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PRODUCTION OF GRAPHITE ELECTRODES BINDER FROM IRAQI ASPHALT

Abdul Halim A.K. Mohammed **Hussain K. Hussain** **Tariq M.Naief**

Chemical Engineering Department-College of Engineering
University of Baghdad-Iraq

ABSTRACT

Basrah crude oil Vacuum residue 773^+ K with specific gravity 1.107 and 4.87wt. % sulfur, was treated with hexane commercial fraction provided from Al-Taji Gas Company for preparing deasphaltened oil(DAO)suitable for hydrotreating process.

Deasphaltening was carried out with 1h mixing time, 10ml:1g solvent to oil ratio and at room temperature.

Hexane deasphaltened oil was hydrotreated on presulfied commercial Co-Mo/$\gamma - Al_2O_3$ catalyst in a trickle bed reactor. The hydrotreating process was carried out at temperature 660 K,LHSV 1.3 h^{-1}, H2/oil ratio 300 l/l and constant pressure of 4MPa.

The hydrotreated product was distillated under vacuum distillation unit. It is found that the mixture of 75% of vacuum residue with 25% anthracene satisfies with requirements for graphite electrodes binder.

الخلاصة

عومل المتبقي الفراغي لخام نفط البصرة ذو درجة غليان 773 كلفن ووزن نوعي 1.017 و4.87 نسية وزنية كبريت بمقطع الهكسان التجاري الذي جهز من شركة تعبئة الغاز في التاجي لتحضير متبقي فراغي مفصول الاسفلتينيات مناسب لعملية الهدرجة.تم معاملة المتبقي الفراغي بالمذيب بزمن خلط 1ساعة ونسبة مذيب الى المتبقي غم 10:1 مل بدرجة حرارة الغرفة.

تم هدرجة المتبقي الذي عومل بالهكسان بوجود العامل المساعد Co-Mo/γ-Al2O3 الذي تم تحويله لصورة السلفايد في مفاعل ثلاثي الاطوار.تمت عملية الهدرجة بدرجة حرارة 660 كلفن وسرعة فراغية 1.3 ساعة $^{-1}$ ونسبة هيدروجين/المتبقي 300 لتر/لتر تحت ضغط 4 ميكاباسكال.

تم تقطير الناتج من عملية الهدرجة في وحدة التقطير الفراغي. لقد وجد ان خليط المتبقي الفراغي بنسبة 75% مع 25% من الانثراسين وافق متطلبات العجينة الرابطة لاقطاب الكرافيت.

KEY WORDS

Binder, graphite electrodes, asphalt, hydrotreating, deasphalting

INTRODUCTION

Graphite electrodes binders are the residues from petroleum refining for heavy oils,coal-tar pitches, petroleum pitches, natural pitches, and the pyrolysis residues from heavy petroleum materials.These binders usually are solid and high viscous black materials, with low solubility in water but are dissolved in many organic solvents.The properties of graphite electrode binder depend on the nature of material obtained by vacuum distillation and its initial boiling point. Softening point, coke yield, sulfur content,BI and QI,are most important properties of the binder (Hatano 1989, Wagner1988).

It is well known that petroleum asphalt obtained by vacuum distillation of reduced crude oil used as basic component for binder production(Wagner1986).

Deasphalting and hydrotreating of the petroleum asphalt are the most important processes for binder production from heavy petroleum products.

Vacuum residue contained a fraction “asphaltenes” which has a particularly strong influence on the rate of HDS. Therefore,the deasphaltening process with low boiling liquid hydrocarbons for the vacuum residue before the hydrotreating process is very important, because of the most sulfur and metals could be removed with the precipitated asphaltenes.In order to obtain an acceptable level of sulfur and metals in deasphaltened oil,hydrodesulfurization should be applied(Gary (1994).

In this work,first attempt was carried out for obtaining a binder for graphite electrodes from high sulfur and metal content asphalt.Asphaltenes was separated from the vacuum residue by hexane solvent.The deasphaltened vacuum residue was hydrotreated,then ,binder was obtained by mixing the hydrotreated deasphaltened vacuum residue with anthracene.

EXPERIMENTAL WORK

Deasphaltening Unit

The deasphalting unit consists of three main stages as follows:

Mixing stage

The vacuum residue or asphalt was mixed with a light solvent in 2-neck glass flask.

The flask set on a magnetic stirrer and the mixing proceed by 12.5 mm magnetic bar. High efficiency condenser connected with upper neck of the flask for solvent recovery, this condenser already cooled by alcohol chiller at temperature of 256 K, the other neck fitted with the thermometer. The mixing carried out at room temperature with 1h mixing time and at 10ml:1g solvent to oil ratio.

Filtration and drying

The asphalt-solvent mixture introduced to the filtration process, where Buchner funnel (250 mm I.D) connected to the filtration flask fitted with filter paper for medium filtration speed. The filtration flask connected to a vacuum system includes a trap, condenser, and cooling machine. For removing of the remaining precipitate inside the mixing flask, washing solvent (hexane) was added and then filtrated. Then the filter paper placed in a hot electrical furnace (383 K) to evaporate the solvent associated with the precipitated asphaltenes for about 10 to 20 min. The dried filter paper then weighted to evaluate the percentage of asphaltenes yield.

Solvent recovery stage

The DAO-solvent mixture obtained from filtration stage introduced to a stripping stage in order to remove the solvent from the deasphaltened oil.

Hydrodesulfurization Unit

The desulfurization of deasphaltened oil was done in hydrotreating pilot plant continuous

high-pressure unit. Process flow diagram of the hydrodesulfurization unit employing a co-current up-flow. The unit consists of feed pump, reactor, high-pressure separator, and cooler.
The reactor used is a stainless steel with 19 mm inside diameter, 800 mm length and 3 mm wall thickness. The reactor supplied with 4 heaters (150 mm length for each) with 2 insulators (100 mm length). It was packed with 90 ml of the Co-Mo $/\gamma-Al_2O_3$ catalyst between two layers of inert glass balls. Catalyst presulfiding was made by passing commercial gas oil containing 0.6 vol.% Cs_2 through the catalyst bed. Firstly the catalyst treated for 3 h, at temperature 473 K, LHSV of 4 h^{-1} , pressure 2.2 MPa and no hydrogen flow. Then the operating conditions changed to 573 K, LHSV of 1 h^{-1}, pressure 2.2 MPa, H_2/oil 200 l/l and duration of experiment 16 hours. After that, the HDS run employed at reaction temperature 660 K with LHSV 1.3 h^{-1}. The gas flow was measured by gas meter by which controlled the H_2/ oil ratio (300 l/l).
The DAO was pumped co-current up-flow inside the reactor by high pressure-dosing pump (30-600 ml/h). The feed preheated and mixed with H_2 gas and entering the reactor. The reactor products were cooled in a condenser-cooler and separated from unreacted hydrogen, H_2S and hydrocarbon gases by passing into high and low-pressure separators.

Distillation of Hydrodesulfurization Products

The hydrotreating product was distilled at laboratory vacuum distillation for low boiling fractions separation. A 250 ml of the HDS product placed in a 500 ml distillation flask, supplied with a heating mantle of 2.4 kW. A voltage regulator was connected with the heating mantle for controlling the amount of heating supplied. Vertical high efficiency condenser was connected with the distillation flask, where a thermometer (623 K) fitted to measure the temperature of the vapors. Cooling machine was supplied by a cooled water (293 K) to a double shell receiver (outside shell) and though it to the condenser. The collecting flask was connected with the receiver, and a triple connector supplied for vacuum controlling, and it was already connected with the trap, trap (3-neck flask) was supplied for preventing vacuum pump damage. This trap connected with a vacuum pump through one way valve, and connected with a vacuum controller (Büch 165) from the another side. The vacuum distillation proceeded under 3 mmHg and a maximum vacuum temperature 593 K. This temperature equal to 803 K under atmospheric pressure.

Binder Preparation for Graphite Electrodes

The vacuum residue above 803 K obtained from HDS produced at 660 K and 1.3 h LHSV, was used as a basic component for binder production. Operating conditions of HDS was depended on a suitable density, viscosity as well as an acceptable level of sulfur & metals content. Anthracene with melting point 487-489 K and 1.25 specific gravity, was crushed and added at different percentages. Each mixture was mixed very well and introduced in an electrical furnace and heated to 523 K for 3 h to complete dispersion of anthracene particles in the residue media, the mixture then left for cooling overnight. A homogeneous binder was obtained.

Tests for the Feedstock and the Products

Density and Specific Gravity

The density and the specific gravity of the feedstock, deasphaltened oil and asphaltic binder were determined by using (ASTM D-287).

5.2 Viscosity

The viscosity of the feedstock, and deasphaltened oil were determined by using

(ASTM D-446).

5.3 Sulfur

The sulfur content of the feedstock determined by x-ray fluorescence (ASTM D-2622) and by quartz tube method (IP 63/55), while the deasphaltened oil and the hydrotreated product and asphaltic binder sulfur content determined by quartz tube method.

Carbon Residue

The carbon residue of asphalt, deasphaltened oil and asphaltic binder were determined by using ASTM D-189 and IP 13/66.

Ash Content

The ash content of the feedstock, deasphaltened oil and asphaltic binder were evaluated by using IP 4/65.

5.6 Softening Point (Ring and ball Method)

The softening point of the asphalt feedstock and ashaltic binder were determined by using ASTM D36-26.

Benzene and Quinoline Insolubles

The (BI) and (QI) were calculated for the asphaltic binder by using IP 47/74 standard method.

RESULTS & DISCUSSION

The properties of hydrotreated vacuum residue above 803 K distilled from the HDS of deasphaltened oil presented in **Table (1).**The standard range of graphite electrode binder properties((Hatano1989,Wagner1988and Mohammed). is shown in **Table (2).** Sulfur and ash contents are satisfies the required binder properties while softening point,density,BI and QI deviates. Therefore, anthracene is added to the binder basic component (hydrotreated vacuum residue above 803K) with different percentages. The binder properties with different anthracene content are shown in **Table (3). Figs. (1,2,3,4) and (5)** show the relationships between added anthracene weight percent and softening point, atomic C/H ratio, BI and QI respectively. The required binder must have 358K softening point(5). From Fig.1 the mixture with 25wt.% anthracene has the required softening point and could be used as graphite electrodes binder. The properties of this binder are shown in Table 4.

Table (1) The properties of hydrotreated vacuum residue above 803 K.

Property	**Unit**	**Data**
Boiling Range	**K**	**803+**
Specific Gravity	**-**	**1.017**
Softening Point	**K**	**308**
Coke Yield	**%**	**20.36**
Sulfur Content	**%**	**1.775**
Ash Content	**%**	**<0.125**
BI	**%**	**12.55**
QI	**%**	**16.21**

Table (2) The standard Properties of graphite electrodes binder (Hatano1989,Wagner1988 and Mohammed)

Property	Unit	Range
Softening Point	**K**	**312-373**
Specific Gravity	**-**	**1.16-1.3**
Coke Yield	**%**	**40.6-61.3**
Sulfur Content	**%**	**0.43-3**
Ash Content	**%**	**<0.125**
BI	**%**	**14.8-39.3**
QI	**%**	**3.4-14.1**
Atomic C/H Ratio	**-**	**1.64-1.95**

Table (3) Effect of Anthracene on the Binder Properties

Binder Properties	Unit	Anthracene wt.%			
		10	20	30	40
Softening point	**K**	**323**	**335**	**367**	**423**
Density	**g/cm3**	**1.25**	**1.13**	**1.85**	**2.05**
Coke yield	**Wt.%**	**39.9**	**46.0**	**58.23**	**65.60**
Ash	**Wt.%**	**0.023**	**0.023**	**0.02**	**0.02**
Sulfur	**Wt.%**	**1.56**	**1.20**	**1.046**	**0.9**
Atomic C/H ratio	**-**	**1.45**	**1.646**	**1.787**	**1.838**
BI	**Wt.%**	**14.0**	**16.05**	**22.20**	**23.0**
QI	**Wt.%**	**3.60**	**4.0**	**10.50**	**15.15**

Table (4) Properties of the Required Binder

Binder Properties	Unit	Anthracene wt.%
		25
Softening point	**K**	**358**
Density	**g/cm3**	**1.16**
Coke yield	**Wt.%**	**52.7**
Ash	**Wt.%**	**0.021**
Sulfur	**Wt.%**	**1.12**
Atomic C/H ratio	**-**	**1.75**
BI	**Wt.%**	**20.0**
QI	**Wt.%**	**8.60**

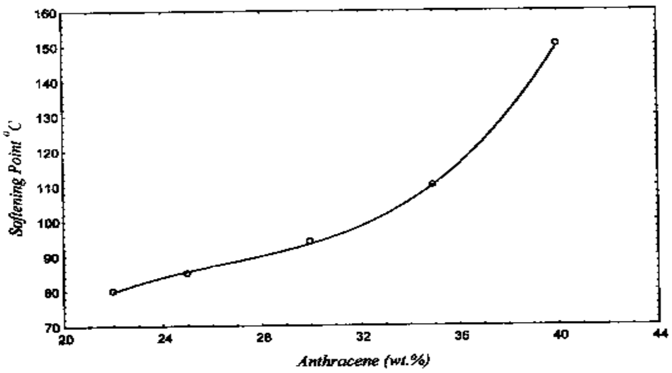

Fig.(1) Effect of Anthracene on the Softening Point

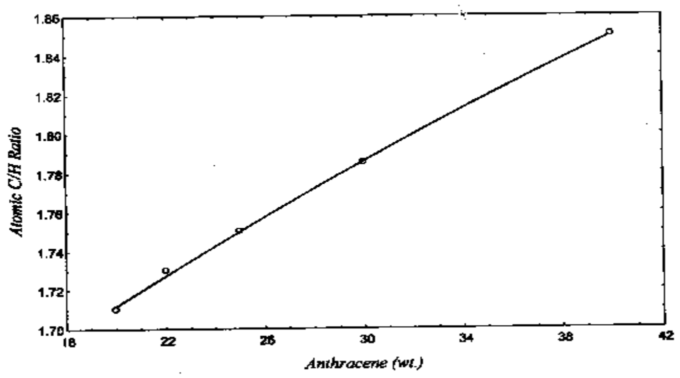

Fig.(2) Effect of Anthracene on the Atomic C/H Ratio

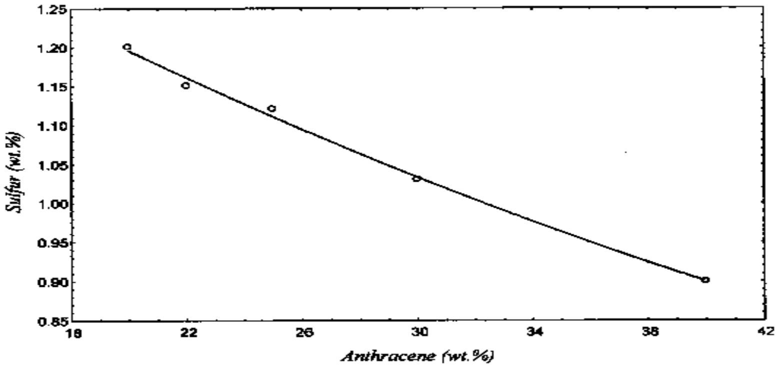

Fig. (3) Effect of Anthracene on the Binder Sulfer Content

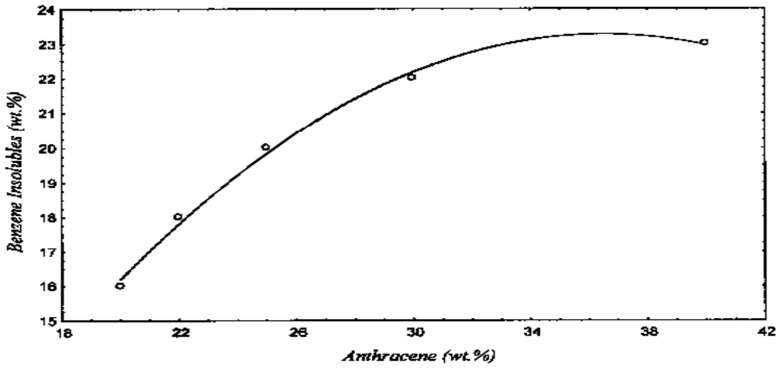

Fig.(4) Effect of Anthracene on the Binder Benzene Insoluble

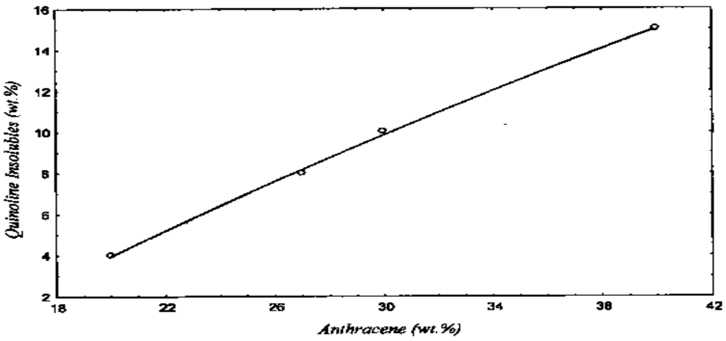

Fig.(5) Effect of Anthracene on the Quinoline Insolubles

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