



The catalytic hydrodesulfurization of coal tar aromatic distillates
by Robert L Jacobson

A THESIS Submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree
of Doctor of Philosophy in Chemical Engineering
Montana State University
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Abstract:

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Light oil produced by Jones and Laughlin Steel Corporation and United States Steel Corporation was desulfurized using Harshaw CoMo 0301-T catalyst crushed and sized to 10-14 mesh. Pure hydrogen and 50% H₂ - 50% N₂ were used as treat gases.

Results of the investigation show that light oil containing less than 1 ppm thiophene can be obtained under a variety of operating conditions. The degree of desulfurization is affected favorably with: (1) increased pressure in the range of 100 to 800 psig; (2) increased temperature in the range of 575 to 850°F; (3) increased treat gas rate in the range of 500 to 1000 ft³/bbl; (4) increased hydrogen to oil ratio in the range of 0.22 to 0.86; and (5) increased contact time.

The degree of desulfurization is also dependent on the boiling range of the light oil; higher boiling material requires more severe process conditions.

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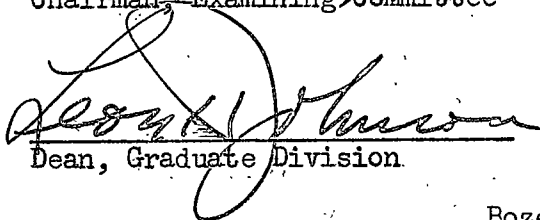
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Chairman, Examining Committee



Dean, Graduate Division

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ABSTRACT

The primary purpose of this investigation was to determine the operating conditions necessary to reduce the thiophene content of crude aromatics from approximately 0.7% to less than 1 ppm in a catalytic hydrodesulfurization pilot unit. The effect of process variables on the degree of desulfurization using a pseudo first-order rate equation and the Arrhenius equation was studied.

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INTRODUCTION

Recent developments in the petroleum industry have brought about the production of extremely pure aromatics. As a result, the producers of coal chemicals have found themselves in a poor competitive position because their aromatics have a relatively high sulfur content (thiophene derivatives). The Jones and Laughlin Steel Corporation, seeking to better their competitive position, consulted Esso Research and Engineering to determine if they could find a process for treating crude aromatics. Esso proposed the possibility of treating coal tar light oil (crude aromatics) in a catalytic hydrodesulfurization unit after they had completed a 24-hour run. They were unable to continue the investigation and it was turned over to chemical engineering graduate students at Montana State College under the direction of Dr. Lloyd Berg for further development.

The Jones and Laughlin crude aromatic light oils (benzene, toluene, and xylene) from the by-product coke ovens contain approximately 0.72 percent (7200 ppm) thiophene derivatives. In order to meet customer specifications the aromatics must contain less than one ppm sulfur and have an acceptable acid color and corrosion test.*

The desulfurization process constitutes hydrogenation of the crude light oil in the presence of a suitable catalyst at elevated temperature and pressure. A substantial savings in investment and operating costs could be effected by hydrofining the crude light oils collectively rather than hydrofining benzene, toluene and xylene separately; therefore, work

*Defined under "Analysis of Processed Light Oil"

was done only on processing crude light oils collectively. A mixture of 50% H₂ - 50% N₂ was used as treat gas for much of the work because hydrogen was to be obtained from the cracking of ammonia. The catalyst used for the hydrodesulfurization comprises "active centers" of cobalt and molybdenum oxide impregnated in an aluminum oxide base carrier of high surface area. This catalyst, used to convert thiophene to hydrogen sulfide and hydrocarbons, is not active enough to hydrogenate the benzene ring.

The principal operating variables studied in connection with catalytic hydrodesulfurization after the catalyst has been determined are pressure, contact time, temperature, composition of hydrogen-rich treat gas and ratio of hydrogen-rich treat gas to crude oil.

A program was set up to determine the technical aspects of using a catalytic hydrodesulfurization process for hydrofining crude aromatics. The initial objectives to be accomplished in the investigation were desulfurization of crude light oil at moderately severe conditions:

(A) To determine whether a satisfactory product could be produced from the standpoint of sulfur content, corrosion test and acid color test.

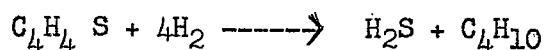
(B) To obtain information concerning operational difficulties which arise and to eliminate such difficulties.

After the above mentioned objectives had been accomplished, it was evident that a commercial plant could be successful. Therefore, a detailed chemical kinetic study was undertaken to determine the effect of operating variables on the degree of desulfurization.

During the initial investigation, Mr. William Hall, a representative from Jones and Laughlin Steel Corporation, was sent to Montana State College to define the quality specifications of processed light oil and to observe work being done. Based on the recommendation of Mr. Hall and representatives of Esso Research and Engineering a commercial light oil hydrofining plant costing approximately three million dollars was built by Badger Manufacturing Company for the Jones and Laughlin Steel Corporation at Aliquippa, Pennsylvania. Much of the data obtained in this investigation was used by Badger in designing the commercial plant. The commercial plant was put on-stream about July of 1957, with a capacity of 1000 barrels of light oil per day.

KINETIC EQUATIONS USED TO DESCRIBE THE REACTION

The principal overall reaction in the process of removing sulfur from light oil is:



The following is a summary of the mathematics used to describe the reaction.

1. Assume that the rate of reaction is dependent on the concentration of thiophene, the concentration of hydrogen, and the concentration of active centers on the catalyst (or some other measure of catalyst activity), and that the physical steps of diffusion involved in the catalytic reaction do not control the rate of reaction. Then the decrease in concentration of thiophene is given by the following equation:

$$\frac{-d(C_{th})}{dt} = k(C_{th})(C_{H_2})^b C_1 \quad (1)$$

Where (C_{th}) is the concentration of thiophene at any time (t) ,
 (C_{H_2}) is the concentration of hydrogen at any time (t) , and
 C_1 is the number of active centers which can enter into the reaction, or some other measure of catalyst activity.

b is the order of the reaction with respect to the concentration of hydrogen.

2. Let x equal the amount of thiophene reacted at any time (t) . The decrease in thiophene will be equal to the amount of thiophene reacted (x) at any time (t) . Then equation (1) can be written:

$$\frac{dx}{dt} = k C_1 (A-x)(B-y)^b \quad (2)$$

Where $\frac{dx}{dt}$ is the rate at which thiophene reacts, or decomposes,

k is the reaction rate constant, dependent on temperature and the particular catalyst,

A is the initial concentration of thiophene,

B is the initial concentration of hydrogen,

x is the amount of thiophene reacted at any time (t), and

y is the amount of hydrogen reacted.

3. Since the amount of H₂ consumed during the reaction is negligible compared with the initial concentration of hydrogen (2), the value of y can be neglected. It follows, then, that:

$$\frac{dx}{dt} = k C_1 (A-x)(B)^b \quad (3)$$

In any set of runs where the concentration of hydrogen and catalyst activity remain constant, equation (3), when integrated between the limits x=0 and x=x, and t=0 to t=t, becomes:

$$\ln A - \ln(A-x) = k (B)^b C_1 t \quad (4)$$

Where x is the amount of thiophene reacted in time (t).

With a flow-type reactor where all reactants are in the vapor phase it is customary to measure (t), which is a measure of apparent contact time, as reciprocal vapor rate (weight of catalyst/feed rate). The apparent contact time varies with the flow of reactants over the catalyst and can be corrected for variations in temperature, pressure, treat gas rate and space velocity (gm oil per hr per gm of catalyst) with the expression:

$$\frac{1}{V.R.} = \frac{1}{\frac{(\text{lb oil}/100 \text{ gm cat.}/\text{hr} \cdot 359 \cdot z + \text{ft}^3 \text{ gas}/100 \text{ gm cat.}/\text{hr})}{\text{Av. M.W. of oil}}} \times \frac{492(P + 13)}{(T + 460)(14.7)}$$

Where T is the operating temperature (°F),

P is the operating pressure (psig),

z is the compressibility factor for light oil, and

$\frac{1}{V.R.}$ is reciprocal vapor rate and is given in cu ft of reactants (at operating conditions) per 100 grams of catalyst per hour.

Reciprocal vapor rate can then be used in the place of (t) the apparent contact time and equation (4) can be rewritten as:

$$\ln \frac{A}{A-x} = K_1 \frac{1}{V.R.} \tag{5}$$

Where K_1 equals $k(B)^b C_1$ in which the reaction rate constant (k) is the only variable with respect to temperature after the correction for contact time is made. The term $(B)^b$ is a function of total pressure and ratio of hydrogen-rich treat gas to charge oil which must be kept constant for a particular value of K_1 .

4. The Arrhenius equation is of the form:

$$\ln k = \ln A - \frac{E_a}{RT} \tag{6}$$

Where k is the reaction rate constant,

A is the frequency factor which is constant,

E_a is the activation energy, and

T is the absolute temperature.

R is the gas constant.

Substituting for the reaction rate constant in terms of K_1 into equation (6) it becomes:

$$\ln \frac{K_1}{(B)^b C_1} = \ln A - \frac{E_a}{RT} \quad (7)$$

Which can be written:

$$\ln K_1 = \ln A + b \ln B + \ln C_1 - \frac{E_a}{RT} \quad (8)$$

Where K_1 and T are the only variables when the pressure term is constant and the catalyst is established to be 100 percent active throughout a given run. Equation (5) can be rewritten:

$$\log_{10} \frac{A}{A-X} = \frac{K_T}{V.R.} \quad (9)$$

and equation (8) can be rewritten:

$$\log_{10} K_T = \frac{-E_a}{2.3 RT} + \log C \quad (10)$$

Equations (9) and (10) were used in the kinetic study and values of K_T were determined at various desulfurization conditions.

EQUIPMENT, METHODS, AND ANALYSIS OF PROCESSED LIGHT OIL

Equipment

Two reactors designed for use at pressures up to 800 psig were used for the investigation. The essential difference in the reactors was the diameter and length of catalyst bed. Auxiliary equipment for both reactors was essentially the same. A schematic diagram of the process is shown in Figure 1.

Reactor No. 1 consisted of an 18-inch length of 2-3/8-inch I.D., schedule 80, stainless steel pipe. The thermowell, extending down through the reactor from the top, was constructed of 1/4-inch, schedule 80, stainless steel pipe. Heat was supplied to the reactor with 33-foot lengths of beaded Nichrome coils connected to 110-volt autotransformers. The reactor was insulated with 1-1/2-inch layer of magnesia mud. Preheat media and catalyst support consisted of 1/8-inch alundum (aluminum oxide) pellets. A catalyst bed of 100 grams was approximately 1-1/4 inches in length.

Reactor No. 2 was constructed from 1-inch, schedule 80, stainless steel pipe approximately 28 inches long. The thermowell, constructed of 1/4-inch stainless steel tubing, extended through the catalyst bed. Five thermocouples spaced approximately three inches apart were located within the thermowell. The preheat section and catalyst support consisted of 1/8-inch alundum pellets. The heating elements comprised four 33-foot lengths of beaded Nichrome coils supplied with current from four 110-volt autotransformers. The coils were wound onto the reactor over a layer of

asbestos tape and insulated with a 2-inch layer of magnesia mud. A catalyst bed of 100 grams was approximately eleven inches in length.

Auxiliary equipment consisted of a pre-vaporizer, calibrated rotometer, wet test meter, water cooled condenser, No. 2 gas cylinders and high-pressure regulators, Jerguson product receiver, and alkali and water product scrubbers. The alkali product scrubber contained 30 percent aqueous NaOH solution.

Methods

Control and measurement of process operating variables were conducted as described in the following paragraphs.

(1) Pressure: The reactor pressure was controlled with a 1/2-inch Mason-Neilan small volume air-to-close regulator valve, and a Fisher-Wizard proportional controller. A high pressure gage down stream from the reactor was used to measure pressure. Measurements were recorded at 1/2-hour intervals.

(2) Temperature: Temperature was controlled by adjusting the input to the Nichrome heating elements with autotransformers. Constant voltage was supplied to the autotransformers with a 2000 watt constant voltage transformer. Temperatures were measured at 30-minute intervals with iron-constantan thermocouples used in conjunction with a Leeds and Northrup indicating potentiometer.

(3) Treat-gas rate: Treat-gas rate was controlled by adjusting the needle valve located downstream from the feed tank, high pressure regulator and calibrated rotometer. Constant pressure was maintained

in the rotometer with the high pressure regulator connected to the feed tank. Measurements and adjustments were made at 1/2-hour intervals.

(4) Space velocity: Space velocity was altered by pump adjustments and determined at the end of each run from calculations involving the weight of oil charged, the catalyst charge, and the on-stream time.

Analysis of Processed Light Oil

Methods for determining the thiophene content, corrosiveness and acid-wash color of the processed light oil are summarized in the following paragraphs. The detailed step by step determinations for acid-wash color and corrosiveness are given in Tables XX and XXI, respectively (3).

(1) Thiophene Determination: Analysis for thiophene in benzene is a standard test proposed by duPont (1). The basis of the test is the reaction of isatin and thiophene in a solution of ferric sulfate in sulfuric acid. A compound called indophenin is formed which has a characteristic deep blue-green color. The intensity of the color is a measure of thiophene concentration. A standard calibration curve with transmission versus thiophene (parts per million thiophene on weight basis) is determined with the aid of a spectrophotometer. A simple distillation is carried out on the processed light oil. The first five percent of light oil distilled over and the material boiling above 90°C are discarded and thiophene determinations are made on the remaining oil (benzene cut). The end point of this fraction is so low that essentially no alkyl thiophenes could be present. Thiophene content of the benzene cut is reported in ppm on a weight basis.

(2) Acid color test: The acid color tests were made on the benzene, toluene, and xylene cuts. These simple distillation cuts are: benzene-I.B.P. to 90°C; toluene-90°C to 110°C; xylene-110°C to E.P. Seven milliliters of reagent grade sulfuric acid and 28 milliliters of sample are placed in a special test bottle and the contents agitated at a specified rate for 15 seconds. The layers are allowed to settle and the color of the acid layer is matched with the color of a standard. The standards are numbered from 0 to 14. The number of the standard which best matches the sample is reported as the acid-wash color number of the sample.

(3) Copper-strip corrosion test: Approximately 50 ml of processed light oil are placed in a 200 ml flask connected to a vertical condenser. A clean polished copper strip is placed in the flask and the oil is refluxed for one-half hour. The oil is said to be corrosive if the copper strip undergoes a noticeable darkening.

DISCUSSION AND RESULTS

Initial Investigation Concerned With The Feasibility Of Hydrofining
Crude Light Oil In A Hydrosulfurization Pilot Plant.

The purpose of the initial investigation was to determine whether crude light oil could be hydrofined effectively in a catalytic hydrodesulfurization unit. A total of nine runs were made, three using light oil produced by Jones and Laughlin (J&L-1, -2, -3) and six runs using light oil produced by United States Steel Corporation (U.S.S.-1, -2, -3, -4, -5, -6). The ASTM Distillation data for Runs J&L-1, -2, and -3 and Runs U.S.S.-1, -2, -3, -4, -5, and -6 are given in Tables I and V, respectively. Reactor No. 1 described under the heading "Equipment" was used throughout the runs. Results for each of the nine runs are described in table form in the appendix. A brief resume of each run is given in the following paragraphs.

Run J&L-1: The conditions chosen for the run to accomplish the desired degree of processing were 600 to 650°F, 400 psig, 2 gm of oil per hour per gm of catalyst, and 1000 ft³/bbl for temperature, pressure, space velocity, and treat gas rate, respectively. Pure hydrogen treat gas was used for the first 245 hours on-stream time and a mixture of 50 percent hydrogen and 50 percent nitrogen was used to complete the run. Freshly distilled crude light oil stored under an atmosphere of nitrogen was used as feed.

The thiophene content in the benzene-cut from the product oil was reduced from approximately 7200 ppm (0.72%) to 0.43 ppm after 27 hours

on-stream time at a space velocity of 2gm/hr/gm. The acid color tests were satisfactory at this time and the corrosion tests became satisfactory after 50 hours on stream.

Two disturbances occurred during the run; the first after 63 hours and the second after 151 hours on stream. Both disturbances, caused by mechanical failure, resulted in poor product (Table II).

After 240 hours on stream, the feed oil was changed from light oil protected from air to a light oil that had been stored for several months in a drum with no prevention from contact with air during storage. Stored light oil tends to darken on standing. Carbon formed within the reactor resulting in excessive pressure drop across the reactor after 260 hours on stream.

Run J&L-2: This run was a continuation Run J&L-1 after carbon formation on the pre-heat media and catalyst within the reaction had been burned off with air. The first part of the run was made using pure hydrogen treat gas and the latter part using 50% H₂ - 50% N₂ treat gas. The latter part of the run (Table III) showed that the thiophene in light oil could be reduced from 7200 ppm to less than 1 ppm at operating conditions of 650°F, 400 psig, 2 gm/hr/gm and 1000 ft³/bbl 50% H₂ - 50% N₂ for temperature, pressure, space velocity and treat gas, respectively. Thus, at these conditions, specification product can be produced when a treat gas containing 50% hydrogen and 50% nitrogen is used.

Run J&L-3: A recurrent operating difficulty was encountered when charge oil which had been stored with no protection from air was used.

A build-up of coke formed where the oil was vaporized, causing excessive pressure drop through the reactor. In the J&L-3 run, a pre-vaporizer (Figure 1) was connected into the oil line leading from the feed pump to the reactor. The pre-vaporizer was maintained at a temperature of 600°F throughout the run. No noticeable pressure drop was encountered during the 72-hour run, and product containing approximately 0.1 ppm thiophene was produced continuously (Table IV). Most of the carbon laydown, resulting when the light oil is vaporized, occurred in the pre-vaporizer rather than in the reactor. Carbon must be cleaned from the pre-vaporizer periodically.

Run U.S.S.-1: Operating conditions for the run were approximately 2 gm/hr/gm and 580°F; pure hydrogen was used as treat gas. No pre-vaporizer was used. The charge oil had a considerably high distillation end point and contained approximately 15 percent more xylene than did the oil used during the J&L runs. A comparison of the results from ASTM distillations for the runs can be made from Tables I and V in the appendix. The charge oil which had not been protected from air during storage contained a small amount of polymerized material.

Results of the acid color tests on the product oil (Table VI) were very poor -- in the range of 12 to 14 for the benzene cut. These results indicated that a light oil having a higher boiling range (containing more xylene) required a higher degree of processing.

Run U.S.S.-2: This run was a continuation of Run U.S.S.-1. Operating conditions were the same except that the temperature was increased

from approximately 580°F to 650°F. Results of this run (Table VII) were better than those of the preceding run, but not as good as the results from J&L runs, although operating conditions for the runs were about the same. This run indicated, as did the previous run, that the higher boiling light oil is more difficult to process than is the lower boiling light oil.

Run U.S.S.-3: Run U.S.S.-3 was conducted for 570 hours at space velocities ranging from 0.7 to 2.5 gm/hr/gm; other conditions were 650°F and 400 psig. The charge oil was the same as that used in Run U.S.S.-2. The pre-vaporizer, used throughout the run, was cleaned twice because of excessive pressure drop caused by carbon formation. As the pressure drop through the pre-vaporizer increased, the space velocity decreased and the treat gas rate increased, causing variations in operating variables.

The results of Table VIII indicate that the light oil from the United States Steel Corporation can be successfully desulfurized at a space velocity of 1.5 gm/hr/gm for at least 400 hours using pure hydrogen treat gas. Results also show that product having a satisfactory acid color test and containing approximately 8 ppm thiophene can be produced at a space velocity of 1 gm/hr/gm using mixed gas.

A comparison of results from the beginning of the run with results near the end of the run show that the catalyst had degenerated somewhat (chemical deactivation of the catalyst was referred to as catalyst degeneration throughout this investigation). Thiophene content of the product had increased from approximately 2 ppm to 9 ppm over a period of

400 hours. During J&L-1 run, catalyst activity remained fairly constant for 245 hours on stream. Thus, a charge oil which has not been protected from air causes more catalyst degeneration as a result of carbon formation on the catalyst.

Run U.S.S.-4: During the run, two temperatures were used -- 600°F and 650°F; and three treat gas mixtures were employed -- 50% H₂ - 50% N₂, 100% H₂, and 50% H₂ - 50% CH₄. A pressure of 400 psig was used.

The results given in Table IX show that better desulfurization is accomplished at 650°F than at 600°F when using 50% H₂ - 50% N₂ treat gas. At 650°F and 600°F, a product containing 0.25 and 4.5 ppm thiophene, respectively, is obtained at space velocities of approximately 1 gm/hr/gm. The results from this run also show, as did the results of Run U.S.S.-3, that a product (Sample 35, Table IX) containing less than 1 ppm thiophene could be produced at 650°F, 400 psig, 1.0 gm/hr/gm and 1000 ft³/bbl pure hydrogen treat gas. A comparison of the results from Samples 39 through 46 with the results from Samples 50 through 62 (Table IX) shows that approximately the same degree of processing is obtained when using either nitrogen or methane as a diluent in the treat gas at the given operating conditions.

Run U.S.S.-5, -6: From the results discussed in the preceding U.S.S. Runs, operating conditions were determined at which U.S.S. light oil could be processed effectively. However, only a small quantity of specification light oil was produced. In the following two runs, specification light oil was produced continuously for 155 and 138 hours, respectively.

Both runs were conducted at approximately 650°F, 400 psig, and 1000 ft³/bbl pure hydrogen.

The charge oil used in Run U.S.S.-5 had a slightly lower boiling range than that used in Run U.S.S.-6. A comparison of the results shown in Tables X and XI indicates that with the lower boiling light oil, a product containing an average of 0.15 ppm thiophene could be produced at a space velocity of 1.33 gm/hr/gm, while with the higher boiling light oil, (Run U.S.S.-6), a product containing an average of 0.31 ppm thiophene could be obtained at 1.0 gm/hr/gm. Acid color and corrosion tests for both runs were satisfactory. No noticeable catalyst degeneration occurred during the runs; however, both runs were interrupted for short periods as a result of carbon formation within the pre-vaporizer.

Conclusion: Results of the foregoing runs show that light oil having a boiling range of approximately 160-280°F can be effectively processed in a hydrodesulfurization unit at 600°F, 400 psig, 1000 ft³/bbl pure hydrogen and 2 gm/hr/gm for temperature, pressure, treat gas rate, and space velocity, respectively. Light oil having a higher boiling range must be hydrofined at more severe conditions. A treat gas containing either 50% H₂ - 50% N₂ or 50% H₂ - 50% CH₄ can be used effectively in the process but more severe conditions are required than when pure hydrogen treat gas is used. More severe conditions can be obtained by increasing such variables as temperature or contact time (decreased space velocity). Charge oil which has been stored for several months without protection from air causes considerably more carbon laydown

within the equipment than does light oil which has been freshly distilled or protected from air during storage.

The Study Of Process Variables Through The Use Of Rate Equations.

A total of fourteen runs designated U.S.S.-10 through U.S.S.-24 was made to investigate the kinetics of the reaction for removing sulfur from light oil with hydrogen. Runs U.S.S.-10 through U.S.S.-19 and Runs U.S.S.-21 and -22 were conducted with light oil which had been previously stored for several months, while Runs U.S.S.-20, -23, and -24 were conducted using freshly distilled light oil. The ASTM distillation data for the various charge stocks are given in Table XII. Reactor No. 1 was used during Runs U.S.S.-10 through U.S.S.-16 and Reactor No. 2 was used throughout the remaining runs.

Short runs were conducted when stored light oil was used as feed, to insure constant catalyst activity. When freshly distilled light oil feed was used, a run lasting 386 hours (Run U.S.S.-23) was conducted with no apparent catalyst degeneration and without noticeable pressure drop across the pre-vaporizer or reactor. Less than 0.01 weight percent of the charge oil was transformed to carbon in the pre-vaporizer when freshly distilled charge oil was used.

The results of the kinetic study were analyzed through the use of the pseudo-first order equation, namely:

$$\log \frac{A}{A-X} = K_T \frac{1}{V.R.} \quad (9)$$

Where A is the initial concentration of thiophene (7200 ppm on wt. basis).

A-X is concentration of thiophene remaining after desulfurization (ppm).

K_T is the overall rate constant ($\text{ft}^3/100 \text{ gm cat/hr}$ at operating conditions and is restricted to a given temperature, total pressure, partial pressure of hydrogen and partial pressure of diluent gas.

V.R. is given as total cu ft of treat gas and oil per 100 grams of catalyst per hour at conditions of the reaction. Values of K_T were determined at various conditions and compared quantitatively.

In Figures 2 and 3, the results shown in Tables XIV and XV from Run -17 and Run -22, respectively, are plotted with $\log A/A-X$ versus reciprocal vapor rate. The figures indicate that the kinetics of the reaction can be described, within experimental accuracy, fairly well by the pseudo-first-order rate equation. The rate equation for these two runs is valid for concentrations of thiophene as low as 0.5 ppm. Results for Runs -19 and -20 shown in Table XV and plotted in Figure 4 ($\log A/A-X$ versus reciprocal vapor rate) also indicate that the rate equation is valid for concentrations of thiophene in the range of 0.25 ppm.

Effect Of Temperature On K_T : The quantitative effect of temperature on the value of K_T has been studied through the use of the Arrhenius equation, namely:

$$\log_{10} K_T = \frac{-E_a}{2.3 RT} + \ln C \quad (10)$$

Where: E_a is activation energy (K cal/mol).

R is the gas constant (K cal/mol $^{\circ}\text{K}$).

T is reaction temperature ($^{\circ}\text{K}$).

Values of K_T were determined at various temperatures from equation (9) at constant total pressure of hydrogen and partial pressure of diluent gas. Variations in apparent contact time, caused by changes in temperature, are compensated for through the use of equation (9). Therefore, the differences in the values of K_T determined at various temperatures should be a result essentially due to the effect of temperature on K_T .

Results of three runs were used to study the effect of temperature on K_T . Runs designated U.S.S.-10 and -11 (Table XIII) were replicate runs with different temperature sequences (5 temperatures for each run) picked at random. Temperatures ranging from 650 to 850°F were employed. Other operating variables were 400 psig and 1000 ft³/bbl 50% H₂ - 50% N₂ treat gas. Run designated U.S.S.-24 (Table XVII) was carried out at temperatures ranging from 525 to 725 °F, 200 psig and 1000 ft³/bbl treat gas. Two temperature sequences were investigated during the run; one sequence was made using pure hydrogen and the other using 50% H₂ - 50% N₂ treat gas.

The tabulated results of Runs U.S.S.-10 and -11 are given in Table XIII and a plot of these results is shown in Figure 5. The term $2 + \log_{10} K_T$ is plotted versus reciprocal absolute temperature (°K). A straight line with a slope equal to $-E_a/2.3 RT$ is obtained. Calculation of E_a , the energy of activation, results in a value of approximately 10 K cal/mol.

Tabulated results of Run U.S.S.-24 are given in Table XVII and plotted in Figure 6. These results are also described quite adequately with the use of the Arrhenius equation. When $1 + \log_{10} K_T$ is plotted versus

reciprocal temperature, a straight line results when either pure hydrogen or 50% H₂ - 50% N₂ treat gas is used for desulfurization. However, it is apparent that the value of E_a (13 K cal/mol) when using pure hydrogen is significantly different from the value of E_a (8 K cal/mol) when using 50% H₂ - 50% N₂ treat gas. The results plotted in Figure 6 also indicate that the values of K_T may be nearly equal at temperatures in the range of 500°F.

Effect Of Pressure On K_T: In order to determine the effect of total pressure and ratio of partial pressure hydrogen to partial pressure oil on the rate of desulfurization, the rate constant (K_T) was calculated from the various plots of log A/A-X versus reciprocal vapor rate. In cases where only one set of conditions was used, the value of K_T was calculated directly from the data with the use of equation (9).

Results from Runs U.S.S.-15, U.S.S.-18, -19, and -21, and U.S.S.-23 given in Tables XIV, XV, and XVI, respectively, were used to show the effect of total pressure on the value of K_T. Values of K_T were obtained at constant conditions, except for pressure and space velocity during each run. A resume of these results is shown in Table XVIII and the values of K_T versus total pressure are plotted in Figure 7.

The results shown in Figure 7 indicate that the value of K_T is, in general, affected adversely with increase in pressure, whether pure hydrogen or mixed gas is used as treat gas. This adverse effect has been attributed to preferential adsorption of oil on the catalyst surface at higher pressures, thus eliminating "sites" or "active centers" capable of adsorbing hydrogen.

TABLE XVIII
Results Plotted in Figure 7

Run No.	Treat Gas	K_T (at following pressures, psig)			
		100	200	400	800
U.S.S.-15	50% H ₂ -50% N ₂	-	0.81	0.63	0.49
U.S.S.-18	50% H ₂ -50% N ₂	-	0.61	0.59	0.39
U.S.S.-19	50% H ₂ -50% N ₂	-	-	0.42	0.39
U.S.S.-19	Pure H ₂	-	-	0.81	0.83
U.S.S.-21	Pure H ₂	-	1.32	0.89	0.55
U.S.S.-23	Pure H ₂	1.34	1.10	1.29	-

The effect of total pressure on the degree of desulfurization can be seen from Figure 8 (Table XV), where $\log A/A-X$ is plotted versus reciprocal vapor rate. The degree of desulfurization was determined at 200, 400, and 800 psig using both pure hydrogen and 50% H₂ - 50% N₂ treat gas. The slope of tangents drawn to the curves is equal to K_T . Again it is apparent that as the total pressure is increased, the value of K_T is decreased. However, it should be noted that the degree of desulfurization is much greater at greater pressures. The value of K_T determined at different pressures and constant weight ratio of feed to catalyst does not relate the true effect of pressure on the degree of desulfurization. An increase in pressure will increase the apparent contact time (reciprocal vapor rate) and this factor has a much greater effect on the degree of desulfurization than does the decrease in K_T caused by increased pressure.

The effect on K_T caused by adding diluent gas such as nitrogen to the treat gas can be determined from comparisons of results shown in Figures 9, 10, and 11 (Tables XIV, XV, XVI, respectively), where $\log A/A-X$ is plotted versus reciprocal vapor rate. These comparisons indicate that the value of K_T , when using 1000 ft³/bbl 50% H₂ - 50% N₂ as treat gas, is

approximately 60-70 percent of that when using 1000 ft³/bbl of pure hydrogen treat gas in the range of 200 to 400 psig and 625 to 650°F. At treat gas rates of 1000 ft³/bbl pure hydrogen and 1000 ft³/bbl 50% H₂ - 50% N₂, the ratios of the partial pressures of hydrogen to oil are approximately 0.86 and 0.43, respectively. Therefore, when the ratio of hydrogen to oil is decreased, the value of K_T decreases.

The effect of decreasing the ratio of partial pressure hydrogen to oil is also shown in Figure 12. Values of K_T calculated at 500 ft³/bbl 50% H₂ - 50% N₂ are considerably lower than values of K_T calculated at a treat gas rate of 1000 ft³/bbl of 50% H₂ - 50% N₂. The ratios of partial pressure hydrogen to oil at treat gas rates of 500 and 1000 ft³/bbl are approximately 0.22 and 0.43, respectively.

From the preceding discussion it appears that the value of K_T depends more on the ratio of the partial pressures of hydrogen to oil than on hydrogen partial pressures alone. This conclusion is supported when considering the effect of total pressure on the value of K_T. As the total pressure is increased, the partial pressures of hydrogen and oil are increased, while the value of K_T is decreased somewhat.

Effect Of High Boilers On K_T: As indicated previously, the degree of desulfurization depends on the boiling range of the charge stock. Two charge stocks, having a boiling range of 158-243°F and 158-282.5°F were desulfurized at 400 psig, 650°F and 1000 ft³/bbl of pure hydrogen treat gas to determine the quantitative effect of high boiling material on K_T. The lower boiling light oil feed, designated "undercut feed", is a zero to 90 percent simple distillation fraction of the regular feed.

The results plotted in Figure 4 (Table XV) show that the undercut feed, ($K_T = 1.13$) can be desulfurized more readily than the regular feed ($K_T = 0.80$). The thiophene content in the benzene cut from both feeds was approximately the same; therefore, the fact that the lighter fraction could be desulfurized more readily may be attributed to the absence of the higher boiling material which is present in the regular feed.

A comparison in the ease of desulfurization of charge stocks having different boiling ranges can also be made utilizing results from Runs U.S.S.-22 and U.S.S.-23. At similar conditions (625°F , 400 psig, and 1000 ft³/bbl pure hydrogen treat gas), values of K_T equal to 0.65 and 1.03 were obtained for Runs -22 and -23, respectively. The charge stocks used in Runs U.S.S.-22 and -23 had boiling ranges of $161-282.5^\circ\text{F}$ and $158-251.5^\circ\text{F}$, respectively. The value of K_T in the case of the higher boiling feed was approximately 60% of that for the lower boiling feed. The higher boiling material made a great deal of difference in the value of K_T .

Contacting Efficiency Of The Catalyst In Reactor No. 1 and No. 2:

Diffusion of reactants from the main gas stream to the surface of the catalyst and diffusion of products from the catalyst surface to the main gas stream are dependent on the velocity of the main gas stream through the catalyst bed. In general, higher velocities will promote better film diffusion. It is desirable to obtain enough velocity so that diffusion does not limit the reaction. A higher velocity can be obtained, while maintaining a constant contact time, by increasing the length of the catalyst bed. The velocity of the gas stream at constant operating conditions

is directly proportional to the length of the catalyst bed.

Results from Samples 9, 11, and 16 in Runs U.S.S.-15, -16, and -17, respectively, are given in Table XIX and plotted in Figure 13. Operating conditions were similar and the light oil feeds were the same for the three samples.

TABLE XIX
Results Plotted In Figure 13

Reactor Number	Run U.S.S.	Sample Number	Catalyst Charge (gm)	V.R. ft ³ /100 gm.cat/hr.	log $\frac{A}{A-X}$	K_T	Cat. Bed Depth (in)
1	15	9	100	0.259	2.404	0.624	1.25
1	16	11	250	0.268	3.338	0.895	3.3
2	17	16	100	0.263	4.032	1.06	11.

The rate constant versus catalyst bed depth (velocity) is plotted in Figure 13. The plot indicates that diffusion has a very definite effect on the rate constant where catalyst bed depths of only 1 or 2 inches are employed, and that the effect becomes less pronounced so that little benefit could be obtained by using a bed depth greater than 10 or 11 inches for this particular reaction and catalyst size (10-14 mesh).

Conclusion:

The results of the kinetic study indicate that:

- (1) The value of the rate constant (K_T) decreases with increased pressure in the range of 100 to 800 psig.
- (2) The degree of desulfurization increases (log A/A-X increases) with increased pressure because contact time also increases.
- (3) The value of K_T using 1000 ft³/bbl of 50% H₂ - 50% N₂ is

approximately 60-70 percent of that using 1000 ft³/bbl of pure hydrogen treat gas in the range of 625 to 650°F and 200 to 400 psig.

- (4) The value of K_T decreases as the ratio of treat gas to oil decreases.
- (5) The value of K_T increases substantially with increased temperature. The energy of activation for the reaction is in the neighborhood of 10 K cal/mol.
- (6) The value of K_T is dependent on the boiling range of the feed; with higher boiling material requiring more severe process conditions.
- (7) Film diffusion has a limiting effect when catalyst bed depths of less than 10 inches are used.
- (8) The value of K_T obtained at similar conditions using Reactor No. 1 with a 100-gram catalyst charge was approximately 50 percent of the value of K_T obtained using Reactor No. 2 with a 100-gram catalyst charge.

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TABLE I

A.S.T.M. DISTILLATION OF LIGHT OIL FEED
USED IN RUNS J&L-1, -2, and -3
(Corrected to 760 mm)

RUNS J&L-1 and -2		RUN J&L-3	
<u>Volume % Dist.</u>	<u>Temp. °F</u>	<u>Volume % Dist.</u>	<u>Temp. °F</u>
I.B.P.	161.5	I.B.P.	160
5	162.5	5	163.5
10	163.	10	164.
20	164.	20	165.
30	165.	30	166.5
40	167.	40	167.5
50	168.5	50	170.
60	171.	60	173.
70	175.5	70	178.5
80	188.	80	189.
90	217.5	90	221.5
95	245.	95	251.
E.P.	268.	E.P.	278.5

TABLE II
TABULATED DATA FOR RUN J&L-1

Catalyst Reference: Harshaw CoMo O301-T 3/16" pills crushed to 8-20 mesh.
 Grams of Catalyst: 250
 Oil Charged: ASTM Dist.
 Range: 161.5-268°F
 Composite Yield: Wt. %: 97%

Sample Number	Total Hours	Cat. Temp. °F	Reactor Press.	Space Vel. gm/hr/gm	Treat Gas Ft ³ /bbl	Thiophene Ppm	Acid Ben.	Color Tol.	Copper-Strip Corro. Test
4	6	617	400	1.9	1050	---	4+	---	---
9	11	612	400	2.0	1000	---	7+	---	---
10	12	608	400	2.0	1000	---	4	---	---
11	13	601	400	---	---	1.0	1-	2-	---
14	16	583	400	2.03	990	3.4	1	1	C
23	25	574	400	2.05	980	---	0+	0+	C
25	27	630	400	2.05	980	0.43	0+	0+	---
28	30	576	400	2.08	960	---	3+	4	C
34-36	36-38	651	400	1.97	1020	0.33	0	0	---
37	39	622	400	1.97	1020	0.6	0+	0+	C
45	47	613	400	---	---	---	---	---	C
46	48	610	400	---	---	---	---	---	C
48	50	608	400	1.97	1020	---	---	---	O.K.
47-50	49-52	610	400	1.97	1020	0.75	0	0	---
51-54	53-56	622	400	1.97	1020	0.95	0+	0+	---
55-62	57-64	622	400	1.92	1040	6.5	0+	0+	---
55-61	57-63	622	400	1.95	1020	4.35	1-	---	---
64	66	669	400	2.06	970	12.0	1-	0+	---
63-70	65-72	653	400	2.06	970	6.5	0+	0+	O.K.
71-78	73-80	642	400	2.07	970	0.76	0	0+	O.K.
79-86	81-88	649	400	2.09	960	0.15	0	0+	O.K.
87-94	89-96	649	400	2.08	960	0.32	0	0	O.K.
95-102	97-104	648	400	2.06	970	0.33	0	0	O.K.
103-110	105-112	649	400	2.08	960	0.17	0+	0+	---

TABLE II (continued)
 TABULATED DATA FOR RUN J&L-1

Sample Number	Total Hours	Cat. Temp. °F	Reactor Press.	Space Vel. gm/hr/gm	Treat Gas Ft ³ /bbl	Thiophene	Acid Color		Copper-Strip Corro. Test
						Ppm	Ben.	Tol.	
111-118	105-112	655	400	1.83	1090	0.10	0	0	----
119-126	113-120	655	400	2.2	910	0.18	0	0	O.K.
127-134	121-128	651	400	2.06	970	0.13	0	0	O.K.
135-144	137-146	648	400	1.96	1020	0.18	0	0	O.K.
143-149	145-151	648	400	1.96	1020	0.37	0	0	O.K.
151-158	153-160	649	400	2.14	930	0.92	0	0	O.K.
159-166	161-168	649	400	2.09	960	0.21	0	0	O.K.
150	152	644	400	----	----	7.3	--	--	----
167-174	169-176	648	400	1.97	1020	T*	0	0	O.K.
175-182	177-184	653	400	1.96	1020	0.10	0+	0+	O.K.
183-190	185-192	651	400	1.86	1080	0.23	--	--	O.K.
191-198	193-200	644	400	1.83	1090	0.54	0	0	O.K.
199-206	201-208	655	400	1.86	1080	0.54	0+	0+	O.K.
207-214	209-216	648	400	1.83	1090	T	0+	0+	O.K.
215-222	217-224	646	400	2.0	1000	0.67	0	0+	O.K.
223-230	225-232	651	400	2.2	910	T	0	0	O.K.
231-238	233-240	651	400	2.04	980	T	0	0+	O.K.
239-243	241-245	651	400	2.15	930	0.26	0+	0+	O.K.

*Trace

TABLE III
TABULATED DATA FOR RUN J&L-2

Catalyst Reference: Harshaw CoMo 0301-T 1/16" pills crushed to 8-20 mesh.
 Grams of Catalyst: 250
 Oil Charged: ASTM Dist. 161.6-268°F
 Composite Yield: Wt. %: 97%

<u>Sample Number</u>	<u>Total Hours</u>	<u>Cat. Temp. °F</u>	<u>Reactor Press.</u>	<u>Space Vel. gm/hr/gm.</u>	<u>Treat Gas Ft³/bbl</u>	<u>Thiophene Ppm</u>	<u>Acid Color Ben.</u>	<u>Color Tol.</u>	<u>Copper-Strip Corro. Test</u>
5-8*	249-256	649	400	----	-----	0.18	0	0	O.K.
9-12*	257-260	648	400	----	-----	0.26	0	0+	O.K.
18-21	267-270	657	400	1.97	1010	0.67	0+	0+	O.K.
33-37	287-291	655	400	2.02	990	0.18	--	0+	C
39-43	293-297	---	400	----	-----	-----	0+	0+	C
38-45	292-298	653	400	2.0	1000	T	0+	0+	C
46-53	300-307	653	400	2.0	1000	0.58	0+	0+	C

* Pure H₂

TABLE IV

TABULATED DATA FOR RUN J&L-3

Catalyst Reference: Harshaw CoMo O301-T 3/16" pills crushed to 12-16 mesh.
 Grams of Catalyst: 200
 Oil Charged: ASTM Dist. Range: 160-287.5°F
 Composite Yield: Wt. %: 96%

<u>Sample Number</u>	<u>Total Hours</u>	<u>Cat. Temp. °F</u>	<u>Reactor Press.</u>	<u>Space Vel. gm/hr/gm</u>	<u>Treat Gas Ft³/bbl</u>	<u>Thiophene Ppm</u>	<u>Acid Color Ben.</u>	<u>Color Tol.</u>	<u>Copper-Strip Corro. Test</u>
4-7	42-54	640	400	2.15	930	0.1	0+	0+	O.K.
8-12	56-64	644	400	2.06	970	0.1	0+	0+	O.K.
13-16	66-72	650	400	2.02	990	0.1	0+	0+	O.K.

TABLE V
 A.S.T.M. DISTILLATION OF LIGHT OIL FEED
 USED IN RUNS U.S.S.-1 THROUGH U.S.S.-6
 (Corrected to 760 mm)

RUN U.S.S.-1		RUNS U.S.S.-2 AND -3		RUNS U.S.S.-4 AND -5		RUN U.S.S.-6	
<u>Volume %</u> <u>Dist.</u>	<u>Temp.</u> <u>°F</u>	<u>Volume %</u> <u>Dist.</u>	<u>Temp.</u> <u>°F</u>	<u>Volume %</u> <u>Dist.</u>	<u>Temp.</u> <u>°F</u>	<u>Volume %</u> <u>Dist.</u>	<u>Temp.</u> <u>°F</u>
I.B.P.	158	I.B.P.	163	I.B.P.	160.5	I.B.P.	162.5
5	178	5	166.5	5	165	5	167
10	178	10	168	10	166	10	168.5
20	188	20	171	20	165.5	20	170.5
30	195	30	173	30	169.5	30	173
40	204	40	175.5	40	172	40	176.5
50	217.5	50	179	50	174.5	50	179
60	236	60	186	60	178.5	60	187.5
70	257	70	199	70	184.5	70	197.5
80	278	80	220	80	196	80	220
90	303	90	259	90	229	90	259
95	329.5	95	294.5	95	259	95	289
E.P.	330.5	E.P.	302.5	E.P.	273.5	E.P.	299.5

TABLE VI
TABULATED DATA FOR RUN U.S.S.-1

Catalyst Reference: Harshaw CoMo 0301-T 3/16" pills crushed to 12-16 mesh.
 Grams Catalyst: 100
 Oil Charged: ASTM Dist. Range: 158-331°F
 Composite Yield: Wt. %: 98%

Sample Number	Total Hours	Cat. Temp. °F	Reactor Press.	Space Vel. gm/hr/gm	Treat Gas Ft ³ /bbl	Thiophene Ppm	Acid Color Ben.	Acid Color Tol.	Copper-Strip Corro. Test
5	41	581	400	2.06	970	--	12	14	----
7	49	583	400	1.98	1010	--	12	14	----

TABLE VII
TABULATED DATA FOR RUN U.S.S.-2

Catalyst Reference: Harshaw CoMo 0301-T 3/16" pills crushed to 12-16 mesh
 Grams Catalyst: 100
 Oil Charged: ASTM Dist. Range: 163-302.5°F
 Composite Yield: Wt. %: 97%

Sample Number	Total Hours	Cat. Temp. °F	Reactor Press.	Space Vel. gm/hr/gm	Treat Gas Ft ³ /bbl	Thiophene Ppm	Acid Color Ben.	Acid Color Tol.	Copper-Strip Corro. Test
3	96	624	400	----	----	---	8+	8+	----
10	124	639	400	2.06	970	---	3+	3+	----
15	144	649	400	2.08	960	---	2	3	----

TABLE VIII
TABULATED DATA FOR RUN U.S.S.-3

Catalyst Reference: Harshaw CoMo 0301-T 3/16" pills crushed to 12-16 mesh
 Grams Catalyst: 100
 Oil Charged: ASTM Dist. Range: 163-302.5°F

Sample Number	Total Hours	Cat. Temp. °F	Reactor Press.	Space Vel. gm/hr/gm	Treat Gas Ft ³ /bbl	Thiophene Ppm	Acid Ben.	Color Tol.	Copper-Strip Corro. Test
2	66	646	400	2.48	753	2.45	0+	2	Corro.
6	82	648	400	2.32	860	2.1	1	2	O.K.
12	106	648	400	1.88	1030	1.0	0+	2	O.K.
18	130	646	400	1.58	1260	2.25	1	3+	O.K.
12-18	106-130	648	400	1.72	1160	1.4	1	3+	O.K.
22	146	648	400	2.21	910	2.22	1	3	O.K.
19-23	134-150	647	400	2.13	940	2.51	2	4	O.K.
24-27	154-166	648	400	2.16	930	1.05	2	3+	O.K.
30	178	642	400	2.28	880	2.95	2	4	O.K.
33	190	648	400	1.67	1200	0.88	1	3	O.K.
36	202	655	400	1.21	1650	0.42	1+	4	O.K.
33-37	190-206	650	400	1.37	1460	0.32	1	3	O.K.
42	226	650	400	2.42	830	1.8	1	3	O.K.
48	250	651	400	0.67	3000	0.26	0+	3	O.K.
54	276	648	400	1.76	1140	0.67	0+	1	O.K.
45-54	238-276	648	400	1.37	1460	0.61	0+	1+	O.K.
60	300	650	400	1.43	1400	0.47	0+	1+	O.K.
63	320	642	400	1.16	1720	0.32	0+	2	O.K.
64	328	642	400	1.13	1716	0.68	0+	2	O.K.
68	360	650	400	0.95	2010	3.35	0+	1+	O.K.
73	400	648	400	1.05	1820	0.62	0+	2	O.K.
64-69	328-368	648	400	1.01	1980	0.35	0+	2	O.K.
77	416	644	400	1.4	1430	2.98	1	3	O.K.
87	462	651	400	2.0	1000	9.0	0+	3+	O.K.

TABLE VIII (continued)

TABULATED DATA FOR RUN U.S.S.-3

<u>Sample Number</u>	<u>Total Hours</u>	<u>Cat. Temp. °F</u>	<u>Reactor Press.</u>	<u>Space Vel. gm/hr/gm</u>	<u>Treat Gas Ft³/bbl</u>	<u>Thiophene Ppm</u>	<u>Acid Ben.</u>	<u>Color Tol.</u>	<u>Copper-Strip Corro. Test</u>
93	486	646	400	2.0	1000	9.0	0+	2+	O.K.
105	530	644	400	2.04	980	3.8	0+	2+	O.K.
107	554	646	400	1.04	670*	8.7	0+	0+	O.K.
108	562	648	400	1.0	670*	8.0	0+	0+	O.K.
109	570	646	400	0.94	670*	6.7	1+	1+	O.K.

* 50% H₂ - 50% N₂

TABLE IX
TABULATED DATA FOR RUN U.S.S.-4

Catalyst Reference: Harshaw CoMo 0301-T 3/16" pills crushed to 12-16 mesh
 Grams of Catalyst: 200
 Oil Charged: ASTM Dist. Range: 160.5-273.5
 Composite Yield: Wt. %: 95%

Sample Number	Total Hours	Cat. Temp. °F	Reactor Press.	Space Vel. gm/hr/gm.	Treat Gas Ft ³ /bbl	Thiophene ppm	Acid Ben.	Color Tol.	Copper-Strip Corro. Test
2	52	586	400	1.13	1770*	7.8	1	1+	O.K.
10	84	605	400	0.99	2020*	7.8	2	3	O.K.
16	108	610	400	1.01	1980*	7.8	1	2	O.K.
22	132	601	400	1.04	1920*	4.5	0+	0+	O.K.
28	156	600	400	1.14	1660*	7.75	0	0+	O.K.
35	188	646	400	1.0	1000#	0.15	--	--	O.K.
39	204	649	400	0.98	2040*	0.25	0+	1	O.K.
37-46	196-232	648	400	0.98	2040*	7.65	1	1	O.K.
46	232	648	400	1.02	1960*	2.7	--	--	O.K.
50-52	248-256	649	400	0.98	2040#	9.0	0+	0+	O.K.
55	274	655	400	1.39	1440#	2.7	--	--	O.K.
62	288	652	400	1.31	1470#	1.52	--	--	O.K.

*50% H₂ - 50% N₂
 #100% H₂
 #50% H₂ - 50% CH₄

