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METHOD FOR RECOVERING AND REFINING CYCLOPENTADIENE

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1 Claim. (Cl. 260—666)

The present invention relates to a process for the recovery of cyclopentadiene from gases or condensates thereof produced in the destructive distillation of coal or of coal to which an amount of mineral oil has been added previous to its carbonization and for subsequent conversion of such cyclopentadiene by simple method and means into a polymer of lower vapor pressure from which the original material is simply recoverable.

An object of the present invention is the provision of a simple and practical method whereby cyclopentadiene can be recovered from gases of the above-stated class and thereafter be converted into a readily storable and relatively safely transportable polymer of a lower vapor pressure and from which the original substance is easily recoverable as required.

The invention has for further objects such other improvements and such other operative advantages or results as may be found to obtain in the process or apparatus hereinafter described or claimed.

In the coke oven gases resulting from the destructive distillation of coal, and the like, more especially at higher temperatures, there are present in addition to the vapors of benzene, toluene, xylene and their aromatic homologs, some amounts of vapors of lower boiling constituents such as carbon bisulphide, mercaptans, olefinic materials and especially cyclopentadiene which has a boiling point of 40.1° C.

Light oil fractions recovered from such coke oven gases and having a boiling range lying substantially between a first drop of 10° C. and an end point of 80° C., contain high percentages of cyclopentadiene as well as others of the above-mentioned low boiling constituents. It has now been found that when such coke oven light oil fractions are heated at substantially the normal boiling point of cyclopentadiene and at substantially atmospheric pressure and with continuous refluxing of volatilized components of said fractions to the heating vessel, the cyclopentadiene content is rapidly polymerized substantially completely to the dimer form even though said fractions contain a large percentage of other hydrocarbons therein that boil at the same or closely adjacent or somewhat higher temperatures. The progress of the polymerization reaction is evidenced by the rapid increases in the specified gravity of such light oil fractions during the described method of heating as is confirmed by the hereinafter given specific example of results obtained by employment of the present improvement.

In the recovery of the above-mentioned compounds from coke-oven gas they are usually either adsorbed in solid media such as charcoal or silica gel or are absorbed in normally liquid fractions derived from mineral oils or coal tars. After being so extracted from the permanent gases of the carbonization process, they are removed from the adsorbing or absorbing media by means including heat in combination usually with some direct steam. After condensation of such direct steam and the hydrocarbonaceous vapors, there is decantable from the condensed mixture an oily admixture, commonly called crude light oil, having a wide distillation range. Segregation from such admixture of the components boiling below the boiling temperature of benzene provides a fraction that contains, if not all, a large percentage of the cyclopentadiene extracted from the gases when the temperatures of condensation are properly low.

In the refining of the above-mentioned crude light oil for the recovery of pure benzene, toluene, and the like, it has more recently been common practice to subject the same to treatment with strong, usually concentrated, sulphuric acid; this practice converted most of the highly reactive low-boiling constituents into sludgy, ill-smelling, noxious materials that were drained from contact with the so-treated light oil along with the residual acid, this waste mixture being frequently disposed of by burning. Such acid treatment converted the cyclopentadiene content into solid, black substances of greatly increased molecular weight from which the cyclopentadiene is not easily recoverable, if at all.

According to the present invention the vapors recovered from the constituents evolved during the carbonization of fuels by any of the above-mentioned adsorbent or absorbent means are subsequent to their extraction from the latter by means of heat, flowed through a well-chilled condenser and the so-formed liquid condensates are thereafter decanted from contact with the associated steam simultaneously condensed. This condensate, i. e., crude coke oven light oil, is then preferably distilled through a fractionating column whereby to separate a fraction commonly called the "forerunnings" fraction that boils substantially completely below about 70° C. During the distillation for separation of such fraction, the evolved vapors are condensed at a temperature as low as practical and prefer-

ably not above 20 to 25° C. If condensation has been carried on at a sufficiently low temperature, there will be contained in the fraction boiling below about 70° C., substantially all the cyclopentadiene contained in the crude light oil and it will be associated therein with such other constituents thereof as carbon bisulphide, mercaptans, lower boiling paraffins and some unsaturated compounds.

The so-recovered liquid "forerunnings" fraction is thereafter flowed to distillation equipment of the type commonly employed in coke-oven by-product plants wherein it is heated, preferably at substantially atmospheric pressure and under constant reflux at temperatures sufficiently low to prevent substantial escape of any of the cyclopentadiene component. During such treatment the "forerunnings" fraction is heated for a time to a temperature preferably about or slightly above the boiling point of the cyclopentadiene. With continuation of the heating without substantial pressure thereon, the cyclopentadiene component of said fraction is relatively rapidly changed into the higher boiling dimer, the reflux serving to return to the zone of reaction the unpolymerized material thereby providing it with further opportunity to be converted into the dimer, which is an object of the invention. After the complete or the preferred degree of polymerization of the cyclopentadiene has been effected—a phenomenon that can be quite easily followed by observance of the changing increase in specific gravity of the liquid portion in the still-kettle—associated liquid materials are separated from the dimerized cyclopentadiene by distilling the heat-treated still contents at a temperature below that at which the dimerized product is unstable, i. e., 170° C.; the maintenance of such temperature is greatly facilitated by employing conditions of vacuum in the distilling apparatus. Following removal of the associated liquid materials, the residual dimer-product can be either drained from the distilling apparatus in relatively pure form after which it is ready for safe storage or shipment to serve as a source of cyclopentadiene which is recoverable in relatively concentrated form by heating the dimer-product at higher temperatures, or it can be immediately so converted without removal from the still.

If, during the said dimerization process as above described, the still-kettle contents have been maintained at a temperature of about 45° C. and at substantially atmospheric pressure, the cyclopentadiene will have been converted primarily into the dimer form, although there may be also present small portions of higher polymers. It is preferable to have substantially only the dicyclopentadiene formed as the result of the present process, because of its relatively easy and efficient reconversion into cyclopentadiene by a simple heating step at relatively low temperatures thus making it possible for the purchaser thereof to convert it into the lower boiling cyclopentadiene at a desired rate of use.

The present invention thus advantageously makes it possible for the coke-plant operator to recover cyclopentadiene from gases of coal distillation and simply and easily to convert it into a form that is relatively pure and is shippable without undue hazard and from which cyclopentadiene itself is easily and readily recoverable whenever a supply of the same is required at the point of consumption.

The following specific example sets forth results realized in carrying out the above-described process in a coke-oven by-product plant. The mixed vapors and gases issuing from the carbonization chambers, after having been flowed through the usual coolers and apparatus adapted for separately removing tar and ammonia, were flowed to a light-oil absorber where they were brought into contact with a petroleum-derived scrubbing oil to absorb light oil therefrom. The so-enriched scrubbing oil was then flowed successively through a preheater and then through a stripping still where it was brought into direct contact with quantities of stripping steam that swept the absorbed light-oil vapors out of the stripping still into condensing equipment; following decantation of the crude light oil from condensed steam, the former was flowed into a fractionation column from which a cyclopentadiene-containing fraction was recovered that showed an end-point of about 52° C. on Barrett standard distillation test for coke-oven light-oil products. Condenser temperatures were maintained at about 15° C. during the recovery of this low-boiling fraction. It was then flowed to the kettle of a still provided with a refluxing column. In the still about 4450 gallons of said material were boiled at substantially atmospheric pressure and at temperatures of from 44° C. to 49° C. for six and one-half hours. The specific gravity of the original charge was about 0.820 at 25° C. and it began immediately to increase and at the end of six and one-half hours, with constant refluxing of all save the most volatile constituents which could not be condensed at 20° C., there was produced in the still about 4000 gallons of a liquid having a density of 0.860 at 25° C. Thereafter a partial vacuum of about eight inches of mercury was provided on the still by appropriate means and the lower boiling materials removed by distillation at a temperature not exceeding 147° C. measured in the still-kettle. This distillation step served to remove from the still-kettle such materials as carbon bisulphide, low-boiling paraffins, and the like, which were present and had remained little changed during the polymerization period.

The liquid dimerized residue remaining in the still-kettle after the above-described treatment amounted to about 1225 gallons, having a specific gravity of 0.985 at 25° C. The said residue gave on thermal depolymerization a yield of 88 per cent by weight of cycopentadiene when heated to about 170° C.

It is now possible with a process as hereinabove described to recover cyclopentadiene from the gases and vapors produced in the carbonization of fuels and to convert it with apparatus normally present in a coke-oven by-product plant into a polymer thereof having a high degree of purity from which cyclopentadiene is readily recoverable. Cyclopentadiene is a product that has more recently become of industrial importance for divers uses. In consequence of its relatively low boiling point, however, its transportation in substantially pure form would require expensive pressure equipment in which the hazards are not completely eliminated. By means of the present invention, this relatively volatile material having a vapor pressure of about 600 mm. mercury at 12° C. can be converted to the dimer that exhibits a vapor pressure of about 10 mm. mercury at the same temperature. The latter compound is shippable without undue hazard and can be easily reconverted to the monomer as required.

It is of course obvious that where those cyclopentadiene-containing fractions treated according to the present process have a content of such other hydrocarbons as raises the distillation end points of the untreated material above the 52° C. end point of the said material cited in the specific example, a higher vacuum than that cited for the complete removal of the associated materials from the dimerized product formed in the specific example may be required and employed without departing from the spirit of the present improvement. It is not intended therefore that the improvement be in any wise limited to specific conditions of the cited example which should be considered as typical but not limiting.

The results realized by actual use of the present improvements show that lower-boiling, cyclopentadiene-containing fractions of light oil derived from gases and vapors evolved from coal, and the like, in the course of its destructive distillation, contain no associated compounds that interfere with the relatively speedy conversion of said fractions' cyclopentadiene content to the dimer form even when the former is present to the extent of only about one-fourth of the fraction being processed, and that the reaction can be substantially completely carried out in simple equipment usually available in coke-oven by-product plants and at about the normal boiling point of cyclopentadiene and at atmospheric pressure with condensation and return of unreacted material to the heating zone.

The invention as hereinabove set forth is embodied in particular form and manner but may be variously embodied within the scope of the claim hereinafter made.

We claim:

A process for producing from cyclopentadiene, and the like, present in gases and vapors evolved from such solid fuels as coal during a carbonization step therefor, a material having at ordinary temperatures a vapor pressure lower than said cyclopentadiene and into which said material is susceptible of re-conversion by simple heating, said process comprising: bringing gases and vapors from said carbonization step into contact with a medium for absorbing cyclopentadiene, and the like, therefrom; removing so-charged medium from contact with residual gases and vapors and thereafter heating such medium to vaporize thereby absorbed constituents of said gases and vapors; cooling the so-vaporized constituents to condense them; fractionally distilling the so-condensed vapors and separating therefrom a liquid product that contains the cyclopentadiene admixed with other constituents thereof and that is substantially completely distillable, at normal pressures, below the boiling temperature of pure benzene; boiling said liquid product at a temperature less than about 60° C. and at substantially atmospheric pressure with return of material volatilized during said boiling to the bulk of the liquid being boiled until the cyclopentadiene is converted into a polymer thereof; and thereafter separating said polymer from more volatile material associated therewith by heating under pressure conditions less than atmospheric.

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