Methods of treating coal tar using reactive distillation are described. The methods include introducing a coal tar stream into a reactive distillation zone which has a reaction zone and a separation zone. The reaction zone contains a hydrotreating catalyst and an absorbent. The coal tar stream is contacted with a hydrogen stream in the reaction zone to remove contaminants from the coal tar stream, and the treated coal tar stream is separated into at least two fractions.
METHOD FOR TREATING COAL TAR USING REACTIVE DISTILLATION

This application claims the benefit of Provisional Application Ser. No. 61/905,912 filed Nov. 19, 2013, entitled Method for Treating Coal Tar Using Reactive Distillation.

BACKGROUND OF THE INVENTION

Many different types of chemicals are produced from the processing of petroleum. However, petroleum is becoming more expensive because of increased demand in recent decades.

Therefore, attempts have been made to provide alternative sources for the starting materials for manufacturing chemicals. Attention is now being focused on producing liquid hydrocarbons from solid carbonaceous materials, such as coal, which is available in large quantities in countries such as the United States and China.

Pyrolysis of coal produces coke and coal tar. The coke-making or “coking” process consists of heating the material in closed vessels in the absence of oxygen to very high temperatures. Coke is a porous but hard residue that is mostly carbon and inorganic ash, which is used in making steel.

Coal tar is the volatile material that is driven off during heating, and it comprises a mixture of a number of hydrocarbon compounds. It can be separated to yield a variety of organic compounds, such as benzene, toluene, xylene, naphthalene, anthracene, and phenanthrene. These organic compounds can be used to make numerous products, for example, dyes, drugs, explosives, flavorings, perfumes, preservatives, synthetic resins, and paints and stains but may also be processed into fuels and petrochemical intermediates. The residual pitch left from the separation is used for paving, roofing, waterproofing, and insulation.

Coal tar has a number of contaminants that need to be removed, such as nitrogen, oxygen, or sulfur-containing compounds, and metals.

There is a need for additional processes for removing contaminants from coal tar.

SUMMARY OF THE INVENTION

One aspect of the invention is a method of treating coal tar using reactive distillation. In one embodiment, the method includes introducing a coal tar steam into a reactive distillation zone, the reactive distillation zone having a reaction zone and a separation zone, the reaction zone containing a hydrotreating catalyst and an absorbent. The coal tar steam is contacted with a hydrogen stream in the reaction zone to remove sulfur compounds, nitrogen compounds, oxygenates and metals from the coal tar stream, and the treated coal tar stream is separated into at least two fractions.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is an illustration of one embodiment of a pre-treatment process for the reactive distillation process of the present invention.

FIG. 2 is an illustration of another embodiment of a reactive distillation process of the present invention.

FIG. 3 is an illustration of another embodiment of a reactive distillation process of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

Coal can be pyrolyzed by heating at high temperature, e.g., up to about 2,000°C (3,600°F), in the absence of oxygen to drive off the volatile components. Pyrolysis produces coke and coal tar. The coke can be used in other processes, such as the manufacture of steel. The coal tar stream comprises the volatile components from the coking process.

FIG. 1 shows one embodiment of a pre-treatment process 5 for the reactive distillation process of the present invention. The coal tar steam 10 is introduced into an optional separation zone 15. Separation zone 15 is designed to recover valuable products that would not survive hydrotreating and/or hydrocracking in the reactive distillation zone (described below). In particular, valuable oxygenated products, such as phenol, cresols or xylene, would be converted to products such as CO₂ and a hydrocarbon skeleton in the reactive distillation zone. These products 20 can be recovered from the coal tar steam 10 before it is sent to the reactive distillation zone by any suitable separation process. Suitable separation processes include, but are not limited to, fractionation, extraction, or other bulk separation processes. The products 20 can be further purified (not shown) using additional separation processes such as additional fractionation or extraction, adsorption or treatment with molecular sieves or resins for removal of trace contaminants, if desired. The residue remaining after removal of the valuable product or products could be further processed separately or sent forward into the reactive distillation zone.

The treated coal tar stream 25 from the separation zone 15 can be sent to a dehydration zone 30 where water is removed from the treated coal tar stream 25. The treated coal tar stream is heated to approximately 150°C with a heater (not shown). The overhead 35 from the dehydration zone 30 contains water and some light oil. The water and light oil are separated in a decanter 40, for example. The water 45 is sent for processing. The light oil 50 can be divided, and a portion 55 is sent forward to the reactive distillation zone, and a portion 60 may be used as reflux for dehydration zone 30.

Bottoms stream 65 is pumped to an appropriate pressure, heated to approximately 350°C, and flashed in pitch flash zone 70. The purpose of pitch flash zone 70 is to recover material in bottoms stream 65 that boils below about 350°C. The overhead stream 75 from pitch flash zone 70 is condensed, pumped to the needed pressure, and combined with the light oil portion 55 to form feed 80 for the reactive distillation zone. Recovery of material from the coal tar having a boiling point below about 350°C is maximized by combining pitch 85 from the bottom of pitch flash zone 70 with bottoms stream 65 from the dehydration zone 30 to form the feed for pitch flash zone 70. A constant level of pitch is maintained in pitch flash zone 70 with overflow recovered in stream 90. This arrangement maximizes recovery of material having a boiling point below about 350°C for the reactive distillation zone, while keeping the viscous, high molecular weight pitch from entering the reactive distillation zone and driving up the bottoms temperature of the pressurized columns. The pitch could also potentially contribute to fouling of the catalyst beds in the reactive distillation zone.

The feed 80 contains a number of contaminants. Examples of contaminants to be removed include, but are not limited to, metals such as antimony, arsenic, beryllium, cadmium, chromium, copper, lead, mercury, nickel, selenium, silver, thallium or zinc; nitrogen containing species, such as pyridines or quinoline; sulfur containing species, such as...
thiophenes or mercaptans; and oxygen containing species, such as phenols or carbazoles. Sulfur, nitrogen, oxygen and metal containing contaminants are present throughout the boiling ranges and must be removed before specific products can be produced, or the coal tar can be used as fuel.

[0017] FIG. 2 illustrates one embodiment of a reactive distillation zone 100. In this embodiment, the reactive distillation zone 100 includes first reactive distillation column 105 and a second reactive distillation column 110. In general, hydrotreating of coal tar requires higher pressure as the molecular weight of the fraction increases. Because of the molecular weight range of components in coal tar feed to be hydrotreated, as indicated by atmospheric boiling points up to 350°C, hydrotreating at two different pressures is desirable. For the catalytic distillation application, it would be desirable to have two columns operating at different pressures. However, in some situations, particularly if a limited number of products are to be produced, the reactive distillation zone could utilize a single column at conditions sufficient to hydrotreat the highest molecular weight fractions.

[0018] The first reactive distillation column 105 includes at least one reaction zone and at least one separation zone. As shown, there are four separation zones 115, 120, 125, 130 alternating with three reaction zones 135, 140, 145. The number of separation zones corresponds to the number of products that the operator wants to produce plus one for the feed inlet.

[0019] Separation zones 115, 120, 125, 130 contain one or more trays. Typically, all of the inlets and outlets from the column are located in the trayed separation zones for ease of introduction of feeds and withdrawal of products. The trayed sections may include equipment that will distribute and mix incoming feeds with column internal streams or will collect products for removal from the column. Potential mixers, distributors and collectors are well known in distillation tower design.

[0020] The reaction zones 135, 140, and 145 are beds containing a hydrotreating catalyst. In some embodiments, the reaction zones will also include an absorbent. All of the beds can be the same catalyst and/or absorbent, or one or more beds can have different catalysts and/or absorbents depending on the specific processing requirements. The purpose of the reaction zones 135, 140, and 145 is the simultaneous removal of contaminants such as metals, nitrogen, sulfur or oxygen containing species, and the separation of the feed into one or more specific cuts defined as useful by the operator. The cuts may correspond to specific products or specific boiling point regions convenient for further processing. The cuts in the drawings (which are referenced to atmospheric boiling points of coal tar components) are for illustration only and can vary depending on operating objectives.

[0021] The catalysts generally used for hydrotreating contain at least one Group VIII metal, such as iron, cobalt and nickel, and at least one Group VI metal, such as molybdenum and tungsten, on a high surface area support, such as alumina. The preferred embodiment is a catalyst containing nickel and molybdenum.

[0022] Placement of the catalyst into the reactive distillation zone requires promotion of intimate contact between the reactants and the catalyst along with appropriate consideration of hydraulics and the potential to flood the column should the catalyst bed provide insufficient passage of vapor rising in the column. Catalyst particles are sometimes larger than those in a conventional fixed bed reactor, and the catalyst within a reactive distillation unit is sometimes supported by contact structures consisting of wire mesh tubes that also provide a mass transfer surface for the distillation as in U.S. Pat. No. 5,730,843. Consideration needs to be given to vapor passage rates as in U.S. Pat. No. 5,449,501, and ease of catalyst replacement within the column as in U.S. Pat. No. 6,299,845.

[0023] The absorbents are typically large surface area materials used to specifically remove metal contaminants from the coal tar. An alumina with a surface area greater than approximately 200 m²/g may be used, for example. The large surface area provides space for metals to deposit. These absorbents are frequently impregnated with metals that promote hydrotreating reactions, such as nickel and molybdenum, to facilitate the absorption of the metal contaminants.

[0024] Typical operating conditions for the reactive distillation zone include a temperature between 300°C and 450°C, at a LHSV between 0.5 and 5/hr and H₂ content between 1000 and 3000 scf/bbl coal tar. Pressure is a function of the hydrocarbon molecular weight processed, with an expected range between about 2.07 MPa (g) (300 psig) and 3.45 MPa (g) (500 psig) for treatment of components with an atmospheric boiling point below 250°C, and an operating range between 3.45 MPa (g) (500 psig) and 6.89 MPa (g) (1000 psig) for components with an atmospheric boiling point between 250°C and 350°C.

[0025] As shown, the feed 80 is introduced into the first distillation column 105 in separation zone 125. The feed 80 is introduced at a point where there is at least one reaction zone above the inlet and at least one reaction zone below it in order to treat as much of the feed as required.

[0026] Hydrogen may be introduced into any or all of the separation zones of the first reactive distillation column 105 for hydrotreating. As shown, hydrogen streams 150, 155, and 160 are introduced into separation zones 120, 125, and 130 respectively.

[0027] The first reactive distillation column 105 can be operated at a pressure consistent with processing material with an atmospheric boiling point up to about 250°C. Typical operating conditions for this would be temperatures between about 300°C and about 450°C, LHSV between about 0.5 and about 5/hr, an H₂ content between about 1000 and about 3000 scf/bbl coal tar, and a pressure operating range between about 2.07 MPa (g) (300 psig) and about 3.45 MPa (g) (500 psig).

[0028] The first reactive distillation column 105 as illustrated contains three beds of catalyst (and optionally absorbent) 135, 140, and 145, and produces three specific distillation cuts referenced to the atmospheric boiling points of the components. For example, overhead 165 can have an atmospheric boiling point up to about 175°C; cut 170 can have an atmospheric boiling point in the range of about 175°C to about 205°C, and cut 175 can have an atmospheric boiling point in the range of about 205°C to about 250°C. The number of separation sections and the number of catalyst beds may vary depending on the processing objectives. For example, an operator may chose to recover cut 170 with overhead 165 and eliminate tray section 120.

[0029] The overhead stream 165 containing hydrocarbon materials and light components including H₂S, CO₂, NH₃, and H₂ is condensed to separate the light components from the hydrocarbons in overhead receiver 180. If desired, a portion or the entire light stream 185 may be recompressed and recycled as H₂ feed to either the first or second reactive dis-
distillation columns 105, 110. Water stream 187 can be removed and sent for treatment. The hydrocarbon stream 190 now free of sulfur, nitrogen, oxygen and metals is recovered as the liquid overhead product 195 and a portion 200 can be used as reflux into the first reactive distillation column 105.

[0030] Hydrogenation reactions through which a portion of the contaminants are removed are exothermic. As material moves through the catalyst beds, heat will be released. In addition to potentially reduced capital requirements, a major advantage of reactive distillation is the ability to consume the heat of reaction as heat of vaporization. Better control of the reaction heat rise leads to better selectivity, more stable catalyst, and lower processing requirements. Heat within the column may also be controlled by the placement and amount of H₂ streams entering the column, as well as the potential for multiple feed streams (not shown), both of which can help regulate heat through their use as quench. Finally, the amount of reflux returned to the column represents another opportunity for control of reaction heat as reflux can serve as a heat sink within the catalyst bed.

[0031] Another advantage of reactive distillation is the counter-current contact of liquid and vapor, and the subsequent promotion of intimate contact between the catalyst and the contaminants to be removed. Organic sulfur and nitrogen species, for example, tend to concentrate in the liquid, while the products (H₂S and nitrogen) are gas phase. Intimate liquid phase contact between the organic species and the catalyst with immediate removal of the products into the gas phase results in lower processing requirements.

[0032] The bottoms 205 of the first reactive distillation column 105 is sent as feed to the second reactive distillation column 110. In this example, second reactive distillation column 110 is processing material with an atmospheric boiling point between about 250°C and 350°C. The second reactive distillation column 110 therefore operates at a higher pressure than the first reactive distillation column 105. Typical expected second reactive distillation column 110 operating ranges are a pressure between about 3.45 MPa (g) (500 psig) and about 6.89 MPa (g) (1000 psig), temperatures between about 300°C and about 450°C, LHSV 1-5/hr, and an H₂ content between 1000 and 3000 scf/bbl coal tar.

[0033] As illustrated, the second reactive distillation column 110 can be divided into three separation zones 210, 215, and 220 and two reaction zones 225 and 230. It produces two specific distillation cuts referenced to the atmospheric boiling points of the components. As with the first reactive distillation column 105, all feeds and products are introduced or withdrawn in trayed separation zones of the column. Hydrogen 235 and 240 can be introduced into any or all of the separation zones. The excellent heat control possible in reactive distillation can be enhanced by the number and position of feed streams into the column and the control of reflux.

[0034] The overhead stream 245 containing hydrocarbon materials and light components including H₂S, CO₂, NH₃ and H₂ is condensed to separate the light components from the hydrocarbons in overhead receiver 250. If desired, a portion or the entire stream 255 may be recompressed and recycled as H₂ feed to either the first or second reactive distillation unit. Water stream 257 can be removed and sent for treatment. The hydrocarbon stream 260 now free of sulfur, nitrogen, oxygen and metals is recovered as the liquid overhead product 265 and a portion 270 used as reflux into the second reactive distillation column 110. The overhead product stream 265 has an atmospheric boiling point in the range of about 250°C to 280°C.

[0035] The bottoms 275 of the second reactive distillation column 110 has an atmospheric boiling range over about 280°C.

[0036] As an example of the usefulness of simultaneous contaminant removal and separation, consider the topmost and bottom cuts in the illustration of the first reactive distillation column 105. The topmost cut 165 (up to 175°C) is high in C₆-C₈ aromatics such as benzene, toluene and xylene. After removal of metal, sulfur, nitrogen and oxygenate components in column 105, the operator may wish to further process this material through a bulk aromatic from non-aromatics separation process, such as the Sulfolane process. The valuable aromatics can then be sent to an aromatics complex for recovery while the non-aromatics can be sent to a catalytic reformer. Valuable products such as naphthalene and methyl-naphthalenes, now free of metal, sulfur, nitrogen and oxygenate contaminants may be recovered from the bottommost cut 175 (205-250°C) via crystallization or adsorption. The fraction remaining after naphthalene recovery may be sent to fuel. Reactive distillation permits a low piece count, efficient processing scheme for maximizing the value of coal tar.

[0037] The cuts from the second reactive distillation column 110 can be used for the production of diesel fuel. Given the composition of some coal tars, the cetane number would be expected to be low. As an alternative to diesel, rather than simply hydrotreating the 250°C+ fraction, a portion of the hydrotreating catalyst in the second reactive distillation column can be replaced with a hydrocracking catalyst, and the 250°C+ fraction can be cracked to produce additional naphtha. Naphtha product offers additional processing outlets; for example, naphtha can go to gasoline or aromatics via reforming or to light olefins via steam cracking.

[0038] FIG. 3 illustrates an alternative second reactive distillation column 305 which provides increased naphtha production. The reactive distillation column 305 has two separation zones 310 and 315 and a reaction zone 320. The feed 325 from the first reactive distillation column (not shown) is introduced into the separation zone 310, and hydrogen is introduced into the separation zone 315. The separation zone 310 is used to fractionate out the naphtha, while the separation zone 315 would remove heavier product. Additional cuts may be withdrawn from 305, depending on the processing objectives of the refiner.

[0039] In addition to the nickel-molybdenum hydrotreating catalyst and the high surface area absorbent, a hydrocracking catalyst, such as a zeolite, would be added for the cracking function. Processing conditions would be about 8.27 MPa (g) (1200 psig) to about 11.03 MPa (g) (1600 psig), 300°C to 450°C, 1000-3000 scf H₂/bbl coal tar, and 0.5 to 3 LHSV. The primary advantage of reactive distillation for hydrocracking, which is exothermic, is control of heat effects via the heat of vaporization. Heat control can be supplemented through the use of feed streams as quenchers and control of reflux.

[0040] The overhead stream 335 containing naphtha and light components including H₂S, CO₂, NH₃, and H₂ is condensed to separate the light components from the naphtha in overhead receiver 340. If desired, a portion or the entire light stream 345 may be recompressed and recycled as H₂ feed to either the first or second reactive distillation columns 105, 305. Water stream 350 can be removed and sent for treatment.
The naphtha stream 355 now free of sulfur, nitrogen, oxygen, and metals can be recovered as the liquid naphtha overhead product 360 and a portion 365 used as reflux into the reactive distillation column 305.

[0041]  The bottoms 370 of the reactive distillation column 305 is the high boiling product that may be used directly as a fuel or fuel blending component or further processed.

[0042]  The first and second reactive distillation columns 105 and 110 may be operated in series, as shown in FIG. 2. Alternatively, the first and second reactive distillation columns may be preceded by a splitter (not shown) which will separate the coal tar into a light and heavy fraction. In this case, the two reactive distillation columns are operated in parallel. The light fraction is sent to the first column, and the heavy fraction is sent to the second.

[0043]  In another embodiment, either the first or second reactive distillation unit can be converted into a hydroprocessing reactor.

[0044]  Previous reactive distillation processes have covered only a gasoline fraction (with a boiling point range of about C5 to 232°C). Using the present invention, it was surprisingly found that reactive distillation could be used to process a coal tar stream over the entire useful range of composition. The range of boiling points for the coal tar stream is from about C5 to about 350°C. (Compounds having boiling points above 350°C are desirably being removed prior to the reactive distillation).

[0045]  While at least one exemplary embodiment has been presented in the foregoing detailed description of the invention, it should be appreciated that a vast number of variations exist. It should also be appreciated that the exemplary embodiment or exemplary embodiments are only examples, and are not intended to limit the scope, applicability, or configuration of the invention in any way. Rather, the foregoing detailed description will provide those skilled in the art with a convenient road map for implementing an exemplary embodiment of the invention. It being understood that various changes may be made to the function and arrangement of elements described in the exemplary embodiment without departing from the scope of the invention as set forth in the appended claims.

What is claimed is:

1. A method of treating coal tar using reactive distillation comprising:
   introducing a coal tar stream into a reactive distillation zone, the reactive distillation zone comprising a reaction zone and a separation zone, the reaction zone containing a hydrotreating catalyst and an absorbent;
   contacting the coal tar stream with a hydrogen stream in the reaction zone to remove sulfur compounds, nitrogen compounds, oxygenates, and metals from the coal tar stream; and
   separating the treated coal tar stream into at least two fractions.

2. The method of claim 1 wherein the reactive distillation zone comprises a first reactive distillation column comprising a first reaction zone and a first separation zone, the first reaction zone containing a first hydrotreating catalyst and a first absorbent, and a second reactive distillation column comprising a second reaction zone and a second separation zone, the second reaction zone containing a second hydrotreating catalyst and a second absorbent.

3. The method of claim 2 wherein an outlet in the first reactive distillation column is in fluid communication with an inlet in the second reactive distillation column, further comprising:
   introducing a fraction from the first reactive distillation column into the second reactive distillation column;
   contacting the fraction from the first reactive distillation column with a hydrogen stream in the second reaction zone to remove sulfur compounds, nitrogen compounds, oxygenate, compounds, and metals from the fraction from the first reactive distillation column; and
   separating the second treated fraction into at least two fractions.

4. The method of claim 3 wherein the second reaction zone further comprises a hydrocracking catalyst and wherein one of the fractions from the second fraction comprises naphtha.

5. The method of claim 2 further comprising;
   separating the coal tar stream into at least two fractions;
   introducing a first fraction into the first reactive distillation column;
   contacting the first fraction with a hydrogen stream in the first reaction zone to remove sulfur compounds, nitrogen compounds, oxygenate, compounds, and metals from the first fraction;
   separating the first treated fraction into at least two fractions;
   introducing a second fraction into the second reactive distillation column;
   contacting the second fraction with a hydrogen stream in the second reaction zone to remove sulfur compounds, nitrogen compounds, oxygenate, compounds, and metals from the second fraction; and
   separating the second treated fraction into at least two fractions.

6. The method of claim 5 wherein the second reaction zone further comprises a hydrocracking catalyst and wherein one of the fractions from the second treated fraction comprises naphtha.

7. The method of claim 2 wherein the first and second reactive distillation columns are operated at different pressures.

8. The method of claim 1 further comprising recovering at least one of the fractions.

9. The method of claim 1 wherein there are at least three separation zones alternating with at least two reaction zones.

10. The method of claim 1 wherein there are at least two reaction zones and wherein the hydrotreating catalyst in the first reaction zone is different from the hydrotreating catalyst in the second reaction zone.

11. The method of claim 1 further comprising removing at least one product from the coal tar stream before introducing the coal tar stream into the reactive distillation zone.

12. The method of claim 1 further comprising removing a pitch fraction from the coal tar stream before introducing the coal tar stream into the reactive distillation zone.

13. The method of claim 1 further comprising removing water from the coal tar stream before introducing the coal tar stream into the reactive distillation zone.

14. The method of claim 1 wherein the coal tar stream includes components having a boiling point from about C5 to 350°C.

15. The method of claim 1 wherein the absorbent has a surface area of at least about 200 m²/g.
16. A method of treating coal tar using reactive distillation comprising:

introducing a coal tar stream into a reactive distillation zone, the reactive distillation zone comprising a first reactive distillation column having a first reaction zone and a first separation zone, the first reaction zone containing a first hydrotreating catalyst and a first absorbent, and a second reactive distillation column comprising a second reaction zone and a second separation zone, the second reaction zone containing a second hydrotreating catalyst and a second absorbent;

contacting the coal tar stream with a hydrogen stream in the reaction zone to remove sulfur compounds, nitrogen compounds, oxygenates, and metals from the coal tar stream; and

separating the treated coal tar stream into at least two fractions.

17. The method of claim 16 wherein an outlet in the first reactive distillation column is in fluid communication with an inlet in the second reactive distillation column, further comprising:

introducing a fraction from the first reactive distillation column into the second reactive distillation column;

contacting the fraction from the first reactive distillation column with a hydrogen stream in the second reaction zone to remove sulfur compounds, nitrogen compounds, oxygenate, compounds, and metals from the fraction from the first reactive distillation column; and

separating the second treated fraction into at least two fractions.

18. The method of claim 17 wherein the second reaction zone further comprises a hydrocracking catalyst and wherein one of the fractions from the second fraction comprises naphtha.

19. The method of claim 16 further comprising:

separating the coal tar stream into at least two fractions;

introducing a first fraction into the first reactive distillation column;

contacting the first fraction with a hydrogen stream in the first reaction zone to remove sulfur compounds, nitrogen compounds, oxygenate, compounds, and metals from the first fraction;

separating the first treated fraction into at least two fractions;

introducing a second fraction into the second reactive distillation column;

contacting the second fraction with a hydrogen stream in the second reaction zone to remove sulfur compounds, nitrogen compounds, oxygenate, compounds, and metals from the second fraction; and

separating the second treated fraction into at least two fractions.

20. The method of claim 19 wherein the second reaction zone further comprises a hydrocracking catalyst and wherein one of the fractions from the second treated fraction comprises naphtha.

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