

NAPHTHALENE DESULFURIZATION WITH SODIUM

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Improving the quality of coke oven naphthalene by treating the product with sodium to remove sulfur compounds and other impurities is of commercial importance to phthalic anhydride producers and other consumers of naphthalene. The treatment of naphthalene with sodium is disclosed in a patent issued in 1930 to G. Schroeter (U. S. Patent 1,763,410). Sodium has been used commercially to remove sulfur compounds, such as thionaphthenes, for a number of years. The available data, however, are inadequate to serve as the basis for designing a continuous process for large-scale operation. This study was undertaken to develop data on reaction rates and other factors essential in preparing preliminary design for a continuous process.

AMOUNT OF SODIUM REQUIRED FOR DESULFURIZATION

In the initial series of tests, crude coke oven naphthalene (74°C melting point) was treated with different amounts of sodium to determine the amount required to achieve essentially complete desulfurization under batch conditions. A 100 g. sample of the naphthalene was added to a 500-ml. round-bottom flask equipped with a heating mantle and reflux condenser. After the naphthalene had reached a temperature of about 210°C, the sodium was added. The mixture was maintained at the reflux temperature of about 217°C. during the reaction period. The contents were then rapidly distilled and the sodium-treated naphthalene was analyzed for sulfur using the Parr bomb method.

The results are given in Table I. In the first four experiments, the sodium used was in dispersion form; in the last three tests, the sodium was in 1/8-in. to 1/4-in. cubes. The results show that 2% by weight of sodium added as a dispersion is very effective in reducing the sulfur. The sulfur is reduced from 8000 ppm. to about 70 ppm. in 30 min. In 60 min., it is reduced to about 5 ppm. The poor results obtained with solid sodium can be attributed to the small surface area of sodium in direct contact with the naphthalene.

Additional tests were made to determine amounts of sodium required to desulfurize higher purity 78°C. naphthalene. Results obtained with 1% and 2% by weight of sodium as a dispersion are shown graphically in Figure 2. These tests were conducted at 187°C. as compared with the reflux temperature of 217°C. in the earlier experiments. The addition of 1% sodium, based on weight of crude naphthalene, reduces the sulfur content from 5000 ppm. to approximately 160 ppm. in 70 min. This is equivalent to removing 98.6% of the sulfur. The reduction in sulfur, as expected, was greater with 2% by weight of sodium.

INFLUENCE OF SODIUM PARTICLE SIZE ON DESULFURIZATION

Additional tests were made to obtain more data on the influence of the particle size of sodium. Crude naphthalene melting over the range of 74° - 78°C. serves as an ideal medium for dispersing sodium. The impurities or foreign components function as very effective dispersing agents. Dispersions containing 50% sodium/50% naphthalene were prepared by subjecting the mixture to high shear agitation with the temperature maintained at 110° - 120°C. The particle size was regulated by using different proportions of purified and crude naphthalene. Apparatus illustrated in Figure 1 was used for these tests. The samples were taken at selected intervals by applying a vacuum to withdraw the vapors from the reaction flask. The vapors were condensed in the sample bottle shown in the flask to the left.

The marked effect of the sodium particle size is illustrated by the data plotted in Figure 3. The reaction proceeds very rapidly with the 20-micron sodium dispersion. For example, the sulfur is reduced to 250 ppm. in 6 min. This is equivalent to removing 99.6% of the sulfur. A reaction period of 125 min., however, is required with the 150-micron sodium dispersion to reduce the sulfur to the same level.

CONTINUOUS DESULFURIZATION WITH OVERFLOW TYPE REACTOR

Data derived from batch-type experiments and reaction rate studies indicated that the sulfur should be reduced to a low concentration with a continuous feed, continuous overflow reactor having an average hold-up time of 3 hr. A series of tests was made by continuously feeding crude naphthalene and 2% by weight of sodium (added as a 50% dispersion in naphthalene) to a well-agitated reactor having an average hold-up time of 3 hr. A resin kettle of 1500 ml. capacity, of the type previously described in Figure 1, was used for this series of tests. The crude 74°C. naphthalene and the 50% sodium dispersion were fed into the reactor by gravity from graduated cylinders. Samples of the overflow product were collected at intervals and analyzed for sulfur.

The results given in Table II show that very effective desulfurization can be obtained with this type of continuous system.

CONCENTRATING THE RESIDUE FROM THE SODIUM-TREATED NAPHTHALENE

The sodium-treated naphthalene contains about 4% - 8% residue and high boiling fractions depending on the degree of purity of the crude naphthalene. Substantially all of the pure naphthalene content of the crude must be recovered for economic reasons. However, no data have been available on the heat transfer and physical characteristics of the mixture containing a relatively high percentage of residue.

The natural circulation evaporator used to boil off naphthalene from the mixture is shown in Figure 4. The rapid circulation is accomplished by applying the required heat in the exchanger indicated by (x). Naphthalene vapors pass overhead and are recovered from the condenser (y) shown on the left. The unit was operated until the mixture in the reboiler contained about 75% residue and 25% naphthalene. The heat transfer conditions in the heat exchanger were good under these conditions of high residue operation. With a properly designed, forced circulation unit, substantially all of the naphthalene could be recovered.

CHARACTERISTICS OF THE SLUDGE

All of the naphthalene from the 75% residue/25% naphthalene mixture obtained from the natural circulation reboiler just described was recovered by further evaporation in a distillation flask. The viscosity characteristics of the sludge after removing substantially all of the naphthalene are shown in Figure 5. The sludge upon cooling is very fluid at temperatures above 100°C. but the viscosity increases rapidly below this value. At room temperature, it may be described as semirigid in consistency.

COMMERCIAL EQUIPMENT FOR DESULFURIZATION

A wide variety of types of reactors for desulfurizing naphthalene can probably be considered in view of the rapid desulfurization rates achieved using fine particle size sodium dispersions. For example, the rate studies indicate that the hold-up time provided in a distillation column may, in some cases, be adequate. This presentation, however, is restricted to an evaporator type of reaction system. The major steps in the process are listed in Table III. The first step consists of preparing a 50% dispersion of sodium in crude naphthalene. The dispersion is mixed with the crude naphthalene feed which is then continuously fed to a desulfurization reaction vessel. High residue bottoms from this reactor are pumped to a second evaporator to recover the remaining naphthalene. The residue is discharged periodically from this vessel. The three major steps of the process are:

(A) Dispersing Liquid Sodium in Naphthalene

The basic equipment required for this step in the process is illustrated in Figure 6. The high-shear dispersion unit is charged with approximately equal parts of liquid sodium and crude naphthalene. Fine particle size dispersions are readily prepared by agitating the contents of the vessel for periods of 5-10 min. The dispersion is then discharged to a holding tank. A continuous feed from this tank is combined with the main naphthalene feed stream and introduced into the evaporator or desulfurization vessel.

(B) Evaporator-Type Desulfurization Reactor

The second step of the process, illustrated in Figure 7, is essentially a continuous flow system. The incoming feed (A) and the vaporized naphthalene (B) plus the side stream (C) going to the second evaporator are regulated to maintain approximately a 50% residue/50% naphthalene mixture in the reactor. The vessel is designed to provide an average product hold-up time of 3 hr. Through-put at this hold-up time with a 2500 gal. vessel is about 30 million lb./yr. of naphthalene, assuming 300 operating days. The mixture is pumped through the external heat exchanger at a rate of about 500 gal./min. which provides extremely turbulent mixing. Volume turnover in the reactor is approximately 18 times/hr. The bottoms from the reactor are pumped to a second smaller evaporator to recover the balance of the naphthalene. Assuming 5% residue including high boilers in the sodium-treated naphthalene, the bottoms flow rate is approximately one-tenth the incoming feed rate.

(C) Final Naphthalene Recovery and Residue Separation

The second evaporator shown in Figure 8 strips essentially all of the remaining naphthalene from the 50% naphthalene/50% residue mixture. It is operated on a semicontinuous basis. When the residue level in the evaporator approaches the capacity of the vessel, the feed from the first evaporator is shut off to permit discharging the vessel. With an 800-gal. capacity evaporator and a through-put rate of 30 million lb./yr., clean out will be required at approximately 8-hr. intervals.

The residue is fluid at the operating temperature and can be discharged by vacuum to a portable tank for conveyance to an incinerator. If the residue is transferred to a slag pile or other area for disposal, it is advisable to destroy small amounts of sodium in the mixture prior to discharging the residue from this evaporator. Although massive amounts of sodium will, under certain conditions, react rather violently with water, commercial experience has demonstrated that finely divided sodium mixed with inert material will react safely with superheated or dry steam in the presence of nitrogen and no hazards are involved. The reaction of sodium with steam to form caustic soda is completed in a matter of minutes.

CONCLUSIONS

Rapid reaction of the fine particle size sodium dispersions with the sulfur compounds present in crude coke oven grade naphthalene have been demonstrated. Basic data have been translated to preliminary design for a continuous process for desulfurizing coke oven grade naphthalene.

ACKNOWLEDGEMENT

We are indebted to H. F. Porter of Du Pont Engineering Department for his assistance in developing some of the basic design features of the process.

REFERENCE

1. Schroeter, G. (to Newport Manufacturing Co.) U. S. Patent 1,763,410 (June 10, 1930).

TABLE I
DESULFURIZATION OF NAPHTHALENE

<u>Run No.</u>	<u>Type Sodium Added</u>	<u>% Sodium Added</u>	<u>Treating Time, Min.</u>	<u>PPM. Sulfur After Treatment*</u>
1	Dispersion	2	30	50-70
2	Dispersion	2	60	5
3	Dispersion	3	30	10
4	Dispersion	4	30	Non-detectable
5	Solid	2	60	4900
6	Solid	3	60	4300
7	Solid	4	60	3900

* Sulfur Content of 74°-75°C Naphthalene Before Treatment-8000 ppm.

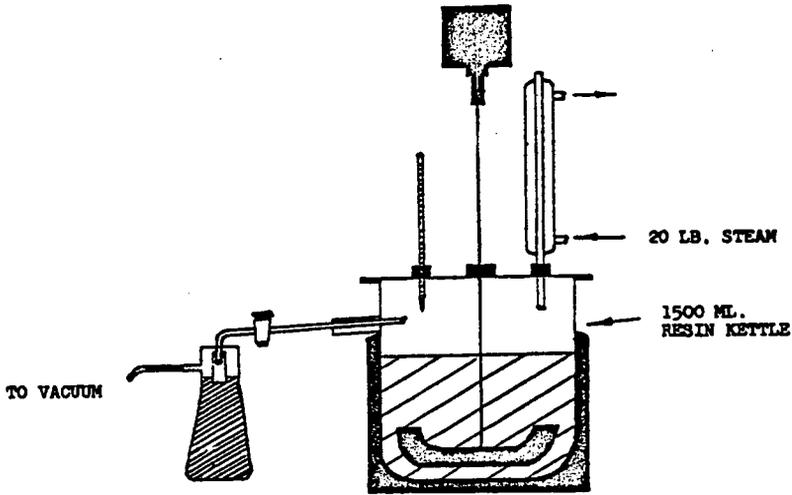
TABLE II
DESULFURIZATION WITH 3-HOUR AVERAGE HOLD UP TIME

<u>Reactor Temperature</u>	<u>Sulfur Content, ppm.</u>		<u>% Sulfur Removed</u>
	<u>Feed</u>	<u>Product</u>	
190°-200°C	3200-6200	30	99-99.8

TABLE III
PROCESSING STEPS IN DESULFURIZING

1. Dispersing the Liquid Sodium
2. Desulfurizing in an Evaporator Vessel
3. Recovery of Remaining Naphthalene
 - (A) Residue Separation

FIGURE 1



DESULFURIZATION APPARATUS

FIGURE 2

DESULFURIZATION RATES

78°C NAPHTHALENE
@ 187°C, 350 mm Hg

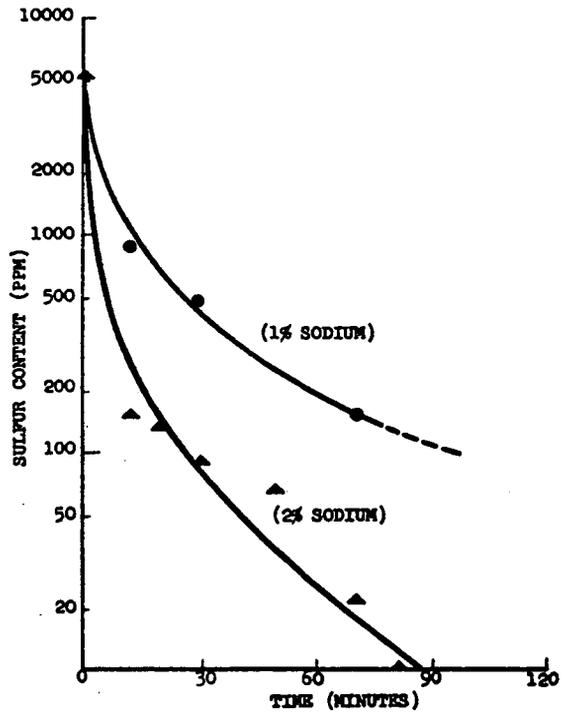


FIGURE 3

DESULFURIZATION RATES
WITH VARYING
SODIUM PARTICLE SIZE

78° NAPHTHALENE
TEMPERATURE 217°

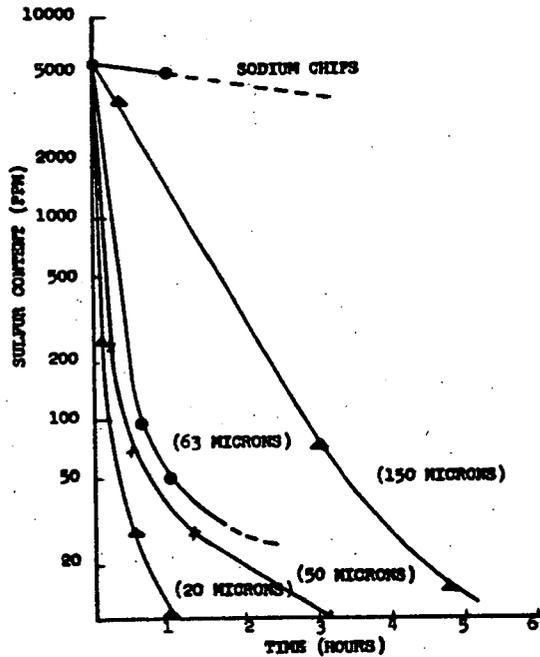
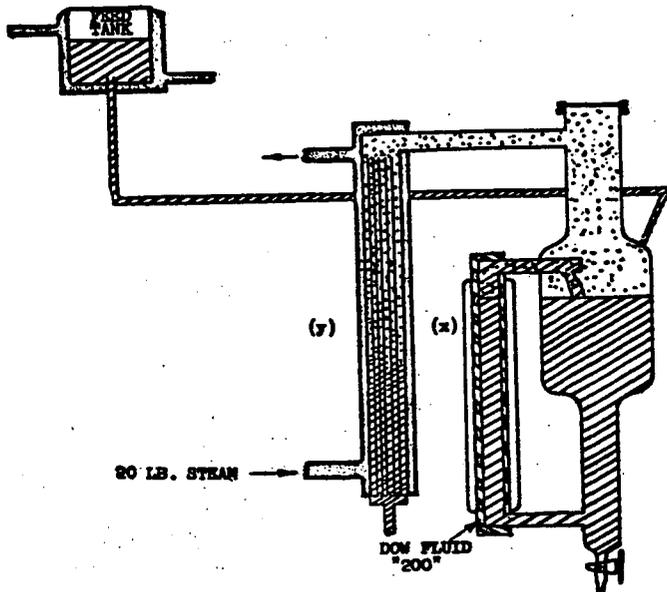


FIGURE 4



NATURAL CIRCULATION REBOILER

FIGURE 5

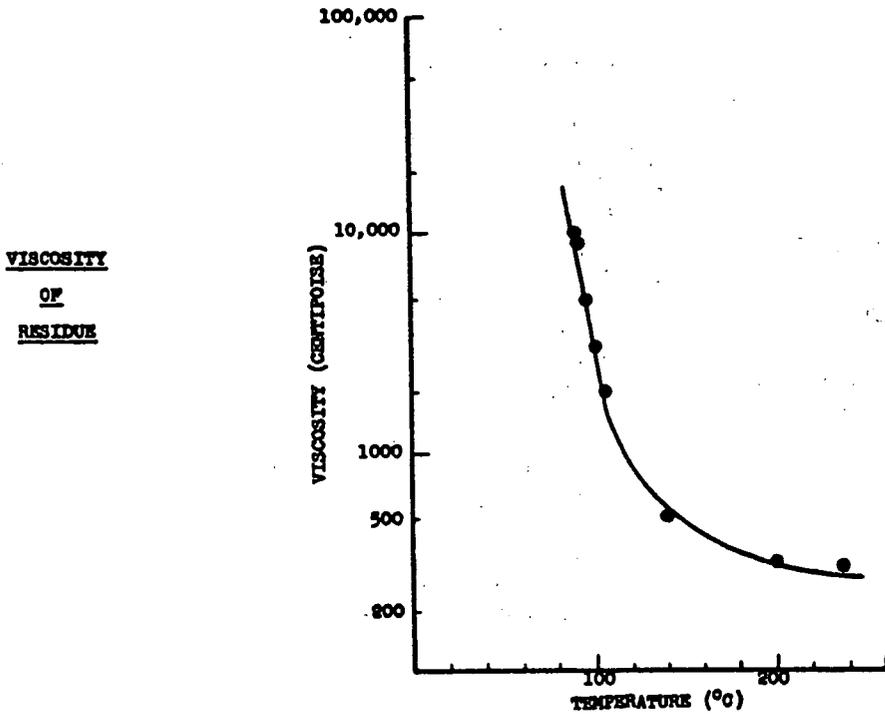
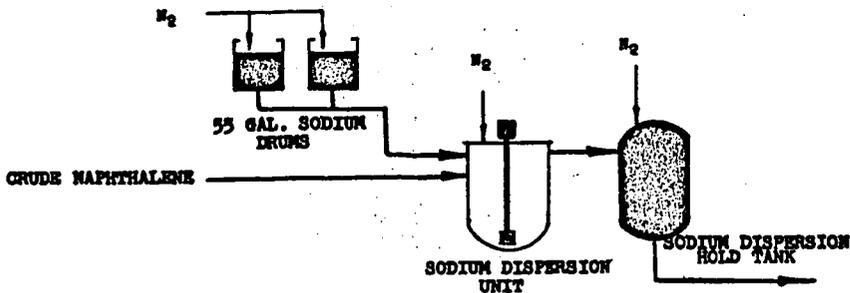


FIGURE 6



DISPERSING LIQUID SODIUM

FIGURE 7

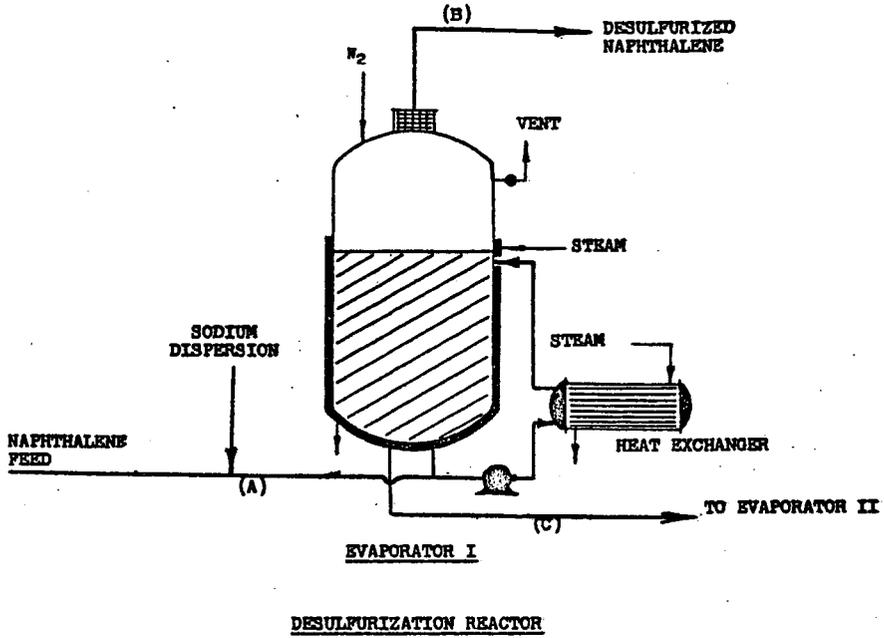


FIGURE 8

