

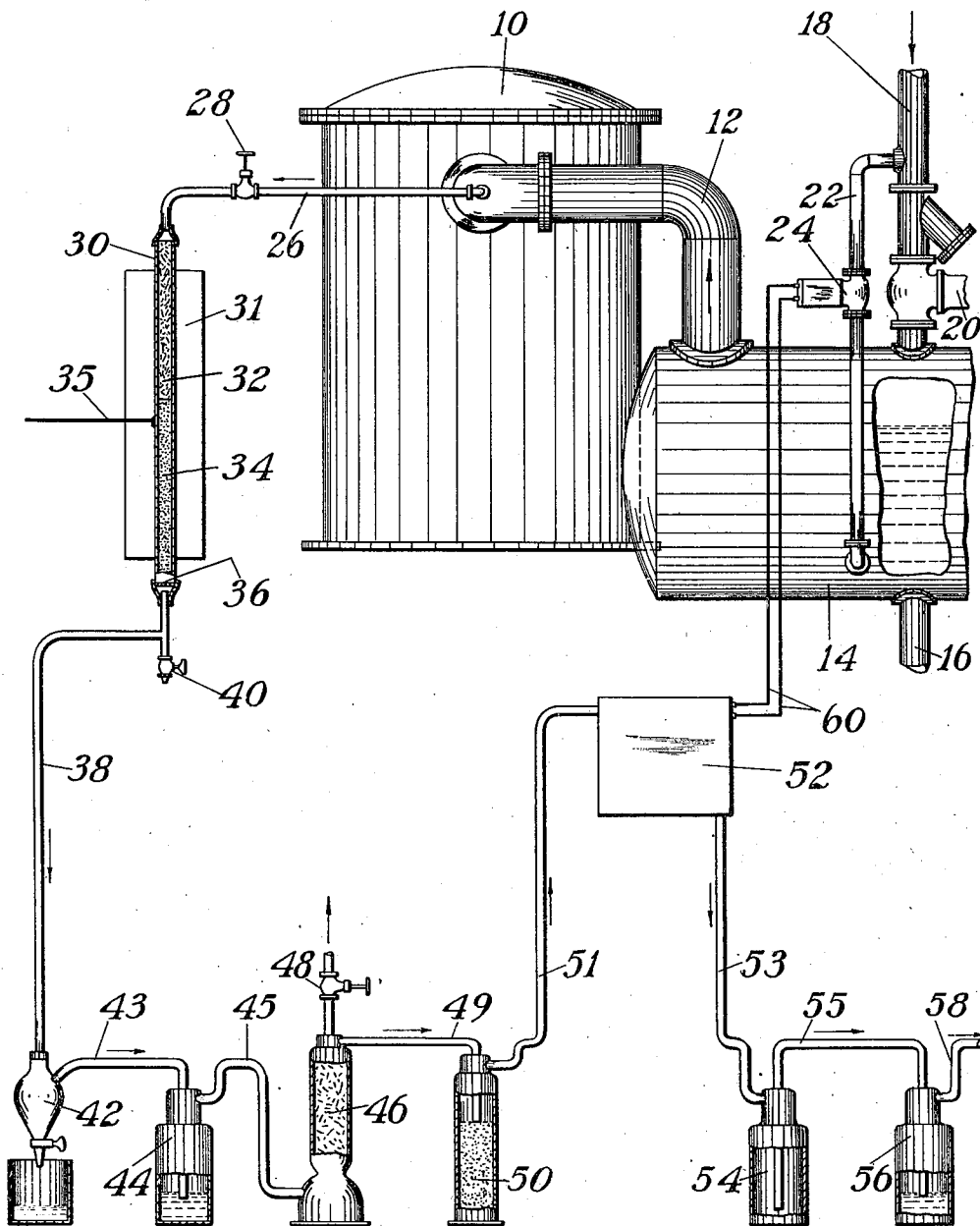
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METHOD AND APPARATUS FOR MEASUREMENT AND CONTROL OF GASEOUS MIXTURES

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METHOD AND APPARATUS FOR MEASUREMENT AND CONTROL OF GASEOUS MIXTURES

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This invention relates to an apparatus and process for determining the proportion of an organic compound present in an oxygen containing gaseous mixture and controlling that proportion in accordance with the determinations made. More particularly this invention relates to the control of the amount of organic compound present in gas mixtures in continuous vapor phase reactions.

Previously the amount of hydrocarbon present in a gaseous mixture such as, for example, a naphthalene-air mixture, was estimated over long periods of time from the total amounts of air and naphthalene used. This estimate was only an average from which the actual ratio of air to naphthalene at any particular moment might vary widely. A method of determining naphthalene content later evolved consisted of passing a portion of the gas through hot concentrated sulphuric acid, which absorbed the naphthalene, measuring the volume of the exit gases, and analyzing the sulphuric acid for naphthalene content. Neither of these methods was satisfactory since the first was apt to be inaccurate for any given moment, and the second involved a laborious laboratory analysis from which immediate determinations were not possible.

This invention has as an object the determination of the organic compound content of an oxygen containing gaseous mixture without the delay normally incident to such analyses.

Another object of the invention is to provide a continuous or intermittent control of the organic compound content of an oxygen-containing gaseous mixture in accordance with determinations made as to such content.

Another object is to provide an apparatus and process for conveniently and rapidly determining the hydrocarbon content of oxygen-containing gaseous mixtures entering into vapor phase reactions, and in accordance with the determinations made adjusting said content to the desired value.

Another object is to provide an apparatus which will automatically determine the hydrocarbon content of an oxygen containing gaseous mixture, and either automatically or with the aid of manual operation adjust the said hydrocarbon content to the desired value.

A further object is to provide an apparatus which will convert the hydrocarbon present in an oxygen-containing gaseous mixture to compounds, such as oxides of carbon, bearing a definite ratio in volume to said hydrocarbons, and which will determine the proportions of such

compounds from which the hydrocarbon content may be easily ascertained.

A still further object is to provide an apparatus which is adapted to maintain the hydrocarbon content of an oxygen-containing gaseous mixture below the proportions at which explosions are apt to occur under the conditions of the reactions in which the mixture is to be employed.

Other objects will appear hereinafter. These objects are accomplished in the following manner:

It is common practice in preparing a mixture of an organic hydrocarbon with air or other oxygen-containing gas such as is used for catalytic vapor phase reactions to pass the gas over or through the liquid hydrocarbon held at a suitable temperature in a vaporizer. The gas stream is partially saturated with vapors of the hydrocarbon in passing over or through the hydrocarbon, and the amount of hydrocarbon vapor becoming mixed with the gas depends upon the temperature of the entering gas, the temperature of the hydrocarbon, the surface of the hydrocarbon exposed to the gas, the speed of the gas over the surface, the turbulence of the gas within the vaporizer, the pressure of the said gas, and whether the gas is passed over or through the hydrocarbon.

In order to obtain the most favorable results from vapor phase reactions it is necessary that all conditions should be maintained as nearly uniform as possible. It is particularly important that the concentration of the hydrocarbon in the reacting gases should not vary appreciably from that proportion which is conducive of the best results from the standpoint of both production and safety of operation. This becomes even more vital as the production per reaction unit is increased since if there be any appreciable variation in the reaction mixture that variation will be reflected by a decreased efficiency for the unit. The above mentioned methods of gas analysis first used were not adequate to high speed production and the development of the process and apparatus hereinafter described was necessary in order to provide a rapid, accurate and continuous method of analysis and control of the gaseous mixture entering into the vapor phase reaction. In the present invention a small portion of the gas stream is bled from the main conduit and passed through a combustion furnace, where the hydrocarbon is completely oxidized to carbon dioxide and water, after which it is passed through suitable drying agents for the removal of water

and water vapor, and then through a carbon dioxide measuring and recording instrument for the continuous measurement and recording of the carbon dioxide contents of the gas stream. The carbon dioxide bears a definite ratio to the hydrocarbon in the original mixture and furnishes a simple method of measuring the proportion of hydrocarbon present in that mixture.

In the drawing which illustrates a preferred embodiment of the apparatus covered by this application, the single figure discloses a diagrammatic view of the vaporizer, catalytic converter, combustion chamber, drying apparatus, carbon dioxide measuring and recording equipment, and control apparatus. It is to be understood, of course, that this showing is entirely diagrammatic, and that the proportions therein are not to scale, but merely for the purposes of representation.

In the drawing the converter 10 is of a usual type employed in catalytic vapor phase reactions, such as the reaction of a mixture of naphthalene and air to produce phthalic anhydride as the end product. This converter is supplied with the mixture of the reacting gases through the pipe 12, which is connected to the vaporizer tank or tanks 14, it being the usual practice to provide at least two of such tanks in order to have a reserve. The tank shown is equipped with an inlet for naphthalene 16, the naphthalene being maintained at any desired level in the tank. The pipe 18 is an inlet for air to the vaporizer tank, said air being admitted to the tank through a reducing valve 20 which lowers the pressure of the entering air. Connected to the pipe 18 at a point more remote from the tank than the reducing valve 20 is a pipe 22, which contains a magnetically controlled valve 24, this pipe 22 being for the purpose of by-passing a certain portion of the air as desired, this air being admitted at or near the bottom of the tank and bubbled through the naphthalene therein. The magnetically controlled valve 24 is automatically adjustable, as hereinafter described, to vary the proportion of air which is bubbled through the naphthalene in order to adjust the proportion of naphthalene present in the reacting gases. A small portion of the reacting gases is bled from the conduit 12 through a pipe line 26 containing a shut-off valve 28. This pipe 26 enters into a nichrome catalyst tube 30 which is surrounded by an electric heater 31 capable of producing temperatures of the order of 625 to 675° C. The upper portion of the catalyst tube 30 is packed with broken porcelain or similar inactive granular material 32, while the lower portion of said tube is packed with the catalyst 34. This catalyst is, in the preferred arrangement, made by dissolving 10.59 grams of ammonium meta vanadate in 225 cc. of boiling water, to which is added 100 grams of a properly sized, partially dehydrated aluminum hydroxide known as "Hydralo".

The mixture is evaporated on a steam bath to dryness with constant stirring, and the coated particles are activated by placing in a tube and slowly raising the temperature to 500° C. while passing a current of moist air through the mass. A five inch length of this catalyst in a three-quarter inch tube functions well as a combustion catalyst for a naphthalene-air mixture at temperatures above 600° C. preferably 650° C. or over, and with a gas flow of 75 to 500 cc. per minute.

A thermocouple 35 is attached to the side of the catalyst tube for the purpose of measuring

the temperature therein, in order that proper adjustment may be made in the electric heater to maintain the desired temperature of reaction. The catalyst is held in place in the tube 30 by means of a wire screen 36 of such a mesh that the particles of catalyst will not pass therethrough. A pipe 38 connected to the catalyst chamber 30, which is provided with a relief valve 40, is in turn connected to a water trap 42 equipped with a valve to permit the removal of water therefrom. The trap 42 is connected by a pipe 43 to a bottle 44 containing sulphuric acid, through which the gases resulting from the combustion are bubbled in order to remove water or water vapor. From the bottle 44 another pipe 45 leads to a bottle 46 containing cotton, which serves to remove any sulphuric acid entrained in the gases. To the upper end of the bottle 46 is attached a vent in the form of a valve 48, which is used to diminish the flow of gases through the remainder of the system by releasing a certain portion thereof to the atmosphere. A pipe 49 connected to the bottle 46 leads the remaining gases through another bottle 50 containing "Dehydrite" a commercial dryer used to remove any residual moisture in the gases. The bottle 50 is connected to a carbon dioxide measuring and recording instrument 52 by means of a pipe 51.

The CO₂ measuring instrument may be of the type identified as a CO₂ indicator made by the Leeds and Northrup Company, of Philadelphia, which consists of the usual potentiometer type of electrical measuring apparatus for gases. In conjunction with this indicator a temperature recorder, produced by the above-mentioned company, is used, the instrument being designated a temperature recorder potentiometer system. This recorder is calibrated to read in percentages of carbon dioxide contained in the gases passed through the instrument 52. A pipe 53 leads the exhaust gases from the instrument 52 to a trap 54, this trap being connected through pipe 55 to a bottle 56 containing glycerine through which the exhaust gases are bubbled, and then vented to the atmosphere through pipe 58. The bottle 56 containing glycerine is provided for the purpose of measuring the exhaust gases, a fairly accurate idea of the volume of those gases being obtained by the number of bubbles appearing per unit of time.

The instrument 52 is connected through appropriate electrical means and wires 60 to the magnetically operated valve 24, this valve being operated in accordance with the carbon dioxide measurements made to bubble more or less air through the naphthalene in tank 14. For example, if the carbon dioxide indication falls below a certain desired value indicating a proportionate drop in the naphthalene content of the reacting gases, the magnetically operated valve is automatically opened to pass a greater portion of the air through the naphthalene in order to entrain a higher percentage of that compound, and thereby enrich the mixture of the reacting gases.

It is obvious from the above description of the apparatus the manner in which this system operates, but a brief description will be given here of its operation.

The naphthalene which is bled from the conduit 12 is passed through pipe 26 to the catalyst chamber 30, where the naphthalene is completely oxidized by the oxygen contained in the reacting gases to form carbon dioxide and water, the resulting mixture of gases passing through pipe 38 to the water trap 42 where any condensed

water is removed. The gases then are led through the sulphuric acid bottle 44, removing the major portion of the remaining moisture present therein, and the gases are then led through bottle 46 in order to remove any entrained sulphuric acid. It is desirable that there be but a very slow flow of gas through the instrument 52, and in order to properly adjust this flow the valve 48 is set at such an opening that the gases passing through that instrument do not exceed in quantity the amount specified for satisfactory operation, this flow being measured as above stated by means of the glycerine bottle 56. The gases, after leaving bottle 46, are further dried in the dehydrite bottle 50 and then passed through the measuring and recording instrument 52. In accordance with the measurements made, the magnetically controlled valve 24 is adjusted to the desired opening to secure the preferred mixture. The following examples illustrate how this method of analysis may be used:

Example I

A sample of a gas mixture consisting of naphthalene vapors mixed with air being used for the catalytic vapor phase oxidation of naphthalene to phthalic anhydride is passed through a combustion catalyst heated in an electric tube furnace where the naphthalene content of the gas is completely oxidized to carbon dioxide and water. The gas sample coming from the combustion furnace is cooled, dried with suitable drying agents and passed through a potentiometer-indicator carbon dioxide gas analyzing cell for the continuous measurement and recording of the carbon dioxide content of the gas. In order to calculate the naphthalene concentration in terms of parts of air per part of naphthalene from the results of the continuous gas analysis which is expressed in volume percent of carbon dioxide, the following formula is used:

$$\frac{\text{Moles CO}_2 \times 100}{\text{Moles CO}_2 + \text{moles air} - \text{moles O}_2 \text{ used in CO}_2 - \text{moles O}_2 \text{ used in H}_2\text{O}} = \text{vol. percent CO}_2$$

but moles O₂ in CO₂=moles CO₂, then

$$\frac{\text{Moles CO}_2 \times 100}{\text{moles air} - \text{moles O in H}_2\text{O}} = \text{vol. percent CO}_2$$

For the combustion of 1 g. of naphthalene in a given ratio of air to naphthalene by weight, the equation becomes

$$\frac{7.809}{M - 0.0156} = \text{vol. percent CO}_2$$

where M=1/29×ratio by weight of air to naphthalene.

The following table has been calculated from the above equation to show the relation between the naphthalene concentration expressed as ratio of air to naphthalene concentration expressed as ratio of air to naphthalene by weight and the volume percent carbon dioxide as measured:

Ratio	Vol. % CO ₂	Ratio	Vol. % CO ₂
20	11.58	28	8.22
21	11.02	29	7.93
22	10.51	30	7.66
23	10.04	31	7.42
24	9.62	32	7.18
25	9.23	33	6.96
26	8.87	34	6.75
27	8.53	35	6.56

Example II

A sample of gaseous mixture of benzene and air used for the catalytic vapor phase oxidation

of benzene to intermediate oxidation products is completely oxidized to carbon dioxide and water in the same manner as that for naphthalene-air mixtures given in Example I. After drying, the oxidized gas is passed through a potentiometer-indicator carbon dioxide gas analyzing cell, or other continuous carbon dioxide gas analyzing apparatus for the continuous measurement and recording of the carbon dioxide content of the gas. In the same manner as in the first example the volume percent carbon dioxide may be calculated to the ratio of air to benzene by weight by means of the following equation:

$$\frac{7.687}{M - 0.0192} = \text{vol. percent carbon dioxide,}$$

where M=1/29×ratio of air to benzene by weight.

The following table, calculated from the above equation, gives the relationship between the volume percent carbon dioxide as measured, and the ratio of air to benzene by weight.

Ratio	Vol. % CO ₂	Ratio	Vol. % CO ₂
20	11.47	26	8.76
21	10.91	27	8.43
22	10.40	28	8.12
23	9.93	29	7.84
24	9.51	30	7.57
25	9.12		

Example III

A sample of a gas mixture of toluene and air used for the partial catalytic oxidation of toluene in the vapor phase is completely oxidized to carbon dioxide and water, dried, and passed through a carbon dioxide gas analyzing apparatus for the continuous measurement and recording of the carbon dioxide content as in the previous examples. The following equation is used to calculate the ratio by weight of air to

toluene from the measured volume percent carbon dioxide:

$$\frac{7.604}{M - 0.0217} = \text{vol. percent CO}_2$$

where M=1/29×ratio.

The following table gives the values for 50 toluene:

Ratio	Vol. % CO ₂	Ratio	Vol. % CO ₂
20	11.38	26	8.69
21	10.83	27	8.36
22	10.32	28	8.06
23	9.86	29	7.77
24	9.44	30	7.51
25	9.05		

Various examples have been given above of a hydrocarbon-air mixture in connection with the above outlined novel method of measurement and control of gaseous mixtures, but the method and apparatus are capable of use with other hydrocarbons than those mentioned as well as with mixtures low in oxygen content.

If it is desired to use this method of control with a gas mixture of an organic compound with air, oxygen-containing gases, or inert gases, in which there is a deficiency of oxygen for the complete oxidation of the organic compound, the sample of the gas may be mixed in known proportions by means of flow meters or other gas flow measuring devices with oxygen or oxy-

gen-containing gases so that there will be an excess of oxygen, and then passed through the combustion furnace. Also, while specific examples of preferred catalysts for use in the combustion furnace 30-34 are specifically mentioned, any catalyst which will completely oxidize the hydrocarbon present in the gaseous mixture at the required speed of gas flow such as copper oxide wire or platinized asbestos may be used in the combustion apparatus.

It is also possible to use any continuous or intermittent carbon dioxide gas analyzing device for the measurement of the carbon dioxide formed by the complete oxidation of the organic compound in place of the indicator and recorder specifically referred to above.

It has been pointed out that the usual magnetic or solenoid operated valve may be employed in connection with the recording apparatus to properly adjust the flow of air or oxygen containing gas through the liquid hydrocarbon, but it should be understood that any other means of control may be employed. For example, in place of the solenoid operation of the valve 24, an electric motor may be supplied to actuate the valve; in place of the electrical connections before mentioned, fluid connections, either hydraulic or pneumatic, may extend from the recording apparatus 52 to the valve 24, whereby said valve may be operated to either open or closed position.

It is intended that this system may be used also in connection with a manual control of the valve 24. An alarm may be attached to the recorder to give warning when the carbon dioxide content of the gases exceeds or falls below a predetermined value, and at the instance of this alarm the valve 24 may be manually adjusted to the desired opening.

It is unnecessary that the moisture content of the gas be removed following oxidation of the mixture, since this precaution is taken only to insure more accurate and trustworthy measurements in the carbon dioxide indicator and recorder. The moisture content of the gases may be determined separately and a correction applied to the readings obtained from the carbon dioxide and recorder. The same procedure, of course, applies to any moisture content of the gas prior to its combustion in the furnace 34. Unless the moisture content of the gas is high, the error introduced by omitting the correction therefor is small and for practical purposes the correction may be disregarded. For the purposes of automatic control, however, it has been found more practicable to eliminate water and water vapor from the gases prior to their entry into the carbon dioxide recorder for the purpose of protecting the recorder as well as in the interest of more accurate measurements.

This invention is extremely useful where a rapid, accurate, and continuous control or measurement of the amount of an organic compound in gaseous mixtures is necessary. It is particularly useful in the control or measurement of the concentration of a hydrocarbon in air or oxygen containing gases being used for catalytic vapor phase oxidations to intermediate oxidation products. Such a control is necessary in order to maintain the yield and quality of the product at the highest possible point under the reaction conditions employed without damaging the catalyst used in such vapor phase reactions. The efficiency of the reaction unit is to a great extent dependent upon the maintenance of a uniform

mixture of the reacting gases and that uniformity may be secured by means of the above described apparatus and process. The control is also valuable in order to prevent the concentration of hydrocarbon from entering the explosive range by means of automatic control, or an alarm system for manual control, for such concentrations might cause an explosion or fire resulting in considerable damage and injury.

This invention not only affords the means of controlling the concentration of hydrocarbon in a gaseous mixture with air or oxygen-containing gases which would otherwise be impossible except in a crude way, but it gives a very accurate measure of the concentration of hydrocarbon. The accuracy may be illustrated in the case of naphthalene air mixtures given in the following table, which shows how a change in the volume percent hydrocarbon in the gas mixture results in ten times as great a change in the volume percent carbon dioxide which is measured and recorded:

Ratio	Vol. % Naphthalene	Vol. % CO ₂
30	0.75	7.66
25	0.90	9.23
20	1.12	11.58

Since many embodiments of this invention, differing widely in one or more respects, may be made without departing from the spirit of our invention, it is to be understood that we do not limit ourselves to the foregoing examples or description except as indicated in the following claims.

We claim:

1. In a process for the catalytic vapor phase reaction of an organic compound and oxygen containing gas, the method of controlling the process which comprises withdrawing a portion of the mixture of compound and gas being supplied to the catalytic converter, converting the compound present in such portion to oxides of carbon, measuring said oxides of carbon and then controlling the proportion of compound present in the mixture being fed to the catalytic converter in accordance with the measurements made.

2. In a process for the catalytic vapor phase reaction of naphthalene and air to produce phthalic anhydride, the method of controlling the process which comprises withdrawing a portion of the mixture of naphthalene and air being supplied to the catalytic converter, oxidizing the naphthalene present in such portion to carbon dioxide, measuring said carbon dioxide and then controlling the proportion of naphthalene present in the mixture being fed to the catalytic converter in accordance with the measurements made.

3. In a process for the catalytic vapor phase reaction of an organic compound and oxygen containing gas, the method of controlling the process which comprises withdrawing a measured portion of the mixture of compound and gas being supplied to the catalytic converter, adding in measured amount to said portion sufficient oxygen containing gas to completely oxidize the compound present in said portion, completely oxidizing the compound present in such portion, thereafter measuring the oxides of carbon and then controlling the proportion of compound present in the mixture being fed to the catalytic converter in accordance with the measurements made.

4. In a process for the catalytic vapor phase reaction of naphthalene and air to produce phthalic anhydride, the method of controlling the

process which comprises withdrawing a measured portion of the mixture of naphthalene and air being supplied to the catalytic converter, adding in measured amount to said portion sufficient oxygen containing gas to completely oxidize the naphthalene present in said portion, completely oxidizing the naphthalene present in such portion, measuring the carbon dioxide and then controlling the proportion of naphthalene present in the mixture being fed to the catalytic converter in accordance with the measurements made.

5. In a system for controlling the amount of an organic compound present in a gaseous mixture containing oxygen, means for causing the oxidation of the organic compound present in a sample of the mixture, such means including a catalytic chamber containing as a catalyst activated vanadium oxide supported on partially dehydrated alumina, means for measuring the oxides of carbon present, and means controlled by the meas-

uring means for controlling the gas to compound ratio in the gaseous mixture.

6. In a system for the catalytic vapor phase reaction of an organic compound and oxygen containing gas, a catalytic converter, a supply receptacle for the organic compound, connections for supplying gas to said receptacle, a delivery connection between said converter and said receptacle, and means for controlling the mixture delivered to said converter, such means comprising means for withdrawing a portion of said mixture from said delivery connection, means for converting the compound present in such portion to oxides of carbon, means for measuring said oxides, and means controlled by said measuring means for adjusting the gas to compound ratio of the mixture supplied by said receptacle.

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