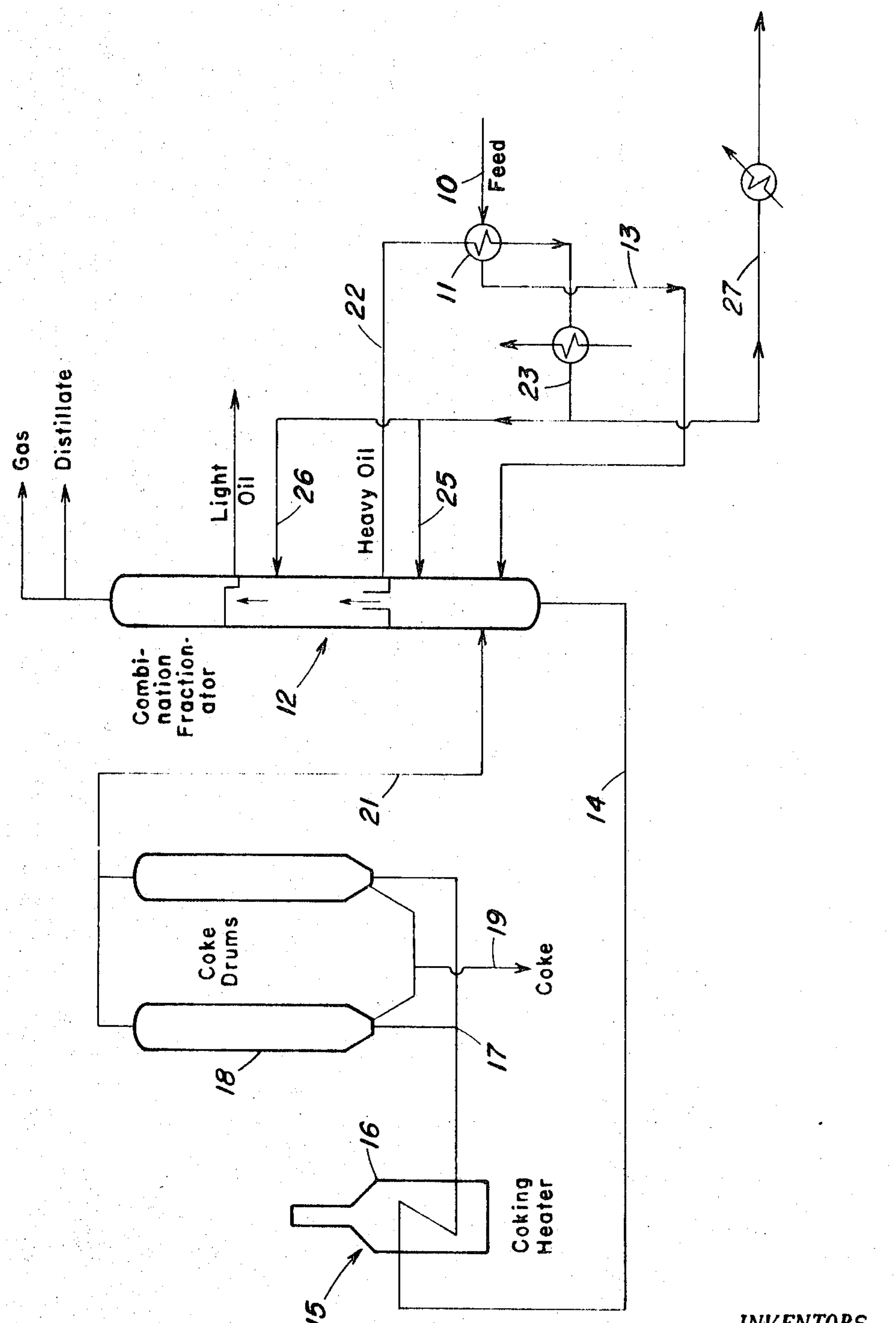
Feb. 16, 1971 W. J. BLOOMER ET AL 3,563,884

DELAYED COKING OF COAL TAR PITCHES

Filed July 15, 1968



INVENTORS
Ward J. Bloomer
WILLIAM P. BRISON, DECEASED
BY: ETHEL N. BRISON, EXECUTRIX
BY Marn & Jangarathis
ATTORNEYS

United States Patent Office

3,563,884

Patented Feb. 16, 1971

1

3,563,884

DELAYED COKING OF COAL TAR PITCHES

Ward J. Bloomer, Westfield, N.J., and William P. Brison, deceased, late of Glen Rock, N.J., by Ethel N. Brison, executrix, Glen Rock, N.J., assignors to The Lummus Company, Bloomfield, N.J., a corporation of Delaware

Filed July 15, 1968, Ser. No. 746,706

Int. Cl. C10g *9/14*

U.S. Cl. 208—81 4 Claims

ABSTRACT OF THE DISCLOSURE

Process for the delayed coking of a liquid feed or a fraction thereof having a high content of condensed ring aromatic compounds and an initial boiling point of not less than 600° F., wherein the unit is operated at a coking heater temperature of 900°–960° F., a coke drum overhead temperature of 840° F.–900° F., and pressure of 15–90 p.s.i.g. and the coker combination fractionator is operated at a temperature and pressure to recover a heavy oil having an initial boiling point of 600° F.–750° F. The recycle of a portion of the overhead from the coking drums introduced into the fractionator is at a volumetric rate of 0.3–0.6:1, based on equivalent feed introduced into the coking heater. Operation of the delayed coking unit under the above conditions prevents the runaway reactions heretofore encountered when attempting to delay coke such feeds.

This invention relates to the production of coke and more particularly to a new and improved process for the delayed coking of liquid feed stocks having a high content of polynuclear aromatic compounds.

The delayed coking of petroleum derived residual oils is one of the more important processes in the petrochemical industry in that both coke and a series of useful gas and liquid products may be produced thereby. Thus, the residual oils may be converted to C_2 and lighter gases, liquefied petroleum gases (LPG), light gasoline, heavy gasoline for catalytic reforming, light gas oil which may be treated to produce diesel or furnace oil and heavy gas oil for feed to a catalytic cracking operation.

Attempts have been made to apply delayed coking techniques to highly polynuclear aromatic feed stocks, such as coal tar pitches, but such attempts have met with little success, mainly due to the unstable nature of such feed stocks. Thus, prior workers have reported considerable coke laydown and foaming in the heater and runaway exothermic reactions in the heater and coke drums. Consequently, attempts to effect delayed coking of such highly polynuclear aromatic feeds have been virtually abandoned.

Accordingly, an object of this invention is to provide an effective process for the delayed coking of liquid feeds having a high content of polynuclear aromatic compounds.

Another object of this invention is to provide a new and improved process for the delayed coking of liquid feed stocks having a high content of polynuclear aromatic compounds that eliminates previously encountered problems.

A further object of this invention is to provide a process particularly adapted to producing coke and other useful products from coal tar pitches.

These and other objects of the invention should be readily apparaent from the following detailed description thereof.

The objects of this invention are broadly accomplished by effecting the delayed coking of a high boiling liquid feed stock having a high content of polynuclear aromatic compounds in a delayed coking unit of the type conventionally employed for the delayed coking of petroleum de-

2

rived feed stocks, except that the unit is operated at a coke drum overhead temperature of between about 840° F. and about 900° F., preferably between about 860° F. and about 900° F., and a volumetric recycle ratio of between about 0.3:1 and about 0.6:1, preferably between about 0.5:1 and about 0.6:1, based on equivalent fresh feed. The term "equivalent fresh feed" as used herein means the total feed introduced into the coking heater after flashing therefrom material boiling below the end point of the light oil to be recovered. Thus, in the conventional delayed coking unit, the feed is introduced into the bottom of the coker fractionator and material below the end point of the light oil to be recovered in the fractionator is flashed therefrom. Thus, the equivalent fresh feed is the total feed introduced into the fractionator minus the material flashed from the feed in the fractionator.

The liquid feeds treated in accordance with the invention have a high content; i.e., generally greater than about 70%, of condensed ring (polynuclear) aromatic compounds, both heterocyclic and isocyclic, and an initial boiling point no lower than about 600° F., generally an initial boiling point between about 600° F. and about 750° F., all converted to one atmosphere. A preferred feed is a coal tar pitch obtained by either the high temperature or low temperature carbonization of coal, as generally known in the art, the former feed particularly being generally characterized as completely comprised of condensed ring aromatic compounds (an estimated 5000 of such compounds), with two-thirds of the aromatic compounds being isocyclic and the remaining third heterocyclic. It is to be understood that the initial feed may be a feed which does not meet the hereinabove characteristics; i.e., a feed with an initial boiling point no lower than about 600° F. and a condensed aromatic ring content of greater than about 70%; e.g., a coal tar, provided the feed is first introduced into the fractionator of the delayed coking unit to remove the lower boiling components. Consequently, the process of the invention is generally applicable to feeds from which may be recovered a liquid fraction having an initial boiling point of no lower than about 600° F. and a condensed aromatic ring content of greater than about 70%.

The invention will now be described in more detail with respect to the embodiment thereof illustrated in the drawing and it is to be understood that the scope of the invention is not to be limited thereby. It is further to be understood that equipment, such as valves, pumps, etc., have been omited from the drawing to facilitate the description thereof and the placing of such equipment at appropriate places is deemed to be within the scope of those skilled in the art.

Referring now to the drawing, a liquid feed, such as, soft coal tar pitch derived from the high temperature carbonization of coal, in line **10** is passed through heat exchanger **11** to effect heating thereof by indirect heat transfer with a heavy oil fraction, as hereinafter described, and introduced into the bottom of the coker combination fractionator **12**, of a type known in the art, through line **13** to flash off material below the end point of the light gas oil to be recovered in the fractionator **12**; i.e., material boiling below a temperature within the range between about 600° F. and about 750° F., preferably below about 600° F. The operation of the fractionator **12** will be hereinafter more fully described.

A combined feed comprised of equivalent feed having an initial boiling point of no less than about 600° F. (the equivalent feed is the feed introduced into fractionator **12** through line **13** minus the material flashed off in the fractionator **12**) plus recycle, as hereinafter described, is withdrawn from the fractionator **12** through line **14** and introduced into a coking heater **15**, of a type known in the art. The coking heater is operated so as to produce an outlet temperature of between about 900° F. and about 960° F. The coking heater **15** is operated as generally known in the art to prevent premature coking therein; i.e., the feed is maintained in turbulent motion or at a high velocity by providing temperature and pressure profiles in the heater that will produce partial vaporization of the feed, thereby preventing the coking problems caused by slow moving feed in the liquid state. In addition, controlled amounts of steam may be introduced into the coking heater **15** through line **16** at appropriate places to obtain the required turbulence or high velocity.

The heated combined feed is withdrawn from the coking heater **15** through line **17** and introduced into coke drums **18**, of a type known in the art, wherein the heavier components of the feed are converted to coke and lighter components. The coking drums are operated at a pressure of between about 15 p.s.i.g. and about 90 p.s.i.g., preferably between about 25 and about 90 p.s.i.g. and an overhead temperature of between about 840° F. and about 900° F., preferably between about 860° F. and about 900° F. The coke is withdrawn from the drums **18** through line **19**.

An overhead is withdrawn from the coke drums **18** through line **21** and introduced into the coker combination fractionator **12** to recover the various components, as known in the art. The fractionator is generally run at an overhead temperature between about 300° F. and about 400° F., a bottoms chimney temperature of about 750° F. to about 810° F. and a pressure between about 25 and about 40 *p.s.i.g.* The overhead from the coke drum, is separated in the fractionator **12** into a light oil generally having cut points between about 400° F. and 750° F., preferably between about 400° F. and about 600° F., a heavy oil having an initial boiling point within the range between about 600° F. and about 750° F., preferably between about 600° F. and 700° F. and an overhead vapor stream comprised of distillate, generally boiling up to about 400° F., and gas.

In accordance with the invention, the heavy oil having an initial boiling point which falls somewhere within the range between about 600° F. and about 750° F., is withdrawn from the fractionator **12** through line **22**, cooled in heat exchanger **11** by indirect heat transfer with the feed in line **10** and further cooled in heat exchanger **23** to a temperature suitable for inducing required recycle in fractionator **12**, generally a temperature between about 400° F. and about 700° F., by indirect heat transfer with a suitable coolant, for example, boiler feed water. A portion of the cooled heavy oil from heat exchanger **23** is introduced into the fractionator **12** through line **25** at a rate to provide a volumetric recycle ratio of between about 0.3:1 and about 0.6:1, preferably between 0.5:1 and about 0.6:1, based upon equivalent feed. Thus, the total recycle is comprised of the heavy oil fraction recovered from the coke drum overhead in fractionator **12**, returned through line **25** and a condensed portion of the coke overhead vapors introduced through line **21**, the condensation being induced by direct contact with the cooled heavy oil fraction. The remaining heavy oil from heat exchanger **23** is passed through line **26** to maintain desired operating conditions in the fractionator **12** and through line **27** to storage and/or further treatment.

Although applicants do not wish to limit the invention by any theoretical reasoning, it is believed that by employing recycle ratios, as hereinabove described, the coke drum overhead temperature is maintained within the hereinabove described limits by vaporization and exothermic cracking of recycle in the coke drums thereby essentially eliminating the tendency toward an exothermic runaway reaction.

Numerous modifications of the invention are possible within the spirit and scope thereof. Thus, for example, the feed may be treated to effect vaporization of material below the end point of the light gas oil to be recovered in the delayed coking process in apparatus other than the coker combination fractionator. Similarly, the various heat transfer steps may be effected otherwise than as hereinabove described, for example, the feed to the combination fractionator may be heated in the coking heater or another heater.

The above modifications and numerous other modifications should be apparent to those skilled in the art from the teachings herein.

The invention is further illustrated by the following example, but the scope of the invention is not to be limited thereby.

EXAMPLE

A soft tar pitch derived from the high temperature carbonization of coal, having the properties of Table I is coked in accordance with the conditions of Table II.

TABLE I

Sp. grav., 60/60° F.	1.2225
Sp. grav., 77/77° F.	1.2188
Visc. SFS, 180° F.	11.5
Visc. SFS, 210° F.	38.0
Pour point, ° F.	75
Conr. carbon, wt. percent	31.2
Ash, wt. percent	0.02
Sulfur, wt. percent	0.6
Naphthalene content, wt. percent	1.21
Distillation, ° F.:	
IBP	431
5%	575
50%	620

TABLE II

	Temp., ° F.	Pressure, p.s.i.g.	Flow rate, #/hr.
Line:			
13	497	30	39,000
14	600	200	65,450
17	920	75	65,450
21	870	30	44,160
25	400	30	10,600

The heavy gas oil recycled through line **25** provides a recycle ratio of 0.5:1 by volume, based on equivalent feed.

The fractionator **12** is operated at an overhead temperature of 355° F. and pressure of 25 p.s.i.g., and a bottoms chimney temperature of 800° F. and pressure of 30 p.s.i.g., whereby the initial boiling point of the equivalent feed is about 600° F. and the following liquid products are recovered, based on total feed.

Component	Amount, #/hr.	Wt. percent, fresh feed
Gas	880	2.25
Distillate, End Point 400° F	97	0.25
Light Oil, 400° F.–600° F	3,880	9.95
Heavy Oil (Line 27) 600°+ F	12,543	32.15

Coke is produced at a rate of 21,600 lbs./hr. (55.40 wt. percent, based on fresh feed) and has the following properties:

Ash (wt. percent)	0.08
Sulfur (wt. percent)	0.36
Volatile matter (wt. percent)	7–14
Fixed carbon (wt. percent)	86–93

In accordance with the invention, liquid feeds having a high content of condensed ring aromatic compounds are upgraded by a delayed coking procedure without either a runaway exothermic reaction or excessive coke laydown and foaming in the heater. The effective delayed coking of such feeds; e.g., coal derived pitches, is advantageous in that apprecibaly higher coke yields, in comparison to feeds derived from petroleum crudes, are secured because of the increased carbon residue of the pitch feeds. In addition, the coke obtained in accordance with the invention, unlike coke obtained from crude petroleum derived feeds, has a very low sulfur content by virtue of decomposition of the predominately organic sulfur content of the pitch; the final product has about one-half the initial sulfur content of the pitch.

Furthermore, the coke produced in accordance with the invention has an extremely low ash content; from nil to a maximum of about 0.1, which makes the coke eminently suitable for the production of high purity metals; e.g., in the electrolytic reduction of alumina.

The liquid products recovered in the coker combination fractionator is similar to a commercial heavy tar distillate; i.e., the total distillate comprises aromatic fractions similar to those characterized in the coal tar industry as tar light oil, carbolic oil, naphthalene oil, and wash oil.

Numerous modifications and variations of the present invention are possible in light of the above teachings and, therefore, within the scope of the appended claims the invention may be practiced otherwise than as specifically described.

What is claimed is:

1. A process for the delayed coking of a coal tar pitch, comprising:

(a) introducing a feed containing coal tar pitch into the bottom of a coker-combination fractionation zone operating at a bottoms chimney temperature from about 750° F. to about 810° F., an overhead temperature from about 300° F. to about 400° F., a pressure from about 25 to about 40 p.s.i.g. and a volumetric recycle ratio of from about 0.3:1 to about 0.6:1 based on equivalent fresh feed;

(b) withdrawing recycle and a fraction having an initial boiling point of no lower than about 600° F. from said coker-combination fractionation zone, said fraction being the equivalent fresh feed;

(c) introducing a mixture of the fraction and recycle into a heating zone to effect heating thereof to a temperature from about 900° F. to about 960° F.;

(d) introducing the heated mixture into a coking zone operated at an overhead temperature from about 840° F. to about 900° F. to effect coking thereof;

(e) recovering coke from said coking zone;

(f) recovering an overhead from said coking zone; and

(g) introducing overhead from the coking zone into the coker-combination fractionation zone.

2. The process as defined in claim **1** wherein the coking zone is operated at a pressure between about 15 p.s.i.g. and about 90 p.s.i.g.

3. The process as defined in claim **2** wherein the coking zone is operated at a temperature between about 860° F. and about 900° F.

4. The process as defined in claim **1** and further comprising: recovering a heavy oil fraction from the coker-combination fractionation zone having an initial boiling point which falls within the range from about 600° F. to about 750° F. and cooling and returning a portion of the heavy oil fraction to the coker-combination fractionation zone to provide said recycle.

References Cited

UNITED STATES PATENTS

3,109,803	11/1963	Bloomer et al.	208—131
3,369,992	2/1968	Henke et al.	208—131
3,375,188	3/1968	Bloomer	208—131
3,379,638	4/1968	Bloomer et al.	208—131
3,440,163	4/1969	Hamner	208—127
2,752,290	6/1956	Beattie	208—131
2,901,416	8/1959	Tate	208—83
2,905,623	9/1959	Moser	208—83
2,922,755	1/1960	Hackley	208—106
3,035,989	5/1962	Mitchell	201—17
3,116,231	12/1963	Adee	208—46
3,338,817	8/1967	Zrinscak et al.	208—46

OTHER REFERENCES

Mekler et al., "New Developments and Techniques In Delayed Coking" presented May 28, 1959, reprinted by The Lummus Co., New York, N.Y., pages 1 to 17.

HERBERT LEVINE, Primary Examiner

U.S. Cl. X.R.

208—83, 131