

Gelsenkirchen-Horst, February 12, 1942.

Method for the Analytical Separation of Asphalt in the
Sump Phase Residue from High-Pressure Hydrogenation.

In the course of the hydrogenation of coal, asphalt is formed which remains in the heavy liquid residue. Although the hydrogenation residues resemble petroleum residual oils, it is not possible to use the same method for the analytical separation of the asphaltic bodies which are used for petroleum residues. The reason lies in the fact that the hydrogenation residue contains, besides asphalt, solid matter which consists of ash components, free carbon and unhydrogenated coal substance. A method has been developed which permits the separation of the hydrogenation residue into several components without the necessity of previously removing the solid matter and without exposing the asphaltic substances to conditions which might change their structures.

One gram of the sample is weighed into an Erlenmeyer flask with ground glass stopper, distributed over bottom and sides of the flask and dissolved in 40 cc. of n-hexane, if necessary under slight warming. The solution is left standing in the dark for 12 hours and filtered. The undissolved residue consisting of solid matter and hard asphalt is washed with n-hexane and extracted with benzol. The benzol solution is evaporated, yielding the "asphalt" fraction. The benzol-insoluble material is extracted with pyridine which treatment yields the "carbene" fraction; the insoluble residue represents the "solid matter". The naphtha solution is treated with 0.5 grams activated charcoal and filtered. Evaporation of the solution yields "neutral oil". The resins which are adsorbed by the charcoal are either estimated by difference (subtraction of the sum of solid matter - asphalt, carbene and oil - from 100) or are determined directly by extraction of the charcoal with chloroform. Results obtained with this method on products containing up to 10% solid matter gave good reproducible results. For products containing more than 10% solid matter, the method has been modified by extracting the sample with n-hexane and permitting the solution to stand for 12 hours; the subsequent treatment is the same as before.

Gelsenkirchen-Horst, September 26, 1938. Analytical Methods.

Removal of Solid Matter.

Oils containing much solid matter (pasting oil, soda oil, sludge) are freed from solid matter by boiling 250 grams sample with about 250 cc. benzol for 20 minutes, filtering and distilling off the solvent.

The ash in the residue is determined on an aliquot portion after washing with hot benzol and drying.

If the oil contains only a small amount of solid matter, boiling with benzol is unnecessary.

This method is used for the analysis of the following products; sludge, pasting oil, soda oil, coal paste, centrifuging residue, centrifuge oil, low-temperature carbonization products, flushing oil.

Determination of Solid Matter.

Two grams of sample are dissolved in hot benzol and filtered through a Gooch crucible. The residue is washed with hot benzol and dried at 105°C.

The determination is used for the analysis of the following products: pasting oil, soda oil, catalysts, coal paste, sludge, centrifuge oil, centrifuging residue, centrifuge charge, residue and oils from low temperature-carbonization.

Asphalt Determination.

Two grams of sample are dissolved under heating in 5 cc. of benzol and treated with 100 cc. naphtha (Normalbenzin).

The solution is left standing in the refrigerator for two hours or at room temperature in the dark for 24 hours. The solution is then filtered, washed with benzol and the filter boiled with benzol until all asphalt has been dissolved. The solvent is distilled off and the residue is weighed.

The determination is carried out on the following products: pasting oil, sludge, centrifuged oil, residue from centrifuging.

Soda Determination.

Five grams of sample are weighed into a 5-liter separatory funnel and treated with steam for about three-quarters of an hour. The condensed water is filtered into a 2-liter Erlenmeyer flask after each 10-to 15-minute steaming period. After cooling the collected water, it is titrated with 0.1 N sulphuric acid, using as indicator a mixture of one part dimethylaminoazobenzene and two parts bromocresol green.

The following products are tested by this method: sludge, centrifuged oil, pasting oil, soda oil.

REMOVAL OF SULFUR FROM THE C₃ AND C₄ FRACTION

Complete removal of sulfur from the C₃, C₄ fraction (middle oil hydrogenation) by means of hydrogenation has been investigated in small-scale equipment. Catalyst 5058 as used for gasoline manufacture was used.

The reactor was filled with 1.95 gals. catalyst; the commercial pellets of 0.39 in. diameter were halved twice to obtain better packing of the reactor.

The experiments were at first carried out at 4400 psig. 19 mV. (probably iron-constantan thermocouple, corresponding to about 700°F.), a gas rate of 530 cu.ft./hour of hydrogenation recycle gas (about 70% H₂) and an injection rate of 2.8 gals./hour (13.2 lbs./hour). Because of difficulties with the pump and ice formation during depressuring of the product satisfactory operation resulted only when the operating pressure was reduced to 745 psig. Further experimenting showed that a satisfactorily purified gas was obtained when operating at 10 mV (probably 410°F.), 294 psig. and a gas rate of 17.6 cu.ft./hour.

Some of the test results are shown in the following table.

Pressure psig.	Approx. Temp. mV. °F.	Gas cu.ft./hour	Injected C ₃ , C ₄ fraction		mg. org. S/100g C ₃ , C ₄	
			gals./hour	lbs./hour	Original	After Treating
1470	10	176	3.8	17.6	0.18	0.00
735	10	176	3.8	17.6	0.16	0.00
294	10	176	3.8	17.6	0.17	0.00
294	10	17.6	3.8	17.6	0.03	0.00

In these experiments a total of 2695 gals. of charge was contacted with 1.96 gals. of catalyst (12,500⁺ C₃, C₄ per 41.8 lbs. of catalyst) and the catalyst did not lose its efficiency.

The sulfur is converted into H₂S by hydrogenation and is removed from the exit gas as usual.

The quantity of hydrogen required has not yet been determined but can be considered small. 1.9 cu.ft./hour of H₂ was used per gallon of C₃, C₄ feed per hour.

Tests were also run with Raffleur spheres as catalyst but no satisfactory results were obtained at pressures ranging from 147-294 psig. and throughput rates even lower than used with catalyst 5058. For these tests the feed stock was freed from H₂S prior to hydrogenation.

Another series of investigations was made using a nickel catalyst. The catalyst was prepared by treating nickel nitrate with hydrogen (353 cu.ft./hour) at slowly rising temperature until a maximum of 608°F. was reached. The temperature of the reactor was then brought to 15 mV (about 570°F.) and the C₃, C₄ fraction was injected at a rate of 3.9 gals./hour. The C₃, C₄ was at first freed from H₂S prior to hydrogenation but this practice was later abandoned.

The efficiency of the nickel catalyst was not as great as that of catalyst 5058 but was better than that of the Raffleur spheres. Nickel is apparently also active as NiS because sulfur removal was obtained when a feed stock containing about 0.1% by wt. of H₂S was processed.

Experimental results are given in the following table.

Pressure psig.	mV.	Approx.	H ₂ cu.ft./hour	Injected C ₃ ,C ₄ fraction		mg. org. S/100g C ₃ ,C ₄	
		Temp. °F.		gals./hour	lbs./hour	Original	After Treating
294	15	570	17.6	3.9	17.6	0.62	0.18
294	15	570	17.6	3.9	17.6	1.40	0.00

The total through-put of C₃, C₄ was 1820 gals. It is calculated that the amount of sulfur removed exceeds by far the amount required to form NiS so that it can be assumed that NiS acts as hydrogenation catalyst.

HS:kg7

ANALYSIS OF COAL

The following determinations are carried out:

1. Determination of ash.
2. Determination of water, using xylene for regular determinations, benzol for water determination, followed by oil determination and carbon tetrachloride for water determination followed by sand elimination.

3. Sand determination.

For the sand determination of brown coal the coal and carbon tetrachloride from the water determination is placed in a separatory funnel, the separated sand is filtered off and the filter containing the sand is ashed. The ash is heated for a short while with concentrated hydrochloric acid, filtered and again ignited.

In a second method which is applicable not only for brown coal but also for intermediate products or residues from the hydrogenation, the solid matter is determined by means of solvents and the solid matter so obtained is ashed. 0.5 grams of the ash are treated in a platinum crucible with about 35 g. of concentrated sulphuric acid, heated for 10 to 15 minutes, cooled to about 80°C. and filtered through a Jena sintered glass crucible of suitable pore size. The residue is washed with warm concentrated sulphuric acid, 20% sulphuric acid and cold water and is dried at 110°C.

4. Alkalinity.

About 1 to 2 g. of coal is moistened with alcohol, 50 cc. of 0.1 N sulphuric acid and enough water are added to give a volume of about 15 cc. The mixture is boiled for 20 minutes, filtered, washed with hot water and titrated with sodium hydroxide, using methylorange as indicator.

ANALYSIS OF COAL PASTE

The following determinations are carried out on coal paste.

1. Determination of water by the xylene distillation method.
2. Determination of solid matter.
20 g. of sample are boiled with 20 cc. of benzol, filtered, dried and weighed.
3. Determination of ash and solid matter.
4. Determination of asphalt.
The filtrate from the water determination is freed from solvent by distillation and 5 g. of the oil thus obtained are treated with 200 cc. of naphtha (Normalbenzin) for determination of the asphalt content.
5. Sieve analysis.
50 to 100 g. of sample is boiled with about 10 to 15 times its weight of benzol and the suspension is passed through a sieve. The residue is washed with benzol, dried and sieved again.
6. Specific gravity, determined by weighing in a graduate at the temperature specified.

DETERMINATION OF HYDROGEN SULPHIDE AND SULPHUR DIOXIDE IN

CLAUS OVEN GAS

Two liters of gas are passed rapidly through two wash bottles containing 15% KOH with 0.1% SnCl_2 . The contents of the wash bottles are transferred to a 500 cc. volumetric flask, filled up to the mark and shaken well. 25 cc. of the solution are added to acidified 0.1 N iodine solution and titrated with thiosulphate to obtain the total sulphur (SO_2 and H_2S).

To another 25 cc. portion of the solution is added 10 cc. zinc acetate, 30 cc. glacial acetic acid and 10 cc. formalin. Addition of iodine solution and titration with thiosulphate gives the amount of hydrogen sulphide.