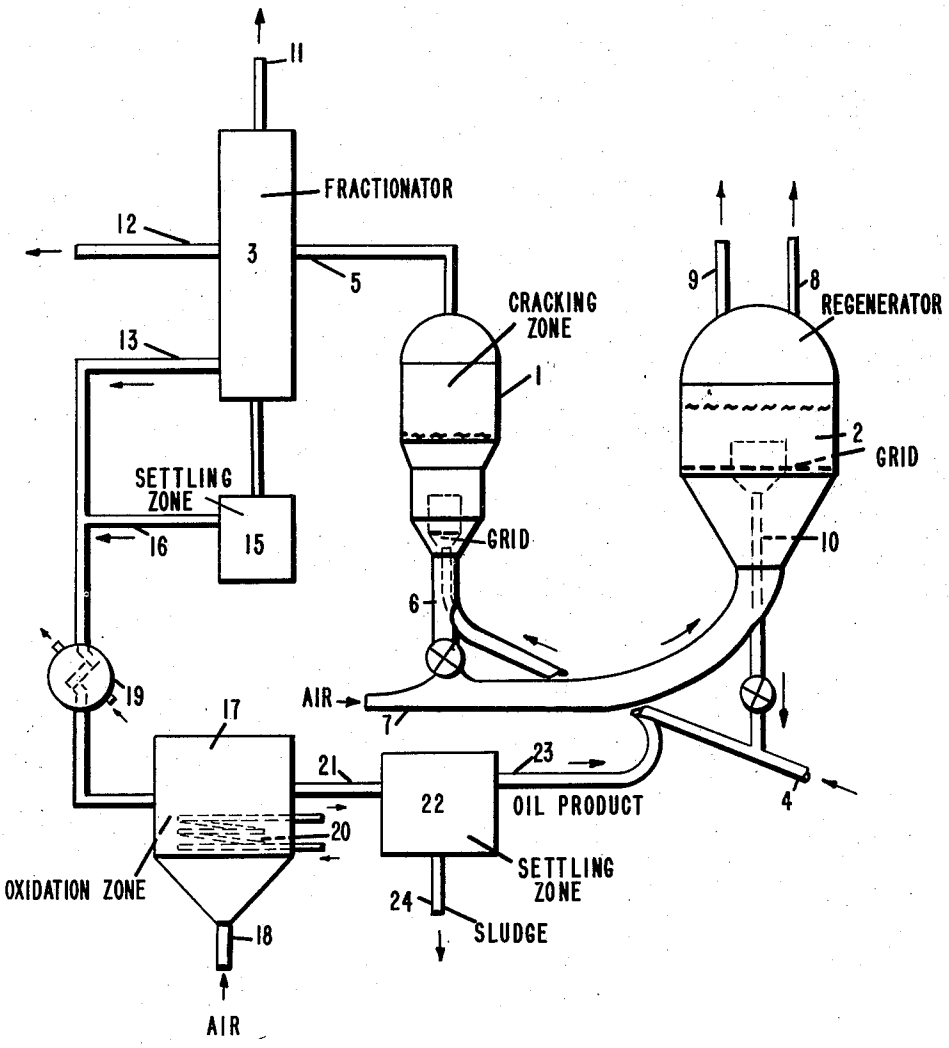
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REDUCTION OF CARCINOGENICITY OF HIGH BOILING CATALYTICALLY CRACKED OIL BY PARTIAL OXIDATION

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JOHN REHNER JR.
LAWRENCE T. EBY INVENTORS

BY W. O. Teilman ATTORNEY

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REDUCTION OF CARCINOGENICITY OF HIGH BOILING CATALYTICALLY CRACKED OIL BY PARTIAL OXIDATION

John Rehner, Jr., Westfield, and Lawrence T. Eby, Linden, N. J., assignors to Esso Research and Engineering Company, a corporation of Delaware

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This invention concerns a novel refining process of application to high boiling catalytically cracked oils. The process of this invention is applied to catalytically cracked products boiling above about 700° F. The process entails the partial oxidation of oils of this character in order to minimize the carcinogenicity of these oils and to improve their value as ultimate products or for further processing.

In the catalytic cracking process, petroleum factions are heated in the presence of a catalyst and large petroleum molecules are broken down into small molecules providing products such as gasoline, kerosene, home heating oils and diesel oils. However, in the catalytic cracking process there is a residual material which contains higher boiling constituents including a substantial concentration of high boiling polycyclic aromatic hydrocarbons. Higher boiling residual material of this character is frequently used for industrial fuels.

Because the residual fractions of catalytic cracking referred to contain polycyclic aromatic hydrocarbons, it was suspected that this material might be carcinogenic in character. At this date it has been established that this is the fact, at least as applied to lower animals. Furthermore, this has been borne out by a limited amount of information indicating that direct contact with certain higher boiling petroleum fractions has caused occupational cancer in man. (W. C. Heuper, "Occupational Tumors and Allied Diseases," page 66, published by C. C. Thomas, Springfield, Illinois, 1942.) As a result of this discovery, it has become important to provide all possible safeguards to prevent any possibility for the occurrence of cancer due to contact with high boiling catalytically cracked products.

This problem has heretofore been met by economically expensive expedients. For example, it has been recommended (Holt, Hendricks, Eckardt, Stanton, and Page, "Archives of Industrial Hygiene and Occupational Medicine," page 333, October 1951), that the high boiling catalytically cracked residues which are suspected of being carcinogenetic must be blended with non-carcinogenic products so as to include no more than 10% of the carcinogenic fraction; such blends have been shown to be safe. This has created some problem in the disposal of the heavy residues from catalytic cracking and has caused a considerable loss in the economic value of the residual cracked products.

Since this problem was first recognized, it has been appreciated that some technique should be found for minimizing the carcinogenicity of heavy catalytically cracked residues. Such methods should be employed in order to further minimize the occupational hazard of handling or processing such stocks and in order to eliminate need for the more expensive safety expedients heretofore used. The present invention is directed to this purpose and for the first time provides a practical and efficient process for reducing the carcinogenicity of heavy catalytically cracked residues.

The process of this invention is a relatively simple process providing for a selective partial oxidation of carcinogenic petroleum fractions. In order to secure the desired results it has been found that the oxidation must be carried out in the narrow temperature range of about 200° to 275° C. This oxidation can be readily achieved by simply blowing air through the residual oil products at this temperature for a period of time ranging from about 2 to 10 hours. If desired, the process may be supplemented by use of ultra-violet energy or sunlight during oxidation, by the use of certain oxidation catalysts, or by the use of ozone. By this process it has been found possible to substantially eliminate the carcinogenicity of the petroleum fractions referred to.

The accompanying drawing diagrammatically illustrates an embodiment of the invention showing the overall processing of petroleum fractions resulting in the formation of carcinogenic products and permitting the destruction of the carcinogenic components in accordance with this invention.

A conventional catalytic cracking system is illustrated in the drawing including the cracking zone 1, the catalyst regenerator 2 and the product fractionator 3. While it will be understood that this invention is of application to catalytically cracked products however obtained, the process illustrated is a fluidized catalytic cracking operation. In this process conventional and well-known cracking catalysts may be used such as silica-alumina mixtures, silica-magnesia mixtures, montmorillonite clay, and the like. In the particular process illustrated, a gas oil feed stock may be introduced to the cracking zone through line 4. This is brought into the reaction zone 1 through a suitable distributing grid so as to be brought in contact with a mass of cracking catalyst maintained in fluidized condition in the cracking zone 1. For this purpose, particles of cracking catalyst of suitable size are employed and the ratio of oil to catalyst is maintained so as to permit the establishment and maintenance of a fluidized condition. In this condition, up-flowing oil vapors passing through the catalyst particles cause the catalyst to have the general characteristics of a liquid. Thus the catalyst bed is characterized as an upper surface and has the general hydraulic properties of a liquid. During passage through the cracking zone at a temperature of about 800 to 1000° F., the oil feed stock undergoes the cracking reaction and the cracked products may be removed overhead through line 5. As will be described, these cracked products are subjected to fractionation in the fractionator zone 3.

Cracking catalyst is continuously withdrawn from the fluidized bed of catalyst in zone 1 through line 6. Air is introduced to intersecting conduit 7 so as to force the catalyst upwardly into the regeneration zone 2. In the presence of the air carbonaceous impurities are oxidized in zone 2 so as to regenerate the catalyst. The products of this oxidation are removed overhead through lines 8 and 9, while the regenerated catalyst is withdrawn from the regenerator through line 10 for recycle to the cracking zone through line 4.

It is not considered necessary to further describe the catalytic cracking operation identified since this is not a part of the present invention. As indicated, however, regardless of the manner of carrying out the catalytic cracking reaction, a cracked product stream is obtained which is fractionated in a distillation tower such as fractionator 3 illustrated. In fractionation zone 3 the catalytically cracked products are separated so as to permit a withdrawal of gaseous products from the uppermost portion of the fractionator through line 11. Low boiling, liquid products such as gasoline may be withdrawn from suitable side stream withdrawals such as line

12. Higher boiling products are withdrawn from other withdrawals positioned at lower portions of the fractionator and from the bottom withdrawal of the fractionator. For example, fractionator 3 may be operated to permit withdrawal of a side stream through line 13 boiling above 700° F. Such a side stream is commonly identified as cycle oil. Still heavier boiling residual products of cracking are then withdrawn from the lowest portion of the fractionator through bottom withdrawal 14. The bottoms product will contain small proportions of catalyst particles carried over from the cracking zone. Consequently, the fraction is passed to a settling zone 15 permitting withdrawal of a clear or clarified slurry oil through line 16.

As described, fractionator 3 is operated to permit segregation of the portion of the cracked products boiling above 700° F. This particular fraction of the cracked products is specified since it has been established that the portion of the cracked products boiling below 700° F. is non-carcinogenic. For this reason, the process of this invention is applied to the products withdrawn from the fractionator through lines 13 and 14 boiling above 700° F. Sharp fractionation is not required however, and lower boiling constituents may be included.

Either or both of the products streams of lines 13 and 14 may be processed. As illustrated, these product streams may be combined and passed together to the oxidation zone 17. Air is introduced to the lower portion of the oxidation zone through line 18 so as to bubble upwardly through the cracked residue. A suitable air distribution grid or other techniques may be used to secure good distribution of the air throughout the oxidation zone. Oxidation must be conducted at a temperature in the range of about 200 to 275° C. and for this purpose suitable heating means must be provided in conjunction with the oxidation zone. For this purpose the oil residue prior to introduction to zone 17 may be passed through a preheater 19 and suitable heating coils 20 may be maintained in zone 17. The oxidation may be carried out on a batch or continuous basis provided the oxidation period be about 2 to 10 hours. Suitable oxidation is obtained under these conditions provided about 0.1 to 1.0 lb. of air per barrel of oil per minute be employed. The air blowing maintains sufficient agitation to keep the oil product in a homogeneous state during oxidation. The oxidized products can be withdrawn from the oxidation zone through line 21 for introduction to a settling zone 22. In zone 22, the oil is permitted to remain in a quiescent state so that sludge may settle from the oil. Thus, it has generally been found that on oxidizing the cracked residues a substantial portion of sludge is formed which will settle from the oil. To facilitate settling, the oil should be maintained at a temperature above about 50° C. for a period of about 0.5 to 5.0 hours or longer. The final oil product may then be withdrawn through line 23 while the sludge may be withdrawn through line 24.

The sludge of line 24 may be used for a variety of purposes. The sludge constitutes suitable material for inclusion in asphalt and for this purpose the sludge may be blended with asphaltic stocks. Alternatively, the sludge may be used as a component of industrial fuels, such as bunker fuels, as a component of wood preservatives, and as a starting material for the production of carbon black by the so-called furnace process.

The oil product of line 23 is rendered substantially inactive or non-carcinogenic by the treatment described. This oil product may therefore be used as fuel oil or may be used for other purposes without danger. However, it is a particular feature of this invention that this oil product be recycled to the catalytic cracking zone 1. The oxidized oil product, by virtue of the removal of carcinogenic polycyclic aromatic hydrocarbons, is greatly improved as a cracking feed stock. For this reason, it becomes attractive to recycle this product for further catalytic cracking. In this connection it is well-known that clarified oil from a catalytic cracking process is sufficiently refractory so as to discourage recycle cracking of this stock. This is particularly true in view of the fact that recycle cracking of a conventional clarified oil does not serve to eliminate the carcinogenicity of this material. In other words, the polycyclic aromatic hydrocarbons which are objectionable are not entirely cracked in recycle cracking which may result in a further build-up in the cracked products of these carcinogenic materials. However, heavy catalytically cracked fractions which have been treated by partial oxidation as described are not subject to these disadvantages and constitute good cracking feed stocks. Furthermore, the removal of the polycyclic aromatic components results in less carbon deposition by the recycled oil on the cracking catalyst, and hence a more efficient catalytic cracking process. It therefore becomes practical and desirable to employ recycle cracking to substantially eliminate or to greatly minimize the final heavy residue obtained from the overall process. By this means the cycle oil and slurry oil are effectively upgraded to the more valuable heating oil and fuel fractions.

In order to fully demonstrate the nature and advantages of this invention reference will be made to typical experiments conducted to evaluate the invention. In a first experiment the fraction of catalytically cracked products boiling above 700° F. was segregated from a commercial cracking operation. This fraction was tested for carcinogenicity according to the procedure identified in the paper "Properties of High Boiling Petroleum Products" by Dietz, King, Priestley and Rehner, published in "Industrial and Engineering Chemistry," vol. 44, page 1818. This procedure permits an identification of the carcinogenicity of a sample by determination of the "tumor potency" of the sample in carefully controlled tests with mice. In the scale employed, tumor potency values of 50 or 60 or more are considered high. Potency values of about 30 or less are low or marginal and commonly indicate that only benign tumors would result. When the identified sample was tested in this general manner it was found to have a tumor potency of about 61.

This same residue of catalytic cracking was then subjected to the process of this invention by air blowing the sample at 200° C. for 7½ hours. The air blowing was conducted in glass equipment by bubbling air through the oil at the rate of 1 liter of air per kilogram of oil. This oxidized oil in total was then tested for tumor potency. It was found that the oxidized oil had a tumor potency factor of only 31. This experiment therefore established that partial oxidation of the heavy residue from catalytic cracking is operative to substantially reduce the carcinogenic nature of the material.

Other experiments were conducted in order to establish the oxidation conditions required to secure this result. In each experiment the fraction employed constituted the portion of catalytically cracked products boiling above 700° F. Air blowing providing 1 liter of air per kilogram of oil per minute was employed for the oxidation. The time of air blowing for each oxidation temperature tested, was two hours, four hours and six hours, with representative results of a similar nature for eight hours. The temperature of oxidation in different experiments was maintained at 100°, 200°, 225°, 250°, 275°, and 300° C.

In these experiments it was determined that oxidation at 100° C. is ineffective. At 100° C. the constituents of the heavy cracked residue underwent substantially no oxidation and the carcinogenic properties of the material were not affected. It was found that a temperature of at least 200° C. is required in order to secure the desired oxidation. Furthermore, it was discovered that at 300° C. oxidation of paraffinic constituents of the material occurs at a faster rate than oxidation of aromatic constituents. For this reason, at a temperature of 300° C.

or higher, there is a build-up rather than a reduction in the aromatic content of heavy cracked residues. These experiments therefore established that oxidation must be carried out between the narrow limits of about 200 and 275° C.

Reference may be made to an experiment conducted at an oxidation temperature of 250° C. to indicate the type of oxidation which is achieved by the process of this invention in order to eliminate carcinogenic materials. The sample employed had an original aromatic content of about 34%. During air blowing extending up to 6 hours under the conditions specified, this aromatic content was linearly reduced to a value of about 26% at the end of 6 hours. Under these conditions, about 28% of sludge was formed as determined by settling at 50° C. The sludge formed was found to have an oxygen content of 2.05%. The oil product separated from this sludge was found to have an oxygen content of 0.94%. It is therefore to be seen that the oxidation treatment applied apparently resulted in the selective oxidation of carcinogenic constituents of the oil so as to permit the separation of these constituents as a sludge. At the same time, however, it should be observed, as indicated above, that even though the sludge be included in the product, this material is also rendered non-carcinogenic by the oxidation. Consequently, while it becomes practical to separate the oxidized polycyclic aromatic compounds this is not required in order to obtain a safe product.

As described, therefore, this invention concerns the partial oxidation of the heavy residue of a catalytically cracked product. The residue to be subjected to oxidation is that portion of the catalytically cracked products boiling above 700° F. normally characterized by inclusion of carcinogenic polycyclic aromatic hydrocarbons. By oxidizing cracked residues of this character at a temperature in the range of about 200 to 275° C. by air blowing for a period of 2 to 10 hours it is possible to selectively oxidize the objectionable constituents. This occurs with little change in the inspections of the oil so that the oxidized product may be used as fuel, may be used for recycle cracking, or the like. As brought out, it is a particular feature of this invention that the partially oxidized catalytically cracked residue be employed for recycling to a catalytic cracking operation.

What is claimed is:

1. A process for reducing the carcinogenicity of a catalytically cracked petroleum oil boiling in excess of about 700° F. which comprises air-blowing said oil at a temperature of from about 200° to about 275° C. with from about 0.1 to 1.0 pound of air per barrel of oil per minute for a period of from about 2 to about 10 hours and oxidizing carcinogenic constituents in said oil to form a sludge.

2. A process as defined by claim 1 wherein said sludge is separated from said oil by settling at a temperature above about 50° C.

3. A process as defined by claim 2 wherein said oil, after separation of said sludge, is recycled to a catalytic cracking operation.

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