7

PRODUCTS FROM SULFONATION OF PETROLEUM RESIDUA

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A B S T R A C T

In a search for new applications for resinous fractions derivable from asphalt, studies of sulfonation reactions of these substances have led to the development of an intermediate product which can be utilized to prepare either strong acid cation exchange materials or an activated gas-adsorbent carbon.

The cation exchange materials have operating characteristics and stability resembling the commercial sulfonated coals, while adsorbent carbons of very high activity have been prepared.

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Processing of low gravity crudes at the Wynnewood, Oklahoma refinery of Kerr-McGee Oil Industries, Inc., affords asphalt as a major product, and among the major efforts of the Kerr-McGee research group has been the investigation of new uses for asphalt and asphalt fractions. The development of commercially feasible methods for separating vacuum reduced crude into the asphaltic components usually referred to as asphaltenes, resins, and oils afforded us ample quantities of these materials for investigation in a search for new uses for these substances as raw materials in the chemical and allied industries.

By proper control of the conditions of separation it is possible to prepare resinous fractions of varying physical properties as reflected by ring and ball softening point, hardness, penetration, etc.

Although these resin fractions have industrial uses of their own as for example in paints, rubber, tile, emulsions, and others, projects were undertaken for the chemical modification of these fractions in search of entirely new utilization of these components as chemical raw materials.

The higher molecular weight fractions of these resins are relatively complex, highly condensed mixed aromatic-aliphatic-naphthenic materials, largely hydrocarbon in nature, but containing minor percentages of sulfur and oxygen most probably present as heterocyclic function. Without extensive fractionation by extremely tedious and expensive processes it appeared that only simple chemical treatment of the resins might result in desirable changes in the properties of these substances, which might give rise to useful products.

Among the reactions investigated which did, indeed, afford useful intermediates or end products was that of treating higher melting resin fractions with a variety of sulfonating agents. The course of the reactions with these reagents apparently involves sulfonation, sulfation, and oxidative condensation and is probably as complex as the somewhat analogous well-known "sulfonation" of coal. However, unlike coal, the asphaltic fractions investigated are fusible at (relatively) low temperatures, and so in the mechanical processing of the latter, dust and fines arising from grinding operations are not lost to chemical processing, inasmuch as the dust and fines can be melted, cast, and reground.

A single sulfonation (the term sulfonation is used with the understanding that the reactions involved are considerably more complex than is implied by this term; however, it is convenient to use this rather than "complex reaction with sulfonating-sulfating agents" which is what it is intended to imply) with, for example, ordinary concentrated sulfuric acid yields, with a variety of asphaltic resinous materials, a product which is readily wet by water and infusible, whereas it will be recognized that the starting material is essentially hydrophobic in nature and is readily fused without more than minor decomposition. The sulfonated product is harder and (from asphaltenes) less friable than the starting material. It possesses poor cation exchange properties, as will be seen from the "Experimental" section.

However, a retreatment of this product with additional sulfonating agents[4] does afford products useful as cation-exchange materials operative in both the

hydrogen and sodium cycle, and of capacity and operating characteristics essentially indistinguishable from commercial "sulfonated coal" cation exchange products, with which the better products were compared. Thus granular materials were prepared having satisfactory ion exchange capacity, good physical stability and resistance to attrition; they are economically regenerated, are free from color throw-off in the alkali metal forms and are washed free of excess regenerant with a reasonable volume of wash water.

The hardness and infusibility of the once sulfonated "intermediate product" led to the testing of these substances as coking materials for the preparation of an activatable adsorbent char(5). It may be pointed out that slow coking of asphaltic resin fractions (resins or asphaltenes) is preceded by fusion, evolution of gaseous pyrolysis products with concomitant profuse foaming until the material is well carbonized, whereupon a light porous friable product is left having essentially no utility as an activatable char. On the other hand, slow charring of a properly-sulfonated intermediate product derivable from the same resinous material affords in good yield a hard granular carbon, the granules of a size essentially the same as the starting material. No fusing or foaming occurs, and the char is readily activated by the usual well-known methods to give a very active adsorbent of satisfactory hardness characteristics.

The relationship of the original resinous material to the "sulfonated" product is largely that of <u>binder</u> to <u>base material</u> as defined by Morgan and Fink(7). These investigators classified binders as substances which, on carbonization, "swell, become macroporous and yield a lustrous char." During the carbonization the material goes through a plastic, or even a liquid stage, during which effervescence accompanying the expulsion of volatile matter gives rise to the swelling with building of the macroporous structure. Base materials, on the other hand, should not become plastic or fluid during carbonization, but rather should have a rigid oriented structure. Other desirable characteristics of a base material are that it should be "a large ring-chain molecule with oxygen or other volatile constituents in the ring."

Inasmuch as binder materials carbonize to give (after activation) carbons of low activity, these investigations conclude that such substances are in the main not very desirable as raw materials for activated carbon.

Similar, though perhaps not as broad, conclusions were reached by Bureau of Mines Investigators(2) who found that certain bituminous and sub-bituminous coals, natural cokes, pitch cokes and petroleum cokes did not yield satisfactory adsorbent carbons by methods which, with desirable raw materials, were successful.

Apparently the reactions attending the sulfuric acid treatment of the asphaltic resins - e.g., sulfonation, sulfation, and oxidative condensation serve to transform these asphaltic resinous materials from a binder (quality unknown) into a very satisfactory base material. The amount of sulfuric acid which is required to effect the conversion depends upon the relative binder/base characteristics of the asphaltic resin, and is most economically a quantity which will effect enough oxidative condensation to minimize fusion during charring. With pentane-precipitated asphaltenes, about 3.5 parts of 95% sulfuric acid per part of resin effects, during a two-hour "sulfonation" period, conversion into a satisfactory base material. For conversion into an activatable char, the sulfonation product, without isolation or washing is slowly heated to coking temperature (about 550-600°C) in the absence of air. During the heating period, excess acid, some sulfur dioxide, H_2S, and even elementary sulfur are evolved along with water, and later, as temperatures in excess of about 400-450° are attained, carbonaceous pyrolytic decomposition products are evolved. The char can be satisfactorily activated by the usual methods (steam) to afford active adsorbent chars in good yield.

Thus examination of sulfonating reactions on asphaltic resin fractions leads to a product which may be resulfonated to yield useful cation exchange materials or which

can be carbonized and activated to give a good activated carbon.

EXPERIMENTAL

Preparation of Cation Exchange Materials

The reaction between hard asphalts or asphaltic resins and simple sulfonating agent such as concentrated sulfuric acid is very slow at ambient temperatures, becoming more rapid as the temperature rises to about 70°C. Above this temperature the reaction proceeds rapidly, accompanied by vigorous evolution of SO_2 as the acid oxidizes part of the asphaltic material. The mixture foams persistently and in consequence the reaction must be carried out in oversize equipment with adequate stirring. Useful starting materials for preparation of either the cation exchange materials or the activated char were found to be blown asphalts of softening point in excess of about 270° and asphaltic resins, asphaltenes, or mixtures thereof having similar softening point properties. Simple asphaltenes were very useful as starting materials.

1. Sulfonation of Asphaltenes

Fused and subsequently ground pentane-precipitated asphaltenes derived from a vacuum reduced asphalt (penetration 89, softening point 120°F) were screened, and the 20/40 mesh fraction retained. Fines were remelted, cast to solidify and reground. For the preliminary sulfonation 100 parts of the 20/40 mesh material were treated with 540 parts by weight of 95% sulfuric acid in a resin reaction flask equipped with an efficient stirrer and vented for the escape of gases. The sulfuric acid was added to the ground material slowly, the mixture was allowed to reach its equilibrium temperature (about 45°C) and was then slowly heated on a steam bath. Because of the violent foaming which ensues, the temperature must be raised slowly - one-half to one hour being required to reach maximum steam bath temperature which is maintained for a period of about two hours. The reaction had largely moderated at the end of this time under these conditions and most of the acid appeared to be absorbed. The mixture was cooled and poured into a large excess of cold water. Fines produced in the sulfonation were removed by backwashing in a large cylinder. Washing of excess acid from the solid product is a tedious operation and is at best not wholly successful.

To test the product for ion exchange capacity, twelve grams of the washed and dried material was transferred to a half-inch diameter glass column and alternately exhausted and regenerated by treatment with dilute sodium hydroxide followed by dilute hydrochloric acid. After several cycles of this sort, the product was regenerated with 4 Normal hydrochloric acid. To wash out the excess acid required over a liter of water (about fifty column volumes) and the material in the hydrogen form was found by standard column testing methods to have an exchange capacity of only about 0.35 m.e.q./gram. (Twelve grams exchanged hydrogen for the cations in about 550 ml of hard water containing 400 ppm hardness expressed as $CaCO_3$). Thus this product is a very poor ion exchange material.

2. Resulfonation of Intermediate Product

The intermediate sulfonated product prepared (above) was further activated by treating 150 parts of the dried material with 80 parts of 20% oleum in similar equipment. The oleum was added slowly while the mixture was cooled in order to prevent excessive heating and foaming. Again when equilibrium temperature was established, the mixture was heated slowly to steam bath temperatures and maintained for two hours. The product was "drowned out" after cooling and thoroughly washed, finally in the sodium form with hot water. A twelve-gram sample of this product required somewhat less than 100 ml of wash water to free it of excess acid after regeneration, and in standard column operation exchanged hydrogen for the cations in 2,150 ml of 400 ppm hard water before leakage reached 5% of the original total hardness. This much-improved product had a working capacity of approximately 1.43 m.e.q. per gram.

3. Double Sulfonation without Intermediate Isolation of Product

A quantity of 20/40 mesh asphaltene was sulfonated with 5.5 times its weight of concentrated sulfuric acid as in the first example. After the initial sulfonation the mixture was cooled and a quantity of 20% oleum equal in weight to the original sulfuric acid charged was slowly added, after which heating was resumed. More SO_2 was evolved and the mixture again foamed as badly as during the original sulfonation. After an additional two hours at steam bath temperature the reaction was terminated and the product was washed. The material possessed high exchange capacity but exhibited color throw-off on lengthy standing in the sodium form in contact with water. This was believed due to small amounts of lower molecular weight sulfate/sulfonates. To eliminate these, the washed material was soaked in hot (90°C) 20% sodium hydroxide for about six hours and then was thoroughly washed with hot water.

This material exhibited ion exchange capacity in both the hydrogen and sodium cycles comparable with that of commercially available sulfonated coals. Color throw-off was not noticeable, regeneration and washing requirements were essentially those of commercial sulfonated coal. Yield of the twice-sulfonated material was about 1.4 times the weight of pentane asphaltenes charged. Quite similar products were obtained from similar sulfonations carried out on an oxidized asphalt and air oxidized asphaltic resins.

Preparation of Activated Carbons

A special apparatus was constructed of fused quartz for preparing and activating chars from sulfonated materials. The major components of this apparatus were a steam superheater and a carbonizing and activating vessel, both constructed of fused quartz. The superheater was a quartz macro combustion tube 3/4" x 30" with ball joints at the ends and heated by a standard electric combustion furnace.

The activating vessel was somewhat similar but arranged in a vertical position. This vessel was larger in diameter (2") and shorter (10"). It was also heated electrically by furnace elements which fit closely for most of its length. Temperature was controlled by a large variable transformer. The lower end was closed and a socket joint attached near the bottom at right angles to its axis. This joint received superheated steam from the combustion tube. A grating of quartz was included just above the steam inlet. This helped distribute the steam uniformily. The upper end of the tube was bottle shaped with a socket joint finish. This socket accepted a ball joint fitting carrying a thermocouple and a condenser.

Steam rate was measured by pressure drop across a calibrated orifice between the supply line and the inlet to the superheater tube.

Approximately 40 grams of dry, granular, sulfonated material was charged to the vessel and carbonized without steam at 500-550°C. The temperature was then raised to that desired for activation, and steam admitted at a rate sufficient to suspend or fluidize the bed of carbon. At the end of the time of activation, heating of the activation vessel was discontinued but superheated steam was continued until the temperature of the carbon had fallen below 500°C at which time the steam was shut off. The carbon was allowed to cool thoroughly before disconnecting the apparatus.

1. Activated Carbon from Asphaltenes

Two-hundred grams of pentane precipitated asphaltenes were slowly coked in the absence of air. Foaming was severe because of fusion and evolution of volatile matter, so that the rate of heating required careful monitoring to avert mechanical loss of material. The final temperature of coking was 500°C and heating was continued for about ten minutes after essentially all pyrolysis products had been evolved. The cooled porous, friable residue (104 g.) was crushed and screened, the 20/40 mesh fraction (54 g.) being retained. Activation for 30 minutes at 975°C with excess of

superheated steam afforded 19.7 grams (4.8% based on asphaltenes) of an "activated carbon" which had a CCl_4 service time(1,3,8) of 36 seconds. Thus, the activated asphaltene coke would be considered worthless as an active char.

2. Activated carbon from Sulfonated Asphaltenes

100 g. of 20/40 mesh asphaltenes was treated with 200 ml (370 g.) of concentrated sulfuric acid, heated to water bath temperature and maintained for two hours. The temperature was slowly raised until a final temperature of 400°C was attained. Copious evolution of SO_2 attended the whole operation. The dry product was screened to eliminate a small amount of fines and the 20/40 mesh fraction coked at 500-550°C until evolution of gases had ceased. Half the char (38.5 g.) was activated with steam at 800°C for 35 minutes to yield 36 g. of activated carbon having a CCl_4 service time of 185 seconds. The other half of the char was steam-activated at 950°C for 35 minutes to yield 24 g. of activated carbon having a CCl_4 service time of 1028 seconds. The once-tested carbon was regenerated for seven minutes at 975°C and exhibited a CCl_4 service time of 1050 seconds. The products are granular, of fairly satisfactory hardness and have been prepared under conditions which yield carbons having CCl_4 service times as high as 1600 seconds.

The activity of the carbon increased with increasing temperature of activation up to about 850-875°C. Thus, carbon activated at temperatures above 900°C was no more active than that obtained at 850°C. At these temperatures, yield of activated carbon decreased rapidly with increased retention time and with increasing temperature. These facts are in general accord with and confirm observations made by previous investigators.(6)

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