



A study of the thermal decomposition of 2-naphthyl disulfide  
by George Lan-yuh Kan

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of  
MASTER OF SCIENCE in Chemical Engineering  
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**Abstract:**

The pyrolysis reaction of 2-naphthyl disulfide heated at three different rates, 1.40, 2.32, 2.50 °C/min. up to 640°C, was studied by using a thermogravimetric analysis unit. This unit was capable of indicating temperature, weight loss, and amounts, of gaseous products produced as a function of time. The study showed that hydrogen, methane ethane, hydrogen sulfide and a trace of carbon dioxide were liberated during the reaction. Also, naphthalene, and 2-naphthalenethiol were identified as products of reaction. The structure of other condensable products was discussed but not identified.

A complete stoichiometric expression for the pyrolysis reaction with a heating rate of 1.40°C/min. is obtained. The stoichiometric coefficients of hydrogen, methane, hydrogen sulfide increase with decreased heating rate.

The weight loss curve follows the same pattern as the major evolution peaks of noncondensable gases, in other words, the weight loss rate becomes faster when the evolution of gases reaches its maximum.

Carbonaceous residues with various sulfur content are found to remain in the reactor after the pyrolysis, reaction. The percentage of sulfur in the residue decreases with decreased heating rate.

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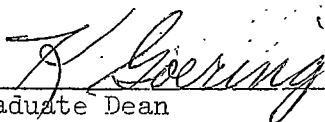
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## ABSTRACT

The pyrolysis reaction of 2-naphthyl disulfide heated at three different rates, 1.40, 2.32, 2.50 °C/min. up to 640°C, was studied by using a thermogravimetric analysis unit. This unit was capable of indicating temperature, weight loss and amounts of gaseous products produced as a function of time. The study showed that hydrogen, methane, ethane, hydrogen sulfide and a trace of carbon dioxide were liberated during the reaction. Also, naphthalene and 2-naphthalenethiol were identified as products of reaction. The structure of other condensable products was discussed but not identified.

A complete stoichiometric expression for the pyrolysis reaction with a heating rate of 1.40°C/min. is obtained. The stoichiometric coefficients of hydrogen, methane, hydrogen sulfide increase with decreased heating rate.

The weight loss curve follows the same pattern as the major evolution peaks of noncondensable gases, in other words, the weight loss rate becomes faster when the evolution of gases reaches its maximum.

Carbonaceous residues with various sulfur content are found to remain in the reactor after the pyrolysis reaction. The percentage of sulfur in the residue decreases with decreased heating rate.

## I. INTRODUCTION

There are several ways to convert heavy petroleum fractions into lighter more valuable ones, namely, hydrocracking, catalytic cracking, and thermal cracking. Among these, thermal cracking yields the largest percentage of fuel oil with a smaller percentage of gasoline.

In the United States, gasoline represents forty-seven percent of the total output from crude processing.<sup>9</sup> But, in other countries, the gasoline demand is less important. In Europe, the need for fuel oils and distillates is growing faster than that of gasoline.<sup>9</sup> It is pointed out that in Western Europe gasoline accounts for twenty percent of the output.<sup>9</sup> Due to more demand for gasoline, thermal cracking is being replaced by catalytic cracking in the United States. But, the charge capacity of 1.3 million bpcd for thermal cracking<sup>9</sup> still makes it worthwhile to investigate the process.

By thermal cracking, gas, gasoline, fuel oil and coke are formed. The ratio of these products depends on feed composition and the conditions being used. Since the feed is essentially heavy residual of a petroleum refinery, the sulfur content is rather high. As a consequence, the sulfur content in the products is rather high too. Sulfur, because it is present in various forms in the products, causes the problems of air pollution, corrosion of equipment and contamination of products. For example, if the coke were used in a furnace, most of the sulfur in it would be converted into sulfur dioxide which would appear in the stack gases and

cause air pollution problems. Besides, the sulfur may be converted to sulfuric acid in the presence of moisture and this leads to corrosion of the air preheater, ducting and stack.<sup>8</sup>

In order to minimize the sulfur content in the products of thermal cracking, basic studies about the way sulfur is present in feed stock, undergoes reaction, and is distributed in various products are necessary.

It is true that both the process and equipment could be improved if more information was known about the mechanism and kinetics of the reaction. Therefore, the purpose of this work is to trace the sulfur of certain compounds similar to those found in feed stocks of the thermal cracking process. There is some reason to believe that heavy polynuclear and heterocyclic aromatics make up part of the feed stock.<sup>12</sup> 2-Naphthyl disulfide was selected for this study because it is a polynuclear aromatic compound and decomposes under heating instead of boiling away as many compounds do.

Throughout the study of pyrolysis of this compound, the products condensable on a water cooled surface, the noncondensables, and the carbonaceous residue remaining in the reactor were analyzed and identified. By doing this and combining the previous information, it might be possible to suggest some methods to improve the thermal cracking process. Also, it will give some basic knowledge in the area of how organic sulfur acts in pure thermal treatment.

## II. EQUIPMENT AND ANALYTICAL PROCEDURES

In order to investigate the pyrolysis reaction of 2-naphthyl disulfide, it is evident that the equipment should be able to detect what compounds have been formed in the reactor at certain temperatures and the rate of formation. The apparatus used to meet this purpose was built in the Department of Chemical Engineering.<sup>5 12 11</sup> Some modifications have been made since then. This equipment consists of a thermogravimetric analysis unit (TGA), a gas chromatograph, and other instruments which were used to analyze and identify the products.

### A. Thermogravimetric Analysis Unit

A sketch of the equipment is shown in Figure 1. It shows the modifications made to a Leeds and Northrup temperature recorder in order to make an automatic recording balance useful for tracing the pyrolysis reaction.<sup>5</sup> The balancing chain was calibrated to get an exact correction factor. It was found that for a weight change of 0.011 grams the pen would give a movement on the recording chart of one smallest division. Tests were made<sup>5</sup> which proved that changing sweep gas flow rate and temperature had essentially no effect on the accuracy of this balance.

Right below the balance is the reaction chamber. They are separated by a water cooled plate. The reaction chamber, (Figure 2), refers to the chamber containing the internal preheater, reactor heater, reactor, condenser and other connecting tubing and supporting stands. For each run, a nitrogen inert gas atmosphere was maintained around the reaction chamber to minimize the effect of oxygen on the reaction.

In the early runs which were made on 2-naphthyl disulfide, there were some heavy condensates condensed on the thermowell and the telescope of the reactor. This gave inaccurate data on weight loss during the run. That problem was solved by using another external preheater and a cap wrapped with a resistance heater, so the temperature of the gases leaving the reactor is too high to condense before entering the condenser.

During each run, the reactor was adjusted so that it was suspended freely below one arm of the automatic balance. It should be tightened by nuts otherwise its thermowell might contact the wall of the diffusion hole of the reactor cap. In case this happened, the weight loss data would not be reliable.

By maintaining a constant suction rate on the line leading from the condenser, the volatile gases formed during reaction in the reactor are pulled through the water cooled condenser to trap the high boiling point products, then through a glass wool filter to stop solid particles, and a tube of drierite to remove water vapor that might be present in the gas stream. The noncondensable gases were pulled through an on-stream gas chromatograph to analyze them.

The reactor heater in the reaction chamber can heat the reactor from ambient temperature up to 700°C. The combination of the preheaters inside and outside the reaction chamber is able to raise the sweep gas entering the reactor heater to a maximum temperature of 270°C. The temperature in the reactor is obtained by a temperature recorder in

conjunction with a thermocouple in the thermowell of the reactor. The temperature of the sweep gas also can be read out on the same temperature recorder by switching the connection to a thermocouple in the outlet of sweep gas.

#### B. Gas Chromatograph

The gas chromatograph used to analyze non-condensable gas contains a thermoconductivity detector and a one-fourth inch diameter column packed with Porapak Q (100-120 mesh). A six and one-half foot length aluminum tubing was used to build the column in order to reduce corrosion problems caused by sulfur compounds. Nitrogen was used as the carrier gas at 65 c.c./min. The column temperature for each run was 119.5°C.

A two-way, solenoid operated sampling valve allows the sample size of each injection to be exactly equal to the sample loop size being used. In the early runs, injection of each sample was manually controlled. In order to make the runs more reproduceable and less tedious, a timer was installed to allow automatic sample injection every five minutes. The on or off period of the timer is adjustable from 2% to 98% of whole time cycle. The whole on-off time cycle also could be adjusted by changing gear and rack assemblies.

An Aerograph 200 gas chromatograph was used to analyze the condensate extracted from the condenser. The column used was a fifteen foot, one-quarter inch aluminum column packed with 5% Se-30 on Anakrom

50/60 ABS. The recommended maximum temperature for this column is 375°C. By inserting a small glass tube into the exit of the column, samples can be collected in higher degree of purity than repeated recrystallization or sublimation and with less effort.<sup>10</sup> These samples were saved for identification purposes.

### C. Infrared and Ultraviolet Spectroscopy

The infrared spectra of the unknown samples collected from the preparative gas chromatograph were used to identify and determine the features of these samples. The Beckman IR-4 Infrared Spectrophotometer was used to get the spectra and the range of scanning is from fifteen microns to two microns. Since potassium bromide does not absorb infrared light in the region of 2.5 to 15 microns<sup>6</sup>, complete spectra of unknown samples were obtained by using potassium bromide "pellet". The pellets were made by grinding potassium bromide and the samples together and pressing in a die under high pressure. In order to get a good spectrum, the optimum amount of each sample in the pellet was found by trying several different ratios of sample to potassium bromide. The typical condition for each run in IR-4 spectrophotometer was double beam with air reference and 0.5 mm. pellet thickness.

For the convenience of comparing unknown spectrum with standard spectrum, polystyrene's characteristic peak at 1600.1 cm.<sup>-1</sup> was located for each spectrum as a calibration point. In identification and spectra interpretation of unknown samples, the Sadtler's Standard IR Spectra and

a correlation chart of infrared group frequencies distributed by Dow Chemical Company were used. It has been found that due to the difference in scales between standard and unknown spectra, it is necessary to be careful in making comparisons.

D. ASTM Quartz-Tube Apparatus

The sulfur content in the residue was determined by the ASTM Quartz-Tube Method. The sulfur in the residue was burned in a porcelain boat into sulfur dioxide and absorbed by 1.5% hydrogen peroxide to become sulfuric acid. The content of sulfur was then determined by titration with sodium hydroxide. The detailed operating procedure is available in the literature.<sup>3</sup>

E. Source of Material

The materials tested to determine their percent weight loss after pyrolysis were purchased from Eastman Organic Chemicals, K & K Chemicals and Aldrich Chemicals (Table I). They are listed to be 95-99% pure and were used in the condition received.

The standard gas which was used to draw the calibration curve of peak height vs. number of moles was obtained from Matheson Company. It contained 5.06% methane, 4.6% hydrogen, 5.67% ethane, 7.48% hydrogen sulfide and 77.19% nitrogen.

The naphthalene used to identify one of the samples in the condensate is available in our laboratory. 2-Naphthalene-thiol which

was used to identify another unknown sample in the condensate was purchased from K & K Chemicals.

F. Analytical Procedure

A detailed operating procedure of the TGA unit is presented elsewhere.<sup>12</sup> The procedure used in this work was essentially the same. However, minor modifications were made. First, the using of a timer allowed automatic injection of gas samples into the chromatograph every five minutes. It was so connected to the circuit that manual push button on-off control could be used if the timer was shut off. By this device, the reliability of gas evolution data and the feasibility of each run was improved. Second, a water filled manometer open to the atmosphere was attached to the suction jar. This permits a quick check of plugging problems. If there were no plugging problems, the pressure difference between the suction stream and the atmosphere should be less than one inch of water.

The operating procedure can be stated simply as follows:

1. Take a sample size of about 1 gram.
2. Assemble the TGA Unit as stated previously.<sup>11 12</sup>
3. Turn on heaters and adjust the Variacs in order to maintain a linear temperature increasing rate in the reactor. The sweep gas pumping rate for each run is kept at 65 c.c./min.
4. For the gas chromatograph, the carrier gas is maintained at 65 c.c./min. and the column temperature is kept at 119.5°C.

5. Watch the gas chromatogram and adjust the attenuation so that the peak height does not go out of the limit of the chart for each different gas.

6. Shut off after the desired temperature is reached.

7. Let the equipment cool down to room temperature

After a run was made, the condensate and the carbonaceous residue could be analyzed individually.

During the run the chromatograph continually analyzed the noncondensable gas components. A typical gas chromatogram is shown in Figure 3. Hydrogen, methane, ethane, hydrogen sulfide that corresponds to peaks 1, 2, 4, and 5 respectively, are identified by comparing their retention times with known compounds. Carbon dioxide that corresponds to peak 3 is identified by comparing the relative position of methane, carbon dioxide and ethane of a known gas chromatogram.<sup>1 2</sup> A supporting evidence is that peak 3 did not show up on the gas chromatogram of Aerograph 660 gas chromatograph equipped with a flame ionization detector.

For quantitative analysis of non-condensable gases, calibration was made by using the known concentration standard gas purchased from Matheson Company. The purpose of this work was to obtain a calibration curve of peak heights vs. moles of gas, which was calculated by a computer program (Table II). By the assumption that the ideal gas law is valid, the number of moles for each gas at a certain average peak height was then calculated by the same program. For each gas a curve

fit program from Paul E. Simacek, a former graduate student here, was used.

For hydrogen, methane, ethane a polynomial of degree four was used to fit the points. For hydrogen sulfide, a polynomial of degree three was used to fit the lower part and a polynomial of degree two was used to fit the upper part. By calling the PLOT subroutine in the IBM 1620 computer, the calibration curves were drawn by an IBM 1627 plotter (Figure 4, 5, 6, 7). A sample program for methane is shown in Table III. The good agreement between the experimental data and the curve drawn can be seen from these Figures.

The calculation of the gas evolution rate at any instant could be obtained by multiplying pumping rate with concentration at that time. The concentration at any time was calculated by converting peak height to number of moles and dividing it by sample loop size. Since the pumping rate was set at 65 c.c./min., a program written in FORTRAN II was used to calculate the gas evolution rate (Table III). The total number of moles of each gas produced in a reaction was determined by measuring the area under the curve of moles per minute per gram of starting material vs. minutes with a planimeter and multiplying it by the weight in grams of starting material.

The condensate was extracted out by chloroform from the condenser. The condensate was then collected and weighed. After trying different columns, a Se-30 column was selected for separating the

different compounds in the condensate. In the early analysis of the condensate, the column temperature was set at 200°C and only two peaks were shown on the gas chromatogram. By raising the column temperature, more peaks began to appear. Finally, a column temperature of 300°C was used and there were nine major peaks with the first peak consisting of solvent and the most volatile constituent in the condensate. That suggested a column temperature programmed from 200°C to 300°C and then held constant at 300°C might give the best resolution of the nine materials present in the condensate. Figure 8 shows a sketch of a typical gas chromatogram under a programming rate of 10°C/min. In Figure 8, with the first peak being solvent, the other peaks were numbered from 1 to 9 from left to right. The nine samples were then collected by preparative chromatography for identification purposes.

There are two methods for determining the stoichiometric coefficients of condensate. One is to approximate the amount of each sample present by evaluation of the gas chromatogram area. The other is to inject a definite amount of condensate and collect all samples by a preparative chromatograph. The exact weight of each sample determines its stoichiometric coefficient, respectively.

The residue is essentially coke. Several sulfur analyses were made on residues either by the Quartz-Tube Method or by Huffman Laboratories, Wheatridge, Colorado. Hydrogen and carbon analysis for Samples 7, 8, and 9 were also carried out by Huffman Laboratories. From these

data, an experimental formula can be calculated for these samples.

Also, the molecular weights of Samples 7, 8, and 9 were determined by Huffman Laboratories.

### III. RESULTS AND DISCUSSION

#### Preliminary Study

The catalogs of K & K Chemicals, Eastman Organic Chemicals, and Aldrich Chemicals were searched thoroughly and all polynuclear and heterocyclic sulfur compounds were taken down for initial study of their possibilities as materials for thorough investigation. To avoid possible complications in further analysis, the compounds selected contained only sulfur in addition to carbon and hydrogen.

Ten compounds were purchased and each was heated at a linearly increasing temperature rate. The first thing that had to be established was whether each compound decomposed or just boiled away. This is easy to ascertain because if a compound is boiled away, the weight loss curve will show a quick change of reactor weight. For each compound the data on percentage weight loss and final temperature were recorded and remarks about the reaction were also taken down. Table I shows the results of initial studies on these compounds.

Table I indicates that all compounds except 2-naphthyl disulfide essentially boil away before the temperature is high enough to cause any thermal decomposition reaction. 2-Naphthyl disulfide was selected for further study mainly because it is a polynuclear compound and decomposes slowly during pyrolysis reaction. A literature search was carried out in the hope of finding some information about thermal decomposition of this compound, but none was found.

Twelve runs were made on the pyrolysis of 2-naphthyl disulfide. Table V gives the heating rate, final weight loss percentage, final temperature, and some general information. In the early runs there was no way to detect whether the product removal line was being plugged or not. After Ex-V was made, a quick check of the plugging problem was allowed by leading out a manometer tube from the suction line. By this device it was found that Ex-V was made while the sampling valve was plugged. There was suspicion that Runs One to Four also had the same trouble and the data from these runs should not be used in quantitative analysis.

From Table V, it is obvious that the weight loss percentage varies from run to run. A possible explanation is that the heating rates are different from run to run and that differences in heating rates caused the difference in weight loss. There was essentially no weight change in the reactor after  $600^{\circ}\text{C}$  and the final temperature did not have much effect on weight loss if it was over  $600^{\circ}\text{C}$ .

It should also be pointed out that Runs Ex-VII, -X, and -XI have more reliable data on gas evolution rate and are being used for both qualitative and quantitative analysis of the reaction. However, the rest of the runs still provide information on qualitative analysis.

#### Gaseous Products

The gaseous products of pyrolysis of 2-naphthyl disulfide are hydrogen, methane, ethane, hydrogen sulfide, and a trace of carbon di-

oxide. These gases were identified by comparing their retention times with standard.

Tables VI through VIII show the evolution rates of these gases in Runs Ex-VIII, -X, and XI. Figures 9 and 10 are plotted according to data from Run Ex-X. They show the rate of evolution of hydrogen, methane, ethane, and hydrogen sulfide as the pyrolysis reaction proceeds.

Although the heating rates of Runs Ex-VIII, -X, and XI were different, they still show similar trends of gas evolution. Hydrogen and hydrogen sulfide start to liberate from the reactor at approximately 325°C. Hydrogen evolution rate increases slowly from 325°C and increases sharply when the temperature approaches 585°C (Figure 9). After 585°C, it decreases rapidly and begins to increase after 600°C is reached (Figure 9). For hydrogen sulfide liberation, three peaks were shown at temperatures close to 370°C, 425°C, and 525°C with the same decreasing order of peak height (Figure 10).

The evolution of methane starts at 527°C and its rate reaches maximum at 585°C. After 600°C, the evolution rate of methane increases just as does the hydrogen evolution rate. For ethane, it starts to liberate at approximately 565°C and reaches its maximum at 580°C. The total amount of evolution of ethane for each run is the smallest compared to the other gases. Carbon dioxide was also found in previous research work.<sup>11</sup>

Since hydrogen and methane still come out in large amounts after 600°C, it is convenient to compare the results of each run at an identical assumed final temperature. Table IX was so constructed that all three runs have the same final temperature of 612°C. From Table IX, the coefficients of hydrogen, methane, and hydrogen sulfide of Run Ex-XI are larger than the other two runs. That is possibly because the gaseous products have a much better chance of being pumped out in a slower heating rate. Since sulfur is the main interest, this also suggests that more sulfur can be liberated in gaseous form at a slower heating rate; in other words, the sulfur content in the condensate should be decreased by doing so.

#### Condensable Products

In order to know more about the mechanism of pyrolysis of 2-naphthyl disulfide, a lot of time was spent in identifying the nine materials shown by peaks 1 to 9 in Figure 8. The samples were collected and spectra were obtained as stated in the previous section. The identification of these compounds proved to be very difficult and it might take a long time to identify all of them. Usually, the spectra on IR, UV, and NMR in addition to a good molecular weight from mass spectrum are needed to make a good guess as to the possible structure of an unknown compound. Finally, an agreement on spectra with a known compound is necessary for positive identification. However, if the IR spectra of an unknown compound and a known compound are identical, that will provide a short-cut for identification.

For Sample 1, an initial identification was made on the gas chromatograph by injecting the mixture of Sample 1 with naphthalene. Since there was still only one peak on the gas chromatogram, the IR and UV spectra of Sample 1 were obtained for positive identification (Figures 11, 12). Also shown in Figure 11 is a spectrum of naphthalene. The good agreement among these two spectra and Sadtler Standard IR Spectrum No. 865 make a positive identification of Sample 1 as naphthalene. As further evidence, the spectrum of Figure 12 also has the same absorption peaks as standard UV spectrum<sup>7</sup>.

Sample 2 was positively identified as 2-naphthalenethiol. The IR spectrum for Sample 2 shown in Figure 13 is identical to the spectrum of 2-naphthalenethiol shown in the same Figure. A comparison between Sadtler Standard IR Spectrum No. 331 and the spectrum of Sample 2 also indicates that they are the same. The UV spectrum of Sample 2 is shown in Figure 14.

A systematic method which allows one to find a standard IR spectrum similar to that of an unknown compound was available in Sadtler's IR Spec Finder Index. This method needs allocation of the strongest absorption band in the whole spectrum region and the strongest absorption band in each micron region. The Beckman IR-4 is not sensitive near the higher micron region so the allocation of the strongest bands are difficult to decide. To make searching for similar spectra more difficult, the IR Spec Finder Index is so arranged that the information in a higher micron region is of utmost importance.

However, a lot of time was spent on this kind of searching work and it was found that there exists some similarity in the standard spectrum of 2-naphthyl sulfide (Figure 15) and that of Sample 7 (Figure 16). In comparing the spectra it should be noticed that the whole spectrum of Sample 7 should be moved to the right about  $10 \text{ cm}^{-1}$  according to the calibration point shift. The agreement between IR spectra of 2-naphthyl sulfide (Figure 15) and Sample 7 (Figure 16) is fairly good except that Sample 7 has shown an extra peak to the right of  $3000 \text{ cm}^{-1}$ . This implies that Sample 7 probably has the same main structure as 2-naphthyl sulfide with an aliphatic substitution<sup>7</sup>. The hydrogen, carbon, sulfur analysis of Sample 7 was reported by Huffman Laboratories as: Carbon, 81.73%; hydrogen, 5.09%; sulfur, 9.54%. Based on this data, the experimental formula of Sample 7 is calculated as  $\text{C}_{23}\text{H}_{17}\text{S}$ . This result suggests that if there is an aliphatic chain it should have approximately three carbon atoms.

The IR spectra of unknown Samples 3, 4, 5, 6, 8, and 9 are shown in Figures 17 and 18. The functional group information for these compounds was obtained by a correlation chart of IR group frequencies distributed by Dow Chemical Company. Table X sums the qualitative information for all nine sample in condensate. The molecular weight and experimental formula shown in Table X are based on Huffman Laboratories analysis data.

A material balance of condensate was made by collecting each sample from the exit of the preparative gas chromatograph and the result

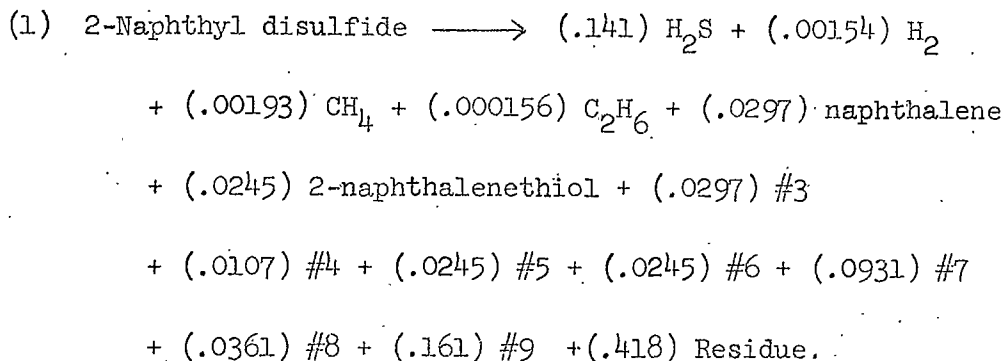
is shown on Table XI together with the carbon, hydrogen, and sulfur content for Samples 1, 2, 7, 8, and 9.

#### Residue

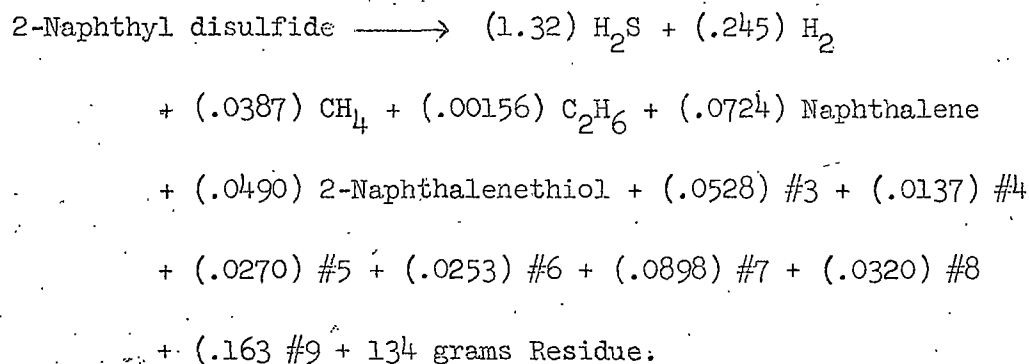
Residue is essentially carbonaceous material. It always contains a very small amount of material which appears in the condensate. Actually, the sulfur content in the residue is of main interest. The residue of Run Ex-X was sent to Huffman Laboratories to analyze. The result was: Carbon, 84.15%; hydrogen, 2.75%; sulfur, 4.79%. When these figures were added up they did not total 100%, so a check of sulfur content was made in our Quartz-Tube sulfur analysis apparatus and the result was 9.74% of sulfur. This data is more reliable in comparison with the other data obtained from different runs (Table XII). Also, the sulfur content in the residue of Run Ex-XI was reported as 9.23%. The result obtained from our apparatus was 9.07%. The value shown in Table XII is an average value. From Table XII, it seems possible that by decreasing the heating rate, the sulfur percentage in residue will also be decreased.

#### Material Balance

A complete material balance was made in Run Ex-XI. For convenience, one gram of 2-naphthyl disulfide is taken as a basis of calculation. If the amount of condensate were determined by subtraction of the amount of residue and gaseous products from the weight of the starting material, a material balance in grams can be obtained:



The molecular weight of Samples 3, 4, 5, and 6 is approximated by comparing their relative positions on the gas chromatogram at 300°C with the positions of those samples of known molecular weight. They were approximated to be 180, 250, 280, and 310, respectively. The stoichiometric expression of the pyrolysis reaction can be written as:



#### Gravimetric Curve

A close examination of the weight loss curve in Figure 10 reveals that the major weight loss periods accompany maximum rates of gas evolution. The weight loss rate becomes faster around the temperature where the evolution of hydrogen sulfide reaches its maximum; i.e., 370°C, 425°C, and 525°C. During the intervals between these tempera-

tures it levels slightly. Figure 10 also shows that the weight loss rate becomes rapid around 585°C and levels off after 590°C. That is because the evolution rates of hydrogen and methane reach their maximum at 585°C and decrease rapidly after 590°C.

#### Discussion of the Possible Mechanism

Hydrogen starts to evolve from the reacting mass at 325°C, which implies that a polymerization reaction occurs and liberates hydrogen-free radicals<sup>12</sup>. Those radicals are reactive with active sites in the reaction mass. Since the active sites are more numerous than the radicals, the probability of radicals combining to form hydrogen atoms is less probable than radicals attacking these active sites. As a result, the S-S bond and the S-C bond in 2-naphthyl disulfide are broken by the attack of hydrogen radicals. Hydrogen sulfide, naphthalene, 2-naphthalenethiol and their corresponding radicals produced by the S-S bond and the S-C bond rupture are formed.

The reaction from 325°C to 525°C is then believed to be the interaction between these radicals and the reaction of radicals with other molecules to give various polycyclic aromatic compounds<sup>4</sup>. At the same time, hydrogen is liberated indicating continuing polymerization. Since no trace of methane and ethane are observed during 325°C to 525°C, it seems that there is no rupture of the naphthalene ring system during this period. The differential thermal analysis<sup>10</sup> indicating no pyrolysis reaction of naphthalene during 300°C to 700°C also provides supporting evidence.

After 525°C is reached, the evolution rate of hydrogen sulfide starts to decrease to zero and the hydrogen evolution rate starts to increase rapidly. This phenomenon suggests that the available reactive C-S and S-S bonds tend to be used up after 525°C.

At 527°C, methane starts to evolve and that means that the ring structure of some polycyclic aromatic compounds starts to rupture. The rate of this rupture reaction follows the same pattern as the evolution rate of methane until 600°C is reached.

After 600°C, the rapid increase of hydrogen and methane evolution rates can be explained as a result of cyclodehydrogenation reactions forming graphite-like molecules<sup>11</sup>.

#### IV. CONCLUSIONS

From the study of pyrolysis of 2-naphthyl disulfide up to 630°C, both qualitative and quantitative information were obtained. Hydrogen, methane, ethane, and hydrogen sulfide are evolved during the reaction. The evolution rate of hydrogen and methane show a maximum at 585°C and tends to decrease rapidly after it, then increase rapidly after 600°C is reached. The hydrogen sulfide evolution rate has three major maximum peaks at 370°C, 425°C, and 525°C, respectively. The liberation rate of ethane is small compared to the other gases and reaches a maximum at 580°C. Hydrogen and hydrogen sulfide start to evolve at 325°C and methane becomes detectable at 527°C. Ethane starts to evolve about 565°C and stops around 600°C.

The stoichiometric coefficients of hydrogen, methane, and hydrogen sulfide increase with decreasing heating rate. The difference in stoichiometric coefficients for ethane is too small to be detected.

The weight loss curve seems to follow the same pattern as the major evolution peaks of noncondensable gases; in other words, the weight loss rate becomes more rapid when the evolution of gases reaches its maximum.

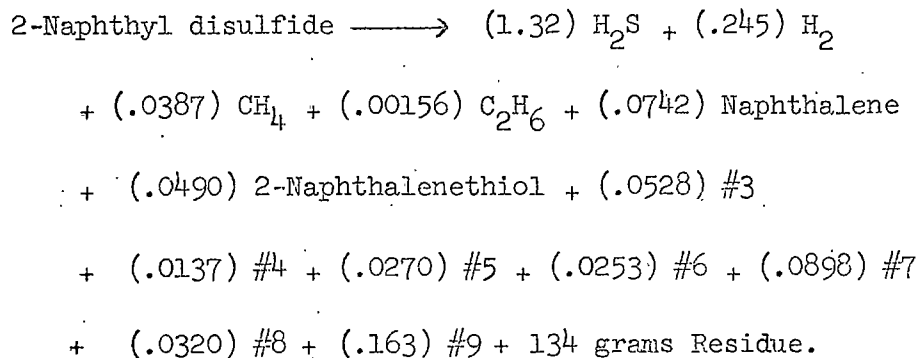
Nine condensable products were found by gas chromatograph analysis. Naphthalene and 2-naphthalenethiol are positively identified by infrared and ultraviolet spectra. The other condensates are mostly naphthalene systems with aliphatic substitutions. For all those con-

densable products the infrared spectra were obtained and their states at room temperature were observed.

Carbonaceous residues with various sulfur content are found to remain in the reactor after the pyrolysis reaction. The sulfur content in the residue decreases with decreasing heating rate.

The true mechanism of the whole reaction is not yet known. A polymerization of starting material to liberate hydrogen radicals is believed to take place at 325°C to 525°C. The hydrogen radicals then attack the reactive C-S bond and S-S bond of the reacting mass to form hydrogen sulfide, naphthalene and 2-naphthalenethiol together with their corresponding radicals. It is also believed that various polycyclic aromatics are being formed during this period. After 527°C, the liberation of methane indicates some ring rupture of these polycyclic aromatics. After 600°C, cyclodehydrogenation causes an increasing evolution rate of methane and hydrogen.

A complete quantitative analysis was made on a run heated at 1.40°C/min. The stoichiometric expression of this reaction is:



APPENDIX

Table I. Preliminary Study of Some Organic Sulfur Compounds by Using TGA Unit

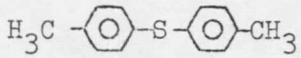
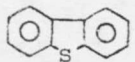
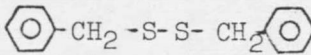
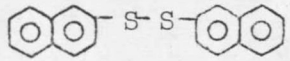
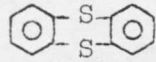
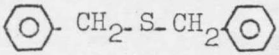
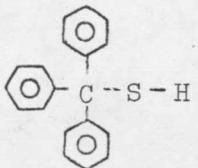
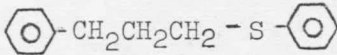
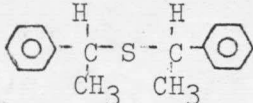
<u>Name of Compounds</u>	<u>Structure</u>	<u>Final Temp. °C</u>	<u>Percent Wt. Loss</u>	<u>Remarks</u>
Di-p-tolyl-sulfide		677	76.4	Boils away at 300°C, K.K.
Dibenzothiophene		395	100.0	Boils away, K.K.
Benzyl disulfide		325	65.0	Boils away, E.C.**
2-Naphthyl disulfide		615	56.5	Decomposes, E.C.
Thianthrene		365	97.1	Boils away, E.C.
Benzyl sulfide		395	80.5	Boils away, E.C.
Triphenyl methyl mercaptan		400	82.0	Boils away, A.C.C.***

Table I. Preliminary Study of Some Organic Sulfur Compounds by Using TGA Unit (Cont.)

<u>Name</u>	<u>Structure</u>	<u>Temp. °C</u>	<u>Wt. Loss</u>	<u>Remarks</u>
		350	90.5	Boils away, A.C.C.
	$\text{CH}_3(\text{CH}_2)_{15}\text{-S-S-(CH}_2)_{15}\text{CH}_3$	410	97.1	Boils away, A.C.C.
		400	86.2	Boils away, A.C.C.

- \* K & K Chemicals Company
- \*\* Eastman Chemicals Company
- \*\*\* Aldrich Chemicals Company

Table II. Program of Set Points in Calibration Curve

```

C      CALIBRATION CURVES OF PEAK HEIGHT VS. GRAM MOLES OF GAS FROM
C      STANDARD GAS MIXTURE
      DIMENSION PEAK(10,10,10), VLOOP(10), CONC(10)
      READ 10, NCOMP, NLOOP, NPEAK
      PRINT 5
      READ 20, (CONC(I), I=1,NCOMP)
      READ 20, (VLOOP(J), J=1, NLOOP)
      READ 25, (((PEAK(I,J,K) , K=1, NPEAK),J=1, NLOOP), I=1, NCOMP)
      READ 25, T,P
C      R=62361(MMHG)(CC)/(GMOLE)(DEG. K)
      R=62361.
      DO 100 I=1, NCOMP
      DO 100 J=1, NLOOP
      YMOL=P*VLOOP(J)*CONC(I)/(R*T)
      PRINT 30, I
      PRINT 40, YMOL
      DO 4 K=1, NPEAK
4      PRINT 50,PEAK(I,J,K)
      AVPEAK = (PEAK(I,J,1)+PEAK(I,J,2)+PEAK(I,J,3)+PEAK(I,J,4))/4.
      PRINT 60, AVPEAK
5      FORMAT(59H HYDROGEN(1)   METHANE(2)   ETHANE(3)   HYDROGEN SULFIDE
1(4))
10     FORMAT(3I3)
20     FORMAT(10F8.4)
25     FORMAT(10F8.2)
30     FORMAT(1H0,15H GAS NUMBER IS ,I3)
40     FORMAT(1H0, 18H   TOTAL MOLES = ,E14.8)
50     FORMAT(22H   PEAK HEIGHT IS = ,F8.2)
60     FORMAT(30H   AVERAGE PEAK HEIGHT IS = ,F8.2)
100    CONTINUE
      CALL EXIT
      END

```

Table III. Sample Program to Plot Calibration Curve of Methane

```
C CURVE PLOT PEAK HEIGHT OF METHANE VS. NUMBER OF TOTAL MOLES
C (DEGREE FOUR)
  XMIN=0.0
  XMAX=1000.
  XL=5.0
  XD=100.
  YMIN=-100.
  YMAX=900.
  YL=5.0
  YD=100.
  IC=101
  CALL PLOT (IC,XMIN,XMAX,XL,XD,YMIN,YMAX,YL,YD)
  IC=0
  X=0.0
  DO 10 K=1,101
  Y=-.39420000E-02+.34423995E+00*X+.65114690E-03*X**2.-.70822228E-06
  1*X**3.+ .41790926E-09*X**4.
  CALL PLOT (IC,X,Y)
10 X=X+10.
  ICC=7
  CALL PLOT (ICC)
  CALL EXIT
  END
```

Table IV. Program to Calculate Gas Evolution Rate for Each Run

```

C      PR=PUMPING RATE
C      S=SAMPLE SIZE OF 2-NAPHTHYL-DISULFIDE
C      CT=COLUMN TEMPERATURE OF GAS CHROMATOGRAPH
C      CR=CARRIER GAS FLOW RATE OF GAS CHROMATOGRAPH
C      H=PEAK HEIGHT OF HYDROGEN
C      XM=PEAK HEIGHT OF METHANE
C      E=PEAK HEIGHT OF ETHANE
C      HS = PEAK HEIGHT OF HYDROGEN SULFIDE
C      T=TIME
C      TEMP=TEMPERATURE OF REACTOR
C      DIV=SMALLEST DIVISION IN WEIGHT LOSS CHART
C      DATA=A NUMBER USED TO END THE PROGRAM
10  FORMAT(1H1,7X, 15HPUMPING RATE IS, F8.2,14H C.C. PER MIN.)
11  FORMAT (46H          SAMPLE SIZE OF 2-NAPHTHYL-DISULFIDE IS, F8.4,
15H GRAM)
13  FORMAT(50H          COLUMN TEMPERATURE OF GAS CHROMATOGRAPH IS, F8.2
1,9H DEGREE C)
14  FORMAT(32H          CARRIER GAS FLOW RATE IS,F8.2,14H C.C. PER MIN.)
15  FORMAT(8F10.4)
16  FORMAT(1H ,37X,24HGAS EVOLUTION RATE*10**8)
17  FORMAT(68H          TIME TEMP. WT LOSS HYDROGEN   METHANE   ETHAN
1E   HYDROGEN)
18  FORMAT(1H ,59X,7HSULFIDE)
19  FORMAT(1H0,67H          MIN. DEG.C PERCENT GM-MOLES/(MIN)(GM. STA
1RTING MATERIAL)//)
20  FORMAT (8F10.2)
21  FORMAT(6X,F5.0, 2X,F5.0,2X,F7.2,2X,F7.2,3X, F7.2,3X,F7.2,2X,F8.2)
      READ 15,PR,S,CT,CR
      PRINT 10,PR
      PRINT 11,S

```

Table IV. Program to Calculate Gas Evolution Rate for Each Run (Cont.)

```

PRINT 13,CT
PRINT 14,CR
PRINT 16
PRINT 17
PRINT 18
PRINT 19
40 READ 20,T,TEMP,DIV,H,XM,E,HS,DATA
   PERW=.011079*DIV*100./S
   IF (DATA) 100,50,10
50 Y1=.22260000E-02+.72730967E-01*H+.37570202E-04*H**2. -.11101874
   1E-07*H**3. + .15786179E-11*H**4.
   Y2= -.39420000E-02 + .34423995E+00*XM + .65114690E-03*XM**2.
   1-.70822228E-06*XM**3. + .41790926E-09*XM**4.
   Y3= .87680000E-02 + .48922380E+00*E + .83716414E-02*E**2.
   1-.21358161E-04*E**3. + .21346391E-07*E**4.
   A=16.25*Y1/S
   B=16.25*Y2/S
   C=16.25*Y3/S
   IF (HS-15.22) 60,70,70
60 Y4= .38250000E-03 + .54737646E+01*HS - .10743039E+01*HS**2.
   1+.12023838E+00*HS**3.
   GO TO 80
70 Y4= -.35435833E+02 + .20405309E+02*HS - .72345327E-01*HS**2.
80 D=16.25*Y4/S
   PRINT 21,T,TEMP,PERW, A,B,C,D
   GO TO 40
100 CALL EXIT
   END

```

Table V. General Information of All the Runs Made on 2-Naphthyl Disulfide

Run	Heating Rate °C/min.	Final Temp. °C	Final % Wt. Loss	Remarks
Ex-I	Not uniform	600	56.5	Sampling valve plugged.
Ex-II	Not uniform	615	73	Sampling valve plugged.
Ex-III	1.89	625	71	Sampling valve plugged.
Ex-IV	2.17	645	57.7	Sampling valve plugged.
Ex-V	1.46	600	58.7	Sampling valve plugged.
Ex-VI	-	-	62.3	Temperature recorder trouble.
Ex-VII	2.90	643	60.2	Condensate was found outside reactor, too fast heating.
Ex-VIII	2.50	648	66.6	
Ex-IX	2.16	643	67.1	Carrier gas leaking.
Ex-X	2.32	643	65.1	
Ex-XI	1.40	638	58.2	
Ex-XII	1.76	632	63	Sampling valve plugged.

Table VI. Results of Ex-VIII

PUMPING RATE IS 65.00 C.C. PER MIN.

SAMPLE SIZE OF 2-NAPHTHYL-DISULFIDE IS 0.9440 GRAM

COLUMN TEMPERATURE OF GAS CHROMATOGRAPH IS 119.50 DEGREE C

CARRIER GAS FLOW RATE IS 65.00 C.C. PER MIN.

GAS EVOLUTION RATE\*10\*\*8

TIME MIN.	TEMP. DEG.C	WT LOSS PERCENT	HYDROGEN GM-MOLES/(MIN)(GM. STARTING MATERIAL)	METHANE	ETHANE	HYDROGEN SULFIDE
0.	308.	0.00	0.0	0.0	0.0	0.0
5.	317.	0.00	0.0	0.0	0.0	0.0
10.	325.	0.23	0.0	0.0	0.0	0.0
15.	335.	0.82	6.31	0.0	0.0	629.98
20.	347.	1.76	10.10	0.0	0.0	2330.82
25.	361.	2.46	13.89	0.0	0.0	7823.75
30.	373.	4.11	16.04	0.0	0.0	8445.28
35.	385.	5.87	13.89	0.0	0.0	5094.01
40.	400.	9.39	15.79	0.0	0.0	4332.33
45.	413.	13.38	19.22	0.0	0.0	4939.62
50.	427.	17.02	19.47	0.0	0.0	5001.45
55.	440.	20.54	20.74	0.0	0.0	2212.74
60.	450.	24.65	22.15	0.0	0.0	1386.05
65.	466.	26.17	23.42	0.0	0.0	1063.01
70.	477.	28.75	27.64	0.0	0.0	1000.73
75.	489.	31.10	33.02	0.0	0.0	1095.40
80.	502.	34.62	49.84	0.0	0.0	1233.55
85.	515.	37.56	.....	0.0	0.0	1307.96
90.	527.	41.08	.....	0.0	0.0	1467.93
95.	538.	45.18	.....	0.0	0.0	1063.01
100.	550.	53.63	312.37	35.89	0.0	858.97
105.	562.	54.81	.....	64.61	0.0	492.29
110.	575.	56.33	955.53	187.47	20.28	691.56
115.	585.	59.85	.....	524.81	66.04	1553.70
120.	600.	62.79	854.96	194.05	22.10	346.68
125.	612.	63.96	801.06	220.55	23.93	238.15

Table VII. Results of Ex-X

PUMPING RATE IS 65.00 C.C. PER MIN.  
 SAMPLE SIZE OF 2-NAPHTHYL-DISULFIDE IS 0.9440 GRAM  
 COLUMN TEMPERATURE OF GAS CHROMATOGRAPH IS 119.50 DEGREE C  
 CARRIER GAS FLOW RATE IS 65.00 C.C. PER MIN.  
 GAS EVOLUTION RATE\*10\*\*8

TIME MIN.	TEMP. DEG.C	WT LOSS PERCENT	HYDROGEN GM-MOLES/(MIN)	METHANE (GM.	ETHANE STARTING	HYDROGEN SULFIDE MATERIAL)
0.	320.	0.00	0.03	0.0	0.0	0.0
5.	330.	0.31	2.27	0.0	0.0	116.93
10.	342.	0.52	10.14	0.0	0.0	1593.50
15.	355.	1.05	19.76	0.0	0.0	5091.09
20.	366.	2.72	22.15	0.0	0.0	7486.04
25.	377.	6.28	19.76	0.0	0.0	5945.45
30.	389.	8.90	16.92	0.0	0.0	3010.73
35.	401.	13.61	19.19	0.0	0.0	2189.45
40.	413.	16.23	23.75	0.0	0.0	2361.93
45.	425.	22.52	24.89	0.0	0.0	4186.20
50.	437.	26.71	23.41	0.0	0.0	1824.19
55.	450.	30.27	22.95	0.0	0.0	1309.88
60.	463.	32.36	26.03	0.0	0.0	720.63
65.	475.	34.98	35.45	0.0	0.0	562.15
70.	485.	37.07	44.47	0.0	0.0	562.15
75.	495.	38.96	62.25	0.0	0.0	766.48
80.	510.	42.52	87.00	0.0	0.0	948.56
85.	521.	44.51	125.98	0.0	0.0	1167.14
90.	533.	47.13	195.46	7.89	0.0	977.46
95.	544.	49.43	281.44	21.25	0.0	977.46
100.	556.	51.53	437.31	49.97	0.0	677.36
105.	567.	53.10	683.10	109.61	7.78	413.47
110.	576.	55.30	1274.53	221.95	23.83	389.44
115.	589.	59.17	1927.30	331.89	19.72	378.06
120.	598.	61.37	795.31	64.81	0.0	0.0
125.	612.	62.31	844.41	112.45	0.0	0.0
130.	623.	62.84	890.77	143.99	0.0	0.0
135.	635.	63.46	1086.14	174.33	0.0	0.0
140.	643.	63.88	1233.54	184.94	0.0	0.0

Table VIII. Results of Ex-XI

PUMPING RATE IS 65.00 C.C. PER MIN.  
 SAMPLE SIZE OF 2-NAPHTHYL-DISULFIDE IS 0.9440 GRAM  
 COLUMN TEMPERATURE OF GAS CHROMATOGRAPH IS 119.50 DEGREE C  
 CARRIER GAS FLOW RATE IS 65.00 C.C. PER MIN.

TIME MIN.	TEMP. DEG.C	WT LOSS PERCENT	GAS EVOLUTION RATE*10**8			
			HYDROGEN GM-MOLES/(MIN)	METHANE (GM.	ETHANE STARTING	HYDROGEN SULFIDE MATERIAL)
0.	322.	0.00	8.80	0.0	0.0	77.50
5.	329.	0.00	8.80	0.0	0.0	212.63
10.	335.	0.00	11.19	0.0	0.0	1302.71
15.	342.	0.00	15.73	0.0	0.0	4220.95
20.	351.	0.23	20.15	0.0	0.0	4827.25
25.	359.	0.82	21.42	0.0	0.0	4981.40
30.	367.	2.81	15.09	0.0	0.0	2443.78
35.	375.	4.21	57.44	0.0	0.0	.....
40.	384.	5.84	.....	0.0	0.0	.....
45.	392.	7.25	.....	0.0	0.0	.....
50.	400.	8.77	57.44	0.0	0.0	1547.47
55.	407.	9.70	40.59	0.0	0.0	7132.37
60.	415.	11.69	47.05	0.0	0.0	7016.24
65.	423.	14.38	63.97	0.0	0.0	13716.12
70.	430.	16.13	53.53	0.0	0.0	7276.96
75.	438.	18.00	53.40	0.0	0.0	6311.16
80.	446.	19.52	52.49	0.0	0.0	5134.93
85.	454.	21.04	46.27	0.0	0.0	3129.45
90.	462.	22.44	37.12	0.0	0.0	4672.48
95.	469.	23.73	27.14	0.0	0.0	855.52
100.	470.	25.01	33.15	0.0	0.0	397.95
105.	480.	26.89	54.70	0.0	0.0	1265.20
110.	495.	28.64	90.42	0.0	0.0	2770.82
115.	504.	30.04	124.15	0.0	0.0	2770.82
120.	512.	31.21	83.76	0.0	0.0	461.50
125.	519.	35.30	186.73	5.85	0.0	2321.47
130.	527.	40.44	290.09	13.57	0.0	.....
135.	535.	41.50	226.83	8.81	0.0	909.68


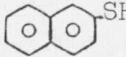
Table VIII. Results of Ex-XI (Cont.)

140.	541.	43.02	401.95	29.72	0.0	1341.14
145.	548.	44.65	524.00	50.29	0.0	855.52
150.	555.	45.59	833.56	125.51	13.05	996.71
155.	561.	46.41	920.50	152.34	19.29	386.60
160.	568.	47.34	1614.61	274.78	31.25	505.50
165.	572.	48.28	1874.07	206.43	28.45	537.49
170.	580.	48.86	1916.24	384.60	22.01	461.50
175.	585.	49.91	1245.26	257.16	4.38	191.23
180.	591.	51.32	851.53	216.35	0.0	42.58
185.	597.	52.02	665.07	1056.59	0.0	0.0
190.	604.	52.60	398.81	63.12	0.0	0.0
195.	611.	53.19	602.16	74.19	0.0	0.0
200.	620.	53.77	692.63	.....	0.0	0.0
205.	630.	54.35	960.92	154.92	0.0	0.0
210.	638.	54.71	1169.93	188.68	0.0	0.0

Table IX. Stoichiometric Coefficients of Gaseous Products for One Mole 2-Naphthyl Disulfide

Run	Heating Rate <u>°C/min.</u>	Final Temp. <u>°C</u>	H <sub>2</sub> <u>mole/mole</u>	CH <sub>4</sub> <u>mole/mole</u>	C <sub>2</sub> H <sub>6</sub> <u>mole/mole</u>	H <sub>2</sub> S <u>mole/mole</u>
Ex-VIII	2.50	612	0.0827	0.0192	0.0016	0.801
Ex-X	2.32	612	0.102	0.0136	0.0016	0.722
Ex-XI	1.40	612	0.196	0.0316	0.0016	1.32

Table X. Qualitative Properties of Condensate from Pyrolysis of 2-Naphthyl Disulfide

Sample No.	State at Room Temperature	Remarks
1	White crystal	 Naphthalene (positive identification).
2	White powder	 2-Naphthalenethiol (positive identification).
3	Red powder	-CH <sub>3</sub> , -CH <sub>2</sub> -, possibly naphthalene system with aliphatic substitution.
4	Yellow green liquid	-CH <sub>3</sub> , -CH <sub>2</sub> -, -OH, possibly naphthalene system with aliphatic substitution.
5	Yellow green liquid	-CH <sub>3</sub> , -CH <sub>2</sub> -, possibly naphthalene system with aliphatic substitution.
6	Pale green liquid	-CH <sub>3</sub> , -CH <sub>2</sub> -, possibly naphthalene system with aliphatic substitution.
7	Yellow green crystal	-CH <sub>3</sub> , -CH <sub>2</sub> -, possibly naphthalene system with aliphatic substitution, MW=332, exp. formula=C <sub>23</sub> H <sub>17</sub> S.
8	Yellow solid	-CH <sub>3</sub> , -CH <sub>2</sub> -, -OH, possibly a naphthalene system with a rather long aliphatic substitution, MW=396.5, exp. formula = C <sub>26</sub> H <sub>19</sub> S <sub>2</sub> .
9	Yellow solid	-CH <sub>3</sub> , -CH <sub>2</sub> -, possibly naphthalene system with aliphatic substitution, MW=317, exp. formula=C <sub>21</sub> H <sub>13</sub> S.











































