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54 **Delayed coking of a heat-treated ethylene tar.**

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Description

This invention relates to delayed coking, and more particularly to delayed coking of premium coking feedstocks at conditions under which premium coke suitable for graphitization is formed.

It is well known that certain feedstocks, such as fluid catalytic cracking gas oil, thermal tar, coal extracts, mixtures thereof, and blends of the foregoing with limited amounts of residual petroleum fractions can be coked at conditions which produce a premium coke suitable for manufacture of graphitized articles such as graphite electrodes for use in the electric arc steel making process.

It is also known that ethylene tars from the steam pyrolysis ethylene process may be used as a feedstock component in a premium coking process.

The steam pyrolysis ethylene process which is the source of ethylene tar as used in this invention is described in *Hydrocarbon Processing*, November 1975, pp. 141—143.

In at least one commercial premium coking operation, ethylene tar was used as the entire feedstock, although the success of the operation has not been clearly established.

Generally, ethylene tars have lowered the quality of premium coke proportionately with their ratio in the feedstock. The reasons for this are not clear, and the extent of lowering varies with the source of the ethylene tar and probably with many other variables. One theory is that ethylene tars contain heavy asphaltenes which not only lower coke quality but also tend to produce furnace coil coking, which in turn necessitates costly shutdowns for furnace cleaning.

One method of determining characteristics of premium coking feedstocks is described in U.S. 4,043,898.

A process for producing premium coke using up to 10 percent ethylene tar as feedstock is described in U.S. Patent 4,130,475.

A method of heat soaking heavy hydrocarbons to increase the amount of toluene insolubles is described in U.S. Patent 3,673,077. This process does not utilize a hydrogen donor solvent.

French Patent 2,090,798 and United Kingdom Patent 1,351,295 both describe the pre-heating of an ethylene tar feedstock prior to coking. Neither process utilizes a hydrogen donor solvent.

According to the present invention there is provided a delayed coking process in which a premium coking feedstock including ethylene tar is introduced to the lower portion of a coker fractionator, transferred from said coker fractionator, to a coking furnace and then to a coking drum, and wherein said ethylene tar is heat soaked in the presence of a hydrogen donor at a temperature of from 260 to 430°C and for a time sufficient to substantially reduce the toluene insolubles content thereof prior to introduction to said coker fractionator.

The described embodiment of the invention

involves heat soaking ethylene tar in the presence of a hydrogen donor solvent and then utilizing the treated ethylene tar as feedstock to a premium coking operation.

Ethylene tar has been used as a feedstock component in premium coking operations. However, the use of ethylene tar has generally led to coke formation on the furnace coils and to a deterioration of the quality of the coke product, particularly in the area of the coefficient of thermal expansion of the graphitized coke. It is believed that both of these problems are the result of the presence of heavy asphaltenes in the ethylene tar. This invention is primarily directed to a process of treating ethylene tar to reduce the amount of heavy asphaltenes therein, with a resultant elimination of or reduction of the problems normally associated with coking material containing ethylene tar.

The process will be described generally with reference to the Figure. Coker feedstock enters coker fractionator 10 from line 12, and passes to coker furnace 14 where it is heated to coking temperature. The heated feedstock then passes into one of the two coke drums 16 and 18 which are filled alternatively while the other is being cooled and emptied. Vapors from the coke drum being filled are returned to the coker fractionator through line 20, and products are recovered from the coker fractionator in a conventional manner.

Ethylene tar is added through line 24 as a feedstock component, and prior to being introduced to the coker fractionator it is heat soaked in a vessel 22 in the presence of a hydrogen donor added through line 26.

The feedstock to the coker fractionator may be made up entirely of donor soaked ethylene tar, but preferably would comprise from 5 to 20 volume percent ethylene tar with the balance being thermal tar, decant oil from a fluid catalytic cracking operation (sometimes referred to as cycle oil or gas oil). Coal tars are sometimes utilized as premium coker feedstocks when they are available. Generally, premium coking feedstocks are highly aromatic hydrocarbon streams having relatively high boiling ranges.

The hydrogen donor material is generally a hydrocarbon which has the ability to take up hydrogen in a hydrogenation zone and readily release it in a thermal treating zone. It is believed that the hydrogen donor operates by yielding hydrogen atoms, thereby upgrading the ethylene tar and preventing condensation and/or polymerization of the ethylene tar. Hydrogen donor materials may be relatively pure chemicals such as tetralin or decalin or they may be a partially hydrogenated catalytic cycle oil, a partially hydrogenated lubricating oil extract or other partially hydrogenated aromatic material. Hydrogen donors usually contain condensed ring aromatics in sufficient quantities to serve as a hydrogen carrier. These aromatics are partially hydrogenated by addition of easily removable hydrogen atoms. After use in the heat soaking vessel 22, the hydrogen donor may be recovered

from fractionator 10, rehydrogenated, and reused as hydrogen donor solvent in the process.

The amount of hydrogen donor in relation to the amount of ethylene tar may vary considerably, but practical limitations suggest a range of from 0.2 to 5.0 times the volume of ethylene tar. A preferred amount of hydrogen donor is a volume of from 0.5 to 2.0 times the volume of ethylene tar.

The temperature in the heat soaking step may also vary considerably, but generally should be above 260°C to provide a reasonable rate of hydrogen transfer, and the maximum temperature is a temperature where thermal cracking becomes significant. Thermal cracking may occur to a significant amount at temperatures above about 450°C, and that should be considered an upper limit in the process.

The residence time in the heat soaking step varies inversely with the soaking temperature. At lower temperatures, such as 260°C or slightly greater, a time of many hours may be required to effect a substantial reduction in the amount of heavy asphaltenes in the ethylene tar. At temperatures near the upper limit, such as from 425—450°C, the time required is much shorter, such as a fraction of an hour. A soaking temperature of from 300°C to 380°C for a time of from one to three hours is preferred. However, there are situations in which a very long residence time is desirable or expedient, and in such cases a similar result can be obtained by maintaining the lower soaking temperature for a longer period of time.

The effectiveness of the process of this

invention in reducing the heavy asphaltenes in ethylene tar is demonstrated in the following examples in which the toluene insoluble material in the tar is reduced by heat soaking in the presence of a hydrogen donor.

Example 1

In this Example, the toluene insoluble material in an ethylene tar was determined to be 15.4 weight percent. The tar was then heat soaked at a temperature of 357°C for a time of 40 minutes, and the toluene insoluble material increased to 16.0 percent by weight. The same ethylene tar was then mixed with hydrogen donor material. The mixture was heat soaked at a temperature of 357°C for a time of 40 minutes, and the toluene insoluble material in the donor soaked tar was determined to be 10.5 percent by weight.

Example 2

In this example, the pentane insoluble fraction of an ethylene tar was run straight, diluted with a cutter solvent, and blended in varying proportions with cutter solvent and hydrogen donor. Each of the blends was soaked at a temperature of 357°C for a time of two hours, and the toluene insoluble fraction and the tetrahydrofuran insoluble fraction of each blend was determined. As illustrated in Table I, the amount of insoluble material was dramatically reduced for the case where one volume of hydrogen donor was heat soaked with one volume of asphaltenes from the ethylene tar. In the absence of the hydrogen donor material, the toluene insolubles and the THF insolubles increased significantly.

TABLE I

Feed	Temp. (°C)	Time (hours)	Toluene insol. wt. %	THF insol. wt. %
Ethylene tar asphaltenes	—	0	26	1
Ethylene tar asphaltenes	357	2	47	37
1:1 Asphaltenes: cutter solvent	357	2	33	14
1:0.9:1 Asphaltenes: cutter: donor	357	2	29	8
1:0.8:0.2 Asphaltenes: cutter: donor	357	2	26	1
1:0.5:0.5 Asphaltenes: cutter: donor	357	2	20	4
1:1 Asphaltenes: donor	357	2	5	0

Claims

1. A delayed coking process in which a premium coking feedstock including ethylene tar is introduced to the lower portion of a coker fractionator, transferred from said coker fractionator to a coking furnace and then to a coking drum, and wherein said ethylene tar is heat soaked in the presence of a hydrogen donor solvent at a temperature from 260 to 430°C and

for a time sufficient to substantially reduce the toluene insolubles content thereof prior to introduction to said coker fractionator.

2. A process as claimed in claim 1 wherein the amount of said ethylene tar is from 5 to 20 percent by weight of the total feedstock to said fractionator.

3. A process as claimed 1 or claim 2 wherein said ethylene tar is heat soaked at a temperature of from 310—380°C.

4. A process as claimed in any one of the preceding claims wherein said hydrogen donor is a partially hydrogenated gas oil from a fluid catalytic cracking operation.

5. A process as claimed in any one of the preceding claims wherein said ethylene tar is heat soaked in the presence of a volume of hydrogen donor of from 0.2 to 5.0 times the volume of ethylene tar.

6. A process as claimed in claim 5 wherein said hydrogen donor is present in a volume of from 0.5 to 2.0 times the volume of ethylene tar.

7. A process as claimed in claim 6 wherein said ethylene tar is heat soaked at a temperature of from 310 to 380°C for a time of 1 to 3 hours.

Patentansprüche

1. Verzögertes Verkokungsverfahren, bei dem ein Premiumverkokungsmaterial mit Äthylenteer in den unteren Teil einer Verkokungsfractionierkolonne eingeführt wird, von dort in einen Verkokungs-Ofen überführt wird und dann zu einer Verkokungstrommel, wobei der Äthylenteer in Anwesenheit eines Wasserstoffdonatorlösungsmittels bei einer Temperatur von 260 bis 430°C heiß eingeweicht wird für einen Zeitraum, der ausreicht, um den Anteil unlöslicher Toluole vor dem Eintritt in die Fraktionierkolonne wesentlich zu reduzieren.

2. Verfahren wie in Anspruch 1 beansprucht, bei dem die Menge des Äthylenteers 5 bis 20 Gew.% der gesamten Menge des der Fraktionierkolonne zuzuführenden Verkokungsmaterials ist.

3. Verfahren wie in Anspruch 1 oder 2 beansprucht, bei dem der Äthylenteer bei einer Temperatur von 310 bis 380°C eingeweicht wird.

4. Verfahren wie in einem der vorhergehenden Ansprüche, beansprucht, bei dem der Wasserstoffdonator ein teilweise hydriertes Gasöl aus einem katalytischen Fluidcrackprozess ist.

5. Verfahren wie in einem der vorhergehenden Ansprüche beansprucht, bei dem der Äthylenteer in Gegenwart des Wasserstoffdonators eingeweicht wird und die Menge des Wasserstoffdonators das 0,2 bis 5,0-fache der Menge des Äthylenteers beträgt.

6. Verfahren wie in Anspruch 5 beansprucht, bei dem die Menge des verwendeten Wasserstoff-

donators das 0,5 bis 2,0-fache der Menge des Äthylenteers beträgt.

7. Verfahren wie in Anspruch 6 beansprucht, bei dem der Äthylenteer bei einer Temperatur von 310 bis 380°C für die Dauer von 1 bis 3 Stunden eingeweicht wird.

Revendications

1. Procédé de cokéfaction retardée dans lequel une charge d'alimentation de cokéfaction de premier choix comprenant du goudron d'éthylène est introduite dans la partie inférieure d'une colonne de fractionnement d'une installation de cokéfaction, transférée depuis ladite colonne de fractionnement dans un four de cokéfaction et ensuite dans un tambour de cokéfaction, et dans lequel ledit goudron d'éthylène est trempé à chaud en présence d'un solvant donneur d'hydrogène à une température de 260 à 430°C et pendant une durée suffisante pour réduire sensiblement leur teneur en insolubles de toluène avant l'introduction dans ladite colonne de fractionnement de l'installation de cokéfaction.

2. Procédé selon la revendication 1, dans lequel la quantité dudit goudron d'éthylène est de 5 à 20% en poids de la charge d'alimentation totale destinée à ladite colonne de fractionnement.

3. Procédé selon la revendication 1 ou la revendication 2, dans lequel ledit goudron d'éthylène est trempé à chaud à une température de 310 et 380°C.

4. Procédé selon l'une quelconque des revendications précédentes, dans lequel le donneur d'hydrogène est un gazole partiellement hydrogéné provenant d'une opération de craquage catalytique fluide.

5. Procédé selon l'une quelconque des revendications précédentes, dans lequel ledit goudron d'éthylène est trempé à chaud en présence d'un volume de donneur d'hydrogène de 0,2 à 5,0 fois le volume de goudron d'éthylène.

6. Procédé selon la revendication 5, dans lequel ledit donneur d'hydrogène est présent dans un volume de 0,5 à 2,0 fois le volume de goudron d'éthylène.

7. Procédé selon la revendication 6, dans lequel ledit goudron d'éthylène est trempé à chaud à une température de 310 à 380°C pendant une période de 1 à 3 heures.

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