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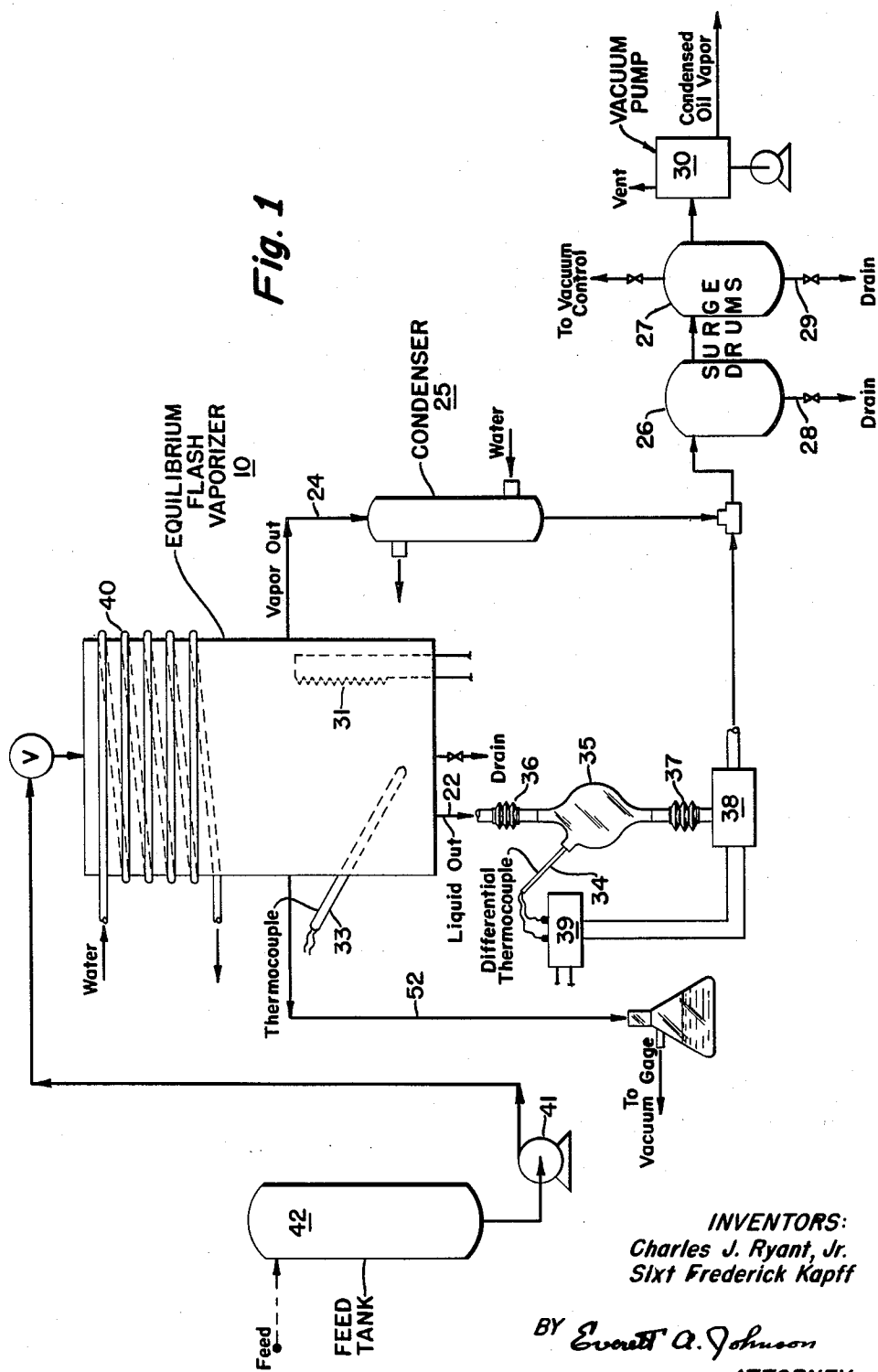
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VACUUM EQUILIBRIUM FLASH VAPORIZATION EQUIPMENT

Filed May 7, 1957

3 Sheets-Sheet 1



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3 Sheets-Sheet 2

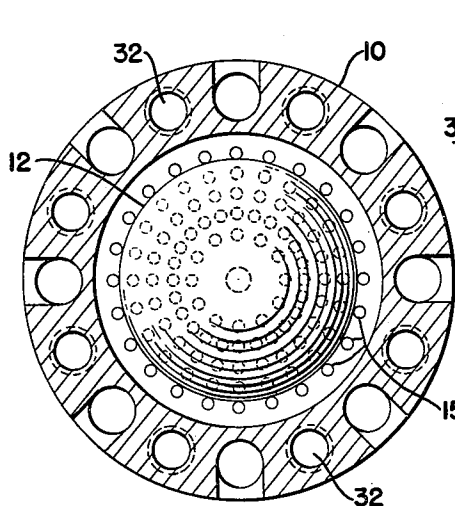


Fig. 3

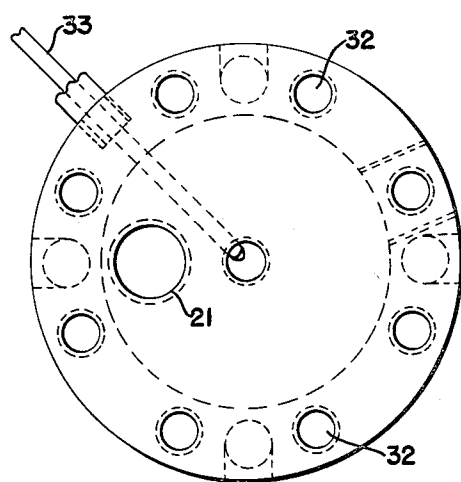


Fig. 4

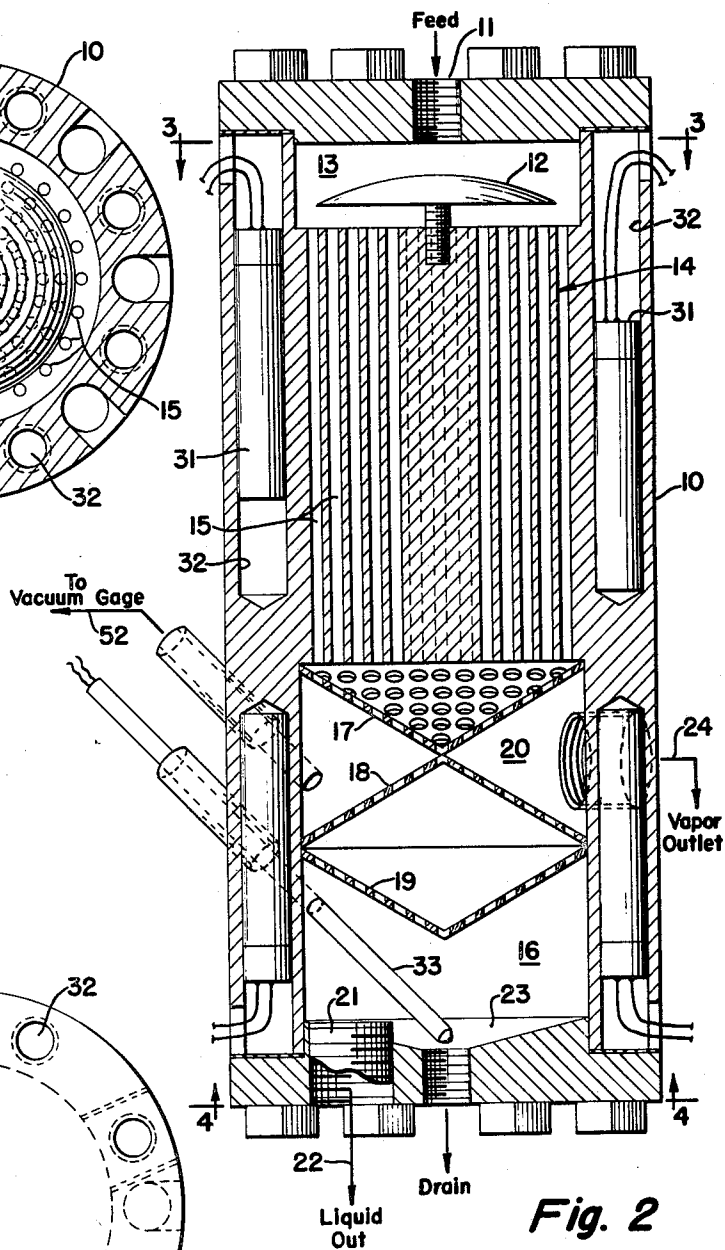


Fig. 2

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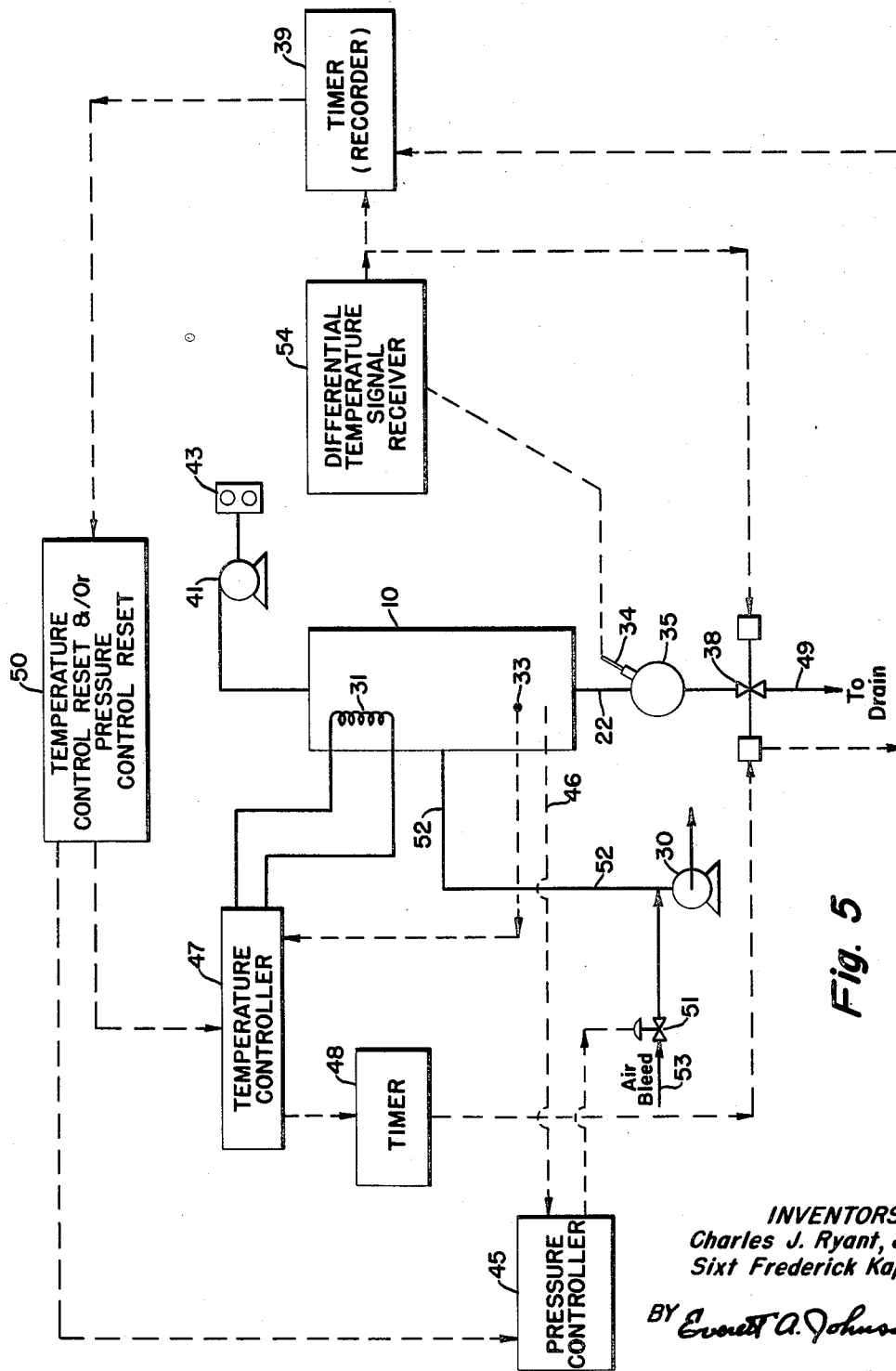
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VACUUM EQUILIBRIUM FLASH VAPORIZATION EQUIPMENT

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9 Claims. (Cl. 73—53)

This invention relates to the problem of establishing the phase diagram for a petroleum fraction. More particularly, the invention relates to a system for determining the phase diagrams of petroleum fractions in order to predict temperature profiles for furnaces as well as to establish the requisite furnace duty.

Among the more important data required in the design of petroleum refinery equipment are the phase conditions of the petroleum fractions. In spite of its importance and frequent occurrence in the design of petroleum refinery equipment, the prediction of the phase condition for petroleum stocks has received very little experimental attention. More particularly, data on "heavy" stocks has been very meager inasmuch as equilibrium flash vaporization of such "heavy" stocks should be obtained under subatmospheric pressures in order to lower the temperatures and eliminate cracking.

Interest in low pressure flashing of high boiling residua has introduced a need for reliable vapor pressure data for high boiling hydrocarbons and has promoted development of methods which enable the designer to estimate the quantity of materials that will be vaporized in a flashing chamber.

The known methods inestimating flash vaporization, include, for example, that described in an article entitled "Phase Relations and Petroleum Fractions," by Edmister and Pollock, Chemical Engineering Progress, volume 44 (1948), page 905, which is a basis for an empirical method for predicting equilibrium flash vaporization conditions of low boiling hydrocarbons. However, low pressure extrapolation of the correlations have not been practical since some attempted correlations differ widely in the high boiling temperature range.

Heretofore, the following time-consuming procedure has been used in constructing a phase diagram:

- (1) Determine the API gravity.
- (2) Run an atmospheric ASTM distillation until cracking begins. For reduced crudes this generally occurs before the 30% vaporization point.
- (3) Run a 10 mm. vacuum distillation.
- (4) Correct the 10 mm. vacuum distillation by an empirical curve to some unknown pressure so that the corrected vacuum distillation curve will agree with the incomplete curve of the atmospheric ASTM distillation.
- (5) Extrapolate the "derived" atmospheric ASTM distillation so it will indicate a temperature at which 90% of the original charge would be vaporized in an atmospheric ASTM distillation.
- (6) From an empirical correlation involving the ASTM 50% point and the ASTM 10% to 30% slope of the atmospheric ASTM distillation curve, determine the atmospheric equilibrium flash vaporization (E.F.V.) 50% point.
- (7) From an empirical correlation involving the ASTM slopes, determine the E.F.V. slopes.
- (8) Knowing the 50% E.F.V. point and the E.F.V. slopes, draw an atmospheric E.F.V. curve.

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(9) From an empirical correlation involving the ASTM volumetric average boiling point and the API gravity of the substance, determine the critical temperature for the petroleum fraction.

(10) From an empirical correlation involving the ASTM 10% to 90% slope, the ASTM volumetric average boiling point, and the API gravity of the substance, determine the critical pressure for the petroleum fraction.

(11) From an empirical correlation involving the ASTM 10% to 90% slope, the ASTM volumetric average boiling point, and the critical temperature, determine the focal temperature for the petroleum fraction.

(12) From an empirical correlation involving the ASTM 10% to 90% slope, the ASTM volumetric average boiling point, and the critical pressure, determine the focal pressure for the petroleum fraction.

(13) On coordinate paper of log of absolute pressure versus the reciprocal of the quantity of temperature in ° F. plus 382, plot the atmospheric E.F.V. (10% pt., 20%, 30%, etc.) and the focal point (focal temperature and focal pressure). Draw straight lines between the atmospheric E.F.V. points and the focal point. These straight lines are lines of constant vaporizations.

Thus, the need for an inexpensive, accurate and rapid system for determining the equilibrium flash vaporization of petroleum fractions is evident. However, devices and systems heretofore proposed required a very large sample, were not easily controlled, could not be readily operated at atmospheric pressure or sub-atmospheric pressure and involved time-consuming operations under the supervision of highly trained technical personnel. Thus, the systems were not adaptable for routine use on micro samples and have not been generally adopted.

It is, therefore, a primary object of our invention to provide a system which is simple in operation and adapted for routine determinations by non-professional personnel. A further object of the invention is to provide an apparatus which requires a minimum volume of sample. Another object of the invention is to provide a system which may be operated over wide pressure ranges and which is easily controlled. Still another object of the invention is to provide an apparatus and method for determination of equilibrium flash vaporizations which is well suited for quality control by plant technical service groups in refineries and in acceptance performance testing of processing units charging and producing high boiling hydrocarbon mixtures. These and other objects of the invention will become apparent as our description thereof proceeds.

Briefly, according to our invention, we provide a system for constructing a phase diagram by obtaining the equilibrium flash vaporization directly and using one empirical correlation for determining the focal point. When the equilibrium flash vaporization curve is obtained at two pressures, there is no need for determining the focal point per se.

Our system employs the principle of measuring the portion of the charge that is not vaporized, in contradistinction to other systems wherein the vaporized portion was condensed to determine the amount of vaporization. An important feature of our equilibrium flash vaporization equipment is a downflow liquid vaporizer which avoids difficulties heretofore encountered in controlling back pressure. In earlier systems there is a tendency for the fluid to "slug" due to the fact that pressure must build up within the vaporizer to force the fluid out of the reboiler. Such operation results in erratic conditions and causes a drop in temperature as a result of the additional self-cooling due to flashing of the charge

which is caused by sudden decrease in the pressure when the "slug" is released.

Our apparatus comprises a downflow vaporizer chamber having a plurality of parallel flow channels, means for controlling the temperature of the vaporizer chamber, a feeding device for supplying the sample at a definite constant rate, an equilibrium chamber in which the vapor produced is contacted with liquid containing the same components, separate means for removing vapors and unvaporized portion, and means for accumulating and timing the accumulation of a selected standard volume of unvaporized sample under preselected temperature and pressure conditions.

The downflow equilibrium flash vaporizer is provided with controllable electrical cartridge heaters, thermocouple means and pressure gauge means. The inlet portion of the vaporizer is also provided with a water cooling coil or jacket to assist in the temperature control of the unit.

Further details of the construction and advantages of our system will be described by reference to preferred embodiments thereof illustrated in the accompanying drawings wherein:

Figure 1 is a schematic diagram of the equipment;

Figure 2 is a vertical section of the vaporizer unit in Figure 1;

Figure 3 is a section taken along the line 3—3 in Figure 2;

Figure 4 is a bottom view taken along the line 4—4 in Figure 2; and

Figure 5 is a schematic and circuit diagram illustrating a continuous and automatic embodiment of the apparatus.

Referring to the drawings, feed enters the top of the block vaporizer 10 through port 11 and impinges upon the deflector plate 12 supported within the manifold section 13 above the heat exchanger section 14 in the vaporizer 10. The feed passes down through the many parallel channels 15 in the heat exchanger section 14 into the bottom separator chamber 16 after passing through the perforated metal cones 17, 18 and 19 in the disengager section 20 immediately below the heat exchanger section 14 and above the separator chamber 16.

The unvaporized liquid leaves the separator chamber 16 by overflowing a circular weir 21 formed by the outlet line 22 in the concave end plate 23 forming the bottom wall of the separator chamber 16. The vapor passes out through a relatively large diameter take-off conduit 24 communicating with the disengager section 20 between perforated cones 17 and 18. The withdrawn vapor may be condensed by passing through condenser 25 and the fluids passed to the series surge drums 26 and 27, provided with drains 28 and 29. A vacuum pump 30 takes suction on drum 27.

A plurality of electrical heating elements or cartridges 31, disposed within cylindrical recesses or chambers 32 in the walls of the vaporizer 10, may be separately controllable to rapidly attain equilibrium of vapor and liquid. Temperature and equilibrium are indicated by a thermocouple 33 maintained in the liquid phase of the separator chamber 16. For a given temperature, the degree of vaporization is obtained by calculation from the length of time for the receiver or accumulator 35 to be filled as sensed by the differential thermocouple 34.

The volumetric receiver or accumulator 35 is mounted between a pair of conduits including bellows 36 and 37, the upper conduit receiving the liquid from the separator chamber 16 in the vaporizer 10 and the lower conduit 37 being controlled by normally open solenoid valve 38. When on test, the valve 38 is closed after equilibrium temperature is attained in disengager section 20 and remains closed until the differential thermocouple 34 in the flask 35 indicates that the desired level of liquid has accumulated therein. Simultaneously, the length of time for accumulating this standard volume of unvaporized liquid is automatically indicated by timer 39 and the

valve 38 is opened for discharge of the collected volume of liquid.

Suitable means can be provided for controlling the temperature of the vaporizer 10 and this may include the cartridge heaters 31 as well as a supplementary cooling coil or jacket 40 surrounding the manifold chamber 13 and a portion of the heat exchanger 14 in the vaporizer 10. Other controls and recorders are well known in the art and may be applied to our system to make it fully automatic. We may, for example, provide for repeated tests at the same temperature and different pressure; likewise, we may electrically determine the ratio of the times for collecting the standard volume of liquid under the selected temperature and pressure conditions.

To operate our equilibrium flash vaporizer apparatus, we perform the following steps:

(1) The constant volume flow into the vaporizer unit 10 is established;

(2) The desired flashing pressure is provided by vacuum pump 30;

(3) The temperature of the vaporizer 10 is adjusted by control of the electrical cartridge heater 31 so that it is only about 1 degree higher than the desired flashing temperature;

(4) The time necessary to accumulate the standard volume of unvaporized charge in flask 35 at the established temperature and pressure of the vaporizer 10 is determined;

(5) Step 4 is repeated at the same temperature, but at a pressure where there will be no vaporization;

(6) Ratio of the times obtained in steps 4 and 5 gives the volume percent of the original charge which is not vaporized at a given temperature and pressure; and

(7) Steps 4 and 5 are repeated at a series of temperatures to obtain sufficient points to establish the entire flash curve.

A complete set of points for an E.F.V. curve can be established rapidly and even heavy stocks can be run under reduced pressures through the vertical downflow vaporizer 10. Feed enters the top of the vaporizer 10 supplied at a constant rate by pump 41 from feed tank 42 and passes downwardly through parallel channels 15 in the body of the vaporizer 10. A solid deflector plate 12 above the exchanger section 14 assures uniform distribution of liquid feed to the parallel exchanger channels 15. Perforated metal cones 17, 18 and 19 disposed immediately below the exchanger section 14 mix the liquid and vapor coming out of the parallel channels 15. The deflector plate 12 and the perforated metal cones 17 eliminate any sensitivity to feed rate variations thus assuring uniformity and reproducibility of data.

The downflow liquid vaporizer 10 employed in our system is self-draining and is designed with a ratio of heat transfer surface to cross-sectional flow area which insures that all the charge will vaporize at a given temperature and pressure by the time it reaches the outlet of the vaporizer. Thus we achieve virtually instantaneous equilibrium and the apparatus is designed so that the force of gravity on the liquid is sufficient to separate liquid from vapor without the existence of a pressure differential. In addition, we provide a plurality of flow paths 15 so that the pressure of the fluid at the inlet 11 of the vaporizer 10 is equal to the pressure at which the outlet of the liquid-vapor separator 16 is being operated.

To operate the equipment illustrated in Figure 5, the control button 43 is depressed to start the pump 41, to supply current to the heaters 31 in the E.F.V. equipment 10, and to start the vacuum pump 30. A pressure controller 45, which is connected to the E.F.V. equipment 10 by line 46, is set for some selected initial pressure of about 10 mm. mercury. A temperature controller 47 is set for some selected initial temperature of about 300° F. and the thermocouple 33 in the E.F.V. equipment 10 is used to indicate the temperature and to govern the

temperature controller 47. The timer 48 is actuated when the temperature controller 47 reaches the selected initial temperature. If the temperature within the E.F.V. equipment 10, as sensed by the thermocouple 33, has been maintained at about $\pm 0.5^\circ$ F. for a period of approximately 10 minutes, then the valve 38 will close.

When the valve 38 closes, it actuates the second timer 39 and causes the liquid to rise within the collection bulb 35. The bulb 35 is provided with a level sensing means, such as differential temperature thermocouple 34. Other level detectors and telemetering means well known in the art may be used. However, in the illustrated embodiment, when there is a decrease in the differential temperature, the second timer 39 is stopped and the valve 38 is automatically opened to permit the flow of liquid from the bulb 35. The total liquid flow being pumped by pump 41 then flows through the E.F.V. equipment 10 and down the drain 49.

When the second timer 39 is stopped, the elapsed interval will indicate the length of time required to accumulate within the bulb 35 the standard volume of liquid. Simultaneously the pressure controller 45 communicating with the E.F.V. equipment 10 is reset to either a high or low pressure as the case may be, and then the cycle is repeated.

When the second timer 39 stops, two events occur alternately; first the pressure controller 45 will be reset to either a high or a low pressure, as the case may be. In other words, if the E.F.V. equipment 10 was operating at about 10 mm. of pressure and the second timer 39 is stopped, then the pressure control 45 resets the pressure to another predetermined pressure and the cycle is repeated. When the second timer 39 stops, it also causes the temperature control reset 50 to advance the temperature controller 47, for example, about 10° , and begin the complete cycle again. The pressure in the E.F.V. equipment 10 is controlled by providing a pressure connection 46 between the equipment 10 to a pressure controller 45 which in turn actuates a valve 51 which bleeds air into the suction line 52 of the vacuum pump 30. In other words, constant pressure is maintained by running the vacuum pump 30 steadily and by controlling the air bleed 53.

"High pressures" as used herein is that pressure where there is no vaporization at a given temperature and "low pressure" is here considered as of the order of 10 mm. of pressure.

Second timer 39 also is a recorder and may be provided with a computing circuit which permits the plotting of a flash curve as the results are received. The curve is plotted on an X—Y recorder rather than a circular chart where the temperature is along one axis and the ratio of the time intervals (which is actually a volume percent not vaporized) along the other axis.

The second timer may be provided with a program cam or other apparatus incorporated in it which permits any number of determinations to be made at a given temperature or pressure, as the case may be.

If the operator desires to have a high and a low pressure comparison, we provide a selective switch which would automatically initiate a test at a different temperature. Thus we may provide a control switch means associated with the second timer 39 which is capable of repeating a first event following which a second event is initiated when the prescribed number of occurrences of the first event has been reached.

Although we have described the invention in terms of examples set forth in some detail, it should be understood that these are by way of illustration only and that the invention is not limited thereto. Alternative embodiments will become apparent to those skilled in the art in view of our description of the invention, and accordingly it is contemplated that modifications may be made

in the invention without departing from the spirit thereof.

What we claim is:

1. An apparatus for determining vacuum equilibrium flash vaporization of liquids which comprises means for flowing a liquid at a selected constant rate, downflow means for incompletely vaporizing the said liquid under controlled temperature and pressure, baffled means subjacent to said downflow means for separating the evolved vapors, means for accumulating from said baffled means a standard volume of unvaporized liquid under the selected conditions of temperature and pressure, and means for determining the time necessary to accumulate said standard volume as a measure of vacuum equilibrium flash vaporization.

2. A vacuum equilibrium flash vaporization apparatus which comprises in combination a constant volume flow feed pump, a downflow flash equilibrium vaporizer, said vaporizer including an upper manifold section, a heat exchanger section consisting of a plurality of parallel channels, means for controlling the temperature of said vaporizer, a disengager section subjacent to said heat exchanger section, said disengager section including a plurality of perforated cones arranged apex-to-apex and base-to-base, a separator chamber, means for withdrawing vapor from said vaporizer, an accumulator into which unvaporized feed flows from said separator chamber, means for maintaining the apparatus at a desired pressure, and means for timing the period within which the accumulator collects.

3. An apparatus for determining vacuum equilibrium flash vaporization of liquids comprising vaporizer chamber means, downflow heat exchanger means in said vaporizer chamber means, vapor-liquid separator means in a lower portion of said vaporizer, means for withdrawing vapor from said vaporizer chamber, means for controlling the temperature of said vaporizer, means for introducing sample liquid at a constant rate into an upper portion of said vaporizer, means for withdrawing unvaporized liquid from a lower portion of said vaporizer, accumulator means accumulating unvaporized liquid withdrawn from said vaporizer, said accumulator means including flask means, differential thermocouple means extending within said flask means, and solenoid-operated valve means controlling the outlet from said flask means, and vacuum pump means for maintaining subatmospheric pressure on said apparatus.

4. Vaporizer chamber means adapted for use in vacuum equilibrium flash vaporization tests which comprises a temperature-controlled block, a recess in one end of said block providing a manifold chamber, a plurality of parallel flow channels extending downwardly from said manifold chamber, an inlet to said manifold chamber, deflector means interposed said inlet and the top of said parallel channels, electrical means for controlling the temperature of the said block, an equilibrium chamber subjacent to said flow channels, outlet means from said equilibrium chamber for withdrawing liquid therefrom, vapor outlet means in an upper part of said equilibrium chamber, and a plurality of perforated cones in an upper portion of said equilibrium chamber, one cone being arranged with its base across the lower end of said channels, a second cone arranged apex-to-apex with the first, and a third arranged base-to-base with the second, said vapor outlet communicating with the space between said first and second cones.

5. An equilibrium flash vaporization still comprising a vertically elongated housing, a manifold chamber in the upper portion of said housing, a heat exchanger chamber in an intermediate portion of said housing, and an equilibrium chamber in a lower portion of said housing, an inlet at the top of said housing discharging into said manifold chamber, deflector means in said manifold chamber onto which the inlet stream impinges, a plurality of parallel channels forming said heat exchanger

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chamber, a first perforated cone across the flow area of said equilibrium chamber and having its base across the lower end of said heat exchanger chamber, a second perforated cone similar to the first and arranged apex-to-apex with the first cone, and a third such perforated cone arranged base-to-base with the second perforated cone, liquid outlet means in the bottom of said housing, said outlet including a weir over which unvaporized liquid flows, vapor outlet means from said separator chamber communicating with the space between said first and second perforated cones, electrical heating means in the walls of said housing, and thermocouple means extending through the walls of said housing to a point below the upper edge of said weir.

6. An apparatus for continuously determining the vacuum equilibrium flash vaporization characteristics of a high boiling hydrocarbon liquid which comprises in combination a downflow vaporizer including a manifold section, a tubular heat exchange section and a liquid-vapor separator section, means for maintaining said vaporizer at a constant temperature, means for providing controlled pressure in said vaporizer, means for accumulating unvaporized liquid exterior of said vaporizer, outlet conduit means for withdrawing vapors from said separator section, means for detecting the accumulation of a preselected volume of unvaporized liquid in said accumulating means, electrical circuit means including thermocouple means, a timer and a means for programming the discharge of the accumulated liquid from said accumulating means, means for controlling the heating of said vaporizer in response to the temperature within the said separator section, and vacuum pump means for maintaining said vaporizer at the desired pressure via the said vapor outlet conduit therefrom.

7. The apparatus of claim 1 which includes temperature responsive means for monitoring the liquid level in said accumulating means and means for programming the discharge of the accumulated liquid therefrom.

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8. An apparatus for determining vaporization characteristics of liquids which comprises means for flowing a liquid at a selected constant rate, downflow means for incompletely vaporizing the said liquid under controlled temperature and pressure, means subjacent to said downflow means for separating evolved vapors, means for accumulating from said subjacent means a volume of unvaporized liquid under selected conditions of temperature and pressure, means for sensing the temperature of the accumulated liquid as a measure of its level, and means responsive to the predetermined level measurement of said accumulated liquid for adjusting the temperature of the downflow means.

9. A vaporization apparatus comprising in combination a constant volume flow feed pump, a downflow vaporizer, said vaporizer including an upper manifold section, a heat exchanger section consisting of a plurality of parallel channels, means for controlling the temperature of said vaporizer, a separator section subjacent to said heat exchanger section, said separator section including an accumulator into which unvaporized feed flows, means for withdrawing vapor from said accumulator, means for maintaining the apparatus at a desired pressure, and means responsive to the temperature of the liquid in said accumulator, said last named means actuating said means for controlling the temperature of said vaporizer.

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