[54] APPARATUS FOR DETERMINING DISTILLATION CUT POINTS

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[57] ABSTRACT

An apparatus for automatically performing distillation analysis of liquids wherein a sample of the liquid is vaporized while the temperature of the vapor and the weight of the sample are continuously measured and recorded. The data is supplied to a computer programmed to provide preset percent distillation points for the sample and hold circuits that can be set to trigger at any preselected boiling point or cut point.

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FIG. 6

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FIG. 8

HEATER VOLTAGE TIME PER
VOLTAGE SAMPLE
1 - 115 VAC , 4.1 MINS
2 - 98 , 4.2
3 - 82 , 4.8
4 - 67 , 5.3
5 - 63 , 6.0
6 - 60 , 6.5

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FIG. 9

TEMP
(°F)

% BOILED (BY WEIGHT)

PURGE

HEAT

FILL

ZERO
APPARATUS FOR DETERMINING DISTILLATION CUT POINTS

BACKGROUND OF THE INVENTION

The present invention relates to a method and apparatus for determining the distillation cut and boiling points of materials and particularly liquids. The problem arises in all process industries, particularly chemical and petroleum industries, of determining the distillation cut and boiling points of liquid samples. In the past a recognized method known as an ASTM method (D86) has been developed for determining distillation cut points. This method comprises placing a measured amount of the liquid in a container and heating the liquid to vaporize it with the vapor being collected and condensed. The various cut points are determined by measuring the amount of liquid as it is condensed and recording the temperature. It requires a skilled operator and 45 minutes to perform a complete distillation analysis of a liquid by this method.

The results obtained with the ASTM method depend to a large extent on the skill of the operator and his attention to the process. Even when the operator is skilled and attentive the method still suffers from incomplete condensation of the sample. When unskilled operators are used the sample size, initial sample temperature and sample recovery may all vary to produce inaccuracies and variations in the results.

Various apparatus have been developed to automate or at least partially automate the above method to eliminate the dependence on the operator. These apparatus have comprised the boiling of a known amount of liquid and collecting the vapors to determine the various distillation cut points of the liquid. These methods while eliminating the need for a skilled operator are time consuming since they substantially duplicate the steps of the ASTM method. Also, the automated methods require equipment to condense and measure the quantity of condensed liquid to determine the various distillation cut-points.

In addition to the above problems with available apparatus they are substantially batched-type apparatus and relatively slow. The slow operation produces a time lag between taking of a sample and the obtaining of the distillation points. The time lag prevents the use of present systems with process controls since the information they supply is out-of-date and not related to the present state or operating levels of the process.

BRIEF DESCRIPTION OF THE INVENTION

The present invention solves the above problems by providing a method and apparatus which is completely automatic and provides a complete distillation analysis of the sample in a short time. The method measures the loss-in-weight of a sample of material as it is heated to determine the various percentage cut-points of the material. As the various percentage cut-points of the material are determined the temperature of the vapor which is being continuously measured, is recorded. The cut-points and temperature can be made to correspond closely to the cut-points obtained by the ASTM method. The analyzer can be adjusted to operate either as a cut-point analyzer or a boiling point analyzer.

The apparatus comprises a sample holder for holding a sample of material with the sample holder being attached to one end of a beam balance. A weight detector is positioned at the opposite end of the beam balance to measure the loss-in-weight of the material as it is heated. The apparatus includes controls for supplying a preset amount of sample to the sample holder and controlling the heating of the sample to obtain the desired rate of evaporation of the sample. After the sample is evaporated the sample holder is purged to both cool it and remove the remaining traces of the sample. The system is automatically zeroed before each new sample is placed in the sample holder. This is done to compensate for build-up of residue in various portions of the sample holder and low frequency drift of the electronic circuits.

The weighing means may be either a device which actually weighs the sample and sample holder or a device which determines the displacement of the end of the beam. The signals representing the temperature and the loss-in-weight of the sample can be recorded in correlation so that the various percentage cut-points and corresponding temperatures may be determined. These variables can be sampled at preset positions to give output data on specific cut-points and/or temperatures. The signals from the temperature and weighing means may also be supplied to an analog-to-digital converter for conversion to digital numbers. The digital numbers can then be supplied to a computer which will compute the various percentage cut-points and print out the corresponding temperatures. Of course, the computer can also be used to control the process utilizing the information from the apparatus.

The system requires a relatively short time to perform a complete distillation analysis, for example, a 10 cc sample can be evaporated in approximately 5 minutes to obtain the same degree of accuracy that is obtained using a skilled operator and following the ASTM method. This time can be further reduced to a minimum of approximately 3 minutes if a smaller sample is used. When a small sample is used the accuracy is not as good as the ASTM method but is normally satisfactory for most control purposes.

The system can also be used directly to control a process. For example, when two streams of product from distillation columns are blended to form a finished product having a specified boiling or cut-point the system can monitor the column streams and control the columns. This is accomplished by supplying the sample holder with a ratio of the two column streams, the ratio being determined by the finished product. If the analyzer determines the ratio it does not supply a finished product having the desired characteristics, then its signal can be used to vary the column streams to obtain a more accurate ratio.

BRIEF DESCRIPTION OF THE DRAWINGS

The present invention will be more easily understood from the following detailed description of a preferred embodiment when taken in conjunction with the attached drawings in which:

FIG. 1 is an elevation view of an instrument constructed according to this invention;
FIG. 2 is a schematic diagram in block form of the control circuits of this invention;
FIG. 3 is a block diagram of the system used to control the blending of two column streams;
FIG. 4 is a curve of the distillation cut-points of a turbine fuel containing various additives;
FIG. 5 is a comparison of the cut-points for gasoline obtained using the processes of the invention with those obtained with the ASTM method;

FIG. 6 is a similar comparison for kerosene;

FIG. 7 illustrates the effect of thermocouple position on the cut-points for kerosene;

FIG. 8 illustrates the effect of heating rate on the cut-points for kerosene; and

FIG. 9 illustrates the effect of varying the temperature of the sample holder on the cut-points of kerosene.

DESCRIPTION OF THE PREFERRED EMBEDDING

Referring to FIG. 1 there is shown an elevation view of a complete instrument constructed according to this invention. The instrument utilizes loss-in-weight to determine the percentage distillation cut-points of a liquid sample. A preset quantity of sample is placed in a sample holder 10 which is attached to one end of the beam 11. The beam is flexurally pivoted at its center 13, for example Bendix and Rex pivots, and the movement of the opposite end of the beam is measured by means of a linear displacement device 12 (LVDT).

The sample holder comprises a sample tube 20 which holds the liquid sample and a heating section or outer housing 21. The heating section contains a suitable heating means, for example a resistance heater which is coupled by means of a lead 22 to a source of power. The leads 22 pass through the center of the beam and are taken out near the flexure pivot to eliminate the possibility of the leads creating a load on the beam and destroying the accuracy of the measurement.

The liquid sample is supplied through a line 30 to a solenoid valve 31 that controls the flow of the sample to the sample tube 20. The outlet of the solenoid valve is coupled by means of a line 32 to the top of the sample tube. Also disposed in the top of the sample tube are thermocouple 33 and an outlet 41 for the purge line. All of the elements 32, 33 and 41 should be positioned so that they do not contact the sides of the sample tube or interfere with the free movement of the beam and the sample holder.

Purging air is supplied by means of a line 35 to a solenoid valve 36 that controls the flow of purging air to the sample tube in response to signals received from the control system described below. The discharge from the purge control solenoid is coupled by means of a line 37 to a vortex tube 38 with the hot end 39 of the vortex tube discharging to the atmosphere while the cold discharge from the vortex tube is connected by a lead 40 to the purge inlet 41 in the top of the sample tube. The use of the vortex tube provides cold air for both purging and rapidly cooling the sample holder so that all samples may be run under the same conditions.

The vapors which are evolved from the sample as it is heated are swept from the top of the sample tube by means of a flow of air through the inlet opening 45 and the exhaust opening 46. This flow of air may be supplied from the same external source as the purge air. The inlet 35 can be coupled directly to a line 47 that discharges from its open end 48 into the housing 54 containing the electronic circuits. The air escapes from the housing 54 at the right hand end and flows out the opening 45-46 to sweep the vapors from the housing. This air flow insures that vapors do not flow into the electronic circuits and that at the same time cools the circuits. A counter-weight 50 is provided on beam 11 to counter-balance the weight of the sample holder. The placement of the counter-balance is not critical since the actual displacement of the beam is measured by means of the device 12. An adjustable dashpot member 51 is coupled to the beam to limit or control sudden movements of the beam and for stabilizing the beam. The linear measuring device may be a linear displacement device that supplies a proportional signal to the displacement of its core member 53 that is coupled to the end of the beam by a suitable clamp. A Schaevitz motion transmitter manufactured by Schaevitz Engineering of Pennsauken, N. J., may be used for the linear displacement measuring device. A drain 55 provides for disposal of sample resulting from overflow or leakage.

The control circuit for the apparatus is shown in FIG. 2 in a block diagram form. The control system utilizes a series of solenoid valves and relays 61-63 to control the flow of the sample to the sample tube, the flow of purging air for purging the sample tube and the flow of electrical current supplied to the heater element of the sample container. The position of the solenoid valves is controlled by a controller in response to various conditions existing in the device as explained below. The control system also utilizes a zero adjustment circuit 60 which adjusts the signal from the position-measuring device to a zero level after the sample holder has been purged. This compensates for residues remaining in the system, the build-up of foreign matter and low frequency drift of the circuits.

The linear motion transmitter is coupled to a loss-in-weight measuring circuit comprising an amplifier 66. The zero adjustment circuit is also connected to the amplifier 66 to adjust the amplifier to a zero output after the sample tube has been purged. The thermocouple is coupled to a temperature measuring circuit also consisting of an amplifier 67. The signals from amplifiers 66 and 67 representing the loss-in-weight of the sample and the temperature of the vapor are supplied to an X-Y recorder 68 that records the loss-in-weight of the sample in correlation with the temperature of the vapor. The two signals are also supplied to an analog-to-digital converter 70 whose output is supplied to a computer 71 programmed as set forth below so that it will supply a print-out indicating the percentage distillation cut-points and the corresponding temperatures as selected.

The controller for automatically controlling the operation cycle of the instrument is shown on the right of FIG. 2 and utilizes a series of operational amplifiers 80-83 coupled as OR gates and disposed in closed loop so that when any one conducts the remainder are latched out. In this type of circuit the output signal of one OR gate is used to latch out the remaining gates with the coupling to the next succeeding gate having a switch disposed in its circuit. For example, the output of OR gate 80 is coupled by a lead 84 to OR gates 82 and 83 and by a lead 85 to OR gate 81 with a switch 86 disposed between the take-off points of the two leads 84 and 85. Thus, the OR gates 81-83 remained latched out as long as OR gate 80 is triggered or until relay switch 86 is opened. When relay switch 86 opens the OR gate 81 will be triggered since the output signal from OR gate 80 is no longer applied to the input of OR gate 81. The remaining OR gates will remain latched out and OR gate 80 will be latched out when OR gate 81 is triggered. This cycle of operation will continue as
the relay switches 86, 87, 88 and 89 are opened and closed. The opening of the relay switches is controlled by signals from various portions of the apparatus as explained below while the relay switches return to a normally closed position in the absence of a signal.

The relay switch 86 is controlled by output signal of the loss-in-weight circuit so that it opens whenever the weight of the sample reaches a preset high value. This is accomplished by a comparing circuit 90 that compares the weight signal with a preset value 91 and supplies a signal on lead 92 to open relay switch 86 when the weight of sample equals the preset value. In a similar manner comparing circuit 93 compares the weight signal with a preset value and supplies a signal on lead 94 to open relay switch 87 when the weight of sample reaches a preset low value. The temperature signal is supplied over a lead 95 to a comparing circuit 96 where the temperature is compared with a preset value 97. The signal from the comparator 96 is supplied over lead 98 to open relay switch 88 when the temperature of the interior of the sample holder reaches a lower limit. The switch 89 is a time delay relay whose coil is coupled in the output lead of the OR gate 83. The time delay is set sufficiently long to permit the weighing circuit to adjust to zero, for example 10 seconds. The output signals of the OR gates 80-83 are supplied over leads 90-93 to the fill solenoid 62, heater relay 61, purge solenoid 63 and zero adjustment circuit 60, respectively. The sequence of operation of the circuit is described below.

In addition to recording the temperature versus weight curve on the X-Y recorder 68 the temperature and weight signals are also supplied to a sample and hold circuit that records any preset cut-point or boiling point. The sample and hold circuit uses a comparator 100 that compares either the temperature or weight, for example the temperature as shown in FIG. 2, with a preset value 101 to give the cut-point for the temperature. The output signal from the comparator is supplied to a monostable circuit 102 that closes the relay switch 103 to complete the input circuit to the amplifier 104. The signal from the amplifier 104 can be recorded on the recorder 105 to give the cut-point for the preset temperature or supplied to a process controller 106. The process controller can position the controls of a distillation column to control the column reflux and reboiling to supply the proper top and bottom products. FIG. 3 illustrates the use of the apparatus to control the blending of two streams to produce a final product whose density and cut-points meet preset specifications. As an example the product may be gas turbine fuel blended from the top product of a column 100 and the product from a side stripper 101. The bottom product from the column 100 is used as the feed for the side stripper. The top product is stored in a tank 104 while the product of the side stripper is stored in a tank 105. While the storage tanks are desirable they can be eliminated if desired. The products in the two storage tanks are blended and supplied as turbine fuel through the pipeline 106.

It is assumed that the specifications for the turbine fuel require that it have a density that falls between upper and lower limits and 10 percent and 90 percent cut-points that also fall within set limits. The density of the products from the two storage tanks are measured by a density measuring circuit 107. The density measuring circuit 107 also computes the approximate quantity of each product and supplies voltage signals on leads 108 and 109 that can be used as set points for the fill controllers 110 and 111. The fill controllers are identical to the controller 90 of FIG. 2 and control the operation of two OR gates in the controller 112. An additional fill OR gate is used with the fill control 110 controlling one to supply a first percentage of the total sample and the fill control 111 controlling the second to supply the remainder of the sample. The controller 112 supplies signals over leads 113 and 114 to control the opening of the solenoid valves 115 and 116 that control the flow of two products into the sample holder. The controller 112 also determines the 10 percent and 90 percent cut-points of the sample using the same circuits as shown in FIG. 2. The 10 percent cut-point can be processed by a controller 117 and supplied over a lead 118 to control the positioning of a valve 119 in the reflux line of the column 100. The operation of distillation columns and various control systems are shown in the prior art, for example see U.S. Pat. No. 3, 342, 698. The information on the 10 percent cut-point can be used to control the reflux to vary the quantity of the light product supplied to the blend. The 90 percent cut-point can be used in a similar manner to control the quantity of the heavy product supplied to blend to vary the density of the blend.

The computer 71 may be programmed in any desired language, for example, a program language known as BASIC wherein the commands to the computer are supplied in a substantially conversational language. An example of this programming is set forth below:

```
LIST
91 FOR K=1 TO 4
92 CALL (4, K, φ)
93 NEXT K
95 PRINT "STARTING"
100 LET C=φ
101 LET DL=’5
110 LET K=φ
120 CALL (4, K, P)
121 IF P<φ THEN 9999
122 GOSUB 2400
130 CALL (4, 1, φ)
131 IF K=2 THEN 150
132 IF K=4 THEN 130
140 WAIT (1,φ)
150 GOTO 120
200 LET C=C+1
210 REM 2200=FURGE, 2300=WAIT, 2400=FILL, 2600=CHECK, 2800=HEAT
250 IF K=0 THEN 2200
260 IF K=1 THEN 2300
270 IF K=2 THEN 2400
280 IF K=3 THEN 2600
290 IF K=4 THEN 2800
310 CALL (1, 5, T)
311 LET T=T+60
```
From the above program it can be seen that the first steps are to command the computer to recall from memory preprogrammed data and set various constants equal to various values. The computer is then told to let various constants perform various functions if various temperature and weight conditions exist in the system. The system is then operated until the steps for commanding the computer to print-out the various percentage boiling points when w equals a certain percentage of the initial weight. Thus, if all the steps up to 2800 have been satisfied the computer will commence to print-out the temperatures for the various percentage boiling points as they are reached. Also the signal from the computer indicating the temperature per percentage boiling point can be transmitted to a separate control system, not shown, in FIG. 1 to be used in a process control.

The following are four distillation cut-point analyses as measured by the instrument and computed by the computer following the above instructions.
As explained, the system operation is substantially automatic and once the quantity of sample to be used and the heating rate have been set no further adjustments are required. Of course, a supply of sample under suitable pressure, 5-100 psig and a source of compressed air for purging the device and ventilating air for removing the vapors as they are evolved from the sample are all essential. With necessary services coupled the instrument can be started by the controller. The first step performed by the controller is the zeroing of the sample holder. This can be done by applying a temporary large voltage signal to the heating circuit which triggers the OR circuit 81. When the large voltage signal is removed the relay switch 87 will open since the sample holder is empty. The opening of the relay switch 87 will trigger purge OR gate 82 and the relay switch 88 will open when the purge air has cooled the sample holder. When the relay switch 88 opens the zero OR gate 83 will trigger and zero the loss in weight amplifier 66. When the time delay relay 89 times out the switch 89 will open and trigger the fill OR gate 80. The quantity of sample supplied depends on the level of the set point 91 that controls the time that OR gate 80 remains triggered. After the sample has been supplied the relay switch 86 will open and trigger the heating OR gate 81 to supply a predetermined voltage to the heating element. By selecting the voltage in relation to the quantity of sample supplied one can obtain the desired heating rate of the sample. The sample will then be evolved as the weight of the sample is continuously measured by the linear displacement device 12. In the sample system the weight of the sample will be recorded in relation to the temperature of the sample and various percentage cut-points can be determined by either inspecting the record or the sample and hold circuit. After the sample has been evaporated the relay switch 87 will open and trigger the purge OR gate 82 to open the purge solenoid and supply purge air to the system. When the temperature of the sample holder (as measured by the thermocouple) reaches a preset level the relay switch 89 opens closing the purge solenoid and triggering the zero OR gate 83. The system will repeat the above sequence of operation and supply distillation analysis of the sample stream connected to the system.

The sample stream connected to the system may be a stream from a process or may consist of previously collected samples which are supplied individually to the system. In the case of a process suitable timing de-

vices can be coupled to the instrument so that it only analyzes the sample at set time intervals or the instrument can be set to continuously analyze the process to provide data for controlling the process.

FIG. 4 shows the distillation cut-points for a turbine fuel that is diluted with various percentages of impurities. From FIG. 3 it is seen that if the turbine fuel is blended with a heavy gas oil the temperature of the higher cut-points is raised while if the turbine fuel is diluted with a lighter hydrocarbon as for example, gasoline, its initial cut-points are lower. Thus, the instrument responds to compositional changes in the same manner as the ASTM method.

FIGS. 5 and 6 show a comparison between the cut-points obtained using the present instrument and the ASTM method where the amount of liquid evaporated is measured and the temperatures at which it evaporated recorded. From a comparison of these two chart records it is seen that the present instrument provides results which are within approximately five percent of the ASTM recordings. This is sufficiently close for all practical purposes and can be used in control processes.

Referring to FIG. 7 there is shown a comparison of results obtained using various distances between the thermocouple and the top of the sample tube. Also shown is an ASTM distillation analysis for the same sample. From the information shown it can be seen that if the thermocouple projects approximately 1.2 inches into the same tube wherein the sample tube comprises a tube of 1.1 inch diameter and 4.5 inch length containing 10 cc. of sample, the results obtained will be substantially equal to the ASTM method. The same results would be obtained regardless of the size of the sample tube provided the thermocouple projects into the tube at least a distance equal to approximately 25 percent of the overall length of the tube. This insures that the temperature measured by the thermocouple is substantially the true temperature of the vapor evolved from the sample.

Referring to FIG. 8 there is shown a comparison between an ASTM distillation curve and the data obtained with the apparatus of this invention utilizing various heating rates. From the data it can be seen that if the heating rate is set to completely evaporate a 10 cc. of sample in approximately four minutes the results substantially equal the results obtained on the ASTM method.

Referring now to FIG. 9 there is shown a comparison between the temperature at which the purging air was shut off and the filling of the sample tube commenced. It can be seen that regardless of the temperature at which the purging air was shut off and the sample tube filled one obtained substantially the same distillation curve. Thus, the final temperature of the sample tube after purging is not critical and can vary over a relatively wide range.

We claim as our invention:

1. An apparatus for automatically conducting distillation analysis of liquids comprising:
   a sample tube;
   a support beam flexurally mounted at a point between its ends, said sample tube being attached to one end of said beam;
   heating means disposed to heat said sample tube to vaporize a liquid sample disposed therein;
purge means disposed to purge said sample tube after said liquid sample is vaporized; temperature measuring means disposed to measure the temperature of the vapor evolved from said sample tube and supply a signal related thereto; weighing means disposed to determine the weight of the sample tube and sample contained therein and supply a signal related thereto; fill means disposed to supply a sample of said liquid to said sample tube; a control circuit, said control circuit being responsive to said temperature measuring means and said weighing means to operate said fill means to fill said sample tube with a preset quantity of a liquid sample, energize said heating means, energize said purge means after said liquid sample is vaporized and adjust said weighing means for the weight of the sample tube after said sample is vaporized; and recording means, said temperature measuring means and said weighing means being coupled to said recording means to record said related signals in a correlatable manner.

2. The apparatus of claim 1 wherein said weighing means comprises linear displacement measuring means disposed to measure the movement of said beam as the sample is vaporized.

3. The apparatus of claim 1 wherein said weighing means comprises a strain gauge weigh cell disposed to weigh said sample tube and sample.

4. The apparatus of claim 1 wherein said control circuit includes means for setting said pre-set quantity of sample supplied to said sample tube.

5. The apparatus of claim 1 wherein one of said temperature measuring means and weighing means is coupled to comparing circuit means, said comparing circuit means comparing the temperature or weight of the sample with a set joint and supplying the other of said temperature or weight measurements of the sample to a process control means.