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PROCESSES OF REFINING AROMATIC HYDROCARBONS

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3 Claims. (Cl. 260—674)

Aromatic hydrocarbons of the type obtained from the light oil and tar produced in by-product coke plants, contain impurities which necessitate the refining of the hydrocarbons for adapting the said hydrocarbons to commercial use. Such impurities include paraffinic, naphthenic, and sulphur compounds, together with unsaturated hydrocarbons. The presence of such impurities prevents the hydrocarbons containing them from being used in many industrial operations.

Many processes have been devised for the removal of such impurities from the aromatic hydrocarbons, such removal being inexpedient by fractionalization procedures owing to the closeness of the boiling points of the impurities. No complete analysis of the impurities present in benzol, toluol, or xylol, has ever been made, but some of the compounds have been identified and analyses made for their concentrations. Thus, in one nitration grade of benzene, the presence of one per cent impurities was found. Roughly one-third of these impurities was found to be cyclohexane. Other naphthenes and paraffinic hydrocarbons boiling up to about 100°C. were present, but were not identified owing to analytical difficulties. The total sulphur amounted to 0.05 per cent and included thiophene. Possibly carbon disulphide was present among the other sulphur compounds.

In another analysis of a benzol containing 0.5 per cent by volume of impurities, the impurities which were isolated distilled from 80°C. up to about 100°C. The greater portion, over 90 per cent, distilled above 90°C. The presence of cyclohexane, methyl cyclohexane, 2,2,4-tri-methyl pentane, n-heptane, 1,1-dimethyl cyclopentane in the mixture was indicated by the boiling points and refractive indices. Thiophene was believed to be present as well. The information available on the impurities in toluol indicates that they consist to a large extent of the higher homologs of the impurities present in benzol.

The presence of these impurities often is undesirable to consumers of the commercial products. In the first place, they represent a diluent of the benzol or the other aromatic hydrocarbons. In the second place, they give rise to undesirable side reactions in manufacturing processes which reduce the yield of final product or affect its quality. Thus the sulphur compounds have affected the color of dyes or the quality of pharmaceuticals in which benzol has been used. The yields of trinitrotoluene produced in the nitration of toluene is reduced by the presence of the "paraffins," as the impurities are known collectively in the industry.

The concentrations of the impurities have been reduced by various methods to which it is superfluous to refer, these being simple methods of separation, such as fractional distillation, which, however, is inexpedient because of the closeness of boiling points of the impurities to that of the hydrocarbon.

In accordance with the present invention there is provided a simple process for the substantially complete elimination of the impurities contained in the usual commercial grades of benzol, toluol, and xylol, the process of the invention being based upon a catalytic conversion of the impurities into compositions that may be removed readily from the hydrocarbons, by further expedient and known refining operations.

The process of the present invention comprises contacting vapors of the hydrocarbon which is to be refined, with a combination of cracking and dehydrogenating catalysts at elevated temperatures. By the action of the catalysts, the impurities are broken down to lower molecular weight compounds, which can be removed more readily from the hydrocarbon after condensation of the catalytically-treated vapors by well-known procedures, such as a combination of acid refining and distillation.

By a cracking catalyst is meant one in which the principal reaction is a breaking of the bonds connecting carbon atoms in the molecule of a hydrocarbon, or between carbon and carbon, or carbon and sulphur in an organic sulphur compound. It may be illustrated, for example, by the simple equation:

\[ \text{C}_8\text{H}_8 + (\text{heat and catalyst}) \rightarrow \text{C}_6\text{H}_6 + \text{C}_2\text{H}_4 \]

By a dehydrogenating catalyst is meant one in which the principal reaction is a separation of hydrogen from the molecule. A reaction illustrating it is as follows:

\[ \text{C}_8\text{H}_8 + (\text{heat and catalyst}) \rightarrow \text{C}_6\text{H}_6 + \text{H}_2 \]

Actually, with a given cracking catalyst, some dehydrogenation may occur along with the cracking. In the case of the dehydrogenating catalyst, some cracking usually occurs, as manifested by formation of a carbon deposit on the surface of the catalyst along with the dehydrogenation.

Illustrative of the catalyst materials employed in accordance with the present process are a silicate for cracking and chronic oxide for dehydrogenation. The chronic oxide may be supported on the silicate, thus enabling the cata-
is pumped by pump 102 through line 104 provided with a control valve 110 for controlling flow of the hydrocarbon, for example, benzol, through pipe 111 to catalyst chamber 112, that contains a bed of a cracking catalyst, such as a siliceous catalyst, which is in intimate contact with a heating fluid maintained in the jacket 114, so that the catalyst chamber 112 at a temperature ranging between about 250° C. to 500° C.

In the catalyst chamber 112, there is effected a preliminary treatment of impurities present in the hydrocarbons by cracking such impurities as are amenable to such treatment. Carbon deposits on the catalyst bed and, as described above, lessen the activity of the catalyst. A pipe 118 connects to the bottom of catalyst chamber 112, pipe 118 being provided with a valve 118 and opening into a stack not shown.

Connected to pipe 118 above the valve 118 is a pipe 120, for transferring the initially treated hydrocarbon vapors to pipe 122 that enters the second catalyst chamber 124. The pipe 120 is provided with valves 126 and 127 for controlling flow of vapors therethrough. Pipe 122 has a valve 131 therein between pipe 120 and the catalyst chamber 124.

The catalyst chamber 124 has a bed of dehydrogenating catalyst 128 therein, which bed may be a chromium oxide, for example. This bed of catalyst 128 is heated to a temperature of from 500° C. to 600° C. by a heating fluid circulating through jacket 130 enclosing the chamber 124. The catalyst chamber 124 is the conversion engine for substantially all of the impurities in the hydrocarbon vapors, such impurities being dehydrogenated into compounds that, together with the cracked compounds from cracking chamber 112, are removable readily from the condensate that is recovered from the dehydrogenation chamber 124.

For this purpose, a condenser 134 is provided, the condenser 134 being connected to the catalyst chamber 124 by a pipe 132. Outlet pipe 132 is provided with a valve 137.

As the vapors pass through the catalyst bed 120, carbon deposits on the catalyst and reduces the activity of the catalyst so that this carbon has to be removed from time to time, although this carbon deposit is not as heavy as that formed in chamber 112.

The carbon deposited in both chambers 112 and 124 is removed conveniently by burning it off with air which is admitted periodically to both chambers 112 and 124 during which periods the flow of hydrocarbon vapors to the system is interrupted.

For admission of air, pipe 138 is provided, which is connected to a source of compressed air, and which connects with catalyst chambers 112 and 124 through pipes 111 and 122 respectively. Since, however, the system will be filled with hydrocarbon vapors in order to avoid explosion, the pipe 138 is connected through pipe 140 to a source of inert gas such as steam or nitrogen. Pipe 138 is provided with a valve 142 between pipe 140 and the source of air, and pipes 111 and 122 are provided respectively, with valves 144 and 146 between the pipes 111 and 112 and the connections therewith of the hydrocarbon vapor lines. Pipe 140 is supplied by a valve 148.

In order to regenerate the catalyst, valves 110, 126, 127, 137 and 142 are closed, and valves 148, 144, 118, 146, 131 and 150 are opened until the system is flooded with inert gas. After filling the system with inert gas, valve 142 is closed, and valve 146 is opened.

When the catalyst has been revivified as indicated by the absence of carbon dioxide in the gases exiting through pipes 132 and 136, valves 142, 148, 144, 118, 146, and 150 are closed, and valves 110, 126, 127, 131, and 137 are open for readmission of the hydrocarbon vapors to the system. However, after the carbon has been burned from the surface of the catalyst beds, it is important to fill the system again with inert gas as described above. Obviously, if needed, the air supply may be diluted with inert gas for controlling the rate of combustion of the deposited carbon, for preventing excessive rise in temperature in the catalyst beds.

The condensate collected in receiver 136 is ready for further refining.

The two catalyst chambers 112 and 124 are heated by a hot fluid circulating around them. Such fluid may be hot combustion gases from burning coke-oven gas, or any other available gaseous material heated sufficiently high to raise the catalyst chambers 112 and 124 sufficiently high to bring about the desired reactions. Chamber 124 is substantially hotter than is chamber 112, as previously mentioned. However, a fused salt bath may be employed as the heating medium, or the catalyst chambers may be heated electrically. When a hot gaseous heating medium is employed, it may be introduced through pipe 144 into jacket 130 enclosing catalyst chamber 124, and then through pipe 150 into jacket 114 around the catalyst chamber 112, and out through outlet 158 to a stack, not shown.

We claim:

1. The process of purifying aromatic hydrocarbons containing not more than approximately five per cent of impurities including paraffinic, naphthenic, and sulphur compounds together with, possibly, unsaturated hydrocarbons, which comprises passing the hydrocarbon to be purified through successive catalytic environments, one of which contains a dehydrogenating catalyst and another contains a cracking catalyst, maintaining dehydrogenating catalyst at a temperature of from approximately 500° C. to approximately 540° C. and at substantially atmospheric pressure, with the cracking catalyst maintained at a temperature of from approximately 250° C. to approximately 500° C. and at substantially atmospheric pressure, thereby converting the said impurities into a condition readily removable from the aromatic hydrocarbon while leaving the aromatic hydrocarbon substantially unaffected.

2. The process of purifying an aromatic hydrocarbon of the group consisting of benzol, toluol, and xyol, obtained from light oil produced in the by-product coking of bituminous coal, of the hydrocarbon containing not more than approximately five per cent of impurities including paraffinic, naphthenic, and sulphur compounds, together with, possibly, unsaturated hydrocarbons, which process comprises contacting successively the aromatic hydrocarbon to be purified with a dehydrogenating catalyst maintained at substantially atmospheric pressure and at a temperature of from approximately 500° C. to approximately 540° C. and with a cracking catalyst maintained at substantially atmospheric pressure and at from approximately 250° C. to approximately 500° C., thereby converting the said impurities into a condition readily removable from the aromatic hydrocarbon, condensing the resulting vapors, and further refining the resulting...
condensate of aromatic hydrocarbon, for removing the said impurities therefrom.

3. The process of purifying aromatic hydrocarbons containing not more than approximately five per cent of impurities including paraffinic, napthenic, and sulphur compounds together with, possibly, unsaturated hydrocarbons, which comprises passing the hydrocarbon to be purified through successive catalytic environments, one of which contains chromic oxide as a dehydrogenating catalyst and another of which contains a silicate as a cracking catalyst, maintaining the chromic oxide catalyst at a temperature of from approximately 500° C. to approximately 540° C. and at substantially atmospheric pressure, with the silicate catalyst being maintained at a temperature of from approximately 250° C. to approximately 500° C. and at substantially atmospheric pressure, thereby converting the said impurities into a condition readily removable from the aromatic hydrocarbon while leaving the aromatic hydrocarbon substantially unaffected.

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