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PAPER A CHEMISTRY

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CLIENT'S LETTER

PetroFuel

From: R&D, Crude refining unit

To: Patent Department

Re: European Patent application to be filed

As you probably read on the "Intranet", PetroFuel acquired the exploration and exploitation rights for a part of the "Palunka" oil field. The exploration was successful and the exploitation of this field will start soon. The crude produced in this field will be processed in the nearby refinery, which will be revamped in order to be able to treat it. "Palunka" crude has a high sulphur content. The refining of the crude thus needs to include a sulphur removal treatment.

Removing sulphur from petroleum products is a well established process and many processes have been proposed to deal with this problem. In our unit, we considered various techniques and came to the conclusion that a process used previously at some PetroFuel refineries could be modernised. A new treatment solution has also been developed which has proven to be effective in our sulphur removal process. The improvements seem important enough to be patented.

In the attachments, you'll find background information, a description of the invention and some older patents dealing with this matter.

Please treat this application with great speed as the other operators of the "Palunka" field face the same problem and might try to file similar applications. In order to speed up the drafting procedure, the attachments are drafted in a way your department normally uses when filing patent applications.

Description of the process for which a patent application has to be filed

Background of the invention

Crude oil often contains significant amounts of sulphur compounds. In a standard refining process the sulphur compounds in the crude oil are typically carried through into the petroleum products. The presence of sulphur compounds in automotive or aviation fuels is increasingly seen as an environmental hazard and governments worldwide are legislating for lower maximum sulphur contents in petroleum products. Petroleum products intended for the petrochemical industry also often have to have low levels of sulphur.

The fractional distillation of the crude oil is an important initial step of refining processes. The distillation of the crude results in a number of hydrocarbon distillate fractions having particular boiling point ranges. In the fractions boiling below 200°C the major amount of the sulphur contaminants is present in the form of mercaptans (R-SH, also known as thiols), often as C₂ to C₆ mercaptans (that is mercaptans containing between 2 and 6 carbon atoms). The present invention concerns a treatment solution which is able to remove mercaptans from hydrocarbon distillate fractions boiling below 200°C. The solution has no utility for fractions boiling above 200°C, since the mercaptans in such higher boiling fractions cannot be removed economically with the present treatment solution.

The textbook method for removing mercaptans from hydrocarbons is to use an extraction process in which the hydrocarbon is brought into contact with an aqueous alkaline solution. The mercaptans are preferentially dissolved as mercaptides (for example R-SNa if the alkali is NaOH) in the aqueous alkaline solution and are thereby extracted from the hydrocarbon stream. The mercaptide-containing alkaline solution is then subjected to a procedure referred to as regeneration which consists of oxidising the mercaptides to water insoluble disulfides (R-S-S-R) and separating the disulfides from the aqueous solution by decantation in a phase separation zone. The aqueous solution is then recycled to the extraction zone.

The efficiency of the sulphur removal depends upon which mercaptans are present. C_2 and C_3 mercaptans are extracted into an aqueous alkaline solution far more readily than C_4 to C_6 mercaptans. Thus if the hydrocarbon to be treated contains significant amounts of C_4 to C_6 mercaptans the standard mercaptan removal method may not be able to reduce the sulphur content to the levels now required.

Objective of the invention

An objective of the invention is to provide a treatment solution which is very effective for removing mercaptans from hydrocarbon fractions boiling below 200°C .

A further objective of the subject invention is to provide a process for efficiently extracting mercaptan compounds from a hydrocarbon fraction which boils below 200°C . The process is particularly useful when the hydrocarbon fraction being treated contains a high proportion of C_4 to C_6 mercaptans.

Description of the process

The invention is thus a treatment solution for hydrocarbons which comprises an aqueous alkaline solution of sodium or potassium hydroxide which contains an alcohol or a carboxylic acid as a co-solvent in a weight ratio of hydroxide to co-solvent of 5:1 to 1:2.

The invention also provides a process for removing mercaptans from hydrocarbon feed streams which boil at temperatures below 200°C , which comprises the steps of

- (a) contacting a hydrocarbon feed stream with the above treatment solution in a first extraction zone and thereby forming a product hydrocarbon stream and a mercaptide-rich aqueous solution,
- (b) passing the mercaptide-rich aqueous solution and air into an oxidation zone where the mercaptides are converted to oily disulfides and producing an oxidation effluent stream which comprises the oily disulfides and an aqueous solution,

- (c) removing the disulfides from the oxidation zone effluent in a phase separation zone by forming a regenerated sulphur-lean aqueous alkaline solution, which is recycled to the final extraction zone of step (a).

The treatment solution must contain either sodium or potassium hydroxide since only alkaline solutions based on these compounds may be regenerated in the manner described. Sodium hydroxide may be used in concentrations of from 1 to 50 wt.%, with a preferred concentration range being from 5 to about 25 wt.%. The co-solvent used to increase the solubility of the mercaptans in the solution may be any alcohol or carboxylic acid. It is essential that the co-solvent and hydroxide are used in a weight ratio of 1:5 to 2:1 since otherwise no increase in solubility is observed. In addition when the co-solvent is a carboxylic acid, the hydroxide to co-solvent ratio must be selected such that the pH of the solution is above 7. An aliphatic alcohol, preferably selected from methanol or ethanol, is the most effective co-solvent. Aromatic alcohols such as phenol or cresol have also successfully been employed. The treatment solution may be manufactured as a concentrate with the correct weight ratio of alkaline compound to co-solvent and diluted for use on site.

The present mercaptan extraction process is believed to be particularly economically viable for hydrocarbon distillate fractions boiling in the range 80°C to 130°C. Such fractions often contain over 50% of the sulphur in the form of C₄ to C₆ mercaptans. Such fractions were not readily amenable to treatment with the standard mercaptan extraction process. The use of the alcohol or carboxylic acid ensures that the C₄ to C₆ mercaptans are effectively extracted.

During the initial testing of the present process it was found that feed streams consisting of hydrocarbon distillate fractions containing significant concentrations of olefinic hydrocarbons cause problems when treated using the present process. One reason for this is that olefinic hydrocarbons are partially soluble in the aqueous alkaline solution. Therefore, in treating a highly olefinic stream with the aqueous solution, a significant amount of the olefinic hydrocarbons begins to enter the aqueous solution. This by itself will result in some loss of the hydrocarbon being treated. However, more importantly, the entrance of these olefinic hydrocarbons into the mercaptide oxidation zone results in a significant amount of polymerisation. This polymerisation is undesirable as it results in a loss of the valuable olefinic hydrocarbons and forms polymers or polymeric deposits which can clog the equipment employed in the process and in other ways interfere with or degrade the performance of the overall treating process.

In a preferred embodiment of the present process, the problems associated with the dissolution of olefinic hydrocarbons are overcome by a step of extracting the olefinic hydrocarbons from the alkaline solution stream prior to the oxidation. This step involves the removing of the olefinic hydrocarbons from the mercaptide-rich aqueous solution with a saturated (that is olefin-free) hydrocarbon stream in a second extraction zone and thereby forming a treated mercaptide-rich aqueous solution.

In this extraction step, the mercaptide-rich alkaline solution is contacted with a saturated hydrocarbon stream under conditions which result in a transfer of a significant percentage of the olefinic hydrocarbons into the saturated hydrocarbon stream employed in this extraction step. The concentration of olefinic hydrocarbons in the extracted mercaptide-rich alkaline solution stream may thereby be reduced to a level which is acceptable for passage of the mercaptide-rich alkaline solution into the oxidation zone. It has been surprisingly found that not only does this second extraction remove olefinic hydrocarbons but it also results in a higher percentage of sulphur removal.

The operation of a preferred mercaptan extraction process is now described.

The feed stream is passed into a first extraction zone. The hydrocarbon stream usually passes upward, counter currently to a descending stream of the aqueous alkaline solution. During passage through the extraction column, mercaptans originally present in the feed stream are converted to mercaptides and transfer into the descending alkaline solution, which results in the removal of the mercaptans and the production of a treated hydrocarbon stream which is removed from the process.

The mercaptide-rich alkaline solution is admixed with a saturated hydrocarbon stream in a second extraction zone. A mixture of saturated hydrocarbons boiling in a similar range to the feed is preferred, since the saturated hydrocarbon stream (after its use in the second extraction) can then be mixed with fresh feed. This saturated hydrocarbon stream is readily available from hydrocracking units, which most modern refineries contain.

A settling vessel which functions as a phase separation zone is then used to separate the less dense hydrocarbon phase from the denser aqueous alkaline solution. This second extraction process produces a treated mercaptide-rich aqueous alkaline solution. The treated mercaptide-rich aqueous alkaline solution is then passed into an air oxidation reactor, in which the mercaptides are oxidised to disulphides. The effluent stream of the oxidation reactor, which comprises an admixture of any residual air, the aqueous alkaline solution and disulphide compounds is passed into a three-phase separator. The residual gaseous components are withdrawn from the top of the separator. The disulfides formed by the oxidation are relatively insoluble in the aqueous alkaline solution and may therefore be separated by decantation and withdrawn from the process. There remains an aqueous alkaline solution containing the co-solvent which is withdrawn from the separator and recycled to the first extraction zone.

The temperature in the first extraction zone is normally within the range of 10 to 120°C, preferably from 25 to 50°C. The pressure used is sufficient to ensure that the feed stream is liquid. The ratio of the volume of the alkaline solution required per volume of the feed stream will vary depending on the mercaptan content of the feed stream. Normally this ratio will be between 0.01:1 and 1:1, although other ratios may be desirable. Optimum extraction is obtained with a flow velocity of from 1.5 to 3 m/sec. The second extraction zone and the oxidation zone are usually operated under the same temperature, pressure and flow velocities as the first extraction zone. The oxidation zone may contain a packed bed of a mixture of alumina and oxidation catalyst particles (such as for example copper phthalocyanine on activated carbon). The bed promotes mixing and the catalyst enhances the reaction rate.

The phase separation zones may be of any suitable configuration. The phase separation zones are sized to allow the denser alkaline solution to separate by gravity from the treated hydrocarbons.

Example 1

A hydrocarbon distillate fraction boiling in the range 80°C to 130°C and containing 10% olefins and 1000 ppm total sulphur in the form of mercaptans (of which 50% was in the form of C₄ to C₆ mercaptans) was treated on a laboratory scale in accordance with the present invention.

The alkaline solution used consisted of 15 wt.% sodium hydroxide, 10 wt.% of the co-solvent (when present) and balance water. All of the steps were performed at 40°C and atmospheric pressure. No catalyst was used in the oxidation zone.

A number of runs with different co-solvents were performed. In two runs the second (olefinic hydrocarbon extraction) zone was omitted. The feed stream was passed through the apparatus at a constant flow rate. The alkali solution was recycled and used saturated hydrocarbon from the second extraction step was mixed with the feed stream. This continuous process was allowed to equilibrate for two hours and then the sulphur content of a sample of treated hydrocarbon was measured. After a further hour the run was stopped, the apparatus was dismantled and cleaned and the presence or absence of polymers in the oxidation zone was determined.

Run	Co-solvent	Final Sulphur content	Polymers present
1	None	460 ppm	No
2	Methanol	45 ppm	No
3	Ethanol	40 ppm	No
4	Phenol	55 ppm	No
5	Cresol	60 ppm	No
6	Butanoic acid	100 ppm	No
7*	Ethanol	200 ppm	Yes
8*	Butanoic acid	150 ppm	Yes

* Runs 7 and 8 are runs in which the olefinic hydrocarbons were not extracted.

DOCUMENT DI (State of the Art)

Petrol or gasoline is a very important fuel. Petrol can be regarded as a mixture of saturated, olefinic and aromatic hydrocarbons. The boiling point range for petrol is most commonly 80°C to 130°C. An important source of petrol is the fractional distillation of crude oil into hydrocarbon distillate fractions. An important impurity in petrol derived from this source is sulphur which is typically present at concentrations of above 100 ppm in the form of C₂-C₆ mercaptans.

The present invention addresses this problem and provides a process for removing this sulphur from the petrol, without degrading the petrol. The present invention thus provides a continuous process for the removal of mercaptans from a petrol stream comprising at least 100 wt. ppm mercaptans which includes the steps of:

- (a) contacting the feed stream with an aqueous alkaline solution containing a carboxylic acid co-solvent in a first extraction zone and thereby forming a sulphur-lean hydrocarbon stream and a mercaptide-rich aqueous solution,
- (b) passing the mercaptide-rich aqueous solution from step (a) and air into an oxidation zone where the mercaptides are converted to disulfides and producing an oxidation effluent stream which comprises disulfides and an aqueous solution,
- (c) removing the disulfides from the oxidation zone effluent in a phase separation zone thereby forming a regenerated sulphur-lean aqueous alkaline solution, which is recycled to the first extraction zone of step (a).

The process may also include a further step (a') which comprises contacting the sulphur-lean hydrocarbon stream from step (a) with fresh aqueous alkaline solution in a second extraction zone, thereby forming a hydrocarbon stream with an even lower concentration of sulphur.

The use of an alkaline aqueous solution which contains a carboxylic acid as a co-solvent in the first extraction step has been found to extract the sulphur compounds very effectively. This solution is also readily separable from hydrocarbon streams.

- 5 The alkaline aqueous solution extracts the sulphur compounds as mercaptides. These mercaptides are converted to disulphides by the oxidation step (b). This step may be performed catalytically in a packed bed of a mixture of alumina and copper phthalocyanine on activated carbon as is well known in the art.
- 10 The resulting disulphides are water insoluble oils and can thus be separated from the aqueous solution by decantation. The residual aqueous alkaline solution may then be recycled to the first extraction zone.

The treatment solution used may utilize any alkaline compound which is capable of extracting mercaptans from the feed stream at practical operating conditions and which may be regenerated in the manner described. A preferred alkaline reagent comprises an aqueous solution of an alkaline metal hydroxide, such as sodium hydroxide or potassium hydroxide. Sodium hydroxide may be used in concentrations of from 1 to 50 wt.%, with a preferred concentration range being from 5 to about 25 wt.%. The co-solvent used may be any carboxylic acid. This carboxylic acid may be used in any amount provided the pH of the treatment solution is not reduced to 7 or below. A preferred carboxylic acid is butanoic acid.

Example

25 A hydrocarbon distillate fraction boiling in the range 80°C to 130°C (ie petrol) containing 400 ppm total sulphur in the form of mercaptans was treated in accordance with the present invention. The alkaline solution used consisted of 15 wt.% sodium hydroxide, 10 wt.% of butanoic acid and balance water. The feed was extracted in a single extraction zone. All of the steps were performed at 40°C and atmospheric pressure.

30 The feed stream was passed through the apparatus at a constant flow rate. The alkali solution was recycled. The whole apparatus was allowed to equilibrate for two hours and then the sulphur content of the treated petrol was measured. The sulphur content was determined to have been reduced by about 85 wt.%.

Claims

Claim 1

A continuous process for the removal of mercaptans from a petrol stream comprising at least 100 wt. ppm mercaptans which includes the steps of:

- (a) contacting the feed stream with an aqueous alkaline solution containing a carboxylic acid co-solvent in a first extraction zone and thereby forming a product hydrocarbon stream and a mercaptide-rich aqueous solution,
- (b) passing the treated mercaptide-rich aqueous solution and air into an oxidation zone where the mercaptides are converted to disulfides and producing an oxidation effluent stream which comprises disulfides and an aqueous solution,
- (c) removing the disulfides from the oxidation zone effluent in a phase separation zone thereby forming a regenerated sulphur-lean aqueous alkaline solution, which is recycled to the first extraction zone of step (a).

DOCUMENT DII (State of the Art)

The present invention relates to the separation of pyridines from hydrocarbon distillate fractions obtained from oil and to a treatment solution able to perform this separation. The fractional distillation of crude oil results in a number of hydrocarbon distillate fractions which are classified by their boiling point ranges. It has been determined that the fractions boiling in the range 200°C to 250°C often contain significant amounts of valuable pyridines. A method has thus been sought to extract these pyridines.

The present inventors have determined that the pyridines can be extracted from the hydrocarbon distillate fraction by contacting the fraction in a counterflow extractor column with an aqueous alkaline treatment solution comprising 1-50 wt.% of an alkali metal hydroxide, and an alcohol where the weight ratio of alkali metal hydroxide to alcohol is 5:1 to 1:2. The alcohol is preferably an aromatic alcohol most preferably phenol or cresol. Sodium hydroxide is preferably used as the alkali metal hydroxide in view of its low cost. The pyridines are then purified and recovered by first distilling the resulting aqueous solution loaded with pyridines, then scrubbing the resulting vapours with dilute sulphuric acid and finally neutralising the sulphuric acid.

Oils which contain significant proportions of olefinic hydrocarbons boiling in a temperature range which is similar to the boiling range of the pyridines which are being extracted are difficult to treat by the method described above. The olefinic hydrocarbons are extracted into the aqueous alkaline solution and contaminate the pyridines during the distillation. The olefinic hydrocarbons extracted into the aqueous alkaline solution can be removed from the solution by contacting it in a further counterflow extractor with a flow of saturated hydrocarbons.

The treatment solution is prepared as a concentrate in a minimum amount of water by blending the alkali metal hydroxide and the alcohols in the requisite weight ratio. The solution at an appropriate concentration is then made up in situ.

Claims

Claim 1

An aqueous alkaline treatment solution comprising 1-50 wt.% of an alkali metal hydroxide characterised in that the solution also contains an alcohol and in that the weight ratio of alkali metal hydroxide to alcohol is 5:1 to 1:2.

Claim 2

A concentrate for preparing the treatment solution of claim 1, characterised in that it contains an alkali metal hydroxide and an alcohol at a weight ratio of 5:1 to 1:2 dissolved in a minimum quantity of water.

Claim 3

A process for extracting pyridines from oil distillate fractions boiling in the range 200°C to 250°C, which comprises contacting in a counterflow extractor column the oil distillate fraction with a treatment solution as defined in claim 1 and distilling the pyridines from the resulting aqueous solution.

Claim 4

A process according to claim 3 where the aqueous stream is contacted with a stream of saturated hydrocarbons prior to the distillation.