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REMOVAL OF VANADIUM FROM PETROLEUM OILS BY OXIDATION

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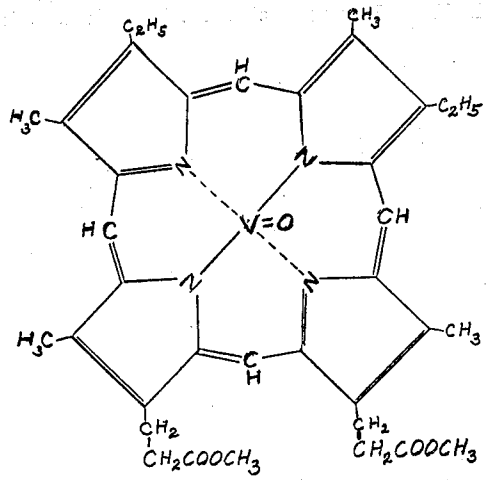
5 Claims. (Cl. 208—251)

This invention is directed to a method for the removal of vanadium from hydrocarbon oils such as petroleum crudes and distillates therefrom, and particularly from the gas oils used in catalytic cracking.

It is well known that some petroleum crudes contain vanadium compounds of a nature such that they are volatilized when the petroleum crudes are distilled and therefore contaminate the distillates. Such vanadium compounds are particularly objectionable in gas oils and other cracking stocks that are to be treated by catalytic cracking since the vanadium contaminates the catalyst and deteriorates its activity. It is a principal object of the present invention to provide a commercially feasible process for reducing the vanadium content of petroleum hydrocarbons to a level at which objectionable contamination of cracking catalysts is avoided.

Some crude petroleums, such as those obtained in Louisiana, contain practically no vanadium compounds, and therefore do not require treatment. West Texas crudes represent another class of natural petroleum that has a low vanadium content; typical samples contain only about 14 parts per million of vanadium of which only a portion is carried over into the gas oil fraction upon distillation. Venezuelan crudes and those found in certain areas of California, on the other hand, have a relatively high vanadium content, and these crudes and the distillates obtained therefrom may advantageously be purified by the process of the present invention.

It has been shown that the vanadium in crude petroleum and in petroleum fractions is present as porphyrin complexes. Thus, in Industrial and Engineering Chemistry, vol. 44 (1942), pages 1159–1165, it is shown that the crude oil from Santa Maria Valley, California, contains a vanadium complex that is similar if not identical to the vanadium complex of mesoporphyrin IX dimethyl ester having the provisional structural formula:



On pages 2591–2596 of the same volume it is shown that such complexes are partially volatilized when the petroleum crudes are distilled and thus appear in the distillates including the gas oil fraction.

My present invention is based on the concept of treating petroleum hydrocarbons containing such vanadium-porphyrin complexes with an oxidizing agent capable of changing the oxidation state of the vanadium, thereby permitting its liberation from the complex and facilitating its removal from the oil. Although the above formula is merely illustrative of many porphyrins which may be present in the oils, and which may contain different substituent groups such as —CH=CH$_2$, —COOH,

—CH$_2$CH$_2$COOH

and the like instead of or in addition to the substituents noted, it will be seen that the molecules in question are planar and form inner complexes of great stability with metal oxides that are normally four-covalent; i.e., which have a coordination number of 4 and are divalent. By oxidizing the vanadium of the divalent V-O structure the stability of the complex is destroyed and removal of the vanadium from the oil is facilitated.

The process of my invention in its broadest aspects is therefore carried out by treating the vanadyl complex-containing petroleum oils with an oxidizing agent capable of attacking the vanadium therein and converting it into a more readily removable form, probably one containing pentavalent vanadium, followed by separation of the vanadium from the oil. Thus, the oxidation may be followed by a solvent treatment for the vanadium removal or the separation may be accomplished by distillation, which is effective since vanadium pentoxide is non-volatile under distillation conditions and therefore remains in the still residue. If desired, the oxidized vanadium may first be converted into a metal vanadate by adding a suitable reactive metal compound such as sodium or calcium hydroxide to increase its solvent solubility or to decrease its vapor pressure.

Oxidation of the tetravalent vanadium in the porphyrin complex is preferably accomplished by adding a suitable oxidizing agent to the oil and then heating until the vanadium oxidation has proceeded to the desired extent. The oil may then be extracted by washing with water or with oil immiscible solvents such as one of the lower monohydric alcohols. Mixtures of water and water soluble alcohols have been used with success. Instead of extracting the oil it may be separated from the oxidized vanadium by any suitable distillation procedure, as by vaporization of the oil at atmospheric or subatmospheric pressures.

The invention will be further illustrated by the following specific examples. It will be understood, however, that although these examples may describe in detail certain preferred features, the invention in its broader aspects is not limited thereto.

Example 1

A sample of a heavy gas oil produced by deep vacuum reduction of Mara Western Venezuela crude petroleum, which sample contained 33 parts per million of vanadium, was diluted for greater ease in handling by admixture with an equal volume of n-hexane. A 150 ml. sample of the diluted oil was treated by adding 0.5 gram of CrO_3 and refluxing at 106° C. for 6½ hours. After cooling it was transferred to a separatory funnel and washed 5 times with 50 ml. portions of a 1:1 isopropanol-water mixture. A filtered sample was analyzed and found to contain 6 parts per million of vanadium.

Example 2

Another sample of the heavy gas oil of Example 1 was diluted with an equal volume of n-heptane and washed six times with a 1:1 water-isopropanol mixture

and a sample of the washed oil-heptane mixture was analyzed for vanadium. It contained 18 parts per million of vanadium, indicating that none was removed by washing.

Example 3

Another sample of the heavy gas oil of Example 1 was treated by adding 0.18% of its weight of CrO_3 followed by heating at 200° C. for 15 hours. It was then distilled by the following procedure.

A vacuum distillation apparatus was set up employing a distillation flask surmounted by a 6-inch heated column packed with glass helices. The treated oil was distilled in this equipment using the temperatures and pressures shown below and four overhead fractions and a still residue were obtained and analyzed for vanadium. The results were as follows:

Fraction	Wt. Percent	Head Temp., ° C.	Pot Temp., ° C.	Pressure, mm. Hg	V Content, p.p.m.
1	20.4	to 180	to 274	0.1	0.1
2	10.5	180–202	274–295	0.1	0.1
3	11.8	202–227	295–319	0.2	0.1
4	19.6	227–258	319–348	0.2	0.1
Residue	42.4				47

The results of these examples show that the vanadium in the porphyrin complex is effectively converted by oxidation into a form in which it can be removed either by solvent extraction or by distillation of the treated oil. The quantity of oxidizing agent to be used for this purpose may vary between rather wide limits, depending on the amount of vanadium in the oil, but should at least be sufficient to oxidize all of the vanadium to be removed to the pentavalent condition. Thus when chromic acid is used the quantity should be at least three times the weight of the vanadium to be oxidized. Other oxidizing agents capable of oxidizing vanadyl vanadium to V_2O_5 may be used such as potassium permanganate, $NaClO_3$, hydrogen peroxide and the like, but the best results have been obtained with chromic acid.

The rate of oxidation of the vanadium in the oil can be increased by adding excess oxidizing agent or by heating the oil after its addition to temperatures of 100°–300° C. or higher, or both. Preferably a quantity of oxidizing agent within the range of about 10 to 200 times the weight of vanadium in the oil is employed, since this permits completion of the oxidation reaction with heating times of about 5–20 hours or less. The optimum treating temperatures, quantity of oxidizing agent and reaction time will of course vary with different oils but can readily be determined by applying the procedures of the foregoing examples to a sample of the oil to be treated.

It will thus be seen that the present invention provides a commercially feasible method for removing combined vanadium from petroleum hydrocarbon oils including both crude petroleum, topped petroleum and distilled petroleum fractions. Ordinarily such petroleum hydrocarbons do not require treatment when they contain less than about 10 parts per million of vanadium but when larger quantities of this metal are present the oils or the distillates can cause an accelerated deactivation or poisoning of cracking catalysts and their complete or partial removal is highly desirable.

By oxidizing the tetravalent vanadium in the oil the stability of its porphyrin complexes is destroyed, and the vanadium is thereby converted into a condition in which it can be more readily separated from the oil.

What I claim is:

1. A method of removing vanadium from petroleum hydrocarbon oils containing vanadium combined therein as a tetravalent vanadium porphyrin complex which consists essentially in the steps of oxidizing said vanadium to the pentavalent condition and then separating it from the oil.

2. A method according to claim 1 in which the tetravalent vanadium is oxidized by reacting the oil with CrO_3.

3. A method of removing vanadium from petroleum hydrocarbon oils containing vanadium combined therein as a tetravalent porphyrin complex which consists essentially in first oxidizing said vanadium and thereby rendering its porphyrin complex unstable and then extracting the oxidized vanadium from the oil.

4. A method according to claim 3 in which the vanadium is extracted by washing the oil with an aqueous lower aliphatic monohydric alcohol.

5. A method of removing vanadium from a petroleum hydrocarbon oil containing vanadium combined therein as a tetravalent vanadium porphyrin complex which consists essentially in first oxidizing said vanadium and thereby rendering its porphyrin complex unstable and then distilling said oil.

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