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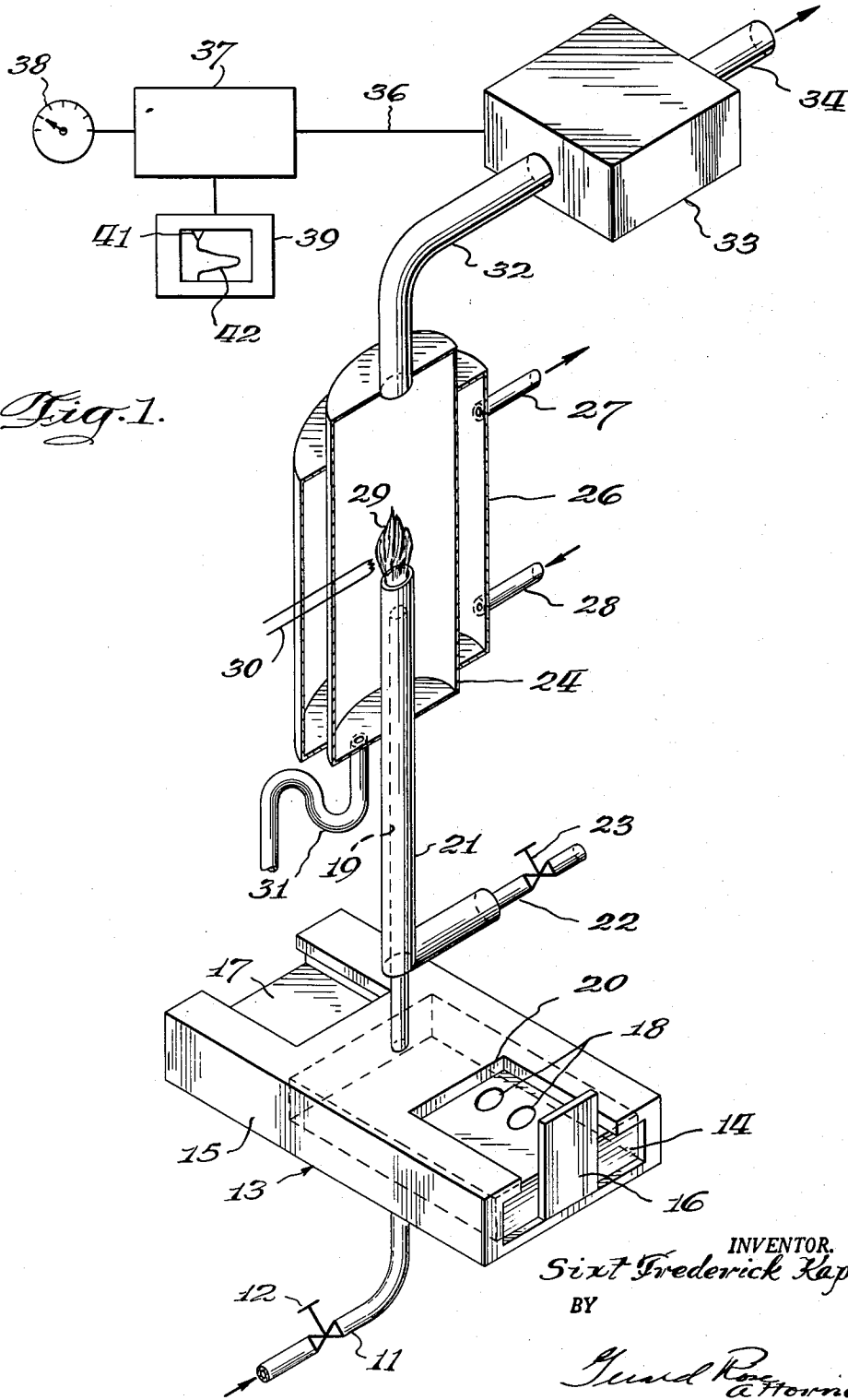
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3,116,979

MEANS FOR DETERMINING CARBON CONTENT

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2 Sheets-Sheet 1



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3,116,979 MEANS FOR DETERMINING CARBON CONTENT

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This invention relates to means for determining the carbon content of a finely divided solid, and especially concerns the provision of an apparatus for accurately and rapidly determining the carbon content of fluidized solid catalysts.

In the operation of commercial processes embodying fluidized solids techniques, such as fluid catalytic cracking, it is frequently desirable to ascertain the carbon content of either spent or freshly regenerated catalyst. This is commonly done by collecting a catalyst sample and laboriously conducting a laboratory determination of its carbon level. These analyses however are time consuming and require the full attention of a laboratory technician. While the desirability of providing a simple carbon-on-catalyst analyzer for use at the unit site is manifest, no equipment is presently available which can afford the requisite accuracy without disproportionate investment and operating costs.

Accordingly, a primary object of the present invention is to provide an apparatus for determining the carbon content of finely divided solid materials, which apparatus is exceedingly accurate yet rugged, low in cost, and suitable for on-site use. A further object is to provide a rapid acting carbon-on-catalyst instrument. Other and more particular objects will be apparent as the description of this invention proceeds.

Briefly, in accordance with the invention, a gas stream is passed into a heated combustion zone at constant flow rate. To this stream is added a known amount of finely divided carbon-containing solid, and the resultant entrained solid is permitted to enter the combustion zone where oxidation of carbon to carbon dioxide occurs. Since the solid is finely divided and well distributed oxidation occurs rapidly and quantitatively. The gas exhausted from the combustion zone is then analyzed for its carbon dioxide content, suitably by a thermal conductivity cell, and this carbon dioxide content is directly related to the original carbon content of the finely divided solid sample.

In one embodiment of the invention, the carrier gas comprises hydrogen which is mixed with an oxygen-containing stream to provide heat to the combustion zone. The oxygen-containing gas stream is likewise supplied at constant flow rate, so the final carbon dioxide content bears a direct correlation with the carbon content of the finely divided solid. This embodiment provides extremely rapid and complete combustion of the carbon deposits.

In another embodiment, the carrier gas comprises oxygen, and heat for the combustion zone is provided by an electric heater or furnace. In this embodiment, no hydrogen supply is required.

The invention also contemplates the provision of means for entraining a known amount of finely divided solids in the carrier gas stream. Such means may comprise a slidable valve block in a valve body, the body having axially aligned conduits for an ascending carrier gas stream and the block having at least one sample-metering cavity which is brought into register with the conduits to effect entrainment of the solids in the gas.

The invention will be further described in the ensuing

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specification which is to be read in conjunction with the attached drawings wherein:

FIGURE 1 is a schematic view, partly in section, showing the first-described embodiment which employs hydrogen to furnish heat to the combustion zone; and

FIGURE 2 depicts the embodiment wherein the combustion zone is heated by electricity, and wherein an optional system is provided for conducting completely automatic carbon content measurements.

Referring to FIGURE 1, the major components of this embodiment include a hydrogen-containing carrier gas inlet conduit 11, a sample metering valve 13 for effecting entrainment of a mass of carbon-containing solids in the carrier gas, a conduit 22 for introducing oxygen-containing gas, a combustion zone 24 where a hydrogen flame 29 burns carbon on the solids to carbon dioxide, and a thermal conductivity cell 33 for determining or measuring the carbon dioxide content of gases leaving combustion zone 24.

Hydrogen-containing gas is supplied to the system via conduit 11 and valve 12 from a constant pressure source. Thus regulation of valve 12 effects control of the hydrogen-containing gas inlet rate, which is a requisite for obtaining a direct correlation between carbon dioxide content as measured by cell 33 and carbon content on the original finely divided sample. This hydrogen-containing stream advantageously is purified 99+ % cylinder hydrogen.

Samples of finely divided carbon-containing solids are metered in known amounts by means of sample metering valve 13. This valve comprises a valve body 15 and a valve block 14 which is slideably received in channel 17 of body 15. Valve block 14 has at least one, and preferably two or more, sample-metering cavities 18 of known volumetric capacity.

Axially aligned with the hydrogen-containing gas inlet conduit 11 and passing through valve body 15 is an outlet conduit 19. Solid sample metering cavities 18 are positioned to register with the inlet and outlet conduits 11 and 19 when block 14 is suitably positioned. Ordinarily at least one sample cavity is not filled so as to permit continuous flow of hydrogen-containing gas into the apparatus.

Outlet conduit 19 extends in a generally vertical direction from valve body 15 and communicates into combustion zone 24. Surrounding a portion of conduit 19 is a coaxial conduit 21, into which a oxygen-containing stream is admitted via conduit 22. This stream is supplied at constant flow rate by suitable regulation of valve 23, and advantageously consists of water-pumped 99+ % cylinder oxygen.

Combustion of carbon deposits on the finely divided solid takes place in combustion zone 24. In zone 24 a hydrogen gas flame 29 is maintained, and ignition of this flame is initiated by an electrically heated resistance filament 30. Combustion zone 24 is shown in partial cross section for purposes of clarity.

A water cooling jacket 26 surrounds at least part of zone 24, and is provided with cooling water via inlet conduit 28 which exhausts at outlet conduit 27. This jacket serves several functions. It prevents zone 24 from becoming heated and thereby increases its life span, and also condenses at least part of the water vapor resulting from combustion of hydrogen gas and/or hydrogen which may be chemically associated with deposits on the finely divided solid material. For maximum accuracy in subsequent analysis of the effluent gas by thermal conductivity means, it is desirable to remove as much as possible of this water inasmuch as water vapor and carbon dioxide have similar thermal conductivities. Condensate may be released continuously through condensate

line 31, which maintains a liquid seal to prevent bypassing of gas around outlet conduit 32.

The effluent gas withdrawn from combustion zone 24 is conducted via conduit 32 to a device for determining the carbon dioxide content of this stream. This device is advantageously thermal conductivity cell 33, which is sensitive to the thermal conductivity difference between carbon dioxide and either oxygen or nitrogen.

Thermal conductivity cell 33 may be connected via symbolic line 36 to an electrical measuring system such as a Wheatstone bridge circuit 37 to detect the electrical response to cell 33. Circuit 37 may be connected to either a meter 38 or a recorder 39 to indicate this response. As shown in the figure, the response is a peak 42 on a curve drawn by recorder pen 41. The integral under this peak 42 is related to the absolute amount of carbon dioxide in the effluent gas, and hence to the carbon content of the finely divided solid sample. To a first approximation, particularly when careful control of the hydrogen and oxygen streams are maintained, the height rather than area of this peak may be related to the carbon level, and for especially low cost operation an indicator such as galvanometer 38 upon which can be observed the maximum peak height may be employed.

In operation, the device of FIGURE 1 is exceedingly simple. The operator moves tab 16 to position block 14 so that one cavity 18 is in alignment with hydrogen inlet conduit 11 and outlet conduit 19. Accordingly, hydrogen gas is free to flow at a constant rate into combustion zone 24 via conduits 11 and 19. Similarly oxygen is admitted via conduits 22 and 21 into zone 24, and the two gases mix and are ignited via filament 30 to establish a flame 29. If desired, a ceramic element may be located in the flame to serve as a reigniter should the flame 29 be extinguished momentarily.

As sample of carbon-containing finely divided solid material such as spent or regenerated silica-alumina cracking catalyst having a particle size within the range of about 10-200 microns, is poured into a solid metering cavity in block 14. Block 14 is then slid along channel 17 so that the solid-containing cavity is in register with conduits 11 and 19; suitable indexes may be provided on block 14 and body 15 for this purpose. The top portion 20 of block 15 strikes off excess catalyst so that the volume of catalyst in cavity 18 is exactly equal to the volume of cavity 18.

As soon as a solids-containing cavity is placed in register with conduits 11 and 19, the hydrogen-containing carrier gas flowing through these conduits entrains the catalyst and lifts it through conduit 19 into the combustion zone. There the catalyst passes through hydrogen flame 29 where carbon on the catalyst is burned to carbon dioxide. Because the cross sectional area of combustion zone 24 is much greater than conduit 19, catalyst from which the carbon has been removed tends to fall by gravity to the bottom of combustion zone 24 from whence it may be periodically removed.

The combustion gases above flame 29 consist chiefly of carbon dioxide, oxygen, and water vapor. Much of the latter is removed by condensation on the water-cooled walls of combustion zone 24, while the remainder discharges via line 32 and thermal conductivity cell 33 to the atmosphere 34. Cell 33 is responsive to carbon dioxide content, and deliver its signal via electrical circuit 37 to indicator 38 or recorder 39.

Turning now to FIGURE 2, an alternative embodiment of the invention is shown. This embodiment substitutes an electrical furnace 54 for the gas flame (29 of FIGURE 1) and thus eliminates the need for hydrogen gas.

The construction of valve 13 is identical to that of valve 13 in FIGURE 1, and accordingly no separate description of its components or function need be given. In the embodiment of FIGURE 2 however, it is advantageous to employ a stream of air as carrier gas and as

a source of molecular oxygen for combustion. This air is admitted via inlet conduit 51, and its associated flow regulating valve 52.

Outlet conduit 53 leaving valve 13 passes into vertically elongated combustion zone 52 which may be a tube having cross sectional area a few times greater than the cross sectional area of outlet conduit 53 at its end 56. For optimum operation, the size of combustion zone 57 is selected to permit continued entrainment of the catalyst through combustion zone 57 and outlet conduit 58, relying on filter or baffles 59 to remove and collect carbon-free catalyst.

Combustion zone 57 is deposited within an electrically heated furnace 54. Zone 57 is maintained at the center of furnace 54 by insulating spacers 55.

Beyond filter 59, conduit 61 conducts combustion gases withdrawn from combustion zone 57 into a thermal conductivity cell 33, or other apparatus such as an infrared detector, which is sensitive to carbon dioxide content.

An optional accessory which may be employed with either embodiment of the invention is a system for conducting a carbon analysis automatically. This system is shown associated with the embodiment depicted in FIGURE 2, and comprises a controllable valve assembly 64 for diverting a portion of solid material normally descending through conduit 67 into conduit 69 and chute 66 into a solid metering cavity 18 in valve block 14. Actual diversion is effected by flapper valve 68, which is moved in response to an electrical signal.

Positioning of block 14 is accomplished automatically by means of solenoid 62 and armature 63. The adjustment of spring loaded armature 63 is made so that solenoid 62 positions valve block 14 to enable gas to flow either through a solids-containing metering cavity 18 or through an unfilled cavity to maintain continuous air flow irrespective of whether a sample is being added.

Automatic sequential operation of valve 64 and valve 13 is effected by means of cam 71, lobes 72 and 73, and micro-switches 74 and 76. Cam 71 is driven by motor 79 via shaft 82; motor 79 may be controlled by switch 82, which is activated either manually or automatically at occasional intervals when sampling is desired.

When switch 82 is closed, motor 79 commences operation and begins rotating cam 71 in a counterclockwise direction. Lobe 72 engages micro switch 74 which intermits an electrical signal via line 77 to valve 64, ordering this valve to shift flapper 68 and collect a sample of solids flowing through conduit 67. The sample pours into solids metering cavity 18 for a time determined by the length of lobe 72. During this time, valve block 14 is in a position to permit air to flow into combustion zone 57 via an unfilled cavity in block 14.

Upon further rotation of cam 71, lobe 73 engages micro switch 76. This intermits a signal to solenoid 62, causing it to move armature 63 and valve block 14 into a position whereby solids in metering cavity 18 are placed in register with the inlet and outlet air conduits 51 and 53. Excess catalyst is removed by the top portion 20 of valve 13, enabling only a predetermined quantity of solids to be entrained in the ascending carrier air stream.

Combustion of carbon on the entrained solids occurs when the gas-entrained solids pass through combustion zone 57, and the resultant carbon dioxide content is determined by thermal conductivity cell 33.

In a test of the embodiment shown in FIGURE 2, without the automatic installation, unusual precision was attained. Furnace 54 was operated at a temperature of 850° F., and the air flow rate was maintained at 145 cc./min., measured at 60° F. and at atmosphere pressure. The amount of catalyst was 0.063 gram. Using a commercially Fisher thermistor type thermal conductivity cell operated at 20 ma. in a conventional bridge circuit and recording the results on a 0-5 mv. recorder, the recorder deflection was substantially linear up to about 2% carbon on the catalyst. A deflection of 5 mv. corre-

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sponded to approximately 2.5% carbon, and the instrument demonstrated its ability to determine carbon levels in excess of 5% by weight.

Thus it is apparent that an exceedingly simple, yet rapid and accurate carbon-on-catalyst measuring device has been provided. In addition to the modifications suggested, various other accessories may be added; for example, either of the embodiments depicted may be operated continuously rather than batchwise by introducing catalyst at a constant and continuous flow rate.

Other alternatives, modifications, and variations will be apparent to those skilled in the art in light of the foregoing description, and accordingly it is intended to embrace all such alternatives, modifications, and variations that fall within the spirit and broad scope of the appended claims.

I claim:

1. In an apparatus for determining the carbon content of a finely divided solid, the improved combination of a vertically elongated combustion zone, a valve body having axially aligned inlet and outlet conduits and said body having a channel therein, a valve block slideably received in said channel and having at least one solid-metering cavity extending therethrough, said at least one cavity being registrable with said inlet and outlet conduits, means for passing to said inlet conduit a stream of carrier

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gas at constant flow rate to entrain finely divided solids in said at least one cavity when said cavity registers with said inlet and outlet conduits, a generally vertical conduit for passing said gas-entrained solid into said combustion zone to effect combustion of carbon to carbon dioxide, a conduit for withdrawing a gas stream containing said carbon dioxide from the combustion zone, and means for determining the carbon dioxide content of said withdrawn gas stream as a measure of the carbon content of said finely divided solid.

2. Apparatus of claim 1 wherein said carrier gas is a hydrogen-containing gas, and said apparatus includes means for passing a stream of oxygen-containing gas at constant flow rate into said combustion zone.

3. Apparatus of claim 1 wherein said carrier gas is an oxygen-containing gas, and wherein said combustion zone is an electrically heated combustion zone.

4. Apparatus of claim 1 including means for introducing a carbon-containing finely divided solid into said solid metering cavity and for sliding said valve block to register said cavity with the inlet and outlet carrier gas conduits.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,116,979

January 7, 1964

Sixt Frederick Kapff

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

In the drawing, Sheet 2, Fig. 2, the column labeled "52", which is shown having a concentric axis with furnace 54, should be -- 57 --; column 3, line 12, for "to", first occurrence, read -- of --; line 36, for "As" read -- A --; same column 3, line 64, for "deliver" read -- delivers --; column 4, line 5, for "52" read -- 57 --; line 40, for "82" read -- 81 --.

Signed and sealed this 9th day of June 1964.

(SEAL)

Attest:

ERNEST W. SWIDER
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