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3,817,853

COKING OF PYROLYSIS TARS

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No Drawing. Filed May 30, 1972, Ser. No. 257,605

Int. Cl. C10g 9/14

U.S. Cl. 208—50

9 Claims

ABSTRACT OF THE DISCLOSURE

Pyrolysis tars which are formed in the high temperature cracking, generally in the presence of an inert diluent, of a hydrocarbon distillate or gas fraction to prepare olefins such as ethylene, propylene, butene, styrene, etc., can be subjected to an improved coking process according to this invention. This invention comprises the pretreating of the pyrolysis tars prior to coking by a hydrogenation treatment, preferably at mild conditions, which can be effected in the presence or absence of a catalyst and/or inert diluent for the tar. The hydrogenation conditions can include temperatures from about 250° to about 800° F. and, when catalysts are employed, liquid hourly space velocities from 0.5 to about 10 volumes per volume per hour. The hydrogenation is effected to consume from 100 to about 2000 cubic feet of hydrogen per barrel of feedstock. Following this hydrogenation, the resulting partially hydrogenated pyrolysis tar is then coked in a conventional delayed coking operation employing coke drum temperatures from 775° to about 900° F. and pressures from atmospheric to about 250 p.s.i.g. to obtain an improved yield of distillate product, reduced yield of coke, and a coke of higher quality than can be obtained in the absence of such hydrogenation.

DESCRIPTION OF THE INVENTION

This invention relates to a coking process, and, in particular, to a process for coking of a pyrolysis tar wherein the yield of distillates is improved and the quality of coke produced by the coking process is also improved.

There is an increasing demand for coke which can be processed into premium quality graphite and, in particular, into graphite having a relatively low coefficient of the thermal expansion. This graphite is used as anode material by the steel industry. Unfortunately, there is also an increasing scarcity of the highly aromatic, suitable feedstock for the production of such premium coke. Ideally, the feedstock for production of premium coke is highly aromatic and major sources of such coke have been highly thermally or catalytically cracked cycle stocks such as the decant oil from a fluidized bed catalytic cracking unit. The recent advances in catalysis such as use of molecular sieve catalysts in catalytic cracking and the hydrogenation of catalytic cracker feedstocks have substantially increased the conversion of cycle stocks to lower boiling, useful distillates and the available supply of the decant oil for delayed coking and production of premium grade coke has been drastically curtailed.

Coincident with this decreasing supply of suitable stocks for production of premium grade coke has been an ever increasing supply of pyrolysis tars. These pyrolysis tars are produced in the high temperature thermal cracking of naphtha condensates and gas oils as well as low-boiling hydrocarbons such as ethane and propane. This cracking is performed at temperatures from about 1200° to 1800° F. and at pressures from 15 to about 30 p.s.i.a., often in the presence of an inert diluent such as steam. The products of this cracking operation are low-boiling olefins, principally ethylene, with approximately 15 to 30 percent propylene, depending upon the particular choice of feedstock. At higher temperatures, acetylene is produced in

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varying amounts. Butenes are also produced. A related process is the high temperature cracking at similar conditions of alkyl aromatics such as ethylbenzene for the production of styrene.

The increasing demand for plastics and finished products based on these olefinic monomers has resulted in a very substantially increased worldwide production of the monomers with an unavoidable coproduction of pyrolysis tars. The pyrolysis tars are highly aromatic and would, superficially, appear to comprise premium feedstocks for the production of quality coke products. Indeed, several investigators have patented processes for the production of premium coke from such feedstocks; see U.S. Pats. 3,326,796 and 3,451,921.

Unfortunately, however, the feedstocks are usually highly olefinic in nature, containing large amounts of alkenyl aromatics. When such olefinic feedstocks are heated to the necessary temperatures for delayed coking operations, coke is prematurely deposited in the heater tubes and the extent of this coke formation can be so great as to actually plug the tubes in a very short operating period. Some investigators have suggested admixing of the pyrolysis tar with a suitable low-boiling diluent to sweep the tar through the heater tubes without premature coke deposition; see U.S. Pat. 3,547,804. Unfortunately, however, even when special precautions are taken to avoid premature coke deposition with the highly olefinic aromatic pyrolysis tars, a quality coke product is still not obtained. Instead, it is a more common experience to obtain coke which, when graphitized, yields products having coefficients of thermal expansion of 25 to about 35×10^{-7} inch per inch per degree centigrade when measured in the range of around room temperature to about 200° C. Quality graphite should have coefficients of about 3 to 15×10^{-7} , preferably of 3 to 7×10^{-7} inch per inch per degree centigrade.

It is an object of this invention to provide an improved method for the efficient disposal of pyrolysis tars.

It is also an object of this invention to provide a process for the conversion of pyrolysis tars into high yields of useful distillate products.

It is an added object of this invention to provide a process for the production of a reduced quantity of coke from pyrolysis tars.

It is a further object of this invention to provide a process for the production of quality coke products from pyrolysis tars.

Other and related objects will be apparent from the following description of the invention.

I have now found that pyrolysis tars can be coked to produce an increased yield of useable distillate products and decreased yield of coke, which coke has, furthermore, an improved quality and is better suited for graphitizing into graphite products. I have found that these results can be achieved by subjecting the pyrolysis tar to a hydrogenation treatment preparatory to the coking operation. The hydrogenation treatment is effected at mild conditions, thermally or catalytically, at temperatures from 250° to about 800° F.; preferably from 375° to 600° F.; so as to consume approximately 100 to about 2000; preferably from 300 to 1000; cubic feet of hydrogen per barrel of pyrolysis tar feedstock. When catalysts are used, the space velocity employed should be from 0.5 to about 10, preferably from 1 to about 7, liquid volumes per catalyst volume per hour.

The result of the production of a coke which can be graphitized into premium grade graphite from a hydrogenated feedstock is quite surprising. It is generally believed that the more highly aromatic the feedstock, the higher quality is the coke product. Hydrogenation, however, destroys aromatics by their conversion to the satu-

rated cyclohexyl hydrocarbons. The mild hydrogenation of a feedstock prior to coking would, therefore, to all expectations, lead to degradation of the quality of the coke product. I have found, however, that the opposite is true, particularly when the hydrogenation is effected at relatively mild conditions as set forth herein. The hydrogenation treatment also permits a more facile heating of the feedstock since the tendency of the feedstock to deposit coke prematurely in the heater tubes is substantially eliminated. Finally, the yield of coke is reduced in favor of increased production of the more valuable and useable distillate products, particularly the increased production of gasoline and gas oil fractions.

The pyrolysis tar which is subjected to the treatment of this invention can be any tar produced by the high temperature thermal cracking in pyrolysis furnaces to produce low molecular weight olefins. In general, olefins comprising chiefly ethylene with lesser amounts of propylene, butene and isobutylene are produced by the severe cracking of petroleum distillates or residues at temperatures from 1200° to about 1800° F., preferably from 1300° to about 1600° F. at pressures from atmospheric to about 15 p.s.i.g. and in the presence of a diluent gas. Typical diluents employed are low-boiling hydrocarbons such as methane, ethane or propane, although steam is the preferred and most commonly employed diluent. Ethane and propane can also serve as the cracking stock. The products of this cracking operation are predominantly olefinic gases such as ethylene, propylene and butene. A heavy pyrolysis tar is obtained from this cracking operation and is removed with the effluent therefrom and separated by condensation. The pyrolysis tar has a high olefinic content and is therefore unstable to subsequent heating since it has the aforementioned tendency to deposit coke prematurely in the heating tubes of furnaces employed for its subsequent conversion. The material, however, also has an appreciable content of condensed polycyclic aromatic hydrocarbons.

The pyrolysis tar is processed in accordance with this invention by subjecting it to relatively mild hydrogenation conditions. The hydrogenation temperatures should be from 250° to 800° F., preferably from about 375° to about 600° F. The hydrogenation should be effected at a pressure of from 100 to about 1500 p.s.i.g., preferably from about 200 to about 1000 p.s.i.g. with hydrogen being added as necessary to maintain the pressure. Most preferably, the hydrogenation is effected in the presence of a catalyst which comprises a hydrogenation component deposited on a suitable inert carrier. Examples of the various hydrogenation components include the metals, salts, oxides or sulfides of the metals of Periodic Groups VIII and VI-B, e.g., chromium, molybdenum, tungsten, iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium and platinum. The particular catalyst employed is not critical to the invention and any of the conventional catalysts used for hydrogenation can be employed.

These catalysts are typically distended on a suitable inert support of carbon, e.g., activated carbon, or a dried and calcined gel of an amphoteric metal oxide, e.g., alumina, titania, thoria, silica, or mixtures thereof. Perhaps the most commonly employed carriers are the silica and alumina-containing carriers or mixtures thereof. The mixtures can be physical or co-gelled mixtures of silica and alumina or can be various naturally occurring aluminosilicates, e.g., clays such as montmorillonites, kaolinites, etc., zeolites such as faujasite, gnelenite, chabazite, etc. Any of the various synthetic prepared zeolites can be used such as the synthetic molecular sieves which are characterized by a relatively uniform pore diameter from 5 to about 15 Angstrom units and a crystalline structure. Methods for the preparation of such zeolites are disclosed in U.S. Pats. 2,882,243 and 2,882,244, as well as a large number of subsequently

patented zeolites of the X, Y, J, L and other crystal designations.

The catalytically active component for the hydrogenation is distributed or distended on such an inert support by various methods including ion exchange for use on the supports having base exchange capacity such as the zeolites and synthetically prepared molecular sieves, impregnation, coprecipitation, or simply physical mixture of a compound such as an oxide or salt of the metal with the gelled carrier.

Various methods of contacting can also be employed for effecting catalysis of the hydrogenation. The catalyst can be finely subdivided with particles having diameters in the range of 1 to about 50 microns and can be suspended in the charge stock during its hydrogenation. Similarly, the particles can be slightly larger particle size, e.g., in the size range passing about a 60 mesh but retained on a 325 mesh screen and can be maintained as a fluidized bed in a typical fluidized operation through which the pyrolysis tar and hydrogen are passed. Most preferably, the particles are prepared with average diameters from $\frac{1}{32}$ to $\frac{1}{4}$ inch and are maintained as a fixed bed of particles in a reactor through which the pyrolysis tar and hydrogen are passed. Regardless of the contacting technique, space velocities from 0.5 to about 10 liquid volumes per volume per hour, preferably from 1.0 to about 4.0 liquid volumes per volume per hour are employed.

If desired, the pyrolysis tar can be admixed with a suitable inert diluent during the hydrogenation to minimize the tendency of the stock to deposit coke in the heating tubes of the furnace used for its preheating to the necessary hydrogenation temperatures. Various inert diluents can be used such as petroleum distillates, e.g., naphtha, gas, oil, kerosene, etc. Other diluents that can be used comprise relatively highly aromatic materials such as naphthalene, tetralin, decalin, benzene, alkylbenzenes, e.g., toluene, xylene, pseudocumene, durene, etc. The amount of inert diluent is preferably minimized for most efficient processing. Generally, the amount of diluent employed can be from 5 to about 45, preferably from 10 to about 25 percent of the pyrolysis tar subjected to the hydrogenation.

Upon completion of the hydrogenation reaction, the pyrolysis tar can be distilled to separate any low boiling distillate products which are formed during the hydrogenation and to separate any of the inert diluent that may have been used in its processing. The production of low boiling distillate products is minimized in the hydrogenation treatment by the mild conditions of temperature and space velocity employed. Generally, the degree of conversion to lower boiling products will be less than about 5 volume percent and, often, will be negligible. Accordingly, the pyrolysis tar can be directed to the coking operation without any intervening distillation or removal of the inert diluent. The inert diluent, when used in such direct processing, can therefore be also passed through the heater tubes of the heater in the coking operation and be removed from the coking operation as an effluent from the coking drum.

The coking process employed in the invention is fairly conventional in conditions and operations, the significant change comprising the mild hydrogenation of a pyrolysis tar prior to the coking. The coking operation generally employs a furnace with heating tubes through which the oil to be coked is passed and heated therein to temperatures from about 900° to about 970° F., preferably from 920° to about 970° F. at pressures from atmospheric to about 250 p.s.i.g., preferably from about 15 to about 150 p.s.i.g. coil outlet or drum pressure. Upon reaching the desired preheat temperature, the charge stock is discharged into a coking vessel, generally by being introduced into the bottom of the vessel and permitted to flow upwardly therethrough.

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The coking vessel has an overhead line from which vaporous products from the coking operation can be withdrawn and passed to a fractionator. The remaining residue undergoes cracking and becomes reduced to dry coke and vapors which are removed overhead, condensed, fractionated and processed in accordance with the particular refinery's requirements.

The dry coke accumulates in the coking vessel until the vessel has become substantially filled with coke and, at that time, the charge stock is diverted into another, adjacent vessel. The coke is stripped of any remaining liquid products and the coke drum is then cooled, opened and the coke is removed therefrom by the use of water jets, drills, rams or other equipment for dislodging the coke from the vessel.

Absolute coke yields from pyrolysis tars will vary greatly depending upon the specific gravity, source and carbon residue of the pyrolysis tar and also upon the operating conditions, especially pressure and recycle ratio employed in the coking operation. Thus, coke yields from about 15 to 60 percent may be obtained depending upon the variables of charge stock and operating conditions outlined above. However, it has been found that in a typical coking operation with the mildly hydrogenated pyrolysis tars employed in this invention, the yield of coke produced is from about 30 to 75 percent of that which is produced when the pyrolysis tar is subjected to coking without any prior treatment. This reduced quantity of coke production is also reflected in the increased yield of more valuable and useable distillate products, chiefly a coker naphtha distillate. It has also been observed that the mildly hydrogenated pyrolysis tar is much less prone to premature deposition of coke and substantially no problems are encountered in the preheating of the pyrolysis tar to the necessary coking temperature even when such preheating is performed in the absence of any diluent or other low-boiling hydrocarbon. Finally, the quality of the coke product is improved and coke which has been produced in accordance with this invention, when graphitized, will yield products having lower coefficient of thermal expansions than coke products which are obtained from the coking of pyrolysis tar which has not been prehydrogenated.

The invention will now be described in reference to the following examples which will illustrate modes of practice thereof and demonstrate the results obtainable thereby.

EXAMPLE 1

The experiments were performed in a laboratory coking unit in which the oil is preheated in a coking coil 0.4 inch internal diameter and 10 feet in length. The preheated oil is discharged into the bottom of a cylindrical chamber having a 6-inch inside diameter and 36 inches in height. The oil is discharged into the bottom of the cylindrical chamber which is in an upright position and the coke accumulates therein as the level of oil rises in the chamber. The top of the vessel has a vapor withdrawal conduit of 0.4 inch diameter and vapors are removed from the drum. In the coking, the charge stock is heated to a temperature of 915° F. and is discharged into the coking zone at a pressure of 50 p.s.i.g. The coking is performed for a period of 4 hours and the temperature in the coking drum is observed to vary between 849° and 853° F. during the coking operation. The coking is operated on a once-through basis with no recycle.

Prior to coking of the pyrolysis tar, the tar is subjected to mild hydrogenation. The hydrogenation is effected by admixing, with the pyrolysis tar, 29.6 weight percent of tetralin and the combined mixture is passed to a fixed bed catalytic hydrogenation unit. The catalyst employed in this hydrogenation is a cobalt molybdate catalyst on an alumina support which is stabilized with approximately 5 weight percent silica. The catalyst has a particle diameter of about 1/8 inch and is disclosed as a packed bed in the hydrogenation reactor.

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In separate experiments, a mixture of the pyrolysis tar with 29.6 weight percent tetralin is subjected to hydrogenation in the presence of 1500 standard cubic feet of hydrogen per barrel of tar. The hydrogenation is performed in both experiments at 1000 p.s.i.g. with space velocities of 2.0 liquid volumes per volume per hour. The temperature in one hydrogenation experiment is 550° F. and in the second experiment is 750° F. The hydrogen consumption in the first experiment is 429 standard cubic feet per barrel and 665 standard cubic feet per barrel in the second experiment. The conversion to liquid product in the first experiment is about 3.2 percent and 4.3 percent in the second experiment.

Upon completion of the hydrogenation, the hydrogenated effluent is distilled to remove the tetralin and minor amounts of low-boiling products formed from the hydrogenation and the residue is then subjected to coking at the aforementioned conditions in the laboratory coking apparatus. A third coking experiment is performed on the non-hydrogenated pyrolysis tar. The following table summarizes the results of the coking experiments:

TABLE 1

	Experiment		
	No. 1 ¹	No. 2 ²	No. 3 ³
Product distribution:			
Coke.....	6.7	11.2	17.2
Distillate.....	90.1	84.3	74.8
Slops.....	1.4	2.4	6.7
Gas.....	1.8	2.1	1.3
Product properties:			
Gas mol weight.....	18.68	18.05	19.21
Distillate gravity, ° API.....	9.5	9.8	8.1
Coke VCM, ⁴ weight, percent.....	10.4	15.2	9.4

¹ 550° F.

² 750° F.

³ Non-hydrogenated.

⁴ Volatile combustible material.

The coking Experiment No. 3 on the non-hydrogenated pyrolysis tar is terminated a short time after starting because the heating equipment becomes plugged by the coke and tar. The run is continued for a sufficiently long time, however, to obtain reliable data.

The coke obtained in the coking experiments is calcined by heating to a temperature of about 2500° F. and the resulting calcined coke is comminuted and blended with a coal tar binder, the blend is extruded and the extrudate is baked by heating to a temperature of about 1800° F. The baked carbon is then graphitized by heating to a temperature of about 3900° F. in an electrical graphite resistance graphite furnace to obtain samples of graphite. The graphic samples are analyzed to determine its coefficient of thermal expansion over a range of temperatures from 50° to 125° C. using a Theta CTE instrument having a differential transformer unit manufactured by Labtronics, Inc. The following table sets forth the results obtained by these experiments:

TABLE 2

Exp. No.	Charge stock	Graphite properties		
		Apparent density	Resistivity	CTE
1.....	Hydrogenated at 550° F.....	1.471	6.2	15.8
2.....	Hydrogenated at 750° F.....	1.462	7.2	22.6
3.....	Unhydrogenated tar.....	1.539	4.6	25.0

The preceding data evidence that the mild hydrogenation of the pyrolysis tar is effective to reduce substantially the yield of coke, to reduce the VCM content of the coke and thereby reduce the calcining requirements, to increase the yield of useable distillate products and to increase the quality of the coke by producing a coke which can be graphitized to a product having improved properties.

The pyrolysis tar used in the preceding experiments has the following analysis:

Gravity -----	° API--	1	
Average molecular weight -----		225	
Pour point -----	° F--	-150	5
Sulfur -----	percent--	0.3	
Nitrogen -----	do--	0.003	
Carbon -----	do--	93	
Hydrogen -----	do--	7	
Viscosity, SSU/210° F. -----		45	10
Carbon residue -----	percent--	11	
Initial boiling point -----	° F--	383	
50 percent boiling point -----	° F--	590	
95 percent boiling point -----	° F--	915	
Aromatic content -----	percent--	90.5	15
Aliphatic olefins -----	do--	2.1	
Saturates -----	do--	0.3	
Olefinic materials ¹ -----	do--	69.5	

¹ Present as alkenyl aromatics.

The preceding example has been set forth solely to illustrate a mode of practice of the invention and to demonstrate results obtainable thereby. It is not intended by this illustration to limit the invention; instead, it is intended that the invention be defined by the materials and steps and their obvious equivalents set forth in the following claims.

I claim:

1. The method for producing useful products from a pyrolysis tar which comprises subjecting a feedstock which is a high-boiling residue produced in the high temperature thermal cracking of petroleum distillate feedstocks at temperatures from 1200°-1800° F. and the presence of a diluent gas to produce light olefins to mild hydrogenation by contacting said pyrolysis tar with hydrogen at a temperature from about 250° to about 800° F. under conditions sufficient to effect a consumption of hydrogen from 100 to about 2000 standard cubic feet per barrel of said pyrolysis tar and thereby produce a mildly hydrogenated pyrolysis tar without producing more than about 5 volume percent lower boiling products, heating said mildly hydrogenated pyrolysis tar to a temperature

from 850° to about 1000° F. and passing said heated pyrolysis tar to a soaking drum and permitting said tar to crack and form vapors and coke therein.

2. The method of claim 1 wherein said hydrogenation is performed at a temperature no greater than about 600° F.

3. The method of claim 1 wherein said hydrogen consumption is from 300 to about 1000 standard cubic feet per barrel of said tar.

4. The method of claim 1 wherein said hydrogenation is performed in the presence of a diluent.

5. The method of claim 4 wherein said hydrogenation is performed in the presence of catalytic amounts of the metal, salt, oxide or sulfide of a Group VI-B and VIII metal distended on an inert support.

6. The method of claim 5 wherein said hydrogenation is effected at hourly space velocity of from 0.5 to about 10 liquid volumes per catalyst volume.

7. The method of claim 1 wherein said coking is effected in a delayed coking process wherein the preheated and hydrogenated pyrolysis tar is introduced into the bottom of a vertically disposed drum and the vapors are removed overhead therefrom.

8. The method of claim 1 wherein said hydrogenated pyrolysis tar is heated to a temperature of from 920° to about 970° F.

9. The method of claim 1 wherein the pressure on the tar in said drum is maintained from 15 to about 150 p.s.i.g.

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HERBERT LEVINE, Primary Examiner

U.S. Cl. X.R.

208—89, 131