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2,990,364

DESULFURIZATION AND DENITROGENIZATION OF COAL TAR AROMATIC FRACTIONS

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2 Claims. (Cl. 208—209)

This invention relates to a method for the desulfurization and denitrogenization of aromatic hydrocarbon-containing fractions produced from the destructive distillation of coal and more particularly this invention relates to a thermal conversion method for the removal of sulfur-containing compounds and nitrogen-containing compounds from aromatic hydrocarbon-containing fractions obtained from coal-tar light oil and coal-gas light oil.

The tars produced by the destructive distillation of coal contain major quantities of hydrocarbons and minor amounts of sulfur and nitrogen-containing compounds. For a number of years it has been the practice to distill from coal-tars a light oil fraction, generally a fraction boiling below about 400° F., containing substantial quantities of benzene, toluene, xylenes and some higher molecular weight alkylated benzene hydrocarbons. In addition to these aromatic hydrocarbons, such light oil fractions contain rather large amounts of solvent naphtha which is composed of paraffins and more complex hydrocarbons.

During the destructive distillation of coal there is also produced coal-gas in rather large amounts. When this coal-gas is scrubbed with so-called wash oils obtained from coal-tars rather large quantities of benzene, toluene and xylenes are scrubbed from the coal-gas to produce a coal-gas light oil fraction which is highly aromatic. The coal-tar light oil fraction and the coal-gas light oil fraction form the preferred charge materials for the process of the instant invention. Each of these fractions will contain small quantities of sulfur-containing compounds such as thiophene and derivatives thereof as well as nitrogen-containing compounds typified by indole and its derivatives. Since the major uses for benzene, toluene and xylenes from the destructive distillation of coal is in chemical processes rather than as fuel, it is preferable that such materials be free of nonhydrocarbon material particularly sulfur- and nitrogen-containing compounds.

A method now has been found for the removal of sulfur-containing compounds and nitrogen-containing compounds from aromatic hydrocarbon-containing fractions produced from the destructive distillation of coal which involves thermal conversion in the presence of hydrogen and under specific reaction conditions.

It is an object of this invention, therefore, to provide a method for the desulfurization and denitrogenization of aromatic hydrocarbon containing fractions produced from the destructive distillation of coal by thermal conversion of such fractions in the presence of hydrogen.

It is a further object of this invention to provide a method for the desulfurization and denitrogenization of light oil fractions from coal-tar and coal-gas by thermal conversion of such light oil fractions in the presence of hydrogen.

Further objects of this invention will be apparent from the description and claims that follow.

In accordance with the instant invention the light oil fraction obtained by distillation from coal-tar or by scrubbing coal-gas with wash oil is subjected to thermal conversion in the presence of hydrogen to remove the sulfur-containing compounds and nitrogen-containing compounds from such fractions. Since these light oil fractions contain rather large amounts of paraffinic type hy-

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drocarbons they may be treated by any of the well known commercial selective solvent processes to remove paraffinic constituents and to concentrate the aromatic content of such fractions. It has been found that the selective solvent treatment of these light oil fractions while removing paraffinic type constituents will remove only minor portions of sulfur-containing and nitrogen-containing compounds since the latter are in the form of heterocyclic ring type compounds and therefore remain in the aromatic fraction. As has been pointed out, these light oil aromatic hydrocarbon-containing fractions generally boil below about 400° F., and accordingly are particularly suitable for thermal conversion processes since they may be vaporized rather easily.

It has been found that the thermal conversion of these light oil fractions to remove sulfur-containing and nitrogen-containing compounds therefrom is best accomplished at temperatures ranging between 850° F. and 1350° F. at pressures in excess of 1000 pounds per square inch and ranging up to 10,000 pounds per square inch with reaction times in the range between 1 and 900 seconds and with an amount of hydrogen in the range between 1 and 20 moles of hydrogen per mole of hydrocarbon charge based on the average molecular weight of the hydrocarbon charge.

Somewhat more preferred reaction conditions employ temperatures in the range between 950° F. and 1250° F., pressures between 2000 and 6000 pounds per square inch with reaction times in the range between 10 and 600 seconds and with amounts of hydrogen in the range between 2 and 10 moles of hydrogen per mole of hydrocarbon charge based on the average molecular weight of the hydrocarbon charge. Under these conditions it has been found that from about 20 to 85 percent of the sulfur contained in the charge may be removed in a single treatment while from 10 to 55 percent of the nitrogen contained in the charge may be removed simultaneously.

The process hydrogen which may be supplied entirely from an outside source is introduced into the process along with the charge hydrocarbons. Since there is a small amount of hydrocracking of hydrocarbons in the process some hydrogen will be consumed and, of course, some hydrogen will be consumed in converting the sulfur-containing compounds into hydrocarbons and hydrogen sulfide and the nitrogen-containing compounds into hydrocarbons and ammonia. The hydrogen together with portions of the hydrogen sulfide and ammonia may be separated from the hydrocarbon effluent by means of a conventional high pressure separator. The amounts of hydrogen sulfide and ammonia which will be separated from the hydrocarbons will depend, of course, upon the operating pressure of the high pressure separator. The hydrocarbon effluent from the high pressure separator may then be flash stabilized to remove the low molecular weight hydrocarbons produced by hydrocracking. In addition to removing these normally gaseous hydrocarbons in the stabilizing operation, the residual hydrogen sulfide and ammonia likewise will substantially be completely removed leaving only the purified aromatic hydrocarbon fraction. The separation of hydrogen sulfide and ammonia from hydrocarbon streams may be accomplished by any one of several well known conventional methods and since such methods are not a part of this invention further discussion thereof is believed unnecessary.

The hydrogen which is separated from the hydrocarbon fraction may be recycled to the process without further treatment to remove any ammonia or hydrogen sulfide since these gases will reach an equilibrium concentration and not accumulate in the hydrogen. The use of recycle

hydrogen will, of course, reduce the amount of make-up hydrogen required to operate the process.

The example which follows comprises a number of experiments designed to illustrate certain specific embodiments of the invention.

Example

A light oil fraction from a steel-mill coke oven was employed as a charge material. This material contained a hydrocarbon fraction having the composition shown in the table under "Charge" and also it contained 0.35 percent by weight of sulfur and 0.04 percent by weight of nitrogen based on the weight of the entire light oil fraction. This charge material was treated in a thermal conversion process employing a tubular reactor at a pressure of 4900 pounds per square inch pressure under the conditions shown in the table. The products resulting from such treatments are likewise shown in the table.

Experiment No.	1	2	3	4	5	6	
Conditions:							
Temperature, ° F.....	950	950	1,000	1,000	1,050	1,100	
Contact time, sec.....	150	300	150	300	300	600	
Hydrogen to hydrocarbon mole ratio.....	3:1	3:1	3:1	3:1	3:1	3:1	
Liquid Recovery wt. percent.....	98.8	94.2	97.3	92.7	90.4	89.3	
Comp. of Hydrocarbon Product, wt. percent no loss basis.....	Charge	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6
C ₁ to C ₈ paraffins.....		1.1	5.8	2.6	7.2	9.6	10.6
C ₉ and heavier paraffins, cyclo- and dicycloparaffins.....	4.1	4.8	2.6	1.8	3.8	2.8	0.4
Total Aromatics.....	95.9	94.1	91.6	95.6	89.0	87.6	89.0
Benzene.....	48.8	56.3	56.1	55.7	53.8	63.5	81.0
Toluene.....	29.4	23.4	22.3	24.7	22.7	17.7	6.3
Xylenes and ethylbenzene.....	13.6	10.9	10.4	11.4	9.7	5.4	1.3
Heavier alkylated benzenes.....	4.1	3.5	2.8	3.8	2.8	1.0	0.4
Average mol wt. of aromatics.....	87.1	85.5	86.0	86.7	86.0	83.0	79.5
Wt. percent sulfur in liquid.....	0.35	0.28	0.23	0.22	0.20	0.06	0.06
Wt. percent nitrogen in liquid.....	0.04	0.031	0.027	0.028	0.024	0.036	0.018
Wt. percent desulfurization.....		20	34	37	43	83	83
Wt. percent denitrogenization.....		22	32	30	40	10	55

These data show that substantial amounts of the sulfur-containing and nitrogen-containing compounds may be removed in a single pass through the reactor. These data also show that if the primary purpose of the thermal conversion treatment is to remove sulfur-containing and nitrogen-containing compounds without substantially changing the aromatic hydrocarbon distribution long reaction times and temperatures below about 1050° F. should be employed. Stated in other words, within the preferred reaction conditions, the longer reaction times and lower temperatures should be used to obtain only sulfur and nitrogen removal and only minor changes in the aromatic hydrocarbon distribution.

If, to the contrary, it is desired not only to remove the sulfur-containing compounds and nitrogen-containing compounds but also to convert the other aromatic hydrocarbons to benzene, then temperatures above about 1050°

F. and shorter reaction times within the preferred conditions should be employed.

We claim:

1. A method for the desulfurization and denitrogenization of aromatic hydrocarbon-containing fractions produced from the destructive distillation of coal which comprises subjecting such a fraction solely to thermal conversion in the presence of hydrogen at a temperature in the range between 850° F. and 1350° F., a pressure in excess of 1000 pounds per square inch and ranging up to 10,000 pounds per square inch, for a time in the range between 1 and 900 seconds, the amount of hydrogen ranging between 1.0 and 20 moles of hydrogen per mole of hydrocarbon charge, and separating the hydrogen sulfide and ammonia produced during the conversion from the hydrocarbon products of the conversion reaction.

2. A method for the desulfurization and denitrogenization of aromatic hydrocarbon-containing fractions produced from the destructive distillation of coal which com-

prises subjecting such a fraction solely to thermal conversion in the presence of hydrogen at a temperature in the range between 950° F. and 1250° F., a pressure of from 2000 to 6000 pounds per square inch, for a time in the range between 10 and 600 seconds, the amount of hydrogen ranging between 2 and 10 moles of hydrogen per mole of hydrocarbon charge, and separating the hydrogen sulfide and ammonia produced during the conversion from the hydrocarbon products of the conversion reaction.

References Cited in the file of this patent

UNITED STATES PATENTS

2,705,733	Nonnenmacher et al.	Apr. 5, 1955
2,706,209	Reitz et al.	Apr. 12, 1955
2,708,180	Fuener et al.	May 10, 1955
2,883,441	Sawyer	Apr. 21, 1959

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

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It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 3, line 3, for "comprises" read -- compares --.

Signed and sealed this 21st day of November 1961.

(SEAL)

Attest:

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