1 535 944

PATENT SPECIFICATION (11) 1 535 944

(21) Application No. 16989/76 (22) Filed 27 April 1976
(31) Convention Application No. 572603.
(32) Filed 28 April 1975 in
(33) United States of America (US)
(44) Complete Specification published 13 Dec. 1978
(51) INT CL² G01N 1/10
(52) Index at acceptance
B8N 12D 12X

(19)



(54) CATALYST SAMPLING METHOD

(71) We, UOP INC., a corporation organized under the laws of the State of Delaware, United States of America, of Ten UOP Plaza, Algonquin & Mt. Prospect Roads, Des Plaines, Illinois, United States of America, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following Statement:—

The prior art has recognised the importance of obtaining samples of catalyst from within an operating catalytic reactor. This provides useful information on such factors as the amount of coke on the surface of the catalyst, the amount of metals deposited on the catalyst, the halogen content, surface area, platinum crystallite size or oxidation state of the catalyst. One type of sampler developed to supply this information mechanically opens and closes the sampling port located at the end of the probe. This type of sampler is represented by the device shown in U.S. Patent 3,348,419. In this reference, a hollow withdrawal conduit is rotated within a hollow shaft to open and close an opening into the withdrawal conduit. U.S. Patent 3,442,138 describes a nonrotating shaft which slides in a reciprocating manner within an outer shaft to operate the catalyst outlet. These samplers have several disadvantages which the prior art has regognised. The movement associated with their operation tends to crush catalyst and the mechanical nature of the probe requires close tolerances. The temperature differences experienced by the sampler and the fine particles combine to make operation difficult. It also results in binding and galling of the moving parts.

A second type of sampling device produces or controls the flow of catalyst pneumatically. For instance, in U.S. Patent 3,653,265, the differential pressure between the reaction vessel and a solids receiver is used to create a gas stream which carries catalyst upward and out of the vessel. The rate of catalyst withdrawal is regulated by a flow of purge gas delivered to the inlet of the withdrawal conduit. An increase in the purge gas rate decreases the flow of gas from the vessel and therefore the catalyst transfer. A second system shown in U.S. Patent 3,786,682 delivers a high velocity gas flow to the end of the withdrawal conduit via a small tube contained within the conduit. This high-velocity flow prevents catalyst from entering the tube except for when it is reduced, and the construction allows removal of all catalyst from the conduit. This second type of sampling device removes the mechanical problems, but the required gas flows to remove small amounts of catalyst are difficult to control and measure. The second system also has a second disadvantage in that the high gas rate forms an unrepresentative environment near the catalyst sampling port and therefore tends to produce unrepresentative samples.

U.K. Patent Specification No. 1,296,025 discloses a withdrawal conduit similar in construction to that preferred for use with the method of the invention. However, the operation used to withdraw catalyst differs. The pressure within the sample receiver is equilibrated with the reactor, and the two volumes are brought into open communication through the withdrawal conduit. The catalyst is then transferred by a gas flow produced by briefly venting the sample receiver to an external point.

In our invention, representative catalyst samples are removed from a sampling point within a vessel containing fixed bed of catalyst in a mechanically simple system without the use of large gas streams.

According to the present invention there is provided a method of transferring a catalyst sample from a sampling point within a vessel containing a bed of catalyst into a withdrawal conduit having a downwardly-facing catalyst entrance port and of transferring the catalyst sample along the conduit into a sample receiver located outside of the vessel at the end of

the conduit, which method comprises the steps of: (a) sealing the withdrawal conduit to gas flow at a point intermediate the sampling point and the sample receiver; (b) evacuating the sample receiver and creating a pressure therein lower than that maintained in the vessel; and (c) rapidly unsealing the withdrawal conduit, which causes a short and rapid gas flow to pass through the withdrawal conduit to equalise the pressures within the vessel and the sample receiver, and which thus effects a fluidisation of catalyst into the downwardly facing catalyst entrance port of the withdrawal conduit and the transfer of catalyst through the withdrawal conduit to the sample receiver.

Of the accompanying drawings Figure 1 presents a vertical cross-section of a fixed bed catalytic reactor in which a system adapted to the use of the method of the invention has been installed. Figure 2 illustrates the preferred construction of the upper end of a catalyst withdrawal conduit 5 for Figure 1 in which the conduit is installed at an angle to the vertical. Figure 3 illustrates the relationship between the pressure differential applied to one specific system and the amount of catalyst transferred.

Referring now to Figure 1, the outer wall 1 encloses a reactor containing a fixed bed of catalyst particles 2. The reactor is shown as it would appear in cross-section when an annular bed of catalyst is used. A cylindrical porous wall 3 of catalyst retaining screen and a porous cylindrical centre pipe 4 define the outer extremities of the catalyst bed. The reactants may flow radially in either an inward or outward direction. The catalyst sampling system includes a withdrawal conduit 5 which extends upward into the catalyst bed at an angle to the vertical. A downwardly facing catalyst entrance port 6 is located near the upper end of the withdrawal conduit 5. The withdrawal conduit 5 passes into the reactor 1 through a catalyst removal nozzle which is filled with inert spheres 7 of a larger diameter than the catalyst. Line 9 carries a small stream of a heated purge gas at a rate controlled by valve 10 and delivers the purge gas to the base of the withdrawal conduit. Just below this point is located a valve 8 which can form a pressure tight seal across the withdrawal conduit. A second line 11 connects with the conduit 14 extending downward from the valve 8. This line may lead to a vacuum source or may be a simple vent line. Line 11 can also supply purge gas to the conduit. The flow through this line is controlled by valve 12. A second valve 15 is provided in the withdrawal conduit below line 11. Either valve 8 or valve 15 may be utilised as the main sealing or surge valve. Two valves are provided as a safety measure. A cylindrical sample receiver 13 is located below valve 15.

Figure 2 illustrates the preferred construction of the downward facing catalyst entrance port 6, which is located at the upper end of the withdrawal conduit 5, when this conduit is to be mounted in the reactor at an angle to the vertical. The entrance port 6 is the unsealed lower end of a small tube 16 which extends within the withdrawal conduit 5 and points upward toward the cap 19 sealing the upper end of the conduit. The upper end 20 of the tube 16 will preferably be near horizontal when the conduit is installed.

Figure 3 presents a summary of experimental data on the relationship of the pressure differential applied between the vessel and the sample receiver to the amount transferred under one specific set of conditions. The data is presented as a band since the amount transferred was found to vary slightly with different configurations of the entrance port and upper portion of the withdrawal conduit. This data was obtained using 1/16 in. (0.16 cm.) reforming catalyst base material with nitrogen as the pressurised gas. The volume of the sample receiver and tubing below the main valve was about 55 cu. in. (900 cc).

The invention is carried out by producing a sudden but small flow of the gas which fluidises the desired small quantity of catalyst and carries it in an upward direction into a catalyst withdrawal conduit. The catalyst is then transported downward through the withdrawal conduit by the action of gravity and/or the gas. This small gas flow is produced by first sealing the withdrawal conduit to gas flow at a point between the point in the reactor at which the sample is desired, referred to herein as the sampling point, and the sample receiver. The sample receiver is then evacuated, that is, the pressure in the sample receiver is reduced below that in the reactor. Preferably, the pressure differential created in this way is in excess of 20 psig (2.3 atm.). The obstruction in the withdrawal conduit is then rapidly removed. This produces a sharp pulsed flow of a regulated volume of gas into the area of lower pressure, which flow stops in the short time required for the two pressures to equalise. The volume of the gas flow is controlled by the evacuated volume and the pressure differential used.

The method of the present invention has an advantage over the pneumatic systems of the prior art in its ability to automatically regulate the amount of catalyst withdrawn with a good degree of precision. This is an improvement over monitoring the amount withdrawn by such means as a sight glass,

which presents a severe safety hazard due to the pressure and thermal shock to which the glass is subjected. The intrinsic control of the quantity of flowing gas ensures that the system will not remove an excessive amount of catalyst which could fill the withdrawal conduit or lead to loss of the seal at the top of the catalyst bed. The method of the invention also does not require any time measurements to monitor the amount transferred.

The amount of catalyst withdrawn is dependent on two variables, the volume of the receiver and conduits below the main seal valve and the pressure differential between this volume and the reactor. Experimental work has determined that the amount of catalyst withdrawn bears a non-linear relationship to the pressure differential between the reactor and the sample receiver. The amount withdrawn can therefore be adjusted in an installed system of unknown volume by changing the pressure differential. The relationship between a pressure differential and the sample obtained is shown in Figure 3 for one specific set of conditions. The performance of other systems will vary according to the configuration of the withdrawal conduit, type of catalyst sampled, etc. However, the information required to produce a graph similar to Figure 3 may be obtained with only a few test runs. For a newly installed system, the first sampling should be attempted with a low pressure differential of about 20—30 psig (2.3—3.0 atm.) in order to ensure only a small amount is withdrawn. This amount is measured, and if different from the desired amount, Figure 3 may be consulted to estimate the pressure differential required. The size of the sample withdrawn should theoretically also bear a linear relationship to the volume of the evacuated part of the system. Varying the size of the receiver may therefore be used as an alternative to adjusting the pressure differential. The size of the sample receiver should be varied if the optimum pressure differential arrived at is either excessive or so small that minor inaccuracies in pressure measurement produce sizable variances in the amount of catalyst withdrawn.

The system may be applied to either fixed or moving beds of catalyst although normally sampling is done only in vessels containing a fixed bed of catalyst. The invention may be used to sample catalyst in vessels other than a reactor or reaction zone. For instance, it may be used to monitor a treatment process or step, such as halogenation, conducted in a regeneration zone or during ths production of the catalyst.

Those skilled in the art will recognise other applications to which this method is adaptable and will also realise that mechanical systems for carrying out the process may have a different configuration from that described herein. Experiments have proven the method workable with different configurations for the catalyst entrance port and the upper end of the withdrawal conduit. For instance, the end may be bent to curve downward in a manner similar to the top of a cane, or a cone may be spaced slightly above the open end of the conduit. Other usable configurations are shown in U.K. Patent Specification No. 1,296,025. The catalyst entrance port must however face downward to prevent catalyst from falling into the withdrawal conduit between samples. It is preferred that the upper end of the conduit has the same outer diameter as the rest of the conduit to allow its easy insertion into and removal from the vessel. The conduit may be inserted through the unloading nozzle usually provided at the bottom of the reactor, and is adaptable for use with either vertical or inclined nozzles. It is especially preferred that the conduit is constructed as shown in Figure 2. This design satisfies the criterion of holding the dead space in the entrance to the withdrawal conduit to a minimum and thereby ensures a more representative sample.

Since the vessel from which the catalyst is to be removed may be operated at a pressure greatly in excess of atmospheric pressure, the optimum pressure differential may require the sample receiver to also be above atmospheric pressure. The term "evacuating" is therefore used herein in reference to the pressure within the vessel and may require simply bleeding off a portion of the pressurised contents of the receiver or connecting the receiver to a vacuum source. The catalyst should be kept in an inert atmosphere after its removal from the bed. It is therefore preferred that the sample receiver be purged with nitrogen and placed under a positive pressure if possible.

One step in the process of the invention comprises "isolating" the sample receiver. This is intended to mean a sealing off of the receiver and the conduit between it and the main sealing valve from such external connections as purge or vent lines. In other words, when the sample receiver is isolated, there is no avenue by which reactants may escape. This is a significant difference from those sampling methods which fluidise the catalyst by bleeding off a constant or variable stream of gas from the vessel containing the catalyst bed.

A small continuous stream of heated purge gas is preferably passed into the bottom of the withdrawal conduit at a point

just above the main sealing valve. This is to prevent the condensation of hydrocarbons, and the concomitant coke formation, from occurring in the withdrawal conduit. The flow rate of this stream is preferably controlled by a restriction orifice. The purge stream may be shut off during the sampling procedure, but such a small stream is required that it does not interfere with the withdrawal if it is not shut off.

To further illustrate the construction and operation of the invention, a sampler adapted for use on fixed bed radial flow reformers utilising 1/16 in. (0.16 cm.) nominal spherical catalyst will be described. This sampler is constructed substantially as shown in Figures 1 and 2. The withdrawal conduit 5 is formed from a 1 in. (2.5 cm.) schedule 40S pipe which preferably extends upward to a point equidistany the reactor wall and the edge of the centrepipe screen. Samples may of course be obtained with a plurality of samplers to profile catalyst characteristics in the bed. A 1/2 in. (1.3 cm) O.D. (outside diameter) 16 gauge tube is used to form the catalyst inlet tube 6 to the withdrawal conduit 5. It is welded to an opening in the conduit at an angle of 30° from the longitudinal axis of the conduit. The conduit is installed with the opening orientated perpendicular to the reactant flow. The top of the withdrawal conduit is sealed with a 1 in. (2.5 cm.) weld cap 19, and the upper end of the 16 gauge tube is centred within the withdrawal conduit. The withdrawal conduit 5 is sealed by means of a 1½ in. (3.7 cm.) stainless steel ball valve 8 with extended bonnet and metal seats. The sample receiver 13 is a 1½ ft. (45.7 cm.) long section of 2 in. (5.1 cm.) schedule 80 pipe. This arrangement is suitable to deliver a sample of approximately 100 cc. in volume with the correct pressure differential between the reactor and the sample receiver. The sample receiver itself is provided with a gate valve at each end (the upper valve corresponding to valve 15) and a pressure gauge.

The preferred operation of the system comprises first attaching the sample receiver to the withdrawal conduit, purging the receiver with nitrogen and then closing valve 8 and evacuating the receiver to a slight positive pressure (lower than that in the vessel) by means of line 11. The vent line 11 is closed, and the main valve 8 is then quickly opened to allow a quantity of the reactants to rush into the sample receiver and associated lines. This produces a short pulse of gas flow into the withdrawal conduit, which fluidises a quantity of catalyst and transfers this quantity into the withdrawal conduit through the catalyst entrance port and upward extending tube. The catalyst is then carried downward by the gas, or it simply falls through the withdrawal conduit and into the sample receiver. The main valve 8 is then closed and the vent line 11 is opened. The vent line is kept open and the second valve 15 just above the sample receiver is closed as a safety precaution. This forces any leakage through the main valve to be vented rather than contact the person removing the sample receiver. The receiver is allowed to cool and is the removed from the withdrawal conduit. At this point, the receiver is depressurised and may be purged with nitrogen if desirable.

WHAT WE CLAIM IS:—

1. A method of transferring a catalyst sample from a sampling point within a vessel containing a bed of catalyst into a withdrawal conduit having a downwardly facing catalyst entrance port and of transferring the catalyst sample along the conduit into a sample receiver located outside of the vessel at the end of the conduit, which method comprises the steps of: (a) sealing the withdrawal conduit to gas flow at a point intermediate the sampling point and the sample receiver; (b) evacuating the sample receiver and creating a pressure therein lower than that maintained in the vessel; and (c) rapidly unsealing the withdrawal conduit, which causes a short and rapid gas flow to pass through the withdrawal conduit to equalise the pressures within the vessel and the sample receiver, and which thus effects a fluidisation of catalyst into the downwardly facing entrance port of the withdrawal conduit and the transfer of catalyst through the withdrawal conduit to the sample receiver.

2. The method of Claim 1 wherein the pressure within the sample receiver is lowered to a subatmospheric pressure in step (b).

3. The method of Claim 2 wherein a portion of the withdrawal conduit is evacuated in step (b) in addition to the sample receiver.

4. The method of any of Claims 1 to 3

wherein the pressure difference set up in step (b) is in excess of 20 psig.

5. A method of transferring a catalyst sample carried out substantially as hereinbefore described with reference to Figure 1 or Figures 1 and 2 of the accompanying drawings.

J. Y. & G. W. JOHNSON,
Furnival House,
14—18 High Holborn,
London WC1V 6DE.
Chartered Patent Agents,
Agents for the Applicants.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1978
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

* C L M S *