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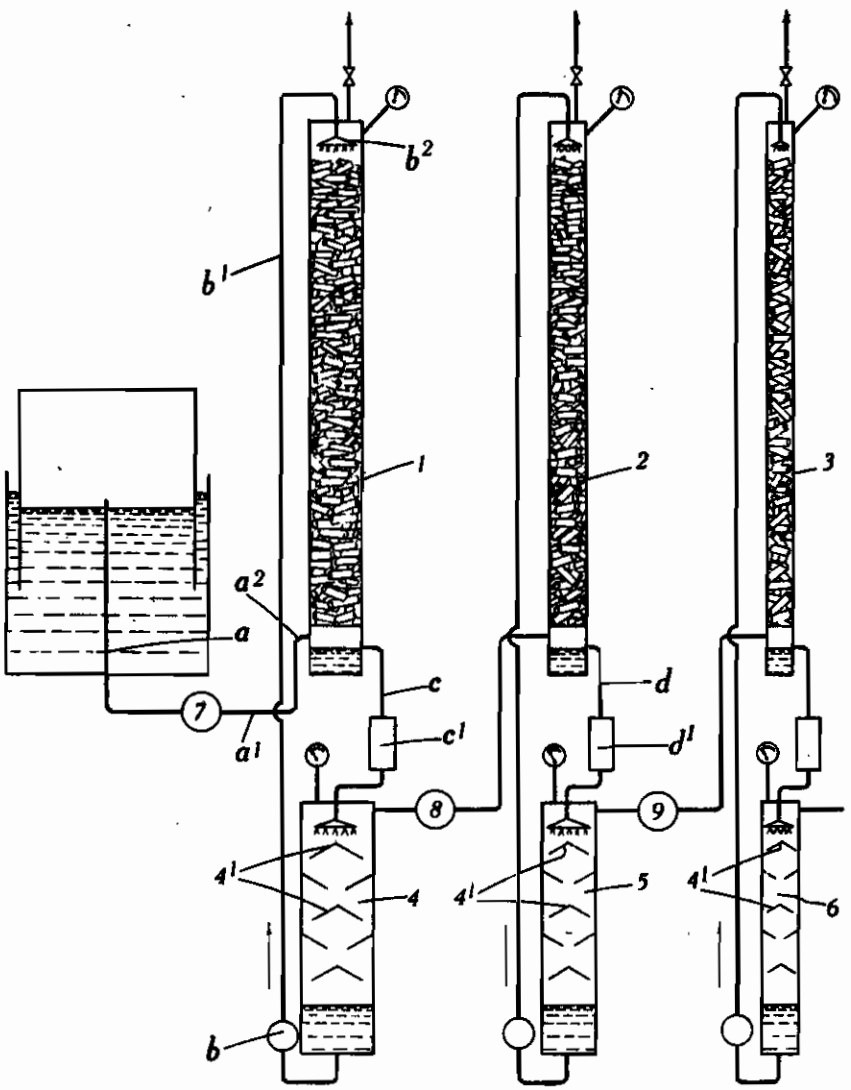

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ALIEN PROPERTY CUSTODIAN

PROCESS OF SEPARATING OLEFINES FROM GASEOUS MIXTURES

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The necessity for utilising hydrocarbons of higher and higher octane number for supplying modern internal combustion engines has led to the practice of adding certain compounds such as the aliphatic alcohols and their ether oxides to the hydrocarbons customarily used. These substances are obtained in the most economical manner by starting from the olefines which are found either in the natural gases collected in certain countries or in the cracking gases provided by the pyrolysis of mineral oils or their heavy fractions of small value.

In any case, the olefines are generally obtained very much diluted in a large proportion of gases such as the corresponding saturated hydrocarbons, methane and hydrogen, and this complicates the problem of the ultimate transformation of these olefines into alcohols or ethers.

Furthermore, methods employing simple liquefaction followed by fractional distillation are of little use in separating the olefines because the boiling point of the olefines and the corresponding saturated hydrocarbons are mixed up in an inextricable fashion in the case of the C_4 and higher hydrocarbons, as the table below shows:—

		Boiling points at ordinary pressure
Ethylene		−103° C.
Ethane		−88°3 C.
Propene		47°8 C.
Propane		−44°5 C.
Butenes	Butene I	−6°6 C.
	Butene 2	+0.3° C.
		+3° C.
	Isobutene	−6° C.
Butanes	Butane-n	−0.6° C.
	Isobutane	−10°2 C.

The present invention has for its object a simple and efficacious process for increasing the proportion of olefine in a gas mixture, or for separating the olefines from cracking or other gases.

Broadly speaking this object is attained by repeated extraction of olefines from a gaseous mixture by means of a solvent having a preferential solvent capacity for the olefines as compared with the diluent gases. This results in the gaseous mixture dissolved in the solvent containing a higher proportion of olefine than the gas in equilibrium with the solution. Hence by recovering the dissolved gases and treating them with solvent and repeating this solution and recovery as often as desired, olefines of any desired degree of purity may be obtained.

Thus according to the present invention a mixture of olefines and diluent gases is treated with a solvent having a preferential solvent capacity for olefines, in a plurality of stages, each of which comprises a solution step, where the gases are dissolved, and a recovery step, where the dissolved gases are recovered from the solvent, the gases recovered from one stage being passed to the solution step of the succeeding stage.

Pressure above atmospheric is preferably used in the solution steps since it renders recovery of the gases easier and also increases the total amount of gas dissolved in a given amount of solvent. On the other hand, the difference between the respective solubilities of the olefines and the saturated hydrocarbons increases with temperature, so that, within certain limits, it is well not to carry out the separation at too low a temperature.

As solvent, there can be used pure water or water to which has been added a certain quantity of a liquid which has the property of increasing the solubility of all the gases forming the mixture, without however diminishing the difference between the solubility coefficients of the olefines on one hand and the diluent gases on the other hand.

It has already been proposed, for the separation of olefines from mixtures containing these substances, to use aqueous solutions of certain salts such as cuprous chloride, which are capable of exerting a chemical action on the olefines by attacking the double bond, to give unstable derivatives capable of being ultimately decomposed by heat to liberate the olefine. Contrary to this known method, the present invention does not bring any chemical reaction into play and only uses the phenomena of solution.

The following example, for the practical carrying out of which there can be used the installation diagrammatically shown on the accompanying drawing, will make the operation of the invention easily understood.

It will be supposed that it is desired to separate propylene from a fraction of cracking gas made up of:—

	Volumes
Propylene	20
Propane	80

and that the solvent used is pure water.

At the temperature of 20° C. and at atmospheric pressure, a litre of water can dissolve respectively 0.165 litre of propylene and 0.037 litre of propane.

To the base of a washing tower 1 provided with Raschig rings, there is admitted at a^2 through a

pipe a^1, the gas to be treated, which is fed by a compressor 7 at a pressure of 6 kg/cm² for example. To the top of the tower the washing water under pressure, to the extent of about 101 m³ for each 100 m³ of gas (reckoned at atmospheric pressure) to be washed, is supplied at b^2 through a pipe b^1 with the help of a pump b.

The height of the washing tower is sufficient for propane practically free of propylene to escape from the top. 62.27 m³ of propane for each 100 m³ of gas treated escape from the tower. At the base of the tower there is obtained water containing in solution such a proportion of the two gases propane and propylene that it is substantially in equilibrium with the mixture treated.

This water is sent through a pipe c, through a valve c^1, into a gas recovery tower 4, where there obtains a slight vacuum produced by a pump 8 and where, flowing over the baffles 4', the water completely gives up the gas which it held in solution: this gas is found to have a volume of 37.73 m³ at ordinary pressure and to have its proportion of propylene increased to 53% by volume. It is again compressed by the pump 8 and sent under a pressure of 6 kg/cm² to a tower 2, washed with 38 m³ of water for each 100 m³ (at atmospheric pressure) of gas initially treated.

There is thus separated, at the top of the tower 2, 13.61 m³ (at atmospheric pressure) of substantially pure propane which is sent to join the propane previously separated in the tower 1 and withdrawn from this latter. At the base of the tower 2, there is obtained a saturated aqueous solution in equilibrium with gas containing 55% of propylene. It is sent through a pipe d and through a valve d^1 into a gas recovery tower 5 where it gives up 23.92 m³ (at atmospheric pressure) of gas containing 83.5% of propylene by volume.

This gas is again taken by a compressor 9 and treated in a tower 3 associated with a gas recovery tower 6 like the towers 1 and 2 and which, in this recovery tower, will give propylene of 96.5% purity and a volume of 20.72 m³ at atmospheric pressure.

If it is desired to obtain greater purity, the gas could be subjected to other successive treatments so as to achieve the result sought.

In order to reduce as much as possible the costs of pumping inherent in the transference of large quantities of water under pressure, there can be added to the water, as has been stated above, a certain proportion of a carefully selected solvent so as to increase the solubility of the gases to be treated, without thereby substantially reducing the difference between the respective solubilities of the olefines and the corresponding saturated hydrocarbon.

It has already been proposed to employ the customary solvents such as the alcohols, the ether oxides and the esters, which are excellent solvents for the olefines, for the separation of olefines, but these liquids dissolve saturated hydrocarbons practically as well as they dissolve the olefines themselves, so that they cannot be used even in aqueous solutions for the separation in question, since the difference between the solubility coefficients of the gases to be separated, which difference alone permits efficacious separation, is then much less as will be seen clearly from the following figures which relate to the propane-propylene mixture at a temperature of 20° C. and at ordinary pressure:

—solubility of propylene in pure water: 0.165 litre/litre H_2O

—solubility of propane in pure water: 0.037 litre/litre H_2O.

With pure ethyl alcohol the solubilities of propylene and propane under the same conditions are respectively 8.9 1. 6.3 1.

It will thus be seen that the solubility of the mixture of the two gases considered is considerably augmented by the employment of alcohol. On the contrary, the ratio of the solubilities which is 4.45 in the case of pure water, is not more than 1.4 in the case of alcohol, which makes any practical separation impossible.

In the same way with normal propanol, the solubilities of propylene and propane are respectively 10.8 1. and 7.7 1. per litre propanol, which again gives a solubility ratio of 1.4.

This characteristic effect of ordinary solvents persists even in aqueous solutions. Thus with an aqueous solution of normal propanol at 20%, the solubility figures are 0.200 1./litre solution for propylene and 0.068 1./litre solution for propane. The improvement in solubility in comparison with pure water is therefore relatively small; the ratio of the solubilities however is reduced by the presence of 20% of propanol to 2.95 against 4.45 in the case of pure water. The employment of these solvents is therefore of no advantage.

A liquid such as carbitol (hydroxy-ethoxy-ethyl-ether) can, however, be used according to the present invention, since the mixtures of this substance with water comply with the desired conditions regarding the difference between the respective solubilities of the olefines and the diluent gases; thus for propane-propylene mixtures the following figures are found:

solubility of propylene in a solution of 50% of carbitol ---------- 0.41 1./litre solution
solubility of propane in a solution of 50% of carbitol ----------0.095 1/litre solution

It will be seen immediately that the difference between the respective coefficients of propane and propylene remains excellent (4.31 instead of 4.45 for pure water) which is essential, whereas the solubility of the whole has however increased in a substantial degree.

It is within the scope of the invention to utilize solvents of different composition in the various stages of the apparatus described.

The filled towers can be replaced by arrangements tending to the production of the same result, for example, by columns having plates or devices having means for agitation. The power used for compression can be recovered by utilising in an appropriate manner the release of gases leaving the washing towers, for example to operate turbines or other similar devices.

Finally, it is within the scope of the invention to make various modifications to the apparatus described and shown while maintaining the principle of separation explained above. In particular, it is sometimes advantageous to reduce the height of the washing towers 2, 3 etc. so as to obtain at the head, not practically pure saturated hydrocarbon, but a mixture of saturated hydrocarbon and olefines, this mixture being immediately returned, without preliminary release, to a suitable place in the tower 1, the diameter of which can be consequently augmented.

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