
Candidate's Answer – A (Chemistry)

Renewal of mercaptans from hydrocarbon feed streams

The present invention relates to a process for removing mercaptans from hydrocarbon feed streams which boil at temperatures below 200 °C.

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. C₂ and C₃ mercaptans are extracted into an aqueous alkaline solution far more readily than C₄ to C₆

mercaptans. Thus if the hydrocarbon to be treated contains significant amounts of C₄ to C₆ mercaptans the standard mercaptan removal method may not be able to reduce the sulphur content to the levels now required.

One known process for removal of mercaptans from hydrocarbons is described in DI for treatment of petrol comprising at least 100 wt.ppm mercaptans. This process comprises 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.

However, it has been 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.

We have now identified a new process for removing mercaptans in which 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.

According to the invention there is provided <claim 1>

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.

[Need to refer to DII here, but no time – it does not disclose treatment solution with aliphatic alcohol, or or

There is also provided according to the invention a treatment solution <claim 7> and a concentrate <claim 9> and use of a treatment solution <claim 10>.

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.

<i>Run</i>	<i>Co-solvent</i>	<i>Final Sulphur content</i>	<i>Polymers present</i>
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.

Claims

1. 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 a treatment solution comprising 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 in a first extraction zone, the hydroxide to co-solvent ratio being selected such that the pH of the solution is above 7 when the co-solvent is a carboxylic acid, and thereby forming a product hydrocarbon stream and a mercaptide-rich aqueous solution,
 - a_) removing olefinic hydrocarbons from the mercaptide-rich aqueous solution with a saturated (that is olefin-free) hydrocarbon stream in a second extraction zone under conditions which result in a transfer of a significant percentage of the olefinic hydrocarbons into the saturated hydrocarbon stream and thereby forming a treated mercaptide-rich aqueous solution,
 - b) passing the treated mercaptide-rich aqueous solution and air into an oxidation zone where the mercaptides are converted to oily disulphides and producing an oxidation effluent stream which comprises the oily disulphides and an aqueous solution,
 - c) removing the disulphides 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).

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2. A process according to claim 1 characterised in that the treatment solution contains an alcohol.
 3. A process according to claim 2 characterised in that the treatment solution contains an aliphatic alcohol, preferably selected from methanol or ethanol.
 4. A process according to any preceding claim characterised in that the flow velocity of the hydrocarbon feed stream in step (a) is from 1.5 to 3 m/sec.
 5. A process according to any preceding claim characterised in that a mixture of saturated hydrocarbons boiling in a similar range to the feed is used in step (a_)
 6. A process according to any preceding claim for hydrocarbon distillate fractions boiling in the range 80°C to 130°C.
 7. A treatment solution for hydrocarbons which comprises an aqueous alkaline solution of sodium or potassium hydroxide which contains an aliphatic alcohol as a co-solvent, the co-solvent and hydroxide being in a weight ratio of 1:5 to 2:1.
 8. A treatment solution according to claim 7 characterised in that the aliphatic alcohol is selected from methanol or ethanol.
 9. A concentrate for preparing the treatment solution of claim 7 or 8 characterised in that it contains an aliphatic alcohol and sodium or potassium hydroxide at a weight ratio of 1:5 to 2:1.
 10. Use of a treatment solution comprising an aqueous alkaline solution of sodium or potassium hydroxide which contains an alcohol as a co-solvent in a weight ratio of hydroxide to co-solvent of 5:1 to 1:2, for removing mercaptans from hydrocarbon fractions boiling below 200°C.
 11. Use according to claim 10 characterised in that the hydrocarbon fractions boil in the range 80°C to 130°C.
 12. Use according to claim 10 or 11 characterised in that the alcohol is an aliphatic alcohol, preferably selected from methanol or ethanol.

Divisional Application

Subject matter – the process outlined in steps (a), (b) and (c) at p. 3 - p. 4 of the client's letter but limited to use of an alcohol in the treatment solution.