STUDIES ON THE PREPARATION OF ALCOHOLS FROM PETROLEUM ACID SLUDGE

by

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INTRODUCTION

A waste product, acid sludge, results from the treatment of petroleum products with sulphuric acid. Since the beginning of the petroleum refining industry, sulphuric acid has been used as a treating agent to improve color, odor and burning characteristics, and to lower sulphur and gum content of the petroleum products. Gruse (1) mentions that Benjamin Silliman, as early as 1855, advocated its use for such purposes. While various other treating methods have been put into commercial operation in the last ten years, the sulphuric acid method of treating petroleum naphtha continues to be the most widely used.

Some refineries use their acid sludge as a fuel, burning it under the boilers; but in most plants it is usually discarded. Rather (2) points out that acid sludge disposal is still an unsolved problem in refining plants. Experimentation on acid sludge, recorded in the literature, is divided in general between two heads: (a) recovery of the sulphuric acid therefrom and (b) preparation of the sludge for use as a fuel.

This investigation has been limited to a study of the possibilities of obtaining the various alcohols from the sulphuric acid sludge. Three separate methods of approach were used. Experiments were carried out (a) in an attempt to recover alcohols from acid sludge furnished by a refinery, (b) in an attempt to prepare alcohols by cracking the acid sludge from a refinery with subsequent absorption of the gases therefrom in sulphuric acid, followed by hydroly- and (c) attempting to prepare alcohols from acid sludge made in the laboratory from pressure distillate.

Acid sludge, resulting from the treatment of pressure distillate with sulphuric acid in the normal factory operation, was obtained from the Derby refinery at Wichita, Kansas. The crude oil used in the refinery came from the McPherson field in Kansas.

LITERATURE

An investigation of the literature was made to determine what work, if any, had been done on the preparation or recovery of alcohols from acid sludge.

Mann (3) succeeded in preparing propyl alcohol from refinery gases, after a large number of futile attempts, by a method based upon the research of Ellis (4). His method of preparation is used by the Standard Oil Company of New Jersey for the production of commercial propyl alcohol.

The method of manufacture consists of first removing the hydrogen sulphide from the refinery gases by suitable absorbents in towers. The olefins are then converted to alkyl sulphates continuously in towers or by agitated batch methods. This is followed by settling to remove oils. The acid solution is then hydrolyzed by mixing with several volumes of water. The alcohols formed are then distilled and rectified. Finally, the acid is reconcentrated from a density of 1.4 to 1.8. This is also mentioned by Grant and Johns (5).

Clough and Johns (6) state that isopropyl, secondary butyl, amyl, hexyl, heptyl and octyl alcohols are being prepared from the olefins formed during the pyrolytic distillation of petroleum fractions on a commercial scale by the Standard Oil Company of New Jersey. All of the alcohols made thus far in a pure state have been normal secondary alcohols--that is alcohols containing the hydroxyl group on the second carbon atom of a straight chain hydrocarbon.

Reed and Prisley (7) state that a commercial grade of amylene is very readilly dissolved when shaken with fifty per cent sulphuric acid in a salt-ice bath. They draw attention to the ease with which trimethyl-ethylene may be converted into tertiary amyl alcohol by the preliminary formation of amyl sulphuric acid and subsequent neutralization. They also state that the absorption of gaseous isobutylene by dilute and concentrated sulphuric acid is very slow at low temperatures; and, while quite rapid at higher temperatures, leads mainly to polymerization products.

Beard (8) maintains that unsaturated hydrocarbons are exceedingly reactive with sulphuric acid and undergo various combinations of the following conversions. The sulphuric acid molecules may add to the double bonds of the olefins with the formation of either neutral or acid esters of sulphuric acid. A considerable amount of polymerization of the olefins may occur. If dilute sulphuric acid is used, the water may combine with the olefins to form alcohols. Inasmuch as sulphuric acid is a strong oxidising agent, the olefins may be actually oxidised.

He also points out that the neutral esters are not removed by aqueous alkalies, and remain dissolved in the treated oil; while the acid esters are removed by aqueous alkalies. He further claims that the larger the relative amount of sulphuric acid used, the smaller is the proportion of neutral esters which remain in the treated oil. Increasing the temperature of treating increases the oxidation, polymerization and sulphonation of the treated oil, according to Beard (8).

According to Trusty (9) of the Louisiana Oil Refining Corporation, di-alkyl esters are soluble in the oil and are not removed by the water wash nor by caustic neutralization.

The most comprehensive recorded research on the action of sulphuric acid on olefins is that done by Brooks and Humphrey (10). They state that the principal results of such action are polymerization of the olefins, the formation of secondary and tertiary alcohols and mono- and dialkyl esters of sulphuric acid. Relative importance of these reactions vary widely with the concentration of acid, molecular weight of olefins and time. The tendency to form alkyl sulphuric esters and alcohols decreases with increasing molecular weight, this result appearing to be maximum with the amylenes and hexenes, according to Brooks and Humphrey (10).

The general procedure used by these men consisted in the preparation of the solution of the pure olefin in the cold acid, addition of ice, separation of the pale, yellow liquid immediately precipitated and extraction of the alcohols therefrom. They conclude that the water which is present in the reaction mixture at low temperatures, and not the water in the subsequently diluted solution, enters into the reaction forming alcohols. They found that the decylenes were almost quantitatively polymerized by sulphuric acid.

Messer (11), however, in work on olefins of sixteen and more carbon atoms was able to separate calcium salts of the acid esters. These were hydrolyzed to give small yields of alcohols, varying in different cases.

Winkler and Pilat (12) state that the optimum temperatures for the formation of olefinic gases which can be converted into secondary alcohols on cracking gas oil in the vapor phase lie between six hundred and six hundred seventy degrees centigrade. They also state that in this temperature interval a maximum yield of five and one-half per cent of such olefins was obtained, figuring on the basis of the gas oil as a starting material.

Brooks (13) points out that in the formation of pintsch gas that the temperature of approximately six hundred degrees centigrade forms the maximum quantity of olefins; while in the Hall cracking unit, which operates at a pressure of seventy-one pounds per square inch, the maximum yield of olefins is at six hundred fifty degrees centigrade. He states, however, that the yields did not fall off appreciably even in going to eight hundred fifty degrees centigrade.

According to Brooks (13) as early as 1828, Hennell (14) pointed out the relationship between ethylene, ethyl hydrogen sulphate, ethyl ether and ethyl alcohol. He stated, "Thus ether may be formed from alcohol, and alcohol from ether at pleasure by throwing the hydrocarbon of these bodies into that peculiar state which it assumes when combined with sulphuric acid. We may even proceed beyond this and form either alcohol or ether, using olefiant gas, which by combining with sulphuric acid, forms sulfovinic acid, and the acid so produced forms either ether or alcohol according to circumstances which are under perfect control."

Brooks (13) points out that as early as 1855 Berthelot (15) absorbed ethylene in concentrated sulphuric acid, diluted the acid mixture with five to six volumes of water and distilled, thus obtaining a very good yield of ethanol. Berthelot also prepared a mixture of hydrocarbon polymers and iso-propyl alcohol by absorption of propylene in concentrated sulphuric acid at eighteen degrees centigrade and subsequent hydrolysis.

Perhaps the most recent and thorough investigation of the formation of butyl alcohol from the butylenes was carried out in Russia by Pigulevskii and Nazarov (16). The following observations were made in their work. During a twelve hour treating period, changing from sixty-five per cent sulphuric acid to eighty per cent acid increased the yield of polymers from seven per cent to seventy-eight per cent. Alcohol formation reached a maximum at seventy per cent acid with formation of a thirty-two per cent yield.

They found that by shortening the treating conditions from twelve to five hours that both the yield of polymers and alcohols fell off, the best yield of alcohol dropping to twenty-eight per cent. By use of vigorous agitation the maximum yield of alcohol, forty-two per cent, was obtained with an acid strength of sixty-five per cent.

When they held the temperature at zero degrees centigrade, the yield of polymers was cut materially; but the maximum alcohol yield obtained was only thirty-five per cent. By dropping the temperature to minus twenty degrees centigrade, polymerization was cut to forty per cent at a concentration of eighty per cent acid, at which concentration the butyl alcohol yield was maximum, twenty- eight per cent.

According to Curme and Reid (17), if a gaseous mixture of olefins is first treated with sulphuric acid under conditions that absorb the higher olefins, permitting the propylene and ethylene to pass unabsorbed; by a second treatment the propylene only may be absorbed in strong sulphuric acid, and a solution of isopropyl sulphates in sulphuric acid may be built up.

Gerr, Pipik and Mezhebovskaya (18) have recently done work on the preparation of ethanol from ethylene selectively absorbed from petroleum gases by charcoal.

Ethyl, propyl and tertiary butyl alcohols are infinitely soluble in cold water (19). The solubility of the higher alcohols decreases rapidly as one progresses up the homologous series, amyl alcohol being two and one-half parts soluble in a hundred parts of cold water.

The reaction between ethylene and sulphuric acid to form ethyl hydrogen sulphate may be followed, according to Chamberlain (20), by one of three subsequent reactions: (a) The heavilly diluted solution may be distilled forming ethanol. (b) The undiluted solution may be heated to between one hundred sixty and one hundred ninety degrees centigrade with the liberation of the ethylene. (c) The temperature of one hundred forty degrees centigrade is unique in that ethyl hydrogen sulphate may react with any alcohol present to form the diethyl ether.

One might suppose that these are general reactions, holding for all of the olefins; however, it appears that the probability of their occurring is much less for the other olefins. Apparently, the conditions favoring the formation of the alkyl hydrogen sulphates from higher olefins are very limited.

According to Brooks and Humphrey (10), the alkyl hydrogen sulphates are not necessarilly formed as intermediate products in the formation of the higher alcohols from olefins by use of sulphuric acid.

Material found in the literature may be summarized briefly as follows. Ethylene may be easilly converted into ethanol with a fair yield, by proper control of conditions. With very limited conditions propylene may be converted to secondary or tertiary butanols, with even greater difficulty; the highest recorded yield, observed in the literature, being forty-two per cent.

It appears that the difficulty of preparing alcohols by treatment of olefins with sulphuric acid increases with the molecular weight of the olefins used. It seems that polymerization of the olefins increases, becoming almost quantitative for the decylenes. Apparently, polymerization losses increase with increasing treating temperature, time of contact, agitation and strength of acid used.

Cracking temperatures ranging from six hundred to eight hundred fifty degrees centigrade seem to give the best yields of gaseous olefins.

EXPERIMENTAL

The experiments performed may be classified into three groups: (a) Hydrolysis of the acid sludge from the refinery. (b) Preparation of acid sludge from pressure distillate and subsequent experimentation with the treated distillate and the sludge formed. (c) Deacidification of the refinery acid sludge, cracking, absorption of the gaseous olefins in sulphuric acid and hydrolysis.

The first two phases of the work were carried on simultaneously, while the third group of experiments was begun after the first two were completed.

Raw Material. A sample of the sludge was obtained from each of the settling tanks of the treating department in the Derby refinery at Wichita, Kansas. That from the first settling tank was a black, viscous, tarry material with a specific gravity of approximately 1.3333 at twenty-three degrees centigrade. Titration showed an acid normality equal to 13.16. The sample from the second settling tank was a dark brown, relatively fluid material with a specific gravity of approximately .8510 at twenty-one degrees centigrade. Titration showed an acid normality equal to .0633. The odor of both samples was almost unbearable.

Group I Experiments

Experiment 1. Two hundred cubic centimeters of the sludge from the second settling tank was steam distilled for an hour to give a distillate fraction designated as A. Then one and a half grams of calcium carbonate were added and distillation was continued to give a fraction designated as

B. Because the residue was acid, a decided excess of calcium carbonate was added; and the distillation was continued into fraction B. From the titration data, .633 grams of calcium carbonate should have been sufficient to neutralize the sludge. The fact that much more was necessary indicated that a reaction had occurred, liberating hydrogen-ions.

The aqueous layers of both fraction A and fraction B gave affirmative tests for amyl alcohol using Allen's test (21). The test from fraction A was much stronger than that from fraction B. Also, the water solution, remaining in the distillation vessel, gave an affirmative test. An ether extract of fraction A gave a very strong positive test. The ether, used, gave a negative test for amyl alcohol.

The water solution from the distillation chamber gave a positive alcohol test with Rosenthaler's method (22) without resort to the use of heat. The aqueous layer from both fraction A and fraction B tested positively for alcohols by use of Rosenthaler's method.

An attempt was made to salt out with potassium carbonate the alcohols detected in the aqueous layer of fraction B. A very small amount of oil separated. This gave a positive test for alcohol by Rosenthaler's method (22). However, this material, in all probability, was not composed entirely of alcohols.

Experiment 2. Two hundred cubic centimeters of sludge from the first settling tank were diluted with one hundred cubic centimeters of water and steam distilled for ninety minutes to give the fraction designated as C. Two hundred grams of solid sodium hydroxide were cautiously added to the residue. Because of the large amount of heat evolved, this was a long procedure. After neutralization, the reaction mixture was steam distilled, giving the fraction designated as D.

The result of Allen's test (21) for amyl alcohol was positive on the aqueous layers, both from fraction C and from fraction D. However, the test was not as strong as that from the aqueous layer of fraction A. The water solution in the distillation vessel gave an affirmative test for amyl alcohol using Allen's test (21).

The aqueous solution, remaining in the distillation chamber, gave a positive alcohol test using Rosenthaler's method (22). Likewise, the aqueous layers from fractions C and D gave positive tests but not as strong as the tests from fractions A and B.

An attempt was made to salt out with potassium carbonate the alcohols detected in the aqueous layers of fractions C and D, but without success.

Experiment 3. Fifty grams of sodium hydroxide, one hundred cubic centimeters of water and seven hundred cubic centimeters of sludge from the second settling tank were refluxed in a two-liter round-bottom flask for twenty-four hours. The reaction mixture was steam distilled until two hundred sixty cubic centimeters of water and oil were collected. At this point the material in the distilling flask was noticed to be highly acid. Consequently, the distillation was discontinued. The distillate gave a weak alcohol test with Rosenthaler's method (22).

The material remaining in the round-bottom flask was neutralized with caustic soda and distilled with superheated steam. With Rosenthaler's test (22) the first twenty-five cubic centimeters distilled showed the presence of alcohols. The second twenty-five cubic centimeters showed only a slight trace of red coloration. The test on the third twenty-five cubic centimeters was negative.

Experiment 4. A quantity of neutralized sludge from the first settling tank was refluxed, but the material turned to coke, after several hours.

Experiment 5. A representative sample of the sludges from the refinery was diluted with ice from three and a half liters to five liters. The tar was separated by decantation to prevent foaming. Thirty-seven hundred cubic centimeters of the material remained. This was steam distilled, using superheated steam. It required about six hours to obtain one hundred eight cubic centimeters of oily layer, which were dried by contact with anhydrous sodium carbonate over night.

The dried product was refluxed for four and a half hours under a return condenser with one hundred eighty cubic centimeters of dry ether and a flattened piece of metallic sodium. The small amount of dark brown solid that formed was filtered in a buchner funnel with suction and washed with dry ether. A very large amount of dry ether was necessary. Even then, a pale yellow brown color remained. This material weighed .2327 grams.

This solid was placed in a twenty-five-cubic-centimeter burrette. A few cubic centimeters of water, enough sodium chloride to saturate, and enough hydrochloric acid to neutralize were added to the burrette. Hydrolysis occurred readily. Two-tenths of a cubic centimeter of pale yellow, oily liquid rose to the surface. This small amount of material gave a positive test for alcohol with Rosenthaler's method (22). A test for phenol by use of ferric chloride was negative.

Group II Experiments

The unsaturated compounds, present in the pressure distillate, apparently are the compounds from which the alcohols of the sludge are derived. Therefore, it was thought to be advisable to determine the percentage of unsaturation in the pressure distillate. This was done, using the method of Morrell and Levine (23). They maintain this method to be in absolute error by less than two per cent. A result of 26.53 per cent by volume of unsaturation was obtained.

Experiment 6. Four hundred cubic centimeters of cold ninety-one per cent sulphuric acid were slowly added with agitation to sixteen hundred cubic centimeters of pressure distillate, keeping the temperature below five degrees centigrade by use of a salt-ice bath. Agitation was continued for thirty minutes after all the acid was added. The sludge was allowed to settle to the bottom of the container. The treated pressure distillate was siphoned from the seven hundred seventy cubic centimeters of sludge that had been formed. Fourteen hundred thirty grams of ice were added to the sludge. This mixture was placed in a five-liter round-bottom flask and refluxed under a return condenser at a temperature just below forty-three degrees centigrade for a period of seventeen hours. This was separated by means of a separatory funnel into an oily layer and an orange-colored aqueous layer designated as X.

The oily layer was distilled through a fractionating head. From one hundred seven to two hundred five degrees centigrade, seven cuts were made of approximately seven cubic centimeters each. The neutralized cuts were treated with benzoyl chloride in an attempt to change any alcohols present into the corresponding benzoyl esters. The fraction that distilled between one hundred twenty-eight and one hundred forty-six degrees centigrade and that between one hundred ninety-five and two hundred five degrees centigrade gave almost complete solidification, rather quickly. The other fractions also gave some solid precipitation. This white solid hydrolysed easily with water in all cases, giving a yellow liquid, which, after drying in a desiccator containing sulphuric acid, gave no liberation of gas with metallic sodium, even at seventy-five degrees centigrade. This established the fact that the oil did not contain alcohols and that the white material was not benzoyl esters.

The oil from those fractions which did not completely solidify was distilled. In each case, the end point of the treated oil was from one hundred to one hundred thirty degrees centigrade higher than that of the original material; but the quantities remaining, after the temperatures had reached those values, were too minute to measure.

Three hundred fifty cubic centimeters of oily material were salted out of solution from the aqueous layer designated as X, by saturating with sodium carbonate after neutralization. This oil was also fractionated and treated with benzoyl chloride and the reaction mixtures were subsequently distilled. The distillation temperatures showed that practically no benzoyl esters were present.

Upon benzoylation of the water solution, no precipitation of esters was noted.

Experiment 7. In this experiment, exactly the same general procedure was used as in experiment 6, except that seventy per cent acid was used in order to lessen polymerization of the olefins of the pressure distillate. After benzoylation, no ester formation was noted in the oily layers from distillation temperature data. No esters were precipitated from the aqueous layer of the distillation fraction by addition of benzoyl chloride.

Experiment 8. Twelve hundred fifty cubic centimeters of eighty-five per cent sulphuric acid were added rapidly, with vigorous stirring, to five liters of pressure distillate, surrounded by an ice bath. The temperature was kept below twelve degrees centigrade. The fourteen hundred fifty cubic centimeters of sludge formed were separated rapidly. Twenty-two hundred grams of ice were added immediately and the mixture was transferred to a five-liter round-bottom flask. The mixture was steam distilled during a period of four hours. Ninety-four cubic centimeters of oil were collected over a saturated water solution of sodium carbonate, kept slightly alkaline with sodium hydroxide.

This oil was dried over anhydrous sodium carbonate and refluxed several hours with metallic sodium and one hundred cubic centimeters of ether. The small amount of yellow precipitate was washed with ether. The solid precipitate was hydrolyzed in a burrette to give one-tenth of a cubic centimeter of oily material. This material gave an affirmative test for alcohol with Rosenthaler's method (22).

A liter of the treated pressure distillate from this experiment was dried with anhydrous sodium carbonate and added to an equal amount of ether and refluxed with metallic sodium for several hours. The ether-washed precipitate hydrolyzed to produce .45 cubic centimeters of alcohols.

<u>Experiment 9.</u> The temperature of five liters of pressure distillate was lowered by an ice bath to seven degrees centigrade. Twelve hundred fifty cubic centimeters of eighty-five per cent sulphuric acid were quickly added with agitation. The temperature rose to seventeen degrees centigrade. The mixture was allowed to settle and seventeen hundred seventy cubic centimeters of sludge were separated with a separatory funnel. This was washed with one kilogram of ice. Five hundred twenty-three cubic centimeters of sludge remained insoluble in the wash water. The wash water was made basic with sodium hydroxide and allowed to stand

one week at room temperature. The organic material was then salted out with sodium carbonate. The oil which separated was dried with anhydrous sodium carbonate. The dried oil was refluxed with ether and metallic sodium for several hours. No precipitate of sodium alcoholates was formed.

Experiment 10. Five hundred cubic centimeters of sixty-five per cent sulphuric acid were slowly added with stirring to four liters of pressure distillate over a period of fifteen minutes. The temperature was held below ten degrees centigrade with an ice bath. The sludge was separated and washed with ice. All of the sludge dissolved in the water from the ice. The solution was neutralized with potassium hydroxide, using ice to keep it cool, and allowed to stand for ten days. The organic material was then salted out with anhydrous sodium carbonate and refluxed with ether and sodium for several hours. The solid, formed, was filtered and washed with dry ether. This was hydrolyzed to produce two-tenths of a cubic centimeter of alcohols.

Experiment 11. Five hundred cubic centimeters of seventy-five per cent sulphuric acid were slowly added with stirring to three liters of pressure distillate over a period of one hour. This was done out side the building on a cold winter day. The temperature was held below minus five degrees centigrade. The sludge was allowed to settle for two hours. The six hundred cubic centimeters of sludge, formed, were separated and neutralized slowly with sodium hydroxide solution; so that the temperature did not rise above ten degrees centigrade. This was refluxed under a return condenser for a period of eight hours. This material was then steam distilled to give thirty-five cubic centimeters of yellow oil. This oil was dried over anhydrous sodium carbonate and refluxed with dry ether and metallic sodium. From the precipitate, formed, two-tenths of a cubic centimeter of alcohols were obtained by hydrolysis.

Experiment 18. Four hundred cubic centimeters of seventy per cent sulphuric acid were slowly added, with stirring, to two liters of pressure distillate. The temperature of the mixture did not rise above minus five degrees centigrade. The material was then agitated at irregular intervals for a period of four hours and allowed to settle. Four hundred eighty cubic centimeters of sludge were separated and neutralized with solid calcium carbonate. The temperature was held below seven degrees centigrade by introduction of snow, while stirring. A heavy, thick paste resulted. After standing over night the liquid was allowed to drain from the solid calcium sulphate. This liquid was left in a closed container for twenty-four days. Sixty cubic centimeters of oily material were separated and dried with anhydrous sodium carbonate. This was refluxed with ether and sodium for a period of several hours. From the solid, formed, one-tenth of a cubic centimeter of alcohol was obtained by hydrolysis.

Group III Experiments

In this group of experiments the acid was removed from the refinery sludge. The resulting heavy oil was cracked. The olefins in the cracked vapors were absorbed in sulphuric acid.

Apparatus. A distilling flask was connected to an electrically-heated silica tube, fourteen inches in length, and seven-eighths of an inch in inside diameter. The tube was wrapped with nichrome wire and insulated with asbestos to prevent loss of heat. A rheostat temperature control was used.

The silica tube was followed by a condensing coil of half inch iron pipe, cooled by water, and this, in turn, was connected to a receiving flask for liquids. The gases from the receiving flask were led through rubber tubing to a series of small glass absorption towers, packed with broken glass to increase time of contact between the gases and the liquid in the absorption flasks. From the absorption towers, the gases were discharged to the atmosphere through an ordinary laboratory vacuum aspirator. All of the connections were made gas tight by use of water glass.

Experiment 13. A sample of the sludge from the refinery was washed free of acid with water. A large amount of water remained in the heavy oil in the form of an emulsion and had to be removed by painstaking distillation. Bumping was severe. The small amount of water remaining was removed by contact with anhydrous sodium carbonate.

Three hundred cubic centimeters of this material were placed in the distilling flask with five grams of cupric oxide. Three absorption towers were used in tandem. The first contained seventy per cent sulphuric acid held at zero degrees centigrade; the second, ninety-five per cent sulphuric acid, held at zero degrees centigrade and the third, ninety-five per cent sulphuric acid held at a temperature between one hundred and one hundred thirty degrees centigrade. Silver sulphate was added to the acid in each tower for catalytic effect. The furnace was heated to eight hundred fifteen degrees centigrade. Vacuum was applied by use of the water aspirator and the material in the flask was distilled through the furnace. The end point of the distillation was observed to be three hundred thirty degrees centigrade. Ninety-five grams of coke remained undistilled in the flask.

The hot concentrated acid from the final absorption tower was diluted with five volumes of ice. This material was distilled and the first three cubic centimeters to come over were tested for ethyl alcohol by use of the iodoform test. A considerable quantity of iodoform resulted.

The acid from the second absorption tower was diluted with five volumes of water and distilled. The first ten cubic centimeters distilled were collected and treated with benzoyl chloride. No ester formation was noted.

The acid in the first absorption tower was neutralized with solid sodium hydroxide, holding the temperature below ten degrees centigrade by means of an ice bath. This required two days. The neutralized material was refluxed for two hours and the aqueous solution was filtered and treated with benzoyl chloride. No ester formation was noted.

Experiment 14. An attempt was made in this experiment to form isopropyl alcohol only. Two hundred twenty-five cubic centimeters of refinery sludge were washed with about five volumes of water. The decrease in volume of the sludge was very slight. Two absorption towers were used, each containing three hundred cubic centimeters of eighty-seven per cent sulphuric acid and one hundred fifty cubic centimeters of light lubricating oil. The temperature of these solutions was held between seventeen and nineteen degrees centigrade. The temperature of the silica tube was held between seven hundred five and seven hundred sixty degrees centigrade. The sludge oil was distilled through the system. Practically all of the material leaving the condenser was in the gaseous state. Sixty-six grams of coke remained undistilled in the distilling flask.

The sulphuric acid-oil mixture was diluted and neutralized with sodium hydroxide and heated under a return condenser to eighty to ninety degrees centigrade for four hours. The volume of this mixture was twenty-seven hundred cubic centimeters. The mixture was distilled. Thirty cubic centimeters distilled between eighty and ninety-nine degrees centigrade. An iodoform test was negative in the cold and produced no precipitation of iodoform when heated. The aqueous solution also tested negative with Rosenthaler's method (22). However, the solution contained considerable material of an inflamable nature. A strong aldehyde test was obtained by Schiff's fuchsin-aldehyde reagent. A strong ketone test was obtained by use of phenyl hydrazine.

Experiment 15. Two hundred twenty-five cubic centimeters of sludge were washed first with water and then with caustic solution. This was followed by a water wash. The material was centrifuged to break up the emulsion. Most of the water was separated and the remaining water removed by use of anhydrous sodium carbonate. Five grams of cupric oxide were added and the oil was distilled through the silica tube, held at a temperature between six hundred fifty and seven hundred five degrees centigrade. The cooled, gaseous product was passed successively through three absorption towers. The first contained eighty-seven per cent sulphuric acid held at eighteen degrees centigrade. The second contained seven parts of acid of the same strength with three parts of light lubricating oil. The materials of this vessel were also kept at a temperature of eighteen degrees. The third contained ninety-five per cent sulphuric acid with some silver sulphate held at a temperature of from one hundred to one hundred thirty degrees centigrade.

After the cracked gases had been passed through the acid solutions, each was diluted with five volumes of ice in separate containers. Two hundred cubic centimeters of material were distilled from each. These solutions were neutralized and treated with iodine. The iodoform that formed was filtered, washed with water and dried. The quantities of iodoform obtained in each case were respectively .0782 grams, .0568 grams and .3456 grams. By calculation this would equal .0206 grams of isopropyl alcohol and .2405 grams of ethanol.

Experiment 16. In this experiment the gases, formed, were first passed through two towers containing concentrated potassium hydroxide to make certain that no hydrogen sulphide entered the acid solution. The gases were then led through a tower, filled with flake calcium chloride, to remove any moisture, picked up from the caustic solution. From the calcium chloride tower the gases passed through eighty-seven per cent sulphuric acid held at a temperature of eighteen degrees centigrade and then through ninety-five per cent sulphuric acid held between one hundred and one hundred thirty degrees centigrade. A cracking temperature between seven hundred five and seven hundred thirty-five degrees centigrade was used. Three hundred cubic centimeters of the sludge oil were used.

After the gases had been passed through the towers, both batches of acid were diluted with five volumes of ice. The resulting solutions were distilled until one fifth of the total volume of each was collected. The alcohols present were converted to iodoform by use of sodium hydroxide and iodine. The material resulting from the cold absorption tower yielded .87 grams of iodoform and that from the hot tower yielded .4691 grams. These weights correspond by calculation to .1328 grams of isopropyl alcohol and .0549 grams of ethyl alcohol.

NOTES AND DISCUSSION

Allen (21) states that a solution of amyl alcohol warmed with strong sulphuric acid will give a red coloration which will disappear on distillation. He advocates the use of this fact as a test for amyl alcohol. It is believed that this test is not adapted to the problem at hand because many other substances were present which might also give such a test. Nevertheless, for lack of a better test, this was used in a few cases. In each case it was possible to duplicate almost the exact shade obtained by use of dilute solutions of commercial amyl alcohol prepared in the laboratory. The odors of other materials prevented the use of the common amyl acetate test for amyl alcohols.

The Rosenthaler test (22) for the alcohol group is as follows: "The solution to be tested is treated with a mixture of four parts of 0.5% solution of sulfanilic acid (in approximately normal hydrochloric acid solution) and one part of 0.7% sodium nitrite, then with excess sodium hydroxide, and heated in a water bath. Various shades of red are produced by different alcohols, the time and temperature of the reaction also being somewhat characteristic."

According to Kamm (24) benzoyl chloride reacts only slowly with cold water to give benzoic acid and hydrogen chloride. However, it reacts comparatively rapidly with alcohols, yielding the benzoic esters of the alcohols and hydrogen chloride. Benzoic esters are much less soluble than the alcohols from which derived in water. Sodium benzoate is soluble in water. These facts may be used to extract alcohols from a basic water solution. However, according to Brooks and Humphrey (10) the tertiary alcohols are practically incapable of benzoylation.

Another interesting fact is that the boiling points of these derivatives are uniformly around one hundred thirty-two degrees centigrade above the boiling points of the alcohols from which derived. Even though many of the higher esters of benzoic acid decompose upon boiling, it was thought that perhaps by distillation under vacuum and application of a linear correction to be added to the boiling points that after treating certain neutralized cuts with benzoyl chloride, this one hundred thirty-two degree rise could be noted and that the cut obtained in this neighborhood could be hydrolyzed to give the free alcohols. However, in general, this method was entirely unsatisfactory. A reaction, liberating large amounts of heat, resulted from treatment of the hydrolysed oily layers with benzoyl chloride. This was usually accompanied by heavy precipitation of a white gelatinous material. Some of this was assumed to be due to the reaction between mercaptans and benzoyl chloride.

According to Mulliken (25), all of the alcohols will react with metallic sodium with the liberation of hydrogen if the temperature is raised to seventy-five degrees centigrade.

Mulliken (25) states that iodoform may be produced in the cold from acetone and isopropyl alcohol under concentration conditions that would not produce iodoform from ethanol except by heating to approximately sixty degrees centigrade. It is to be noted that in experiment fourteen that the ketone test obtained could not have been due to acetone, the oxidation product of isopropyl alcohol, because acetone will give an iodoform test easily in the cold. The iodoform test is probably not quantitative beyond establishing the correct order of magnitude. However, in view of the minute quantities of alcohol present, distillation or specific gravity means were not practicable.

Brooks and Humphrey (10) advise use of the fact, that the sodium alcoholates are insoluble in ether, for the extraction of small amounts of alcohols from large amounts of organic material.

The pressure distillate is stabilized at the refinery before treating with sulphuric acid. Also the pressure distillate used in group two experiments had been weathered at room temperature for some time. In view of these facts it is not likely that olefins of less molecular weight than the amylenes would be present when the pressure distillate first comes in contact with the sulphuric acid. According to Moureu (26), the secondary alcohols are formed in preference to the primary and the tertiary in preference to the secondary. Consequently the probable alcohols formed direct from the sludge are the secondary and tertiary amyl, hexyl, heptyl, octyl and perhaps nonyl alcohols. No information was found in the literature with reference to the action of the nonylenes on sulphuric acid. Brooks and Humphrey (10) state that the decylenes are almost quantitatively polymerized by sulphuric acid.

The fact that a distillation curve of the pressure distillate indicates only traces of amylene, hexylene, heptylene, octylene and nonylene; and the polymerization losses indicated by the literature explain the surpridingly low yields of alcohols by direct hydrolysis of the sludge.

Experiment five and all of those of group three were carried out using a fifty-fifty mixture of sludges from the two settling tanks of the refinery. It was thought that if any process of worth should be developed on the mixture that duplicate experiments could be run on the sludge from each settling tank separately.

The literature in general advised that heat, time and high concentration of sulphuric acid caused polymerization of the higher olefins at the expense of alcohol production. It was therefore deemed advisable to prepare sludge from pressure distillate, using dilute acid, shortening contact time and lowering the temperature of the reaction.

The results of experiment eight show clearly that the alcohols, formed, dissolve to a very large extent in the treated pressure distillate. This shows either that most of the hydrolysis of the unsaturated compounds takes place before the separation of the sludge, or that the intermediate products are more soluble in the pressure distillate than in the sludge.

Experiment nine was performed because it was thought that perhaps alkyl hydrogen sulphates might be formed as intermediate products in the formation of alcohols from pressure distillate and that perhaps these were soluble in water. No alcohols were isolated using this as a working hypothesis.

In all of the steam distillations of the refinery acid sludge, a sickening odor of hydrogen sulphide and mercaptans was evolved. The presence of hydrogen sulphide was verified by placing a rag, saturated with lead acetate, over the adapter leading into the receiving vessels.

In all cases the water of the distilled fraction was immediately saturated with sodium carbonate and made basic with sodium hydroxide. Saturation was done to prevent any alcohols from dissolving in the aqueous layer. The acid was neutralized to prevent esterification of the alcohols present. The addition of sodium hydroxide removed the unbearable odor and left in its place one that was very pleasant.

In the third group of experiments, cracking temperatures were used that were somewhat in excess of the most favorable temperatures used by Winkler and Pilat (12) for cracking gas oil to obtain olefinic gases, convertible to alcohols. This was done because the oil to be cracked was an exceedingly high boiling fraction and because the cracking time was short.

In view of the fact that most of the sludge oil was converted into gases in the group three experiments it is surprising that more isopropanol and ethanol were not formed. However, Winkler and Pilat (12) only observed a maximum yield of five and one half per cent of olefins, convertible into alcohols by cracking gas oil.

In the preparation of isopropyl alcohol it was necessary to take precautions for the elimination of hydrogen sulphide from the gases. Placing a quantity of cupric oxide in the heavy oil aided materially in lowering the quantity of hydrogen sulphide evolved. However, the best results were obtained by passing the cracked vapors through a caustic solution.

SUMMARY OF RESULTS

1. Only traces of alcohols were obtained by direct hydrolysis of acid sludge from the refinery.

2. Preparation of sludge in the laboratory from pressure distillate using controlled temperatures and concentrations of acid yielded only traces of alcohols, but in greater quantity than that obtained from refinery sludge.

3. In the preparation of acid sludge from pressure distillate alcohols are formed which dissolve mainly in the pressure distillate. Approximately twenty-three times as much alcohol was obtained from the treated pressure distillate as from the sludge which was formed.

4. Small amounts of ethyl alcohol and propyl alcohol were prepared by first cracking the heavy oils from the acid sludge and then converting the ethene and propylene into alcohols.

5. Passing the gases through caustic solution before absorption in sulphuric acid aided materially in increasing the yield of isopropanol.

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