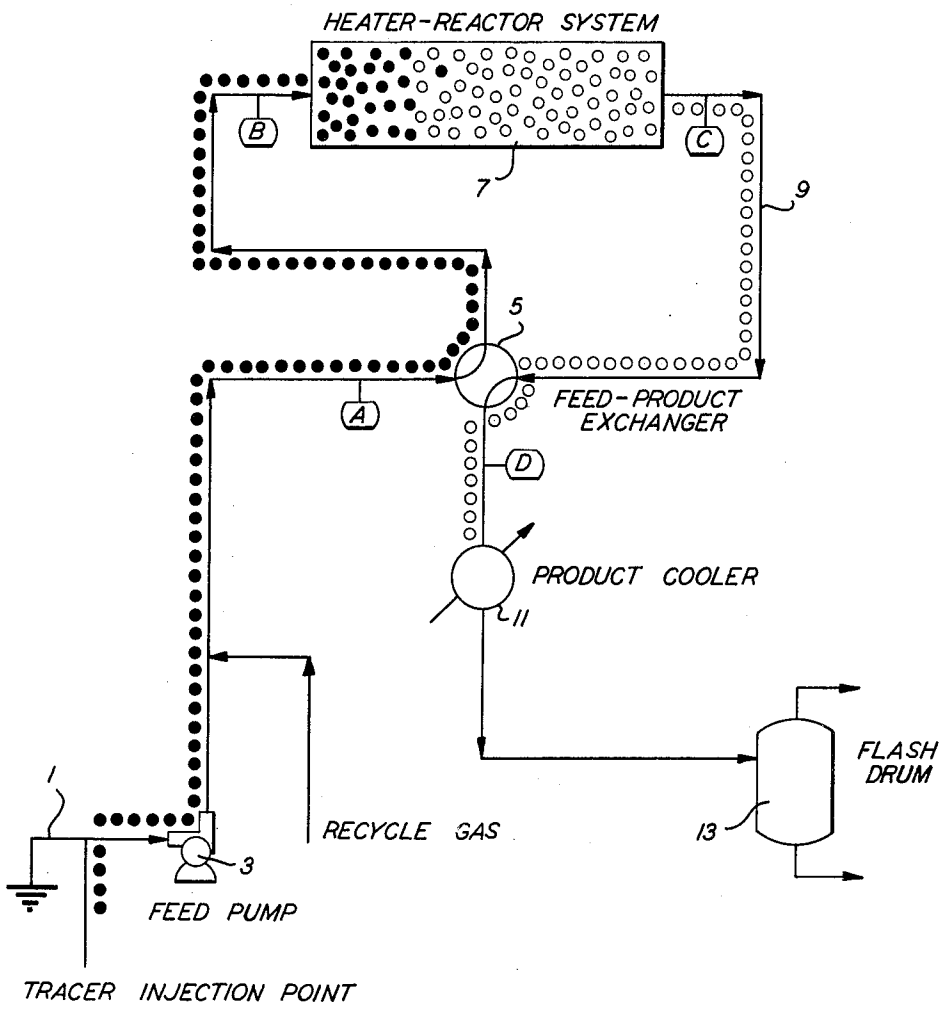
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DETECTION OF HEAT EXCHANGER LEAKS

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Fig. 1.



INVENTORS.
JAY S. CURTICE
ADOLPH I. SNOW
LLOYD A. BAILLIE

BY Adams Forward & McLean

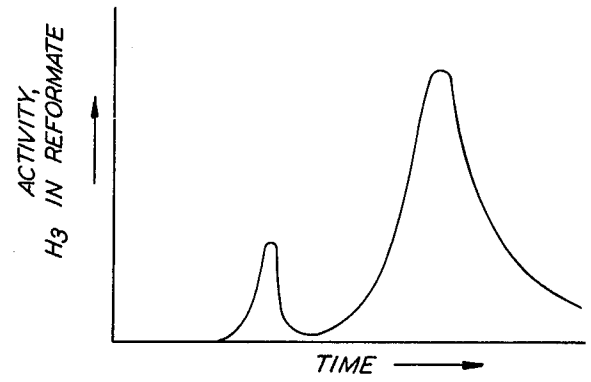
ATTORNEYS

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Fig. 2.



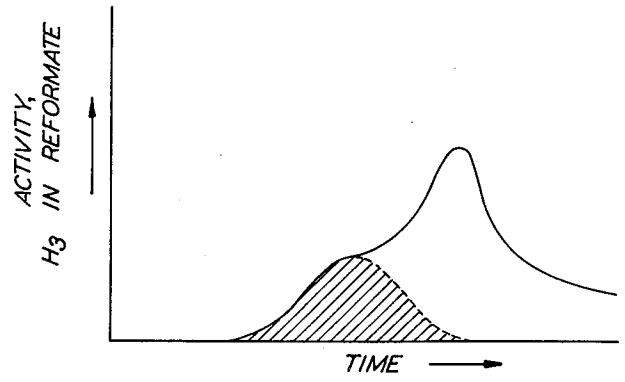


Fig. 3.

INVENTORS.
JAY S. CURTICE
ADOLPH L. SNOW
LLOYD A. BAILLIE

BY Adams Forward & McLean

ATTORNEYS

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DETECTION OF HEAT EXCHANGER LEAKS

Jay S. Curtice, Chicago, Adolph I. Snow, Matteson, and Lloyd A. Baillie, Park Forest, Ill., assignors, by mesne assignments, to Sinclair Research, Inc., New York, N.Y., a corporation of Delaware

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This invention relates to a method for detecting and, if desired measuring, leaks in process equipment such as feed-effluent heat exchangers.

Feed-product heat exchangers are commonly employed in petroleum refining processes as, for example, in reforming, cracking, hydrogenation or other refining methods employing elevated temperatures, i.e. generally from about 200 to 1000° F., usually more than about 500° F. In these processes the feed and effluent product enter a heat exchanger wherein they are kept separate so as to prevent commingling of the feed with the product. In the heat exchanger, the feed material by indirect heat exchange absorbs part of the heat energy contained in the effluent product. It is not uncommon in such systems to have a leak develop in the means separating the feed from the product in the heat exchanger, i.e. generally a metallic means such as plates, tubes, coils, etc. which leak, in addition to creating feed and/or product loss or misdirection, often necessitates an interruption of the operation for repairs.

We have now found that leaks in feed-effluent heat exchangers can be positively detected and measured by the method of this invention. The present invention comprises injecting a suitable radioactive tracer compound into a feed-stock and taking a sample of the reaction product effluent which has left the heat exchanger. The radioactive tracer compound must be one which is chemically converted by the action of the reaction or reactors provided in the flow system between the respective feed and effluent sides of a feed-effluent heat exchanger, to tracer-labelled products which can be separated from any original unconverted tracer bypassing the reactor through an exchanger leak. Thus, detection of unconverted radioactive tracer in the product effluent leaving the heat exchanger means that there must be a leak in the feed-effluent heat exchanger, allowing feed material to flow into the effluent stream without entering the reactor or reactors. It is to be understood that the method of the present invention is applicable to any process where a feed-effluent heat exchanger is employed as, for example, in reforming, catalytic or thermal cracking, hydrogenation, desulfurization processes or other refining or petrochemical processes.

It is evident, therefore, that the radioactive tracer of the present invention is of the type that is converted under reactor conditions. It is also important that the radioactive tracer be relatively thermally stable, and relatively non-active with exchanger surfaces under the heat exchanger conditions of elevated temperature such as about 200° to 1000° F., preferably above 500° F. The ideal case is where you get essentially no conversion of the radioactive tracer in the heat exchanger and substantially complete conversion in the reactor. In actual operation, the ideal case is difficult to achieve. Practically speaking, therefore, generally at least about 50% of the radioactive tracer should be unconverted in the heat exchanger, preferably about at least about 90% unconverted, and at least about 90% of the tracer should be converted in the reactor, preferably at least about 99%. Where there is, for instance, unconverted tracer material present in the stream passing to the product side of the heat exchanger, the leak can be shown by the change in the

amount of this tracer component in the product upon passing through the heat exchanger, i.e. due to the leak more unconverted tracer material is in the product from the heat exchanger than was in the product passing to the heat exchanger.

A particularly suitable radioactive tracer in octane-enhancing naphtha reforming systems is tritiated anisole, such as 4-H^3-anisole or 1-methoxy-4-H^3-benzene. Tritiated anisole can easily be prepared by the hydrolysis of p-anisylmagnesium bromide with high specific activity tritium water. This tracer compound has been found to be essentially completely converted under the reaction conditions used for example in typical platinum-alumina catalyst reforming operations and does not decompose significantly in the heat exchangers employed in such systems. The products of conversion can be separated from any leaked anisole by any suitable separation method such as chromatography. Another suitable tracer in reforming systems is radio-labeled ethyl cyclohexane which during the reforming operation is converted to ethyl benzene and other materials readily separable, e.g. by distillation, from any tagged ethylcyclohexane in the product as the result of a heat exchanger leak. Examples of other tracers that may be employed, for instance, in desulfurization and hydrogenation systems are radioactive olefins. During hydrogenation or desulfurization the olefins are converted to paraffins, thus detection of labelled olefin in a product leaving the heat exchanger indicates a leak. Any means known to the art may be employed to separate the converted from the unconverted tracer as, for instance, by chromatography, chemical separation methods or distillation.

Although reactor conditions may vary depending on the system or process employed they must be such, as aforementioned, as to convert the tracer utilized. The reaction temperatures may be up to about 1000° F. or more, usually more than about 600° F. Catalyzed reaction systems may convert the tracer even at temperatures lower than 600° F. By way of illustration, in reforming the reactor conditions generally fall within the followng ranges: temperatures, between about 850 to 975° F.; pressures, between about 100 to 1000 p.s.i.g.; weight hourly space velocity, about 1 to 8; hydrogen recycle, about 500 to 5000 standard cubic feet per barrel of feed. Preheaters are often used in reforming systems before each reactor to provide the reactor or reactors with hydrocarbon of temperatures that may vary between about 850° F. to 975° F. Desulfurization and hydrogenation operations generally employ the following conditions: temperatures, between about 500 to 800° F.; pressure, about 200 to 800 p.s.i.g. and the reaction is carried out in the presence of a suitable catalyst. The conversion zone in the above processes as well as other processes can constitute a single reactor or multiple reactors. The invention will be best understood by the following examples with reference to the accompanying drawing (FIG. 1).

FIGURE 1 is a fluid circuit diagram of a feed-effluent heat exchanger system in accordance with the present invention.

FIGURES 2 and 3 are graphs representing tracer activity-time patterns in accordance with the invention.

Example I

About one-half curie of tritiated anisole is dissolved in 100 ml. of straight-run naphtha (reformer feed) and injected at a suitable point in the feed line 1, as for example, the feed pump inlet line. The amount of tracer used depends on the volume of the system involved.

Any injection system known to be suitable for radioactive tracer injection can be employed. A particularly

suitable injector system is a 1" I.D. steel bomb about 12" long (in which the radioactive anisole tracer is placed) which is fitted with valves at either end. The bomb is connected to the injection point on the feedline 1 by ½" tubing and at the other end similarly connected to the bottom of a 5–10 liter blowcase, over half full of reformer feed and pressured to about 100 p.s.i. over the pressure at the injection point. From this system the tracer is injected to the feed line as follows:

The valve at the top end of the steel bomb is opened full and the valve at the bottom end is carefully but quickly opened to the point that the rate of delivery of liquid from the blowcase is 2 to 4 gallons per minute in a 16,000 bbl./day reforming unit. The injection should be allowed to continue for 30 to 60 seconds to insure that all of the tracer is washed from the bomb into the injection point. The feed, together with the tracer is pumped via pump 3 into heat exchanger 5. The feed is there heated by indirect heat exchange with the final reactor effluent to a temperature of about 500 to 900° F. and passed to the heater-reactor system 7. The heater-reactor system 7 comprises multiple adiabatic platinum-alumina catalyst bed conversion zones each equipped with a preheater. The preheaters are employed to provide each of the several reactors with inlet temperatures that may vary between about 850° F. to 975° F. The pressure employed in the reactors can vary between about 100 to 1000 p.s.i.g., preferably about 300 to 500 p.s.i.g. An exemplary WHSV is 2 while the H_2 to hydrocarbon mole ratio is about 7 to 1. Under these reformer conditions, tritiated anisole is substantially completely converted to other materials which are easily separable from anisole. The effluent from the heater-reactor system 7 is passed via line 9 back to the heat exchanger 5, through product cooler 11 and on to flash drum 13 for separating recycle gas from liquid gasoline product.

Liquid samples are taken at points A, B, C and D shown in the drawing through sampling lines. Sampling of the liquid product at points C and D is preferably started shortly before the tracer is injected and continued periodically at the rate of one sample per minute for twenty minutes. At lower or higher linear flow rates proportionately lower or higher frequency of sampling can be used. It is preferred that the flow rate through the sampling line be considerably faster than 100 ml./minute to "turn over" the contents of the sampling line as rapidly as possible. Under these flow rates, only 100 ml. of each sample is required. Estimates of residence times for material passing through the unit will be of great help in fixing a specific sampling schedule. One procedure consists of estimating residence times for the extreme cases of "all liquid" flow and "all vapor" flow, and arranging a sampling schedule adequately covering both cases. Samples at points A and B should be taken more frequently, and need not be continued as long as samples from C and D. After the twenty-minute sampling period is over, several more samples should be taken at each point, at intervals increasing with time.

The samples taken at points A, B and C afford the self-checking data necessary for an unambiguous test. Point A samples show the activity-time relationship of the tracer entering the heat exchanger system and they serve as a base point for comparison. If the distance from the injection point to the heat exchanger is sufficiently short, and if no excessive hold up or large inventory exists between the injection point and the inlet of the exchangers, sample point A may be safely omitted. Samples at point B can be used to establish with certainty that the unconverted tracer does survive the heat exchangers, or to measure the extent of any heat induced decomposition. Samples at point C can be used to establish that the tracer has been completely converted or to determine the extent of conversion of the tracer compound in the catalytic reactors. If unconverted tagged anisole appears in the product, i.e. the sample taken at point D, and none appears at point C, a leak is present. If labelled anisole appears at point C, the leak must be calculated from the difference in labelled anisole content of samples from point C and point D.

Samples B, C and D are analyzed by separating the unconverted tracer, if present, from the converted tracer and measuring the radioactivity of each by any known standard method as, for example, by use of a scintillation counter, Geiger counter, etc. The separation step is of course, unnecessary with respect to sample point A, if taken. Any method known to the art can be employed to separate the converted from the unconverted tagged anisole as for instance, by chromatography. A particularly suitable method is by elution chromatographic analysis over activated alumina. Accordingly, by this method a 5 ml. sample of reformate, for example, is dissolved in 200 ml. of n-pentane and introduced into a pentane-soaked alumina column 30 cm. long by 1.75 cm. diameter. Further elutions are made with 300 ml. n-pentane and 200 ml. of toluene. The fractions are counted on the radioactivity counter, corrected for efficiency of counting, and the anisole (unconverted) activity of the reformate sample calculated as dpm i.e. disintegrations per minute (anisole) per dpm (total activity in the sample).

Analysis of samples taken at point D will generally result in two types of activity-time patterns. These are sketched in FIGURES 2 and 3. In the FIGURE 2 case, the tracer proceeding through the leak will appear only in the earlier samples, well separated from the wave of tracer activity from material going through the reactors. The first or "leak" peak will consist only of tritiated anisole, and the second "main" peak will contain virtually no tritium as anisole. The problem of analysis is quite simple in this case. The relative amounts of unchanged tracer and tritium in other forms can be used to calculate the amount of leak.

In the FIGURE 3 case, the unchanged tracer following the leak flow path has been delayed sufficiently that it overlaps with the main wave of activity returning from the reactors, which is often the case in actual commercial operations. Here it will be necessary to analyze several samples, or a suitable blend of samples, into their anisole and non-anisole components. Chromatography over activated alumina provides a rapid and convenient method for such an analysis. The size of the leak can be calculated by comparing the anisole activity in the effluent with the total tritium activity injected. This method, however, appears to be subject to some error. It has been found that a much more reliable figure is obtained where the "relative method" is employed. In the "relative method" the anisole activity is compared with the total activity in the recovered liquid product to give a quantitative figure for the percent leak.

Example II

About one-half curie of tritiated ethylcyclohexane is dissolved in 100 ml. of straight run naphtha (reformer feed) and injected into feed line 1 as in Example I. The feed together with the tagged or labelled ethylcyclohexane is pumped into heat exchanger 5 and then into the heater reactor system 7. Under the reformer conditions the tagged ethylcyclohexane is converted to ethyl benzene and other materials which can be separated by distillation from the ethylcyclohexane. The effluent product is then passed from the heater-reactor system 7 to the heater exchanger 5. Any tagged ethyl cyclohexane which leaks from the feed to the product side of the heat-exchangers does not pass through the reactors and consequently will not be converted. 100 ml. samples are taken at points C and D. If tagged ethylcyclohexane appears at D and none at C, a leak is present.

Samples C and D are analyzed by separating the unconverted tracer from the ethylbenzene and other materials by distillation and measuring the radioactivity, for instance, by use of a scintillation counter. In the activity-

time pattern of analyzed samples taken at D, the leaked material will show up as a first or "leak" peak. The tagged material causing this leak will have a boiling point near the boiling point of ethylcyclohexane. Since this material does not appear in samples taken before the heat exchangers, i.e. point C, but is apparent in samples obtained after the heat exchangers, the source of this ethylcyclohexane is a leak in the heat exchangers. The extent of the leak can be determined as in Example I.

Example III

About one-half curie of tritiated hexene-1 is dissolved in 100 ml. of a 950° F. minus liquid fraction derived from hydrocracking of a Mid-Continent residual oil and injected into the feedline of a hydrodesulfurization unit. The feed together with the tagged hexene-1 is pumped through the heat exchanger provided the unit and then into the hydrodesulfurization zone. The hydrodesulfurization reaction conditions are as follows: temperature, about 650° F.; pressure, about 250 to 300 p.s.i.g.; weight hourly velocity, 5; hydrogen to hydrocarbon mole ratio, about 1000 standard cubic feet per barrel of feed. A suitable catalyst such as cobalt-molybdena-alumina is employed in the desulfurization zone. Under these conditions the tagged hexene-1 will be converted to tagged hexanes and other materials in the reaction zone. Any hexene-1 leaking from the feed to the product side of the heat exchanger will not be converted. The desulfurized product is then passed back through the heat exchanger. 100 ml. samples are taken both after the reactor but before the heat exchanger and after the heat exchanger. If the sample taken after the reactor but before the heat exchanger contains no tritrated hexene-1 but the sample taken after the heat exchangers contains hexene-1, a leak is present in the heat exchanger. The samples are analyzed by separating the hexene-1 from the paraffins, for instance, by chromatography and measuring the radioactivity by use of a suitable counter. The extent of the leak can be determined as in Example I.

It is claimed:

1. A method for detecting leaks in feed-effluent heat exchangers of a chemical reactor system which comprises injecting into a chemical feedstock a radioactive tracer capable of being at least about 90% chemically converted under reactor conditions but at least about 50% chemically unconverted under heat exchanger conditions, passing said feedstock together with the tracer through successively the feed side of the feed-effluent heat exchanger, reactor, and the effluent side of said heat exchanger, taking a sample of said effluent, separating from said sample converted tracer, and detecting the radioactivity of the remaining sample.

2. A method for detecting leaks in feed-effluent heat exchangers of a naphtha reforming system which comprises injecting into the reformer feedstock a radioactive tracer capable of being at least about 99% chemically converted under reforming conditions but at least about 90% chemically unconverted under heat exchanger conditions, passing said feedstock together with the tracer through successively the feed side of a feed-effluent heat exchanger, and a reactor containing reforming catalyst and operating at a temperature of about 850 to 975° F. and a pressure of about 100–1000 p.s.i.g., to produce higher octane reformate, passing the reformate back through the effluent side of said heat exchanger, taking a sample of said reformate, measuring its radioactive content, separating from said sample converted tracer and measuring the radioactive content of the remaining sample.

3. The method of claim 2 wherein the tracer is tritiated anisole.

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