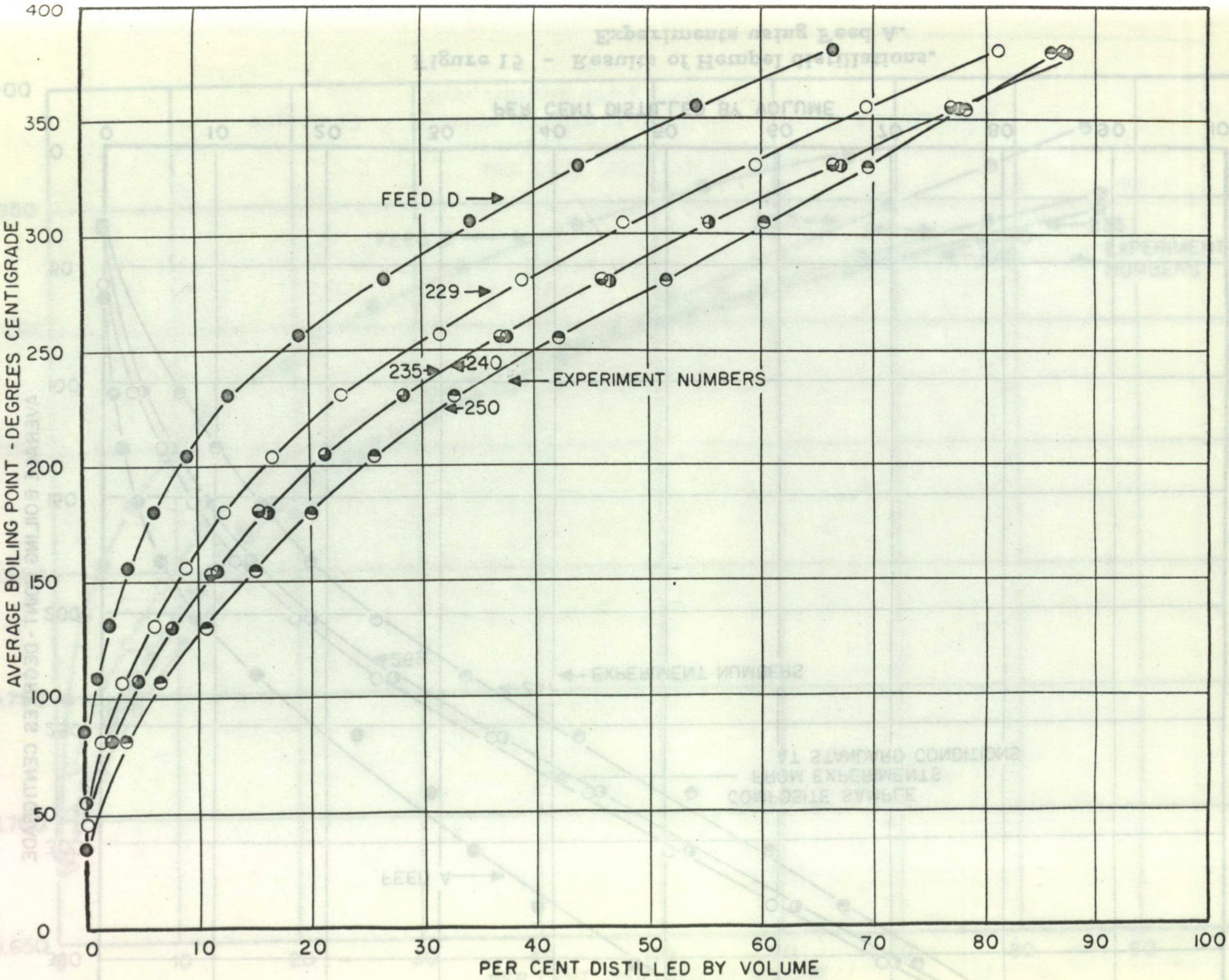

Figure 14 - Results of Hempel distillations.
Experiments using Feed D.

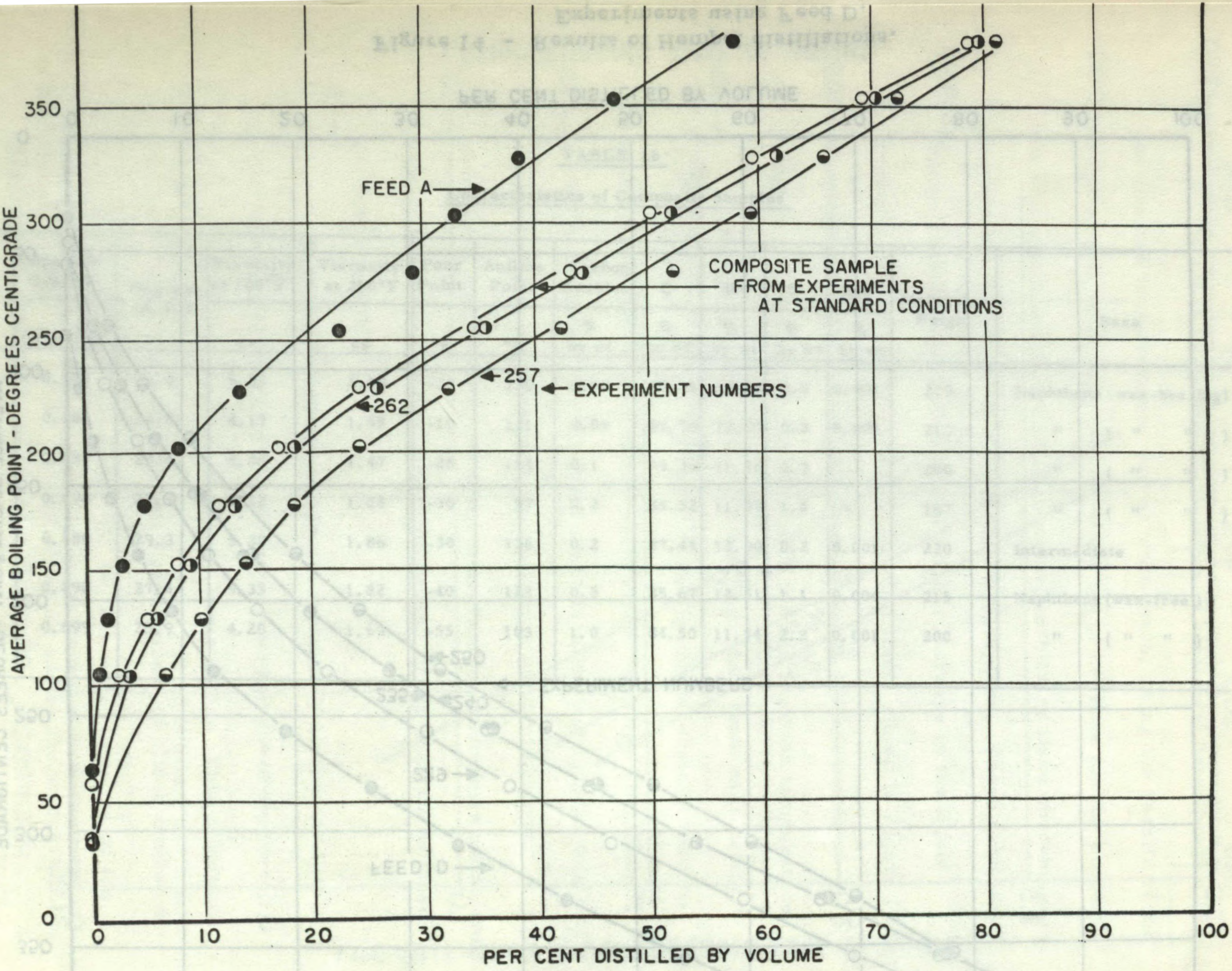

Figure 15 - Results of Hempel distillations. Experiments using Feed A.

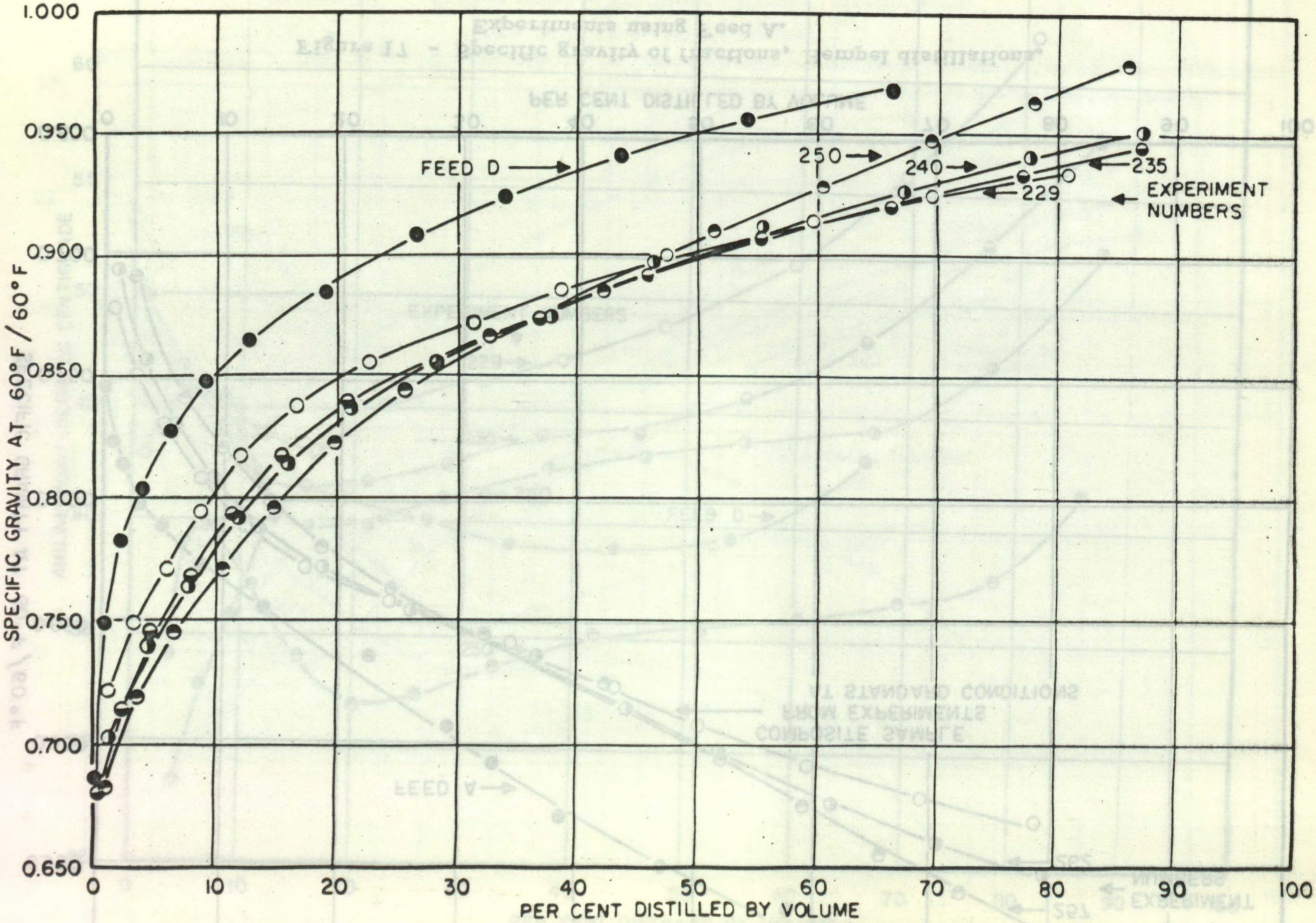

Figure 16 - Specific gravity of fractions, Hempel distillations. Experiments using Feed D.

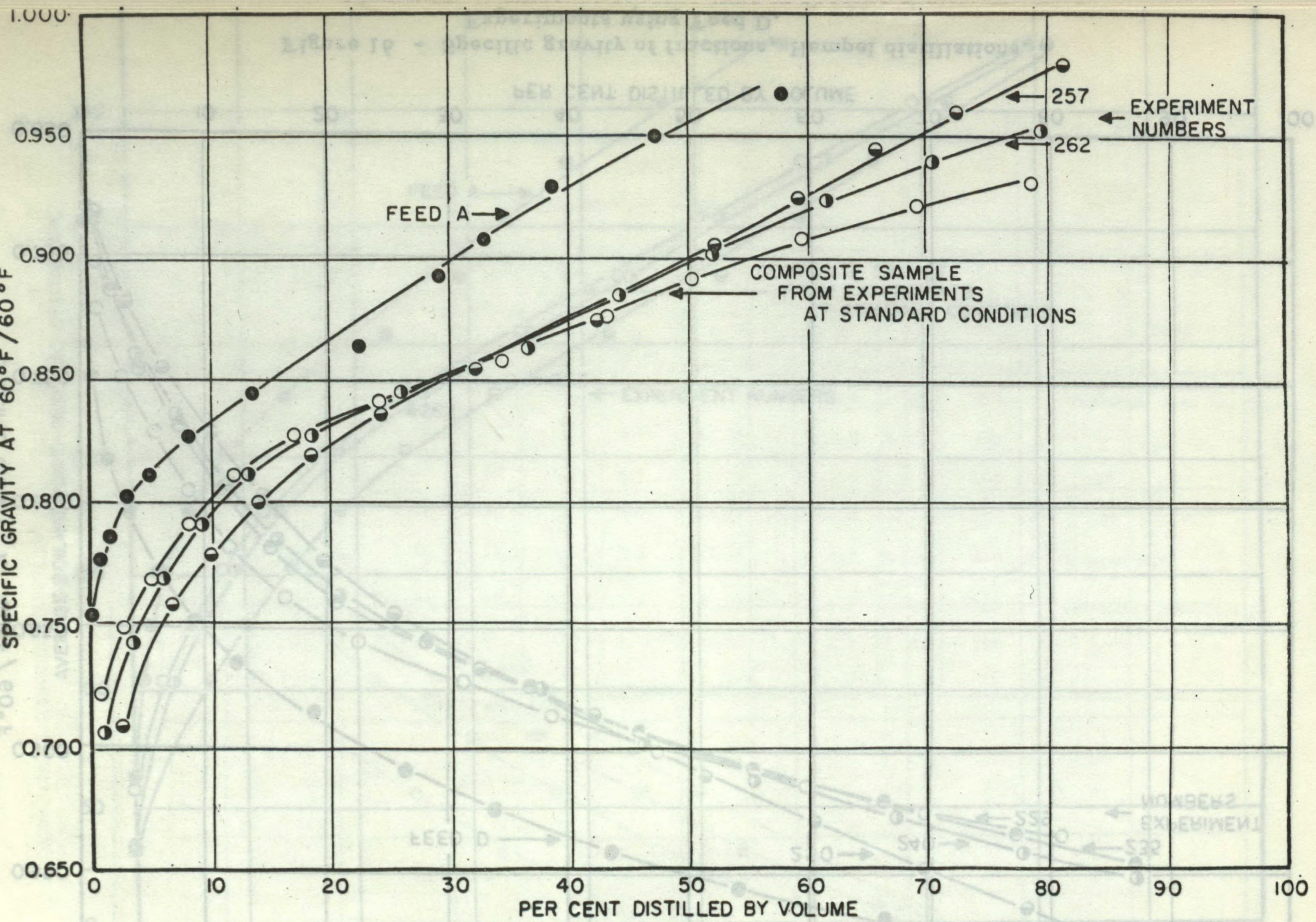

Figure 17 - Specific gravity of fractions, Hempel distillations. Experiments using Feed A.

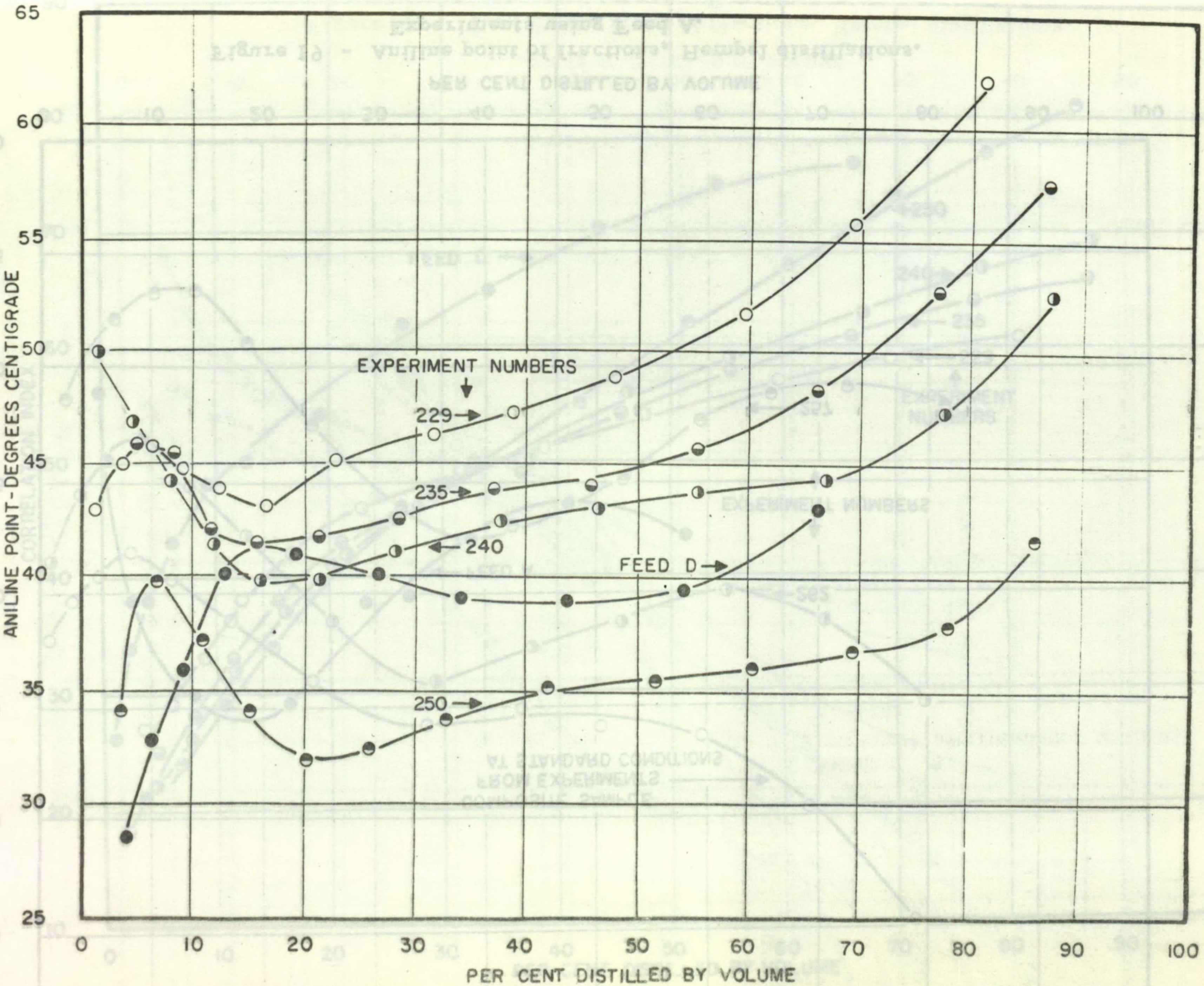

Figure 18 - Aniline point of fractions, Hempel distillations.

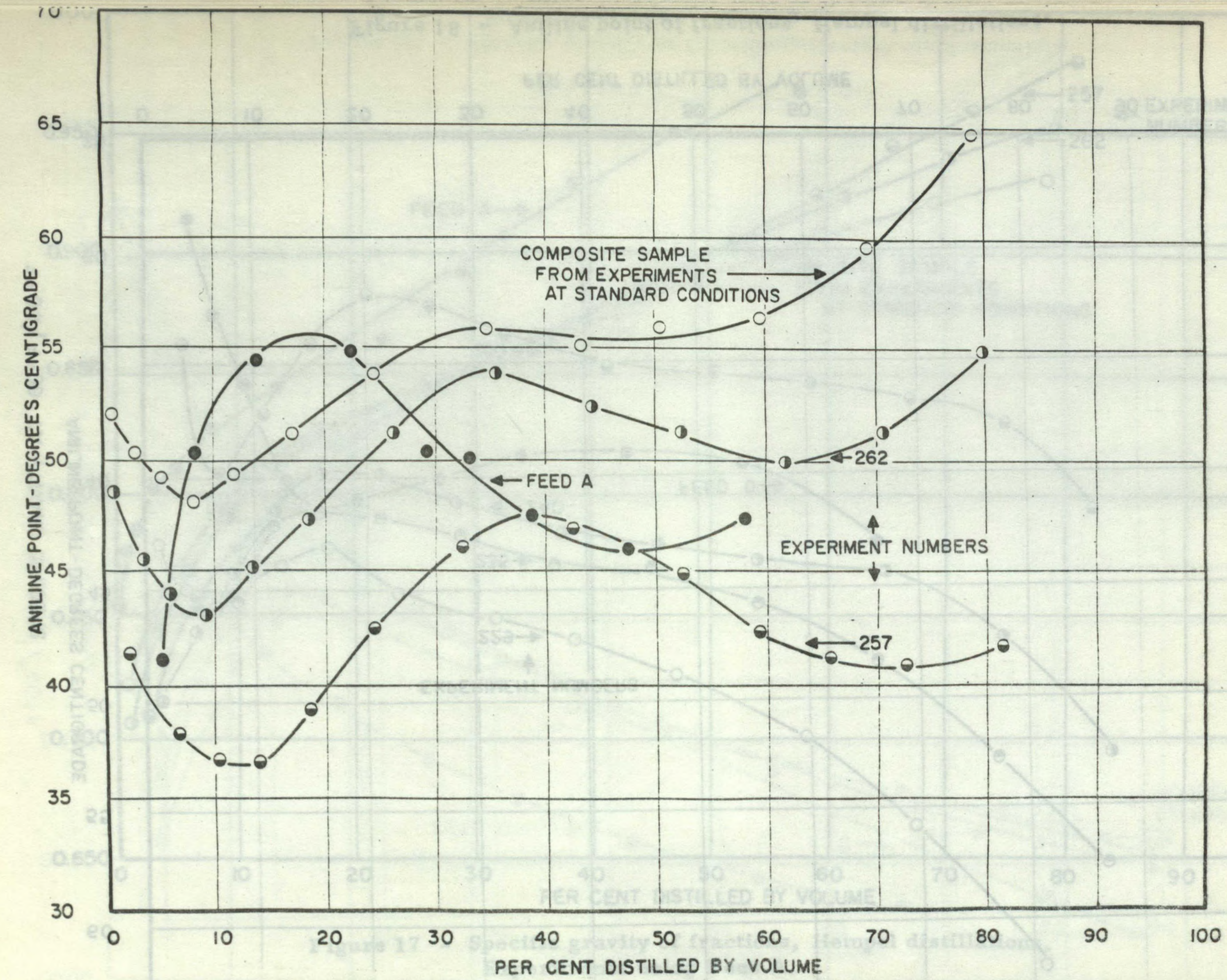

Figure 19 - Aniline point of fractions, Hempel distillations. Experiments using Feed A.

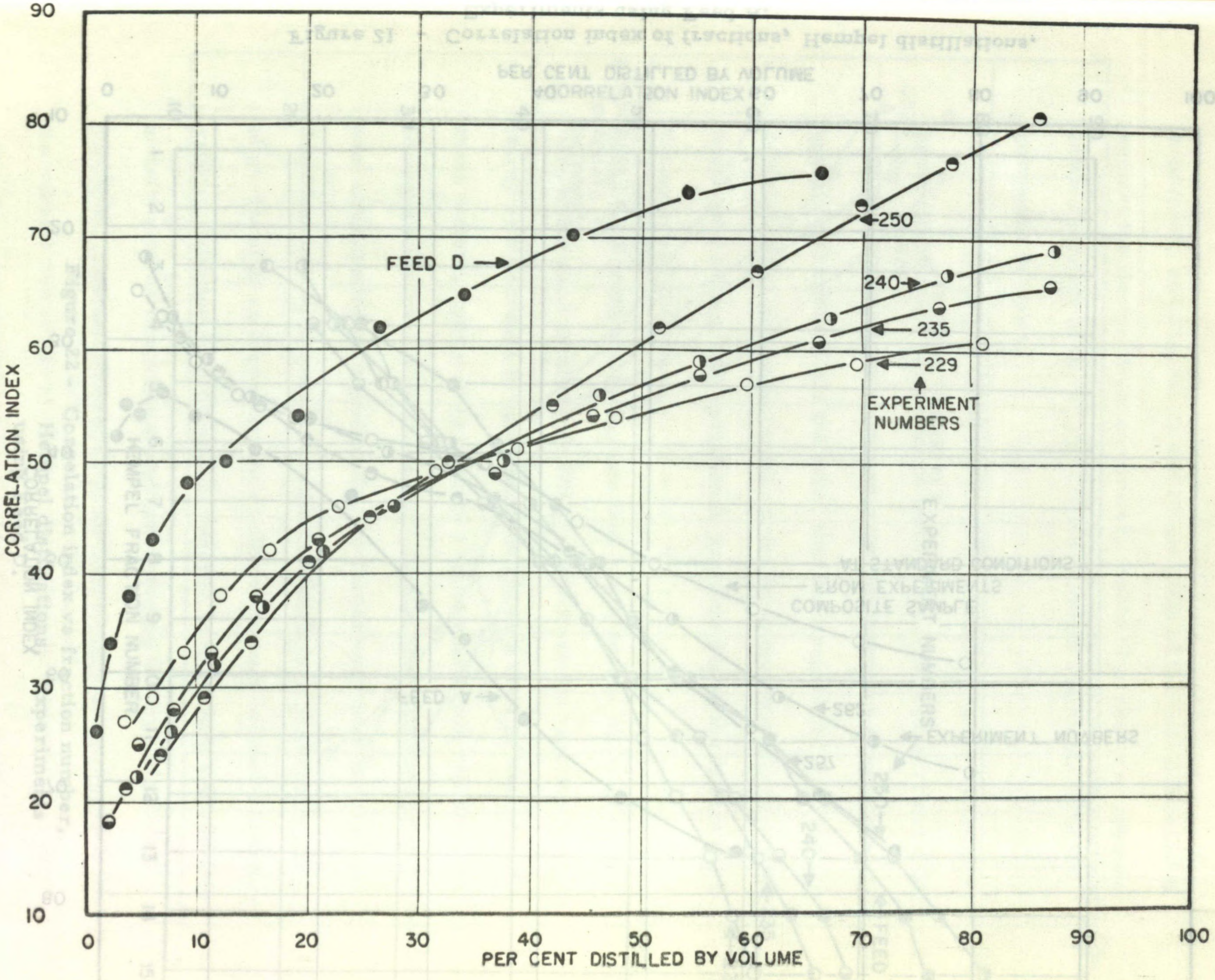

Figure 20 - Correlation index of fractions, Hempel distillations.
Experiments using Feed D.

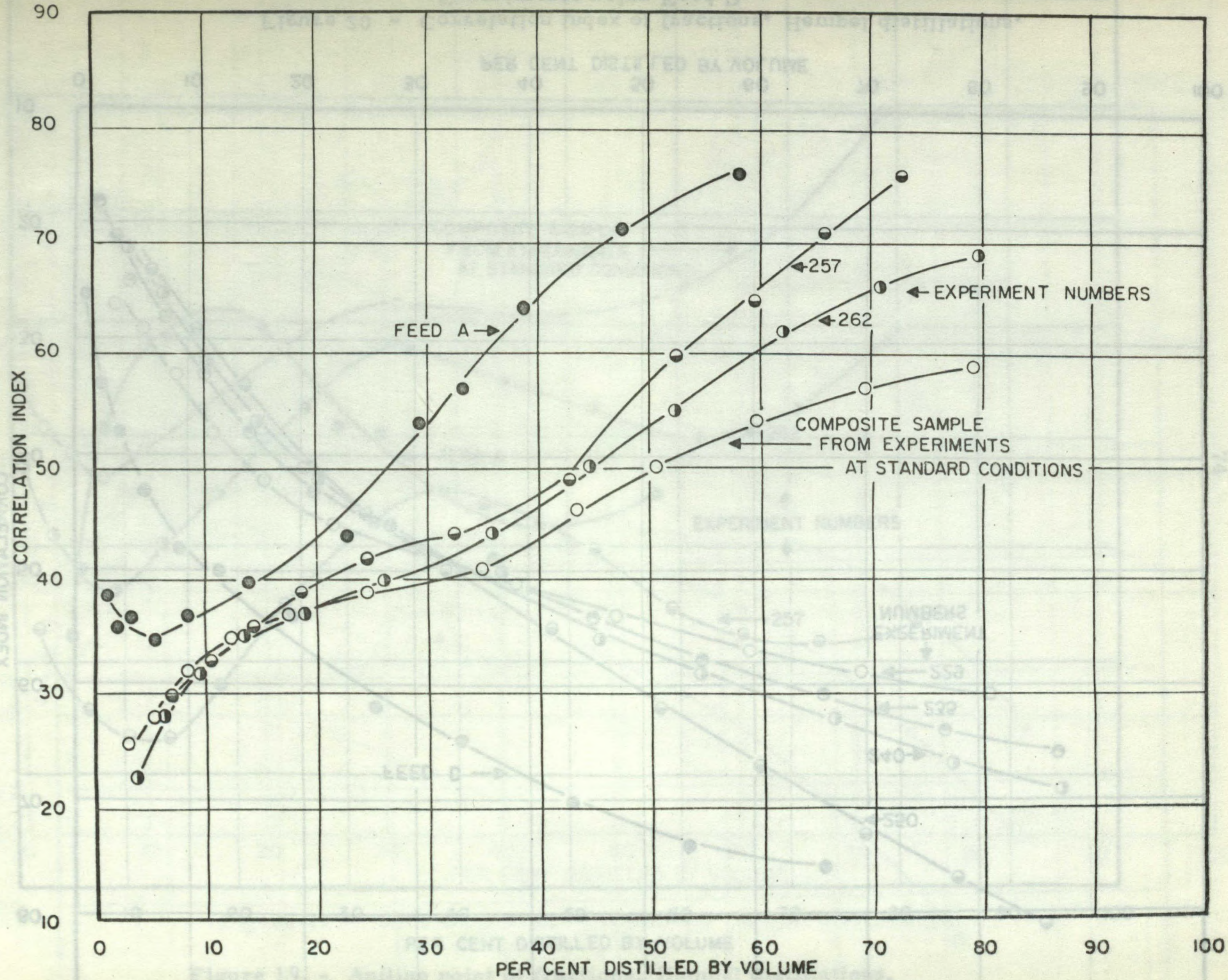

Figure 21 - Correlation index of fractions, Hempel distillations.
Experiments using Feed A.

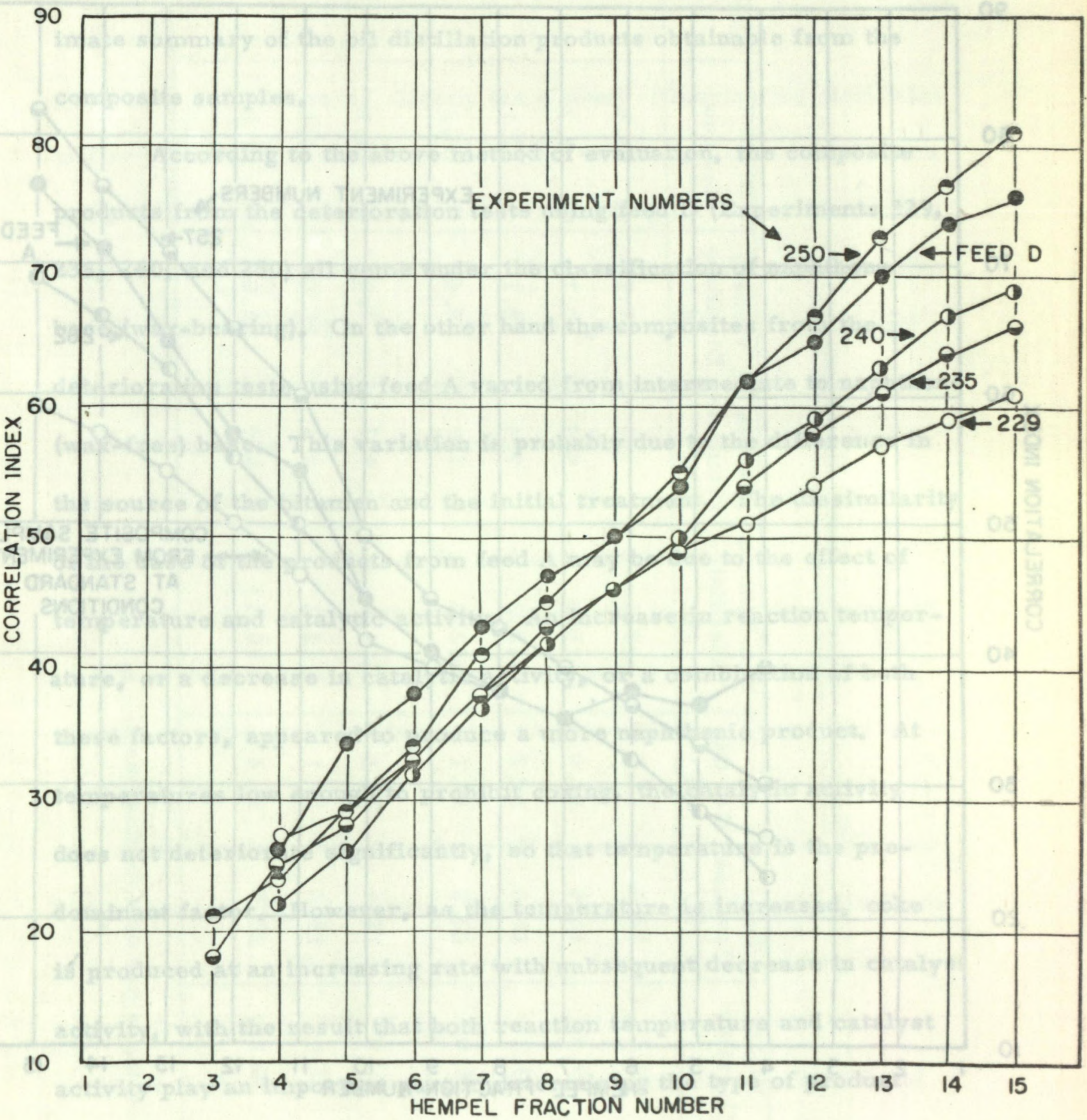

Figure 22 - Correlation index vs fraction number, Hempel distillations. Experiments using Feed D.

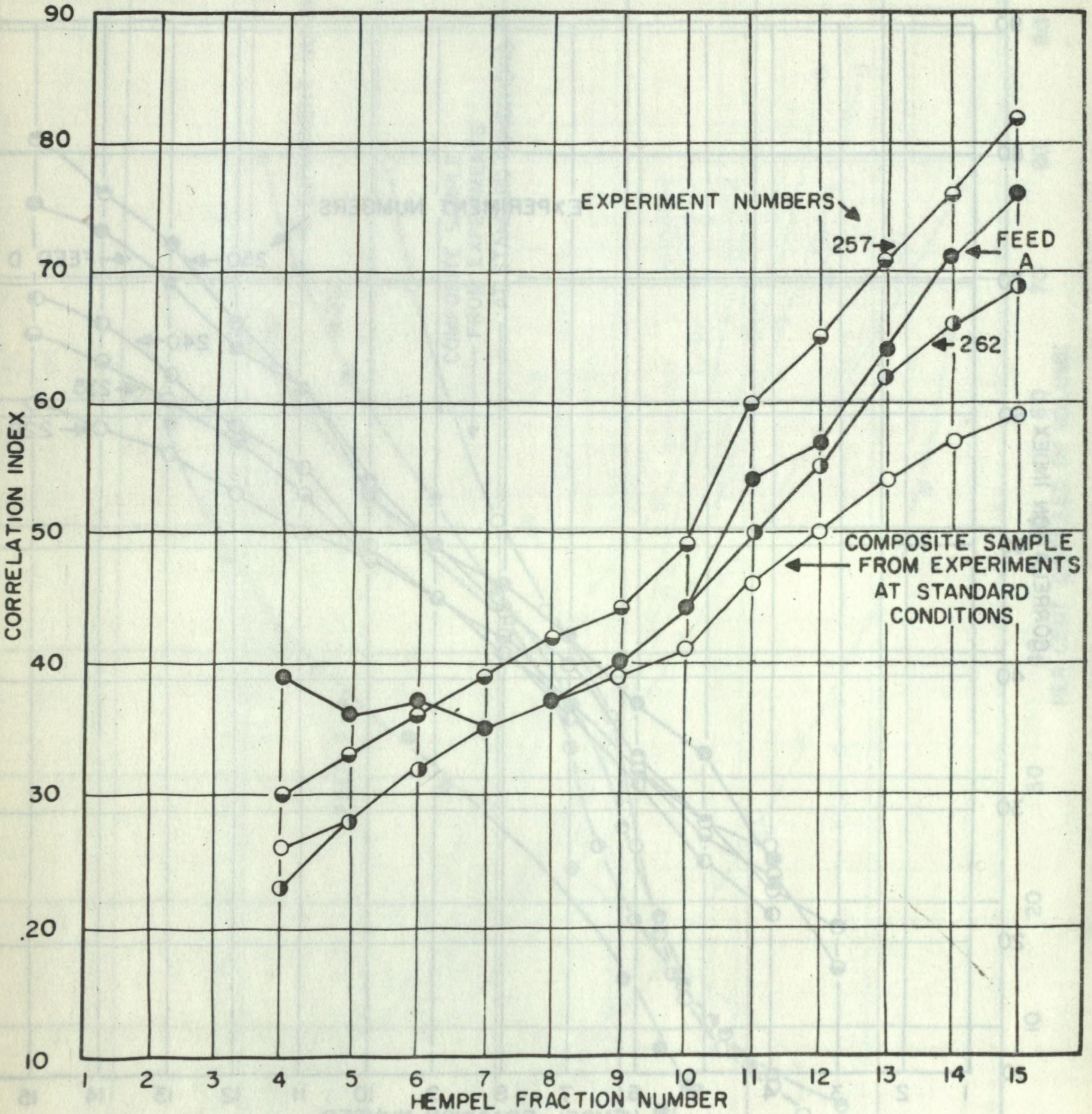

Figure 23 - Correlation index vs fraction number, Hempel distillations. Experiments using Feed A.

recovered, and Figures 22 and 23 are plots of the correlation index against the Hempel fraction number. Table 17 presents an approximate summary of the oil distillation products obtainable from the composite samples.

According to the above method of evaluation, the composite products from the deterioration tests using feed D (Experiments 229, 235, 240, and 250) all come under the classification of naphthene base (wax-bearing). On the other hand the composites from the deterioration tests using feed A varied from intermediate to naphthene (wax-free) base. This variation is probably due to the difference in the source of the bitumen and the initial treatment. The dissimilarity of the base of the products from feed A may be due to the effect of temperature and catalytic activity. An increase in reaction temperature, or a decrease in catalytic activity, or a combination of both these factors, appeared to produce a more naphthenic product. At temperatures low enough to prohibit coking, the catalytic activity does not deteriorate significantly, so that temperature is the predominant factor. However, as the temperature is increased, coke is produced at an increasing rate with subsequent decrease in catalyst activity, with the result that both reaction temperature and catalyst activity play an important part in determining the type of product produced. For this reason, no definite comparison can be made of the various composite products with respect to temperature. However, from the results obtained it is believed that a trend can be

TABLE 17

Summary of Hempel Distillation Products

Composite Sample	Light Gasoline %	Total Gasoline %	Gas Oil %	Non-Viscous Distillate %	Medium Distillate %	Viscous Distillate %	Residuum %	Distillation Loss %
Run 229	2.6	14.2	34.9	18.1	9.3	11.1	12.4	0.0
Run 235	3.3	18.0	38.0	15.2	9.9	10.7	8.2	0.0
Run 240	3.1	18.6	38.2	18.2	7.4	10.1	7.1	0.4
Run 250	5.0	22.8	38.1	12.4	7.0	9.4	8.2	2.1
Standard Conditions	1.9	14.4	37.1	14.8	9.7	7.8	16.2	0.0
Run 262	2.4	15.5	37.1	12.3	9.4	11.0	14.5	0.2
Run 257	5.1	20.9	36.4	10.8	6.9	12.0	13.0	0.0

Note: All percentages are on a volume basis.

established with respect to the temperature effect. An increase in reaction temperature produces a slightly larger fraction in the gasoline range, does not significantly affect the quantity of gas oil produced, and decreases slightly the amount of lubricating distillates and residuum. The aniline points of the various fractions from each composite sample decrease with corresponding increases in reaction temperatures indicating increasing olefin and aromatic content. The correlation index (46) in the range of temperatures employed is not affected materially in the gasoline or light gas oil range. However, from the light gas oils to the lubricating distillates, the correlation index shows a fairly rapid increase with the reaction temperature, also indicating increasing olefin and aromatic content.

The yield of straight run gasoline was low, varying from 14% to 23% of the product. The higher the reaction temperature the greater was the yield boiling in the gasoline range. There was no kerosene fraction produced in any of the tests. The yield of gas oil was approximately the same from all tests and ran between 35% and 38% of the total liquid product. The remaining high boiling distillate yield decreased with increasing reaction temperature. The yields ranged from 29% to 39% of the liquid product. The amount of residuum left, on removal of distillate to approximately 750°F end point, decreased with increasing reaction temperature. The residuum varied between 7% and 16% of the liquid product.

Each of the composite samples from Experiments 229, 235, 240 and 250 was distilled in a five-gallon still to produce a 400°F end point gasoline cut. The results of these distillations are shown in Table 18.

These 400°F end point gasoline cuts were analyzed and the results are shown in Table 19.

The 400°F end point gasoline showed a decrease in gravity with increasing reaction temperature, accompanied by a corresponding increase in sulphur content. The octane number increased with reaction temperature, and the lead susceptibility appeared to decrease slightly with increased temperature. The aromatic hydrocarbon content of the gasoline fraction was not affected by an increase in temperature, although the unsaturated compounds increased at the

TABLE 18

Summary of Distillations in 5-Gallon Still

Experiment No.	Gasoline Cut at 400°F		Residue above 400°F		Gas and Wettage Loss	
	% by wt	% by vol	% by wt	% by vol	% by wt	% by vol
229	12.9	14.7	85.5	83.4	1.6	1.9
235	15.8	18.0	82.6	80.1	1.6	1.9
240	17.3	20.0	81.1	78.5	1.6	1.5
250	22.1	25.5	75.8	72.3	2.1	2.2

TABLE 19

Analyses of Gasoline Cuts at 400°F

	Experiment Number			
	229	235	240	250
Specific gravity, 60°/60°F	0.777	0.774	0.771	0.771
Degrees, A.P.I.	50.6	51.3	52.0	52.0
Sulphur, % by wt	0.13	0.14	0.15	0.32
Saturated hydrocarbons, % by vol	71	67	65	55
Unsaturated hydrocarbons, % by vol	9	14	17	26
Aromatic hydrocarbons, % by vol	20	19	18	19
Octane No., motor method:				
Unleaded	59.8	60.6	63.9	69.0
Leaded with 1 ml TEL/Imp gal	64.1	66.1	68.4	73.5
Leaded with 3 ml TEL/Imp gal	70.2	71.1	73.6	76.1
Distillation, Engler, °F:				
Initial boiling point	139	142	136	134
5% recovered, by vol	200	192	190	174
10% " "	218	211	209	190
20% " "	240	238	234	220
30% " "	260	259	258	246
40% " "	283	280	276	270
50% " "	300	298	294	291
60% " "	317	314	311	309
70% " "	328	330	323	328
80% " "	346	344	343	345
90% " "	362	360	358	363
95% " "	372	370	368	376
End point	394	382	398	388
Recovery, % by vol	99.0	99.0	98.5	97.0
Residue, % by vol	0.4	0.6	0.5	1.1
Loss, % by vol	0.6	0.4	1.0	1.9

expense of a corresponding decrease in saturated compounds.

The gasoline cut at 400°F from Experiment 235 was fractionated with a 1 ft by 3/8 inch distillation column, packed with conical Stedman packing*. The refractive index of each fraction taken was determined with an Abbé-type refractometer at 25°C*. The volumes of the fractions as percentage of charge, the cutting temperatures in °C, and the refractive indices, are given in Table 20 and Figure 24.

Some fractions were then combined and about 1 ml of each of these fractions, or combination of fractions, was used to determine the relative amount of hydrocarbon types by means of the fluorescent indicator absorption method (47)*. The results are shown in Table 20 and Figure 24. It is interesting to note that the percentage of olefins remains practically constant throughout the boiling range. Similarly the aromatic content is fairly constant above the xylene boiling point.

When leaded with 3 ml of tetraethyllead the knock ratings of the gasoline cuts were lower than those shown in a recent Canadian survey of regular grade gasolines, which varied between 80 and 85 octane number (motor method). On the other hand, the sulphur contents met the maximum allowable limit of 0.15% as specified by the Canadian Government Specifications Board, with the one exception of the gasoline from Experiment 250, which utilized the highest

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* This work was done by H. Keller, Division of Applied Chemistry, National Research Council of Canada, Ottawa.

TABLE 20

Characteristics of Fractions from Gasoline Cut from Experiment 235

Fraction or Combined Fraction No.	Boiling Point		Distillate	Refractive Index	Hydrocarbon Type		
	°C	°F	% by vol of charge	N_D^{25}	Sat % by vol	Olefin % by vol	Arom % by vol
	35(IBP)	95					
	70	158	5				
1	75	167	7.5	1.4046	80	10	10
2	86	187	9	1.4263	62.5	15	22.5
3	100	212	16	1.4023	80.5	16	3.5
4	106	223	18.5	1.4200	68	16	16
	115	239	21	1.4223			
5	119	246	24.5	1.4090	80	17	3
6	126	259	29	1.4166	75	17	8
	129	264	30.5	1.4174			
7	140	284	36	1.4379	58	15	27
8	145	293	38.5	1.4338	63	16	21
9	148	298	41	1.4273	76	16	8
	150	302	44	1.4236			
10	155	311	46.5	1.4325	64	13.5	22.5
	158	316	49	1.4399			
	162	324	51.5	1.4429			
	164	327	53	1.4450			
	165	329	55	1.4452			
	166	331	57	1.4451			
	169	336	60	1.4456			
	172	342	62	1.4454			
11	173.5	344	64	1.4452	65	12	23
12	180	356	67	1 4477	62.5	12.5	25
13	184	363	69	1.4529	62	12	26
	187	369	72	1.4545			
	189	372	73	1.4558			
	192	378	75	1.4527			
14	194	381	77.5	1.4507	66.5	10	23.5
	195	383	78.5	1.4518			
	195(?)	383(?)	81	1.4518			
15	200	392	83.5	1.4592	59	10	31

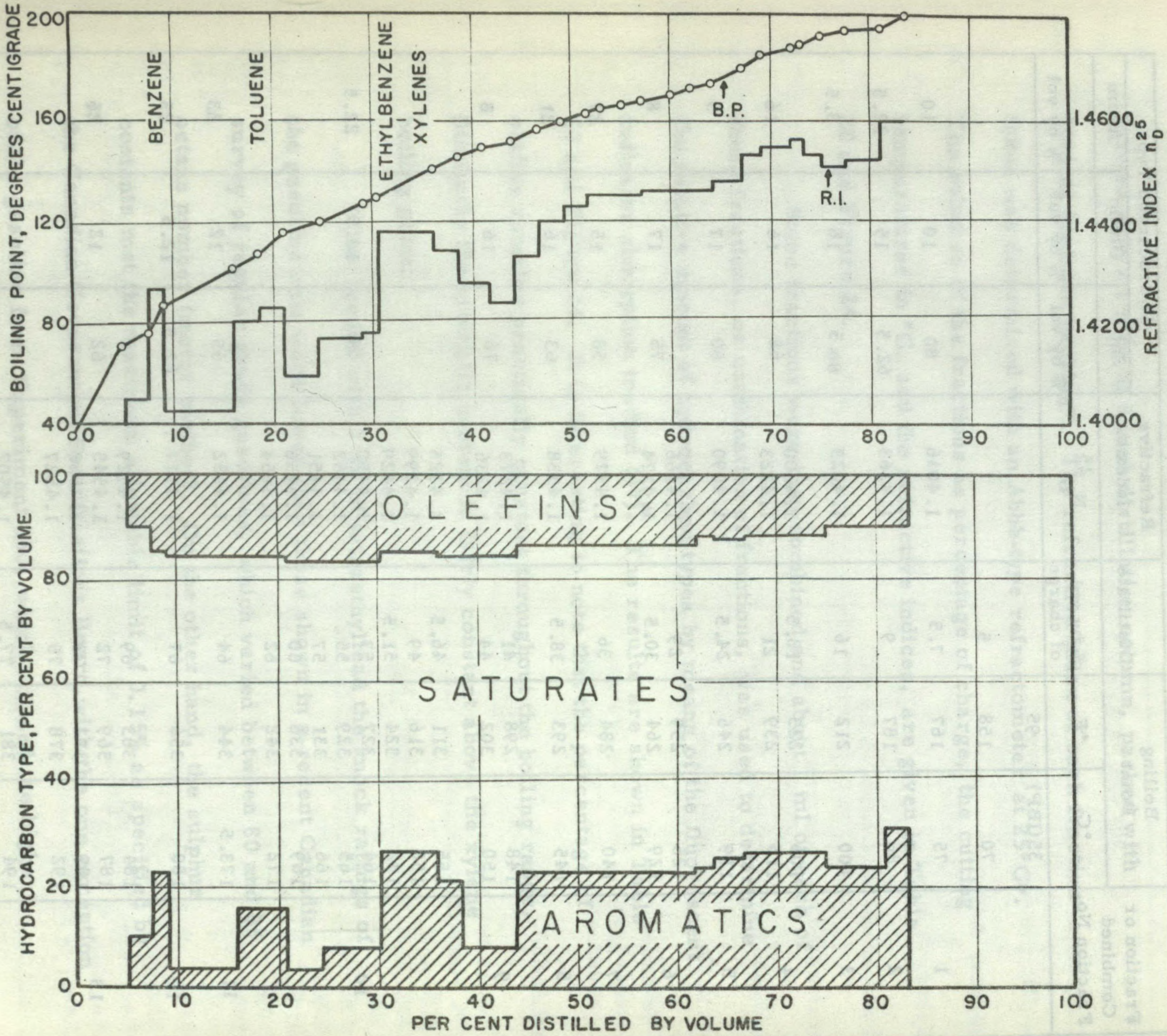

Figure 24 - Refractive index and hydrocarbon type of fractions from distillation of gasoline cut.

operating temperature. The volatility was low and would require quite extensive blending in the lower boiling range to raise it to the required specification.

The Diesel Indices were determined for the gas oil fractions of the Hempel distillations and are given in Table 21. The results show that the Diesel Index decreases as the operating temperature increases, because of the increased content of unsaturates resulting from increased cracking. On the basis of 40 as the minimum Diesel Index requirement for a good grade of diesel fuel, two of the gas oils meet this specification. If the Diesel Index of the remainder could not be raised by the addition of cetane improvers to meet diesel fuel specifications, they could be used as No. 2 fuel oil.

TABLE 21

Diesel Index of Gas Oil Fractions

Experiment No.	Original Feed	Diesel Index
229	D	36
235	D	33
240	D	32
250	D	27
Standard Conditions	A	44
262	A	41
257	A	35

A portion of the remaining high boiling distillate produced at the lower reaction temperatures could probably be blended with the gas oil to increase the No. 2 fuel oil production. The remainder of these distillates could be used as Nos. 4 and 5 fuel oils, or as cracking stock or recycle hydrogenation stock.

ACKNOWLEDGMENTS

The authors wish to acknowledge the contribution of Dr. T.E. Warren, Senior Scientist of the Fuels Division from 1929 to 1952,* under whose direction this investigation was initiated and the earlier portion of the work was done.

They also wish to express their appreciation to the following members of the Fuels Division for their assistance in the operation of the experimental equipment: Dr. Mary L. Boyd and Messrs. G. Hinton, L. Labelle, W.H. Merrill, M.P. Pleet and A. Yates. The analytical work was done by the Liquid and Gaseous Fuels Analysis Section and the Solid Fuels Analysis Section. Illustrations in the text were drawn by Mr. M.P. Pleet.

Fractionation of the gasoline from Experiment 235 and the subsequent determination of hydrocarbon types were done by Dr. H. Keller of the Division of Applied Chemistry, National Research Council of Canada, Ottawa.

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*At present Director, Research Council of Saskatchewan, Saskatoon, Saskatchewan.

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