THE SEPARATION OF HYDROCARBONS WITH MOLECULAR SIEVES

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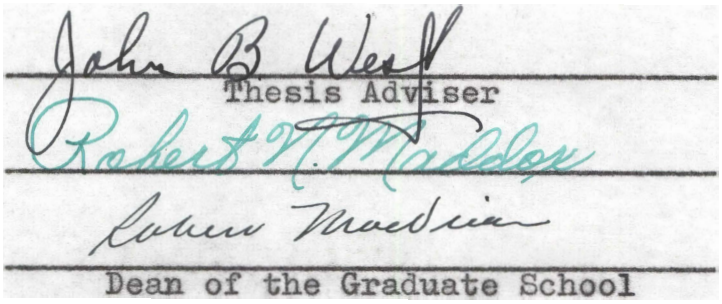

PREFACE

The purpose of this study was to determine the feasibility of separating normal-hydrocarbons from binary or multicomponent mixtures by selective adsorption with Linde Air Products Company "Molecular Sieves".

Specific studies were made on the adsorption capacity of the Molecular Sieves at definite charge rates with charge stocks of known composition.

Particular emphasis was also placed on increasing the octane number of refinery stream samples of catalytic reformate and light naphtha, by the adsorption of their low octane number normal-paraffin components.

The author wishes to express his gratitude to Dr. John B. West for his guidance and suggestions throughout the course of this work.

Sincere appreciation is also due the Continental Oil Company for furnishing the materials and equipment required for the experimental studies.

Above all, the author is most deeply indebted to his wife, Sue, for her patience and consideration throughout his graduate studies.

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CHAPTER I

INTRODUCTION

In the latter part of 1954, a new adsorbent material was announced by the Linde Air Products Company, a division of Union Carbide and Carbon Corporation. The material was trade-named "Molecular Sieves" because it will separate liquid and gaseous materials on the basis of a difference in molecular size.

The material was classified as a synthetic adsorbent with high selectivity. The following possible applications in process operations or research were suggested by Linde[1].

1. Hydrocarbon separation; for example, straight chain from cyclic and branched chain hydrocarbons.

2. Recovering unsaturates from waste gas streams; for example, ethylene, acetylene, propylene.

3. Gas purification; for example, removal of unwanted substances such as carbon monoxide and dioxide, ammonia, hydrogen sulfide and mercaptans.

4. Drying liquids such as transformer oils, ethanol, toluene, benzene, pyridine and others.

[1]Linde Air Products Company, Technical Bulletin, Form 8614, January, 1955

Chemically, the new materials are synthetic zeolites, quite similar to many natural clays and feldspars. The atoms of sodium, calcium, aluminum, silicon and oxygen in the Molecular Sieves (mainly in the form of sodium or calcium aluminum silicates) are arranged in a definite and consistent crystalline pattern. The structure contains a large number of cavities, interconnected by a number of smaller holes or pores. These cavities and pores are very uniform in size. When the water of hydration is driven off, the crystalline structure retains its form and it is strong enough to be brought up to red heat without breaking down.

The empty cavities have a strong tendency to recapture the water molecules driven off during manufacture. If no water is present, they will accept almost any material that can pass through the pores and into the cavities. This property is the reason for the material's ability to separate hydrocarbon molecules selectively.

Linde research groups have been working on the development of Molecular Sieves since the late 1940's and started a test marketing of the material in March, 1954.

Two types of Molecular Sieves have been developed, differing only in the size of the pore diameter.

The first, Linde type 4 A, a sodium aluminum silicate, has a pore opening of about 4 Angstroms in diameter and can adsorb molecules with a diameter of less than 4 Angstroms.

The second, Linde type 5 A, is a calcium aluminum silicate, with a pore opening of about 5 Angstroms diameter.

The Linde 4 A material will permit ethane molecules to enter the pores but will not admit propane or larger molecules. Linde type 5 A material, with a larger pore opening than the 4 A, will permit the adsorption of straight-chain hydrocarbons like normal-hexane, but not branched-chain iso-hexanes or cyclics like benzene or cyclohexane. Table I gives the molecular diameters of some of the molecules separated by Molecular Sieves.

An extremely desireable property of either type of Molecular Sieve is that it may be reactivated to it's original state. The reactivation is performed by simultaneous heating and purging with a dry inert gas. This permits the same batch of Molecular Sieves to be used again and again in a cyclic process.

Due to the unique properties of Molecular Sieves and their availability as a new material in the field of adsorption, it was decided to make a study of their properties in special applications, as a basis for this study.

The initial problem was to determine the effect of varying liquid velocity and charge stock composition to an adsorption column under controlled conditions.

The removal of normal-paraffins from specific refinery streams was also obtained and the accompanying rise in the octane rating of the product was determined.

TABLE I

MOLECULAR DIAMETERS[2]

Material	Angstrom Units
Helium	2.66
Hydrogen	2.76
Oxygen	2.92
Ammonia	3.06
Nitrogen	3.14
Carbon Dioxide	3.24
Methane	4.0
Ethane	4.0
Propane and heavier n-paraffins	4.89
Iso-butane and heavier iso-paraffins	5.58
Benzene	5.6
Methyl Cyclohexane	5.7

[2]Glasstone, Samuel., Textbook of Physical Chemistry, Second Edition, 1946, 1194-1210, D. Van Nostrand Company.

CHAPTER II

REVIEW OF THE LITERATURE

The Linde Molecular Sieves are a synthetic zeolite with a chemical composition and crystalline structure similar to a naturally occuring zeolite known as chabasite. Zeolites are classified as hydrous silicates occuring as natural minerals in volcanic rocks, often in the form of large crystals. Brunauer[3] stated the formula for chabasite is $CaO.Al_2O_3.4\ SiO_2.6\ H_2O$.

Brunauer also stated it has been found from X-ray examination that the water molecules in zeolites are not held by ordinary valence bonds, but merely fit into the vacant spaces in the lattice of the aluminum, silicon, oxygen and metal atoms. On dehydration, part of the water is removed and the spaces can then be filled by other molecules. The six molecules of water can be removed from the chabasite crystal by simultaneous heating and purging or evacuation. The dehydration leaves the framework of the crystal unchanged; only when 93 per cent of the water is removed does the structure begin to collapse.

Crystallographically, chabasite is based on a three dimensional network of silica tetrahedra, in which one-third of the silicon is replaced by aluminum ions.

[3]Brunauer, Stephan. The Adsorption of Gases and Vapors. Volume 1, Physical Adsorption, Princeton University Press, 1945, 366

The replacement gives rise to an excess negative charge, which is balanced by the incorporation of positive ions. In nature, calcium is the most common positive ion but it can be substituted by other positive ions, such as sodium, potassium, barium, copper, etc.

In 1916, Smith[4] presented the chemical analysis of five samples of minerals classified as chabasite.

TABLE II

CHEMICAL ANALYSIS OF CHABASITE

Component	Weight per cent
SiO_2	46.64 - 48.82
Al_2O_3	18.06 - 20.04
CaO	5.01 - 8.81
SrO	0.02 - 0.60
K_2O	0.33 - 2.13
Na_2O	0.33 - 3.81
H_2O	21.56 - 22.09

Investigation of the adsorption properties of chabasite were made in 1921 by Nacken and Wolff[5]. An apparatus was developed for measuring the volume of gas adsorbed under various physical conditions. It was determined that dehydrated chabasite strongly adsorbs

[4]G.F.H. Smith, Mineral Mag., 17, 274-304 (1916)

[5]R. Nacken and W. Wolff, Centr. Min. Geol., 364-72 (1921)

air, nitrogen, carbon dioxide, and illuminating gas. In one experiment, chabasite took up fourteen times it's own volume or 1.3 per cent by weight of nitrogen.

The effect of various temperatures on the dehydration of chabasite is described by Rothmund[6]. Samples of chabasite were allowed to stand over 1 N. sulfuric acid at 25° C. until they took up a definite quantity of water. They were then heated at a definite temperature for thirty minutes and then hydrated as before. This was begun at 100° C. and the temperature raised 50° C. each time until the temperature had reached 1000° C.

It was found that the adsorption of water by chabasite was completely reversible up to 600° C. At 800° C. the chabasite became "dead burnt" and would no longer adsorb water under the prescribed conditions.

In 1928, Schmidt[7] investigated the adsorption of seventeen various gases by chabasite. It was found that the nine smaller molecules with diameters of less than 4 Å. gave normal adsorption values, but the eight larger molecules showed smaller adsorption or none at all. He concluded that ethylene is the largest molecule that gives normal adsorption.

The phenomenon of allowing the smaller molecules to penetrate into the pores of the adsorbent while the larger

[6] V. Rothmund, Rec. trav. chim., 44, 329-39 (1925)

[7] O. Schmidt, Z. phys. Chem., 133, 263 (1928)

molecules are shut out, was termed "persorption" by J. W. McBain[8].

In 1933, Porter[9] reported the adsorption on chabasite of the liquids; water, methanol, formamide, formic acid, and methyl cyanide.

Rabinowitsch and Wood[10] investigated the effect of base exchange on the adsorptive capacity of chabasite. They found that the replacement of calcium by sodium ions had only slight effect on hydrogen adsorption, but eliminated almost completely the nitrogen adsorption. Replacement of calcium by potassium ions cut down very strongly both the hydrogen and nitrogen adsorption. They explained the results by discussing the sizes of the three ions involved.

The sodium ion with a radius of 0.98 Å. was slightly smaller than the calcium ion with a radius of 1.06 Å., but each calcium ion is replaced by two sodium ions in the base exchange. This is sufficient to prevent the entry of the larger nitrogen molecules into the very fine pores of chabasite, but hydrogen can still enter readily. The potassium ion, with a radius of 1.33 Å. is large enough to shut out even the hydrogen molecules.

Adsorption data and thermodynamic properties of

[8]J. W. McBain, Colloid Symposium Monograph,4, (1926)

[9]J. L. Porter, J. Physical Chem., 37, 361-66, (1933)

[10]Rabinowitsch and Wood, Trans. Far. Soc., 32, (1936)

chabasite with various normal and iso-paraffins were presented by Barrer and Ibbitson[11]. The adsorption of helium, argon, nitrogen, methane and ethane occured very rapidly. The adsorption of normal-paraffins (propane, normal-butane, normal-pentane and normal-heptane) occured fairly rapidly at temperatures of 100° C. and higher.

Hydrocarbons with side chains (iso-butane, iso-pentane and iso-octane) were totally excluded under all conditions. When adsorption occured, equilibrium was reversible and could be approached from the sorption or desorption sides.

In 1940, the Linde Air Products Company organized a research group to study adsorption and adsorbent materials. It was during the course of this study that the synthetic zeolites known as Linde Molecular Sieves were developed.

In late 1954, an announcement was made in technical publications[12] that Linde had developed the olecular Sieves to the extent that several tons had been marketed and production of the various types of sieves was sufficient to provide small quantities of the various types to interested laboratories.

An illustrated brochure was distributed by Linde

[11] R. . Barrer and D. A. Ibbitson, Trans. Faraday Society, 40, 195-206, (1944)

[12] Chemical & Engineering News, 32:4786, Nov. 29, 1954

describing the various properties of the Molecular Sieves and some of their applications[13].

The subject of liquid hydrocarbon separation was briefly covered by Linde in their technical bulletin on "Hydrocarbon Purification"[14].

An adsorption column containing Linde type 5 A olecular Sieve pellets one-sixteenth inch in diameter was used in all of their experiments.

The first experiment was the separation of normal-tetradecane from a mixture containing five weight per cent normal-tetradecane in benzene. A loading of 8.8 per cent by weight of normal-tetradecane was obtained on the Molecular Sieves, before the breakthrough of the normal-tetradecane. The breakthrough was determined by measuring the refractive index of the effluent. An equilibrium loading of 10.7 weight per cent normal-tetradecane on the Molecular Sieves was obtained.

After draining the column, the liquid remaining in the pellets was removed by evacuation. The adsorbed normal-tetradecane was then removed by the adsorbent by steaming the bed at 250° C. and condensing the desorbed vapor. Refractive index measurements on the benzene and

[13]Linde Air Products Company, Technical Bulletin, Form 8614, Linde olecular Sieves For Selective Adsorption, January, 1955.

[14]Linde Air Products Company, Technical Bulletin, Hydrocarbon Purification, Form 8603, December, 1954.

normal-tetradecane indicated the materials recovered were approximately 99.9 mol per cent pure.

The second experiment discussed was the separation of normal-heptane from a mixture of 11.3 mol per cent normal-heptane in methylcyclohexane. A loading of 8.2 weight per cent normal-heptane on the adsorbent was determined before the breakthrough of the normal-heptane. An equilibrium loading of 10.4 weight per cent normal-heptane on the adsorbent was obtained. The adsorbed normal-heptane was removed by heating the Molecular Sieves to 350° C. and purging with one liter per minute of dry nitrogen.

The third experiment was the purification of commercial grade iso-pentane by removing its normal-hydrocarbon impurities. The normal-hydrocarbon impurities were present at a concentration of 9 weight per cent. The breakthrough point of the normal-hydrocarbon impurities was not determined. On desorption of the Molecular Sieves a normal-hydrocarbon loading of about 12 weight per cent was obtained. Infra-red analysis on the initial column effluent did not detect any normal-hydrocarbons.

CHAPTER III

MATERIALS AND EQUIPMENT

Materials

The adsorbent used in all of the experiments was a sample of Linde type 5 A Molecular Sieves. The sieves were in the form of extruded pellets, approximately 1/16 inch diameter and 3/16 inch length. Physical and chemical properties for this type of Molecular Sieve are presented in Table X.

The normal-heptane was ASTM normal-heptane prepared by the Phillips Petroleum Company as a Knock Engine Test Reference Fuel. The National Bureau of Standards reported test results on a sample from the original lot. The test results are presented in Table XI.

The nitration-grade toluene was supplied by the Colorado Fuel and Iron Company. Analysis by a General Electric mass spectrometer indicated a purity of 99.1 volume per cent toluene. The refractive index at 68° F. was 1.4960. Doss[15] reported the refractive index of toluene at 68° F. to be 1.49685.

The samples of catalytic reformate, light naphtha, and catalytic cracked gasoline were stream samples from refinery processing units. Physical data on the refinery samples are presented in the Appendix.

[15]Doss, M. P., Physical Constants of the Principal Hydrocarbons, Fourth Edition, 1943, The Texas Company.

Equipment

A schematic diagram of the equipment is shown in Figure 1.

The pump used in all of the experiments was a Milton Roy "miniPump" with a volume metering control. The pump was calibrated before proceeding with the experiments and found to be readily controlled between pumping rates of 100 to 1100 ml. per hour.

The adsorption column was a 2.5 cm. i.d. Pyrex glass tube, 4 feet long, with ball joint connections. A glass tube was added to provide a liquid outlet six inches below the top of the adsorption column.

Indentations in the adsorption column, two inches from the bottom, provided a seat for a 20 mesh stainless steel gauze serving as a packing support.

A 2 mm. i.d. Pyrex tube was sealed at the lower tip and placed 20 inches into the middle of the adsorption column. The tube served as a thermal well for the iron-constantan thermocouple used to control reactivation temperatures.

A total of 403.0 grams of new, Linde type 5 A Molecular Sieves were charged to the column. This was equivalent to a volume of 578 ml. of adsorbent.

The column was completely wrapped with two 6-ft. lengths of Briskeat flexible electric heating tape. The tapes had a maximum rating of 700 watts each and were connected in parallel to provide a maximum heat output

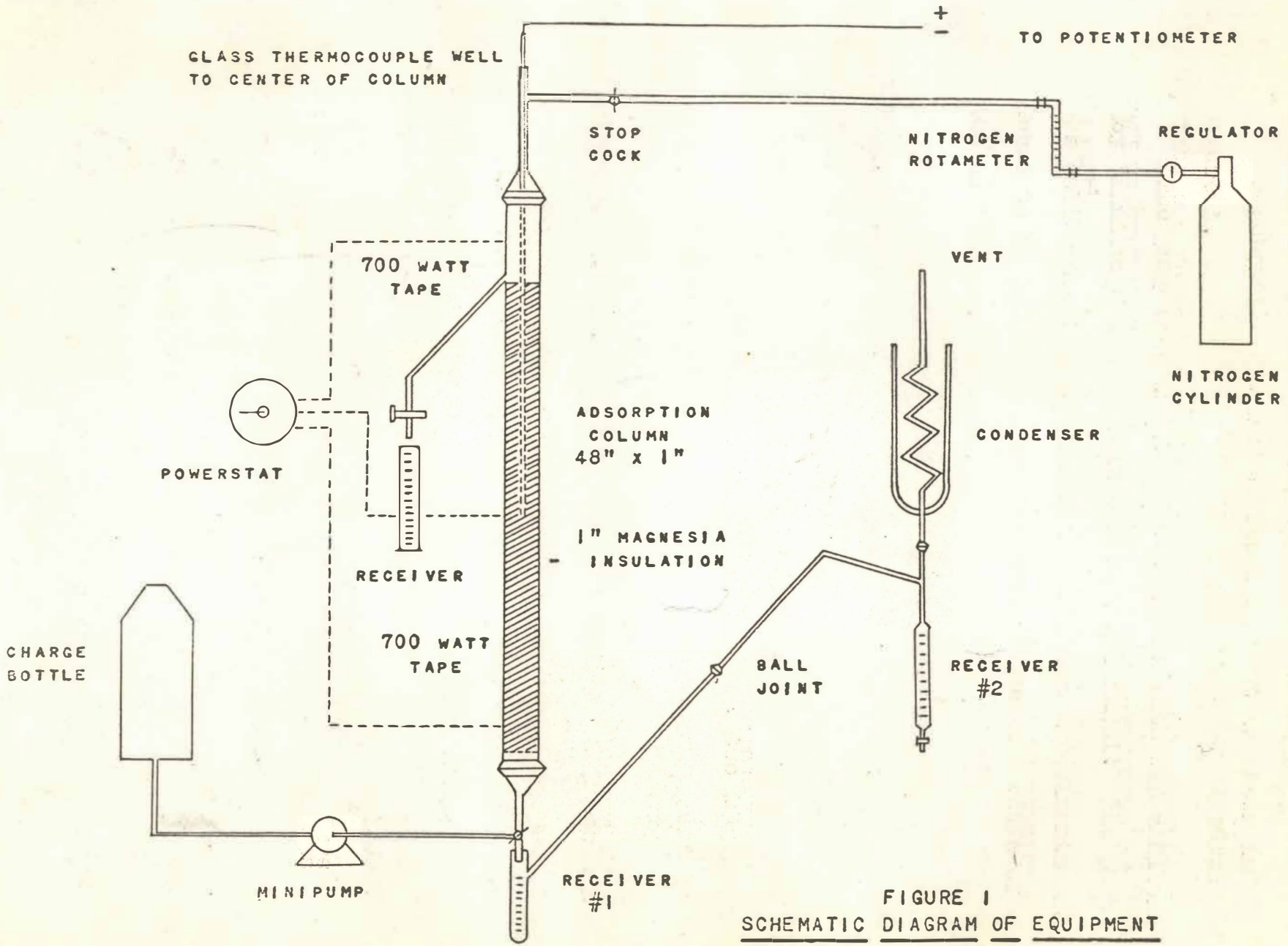

FIGURE 1
SCHEMATIC DIAGRAM OF EQUIPMENT

of 1400 watts.

The heating tape was wrapped with 1-inch wide fiber glass tape to prevent the slipping of the heating tape on heating.

The entire heating section was insulated with one inch of magnesia insulation.

A 110 volt, 15 ampere output powerstat was wired to the heating tape connections. A thorough check was made to insure that the connections were secure and each tape was functioning properly.

Adapters with ball joint connections were designed for each end of the adsorption column to control the liquid or gas flow during the various phases of the operation.

A vacuum-jacketed condenser was constructed with a cooling coil approximately two feet in length. The condenser would hold approximately 0.5 liter of dry ice and acetone at -110° F.

Condensate receiver #1 was a graduated 50 ml. tube with a specially installed gas outlet side-arm.

Stainless steel tubing was used between the liquid charge bottle and the miniPump and also between the miniPump and the base of the adsorption column.

Short sections of polyethylene tubing were used to make the connections between the glass and metal tubing.

The entire system was checked for leaks by evacuation and then observing the rate of pressure increase in the system with a mercury manometer.

The iron-constantan thermocouple wire was number 30 B. & S. gauge. The thermocouple wire was made by the Leeds and Northrup Company.

A Leeds and Northrup standard potentiometer was used in conjunction with the thermocouple wire. The potentiometer was frequently checked during each run to insure that it was standardized.

A single cylinder of Linde high pressure nitrogen was adequate for the purge gas required during the reactivation of the sieves.

The nitrogen regulator was combined with a Hoke-Phoenix nitrogen flowmeter in a single unit. The nitrogen flowmeter had been calibrated at flow rates of 0.25 to 20.0 liters of nitrogen per minute at standard temperature and pressure by the manufacturer. Several runs were made to confirm the indicated calibration.

Silicone stop-cock grease was used on all glass stopcocks to insure proper working action. No grease was placed on the ball-joint fittings in order to reduce sample contamination to a minimum.

Metal spring clamps were placed on each ball-joint connection to maintain a tight seal.

An Abbe "60" refractometer, thermostatically controlled at 68° F., was used for all refractive index determinations. The refractometer was calibrated with standard test samples furnished by the manufacturer before each series of samples was tested.

The analytical balance was a Gram-atic balance made in Switzerland by E. Mettler. All weights were built into the balance. The balance was checked with a set of standard weights supplied by the Fisher Scientific Company.

CHAPTER IV

EXPERIMENTAL WORK

The experiments were all based on liquid adsorption using Linde type 5 A Molecular Sieve pellets with a diameter of one-sixteenth inch.

The experimental work was divided into three phases. The first phase was to determine the equilibrium capacity of new sieves for normal-heptane in a static system.

The second phase was to determine the capacity of the sieves at specific liquid charge rates with synthetic charge stocks of known composition.

Two synthetic mixtures of ASTM normal-heptane and nitration-grade toluene were carefully prepared. The first mixture was a blend containing 5.0 weight per cent normal-heptane in nitration-grade toluene. The second mixture was a blend containing 10.0 weight per cent normal-heptane in nitration-grade toluene.

Four experimental runs were made on each synthetic mixture at liquid hourly space velocities of 0.416, 0.832, 1.248, and 1.664. These specific charge rates were selected to bracket the miniPump pumping range of 0 to 1.872 liquid hourly space velocity.

The third phase consisted of passing several multi-component mixtures through the adsorption bed and determining the extent and type of normal-paraffins

adsorbed by the Molecular Sieves. The materials tested were nitration-grade toluene, catalytic reformate, light naphtha, and catalytic cracked gasoline. Research octane numbers were determined on the catalytic reformate, light naphtha, and catalytic cracked gasoline, before and after the removal of components adsorbed by the sieves.

Equilibrium capacity for normal-heptane.

Approximately 60 grams of new, type 5 A Molecular Sieves were placed in a clean, 250 ml. glass stoppered Erlenmeyer flask. The weight of the flask and sieves was determined with the aid of an analytical balance.

Approximately 100 ml. of ASTM normal-heptane were then added to the flask. A vigorous release of adsorbed gas was noted immediately and bubbles were still being emitted from the sieves five minutes later.

The temperature of the flask increased slightly but was not accurately determined.

The glass stopper was replaced when the gas rate had declined sufficiently. The flask and contents were allowed to stand with periodic agitation for twenty-four hours at a constant temperature of 77° F.

The excess normal-heptane was removed by evaporation with a vacuum maintained at approximately 4 mm. Hg absolute pressure. At thirty minute intervals the flask was removed and the contents were reweighed. After two hours the weight was constant and was recorded.

The amount of normal-heptane adsorbed was found to

be 6.8032 grams for 59.4879 grams of Molecular Sieves. This is equivalent to a weight loading of 11.44 per cent normal-heptane.

Separation of normal-heptane from nitration-grade toluene.

The two charge stocks of normal-heptane and nitration-grade toluene had the following physical properties.

TABLE III

PHYSICAL PROPERTIES OF SYNTHETIC BLENDS OF NORMAL-HEPTANE AND NITRATION-GRADE TOLUENE

	Runs 1-4	Runs 5-8
Weight per cent n-heptane	5.00	10.00
Volume per cent n-heptane	6.25	12.34
Weight per cent nitration grade toluene	95.00	90.00
Volume per cent nitration grade toluene	93.75	87.66
n_D at 68° F.	1.4888	1.4818

Runs 1 and 5 had charge rates of 4.0 ml. per min., runs 2 and 6 had charge rates of 8.0 ml. per min., runs 3 and 7 had charge rates of 12.0 ml. per min., and runs 4 and 8 were made at a charge rate of 16.0 ml. per min.

All runs were made at atmospheric pressure and an initial adsorption bed temperature of 77° F. No attempt was made to maintain the sieves at isothermal conditions.

The first four runs were made with the blend of

5.0 weight per cent normal-heptane in nitration-grade toluene as the charge stock. A total volume of one liter of effluent was recovered during each of the runs. Separate fractions were collected from each 50 ml. of effluent during each run to determine the refractive index of each 5 % increment of effluent. The twenty cuts were more than adequate to determine the breakthrough point of the normal-heptane in the effluent.

The breakthrough point was determined as the point during each run when the refractive index of the effluent toluene was lower than the refractive index of the original nitration-grade toluene.

The refractive index of each fraction was determined and the normal-heptane content could be evaluated from the correlation presented in Figure 8.

Experimental data determined on the cuts from runs 1 through 4 are presented in Table XII.

A temperature rise of 20° F. was noted in the adsorption bed during each run.

Runs 5 through 8 were made with the blend of 10.0 weight per cent normal-heptane in nitration-grade toluene as the charge stock. Since the charge stock contained twice the weight of normal-heptane as the charge in the first four runs, the total column throughput was reduced to 500 ml. The same number of cuts were made as in the first four runs, therefore, the volume of each cut was reduced to 25 ml.

The refractive index of each cut was determined and the composition evaluated from the correlation presented in Figure 8.

Experimental data determined from runs 5 through 8 are presented in Table XIII.

The maximum temperature rise in the adsorption bed during runs 5 through 8 was 20 to 25° F.

The reactivation of the sieves was duplicated as closely as possible to maintain their adsorption capacity. The procedure followed was to drain the liquid from the adsorption column. The liquid trapped in the void spaces was removed by slowly heating the adsorption bed to 150° F., while purging with dry nitrogen flowing down through the sieves at the rate of two liters per minute.

A sharp rise in the adsorption bed temperature was noted when the last traces of liquid were evaporated. When the adsorption bed temperature reached 200° F. the nitrogen purge rate was reduced to 0.5 liter per minute and the powerstat was adjusted to provide a heating rate of approximately 5° F. per minute.

The effluent gas flow was into the #1 condensate receiver and then to the condenser cooled with acetone and dry ice.

When the adsorption bed temperature was 660° F. the powerstat was adjusted to maintain the temperature constant. Purging was continued for one hour at the final temperature to permit the sieves to attain equilibrium.

The volume of condensate recovered during the final thirty minutes of purging was nil.

The column was allowed to cool to room temperature after each run.

Experimental data from the reactivation of the sieves during the eight runs on blends of normal-heptane in nitration-grade toluene are presented in the following table.

TABLE IV

MATE IAL RECOVERED FROM DESORPTION OF THE MOLECULAR SIEVES ON RUNS 1-8

Run No.	Normal-Heptane Recov.		Sieve Lo ding	n_D at 68°F.
	Vol.-ml.	Wt.-gms.	Wt. per cent	
1	53.0	36.4	9.0	1.3889
2	44.1	30.4	7.5	1.3888
3	46.9	32.3	8.0	1.3892
4	47.9	32.9	8.2	1.3889
5	54.4	37.4	9.3	1.3882
6	51.0	35.1	8.7	1.3882
7	51.3	35.3	8.8	1.3882
8	49.6	34.1	8.5	1.3882

Adsorption of hydrocarbons from multicomponent mixtures.

The refractive index values on the toluene effluent from the first eight runs were often higher than the refractive index of the original nitration-grade toluene. Since the refractive index of the nitration-grade toluene was 1.4960 and the refractive index of the ASTM normal

heptane was 1.3878, any value obtained on the effluent toluene higher than 1.4960 would indicate the removal of impurities from the nitration grade toluene by the sieves.

Doss[15] reported the refractive index of pure toluene is 1.49685 at 68° F. Refractive index values obtained on the initial toluene samples during the first eight runs were as high as 1.4968.

In an attempt to determine the impurities present in the nitration-grade toluene a total of 2500 ml. of toluene was passed through the adsorption column. Refractive index values were obtained on the effluent toluene at definite intervals. The charge rate to the column was 10.0 ml. per minute. The rate was equivalent to a liquid hourly space velocity of 1.04.

Experimental data are presented in Table XV.

On regeneration of the sieves, 6.8 ml. of liquid weighing 4.8 grams were recovered. This was equivalent to a sieve loading of 1.2 weight per cent.

The liquid was found to be essentially pure normal octane on analysis by infra-red spectrophotometry. The toluene content of the liquid was less than 0.1 volume per cent. The absorption spectrum was almost identical with a comparison sample of pure normal-octane obtained from the Phillips Petroleum Company.

The normal-octane content of the nitration-grade toluene was determined as 0.54 volume per cent.

The final phase of the experimental work on complex

mixtures was to determine the type and amount of materials adsorbed by the Molecular Sieves from samples of catalytic reformate, light naphtha, and catalytic cracked gasoline.

Research octane numbers were obtained on the catalytic reformate, light naphtha, and catalytic cracked gasoline before and after contact with the sieves.

A charging rate of 10.0 ml. per minute was maintained during the runs. The procedure followed on regeneration of the sieves was the same as that previously established during the initial runs.

Catalytic reformate.

Two runs were made with catalytic reformate as the charge stock. The catalytic reformate contained 46.1 per cent paraffins, 1.0 per cent olefins, 14.5 per cent naphthenes, and 38.4 per cent aromatics.

Physical tests of the catalytic reformate are presented in Table XVI.

A total of 400 ml. of product was recovered during each run. Separate fractions were collected every 100 ml. and the refractive index of each fraction was determined.

A temperature rise of 34° F. was noted in the adsorption bed during each run.

On regeneration of the sieves, 34.7 ml. of liquid, weighing 23.7 grams, were recovered from each run. This was equivalent to a sieve loading of 5.9 weight per cent.

The first three 100 ml. fractions from each run ere combined and tested to determine the octane rating.

The refractive index readings on the first three 100 ml. fractions from each run were found to be essentially the same while the refractive index of the fourth 100 ml. fraction indicated the partial breakthrough of normal paraffins.

The research octane ratings are presented in the following table.

TABLE V

RESEARCH OCTANE RATINGS ON CATALYTIC REFORMATE

	Original Sample	Column Effluent
Unleaded	79.4	88.9
+0.5 cc TEL*	84.8	
+1.0 cc TEL	88.4	
+2.0 cc TEL	91.4	
+3.0 cc TEL	93.6	98.7

*Tetraethyl lead per gallon of sample

Additional data are presented in Table XVI.

Light Naphtha.

Two runs were made with light naphtha as the charge stock. The light naphtha contained 50.1 per cent paraffins, 0.9 per cent olefins, 46.7 per cent naphthenes, and 2.3 per cent aromatics.

A total of 400 ml. of product was passed through the column during the initial run. This was reduced to 300 ml. of product on the final run when the refractive index

values from the initial run indicated almost a complete breakthrough of the materials being adsorbed after 300 ml. of effluent had been recovered. Fractions were taken every 100 ml. and the refractive index of each fraction was determined.

A temperature rise of 24° F. was noted in the adsorption bed during each run.

The effluent receiver was placed in an ice bath during each run to minimize the loss of low boiling materials present in the charge stock.

On regeneration of the sieves a slight amount of non-condensable white smoke with a pleasant odor was emitted from the condenser when the regeneration temperature reached 600° F. in the adsorption bed.

A total of 27.5 ml. of condensate weighing 18.7 grams was recovered from the initial run. This was equivalent to a sieve loading of 4.6 weight per cent.

A total of 27.0 ml. of condensate weighing 18.3 grams was recovered from the final run. This was equivalent to a sieve loading of 4.5 weight per cent.

The two portions of desorbed materials were combined and distilled to determine their boiling range. Physical tests on the charge stock and desorbed material are presented in Table XVII.

The first 300 ml. of effluent from the initial run were combined with the 300 ml. from the second run and the octane ratings determined. Refractive index values

from the cuts indicated that approximately 50 % of the original normal-paraffin content remained in the samples tested for octane rating. The ratings were as follows:

TABLE VI

RESEARCH OCTANE RATINGS ON LIGHT NAPHTHA

	Original Sample	Column Effluent
Unleaded	57.3	64.7
+ 0.5 cc TEL*	63.4	
+ 1.0 cc TEL	68.7	
+ 2.0 cc TEL	75.6	
+ 3.0 cc TEL	78.6	83.3

*Tetraethyl lead per gallon of sample

Catalytic cracked gasoline.

Only one run was made on catalytic cracked gasoline due to difficulties encountered on regeneration.

The catalytic cracked gasoline contained 27.5 % paraffins, 8.3 % olefins, 14.0 % naphthenes, and 50.2 % aromatics.

A total of 400 ml. of product was recovered during the run. Fractions were collected every 100 ml. and the refractive index of each cut was determined.

The column receiver was kept in an ice bath during the charging to minimize the loss of low boiling materials present in the charge stock.

The adsorption bed temperature rise was 24° F.

The charge to the adsorption column had a yellow color while the effluent was initially clear. The color gradually became darker until it was the same color as the charge stock.

On regeneration, a considerable amount of non-condensible white smoke with a pleasant odor was emitted from the condenser when the temperature reached 600° F. in the adsorption bed.

The yield of condensate recovered was very low. A total of 10.1 ml. of condensate weighing 6.9 grams was recovered. This was equivalent to a sieve loading of 1.7 weight per cent.

The first 300 ml. of effluent were combined and the octane ratings were determined. There was sufficient sample for only one rating on the column effluent.

TABLE VII

RESEARCH OCTANE RATINGS ON CATALYTIC CRACKED GASOLINE

	Original Sample	Column Effluent
Unleaded	87.4	88.8
+ 0.5 cc TEL*	91.2	
+ 1.0 cc TEL	92.8	
+ 2.0 cc TEL	94.5	
+ 3.0 cc TEL	95.8	

*Tetraethyl lead per gallon of sample

Physical data are presented in Table XVIII.

CHAPTER V

RESULTS AND DISCUSSION

The ability of the Linde type 5 A Molecular Sieves to adsorb normal-paraffins from a mixture containing iso-paraffins, naphthenes, and aromatics was definitely established during the various runs.

The Molecular Sieve equilibrium loading of 11.44 weight per cent normal-heptane, as determined by a static test, was slightly higher than the value of 11.3 weight per cent determined by Linde in their work.

The maximum capacity of the sieves for normal-heptane was not determined during the runs made on blends of normal-heptane and nitration-grade toluene. As shown by the data in Figure 2 and Figure 3, maximum capacity was almost obtained in the final portion of the runs.

The breakthrough point of the normal-heptane from the sieves was dependent upon the liquid charge velocity and the concentration of the normal-heptane in the charge stock. As the liquid velocity through the column was increased, the yield of normal-heptane free product was decreased for a given charge stock. As the concentration of normal-heptane in the charge stock was increased the yield of normal-heptane free product was lower.

Figures 2 and 3 show the breakthrough point of the

normal-heptane at definite liquid charge rates.

The increase in purity of the initial toluene effluent from the sieves over the purity of the original nitration-grade toluene was due to the removal of 0.54 volume per cent normal-octane impurities present in the nitration-grade toluene.

Figure 4 presents a semi-logarithmic plot of the breakthrough point of the normal-heptane as a function of liquid hourly space velocity and the concentration of normal heptane in the charge stock.

Table IV shows the sieve loading during the runs on normal-heptane and nitration-grade toluene varied from 7.5 to 9.3 weight per cent. For a given charge stock the weight per cent sieve loading should have decreased as the charge rate to the column increased. The sieve loading results for runs 2, 3, and 4, do not show a decreasing trend.

The graphical results of Figure 2 and Figure 3 indicate a consistent lower trend in the amount of material adsorbed as the charge rate is increased.

The inconsistent results for runs 2, 3, and 4, as shown in Table IV, are probably due to slight experimental errors in the regeneration of the Molecular Sieves and subsequent recovery of the desorbed materials.

The adsorption loading of the sieves during runs 5 through 8 was more consistent. The more consistent results were partially due to improved experimental techniques.

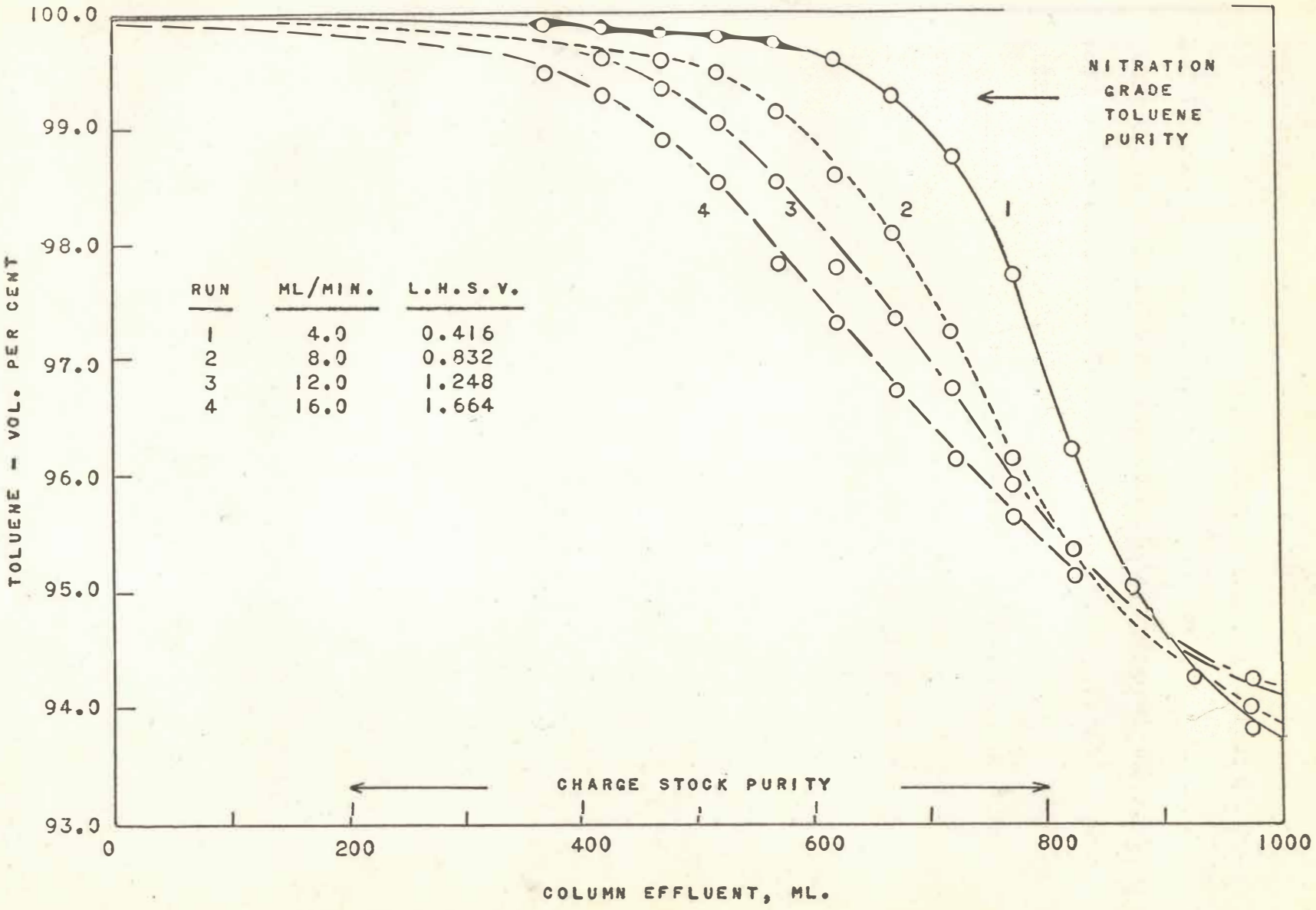

FIGURE 2 SEPARATION OF NORMAL HEPTANE FROM 5.0 WT. PER CENT NORMAL HEPTANE IN NITRATION GRADE TOLUENE

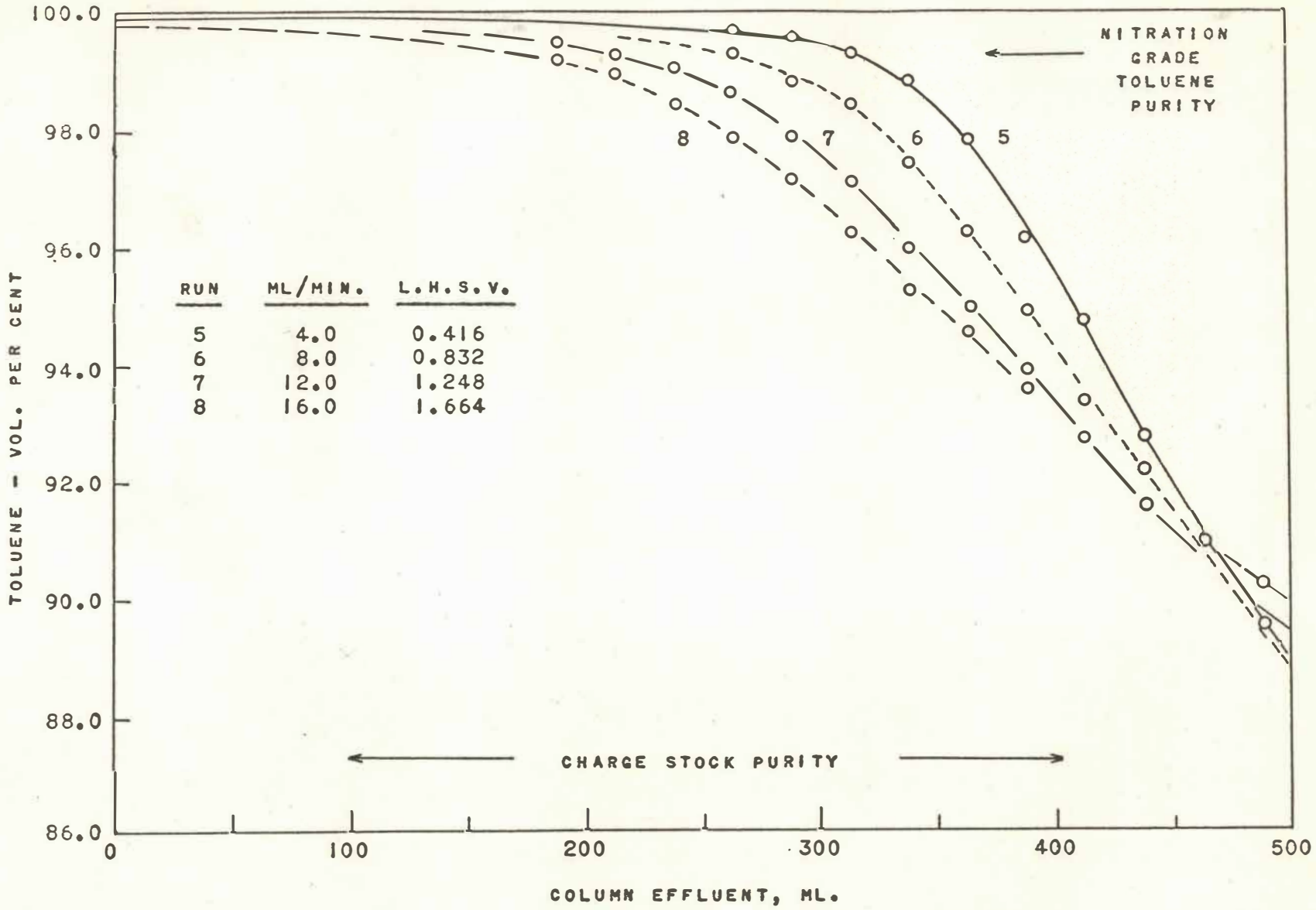

FIGURE 3 SEPARATION OF NORMAL HEPTANE FROM 10.0 WT. PER CENT NORMAL HEPTANE IN NITRATION GRADE TOLUENE

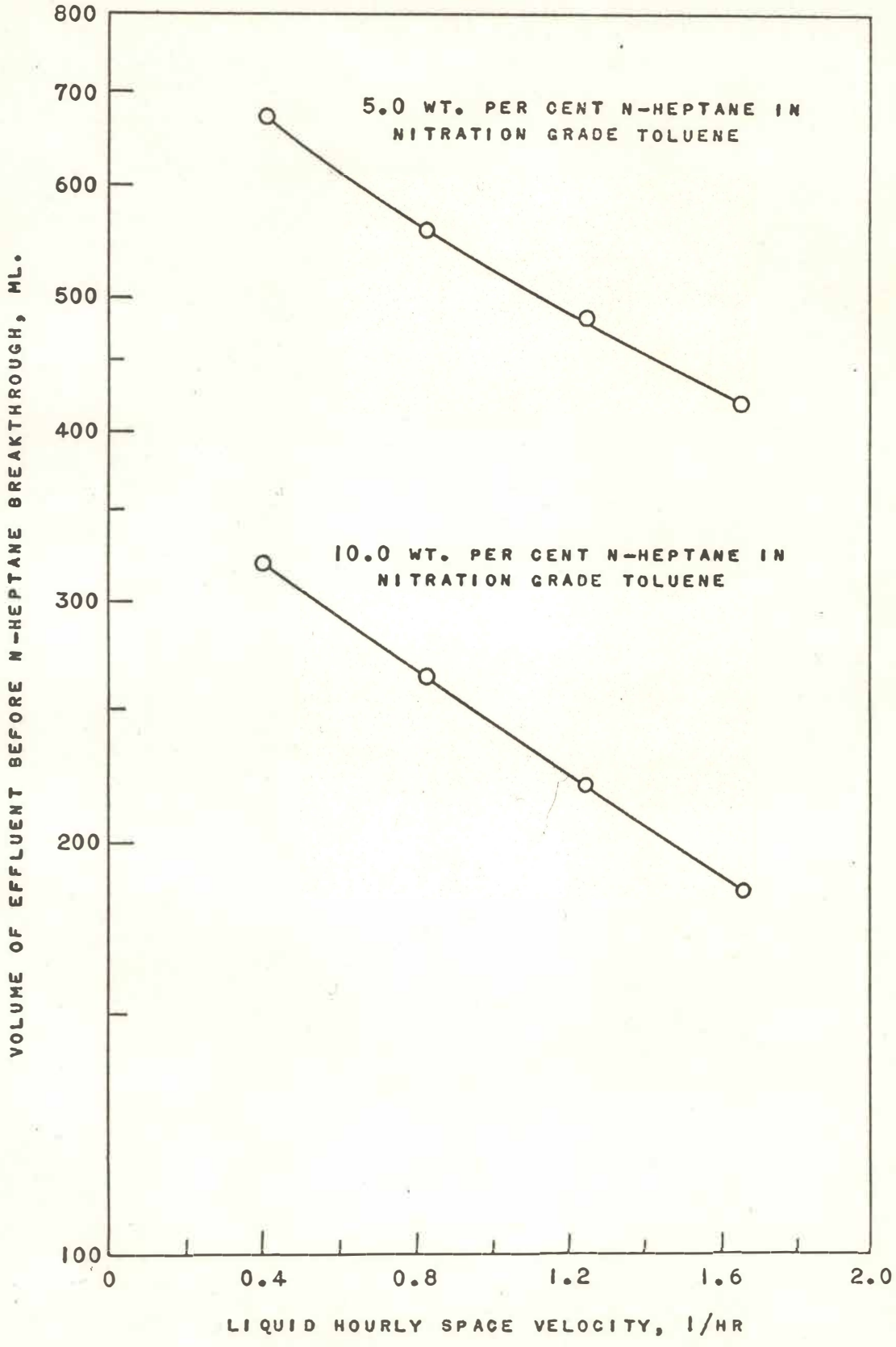

FIGURE 4 THE EFFECT OF CONCENTRATION AND CHARGE RATE ON THE BREAKTHROUGH OF N-HEPTANE

The adsorption forces present in the Molecular Sieves were not evaluated in this work but an indication of their magnitude may be realized from the temperatures required to reactivate the sieves as shown in Table XIV and Table XIX.

Table XIV presents the regeneration data from the initial runs during the separation of normal-heptane from nitration-grade toluene. As indicated by the refractive index values on the desorbed material, the condensate recovered was almost pure normal-heptane with slight traces of normal-octane present.

Normal-heptane has a boiling point of approximately 209° F. at standard conditions, however it was found that little if any normal-heptane was desorbed at 209° F. and over one-half of the desorbed normal-heptane was not recovered until the bed temperature reached approximately 550° F. The vapor pressure of normal-heptane at 550° F. is approximately 500 psia. The normal-heptane was above its critical temperature of 512.6° F. before the desorption of the sieves was at maximum rate.

The Molecular Sieves removed trace impurities of normal-octane from nitration-grade toluene. The capacity of the sieves for the normal-octane was only 1.2 weight per cent but due to the low concentration of the normal-octane a total volume of 500 ml. of practically pure toluene was recovered before the breakthrough of normal-octane.

The sieve temperatures during desorption of the normal-octane as shown in Table XIX, indicate a bed temperature approximately 100° F. higher was required when normal-octane was being desorbed than when normal-heptane was the desorbed material.

The results obtained from the catalytic reformate runs indicated that the presence of iso-paraffins, naphthenes, and aromatics in a charge stock with a considerable boiling range, would not interfere with the removal of the normal-paraffins present.

The sieve loading at equilibrium of 5.9 weight per cent was lower than expected from the results obtained in runs 1 through 8 on the separation of normal-heptane from nitration-grade toluene.

The normal-hydrocarbons removed from the catalytic reformate had approximately the same boiling range as the original catalytic reformate.

The boiling range of the normal-paraffins removed from the light naphtha was also approximately the same as the original sample.

The amount of normal-paraffins present in the catalytic reformate was approximately 10.0 per cent of the original volume or approximately 22 per cent of the total paraffin content.

The octane number improvement of the catalytic reformate by the removal of essentially all of the normal-paraffins by the Molecular Sieves is shown in Figure 5.

The improvement of ten octane numbers on the unleaded samples of catalytic reformate and five octane numbers on the maximum leaded samples definitely established the degrading effect of the normal-paraffins on the octane number of the original catalytic reformate.

Removal of the normal-paraffin content of the catalytic reformate drastically reduced the volume of tetraethyl lead required for a given octane number level.

An equilibrium sieve loading of 4.6 weight per cent was obtained on the light naphtha. This low value may have resulted from the partial fouling of the sieves in a prior run on catalytic cracked gasoline.

The amount of normal-paraffins present in the light naphtha was approximately 16 per cent of the original volume or approximately 50 per cent of the total paraffin content.

The results obtained from the light naphtha runs indicated a substantial octane number improvement may be obtained from the removal of the normal-paraffins.

The octane number improvement of the light naphtha was approximately seven octane numbers unleaded and five octane numbers on the maximum leaded samples. The samples tested had only 50 per cent of the normal-paraffins removed so the octane number improvement on the complete removal of the normal-paraffins could be expected to be double the experimental values. The estimated octane numbers for total normal-paraffin removal are shown in Fig. 6.

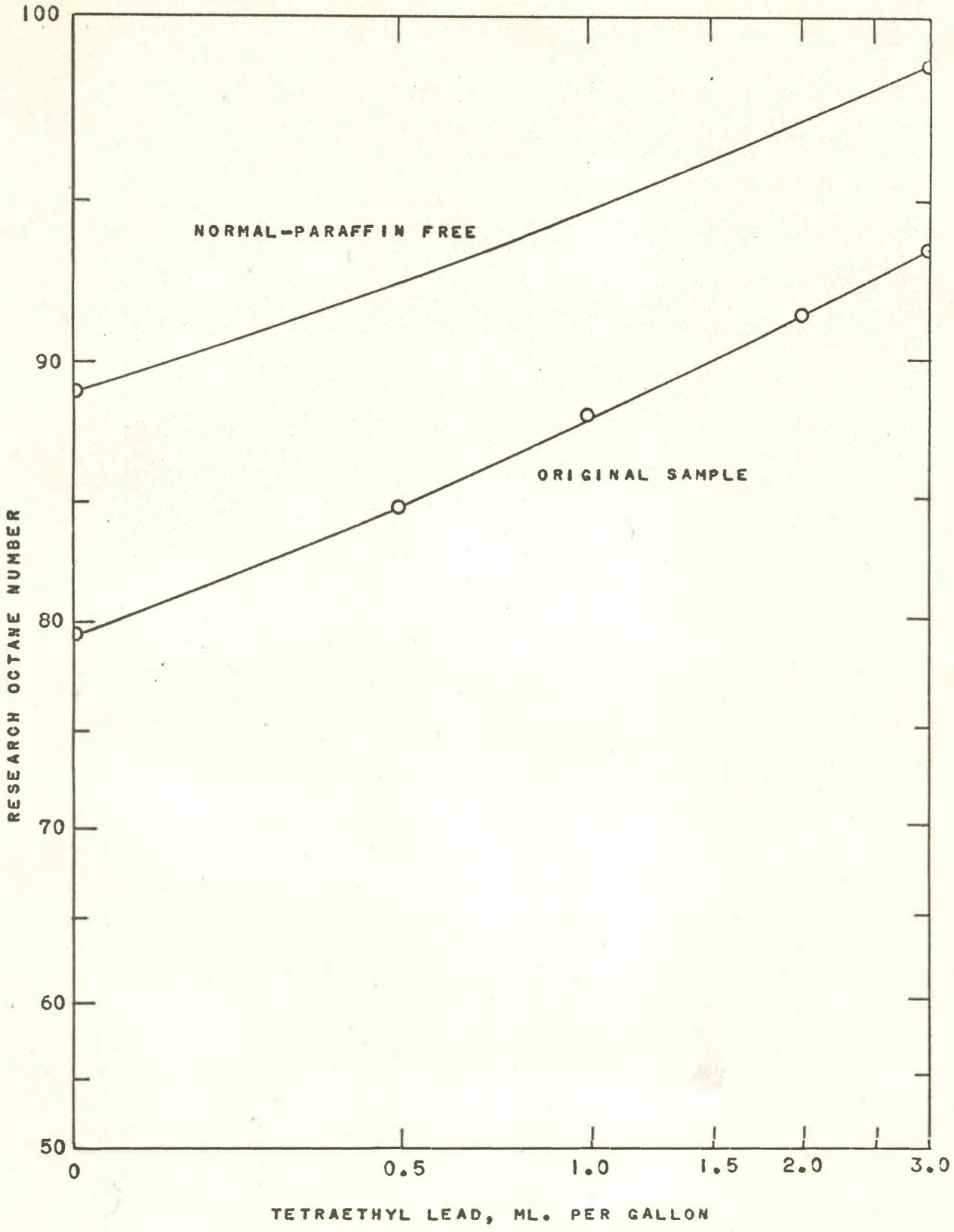

FIGURE 5 TETRAETHYL LEAD SUSCEPTIBILITY OF CATALYTIC REFORMATE

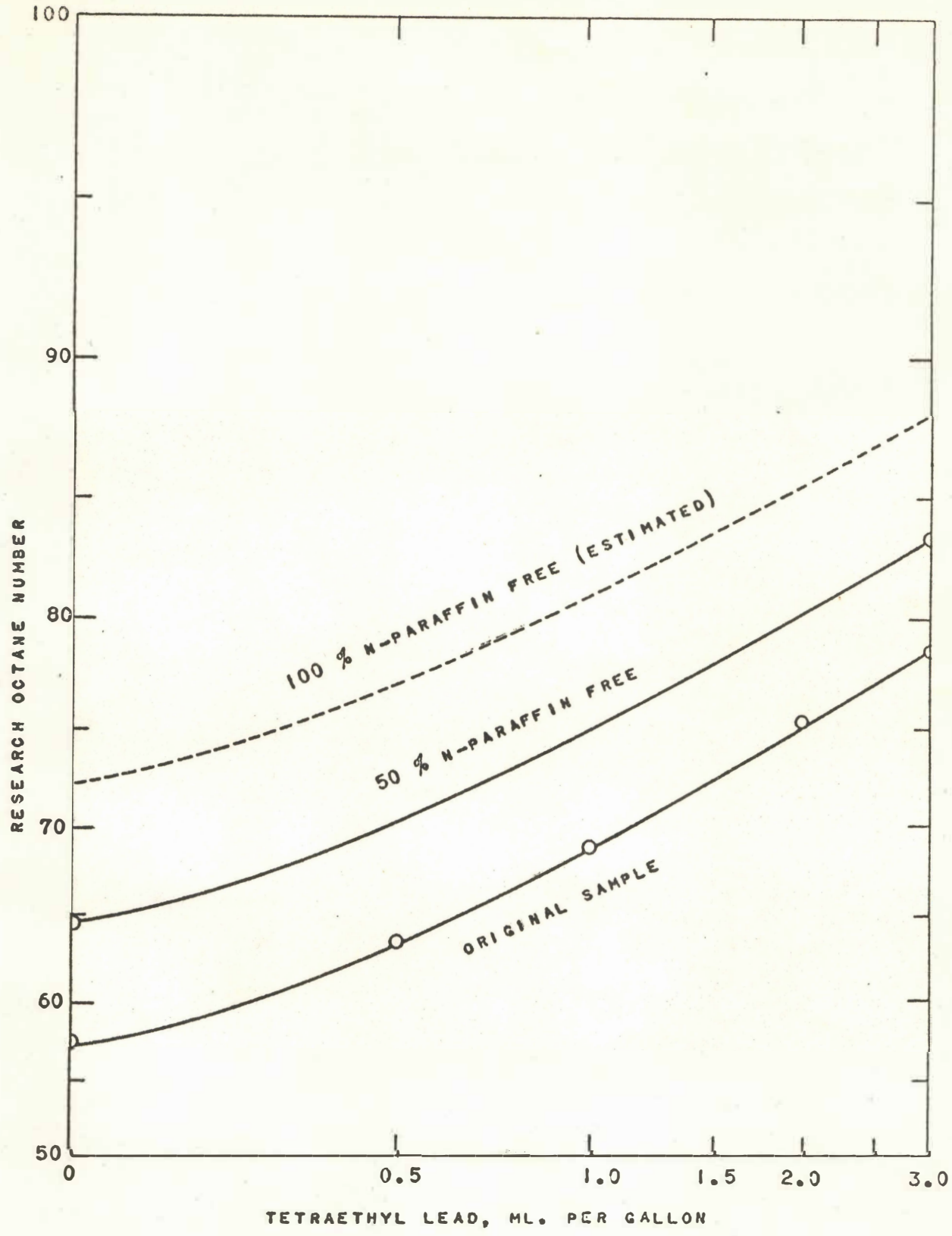

FIGURE 6 TETRAETHYL LEAD SUSCEPTIBILITY OF LIGHT NAPHTHA

The experimental run on catalytic cracked gasoline was very disappointing. On regeneration of the sieves a low yield of desorbed material was recovered and a considerable amount of non-condensable gases were emitted from the condenser.

The adsorption bed temperature rise of 24° F. during the charging portion of the run indicated a considerable amount of materials were being adsorbed on the sieves.

The removal of color bodies from the catalytic cracked gasoline was obtained during the initial stage of the run.

The high olefin content of the catalytic cracked gasoline could have been responsible for the regeneration difficulties. It has been reported by a Linde representative that normal-olefins adsorbed by the Molecular Sieves will polymerize on heating to the required regeneration temperatures. Further work on charge stocks of known composition would be required to definitely establish the reason for the thermal decomposition of part of the adsorbed materials.

Trouble was encountered during several of the runs with the formation of hydrates in the condenser coil. In some cases the vent line was completely plugged and it was necessary to stop the nitrogen purge through the system and back pressure the condenser line to remove the deposits.

Another serious problem was the removal of the

liquid held in the voids between the sieves after the column had been drained.

The most effective method of removal was to evaporate the liquid present by passing warm nitrogen through the adsorption bed until a rapid temperature rise indicated that the bed was dry.

The method of drying the adsorption bed by maintaining a vacuum on the system was found to be very time consuming and inefficient.

In one attempt the adsorption bed temperature dropped to 40° F. during the drying procedure and the rate of evaporation of the trapped liquid at that temperature was negligible.

CHAPTER VI

"PARASORB" UNIT PROPOSAL

To provide further information on the feasibility of utilizing Molecular Sieves in a commercial process, a cursory study is presented on their use in adsorbing the normal-paraffins present in a stream of 4500 bbls. per day of catalytic reformate.

The purpose of the unit would be to remove the low octane number components from the catalytic reformate and provide a superior motor fuel.

The normal-paraffins removed from the catalytic reformate could be used in the manufacture of petrochemicals, or further processed by isomerization to improve the octane rating.

The experimental results obtained from runs 9 and 10 on catalytic reformate served as the basis for yields and operating conditions.

One assumption was made that future developments in the manufacture of the Molecular Sieves will provide a new type of Molecular Sieve as a spherical pellet with high resistance to abrasive action. This feature would permit the use of a moving bed of sieves in an adsorption tower and continuous regeneration in suitable equipment.

A schematic diagram of the proposed process is shown in Figure 7.

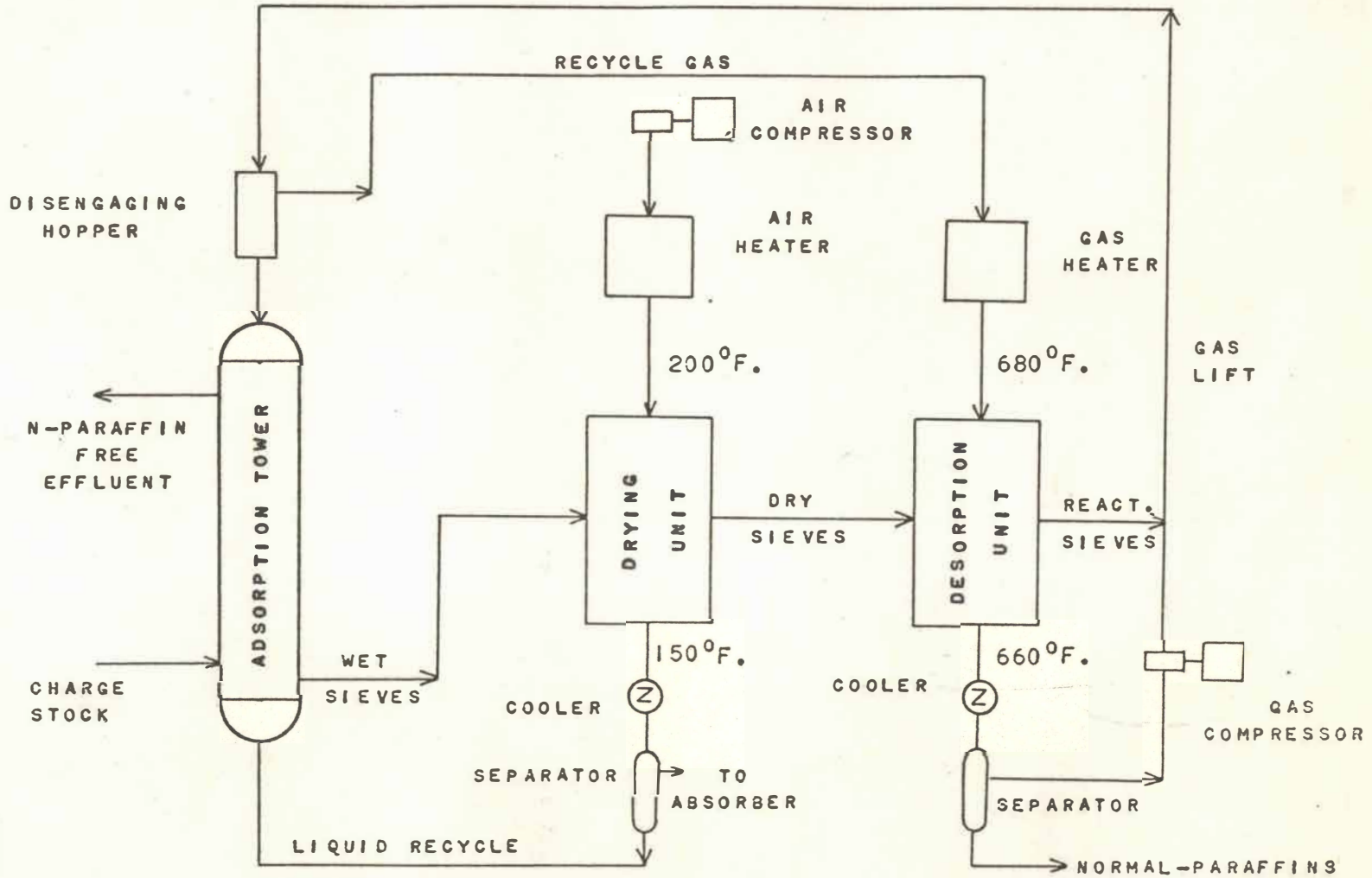

FIGURE 7 SCHEMATIC DIAGRAM OF PROPOSED "PARASORB" UNIT

Charge stock to the unit would be 4500 bbls. per stream day of catalytic reformate from a catalytic reforming unit. The charge stock would have an unleaded octane rating of approximately 80 and a leaded octane rating of 94.

The effluent from the adsorption section would be 4050 bbls. per stream day of essentially normal-paraffin free product. The octane number of the effluent would be approximately 89 unleaded and 99 leaded.

The volume of normal-paraffins recovered would be 450 bbls. per stream day. The normal-paraffins present in the desorbed material would be normal-heptane, normal-octane, normal-nonane, and normal decane.

The weight of Molecular Sieves in the total system would be approximately 100,000 pounds. The circulation rate of the sieves would be 76,000 pounds per hour, with a normal-paraffin loading of 6.0 weight per cent on leaving the adsorption section.

The adsorption tower would contain approximately 45,000 pounds of Linde type 5 A Molecular Sieves. The fresh feed of catalytic reformate would enter the base of the adsorption tower and leave near the top.

The Molecular Sieves would enter the top of the adsorption tower and slowly move down the tower by settling. A mechanical conveyor would remove the spent sieves from the base of the adsorption tower.

The counter-current flow would permit the maximum

saturation of the sieves leaving the adsorption tower.

The sieves would pass to a drying zone where the extraneous liquid would be removed by evaporation. The saturated gases from this section would pass to a cooler and then to a separator. The liquid condensate would be recycled to the adsorption column while the gas would be charged to an absorption system to permit the recovery of the traces of hydrocarbon present.

The dry sieves would proceed to the reactivation section where they would be heated to 660° F. and simultaneously purged with an inert gas.

The hot gases from this section would also pass through a cooler and separator. The condensate would be essentially pure normal-paraffins. The cooled gas would be compressed and then serve as a gas lift to return the reactivated sieves to the top of the adsorption tower.

The flow of compressed gas would cool the sieves and permit the recovery of a substantial amount of the heat required to raise the sieves to 660° F.

The use of an oxygen-free gas in the reactivation system would be required to reduce the hazards of having an explosive mixture in the system and also to prevent the oxidation of hydrocarbons to undesireable compounds.

The main energy requirement of the entire unit would be in the heat input to the drying and desorption sections.

The total heat load is estimated as follows in Table VIII.

TABLE VIII

"PARASORB UNIT" HEATING LOAD

Heating requirement	B.T.U. per hour
Latent heat required to remove the extraneous liquid.	2,080,000
Heat required to raise sieves from 200° F. to 660° F.	9,120,000
Heat of desorption required by normal-paraffins at 900 B.t.u. per pound.	4,110,000
Latent heat of normal-paraffins	617,000
Sensible heat of the normal paraffins	695,000
Allowance for heat loss	1,378,000
TOTAL	18,000,000

Auxiliary heating in the form of internal heating coils would be required in the reactivation section to reduce the volume of gases required to furnish the heating requirements. The flow of the hot gas and the sieves would be counter-current for maximum efficiency.

An elutriation system would be required to remove the Molecular Sieves fines from the system. It was estimated that 300 pounds of new sieves would be required daily to maintain a constant inventory in the total system.

The fines could be returned to the manufacturer for repelleting since the powder would be the same type of material as the original pellets.

An economic study is presented in the following table.

TABLE IX

ECONOMIC STUDY OF PROPOSED "PARASORB" UNIT

	Present System	Proposed System
Daily Value of Product		
189,000 gals. @ 12¢/gal.	$ 22,680	
170,100 gals. @ 14¢/gal.		$ 23,814
18,900 gals. @ 8¢/gal.		1,512
TOTAL	$ 22,680	$ 25,326
Expenses-Daily		
Fuel @ 15¢ per million B.t.u.		70
Labor - 12 hours @ $3.00/hour		36
Make-up Molecular Sieves 300 lbs. @ $1.00/lb.		300
Electricity @ 0.7 ¢/kwh.		10
Water @ 10 ¢/1000 gals.		3
Maintenance		60
Overhead- ins., taxes, etc.		120
Total		$ 635
NET VALUE OF PRODUCT	$ 22,680	$ 24,691
DIFFERENCE		+ $ 2,011
Cost of "Parasorb" Unit*		
4500 bbls. @ $2.75/bbl.		$ 1,237,500
100,000 lbs. Molecular Sieves @ $1.00/lb.		100,000
TOTAL		$ 1,337,500
Annual difference of product values, $2,011 x 350 days annual operation		$ 703,850
Less depreciation - 8 year basis:		167,187
NET PROFIT BEFORE TAXES		$ 535,663
Taxes at 52% annual rate		278,545
ANNUAL PROFIT AFTER TAXES		$ 257,118
Per cent return annually on investment		19.2%

*The Oil and Gas Journal, Vol. 54, No. 50, 135

CHAPTER VII

SUMMARY AND CONCLUSIONS

The adsorption capacity of the Molecular Sieves was found to be a function of the liquid velocity in the adsorption bed and the concentration of the normal-paraffins in the charge stock.

Essentially complete reactivation of the Molecular Sieves was obtained on heating to 660° F. and purging with dry nitrogen.

Trace quantities of pure normal-octane were recovered from nitration-grade toluene.

Equilibrium capacity of the sieves varied from 1.2 weight per cent on the purification of nitration-grade toluene to 11.44 weight per cent on the adsorption of normal-heptane from pure normal-heptane.

The removal of 10.0 volume per cent normal hydrocarbons from catalytic reformate increased the research octane number of the effluent from 79.4 to 88.9 unleaded and from 93.6 to 98.7 with 3.0 cc. of tetraethyl lead.

The removal of 50 per cent of the normal-paraffin content of a light naphtha increased the unleaded octane rating from 57.3 to 64.7 and the leaded ratings from 78.6 to 83.3.

A sample of catalytic cracked gasoline was found to contain materials readily adsorbed by the sieves.

On regeneration of the sieves, however, the majority of the materials adsorbed were thermally unstable and were converted to non-condensible gases and non-volatile deposits on the Molecular Sieves.

Future studies in this field could be wide and varied because of the recent development of the Molecular Sieves.

Possible studies might include:

1. Methods of reactivation of the Molecular Sieves when thermally unstable compounds are adsorbed.

2. Determination of the extent and nature of normal-hydrocarbon impurities in commercial grade samples of benzene, iso-octane, etc.

3. The effect of adsorption bed temperature on the rate of adsorption.

4. The effect of pressure on the rate of adsorption from liquid charge stocks.

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APPENDIX

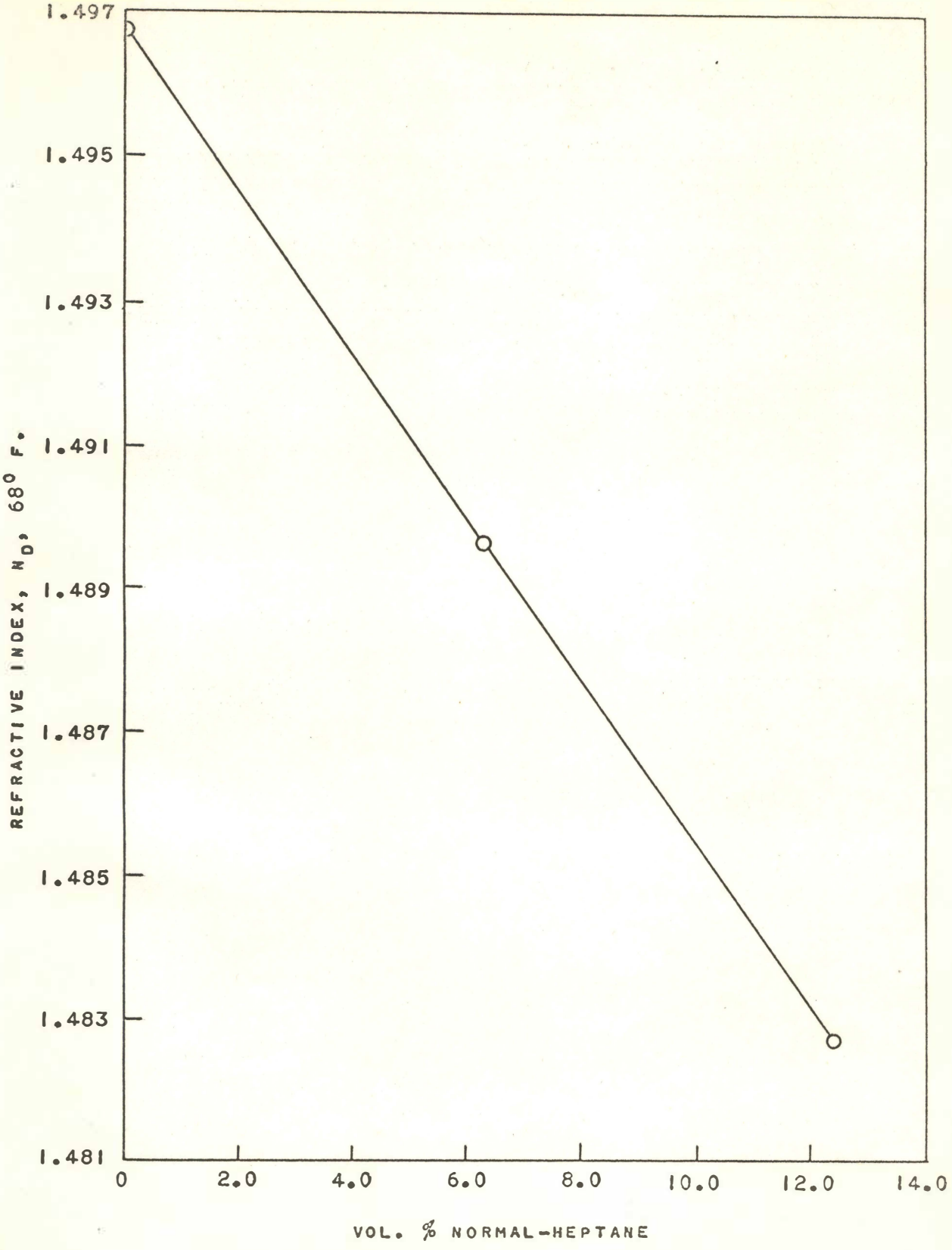

FIGURE 8 REFRACTIVE INDEX OF NORMAL-HEPTANE-TOLUENE BLENDS

TABLE X

PROPERTIES OF LINDE TYPE 5 A MOLECULAR SIEVES[16]

Bulk density	-	43 lbs. per cubic foot
Heat of water adsorption	-	1800 B.t.u. per lb. of water
Specific heat at 250° C.	-	0.24
Surface area	-	750 square meters per gram

[16]Linde Air Products Co., Technical Bulletin, General Information on Molecular Sieves, Types 4 A and 5 A. Form 8605 December, 1954

TABLE XI

PHYSICAL DATA ON ASTM NORMAL-HEPTANE

Boiling point, 760 mm. Hg, °C.	98.418
Freezing point, ASTM, °C.	-90.684
Density at 20° C., gms./ml.	0.68385
Refractive index, n_D at 20° C.	1.38779

TABLE XII

EXPERIMENTAL DATA ON THE SEPARATION OF NORMAL-HEPTANE FROM 5.0 WEIGHT PER CENT NORMAL-HEPTANE IN NITRATION GRADE TOLUENE

Charge rate-ml/min.	4.0	8.0	12.0	16.0
L.H.S.V.	0.416	0.832	1.248	1.664

Refractive Index Data

Cut no.	Fraction	Run 1	Run 2	Run 3	Run 4
1	0 - 50	1.4968	1.4968	1.4968	1.4966
2	50 - 100	1.4968	1.4968	1.4968	1.4965
3	100 - 150	1.4968	1.4967	1.4968	1.4965
4	150 - 200	1.4968	1.4966	1.4968	1.4965
5	200 - 250	1.4968	1.4965	1.4968	1.4965
6	250 - 300	1.4968	1.4965	1.4967	1.4964
7	300 - 350	1.4968	1.4965	1.4966	1.4964
8	350 - 400	1.4967	1.4965	1.4966	1.4963
9	400 - 450	1.4967	1.4964	1.4965	1.4960
10	450 - 500	1.4966	1.4964	1.4964	1.4955
11	500 - 550	1.4966	1.4963	1.4957	1.4951
12	550 - 600	1.4965	1.4958	1.4951	1.4943
13	600 - 650	1.4964	1.4953	1.4944	1.4937
14	650 - 700	1.4961	1.4947	1.4937	1.4930
15	700 - 750	1.4954	1.4936	1.4930	1.4923
16	750 - 80●	1.4942	1.4924	1.4921	1.4918
17	8●0 - 850	1.4926	1.4914	1.4914	1.4913
18	850 - 900	1.4911	1.4907	1.4910	1.4908
19	900 - 950	1.4902	1.4903	1.4904	1.4904
20	950 -1000	1.4893	1.4896	1.4899	1.4900

TABLE XIII

EXPERIMENTAL DATA ON THE SEPARATION OF NORMAL-HEPTANE FROM 10.0 WEIGHT PER CENT NORMAL-HEPTANE IN NITRATION GRADE TOLUENE

Charge rate-ml/min.	4.0	8.0	12.0	16.0
L.H.S.V.	0.416	0.832	1.248	1.664

Refractive Index Data

Cut no.	Fraction	Run 1	Run 2	Run 3	Run 4
1	0 - 25	1.4967	1.4967	1.4967	1.4967
2	25 - 50	1.4967	1.4967	1.4967	1.4967
3	50 - 75	1.4967	1.4967	1.4967	1.4967
4	75 - 100	1.4966	1.4967	1.4967	1.4967
5	100 - 125	1.4966	1.4967	1.4967	1.4966
6	125 - 150	1.4966	1.4967	1.4967	1.4966
7	150 - 175	1.4966	1.4967	1.4966	1.4965
8	175 - 200	1.4966	1.4967	1.4963	1.4960
9	200 - 225	1.4966	1.4966	1.4960	1.4957
10	225 - 250	1.4966	1.4966	1.4958	1.4950
11	250 - 275	1.4965	1.4960	1.4952	1.4944
12	275 - 300	1.4964	1.4955	1.4943	1.4935
13	300 - 325	1.4961	1.4950	1.4935	1.4925
14	325 - 350	1.4955	1.4939	1.4921	1.4913
15	350 - 375	1.4943	1.4925	1.4910	1.4906
16	375 - 400	1.4924	1.4909	1.4897	1.4893
17	400 - 425	1.4907	1.4892	1.4885	1.4883
18	425 - 450	1.4885	1.4877	1.4871	1.4874
19	450 - 475	1.4863	1.4861	1.4861	1.4865
20	475 - 500	1.4847	1.4844	1.4850	1.4856

TABLE XIV

VOLUME OF NORMAL-HEPTANE RECOVERED ON REGENERATION

Sieve temp. °F.	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8
250	2.0		1.4	1.0	3.8	5.2	3.7	3.6
300	7.1	4.6		6.5	10.3		9.2	8.3
350	11.6	6.0	8.2	8.8	14.1	12.5	12.0	12.9
400	12.2	6.8	9.2	10.5	17.5	14.8	15.5	15.8
450		9.8	13.2	13.0	19.0	19.5	18.1	18.5
500	13.9	12.4	16.6	16.4	24.6	27.2	22.0	22.6
550		20.0	23.4		31.0			
600	30.9	28.8	29.5	30.4	37.5		36.6	
650	39.5	34.0	36.5	39.1	45.4	41.2	43.0	41.7
660*	53.0	44.1	46.9	47.9	54.4	54.0	51.0	49.6

*After 1 hour.

TABLE XV

EXPERIMENTAL DATA ON THE PURIFICATION OF NITRATION-GRADE TOLUENE

Charge rate-ml/min. 10.0

L.H.S.V. 1.04

Refractive Index Data

Cut No.	Fraction	n_D at 68° F.
1	0 - 100	1.4968
2	100 - 200	1.4969
3	200 - 300	1.4969
4	300 - 400	1.4969
5	400 - 500	1.4968
6	500 - 1500	1.4966
7	1500 - 2500	1.4961

Normal-octane, n_D at 68° F. = 1.39743^{15}

TABLE XVI

EXPERIMENTAL DATA ON CATALYTIC REFORMATE

Physical Tests	Catalytic Reformate	Effluent Composite	Desorbed Material
API Gravity	53.9	50.6	73.0
Reid Vapor Press. psi.	2.9		
n_D at 68° F.	1.4300	1.4377	1.3896
ASTM Distillation, °F.			
IBP	135		156*
5%	175		176
10%	178		183
20%	200		192
30%	210		200
40%	220		205
50%	231		212
60%	244		218
70%	257		226
80%	276		237
90%	301		260
95%	325		292
EP	363		338
Recovery, ml.	98.5		97.0

*Based on 50 ml. of sample

Refractive Index Values, 68° F.

Cut No.	Fraction	Run 9	Run 10
1	0 - 100	1.4378	1.4376
2	100 - 200	1.4388	1.4383
3	200 - 300	1.4378	1.4374
4	300 - 400	1.4350	1.4342

TABLE XVII

EXPERIMENTAL DATA ON LIGHT NAPHTHA

Physical Tests	Light Naphtha	Effluent Composite	Desorbed Material
API Gravity	62.7		72.8
Reid Vapor Press. psi.	2.6		
n_D at 68° F.	1.4050	1.4077	1.3896
ASTM Distillation, °F.			
IBP	180		186*
5%	190		194
10%	193		198
20%	197		202
30%	200		205
40%	204		208
50%	207		212
60%	212		216
70%	217		222
80%	225		229
90%	240		246
95%	246		268
EP	283		302
Recovery, ml.	99.0		98.5

*Based on 50 ml. of sample

Refractive Index Values, 68° F.

Cut No.	Fraction	Run 13	Run 14
1	0 - 100	1.4103	1.4104
2	100 - 200	1.4073	1.4074
3	200 - 300	1.4057	1.4052
4	300 - 400	1.4050	-

TABLE XVIII

EXPERIMENTAL DATA ON CATALYTIC CRACKED GASOLINE

Physical Tests	Catalytic Cracked Gasoline	Effluent Composite	Desorbed Material
API Gravity	53.8		*
Reid Vapor Press. psi.	4.6		
n_D at 68° F.	1.4304	1.4347	1.3851
ASTM Distillation, °F.			
IBP	124		*
5%	142		
10%	164		
20%	184		
30%	206		
40%	232		
50%	263		
60%	292		
70%	321		
80%	354		
90%	383		
95%	404		
EP	431		
Recovery, ml.	98.5		

*Insufficient sample for tests.

Refractive Index Values, 68° F.

Cut No.	Fraction	Run 11
1	0 - 100	1.4347
2	100 - 200	1.4348
3	200 - 300	1.4345
4	300 - 400	1.4330

TABLE XIX

MATERIAL RECOVERED DURING REGENERATION

Sieve temp. °F.	Run 9	Run 10	Run 11	Run 12	Run 13	Run 14
300	1.0	1.4	2.5		1.3	2.4
350	4.4	4.6	3.5		3.8	4.3
400	6.1	7.0	4.0		8.0	7.9
450	9.0	10.8	5.2		11.2	12.6
500	15.0	15.1	6.1		15.6	16.4
550		22.8	7.8		20.4	20.8
600	25.0	25.4	8.2			23.5
650	28.4	29.2	9.0	1.1	25.3	25.7
660*	34.7	34.7	10.1	6.8	27.5	27.0

*After 1 hour

VITA

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Candidate for the Degree

of Master Of Science

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