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(54) HIGH THROUGHPUT DEVELOPMENT METHOD FOR CATALYTIC HYDROPROCESSING OF DIRTY FEEDSTOCKS

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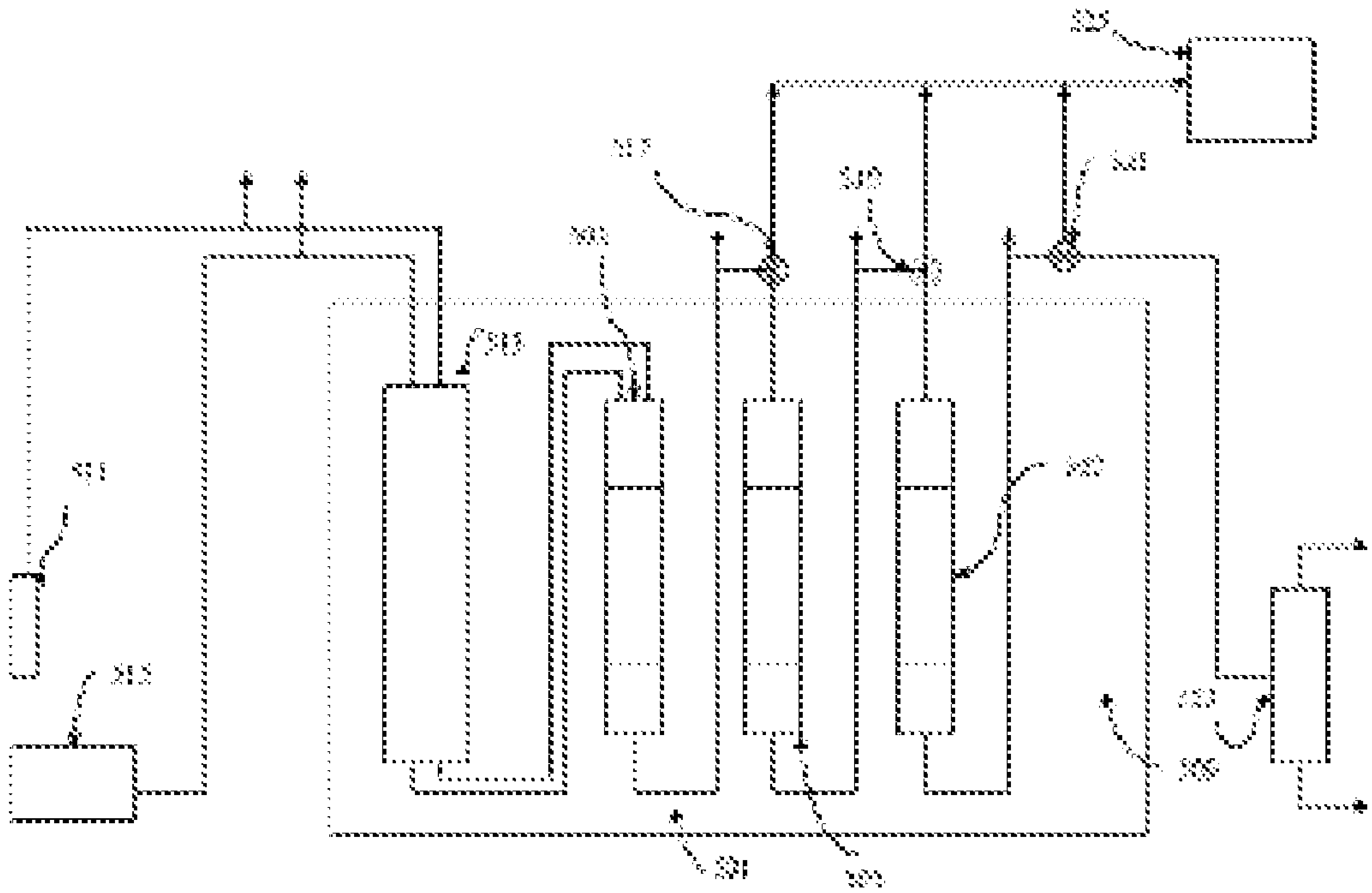
(57) ABSTRACT

A method for determining a set of operating parameters for a commercial scale plug flow catalytic process and reactor system for hydroprocessing dirty feedstocks, comprises the steps of: feeding selected partial pressures of said feedstock and hydrogen to the inlet the first reactor stage of a first composite multi-stage series-connected laboratory scale plug flow reactor including at least three reactor stages, the catalyst beds of each of said reactor stages including catalyst particles capable of catalyzing the removal by hydrogen of heteroatoms from said heterocyclic molecules; sampling the effluents of each of said reactor stages; measuring the concentration of heterocyclic molecules in said dirty feedstock in the concentrations of heterocyclic molecules and intermediate and final products and by products of the catalytic reaction in the effluents of each of said reactor stages.



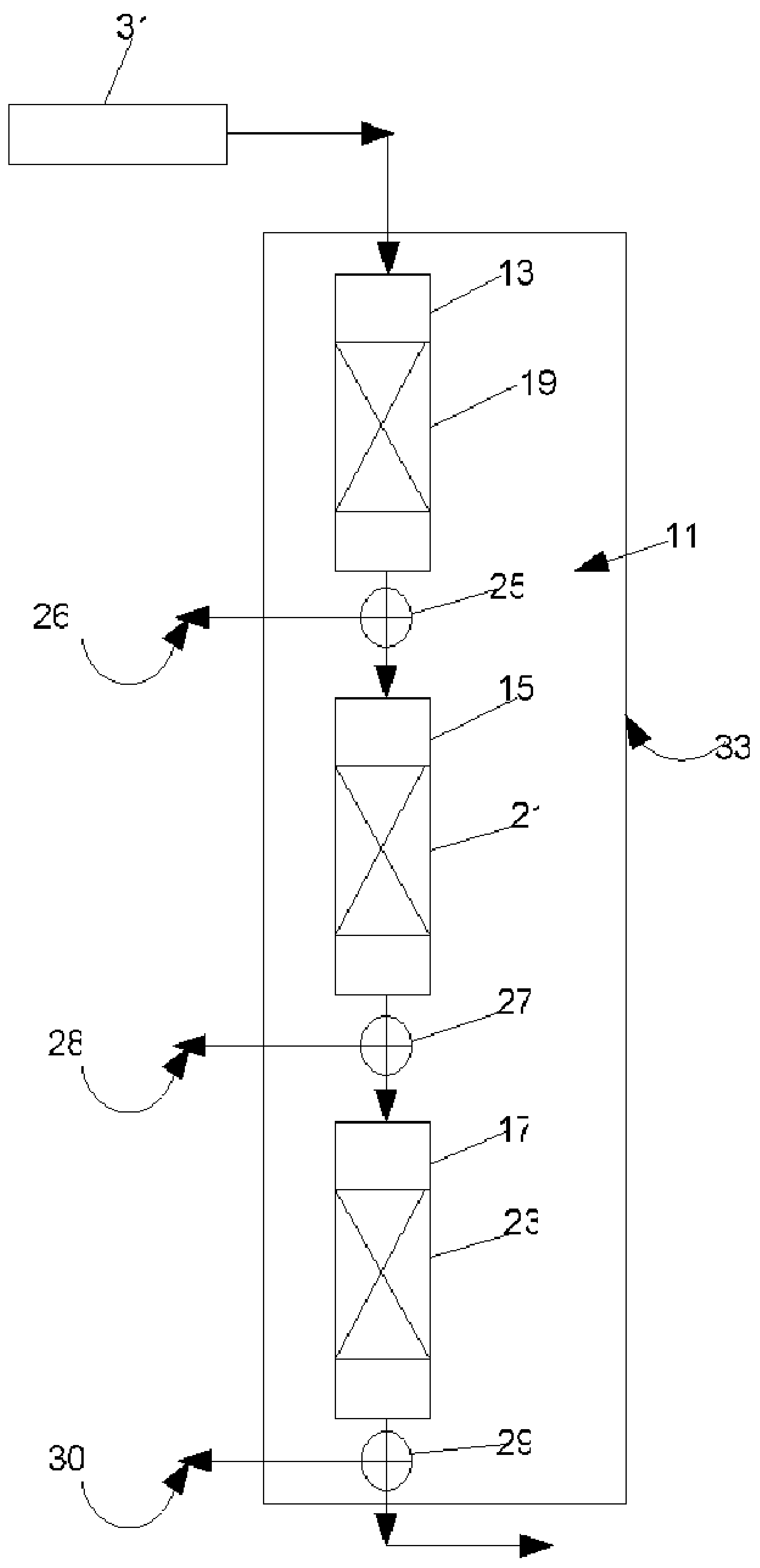


Figure 1

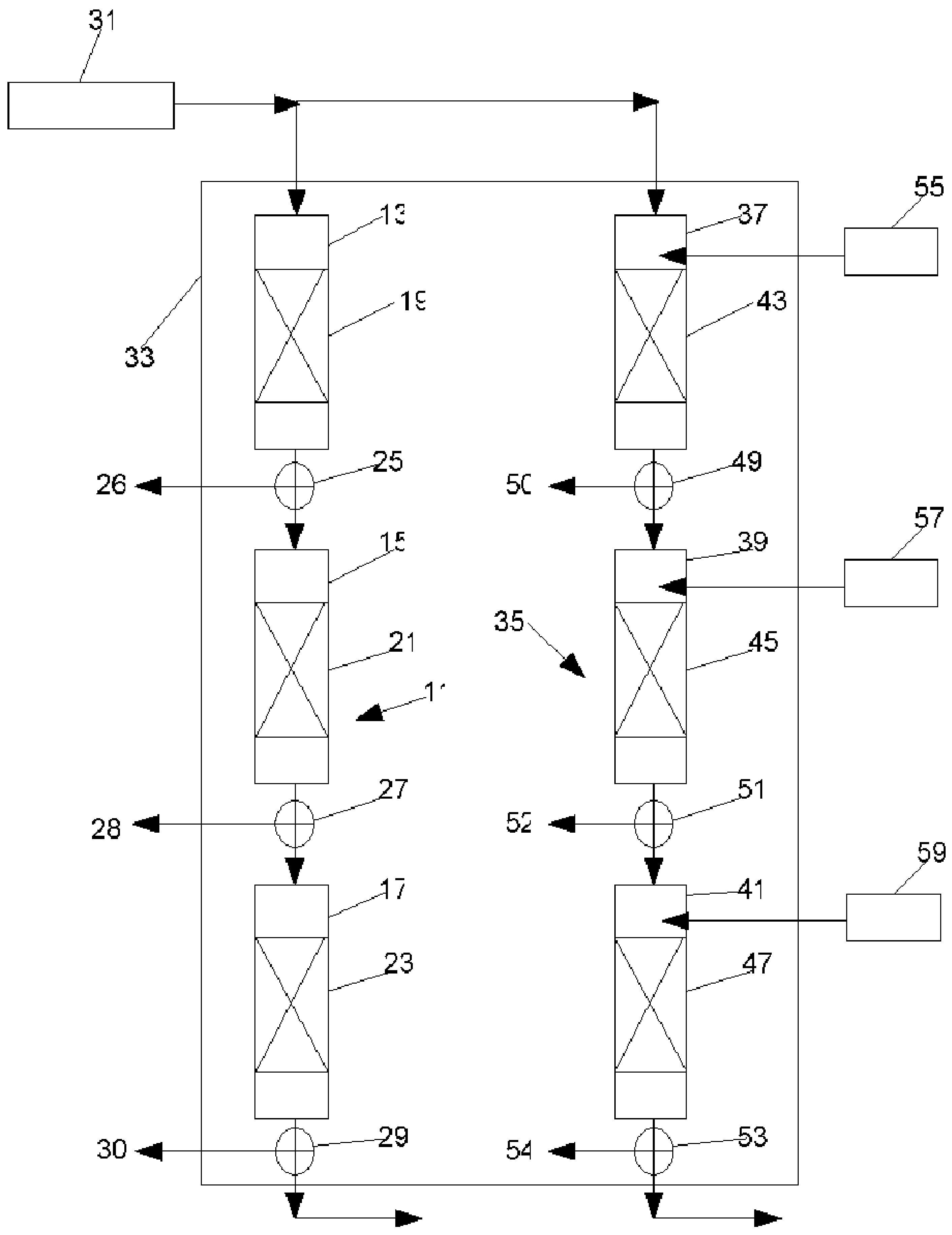


Figure 2

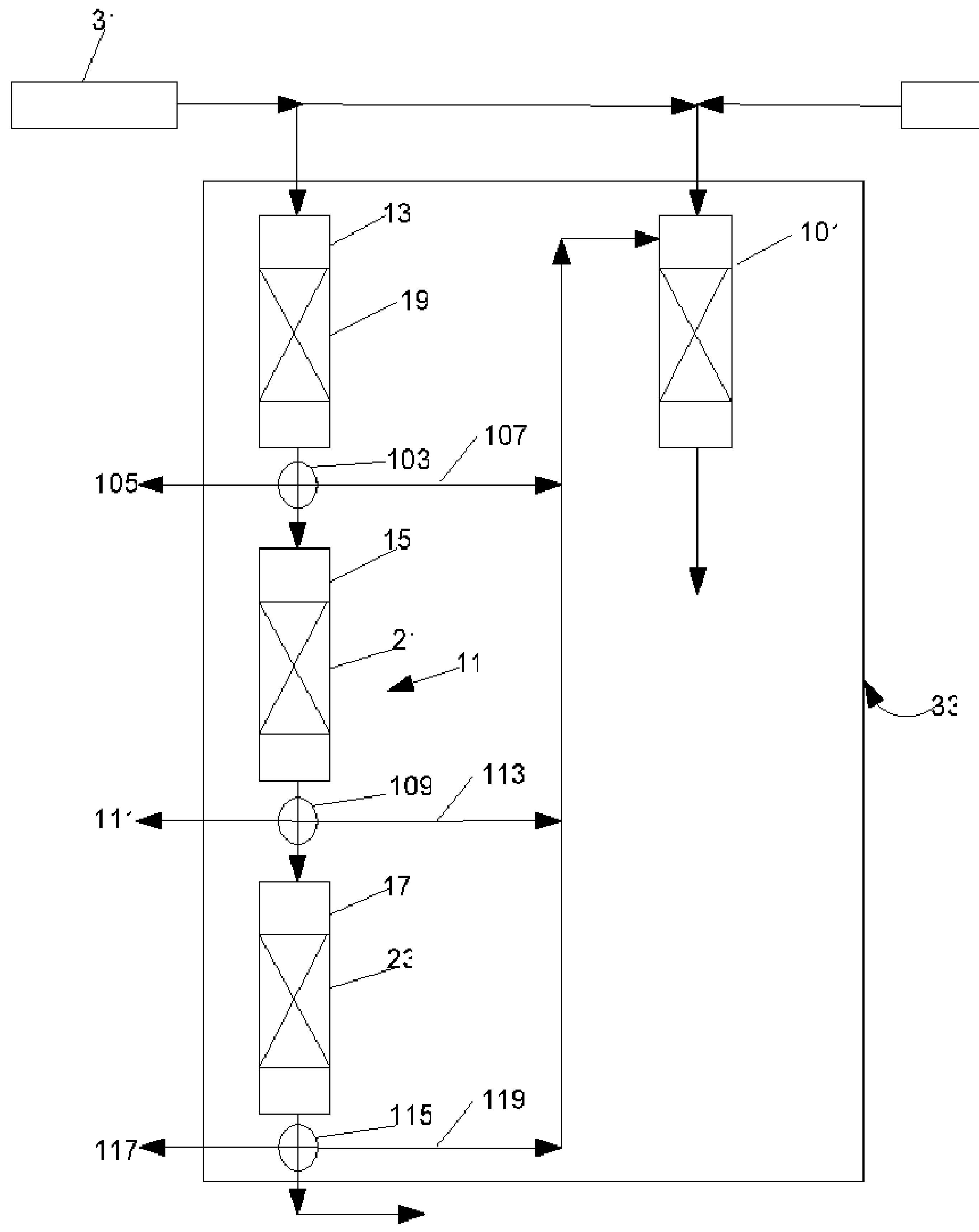
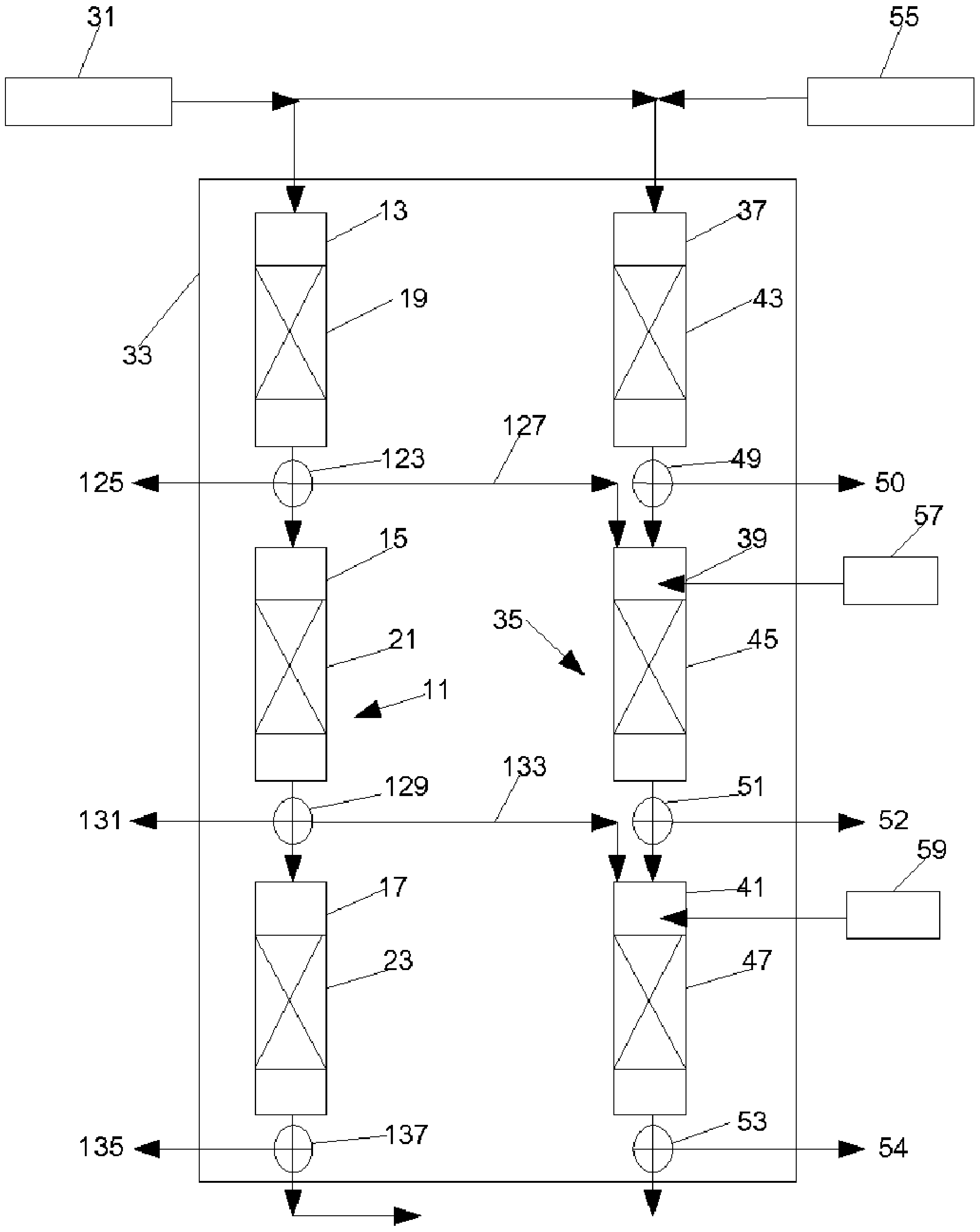


Figure 3



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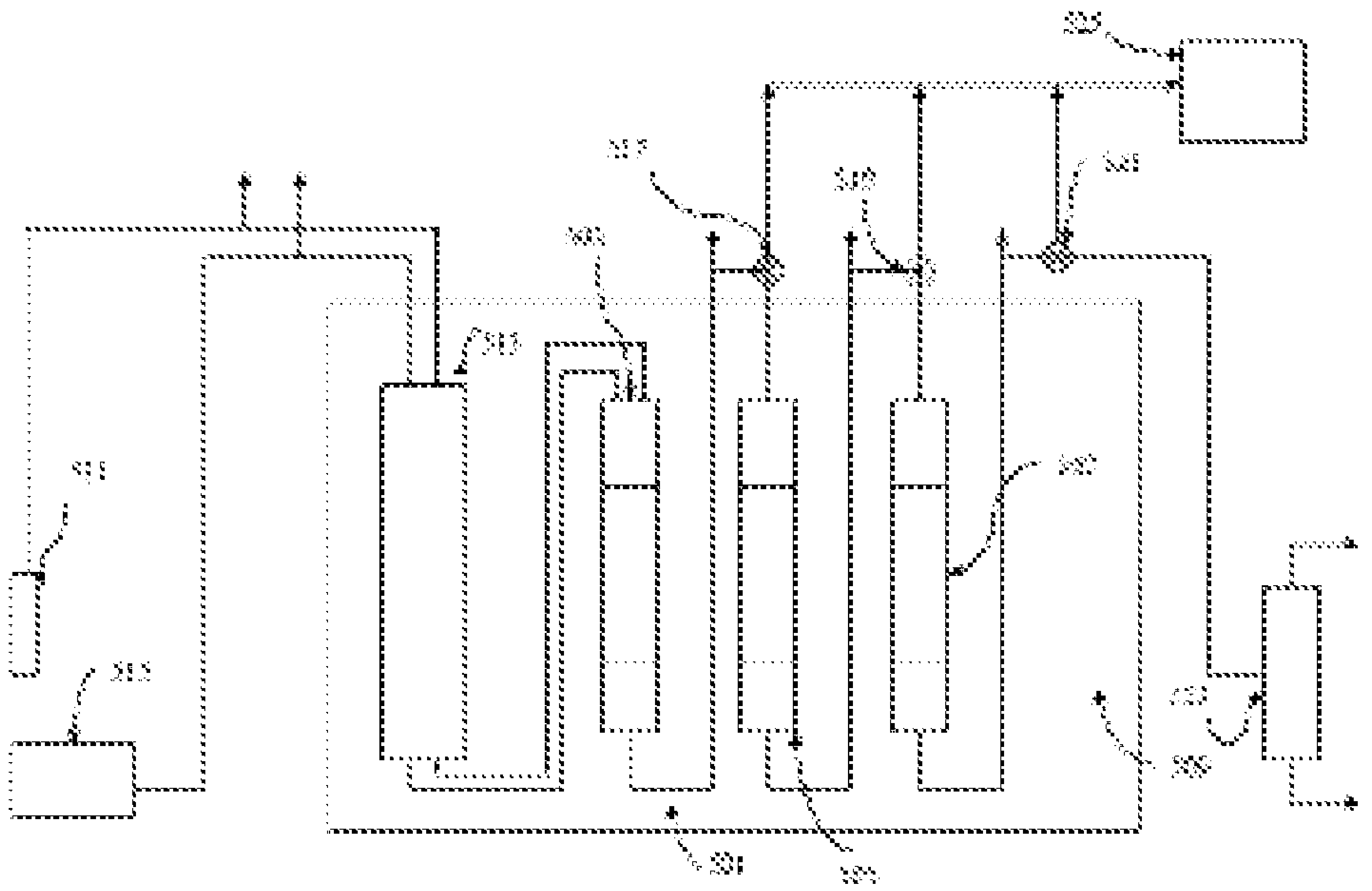

Figure 5

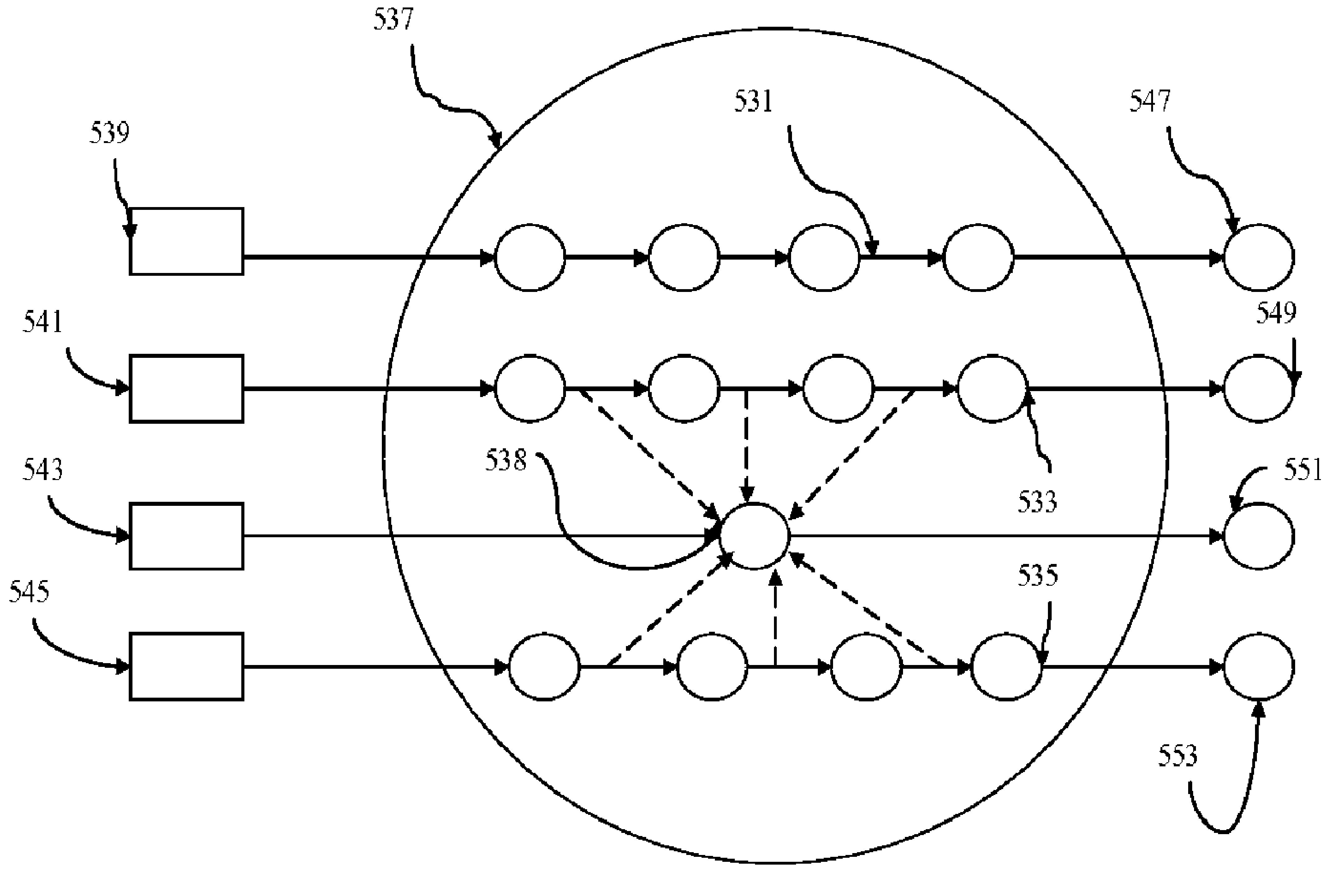

Figure 6

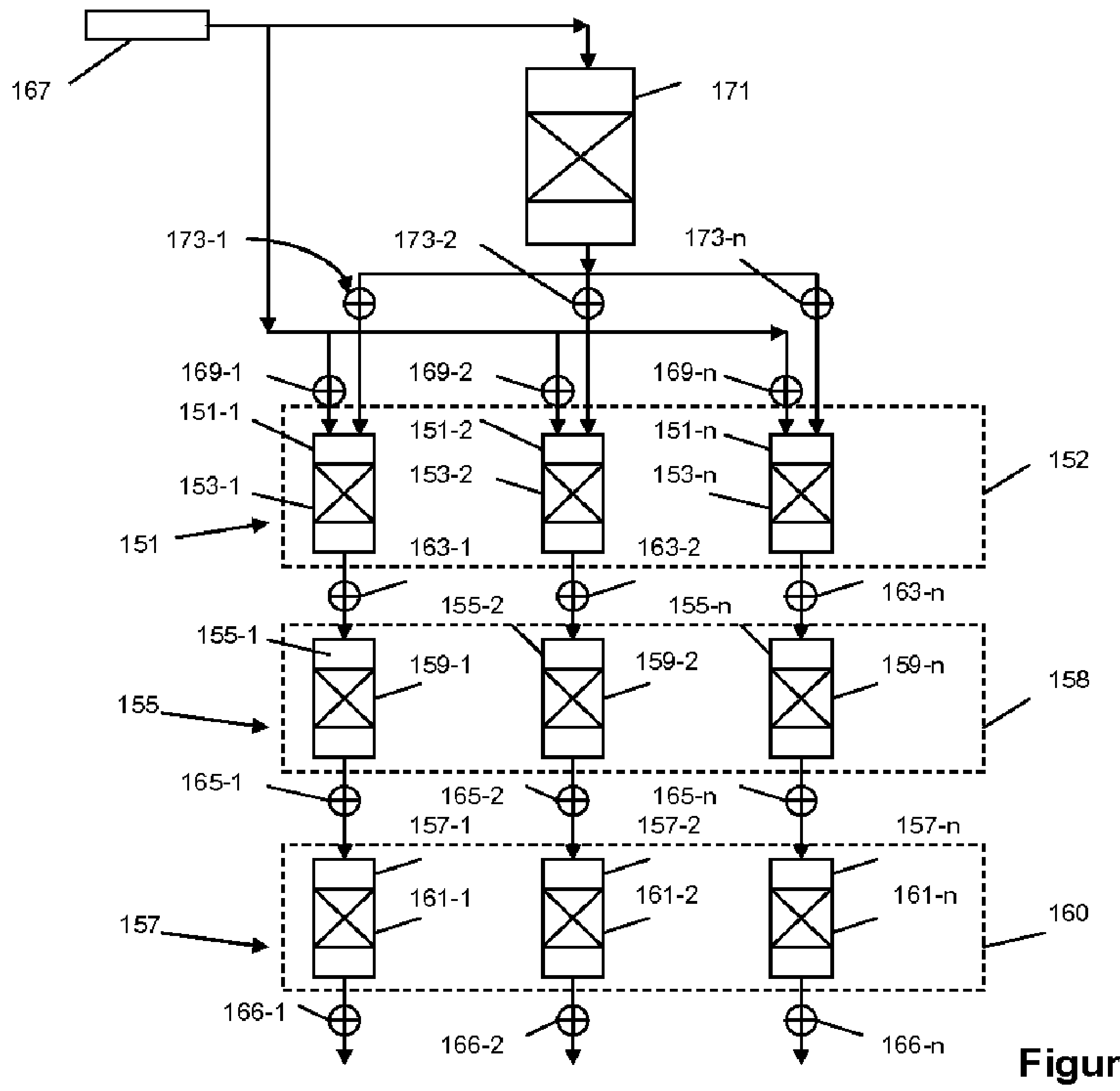

Figure 7

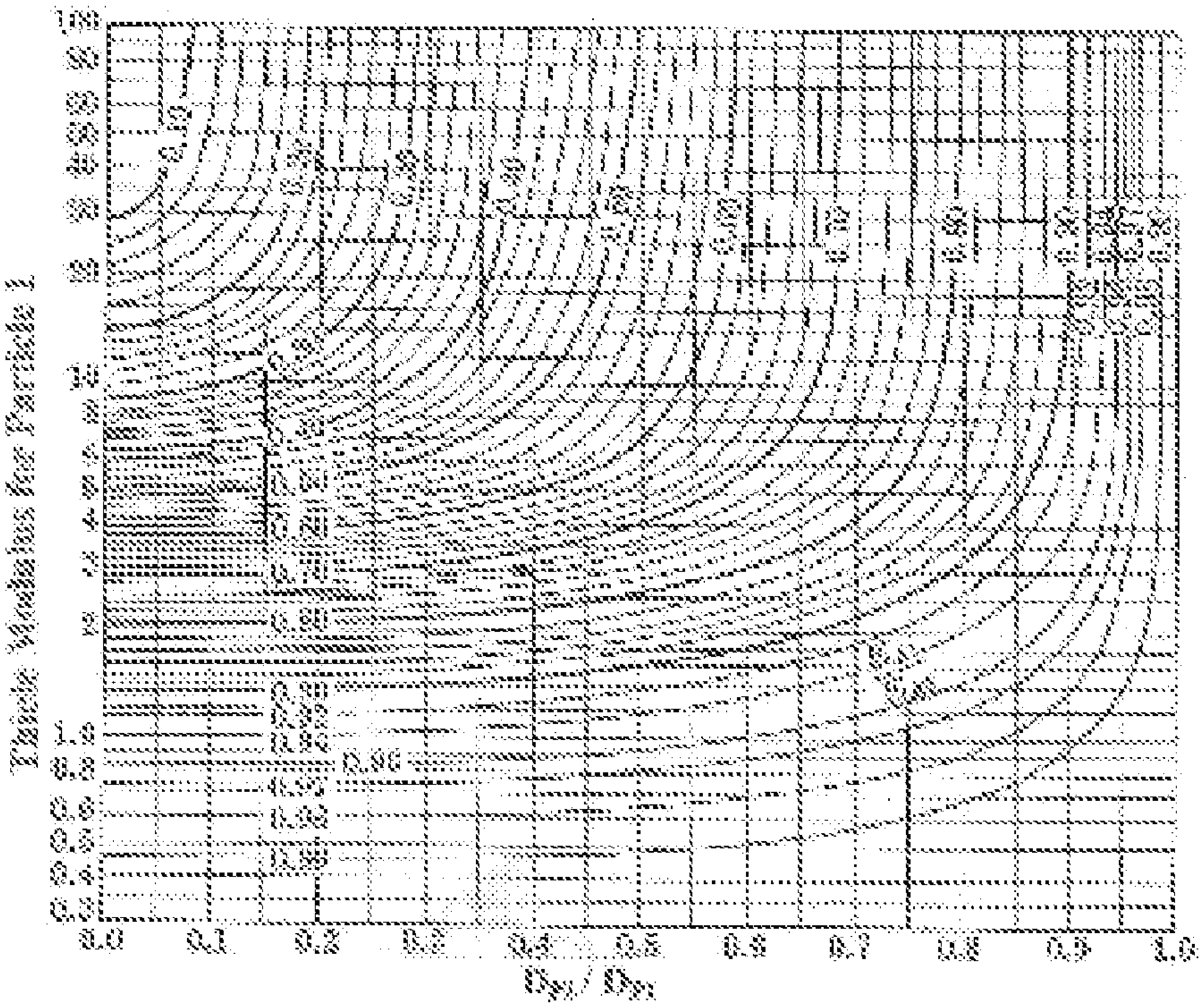

Figure 8

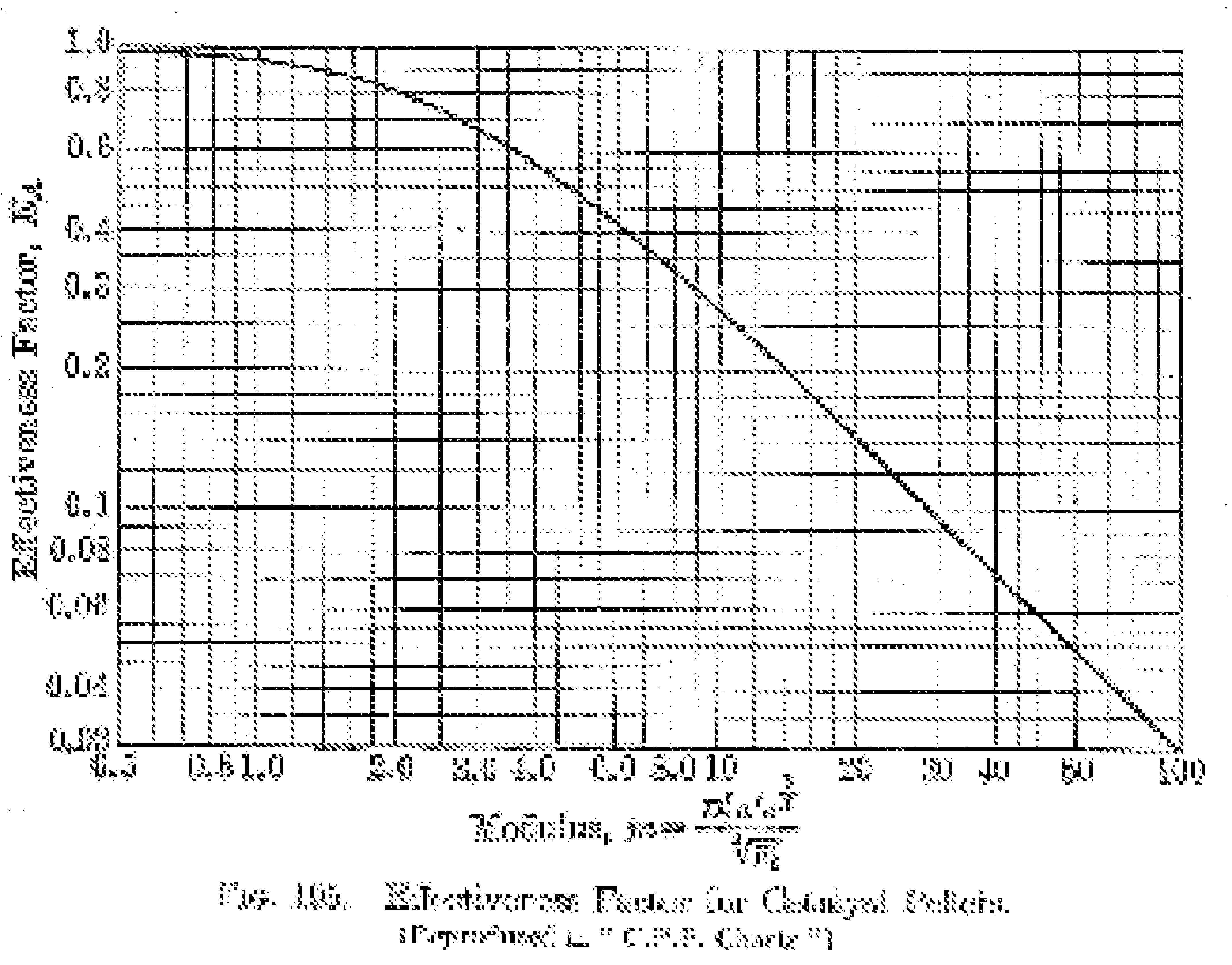

Figure 9

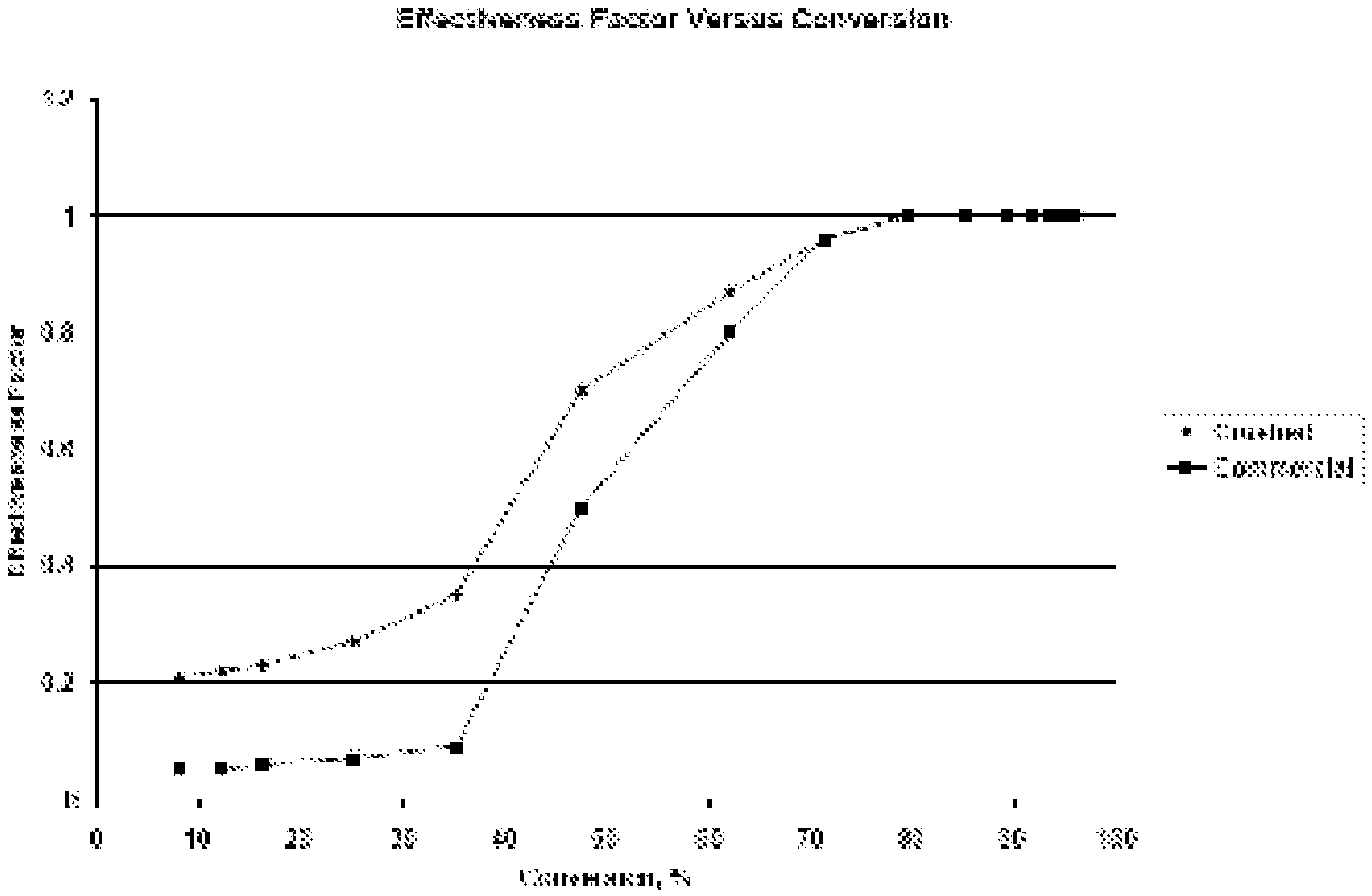

Figure 10

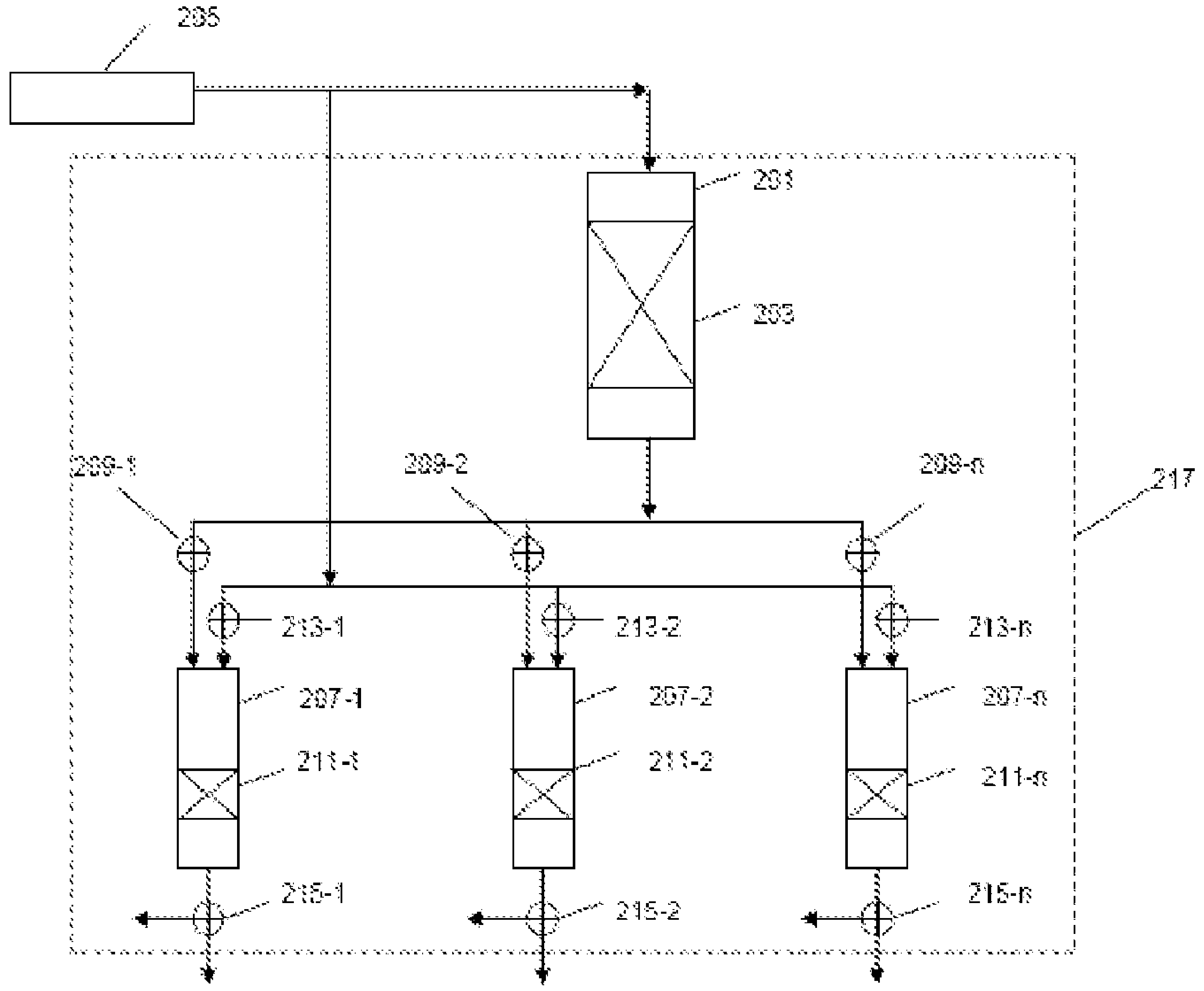

Figure 11

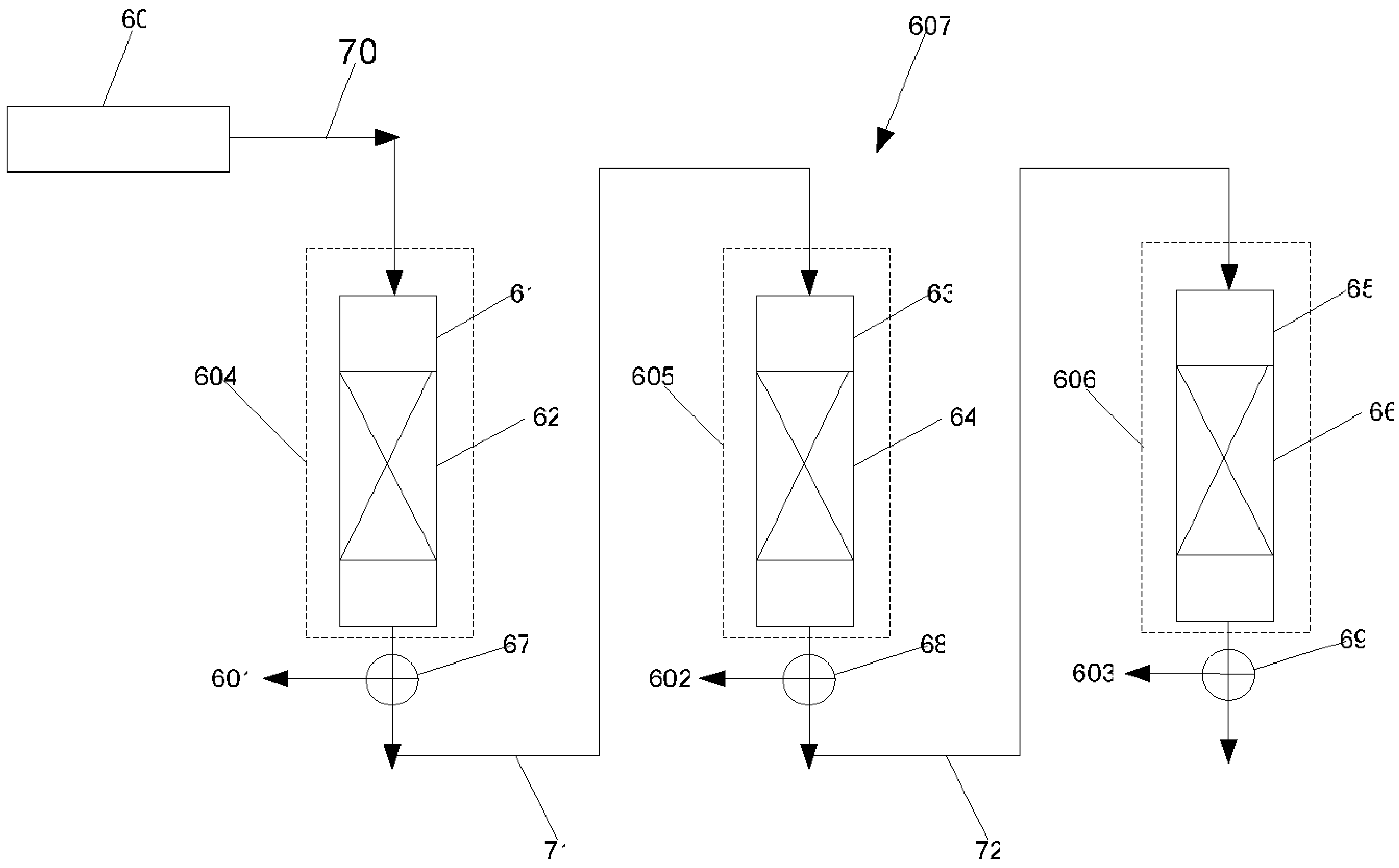

Figure 12

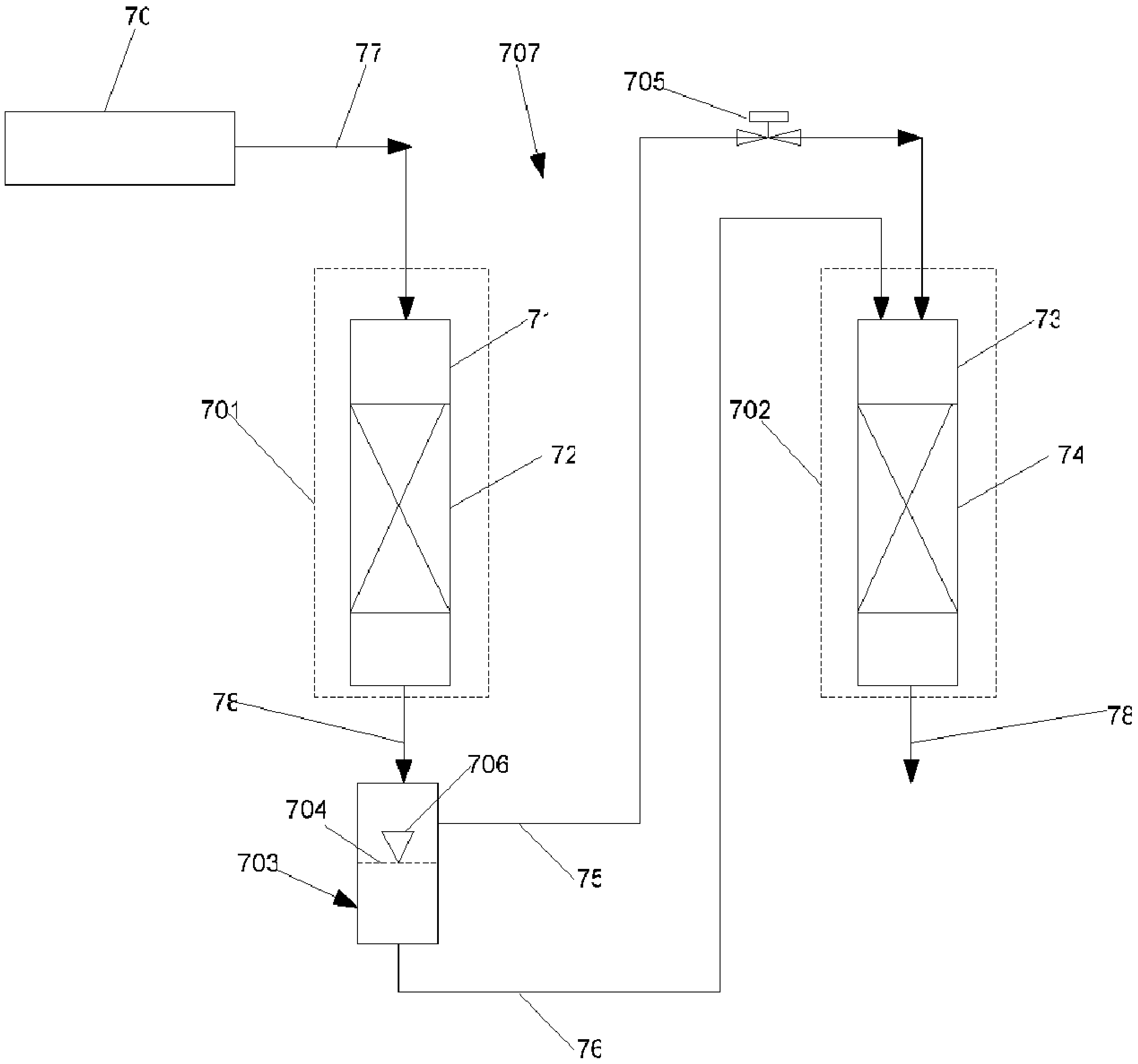

Figure 13

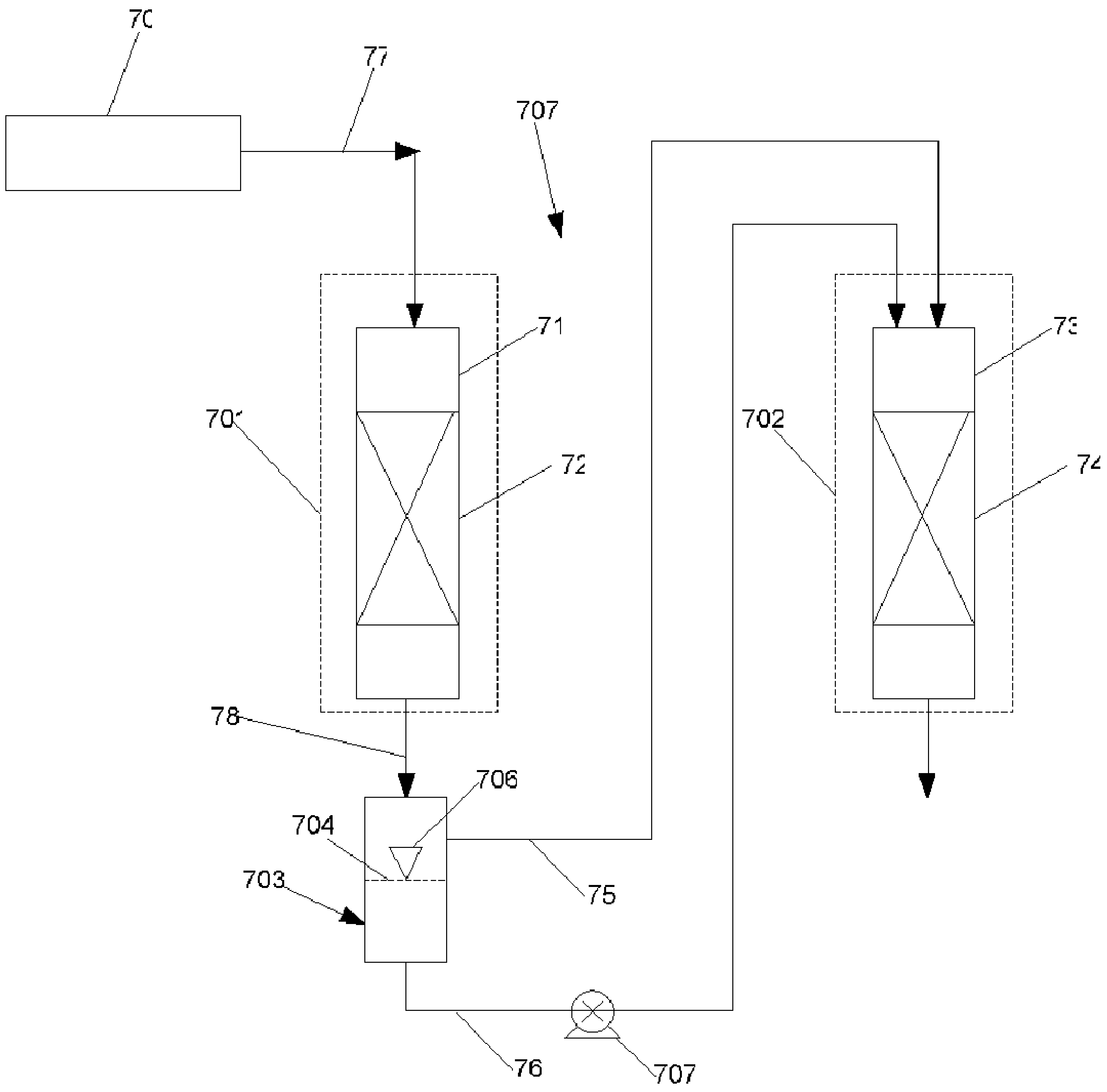

Figure 14

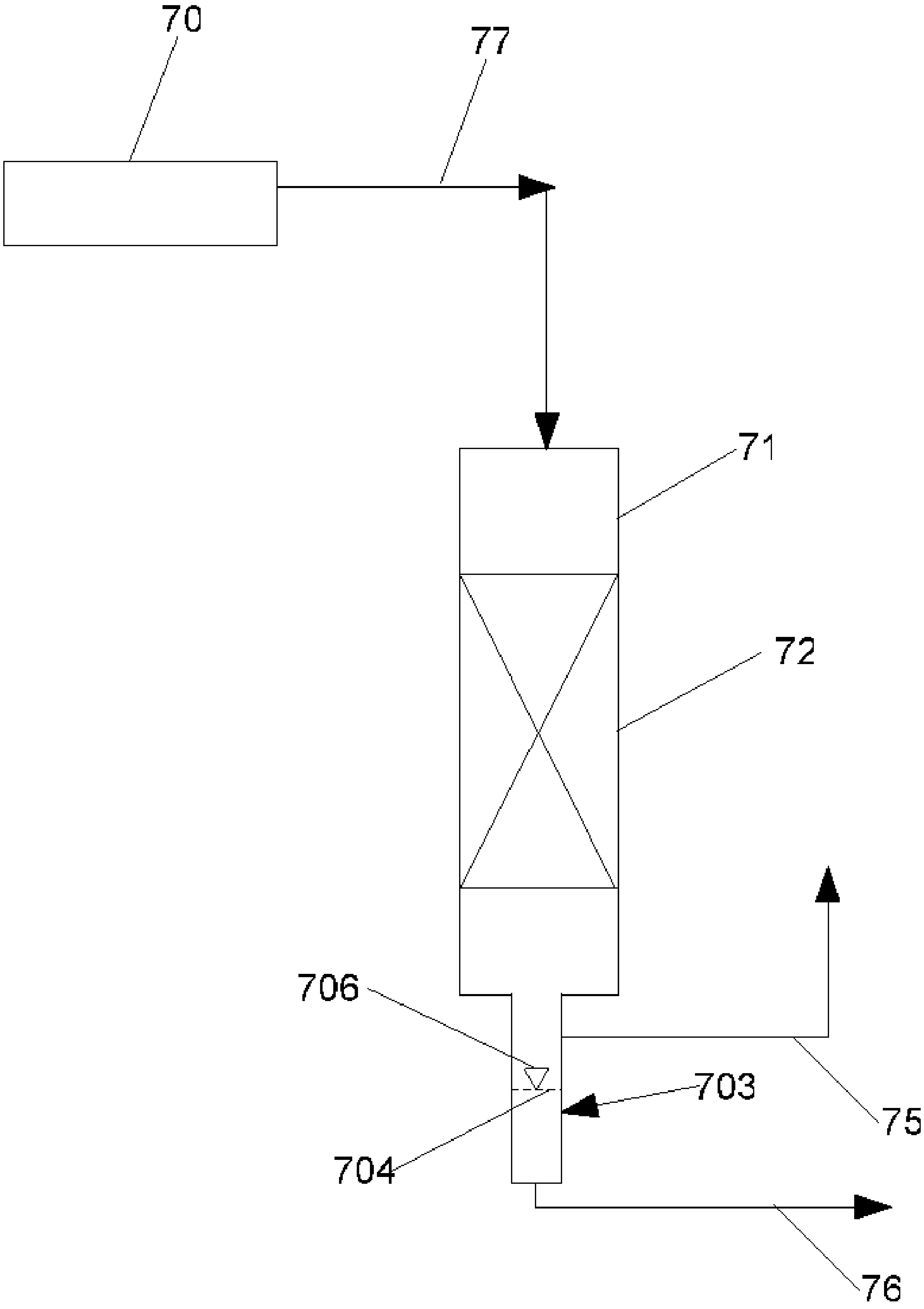

Figure 15

HIGH THROUGHPUT DEVELOPMENT METHOD FOR CATALYTIC HYDROPROCESSING OF DIRTY FEEDSTOCKS

FIELD OF INVENTION

[0001] This invention relates to methods for the low cost, accelerated development from discovery to commercial readiness of catalysts and plug flow catalytic processes for hydroprocessing of dirty feedstocks. By the term "dirty feedstocks" is meant feeds such as C^{10}-C^{20+} distillates from crude oil that contain large heteroatom containing molecules, and cycle oils produced in refinery operations.

BACKGROUND OF THE INVENTION

[0002] In order to scale-up a plug flow catalytic process for hydroprocessing of dirty feedstocks, it is necessary to define the impact of feedstock composition, time on stream, residence time, catalyst particle size, shape and other characteristics, and temperature profile on reaction rate and selectivity. The first step in a traditional scale-up program generally involves the selection, and definition of the intrinsic properties of, the catalyst. This step is typically performed isothermally with a diluted, crushed or powdered catalyst to minimize mass transfer limitations. A process variable study is performed to determine the impact of feed composition, space velocity, pressure, and residence time on reaction rate and selectivity. Activity and selectivity maintenance are then determined over a six to twelve month operating period. At the end of the operation, a second process variable study is performed to determine whether these properties have changed during time on stream.

[0003] Next, a commercial form of the catalyst is tested in an isothermal reactor. The commercial catalyst is of a larger particle size than the crushed catalyst and may have a special shape to minimize pressure drop during operation. The larger particle size generally results in a lower reaction rate and a selectivity loss due to limitations on mass transfer of reactants or products in and out of the catalyst pores. Operations generally consist of performing process variable studies at the beginning and end of an activity and selectivity maintenance run. This operation can be run in a laboratory scale reactor and typically lasts approximately one year.

[0004] In a commercial trickle-bed hydrotreating reactor, catalyst particles with diameters of 1.3-3.2 mm and average lengths of 5-10 mm are commonly used. This range of catalyst sizes reflects the tradeoff between the desire to provide high catalyst utilization (high catalyst effectiveness factors) on one hand, and to maintain a manageable pressure drop across the reactor on the other. Within this range of catalyst particle size, the intraparticle diffusion resistance (the diffusion of sulphur compounds inside the catalyst pores) could significantly reduce the overall HDS reaction rate. Furthermore, the intra-particle diffusion effect varies with operating conditions (particularly with temperature) and sulphur compounds of different intrinsic reactivities. While this issue is very important for a full understanding of HDS mechanisms and processes, it has not been adequately and quantitatively addressed in the open HDS literature, although many HDS studies have been conducted separately with either full-size catalysts or crushed catalyst particles.

[0005] The final step in the scale-up process is to test the commercial catalyst under adiabatic conditions, normally in a demonstration scale reactor containing one or more reactor tubes. The tubes in the demonstration scale reactor would have internal diameter of approximately 1 inch. In some cases, to further explore heat transfer effects, a configuration containing up to about 6-8 tubes arranged at commercial spacing could be used. In an exothermic reaction, the temperature profile depends upon the degree to which heat is continuously removed, as in a tubular reactor, or the reactor is simply a fixed bed reactor without a specific heat removal capability. The temperature profile can have a significant impact on selectivity, reaction rate, and activity maintenance. The test run also provides a measure of the tendency for the catalyst to produce hot spots or temperature runaways. Here again, the operating period can exceed one year.

[0006] This sequential approach typically takes in excess of three years to complete and may not provide all of desired data for scale-up. For many catalysts, the reaction rate and selectivity may be a function of residence time as well as time on stream. This can be the result of changes in the catalyst state or form, due to exposure for extended periods of time, or it may be due to the changing gas and liquid composition from the reactor inlet to the outlet. Examples would include oxidation from water formed during conversion, formation of a support over layer, poisoning, e.g., by reaction with hydrogen sulfide and ammonia, etc. In addition, surface catalytic reactions and buildup of feed and products in the pores can result in reductions in mass transfer rate to the catalyst.

[0007] The hydroprocessing of dirty feeds involves a sequential series of upgrading steps. These include first the removal of a heterocyclic molecules from the feed by a desulfurization, deoxygenation and denitrogenation step, followed by a hydro-dearomatization step to get rid of polynuclear aromatics. The catalysts used for these steps must be substantially immune to sulfur, oxygen and nitrogen poisons and are typically well-known metal sulfide catalysts. Thereafter, the feed may be subjected to ring opening step in which carbon-carbon bonds in ring structures are selectively cleaved to open the rings and some long chain molecules are broken into shorter segments. This step is also typically performed using a metal sulfide catalyst, however the sulfur levels in the catalyst are normally much lower than in the catalysts used for the previous steps. Thereafter, the feed may, if necessary, be subjected to a hydrogenation step for saturating the H—C bonds in the feed. The catalyst used in this step is typically a Zeolite supported or bulk non-precious Group 8 metal, although precious group metal catalysts can also be used. Finally the feed is subjected to a hydrocracking and isomerization step to form saturated hydrocarbons and napthenes of the desired chain length distribution. The catalysts used in the step typically comprise a Zeolite supported Group 8 precious metal. The steps in this process can be performed in separate plug flow reactors. Alternatively, some or all of the steps may be performed in a plug flow reactor having a longitudinally segmented bed, wherein each bed segment comprises a catalyst optimized for the given catalytic process step.

[0008] Despite the relatively large number of patents covering the different unsupported catalysts and their applications in hydroprocessing, there are only a few commercial bulk hydrotreating catalysts. In light of the potentially huge performance benefits demonstrated in the laboratory, this may look somewhat surprising. However, incorporating a catalyst with extremely high activity in existing refinery process equipment is all but straight forward. In many cases the process and the equipment was not designed for the heat release and H2 consumption accompanying a very high activity catalyst. The commercial use of such a catalysts can only be accomplished by close cooperation between the catalyst manufacturer and the refiner to ensure the expected performance benefits are achieved without undesired side effects or operational difficulties. In addition to that, the price plays an important role even if the unsupported catalyst contains only Group VIII and Group VI metals. High concentration of metals and higher density of unsupported, as compared to supported, catalysts will increase the reactor fill price significantly. Consequently, there are only limited offerings of commercial bulk hydroprocessing catalysts, with one being sold in sizable amounts in the present hydroprocessing market. This is the NEBULA1 catalysts family NEBULA-1 and NEBULA-20 are the commercial grades) of the Albemarle Catalyst company. Clearly there are opportunities for other more advanced catalysts to be offered into the market, to help further improve product quality and to reduce overall costs of desulfurization to clean fuels.

[0009] Recently, High Throughput Experimentation (HTE) techniques have been proposed as a source of data for new catalysts and processes. These HTE experiments are normally performed under conditions that minimize heat and mass transfer effects. Small volumes (less than 2 ml) of catalyst and high heat transfer rates are utilized. This approach is useful for comparing the intrinsic properties of an array of candidate catalysts but does not provide the data required for scale-up. See, for example, U.S. Pat. Nos. 6,149,882 and 6,869,799.

[0010] Combinatorial chemistry is in widespread use in the pharmaceutical industry, where it is used to synthesize, purify and evaluate new drugs at a more rapid pace than previously possible. In the field of pharmaceutical chemistry, the reactions are typically performed at a relatively small scale, since only a small amount of each drug is required for testing. Typically, only those drugs which are active in relevant bioassays are scaled up. The type of chemistry used to generate commercial quantities of the drugs is rarely the same as that used in small scale synthesis.

[0011] Combinatorial chemistry is being used in petroleum chemistry for the discovery of new catalytic materials for use in various refining applications. However, to have any commercial meaning, one must be able to correlate the results obtained on a small laboratory scale with those which will be obtained on a commercial scale. One combinatorial chemistry approach used to identify useful catalysts for various reactions involves placing a plurality of catalysts on a metal plate, contacting the plate with a gaseous reactant, and analyzing the products obtained via GC/MS. This approach is limited because, at least for a number of exothermic and endothermic catalytic reactions, it is difficult to correlate the results obtained on this small scale with those obtained on a commercial scale. This limitation exists, in part, because the heat transfer obtained on such a small scale cannot reasonably be correlated with what would be observed in a large reactor. There are many recent examples of this combinatorial approach and some representative ones are found in the following references: U.S. Pat. No. 5,776,359; U.S. Pat. No. 5,853,356; U.S. Pat. No. 5,939,268; U.S. Pat. No. 6,149,882; U.S. Pat. No. 6,790,322; and U.S. Pat. No. 7,025,828. In addition, the issue of process scale up has been addressed to some degree in U.S. Pat. No. 6,806,087. Here too, the approach is one that is unable to adequately address the full range of scale up issues including both heat and mass transfer effects on a commercially relevant scale of catalyst operation.

[0012] Heat transfer effects are very important in endothermic reactions. For example, hydroprocessing such as hydrocracking, hydrodesulfurization, hydroisomerization, which are endothermic reactions, are very sensitive to heat and mass transfer effects. A small scale reaction which provides an acceptable product mixture may provide an unacceptable level of secondary reactions on scale-up due to heat and or related mass transfer effects. Thus, it is quite difficult to extrapolate the results on small scale endo-thermic reactions to large commercial scale reactors. At the same time, it is not possible to take advantage of High Throughput combinatorial chemistry with the use of commercial scale reactors.

[0013] It would be advantageous to provide methods for discovering and evaluating optimal catalyst systems using combinatorial chemistry techniques that are capable of taking the heat and mass transfer effects on product distribution and other reaction characteristics into consideration. The present invention provides such methods.

SUMMARY OF THE INVENTION

[0014] This invention relates to a low cost, accelerated method for determining an advantageous combination of reactor structures, catalyst characteristics, catalyst bed structures and process conditions for scaling up from discovery to commercial readiness a plug-flow catalytic process and reactor system for hydroprocessing dirty feed stocks, and having high productivity and selectivity to desired products.

[0015] The method of the invention involves the use of high throughput laboratory scale catalytic process development apparatus that includes multistage series-connected laboratory scale plug-flow reactors to iteratively investigate each of the separate successive hydroprocessing steps performed on the dirty feed stocks, including removing heteroatoms, saturating polynuclear aromatics, cleaving carbon-carbon bonds in cyclic molecules, saturating unsaturated molecules, and hydrocracking and isomerizing the resulting hydrocarbon molecules. The characteristics and compositions of the effluents of the laboratory scale reactor stages are sampled and measured during each iteration, and the results of such measurements made during one iteration are used to help determine the choice of catalyst bed characteristics and process conditions in subsequent iterations for improving the productivity and selectivity of hydroprocessing operation.

[0016] The process conditions under which the testing is performed include various sets of temperatures, pressures, flow rates and relative partial pressures of reactants and reaction products in the catalyst beds of the various stages of the laboratory reactors. The testing of the catalysts includes determining the effects, in the various sets of process conditions, of the relevant catalyst characteristics such as particle size and shape on the performance of the catalysts in various portions of the series-connected laboratory scale fixed bed reactors over time. The testing of catalyst bed configurations can include the testing of the effects of various configurations of catalyst beds in the laboratory scale reactor stages, including varying the catalyst characteristics from one laboratory scale reactor stage to the next.

[0017] The data generated as a result of this testing enables the design of a commercial scale plug-flow catalytic process and reactor system for hydroprocessing dirty feed stocks in which the catalyst characteristics and operating parameters, including partial pressures of reactants and products, temperatures, pressures and flow rates are optimized. Thus, in accordance with the method of the invention, the longitudinal gradients in kinetics, mass transfer and heat transfer characteristics for the various reactions occurring within the catalyst beds, or catalyst bed segments, for each of the upgrading steps for hydroprocessing dirty feedstocks in a commercial scale reactor or reactors are investigated with the use of composite multistage series-connected laboratory scale fixed bed reactors that effectively permit the segmenting of each individual catalyst bed, or bed segment, in the commercial scale reactors into successive longitudinally distributed slices to permit the taking of measurements to investigate the kinetic, mass transfer and heat transfer characteristics for the different chemistries occurring within each of such slices of the catalyst beds or bed segments. The data gathered based on these measurements allows the development of predictive models using laboratory-scale reactors that describe the behavior is applicable to large-scale catalytic hydroprocessing systems.

[0018] The term “plug flow reactor”, as used herein refers to fixed bed reactors, packed bed reactors, trickle bed reactors and monolithic reactors operating either in a once through or a recycle mode. The term “laboratory scale plug flow reactor” as used herein, refers to a plug flow reactor in which each reactor stage has an internal diameter of less than 4 inches, preferably less than 2 inches, and more preferably less than 1 inch; a length of less than 8 feet, preferably less than 4 feet, more preferably less than 1 foot; and a catalyst charge of less than 800 grams, preferably less than 400 grams, more preferably less than 25 grams (excluding inert diluent particles charged to the reactor).

BRIEF DESCRIPTION OF THE DRAWINGS

[0019] FIG. **1** is a schematic representation of a composite multistage, series-connected, plug flow reactor in accordance with the invention;

[0020] FIG. **2** is a schematic representation of a composite multistage, series-connected, plug flow reactor and a parallel multistage, series-connected, probe reactor in accordance with the invention;

[0021] FIG. **3** is a schematic representation of a composite multistage, series-connected, plug flow reactor and a fluid dynamically linked, single stage probe reactor in accordance with another embodiment of the invention;

[0022] FIG. **4** is a schematic representation of a composite multistage, series-connected, plug flow reactor and a fluid dynamically linked, multistage, series-connected, probe reactor in accordance with the invention;

[0023] FIG. **5** is a schematic representation of a multistage, composite series-connected, plug flow reactor disposed in a constant temperature environment in the form of a fluidized sand bath in accordance the invention;

[0024] FIG. **6** is a schematic representation of a plurality of composite multistage, series-connected, fixed bed reactors disposed in the common fluidized sand bath in accordance with the invention;

[0025] FIG. **7** is a schematic representation of a plurality of composite multistage, series-connected, plug flow reactors configured to receive controlled variable inputs in accordance with the invention;

[0026] FIG. **8** is a graph useful for determining the Thiele Modulus of a catalyst;

[0027] FIG. **9** is a graph of the Effectiveness Factor versus Thiele Modulus for a catalyst;

[0028] FIG. **10** is a graph of Effectiveness Factor versus conversion for crushed and commercial scale catalysts;

[0029] FIG. **11** is a schematic representation of a plug flow reactor arrangement in accordance with another embodiment of the invention;

[0030] FIG. **12** is a schematic representation of a multistage, composite series-connected, isothermal plug flow reactor in accordance with the invention;

[0031] FIG. **13** illustrates an assembled, schematic diagram of reactors and a separator in accordance with one embodiment of the present invention;

[0032] FIG. **14** illustrates an assembled, schematic diagram of the reactors and the separator in accordance with another embodiment of the present invention; and

[0033] FIG. **15** illustrates an assembled, schematic diagram of the reactor and the separator in accordance with yet another embodiment of the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0034] Referring to FIG. **1** of the drawings, the composite multistage laboratory scale plug flow reactor **11** of a first embodiment of the invention is made up of three series-connected plug flow stages **13**, **15** and **17**, in this case fixed bed stages, each of which contains a bed of catalyst particles **19**, **21** and **23**. A sampling valve **25** is connected between the output of the first reactor stage **13** and the input to the second reactor stage **15** and has an output **26** for sampling the effluent from the first reactor stage **13** for analysis. A sampling valve **27** is connected between the output of the second fixed bed reactor stage **15** and the input to the third fixed bed reactor stage **17** and has an output **28** for sampling the effluent from the second reactor stage **15** for analysis. A sampling valve **29** is connected to the output of the third fixed bed reactor stage **17** and has an output **30** for sampling the effluent of the third reactor stage **17** for analysis. The output of the third reactor stage **17** is connected through the valve **29** to, e.g., a product accumulator (not shown). The feed to the multistage fixed bed reactor **11**, which normally is fresh reactant feed, is connected to the inlet of the first fixed bed reactor stage **13** from a source **31**. A sampling valve may also be installed in the line between the feed source **31** and the inlet to the first fixed bed reactor stage **13** in order to permit analysis of the feed.

[0035] The multistage fixed bed reactor **11** is contained in a temperature control device **33** that, for an exothermic reaction such as the Fischer-Tropsch reaction, could contain a material, such as circulating boiling water or a fluidized sand bath, for extracting heat from the reactor **11** in order to maintain the multistage reactor **11** at a substantially constant temperature. For an endothermic process, such as paraffin dehydrogenation or catalytic reforming, the temperature control device **33** could contain apparatus, such as an electrical heater, to supply heat to the fixed bed reactor **11** in order to maintain the substantially constant desired temperature. Alternatively, for both exothermic and endothermic catalytic processes, the temperature control device **33** can consist of a fluidized sand bath heater in which the multistage reactors are immersed.

[0036] Each of the catalyst beds **19**, **21**, and **23** in the reactor stages of the multistage reactor **11** replicates a longitudinal portion of the catalyst bed of a large fixed bed reactor and permits the measurement and analysis of the characteristics and performance of successive longitudinal portions of a large catalyst bed, thereby allowing determination of longitudinal gradients in reactor characteristics and performance that heretofore have been inaccessible. While reactor **11** has been shown as having three series-connected stages, it is equally possible to have a larger number of series-connected stages, e.g., four or six stages, in order to analyze the performance of the composite catalyst bed at a greater number of points along its length.

[0037] Depending on the reaction being studied and the data needed, the analysis of the feed and the effluent from the reactor stages can include, e.g., conventional GC/MS or UV or IR characterization of the reactant and product stream(s), and/or analysis of the catalyst system by XRD, diffuse reflectance IR or other spectroscopic techniques that are well known in the art. These studies would allow the performance attributes of the system to be quantified as a function of the longitudinal position in the catalyst bed. Such knowledge would allow the system to be optimized with direct knowledge of the catalytic reaction kinetics and performance attributes of each point and permit the design of catalyst systems in which, e.g., the catalyst particles may have different chemical or physical characteristics in different portions of the catalyst bed so as to operate at peak productivity or selectivity as a function of the local environment.

[0038] The catalyst beds in the reactor stages **13**, **15** and **17** may be a crushed or powdered catalyst or a commercial-size catalyst. Most measurements made in gathering data for the scale up of a catalytic reactor need to be made with the reactor operating in a substantially isothermal regime. In order for the reactor stages **13**, **15** and **17** to operate in a substantially isothermal regime, the catalysts in the beds **19**, **21** and **23** are diluted with an inert particulate matter, typically in a ratio of up to about 8-10 to 1. For measurements being made with the reactor operating in a substantially adiabatic regime, the catalyst in the beds **19**, **21** and **23** is less diluted, and depends on the heat of reaction of the process under study and reactor diameter. The ratio of catalyst particles to diluent particles in a catalyst bed depends upon a number of factors, including the amount of heat generated by the reaction and the activity of the catalyst particles in the bed. The appropriate ratio for a given reaction, catalyst, reactor diameter and catalyst particle size can easily be determined by one of ordinary skill in the art by a simple experiment.

[0039] A commercial-size catalyst in a fixed bed reactor typically has particle size of about 1 to 5 mm. the catalyst particles can be in any one or more a variety of shapes, e.g., round, tubular, trilobe, toroidal, etc. The crushed or powdered catalyst, which is typically formed by crushing a commercial-size catalyst, typically has a particle size of about 0.10-0.20 mm. the crushed or powdered catalyst particles are normally preferably as small as can be obtained while still retaining a performance qualities of the catalyst. The interior diameter of a reactor stage should be about 10 times the diameter of the smaller of the diluent or catalyst particles and the minimum would typically be in the range of about 10 to 50 mm (0.4 to 2 inches) for a bed containing commercial-size catalyst particles and diluent. Crushed or powdered catalyst particles are typically more active than the commercial-size catalyst particles because of lower mass transfer resistance. Therefore, in order for a reactor containing a bed of crushed or powdered catalyst to operate at the same temperature as a similar reactor containing commercial-size catalyst, the ratio of inert diluent particles to catalyst particles in the bed of crushed or powdered catalyst particles normally needs to be higher than that of the bed containing commercial-size catalyst particles in order that the heat release per unit volume of the to catalyst beds is the same.

[0040] The interior diameter of a reactor containing crushed catalyst, can, if desired, be smaller, in the range of about 5 to 12 mm, than that of a reactor containing the commercial size catalyst. For reasons of flexibility in the use of the multistage reactor **11** in different applications, however, it may be preferable that the crushed catalyst bed have the same interior diameter as that required for a bed containing commercial-size catalyst particles. Alternatively, the interior diameter of a reactor being used with a bed of crushed or powdered catalyst particles may be reduced by the use of a thermally conductive sleeve within the reactor.

[0041] The minimum height of a reactor stage is determined either by mixing or heat release considerations. For isothermal operation, if mixing is the limiting factor, the height should be sufficient to avoid bypassing. Typically, this would be at least about 50 times the average diameter of the particles, or about 50 to 250 mm (2 to 10 inches) for a reactor stage containing a bed of commercial-size catalyst particles. Because the feed is progressively converted as it traverses the stage of the multistage reactor **11**, the concentration of fresh feed in the successive reactor stages decreases from one stage to the next. If it is desired to have constant conversion in each reactor stage, the lengths of the catalyst beds **19**-**23** can be progressively longer in each of the successive reactor stages **13**-**17**. If the reactor **11** is to operate in the adiabatic regime, one would tend to use a lower ratio of inert diluent and a larger diameter reactor.

[0042] Referring to FIG. **2** of the drawings, there is illustrated a second embodiment of the invention in which elements that are the same as in the embodiment illustrated in FIG. **1** are numbered similarly. This second embodiment includes a composite multistage reactor **11** that is the same as the multistage reactor **11** of FIG. **1**. A composite multistage probe reactor **35**, in which each reactor stage can be the same as the corresponding reactor stage of multistage reactor **11**, is operated in parallel with the multistage reactor **11**. Both of the multistage reactor **11** and the probe reactor **35** are contained in a temperature control device **33** that can be the same as the types discussed above. If desired, the probe reactor **35** can be contained in a temperature control device separate from the temperature control device **33** in which the reactor **11** is contained, thereby permitting the operation of the probe reactor **35** at a temperature different from that of the multistage reactor **11**.

[0043] The composite reactor **35** has three series-connected reactor stages **37**, **39**, and **41** that contain catalyst beds **43**, **45** and **47**, respectively. A sampling valve **49** is connected between the output of probe reactor stage **37** in the inlet of the probe reactor stage **39** and has an output **50** for sampling the effluent from reactor stage **37**. A sampling valve **51** is connected between the output of reactor stage **39** and the input of reactor stage **41** and has an output **52** for sampling the effluent from the reactor stage **39**. A sampling valve **53** is connected between the output of reactor stage **41** and, e.g., a product accumulator (not shown), and has an output **54** for sampling the effluent from reactor stage **41**. The fresh reactant feed from source **31** is connected to the inlet of the first probe reactor stage **37**. A control and sampling valve can be connected between the source **31** in the inlet to the first probe reactor stage **37** for selectively controlling the amount of feed to the probe reactor and to permit the sampling of the feed for analysis. Also connected to the inlet to the first probe reactor stage **37** is a source **55** of a material to be controllably added to the input of the first probe reactor stage **37** for ascertaining the effect of such addition on the characteristics and performance of the stages of the probe reactor **35**. A source **57** is connected to the inlet of the second probe reactor stage **39** for selectively adding a material to the input of such a second probe reactor stage for ascertaining the effect of such addition on the characteristics and performance of the second and third probe reactor stages **39** and **41**. A source **59** is connected to the input of the third probe reactor stage **41** for selectively adding a material to the input of such probe reactor stage for ascertaining the effect of such addition on the characteristics and performance of the third probe reactor stage **41**. In this embodiment of the invention, the catalyst beds **43**, **45** and **47** of the probe reactor **35** are preferably the same as the catalyst beds **19**, **21** and **23** of the multistage reactor **11**, respectively.

[0044] The use of the composite multistage probe reactor **35** allows one to measure the transient response of the system to permanent or temporary changes in the feed composition at any stage of the multistage reactor **11** by comparing the characteristics and performance of the relevant stages of the probe reactor **35** over time in response to the change in input with the characteristics and performance of the corresponding stages of the multistage reactor **11**. Introduction of a change in gas or liquid input to the third reactor stage of the probe reactor **35** allows one to measure the impact of the changed component on the reaction rate and selectivity of the third reactor stage catalyst bed of the multistage reactor **11** with time. Introduction of the change to the second probe reactor stage allows one to measure the impact on the second and third stage catalyst beds of the multistage reactor **11**. This is equivalent to measuring the response to a change in conditions of any small segment of the catalyst bed in a commercial-size fixed bed reactor. For example, raising the gas feed rate to any reactor stage of the probe reactor **35** by having one of the sources **55**, **57** or **59** and additional fresh feed into the stage of the probe reactor **35** to which it is connected, would allow the investigation of the changes in incremental performance of that stage and following stages resulting from the change in input over time.

[0045] It is also possible to use the sources **55**, **57** or **59** to vary the concentrations of the trace components present in the fresh feed in a selected probe reactor stage, for instance by adding fresh reactant feed having a higher or lower concentration of such trace components, in order to quantify the effect of such trace components on various parts of the composite catalyst bed under a full range of operating conditions. By doing this it would be possible to map the critical longitudinal portions of the composite catalyst bed in a commercial system in which the catalyst is most vulnerable to poisoning or other inhibitory reactions caused by poisons or other natural byproducts of the reaction being practiced. The probe reactor **35**, and other versions of probe reactor as discussed below with relation to other Figures, can also be used to investigate the transient response of a reactor to temporary changes in the composition of the feed or prior stage effluent to various points in a composite catalyst bed by temporarily adding the materials of interest to a selected stage of the probe reactor **35** and monitoring the time dependent response of that stage and following stages of the probe reactor **35** to such added materials both during and after the time that such materials are added.

[0046] Referring to FIG. **3** of the drawings, there is illustrated another embodiment of the invention in which elements that are the same as in the embodiments of FIG. **1** are numbered similarly. In this embodiment of the invention, the probe reactor **101** can consist of a single plug flow reactor stage whose inlet is selectively fluid dynamically linked to a selected stage of the composite multistage fixed bed reactor **11**. Other configurations for the single stage probe reactor **101** are discussed below. The valve **103** is connected between the output of the first reactor stage **13** and the input of the second reactor stage **15** of the multistage reactor **11** and has outputs **105** and **107** for selectively sampling of the effluent of the reactor stage **13** and selectively connecting a portion of the effluent of the reactor stage **13** to the input of the probe reactor **101**, respectively. The valve **109** is connected between the output of the reactor stage **15** and the input to the reactor stage **17** of the multistage reactor **11** and has outputs **111** and **113** for selectively sampling of the effluent of reactor stage **15** and selectively connecting a portion of the effluent of reactor stage **15** to the input of probe reactor **101**, respectively. The valve **107** is connected between the output of reactor stage **15** and a product accumulator and has outputs **117** and **119** for selectively sampling of the effluent of reactor stage **15** and selectively connecting a portion of the effluent of reactor stage **15** to the input of probe reactor **101**, respectively. The probe reactor **101** also receives inputs from the feed source **31** and from a source **121**. The probe reactor **101** and the catalyst bed contained therein in this embodiment of the invention is preferably the same as the reactor stage and catalyst bed contained therein in the multistage reactor **11** following the one having a portion of its effluent connected to the input of the probe reactor **101**. The single stage probe reactor may, for example, be used to perform the same investigations as were described above with relation to the multistage probe reactor embodiment of FIG. **2**.

[0047] Referring to FIG. **4** of the drawings, there is illustrated another embodiment of the invention in which elements that are common to the embodiments of FIGS. **1** and **2** are numbered similarly. In this embodiment of the invention, the probe reactor **35** consists of a composite multistage series-connected plug flow reactor in which the reactor stages may be the same as the multistage series-connected probe reactor **35** depicted in FIG. **2** of the drawings. In this embodiment, however, the stages of the probe reactor **35** are selectively fluid dynamically linked to selected stages of the composites multistage series-connected reactor **11** by selectively connecting a portion of the effluent of one or more stages of the composite multistage series-connected reactor **11** to one or more selected stages of the probe reactor **35**. The valve **123** is connected between the output of the first reactor stage **13** and the input of the second reactor stage **15** of the multistage reactor **11** and has outputs **125** and **127** for selectively sampling the effluent of the first reactor stage **13** and connecting a selected portion of the effluent of reactor stage **13** to the inlet of probe reactor stage **39**, respectively. The valve **129** is connected between the output of reactor stage **15** and the input to reactor stage **17** of the multistage reactor **11** and has outputs **131** and **133** for selectively sampling the effluent of reactor stage **15** and selectively connecting a portion of the effluent of reactor stage **15** to the input of probe reactor stage **41**, respectively. The fresh reactant feed from the source **31** is connected to the input of the first probe reactor stage **37**. Control and sampling valves (not shown) may be connected in the line between the fresh reactant feed and the probe reactor stage **37** to control the amount of fresh reactant feed supplied to the probe reactor **35** and to permit the analysis of its content. Also connected to the input to the first probe reactor stage **37** is a source **55** of a material to the selectively added to the input of the first probe reactor stage **37** for ascertaining the effect of such addition to the stages of the probe reactor **35**. A source **57** is connected to the input of the second program per stage **39** for selectively adding a material to the input of such a second program per stage for ascertaining the effect of such addition on the second and third probe reactor stages **39** and **41**. A source **59** is connected to the input of the third probe reactor stage **41** for selectively adding a material to the input of such probe reactor stage for ascertaining the effect of such addition on the third probe reactor stage **41**. In this embodiment of the invention, the catalyst beds **43**, **45** and **47** of the probe reactor **35** are preferably the same as the catalyst beds **19**, **21** and **23** of the multistage reactor **11**, respectively.

[0048] Referring again to FIG. **3** of the drawings, the probe reactor **101** can consist of a substantially fully back-mixed reactor instead of a single stage fixed bed reactor stage **101**, such as discussed above. The distribution a catalyst, feed and products in the back-mixed probe reactor **101** a substantially uniform and so, if the probe reactor **101** receives only effluent from a stage of reactor **11**, it corresponds to a single, narrow, horizontal slice at the inlet of the catalyst bed of the stage of multistage reactor **11** following the stage that has a portion of its effluent connected to the input of the probe reactor **101**. By controlling the relative concentrations of fixed bed reactor stage effluent and fresh feed, it will is possible for the back-mixed probe reactor to simulate any selected horizontal slice of the fixed bed reactor stage whose effluent is connected to the back-mixed probe reactor. The back-mixed probe reactor **101** can, for instance, be a two-phase fluidized bed reactor, a three-phase slurry reactor, or a three phase ebulated bed reactor.

[0049] Alternatively, the probe reactor **101**, instead of being a fully back-mixed reactor such as discussed above, can be a two-dimensional catalyst array such as disclosed in Y. Jiang et al, *Chemical Engineering Science*, vol 54, pp 2409-2419 (1999). Such a probe reactor can be used to investigate the intrinsic characteristics of a plurality of crushed catalysts in the presence of different mixes of feed, effluent and product.

[0050] In the embodiments of FIGS. **2**, **3** and **4** of the drawings, stages of the probe reactor **101** and **35** receive as inputs combinations of controlled amounts of one or more of the fresh reactant feed, effluent from a selected stage of the multistage reactor **11** and other feeds. Such other feeds may, for instance, consist of additional fresh reactant feed, additional product gases or liquids produced during the reaction taking place in the composite multistage reactor **11**, or contaminants that may be present in the fresh feed used during operation of a commercial reactor.

[0051] The reactant and other material feeds, and reaction products and byproducts in reactor effluents supplied or generated in the embodiments of the invention described herein may be either gaseous, liquid or mixed phase (such as e.g., gas/liquid or two or more immiscible liquids). Feeds and effluents consisting of gases can be handled using well known conventional back pressure regulators and gas flow control systems with mass flow controllers. Controlled amounts of liquids can be pumped in high-pressure environments using known pumps such as a Ruska pump or a Syringe pump. If the effluent from a reactor stage or the feed contains multiple phases, particularly if such phases are immiscible, such as water and hydrocarbons or liquid and gas, it is important to avoid slug flow. In such case, sampling valves may consist of e.g., iso-kinetic sampling valves such as available from Prosery AS, or splitters such as described in U.S. Pat. No. 4,035,168. Alternatively, the stream may be sampled immediately after a static mixer such as available from Prosery AS, which homogenizes the multiphase stream. In combining immiscible feeds or feeds and effluent to a reactor stage, or in conducting the multiphase effluent from the outlet of one reactor stage to the inlet of the following reactor stage in a series-connected multistage reactor, it is typically the practice to manifold of the streams into a line having a high Reynolds number similar in concept to a fuel injection system in an automobile engine. Alternatively, static mixers such as available from Prosery AS or from Admix, Inc., Manchester, N.H., can also be used. In this case, some simple initial testing may be desirable to confirm that the operating conditions are leading to the homogeneity of the stream passing through the device. If the gas and liquid are well mixed in a transfer line, it is possible, for instance, to take a combined liquid and gas sample in a sample bomb connected to the reactor line via double block valves. The bomb would be at atmospheric pressure or slightly above. The block valves would be opened and liquid and gas would be allowed to flow into the bomb. The two block valves would then be closed, the sample bomb removed from the reactor and the contents analyzed. The presence of a small concentration of an inert gas such as Argon in the stream can be used to allow closure of the material balance. Alternatively, if the phases are not well mixed, one could employ gas/liquid separators and analyze the gas and liquid phases separately with an internal standard such as He or Ar and overall carbon balance analysis to link the two. This could be accomplished e.g., by using a gas sample bomb attached to the top of the line and a liquid sample bomb attached to the bottom of the line. A major area of concern in understanding and controlling the characteristics and performance of a plug flow reactor is the adsorption or reaction of a feed component, product or byproduct with the catalyst surface. For instance, in a hydrocracking processes, materials such as ammonia, carbon monoxide, hydrogen sulfide, can tie up active catalyst sites, reduce reaction rate and adversely impact product selectivity. The reactions caused by these materials can take time to equilibrate and can also take time to be released after removal of the material from the feed stream to the reactor.

[0052] Ammonia is known to react with hydrocracking catalysts, causing activity to decline and line out. Upon removal of the ammonia from the feed, hydrogen can be used to remove the ammonia from the catalyst surface. In investigating the effects of ammonia on different portions of the composite catalyst bed, ammonia can be added to the inlet of any of the stages of probe reactor, thereby replicating the effect of the presence of ammonia in the feed to a selected longitudinal slice of the composite catalyst bed. By controlling the conversion level in a given catalyst slice, e.g., by adjusting temperature and/or flow rate and/or reactant partial pressures in a probe reactor stage, it is possible to define the effect of the ammonia under various operating conditions. By varying the hydrogen concentration in the feed to one or more probe reactor stages, it is possible, for example, to investigate the effect of increased hydrogen on the ammonia-contaminated catalyst in different portions of the composite catalyst bed, e.g., the bed with the greatest activity decline.

[0053] Carbon monoxide is tightly held on many Group VIII metal catalysts, which can reduce available surface for hydrogen, thereby making hydrogen activation the rate limiting step. By varying the concentrations of carbon monoxide (or carbon dioxide) and hydrogen in the feed to selected stages of the probe reactor **35** or **101** and comparing performance of the relevant probe reactor stages with the corresponding stages of the multistage reactor **11**, it is possible to determine the impact of carbon monoxide and hydrogen concentration on reaction rate and selectivity. The use of a multistage probe reactor allows for testing of the impact at various conversion levels by e.g., by adjusting temperature and/or flow rate and/or reactant partial pressures.

[0054] The addition of water to a plug flow reactor in heavy oil upgrading and conversion processes has been shown to have a positive impact under some conditions and a negative impact under others. Adding controlled amounts of water (or other oxygenated molecules) to selected stages of the probe reactor **35** or **101** would permit the study of the impact of the added water on reaction rate and selectivity in selected longitudinal slices of the composite catalyst bed by comparing the characteristics and performance of the relevant stages of the probe reactor with the corresponding stages of the multistage reactor **11**.

[0055] The amount of Conradson carbon is usually utilized in correlations for hydrotreater performance. In general, carbon and heavy wax deposits on a catalyst inhibit the diffusion of reactants to the catalyst surface and the removal of reaction products from the catalyst surface. This tends to lead to activity reduction via unwanted side reactions with deposits on the catalyst surface or with the diffusion limited reactants or both. In the case of beds containing commercial-size catalyst particles where the diffusion path is the longest, this sort of diffusion limitation can limit overall catalyst life and require costly steps to maintain system performance Adding different molecular weight fractions of these materials to a selected stage of the probe reactor **35** or **101** would allow the determination of what portion of the composite catalyst bed is impacted the most. The effects of various regeneration techniques such as by the addition of hydrogen, water, or a light solvent can also be determined my controlling the feeds to the relevant stages of the probe reactor **35** or **101**, thereby to define the preferred rejuvenation technique. These issues will be particularly important in processing of heavy sulfur containing feeds from tar sands, shale, heavy oil deposits, and coal. These feeds are known to carry many contaminants that can lead to catalyst poisoning, and in situ regeneration, in order to avoid the cost of frequent replacement with fresh unused catalyst, is frequently the only means to make the overall process economically viable.

[0056] Polynuclear aromatics are also known to inhibit a catalyst by forming carbonaceous overlayers on catalyst sites that reduce selectivity and activity of hydroprocessing catalysts. The effect of the presence of polynuclear aromatics in the feed at various longitudinal portions of a composite catalyst bed of a plug flow reactor can be determined by adding the polynuclear aromatics to a selected stage of the probe reactor **35** or **101** and comparing the characteristics and performance of the relevant stages of the probe reactor with the corresponding stages of the multistage reactor **11**. This can be used to help define in what portion of the composite catalyst bed the polynuclear aromatics have their greatest impact, and what can be done to improve the process design and catalyst performance, by comparison of the performance and characteristics of the relevant stages of the probe reactor **35** or **101** with the corresponding stages of the multistage reactor **11**.

[0057] Referring again to FIG. **3** of the drawings, the probe reactor **101** can consist of a substantially fully back-mixed reactor instead of a single stage plug flow reactor stage **101**, such as discussed above. The distribution a catalyst, feed and products in the back-mixed probe reactor **101** a substantially uniform and so, if the probe reactor **101** receives only effluent from a stage of reactor **11**, it corresponds to a single, narrow, horizontal slice at the inlet of the catalyst bed of the stage of multistage reactor **11** following the stage that has a portion of its effluent connected to the input of the probe reactor **101**. By controlling the relative concentrations of fixed bed reactor stage effluent and fresh feed, it will is possible for the back-mixed probe reactor to simulate any selected horizontal slice of the fixed bed reactor stage whose effluent is connected to the back-mixed probe reactor. The back-mixed probe reactor **101** can, for instance, be a two-phase fluidized bed reactor, a three-phase slurry reactor, or a three phase ebulated bed reactor.

[0058] Referring now to FIG. **5** of the drawings, the series-connected reactor stages of the composite multistage laboratory scale plug flow reactor, in this case a fixed bed reactor, according to the invention can be arranged in parallel with one another in a temperature control device for a more compact and convenient configuration. In this arrangement the composite multistage reactor **501** is made up of three series connected reactor stages **503**, **505** and **507** which are disposed in temperature control device constituted by a heated or cooled fluidized sand bath **509**. The reactant feed gas is preferably connected from a source file a through a preheat coil **513**, which is also disposed in the fluidized sand bath **509**, to the inlet of the first reactor stage **503**. Liquid, which may be a reactant, is fed from the feed pump **515** through the preheat coil **513** to the inlet of reactor **503**. Sampling valves may be connected in the both the gas and liquid feed lines for sampling the gas and liquid feeds. The preheat coil **513** is used to heat the gas and liquid feeds to the appropriate temperature for being supplied to the multistage reactor **501**. The outlet of reactor **501** is connected to the inlet of reactor **505** through a sampling valve **517**. The outlet of reactor stage **505** is connected to the inlet of reactor stage **507** through the sampling valve **519**, and the outlet of reactor stage **507** is connected through a sampling valve **521** to the separator **523**. Each of the sampling valves **517**, **519** and **521** have an outlet selectively connected to a probe reactor **523** for supplying effluent to the probe actor **523**. Each of the sampling valves **517**, **519** and **521** also has an outlet to permit sampling of the effluent from the respective reactor stage to whose output of the sampling valve is connected.

[0059] Referring now to FIG. **6** of the drawings, there is illustrated schematically, an arrangement of three composite multistage series-connected laboratory scale plug flow reactors **531**, **533** and **535** and arranged in a fluidized sand bath **537**. The stages of each of the multistage reactors are arranged in parallel with one another in the same manner as the stages of the reactor **501** in FIG. **5**, and each of the multistage reactors **531**, **533** and **534** is preferably preceded by a preheat coil that can be the same as the preheat coil **513** illustrated in FIG. **5** of the drawings. A single-stage probe reactor **538**, which can be any of the types described above with relation to probe reactor **101** of FIG. **3** of the drawings, is arranged between the series-connected reactors **533** and **535** in the fluidized sand bath **537** and selectively receives inputs of either the reactant feed or the effluent of any of the reactor stages of the series connected reactors **533** and **535** by means of sampling valves (not shown) that may be the same as the sampling valves **517**, **519** and **521** illustrated in FIG. **5** of the drawings. Each of the reactors **531**, **533**, **538** and **535** receives reactant feed from sources **539**, **541**, **543**, and **545**, respectively, that can be all the same feed source. The outlets of the last stages of each of the reactors **531**, **533**, **538**, and **535** are preferably connected to the separators or product accumulators **547**, **549**, **551** and **553**, respectively, which all may be constituted by a single separator or product accumulator.

[0060] The arrangements of FIGS. **5** and **6** have the advantage that the fluidized sand bath need not be so deep as it would be if the reactors were arranged vertically, and in that the sampling valves **517**, **519** and **521** can be situated above the fluidized sand bath and so are accessible for maintenance or adjustment during operation of the multistage reactors. If the effluents from the stages of the multistage reactors contain multiple phases, the transfer lines connecting the outlet of one reactor stage to the inlet of the following reactor stage need to be configured in such a way as to avoid a slug flow in the lines. As described above, this can be accomplished using lines having high Reynolds numbers or with the use of static mixers. The sampling valves **517**, **519** and **521** can be iso-kinetic sampling valves, although other arrangements such as described above can also be used. Additionally, the conduits connecting the outlet of one reactor stage to the inlet of the following series-connected reactor stage are designed for non-slugging flow, for instance by using static mixers.

[0061] Having a plurality of composite multistage series-connected reactors disposed in a common temperature environment, such as constituted by the fluidized sand bath **537**, or as described above with relation to FIGS. **2** through **4** of the drawings, permits the simultaneous investigation of various characteristics of a catalytic process for substantially accelerating the scaling up of the reaction to commercial application. For instance, using the configuration of FIGS. **5** and **6** as an example, if the multistage reactor **535** contains crushed catalyst particles diluted with an inert diluent for isothermal operation, and the reactor **533** contains commercial scale catalyst particles also diluted with an inert diluent for isothermal operation, and the reactor **531** contains commercial scale catalyst particles in a concentration suitable for adiabatic operation, the kinetic, mass transfer and heat transfer characteristics of the catalytic process can be investigated simultaneously in the isothermal reactors, and the resulting reactor model derived from the data obtained from the isothermal reactors can be confirmed by the data obtained from the adiabatic reactor.

[0062] Other experiments to be performed that aid in the scaling up of a catalytic process include, for example, investigating the characteristics of a plurality of different catalysts simultaneously. Alternatively, a crushed catalyst in the catalyst beds of one multistage series-connected reactor could be compared with a plurality of different shapes or sizes of commercial-size versions of the catalyst in the catalyst beds of other multistage series-connected reactors, all disposed in a common constant temperature department. In an alternative arrangement, it is also possible to have different catalysts in different reactor stages of the multistage series-connected reactor **11** for testing the catalysts in series. Using such an arrangement, one can design a layered composite catalyst bed in which the intrinsic behavior of each catalyst layer is matched to the local kinetic and mass transfer environment, so that the overall response of the system is varied longitudinally so as to obtain behavior characteristics in each longitudinal portion of the composite reactor that are optimum for process performance If a plurality of multistage series-connected plug flow reactors is disposed in separate, independently controllable temperature control devices, a plurality of different heat removal levels can be investigated in parallel.

[0063] Referring now to FIG. **7** of the drawings, the module **151** contains a plurality of parallel laboratory scale plug flow reactor stages **151-1** through **151**-*n*. The module **151** includes a temperature control device **152** surrounding the module **151** for controlling the temperature of the ambient experienced by the reactor stages **151-1** through **151**-*n*. In the case of an exothermic reaction, such as the Fischer-Tropsch reaction, the temperature control device may consist of an enclosure containing circulating boiling water for extracting heat from the reactor stages **151-1** through **151**-*n*. For an endothermic process, such as e.g., dehydrocycloaromatization, steam reforming or hydroprocessing, the temperature control device can comprise apparatus, such as an electrical heater, for supplying heat to the reactor stages **151-1** through **151**-*n*. For either exothermic or endothermic reactions, the temperature control device **152** may alternatively comprise a fluidized sand bath heater in which the multistage reactors are immersed.

[0064] Each of the reactor stages **151-1** through **151**-*n* contain a catalyst bed **153-1** through **153**-*n*. The modules **155** and **157** can be identical to the module **151**, and contain a plurality of parallel plug flow reactor stages **155-1** through **155**-*n* and **157-1** through **157**-*n*, respectively. Each of the parallel reactor stages in the modules **155** and **157** contain catalyst beds **159-1** through **159**-*n* and **161-1** through **161**-*n*, respectively. In the illustrated embodiment, the outlet of each of the reactor stages in module **151** is connected to the inlet of the corresponding reactor stage in module **155**, and the outlet of each of the reactor stages in module **155** is connected to the inlet of the corresponding reactor stage in module **157**. Thus, the series connected reactors stages **151-1**, **155-1** and **157-1** form a composite multistage series-connected fixed bed reactor. Similarly, the other sets of series connected reactor stages in the modules **151**, **155** and **157** also form composite multistage series-connected fixed bed reactors. The modules **151**, **155** and **157** may contain any desired number of parallel reactor stages depending upon the application. For instance, each module might contain four or eight or even 16 parallel reactor stages. Is also possible to have additional modules of parallel reactors stages, with each of said parallel reactors stages being connected in series with the corresponding reactor stages of the preceding and succeeding modules. For instance, there might be four or six modules in a given application.

[0065] The modules **155** and **157** are surrounded by temperature control devices **158** and **160**, respectively, that may be the same as, or common with, the temperature control device **152** that surrounds the module **151**. Sampling valves **163-1** through **163**-*n* are connected between the outlet of each reactor stage in the module **151** and the inlet of the corresponding reactor stage in module **155**. Sampling valves at **165-1** through **165**-*n* are connected between the outlets of each of the reactor stages in module **155** in the inlet of the corresponding reactor stage in module **157**. Fresh reactant feed is fed from a source **167** through control valves **169-1**

through **169**-*n* to the inlets of each of the reactor stages **151-1** through **151**-*n* of module **151** for supplying controlled amounts of reactant feed to the inlets of the respective reactor stages. The plug flow reactor **171** also receives fresh reactant feed gas from the source **167** at its inlet, and has its outlet connected to the inlets of the reactor stages **151-1** through **151**-*n* through control valves **173-1** through **173**-*n*, respectively, for supplying controlled amounts of effluent from the reactor **171** to the reactors **151-1** through **151**-*n*.

[0066] In a commercial-size plug flow reactor, the proportion of fresh feed and reaction products and byproducts varies continuously along the length of the catalyst bed. At the inlet there is 100% fresh reactant feed and zero reaction products and byproducts. As the fresh feed is consumed in the catalyst bed of the reactor, the proportion of fresh feed decreases and the proportion of reactant products and byproducts increases longitudinally along the catalyst bed. The multiple parallel-serial reactor arrangement of FIG. **7** can be used to perform a number of different kinds of experiments. For instance, all of the reactor stages can contain the same catalyst and the composition of the feed can be varied from stage to stage. Alternatively, the composition size or configuration of the catalyst particles can be varied from reactor stage to reactor stage in each of the reactor stages can receive the same feed.

[0067] In accordance with the method of the invention, the longitudinal gradients in kinetics, mass transfer and heat transfer characteristics for the various reactions occurring within the catalyst beds, or catalyst bed segments, for each of the upgrading steps for hydroprocessing dirty feedstocks are investigated with the use of composite multistage series-connected fixed bed reactors that effectively permit the segmenting of each individual catalyst bed, or bed segment, into successive longitudinal slices to permit the taking of measurements to investigate the kinetic, mass transfer and heat transfer characteristics for the different chemistries occurring within each of such slices of the catalyst beds or bed segments. In the initial step of removing the hetero oxygen, sulfur and nitrogen atoms from the heterocyclic molecules, the dirty feedstocks and hydrogen are fed to the inlet of the first reactor stage of a first composite multistage series-connected plug flow reactor in which the catalyst beds contain a catalyst, typically a metal sulfide, that is capable of catalyzing the reaction of hydrogen with the dirty feedstocks to remove the heteroatoms from the heterocyclic molecules in the feedstock. The catalytic chemistry performed in such first composite multistage series-connected reactor initially forms alcohols, thiols and amines as intermediates that are liquid at the reaction conditions. These intermediates are then converted to H_2O, H_2S, and NH_3 that are highly volatile at reaction temperatures and removed from the system as gases. If the reaction conditions are such that the intermediates were not fully converted, they would remain in the system and cause problems in the following processing steps by poisoning the catalysts. By segmenting the heterocyclic molecule processing catalyst bed into a series of three or more longitudinal catalyst bed slices in separate series-connected reactor stages, sampling of the effluents of each of the reactor stages and measuring the amounts of reactants and intermediate and final products in the effluents of each of the stages in order to determine the extent to which the hetero-atoms have been removed from the heterocyclic molecules and intermediate and final products and byproducts of the reaction have been formed in each reactor stage, one can optimize the processing conditions for the step to ensure, e.g., that such intermediates do not remain in the system, but are converted to the volatile products. The compositions of the effluents can be measured by gas or high-pressure liquid chromatic measurements combined with mass spectroscopy. Alternatively, the presence of sulfur can be measured using pulsed flame photometric detectors. Oxygen it can be measured using GCMS or O^{17}NMR, and nitrogen can be measured using chemiluminescence techniques.

[0068] Similarly, the following hydroprocessing steps are each performed in successive composite multistage series-connected fixed bed reactors, each containing three or more reactor stages. Each of such following successive hydroprocessing steps involves feeding effluent from the last stage of the preceding composite multistage reactor and hydrogen to the first stage of the following composite multistage reactor, and measuring the concentrations of the feed to said following composite multistage reactor and the reaction products and byproducts in the effluents of each of the reactor stages of said following composite multistage reactor. The segmentation of the catalyst beds of each of the steps use for hydroprocessing dirty feedstocks and the sampling and measuring the concentration of the various components in the effluents of each of the reactor stages allows one to develop a model for optimizing the processing conditions for each of the steps using small-scale equipment such as described above, which model is applicable to the analysis of the performance of commercial scale catalytic hydroprocessing systems useful for hydroprocessing dirty feedstocks.

[0069] In the step of using hydrogen to saturate the polynuclear aromatics, the progress of the catalytic reaction in each of the reactor stages can be investigated by sampling the effluents of each of the reactor stages and taking measurements using high-resolution P-NMR or C^{13}NMR. The progress of the step of cleaving the carbon-carbon bonds, and the isomerization step, can be measured using gas chromatography with high-resolution mass spectroscopy or high-resolution C^{13}NMR measurements on the effluents of the relevant reactor stages. The identity and concentration of various hydrocarbons can be measured using GCMS.

[0070] Among the process variables that can be investigated using the method of the invention is the effect of low levels of heteroatoms on the functionality of the catalysts in the process stages following the initial heterocyclic molecule treatment step. This can be performed using, e.g., a probe reactor in a manner described above with relation to FIGS. **2** through **4** or **6** of the drawings.

[0071] The data gathered based on these measurements allows the development of predictive models using small-scale reactors that are able to describe behavior applicable to large-scale catalytic hydroprocessing systems.

[0072] Kinetics

[0073] Heretofore, it has been the practice to measure the kinetics of a plug flow catalytic system only by measurements taken at the inlet and the outlet of the catalyst bed, so that the measurements are averaged over the length of a catalyst bed. In analyzing the kinetic performance of such a reactor it was necessary to make assumptions concerning the kinetic order of the reaction. Typically, it was assumed that the order of the reaction remained constant along the length of the catalyst bed in the reactor. Applicants have found that this assumption was in many cases incorrect. With the use of the multistage series-connected plug flow reactor of the present invention as described above with relation to any of the FIGS. **1** through **7**, it is possible to investigate longitudinal variations in the kinetics of a plug flow catalytic system along the length of the composite catalyst bed of the reactor.

[0074] Using the multiple parallel-serial reactor arrangement illustrated in FIG. **7** of the drawings as an example, the multistage series-connected reactor of the present invention can be used in accordance with the method of the invention to develop scale-up data for investigating the integral, differential and intrinsic kinetics of a plug flow catalytic reactor system as a function of the longitudinal position along the catalyst bed of the reactor. For example, to determine the integral kinetics of a fixed bed reactor system, the catalyst beds in the reactor stages of modules **151**, **155** and **157** and the reactor **171** can contain the catalyst intended for use with the system. The parallel reactor stages **151-1** through **151**-*n* in the module **151** receive varying proportions of fresh feed from the source **167** and effluent from the reactor **171**. For instance, the valves **169-1** through **169**-*n* and valves at **173-1** through **173**-*n* can be set such that reactor stage **151-1** receives 100% fresh feed and no effluent, and the reactor stages **151-2** through **151**-*n* receive successively decreasing proportions of fresh feed and increasing proportions of effluent. In this arrangement, the successive reactor stages **151-1** through **151**-*n* are equivalent to successive, longitudinally-spaced slices of the catalyst bed of a fixed bed reactor, with reactor stage **151-1** being equivalent to the slice at the inlet of the catalyst bed and reactor stages **151-2** through **151**-*n* operating at conditions equivalent to slices of the catalyst bed positioned at successive longitudinal positions along the composite bed. The reactor stages in modules **155** and **157** can be used to provide data for slices of the catalyst bed being scaled-up that are intermediate the slices of the successive reactor stages in module **151**. For example, if reactor **171** is operated at 90% conversion, its effluent will contain 10% of the amount of fresh feed at its inlet with the remainder of the effluent being reaction products and byproducts. If reactor stage **151-2** receives 88% fresh feed and 12% effluent from the reactor **171**, the composition of the feed at the inlet to reactor stage **151-2** will be 89.2% fresh feed with the remainder being reaction products and byproducts. If the reactor stages **151-1**, **155-1** and **157-1** are each run at 3% conversion, their effluents will contain 97% fresh feed, 94.1% fresh feed and 92.3% fresh feed, respectively, with the remainder being reaction products and byproducts. Thus, the compositions and proportions of fresh feed and reaction products and byproducts in the reactor stages in modules **151 155** and **157** are equivalent to those at successive longitudinal slices in the catalyst bed of a fixed bed reactor.

[0075] In order to determine the integral kinetics of the catalytic system as a function of longitudinal positions in the catalyst bed, it is necessary to analyze the inlet feed stream and composition and outlet feed stream and composition, normalized, for instance to STP per standard leader of feed, at each of the successive longitudinal slices of the catalyst bed. In this manner it is possible to determine the kinetics of the reaction at each effective slice of the full commercial scale system. If the resulting rate constant vs distance from inlet curve is a straight line, the integral kinetics of the system is a constant along the length of the catalyst bed. If the slope of the line changes from slice to slice, this would be indicative of a change in kinetics (and likely catalyst state) as a function fo distance from the inlet.

[0076] If the resulting kinetic curve on the log-log plot is not a straight line, then the integral kinetics of the system varies along the length of the reactor catalyst bed. In this case, it is necessary to do a regression analysis to fit the curve to an equation relating the reaction rate to the concentration of feed. Differentiating that equation, either graphically or mathematically, gives the Rate Model Correlation as a function of longitudinal position along the catalyst bed. A representative graphic technique is discussed in *Graphical Methods for Data Analysis*, John M. Chambers, Chapman and Hall, May 1983, ISBN: 0412052717.

[0077] In order to determine the effects of temperature and pressure on the integral kinetics of the system, the above-described experiment can be run at different temperatures and at different pressures. The experiment can also be run using different size catalysts. For example, the experiment can be run using the intended commercial size and shape catalyst and also with a diluted crushed or powdered catalyst.

[0078] The intrinsic and differential kinetics, free of mass transfer and heat transfer effects, of the composite multistage series-connected fixed bed catalytic system of the invention can also be investigated for purposes of scale-up to a commercial system using the systems depicted in FIGS. **1-7** of the drawings. Using the system depicted in FIG. **7** as an example, the catalyst beds of the reactor stages include very finely crushed or powdered catalyst particles in order to avoid mass transfer effects, and the catalyst is highly diluted to avoid heat transfer effects. Additionally, the diameter of the reactor should preferably be small, typically about 5 to 12 millimeters to further avoid heat transfer effects. This can be accomplished by using a smaller diameter reactor or by using a heat conductive sleeve in each reactor stage to reduce its diameter. The depth of the catalyst bed in each of the reactor stages is typically between about 5 and 10 centimeters. The same series of measurements and calculations are performed as described above for determining the integral kinetics of the system. In determining the differential kinetics of the system the amount of conversion in each reactor stage should be very small, e.g. less than 20 percent, preferably about 2 to 5 percent. The measurements can be performed at different temperatures and pressures in order to investigate the effects of temperature and pressure on the intrinsic and differential kinetics of the system.

[0079] While these kinetics measurements have been described with relation to FIG. **7**, it would also be possible to use the other disclosed reactor systems such as that described with relation to FIG. **1** or **5** of the drawings, using enough series-connected reactor stages to give the necessary of longitudinal information along the composite catalyst bed. A significant advantage of the system of FIG. **7** of the drawings is that the use of the reactor **171** to supply the effluent to all of the reactor stages in module **151** means that each of the reactor stages in the module **151** receives exactly the same reaction products and byproducts and trace elements, thereby replicating actual reactor conditions more exactly and eliminating errors resulting from variations in the composition of the feed to the reactor stages. Additionally, the composition of the inputs and outputs from all of the reactor stages can be sampled substantially simultaneously to give a snapshot of the reactor's performance at a given moment. The sampling of the composition of the inputs and outputs from the reactor stages can also be repeated periodically while the reactor system continues to operate thereby investigating the performance of the reactor system as a function of time on stream to see what aspects of the reactor performance change and in what longitudinal zones of the overall catalyst bed the changes occur. This data is useful in investigating the catalyst stability, among other things.

[0080] The kinetics of deep desulfurization is governed by the extent to which desulfurization (HDS) occurs by direct sulfur extraction, or by hydrogenation of the sulfur-containing molecule followed by sulfur extraction. The direct route is primarily inhibited by hydrogen sulfide, and the hydrogenation route by specific nitrogen-containing compounds. Certain catalysts are known to exhibit different preferences for the two routes, and this is ultimately important to the overall amount of hydrogen that will be required to process a given amount of sulfur containing feed. Thus, a detailed understanding of the kinetics of deep desulfurization is used to select the most suitable catalyst for a given service and to evaluate the relative advantages of a revamp versus a grass-roots unit with respect to investments, hydrogen costs and product properties.

[0081] The problem of deep removal of sulfur has become more serious due to the lower and lower limit of sulfur content in finished gasoline and diesel fuel products by regulatory specifications, and the higher and higher sulfurcontents in the crude oils. A survey of the data on crude oil sulfur content and API gravity for the past two decades reveals a trend that U.S. refining crude slates continue towards higher sulfur contents and heavier feeds. Consequently there is a growing need for newer and more efficient catalysts for deep desulfurization, and the present invention enables such materials to be developed in a more timely, cost effective and efficient way.

[0082] Mass Transfer

[0083] Methods of investigating the mass transfer characteristics of a catalytic process in a plug flow reactor, such as a fixed bed reactor, typically involve a comparing the conversion versus residence time characteristics at a given set of operating conditions of a finely crushed with that of a commercial-size catalyst. The crushed catalyst is screened to a narrow particle size range, preferably one that is close to the minimum obtainable catalyst particle size that still retains its catalytic properties. This minimum catalyst particle size depends on the characteristics of the specific catalyst being used, and can be determined by simple experimentation. In the more simple method for determining the mass transfer characteristics, the finely crushed and screened catalyst is assumed not to have any mass transfer limitations, so that any difference in the conversion versus residence time characteristics between the crushed catalyst and the commercial-size catalyst is assumed to be the result of mass transfer limitations. For a given feed, the effluent of the two reactors is sampled to determine the amount of conversion. Alternatively, the input flow rates of the two reactors can be adjusted (i.e., the input flow rate to the crushed catalyst in reactor is increased, or the input flow rate to the commercial-size catalyst reactor is decreased) so that each of the reactors has the same percentage conversion, and that difference in residence times is attributed to mass transfer limitations in the commercial-size catalyst.

[0084] In a more rigorous and technically exact method of determining the mass transfer characteristics of a commercial-size catalyst, the finely crushed catalyst is not assumed to have zero mass transfer limitations, and the Thiele Modulus of the commercial catalyst is determined from the ratio of the observed reaction rates of the crushed and commercial-size catalysts and the ratio of their particle sizes. The Effectiveness Factor for the commercial-size catalyst can then be determined from a plot of the effectiveness factor versus the Thiele Modulus. This method is described in Hougen and Watson, Chemical Process Principles, Part III, Kinetics and Catalysts, pp. 998-1000, Wiley, March 1966, which is incorporated herein by reference.

[0085] The intra-particle diffusion effect on hydrodesulphurization of model compounds such as dibenzothiophenic compounds in light cycle oil can be determined experimentally by varying the average particle size and determining the effect of that change on overall catalyst activity and selectivity. The catalyst effectiveness factors can then be determined for a full-size catalyst and its crushed catalyst particles under similar operating conditions. In the full-size commercial catalyst, significant intra-particle diffusion resistance is possible, resulting in reduced sulphur removal reaction rates for all the dibenzothiophenic and related sulfur containing reactants in the feed. The effectiveness factors are a good measure of the degree of intraparticle mass transfer resistance and need to fall in the range of 0.3 or higher, preferably 0.8 to 0.9 to achieve desired performance. It is also important to determine the effect of intraparticle mass transfer resistance as a function of the geometric properties of sulfur bearing reactants and this can be achieved by use of model DBT compounds with various substituent groups that increase their molecular size. A problem with both of these methods is that they does not give any information concerning longitudinal variations in mass transfer performance along the reactor catalyst bed and basically assumes that the mass transfer characteristics are uniform from input to output. This assumption is incorrect for many catalytic systems, and the inability to investigate the longitudinal variations in mass transfer characteristics in a fixed catalyst bed has meant that information which would allow the optimization of the catalyst bed along its length has not been available.

[0086] In accordance with the present invention, the catalyst beds of the plug flow reactors are segmented longitudinally into at least three series-connected stages and the effluent of each of the stages is sampled to determine the amount of conversion occurring in each longitudinal segment of the catalyst bed. Referring again to FIG. **1** of the drawings, in accordance with the present invention, each of the reactors **11** and **35** includes three or more reactor stages with sampling valves between the output of each stage and the input of the succeeding stage for measuring the content of the effluent of each stage. The temperature control device **33** maintains both of the reactors **11** and **35** in a common thermal environment. The reactors **11** and **35** both receive the identical reactant input feed from the source **31**. In performing a basic mass transfer investigation, the sources **55**, **57** and **59** are preferably not used. The catalyst beds **19**, **21** and **23** in reactor stages **13**, **15** and **17** of reactor **11** contain a finely crushed and screened or powdered catalyst mixed with enough inert diluent particles so that the operation of the reactor **11** is essentially isothermal

[0087] The catalyst beds **43**, **45** and **47** in reactor stages **37**, **39** and **41** of reactor **35** are composed of commercial-size catalyst particles that are also mixed with a lesser percentage of inert diluent particles so that the operation of reactor **35** is also essentially isothermal. To investigate the longitudinally-dependent mass transfer characteristics of the commercial-size catalyst in accordance with the method of the invention, each of the reactors **11** and **35** receive the identical reactant feed from the source **31** and the pressure and the feed rate for each of the two reactors is held constant. The conversion versus residence time relationship is obtained for each stage of the reactors **11** and **35** from the difference in the amount of reactant feed at the inlet and outlet of each reactor stage and the flow rate, for a given set of operating conditions.

[0088] In the simplified method of determining mass transfer limitations, the Effectiveness Factor for the commercial-size catalyst is obtained for the commercial-size catalyst at each stage of the reactor **35** by taking the ratio of the Observed Reaction Rates of the commercial-size catalyst and the crushed catalyst for each reactor stage. The Observed Reaction Rate is obtained for each reactor **11** and **35** by plotting the cumulative conversion of reactant and corresponding cumulative appearance of the product and byproducts (if any) versus residence times at the outputs of the reactor stages of each reactor and fitting curves to the data using well-known techniques. See, e.g., *Graphical Methods for Data Analysis*, John M. Chambers, Chapman and Hall, May 1983, ISBN: 0412052717. The slope of the resulting curve for the product at any residence time or conversion level for one of the reactors **11** or **35** is the Observed Reaction Rate, K_o (conversion per unit of residence time) for such reactor for such product. If mass transfer were not limiting, the K_o would be independent of particle diameter. A comparison of the plots of K_o versus conversion for the two reactors defines the longitudinal areas of the composite catalyst bed of the reactor **35** containing the commercial-size catalyst in which mass transfer through the catalyst pores is limiting. The Effectiveness Factor for a catalyst in a reactor is equal to the K_o divided by the Intrinsic Reaction Rate, for such catalyst in the reactor. In the simplified method, the crushed catalyst is assumed not to have any mass transfer limitations, so that its K_o is equal to the K_i for the catalyst. Therefore, the Effectiveness Factor for the commercial-size catalyst at any point along the composite catalyst bed of reactor **35** is equal to the ratio of the K_o of the commercial-size catalyst to that of the crushed catalyst at such point along the catalyst beds.

[0089] If the Hougen and Watson method is used, the K_o of the crushed catalyst is not assumed to be equal to the K_i. According to this method, it is possible, using the graph of FIG. **8** of the drawings, to determine the Thiele Modulus for the commercial-size catalyst at any point along the catalyst bed from the ratio of K_o's at such point and the ratio of the particle diameters of the commercial-size and crushed catalysts. For instance, if the ratio of the particle diameter of the crushed catalyst to that of the commercial-size catalyst is 0.2, and the ratio of K_o of the commercial-size catalyst to that of the crushed catalyst is 0.34 at a given point along the catalyst beds, the Thiele Modulus at that point is about 9. Using the graph of FIG. **9**, the Effectiveness Factor for the commercial-size catalyst at that point along the composite catalyst bed of reactor **35** is about 0.27. The determination of the longitudinally dependent Effectiveness Factor for the catalyst bed containing the commercial-size particles can be performed repeatedly during running of the reactors **11** and **35** to determine the effect of time on stream on the mass transfer characteristics of the fixed bed catalyst system. The measurements can also be repeated at different operating conditions of temperature and pressure in order to investigate the longitudinally dependent effects of changes in these parameters on the mass transfer characteristics of the composite catalyst bed of the plug flow reactor **35**.

[0090] Because the Effectiveness Factor is the ratio of K_o to the it is possible to calculate the K_i for a catalyst from the Effectiveness Factor and the K_o for a given longitudinal point along the catalyst bed. Since K_i is the same for the crushed and commercial-size catalysts, the Effectiveness Factor for the commercial-scale catalyst at any point along the catalyst bed can be determined from the K_o for the crushed catalyst at that point and the K_i.

[0091] For reactions in which different reaction pathways are possible in different longitudinal portions of the catalyst bed of the plug flow reactor, e.g., conversion of sulfur or nitrogen containing feedstocks, carburization, or the production of methane via hydrogenolysis, it is important also to characterize the behavior of the different kinetic pathways producing the product and various byproducts that can exist for the system as they vary along the length of the composite catalyst bed of the reactor in order to explore the longitudinally dependent kinetic and mass transfer space for the system, and to distinguish between the occurrence of mass transfer and kinetic effects in the system. When this space has been explored, the mass transfer performance of reactant to product for the system operating at a given set of conditions that involve an optimal set of trade-offs for the particular catalyst can be investigated.

[0092] An example of the opportunity to optimize the longitudinal characteristics of a catalyst bed of a fixed bed reactor afforded as a result of the data obtained by the method of the present invention is illustrated in connection with the graph in FIG. **10** of the drawings. This graph depicts what is believed to be a typical relationship between the Effectiveness Factors and conversion rates for crushed and commercial-size catalysts in a fixed bed reactor working at a given set of operating conditions of temperature and pressure and with a common reactant feed. Mass transfer limitations are clearly present up to the point in each of the fixed bed reactor catalyst beds at which about 50 to 60% conversion has occurred, but are not present at the portions of the catalyst beds at which greater than about 70% conversion has occurred. The greater mass transfer limitations, evidenced by of the lower Effectiveness Factor, of the bed containing the commercial-size catalyst particles is believed to reflect the differences in the lengths of the reaction pathways in the crushed and commercial-size catalyst particles. This suggests that buildup of material, such as wax, in the catalyst pores is present at the portion of the reactor catalyst bed at which lower conversion has occurred, i.e., close to the inlet of the reactor bed where the catalyst experiences almost entirely fresh feed, but not present at lower portions of the catalyst bed at which higher conversions have occurred.

[0093] In a hydroprocessing reactor, a lower Effectiveness Factor may result in an undesirable higher methane make and/or carbon overlayer formation. Thus, particularly in the reactor containing the commercial-size catalyst bed, the upper portions of the catalyst bed would be producing substantial amounts of methane. This results in a much lower diffusivity of the reactant gases in such pores, so that the active sites within the catalyst become starved of reactants and begin generating large amounts of methane. In order to optimize the catalyst bed structure of the fixed bed reactor to avoid the undesirable high methane make in the inlet portions of the catalyst bed, it is possible, for instance, to use a less active catalyst in that portion of the reactor bed, which would generate lesser amounts of methane.

[0094] As an alternative to using crushed in commercial size catalyst particles of different sizes in an investigating the mass transfer characteristics of the catalyst bed in a plug flow reactor, is possible to use the same size particles with different levels of catalyst loading. The particles would be made up of finely crushed or powdered catalyst dispersed and inert diluent such as alumina or silica. The powder or finely crushed catalyst is uniformly mixed with the finely crushed inert diluent, formed into particles of a given size and sintered. Particles in which the catalyst concentration is selected to be relatively low can correspond to the crushed catalyst in the method described above. Particles in which the catalyst concentration is relatively higher can correspond to the commercial-size catalyst. The concentration of catalyst within the particles appropriate for the particles to correspond to crushed catalyst or commercial-size catalyst depends on the activity of the catalyst and the nature of the reaction.

[0095] In scaling-up a reactor to commercial size, is preferable to confirm the mass transfer characteristics determined under isothermal conditions in the manner described above in an adiabatic reactor. In an adiabatic reactor, the amount of diluent for the commercial-size catalyst is reduced and the tube diameter is controlled so that its thermal performance mirrors that expected for the commercial-size reactor.

[0096] In investigating mass transfer effects in a hydroprocessing reactor, as an alternative to plotting the reaction rate versus conversion or residence times, is to plot the methane selectivity versus conversion. Methane selectivity is greater when mass transfer limitations exist. Mass transfer is an issue only in those parts of the reactor where methane selectivity is widely different for the commercial and crushed catalyst. Between about 35% and 80% conversion, the methane selectivity is very low. In this region, mass transfer is not an issue. In the portion of the catalyst bed where above about 80% conversion has occurred, the methane selectivity increases rapidly and the reaction rate slows down for both the crushed and the commercial catalyst. This is an indication that something other than mass transfer effects is limiting the catalyst activity and increasing the methane selectivity.

[0097] Heat Transfer Effects

[0098] Understanding the heat transfer performance of a plug flow reactor is critical to maximizing the productivity at which the reactor can be run. The temperatures in the catalyst bed of a plug flow reactor can vary both longitudinally and laterally within the catalyst bed. For endothermic reactions, there can be the need to get heat into cold spots in the catalyst bed or the reaction may shut down.

[0099] The reactor system illustrated in FIG. **2** of the drawings can also be used to investigate heat transfer characteristics of a plug flow reactor system. For example, the catalyst beds in the reactor stages **13**, **15** and **17** of the reactor **11** can contain a mixture of crushed catalyst and inert diluent particles, and the catalyst beds in stages **37**, **39** and **41** of the multistage reactor **35** can contain mixtures of full-size catalyst particles and inert diluent particles. And both cases the ratios of catalyst particles to inert diluent particles are selected so that the reactor's **11** and **35** operate substantially isothermally. The catalyst beds of the reactors **11** and **35** are instrumented with thermocouples (not shown) to measure in the temperatures at successive longitudinal positions along the catalyst beds, both in the central portion of the bed cross-section and near its periphery. In addition, the effluent of each of the reactor stages is sampled by sampling valves **25**, **27** and **29** of multistage reactor **11** and sampling valves **49**, **51** and **53** of multistage reactor **35**. Lateral heat transfer effects can be further studied by inserting conductive sleeves in the reactor stages in order to decrease the catalyst bed diameter so that the heat generated in the central portion of the bed has less distance to travel to the heat sink formed by the reactor walls and the temperature control device **33** surrounding the reactor walls. Successively thinner heat conductive sleeves can be used to incrementally increase of the diameter of the catalyst bed until the bed diameter is such that the heat that cannot be adequately removed from the central portion of the bed through the reactor walls.

[0100] Temperature and product measurements are preferably a repeated for different reactor flow rates, pressures, and productivities, both at Start of Run and during the reactor's time on stream as the reactor lines out. The effect on heat transfer characteristics and other process parameters, such as conversion, selectivity and kinetics, of using catalyst particles of various sizes and shapes in the catalyst bed can also be investigated using the method of the invention. The data obtained from such measurements permits one to investigate and gain an understanding of how the heat transfer properties of the reactor system affect reactor performance over the entire multivariable space in which the commercial-size reactor might operate.

[0101] Referring now to FIG. **11** of the drawings, there is illustrated in alternative embodiment of the apparatus of the invention which can be used for investigating the longitudinally dependent mass transfer, kinetics and heat transfer characteristics of a fixed bed reactor. The plug flow reactor **201**, in this case a fixed bed reactor, contains a bed **203** of commercial sized catalyst particles. Reactor **201** is supplied with fresh reactant feed from the source **205**. Effluent from the reactor **201** is supplied to fixed bed reactor stages **207-1** through **207-*n*** through control valves **209-1** through **209-*n*** for feeding controlled amounts of effluent from reactor **201** to such reactors. Each of the reactor is **207-1** through **207-*n*** contains a narrow catalyst bed **211-1** through **211-*n*** of catalyst particles mixed with enough inert diluent particles so that the catalyst beds operate in a substantially isothermal mode. The source **205** also supplies controlled amounts of fresh reactant feed to the inlets of the reactor stages **207-1** through **207-*n*** through control valves and **211-1** through **211-*n***. The effluents from the reactor or stages **207-1** through **207-*n*** can be sampled by means of sampling valves **215-1** through **215-*n***.

[0102] If the reactor **201** is operated at a given conversion level, e.g. 80%, the input to the individual reactor stages **207-1** through **207-*n*** can represent any degree of conversion from zero to 80% by using the control valves **209-1** through **209-*n*** and **213-1** through **213-*n*** to adjust the ratio of reactor **201** effluent to fresh feed being supplied to the individual reactor stages **207-1** through **207-*n***. Thus, if the valves **209-1** and **213-1** are adjusted such that reactor stage **207-1** receives only effluent from the reactor **201**, and the thickness of the catalyst bed **211-1** is such that it performs an additional 5% conversion on such effluent, the catalyst bed **211-1** is equivalent to a cross-sectional slice of a fixed bed reactor in which the conversion between 80 and 85% takes place. Similarly, if the valves **209-2** and **213-2** are adjusted such that the input to reactor stage **207-2** is equivalent to the effluent of a reactor operating at 40% conversion, and the thickness of the catalyst bed **211-2** is such that it performs an additional 5% conversion on such effluent, the catalyst bed to an **11-2** is equivalent to a cross-sectional slice of a catalyst bed in which the conversion between 40 and 45% takes place. Thus, the catalyst beds **211-1** through **211-*n*** can replicate the performance of a cross-sectional slice of a fixed bed reactor positioned at any longitudinal position along the catalyst bed.

[0103] The catalyst beds **211-1** through **211-***n* need not all have the same composition. For instance, the beds **211-1** and **211-2** could contain crushed and commercial-size catalyst particles, respectively, in each case mixed with an amount of inert diluent particles such that the beds operate in isothermal mode. In this case the mass transfer, heat transfer and kinetics characteristics of a cross-sectional slice of a catalyst bed located at any longitudinal position in the catalyst bed can be investigated. In a different application, the catalyst beds **211-1** through **211-***n* could contain catalyst particles of different chemical or physical composition. In order to prevent heat loss or gain in the effluent from the reactor **201** being fed to the reactor stages **207-1** through **207-***n*, the connecting tubing and valves are preferably surrounded by insulating material and the entire system comprising the reactor **201** and the reactor stages **207-1** through **207-***n* can be surrounded by a temperature control device, or alternatively, the reactor **201** and reactor stages **207-1** through **207-***n* can be surrounded by separate temperature control devices, depending on the needs of the application. Additionally, the reactant feed from the source **205** being supplied to the reactor stages **207-1** through **207-***n* can be heated before it is supplied to such reactor stages by well-known indirect heating means such as a coil in a sand bath or an infrared furnace (not shown) in order to have the appropriate temperature conditions in the catalyst bed inlet portions of such reactor stages.

[0104] The apparatus disclosed in FIGS. **2**, **4**, **7** and **11** can also be used to investigate other operating parameters of a plug flow reactor for scale-up or other purposes in accordance with the method of the invention. For example, the longitudinally dependent activity maintenance of a catalyst bed can be investigated as a function of time on stream under different conditions of temperature, pressure and catalyst shape and size. Other longitudinally dependent process parameters that can be investigated using the method of the invention include the effects of different space velocities, reaction products and by-products, different operating temperatures and pressures, time on stream, and different catalyst sizes and shapes, on matters such as e.g., conversion, productivity, kinetics and selectivity, and on changes in catalyst physical and chemical properties such as active site crystal size, oxidation, and growth of an over-layer of support on the surface of the catalyst active sites.

[0105] Using present invention, the time for scale-up of the catalytic process from discovery to commercial scale application can be significantly reduced. For example, in one particularly advantageous configuration, four multi-stage reactors of the type described above can be operated in parallel. In this embodiment, the stages of one of the reactors are loaded with crushed catalyst. This reactor provides Intrinsic Reaction Rate and selectivity data. The stages of the second reactor are loaded with commercial-size catalyst. The data from this second reactor can be used to define the degree of mass transfer limitation (Effectiveness Factor) based on a direct comparison of the relative residence times in the reactors containing the crushed catalyst in the commercial-size catalyst required to achieve a given amount of conversion. By obtaining conversion data at a series of residence times, it is possible to determine the Effectiveness Factor and hence the Effective Diffusivity with conversion or residence time. This data also provides information on the impact of mass transfer on selectivity. A third, probe reactor can be operated in parallel with the previous two reactors. This probe reactor can either be a shallow fixed bed reactor or a back-mixed reactor. Flow can be directed to the appropriate actor from any of the reactor beds in the previous two reactors. In addition, additional gases or liquids can be added to the probe reactor to determine the rates of adsorption or surface property changes on the catalyst. This information can provide valuable insight in modeling the fixed bed reactor. Finally, an adiabatic reactor can be operated in parallel to test the reactor model developed from the previous reactors. Operation of the series reactors in this parallel mode allows for much faster generation of the required scale-up data. In fact, all the required scale-up data, including deactivation and regeneration data, at one temperature can be obtained in one to two years, for a savings of several years of development time. A further improvement to the experimental design would be to operate several four reactor sets at the same time. These sets can be operated at different temperature, pressure, and feed compositions. The set producing the optimum economics can be used for the commercial design. The cost of operating several parallel sets of series reactors simultaneously is a small expense when compared to the potential savings associated with accelerating the scale-up of a new catalyst to a full-scale commercial operation. If the new catalyst results in a $1/barrel savings, a 100 thousand barrel/day plant will produce a savings of over $30 million per year. These savings would easily far more than offset the cost of operating the parallel sets of series reactors.

[0106] In an adiabatic reactor, it is possible to produce hot spots in the reactor, which may cause the adiabatic reactor to run away. Also, in an adiabatic reactor, because reaction parameters, such as temperature, kinetics parameters, etc., can change continuously, it is difficult to measure the reaction parameters by direct measurement. Dividing an adiabatic reactor into multistage series-connected reactor stages can help determine reaction parameters at different locations along a flow direction of the reactor, but it is difficult to keep continuities of the reaction parameters, especially temperature, between adjacent reactor stages.

[0107] Therefore, it is difficult to directly measure reaction parameters in an adiabatic reactor, and to exactly and securely determine reaction characteristics in the adiabatic reactor, such as kinetics, mass transfer, heat transfer etc.

[0108] FIG. **12** illustrates a schematic diagram of a composite multistage laboratory scale plug flow reactor **607**. The reactor **607** includes first, second and third series-connected reactor stages **61**, **63** and **65**, each having a catalyst bed **62**, **64** and **66**. The reactor **607** further includes a fresh reactant conduit **70** which connects an inlet of the first reactor stage **61** to a source **60**, so that the source **60** can provide feeds, which are normally fresh reactants, to the first reactor stage **61**. The reactor **607** further includes connecting conduits **71** and **72** to connect the first and second reactor stages **61** and **63**, and the second and the third reactor stages **63** and **65**, respectively. A first sampling valve **67** is disposed between the first and second reactor stages **61** and **63**, and has an output **601** to facilitate sampling effluents from the first reactor stage **61**. Here in this document, a device is said to be disposed between two stages of the reactor does not necessarily mean that the device is physically disposed between the two stages of the rector but that the device is between the two stages of the reactor along a flow of reactants. A second sampling valve **68** is disposed on the conduit **72** and has an output **602** for sampling effluents from the second reactor stage **63**. A third sampling valve **69** is disposed between an outlet of the third reactor stage **65** and a device, such as a fourth reactor stage or a product accumulator (not shown) and has an output **603** for sampling effluents from the third reactor stage **65**. A sampling valve connected to the fresh reactant conduit **70** may also be provided in order to permit analysis of the feeds.

[0109] In one embodiment, the reactor stages **61**, **63** and **65** are isothermal reactor stages, which are used together to simulate an adiabatic reactor. Thus, temperature control devices **604**, **605** and **606** are provided to control the temperature of the reactor stages **61**, **63** and **65** respectively. A preheater (not shown) may be disposed between the source **60** and the first reactor stage **61** to preheat the feeds from the source **60** so that when the feeds flow into the first reactor stage **61**, the feeds have already reached a desired temperature for the feeds. Alternatively, the preheater can also be disposed in the first reactor stage **61**.

[0110] In one embodiment, when using the isothermal reactor stages **61**, **63** and **65** to simulate the characteristics of an adiabatic reactor, the temperature setting for each of the temperature control devices **604**, **605** and **606** should be determined first. Generally, for a given catalytic process, based on data derived from operating the adiabatic reactor in practice, the temperature setting for the first temperature control device **604** and temperature variation in the first reactor stage **61** can be determined. Then, based on information from the first reactor stage **61**, the temperature setting of the second temperature control device **605** can also be determined, and so on. Thus, after the temperature settings of each of the temperature control devices **604**, **605** and **606** is determined, the reactor stages **61**, **63** and **65** can be used to simulate the characteristics of the adiabatic reactor.

[0111] In this embodiment, the temperature of the temperature control devices **604**, **605** and **606** are defined as T1, T2 and T3, which are different from each other. Different catalytic processes may have different T1, T2 and T3 settings. Alternatively, a common temperature control device (not shown) can be provided to control the temperatures of reactor stages **61**, **63** and **65** together.

[0112] Thus, the isothermal reactor stages **61**, **63** and **65** can respectively simulate successive catalyst bed slices of a catalyst bed of a larger adiabatic reactor. Thus, the characteristics of the catalyst bed, which is simulated by the catalyst beds **62**, **64** and **66**, are determined. Because it is relatively easy to operate the isothermal reactor stages, characteristics associated with the larger adiabatic reactor can be determined by simulating the adiabatic reactor using the isothermal reactor stages. In this embodiment, the first, second and third reactor stages **61**, **63** and **65** can be arranged upright.

[0113] For a particular catalytic process between at least two successive reactors, for example a particular catalytic process in a multistage series-connected reactor stages, if an effluent fluid from one reactor stage is homogeneous, such as in a gas phase, transferring effluent fluid can be quite straightforward by using a properly sized and shaped tube connecting an outlet of one reactor stage to an inlet of a following reactor stage. In many catalytic processes, however, the effluent from a reactor stage may be in a multiphase state, meaning that it includes one or more gaseous fluids, which are fluids in gas phase (such as gases, vapors or mixtures of gases and vapors), and one or more liquid fluids, which are fluids in one or more liquid phases (such as water phase, oil phase, other immiscible phases and partial emulsion phases, etc.)

[0114] The multiphase fluid is often a multi-component fluid, each component being in its own state, which can be a single-phase state or multiphase state. If the multi-component fluid is in thermodynamic equilibrium, the fluid can be transferred directly by a tube connecting two successive reactor stages.

[0115] However, in certain catalytic processes, such as hydrodesulphurization etc., the multi-component fluid may not be in thermodynamic equilibrium. So, when the multi-component fluid is transferred directly through the tube connecting the outlet of one reactor stage to the inlet of the following reactor stage, the states of the components may vary during the transfer such that continuity or consistency of the fluid between adjacent two reactor stages may be broken. Thus, it is difficult to use the multistage series-connected reactor stages to model a plug reactor and to measure and optimize the corresponding catalytic processes.

[0116] FIG. **13** illustrates a schematic diagram in accordance with one embodiment of the present invention. In this embodiment, a catalytic process development apparatus includes a composite multistage laboratory scale plug flow reactor **707** which includes first and second series-connected reactor stages **71** and **73**. The reactor stages **71** and **73** include catalyst beds **72** and **74**, respectively. The catalytic process development apparatus further includes temperature control devices **701** and **702** disposed on the reactor stages **71** and **73** respectively, and a fresh reactant conduit **77**. The fresh reactant conduit **77** is connected an inlet of the first reactor stage **71** to a source **70** so that the source **70** can provide feeds which are normally fresh reactants to the first reactor stage **71**. In this embodiment, the catalytic process development apparatus further includes a separator **703**, first and second effluent conduits **78**, a gas conduit **75** and a liquid conduit **76**. The first conduit **78** is connected an outlet of the first reactor stage **71** to an inlet of the separator **703**. The gas conduit **75** and the liquid conduit **76** connect the separator **703** to an inlet of the second reactor stage **73**. The second effluent conduit **78** connect an outlet of the second reactor to a following device (not shown), such as another separator. The reactants from the source **70** are fed into the first reactor stage **71**. A multiphase effluent fluid from the first reactor stage **71** is sent into the separator **703**, wherein gaseous fluid(s) in the multiphase fluid are separated from liquid fluid(s), and both are introduced into the second reactor stage **73** through the gas conduit **75** and the liquid conduit **76** respectively.

[0117] Referring to FIG. **3**, the catalytic process development apparatus further includes a flow restrictor **705** disposed on the gas conduit **75** to control flow resistance in the gas conduit **75**, resulting in a gas pressure difference (pressure drop) ΔP between two sides of the flow restrictor **705**. Assuming a gas pressure in the first reactor **71** and the separator **703** is P1, a gas pressure in the second reactor **73** is P2. Thus, P1>P2 due to the flow restrictor **705**, and ΔP=P1−P2.

[0118] In one embodiment, ΔP is large enough so that it can drive the liquid fluid in the separator **703** to enter into the liquid conduit **76** and to flow into the second reactor stage **73** but is also small enough so that it can not affect reactions in the second reactor stage **73**. The flow restrictor **705** can be a restricting valve, an orifice, or other restricting means etc. When properly sized and shaped, the gas conduit **75** can function as the flow restrictor **705**. The flow resistance of the gaseous fluid can be adjusted by many ways, such as electrical, electromagnetic, pneumatic, mechanical or thermal ways etc., which are familiar to those ordinary skills in the art. The electromagnetic ways are preferred.

[0119] Additionally, the catalytic process development apparatus further includes a differential pressure sensor (not shown) disposed across the flow restrictor **705** or two ends of the gas conduit **75** to measure the ΔP. Combined ΔP and physical properties of the gaseous fluid, information about a mass flow rate of the gaseous fluid can be determined.

[0120] In one embodiment, if ΔP is too small, the liquid fluid can not flow but accumulate in the separator **703**. If ΔP is too large, the liquid fluid may keep flowing until all the liquid fluid in the separator **703** is transported to the second reactor stage **73**. When the liquid fluid in the separator **703** is drawn out, the gaseous fluid may flow through the liquid conduit **76**. Thus, ΔP is reduced due to an extra pathway for the gaseous fluid. Then, the liquid fluid begins to accumulate in the separator **703** and blocks the liquid conduit **76**. Subsequently, the ΔP restores to a desired value little by little, and the liquid fluid starts to flow again. Thus, the flow rates of the gaseous and liquid fluids may fluctuate with respect to time because of fluctuation of the ΔP, which is disadvantageous to the second reactor stage.

[0121] In a preferred embodiment, the catalytic process development apparatus includes a liquid level sensor **706** disposed in the separator **703**. The liquid lever sensor **706** monitors variation of a liquid level **704** in the separator **703**. Liquid sensor signals from the liquid level sensor **706** are used to control the flow restrictor **705** to generate a suitable ΔP to drive the liquid fluid in such a manner that the liquid level **704** is maintained at a desired substantially constant level. Thus, the fluctuation of the fluids in the separator **703** can be eliminated. When the liquid fluid is transferred stably through the liquid conduit **76**, the liquid mass flow rate information can also be obtained by using the measured ΔP in combination with physical properties of the liquid fluid.

[0122] In one embodiment, in certain low pressure reactions including low pressure FT synthesis etc., a small pressure drop ΔP may still be too big to tolerate, especially when the reactor stage is long or there are many reactor stages. Additionally, in the process of adjusting ΔP to maintain the liquid level **704** by the liquid level sensor **706** and the flow restrictor **705**, the fluctuation of ΔP may also affect liquid flow in the first reactor stage **71**.

[0123] FIG. **14** illustrates a similar schematic diagram as the diagram of FIG. **13**. In this embodiment, the flow restrictor **705** is removed from the gas conduit **75**, so, there is no pressure drop ΔP on the gaseous fluid. Meanwhile, a liquid pump **707** is disposed on the liquid conduit **76**. The liquid level signals are used to control the liquid pump **707** to maintain the liquid level **704** at the desired constant level. Additionally, because an output pressure of the liquid pump **707** is approximately equal to its input pressure, it does not create a pressure drop between the first and the second reactor stages **71** and **73**.

[0124] In this embodiment, the liquid pump **707** includes a positive displacement pump or a centrifuge pump etc. Additionally, the liquid pump **707** can have metering capability, which can be used to obtain the liquid flow rate information directly. In order to cause the liquid fluid to be distributed uniformly in the second reactor stage **73**, a sprayer or similar spraying devices (not shown) can be adopted inside the reactor stage **73**. Alternatively, a check valve (not shown) may be disposed on the liquid conduit **76** and located behind the liquid pump **707** to prevent the liquid fluid in the liquid conduit **76** from reflux.

[0125] In the embodiments of the present invention, the gaseous fluid and the liquid fluid in the effluent of the first reactor stage **71** are separated in the separator **703**, and then transported to the second reactor stage **73**. Thus, possible interactions between the gaseous fluid and the liquid fluid in the effluent during transport can be minimized, and the potential of altering the states of the components in the effluent by fluid distribution and recombination processes can be reduced. The continuity or consistency of the components of the fluid can be maintained between the first and second reactor stages **71** and **73**. Additionally, separation of the gaseous fluid and the liquid fluid also makes it easy for sampling the fluids for species analysis, whether continuously or intermittently, on-line or off-line.

[0126] As mentioned above, in certain catalytic processes, there are different types of liquid phases for the multiphase effluent fluid. In one example of the FT synthesis, its effluent may contain water phase liquid(s) and oil phase liquid(s). In order to transport such multiphase fluid uniformly, an agitation device (not shown) can be provided to cause homogenization of the multiphase fluid. The agitation device may include a mechanical stirring device, a magnetic stirring device or an ultrasonic stirring device etc. In one embodiment, the ultrasonic stirring device is provided, which can be installed near a bottom of the separator **703**. The ultrasonic stirring device can provide sufficient homogenization of the liquid fluid, while having minimum interference to the performance of the liquid level sensor **706** and also without significantly increasing liquid temperature.

[0127] Referring to FIGS. **13-14**, if the separator **703** is operated in a temperature which is higher than that of the first reactor stage **71**, portions of volatile species in the liquid phase in the separator **703** may be evaporated and enter into the gas phase so as to alter the states of the species. If the separator **703** is operated in the temperature which is lower than that of the first reactor stage **71**, portions of vapors in the gas phase in the separator **703** may be condensed and enter into the liquid phase so as to also alter the states of the species. As a result, variations in the effluent from the first reactor stage **71** can be produced during its transfer to the second reactor stage **73**. Therefore, for certain catalytic processes, it is preferred that the temperature of the separator **703** is the same as that of the effluent from the first reactor stage **71**. Thus, the states of the species of the effluent are preserved.

[0128] Referring to FIG. **15**, for example, in order to keep the temperature of the separator **703** being the same as that of the effluent of the first reactor stage **71**, the separator **703** is integrated into the first reactor stage **71**. The integrated first reactor stage **71** and the separator **703** can enjoy operation simplicity and also minimize the potential of altering the states of the components.

[0129] The composite multistage reactor **707** can include three or more series-connected reactor stages. The outlet of each of the reactor stages can connect to a separator. The separator and the reactor stage can be separate from or integrated with each other. All the reactor stages can also be arranged upright along a vertical line.

1. A method for determining a set of operating parameters for a commercial scale plug flow catalytic process and reactor system for hydroprocessing dirty feedstocks, comprising the steps of:

removing heteroatoms from heterocyclic molecules in said dirty feedstock by feeding selected partial pressures of said feedstock and hydrogen to the inlet the first reactor stage of a first composite multi-stage series-connected laboratory scale plug flow reactor including at least three reactor stages, the catalyst beds of each of said reactor stages including catalyst particles capable of catalyzing the removal by hydrogen of heteroatoms from said heterocyclic molecules, said heteroatom removal process being implemented at a selected set of operating conditions of temperature, pressure, and reactant and reaction product flow rates, and the catalysts in the catalyst beds of said laboratory scale reactor stages having selected sets of characteristics;

sampling the effluents of each of said reactor stages;

measuring the concentration of heterocyclic molecules in said dirty feedstock in the concentrations of heterocyclic molecules and intermediate and final products and by products of the catalytic reaction in the effluents of each of said reactor stages;

repeating steps (a) through (c) at different selected sets of said operating conditions, and/or at different selected sets of characteristics of the catalysts in the catalyst beds of said laboratory scale reactor stages; and

using the results of said measurements obtained in one heteroatom removal operation to influence the selection of catalyst bed characteristics and operating parameters in a subsequent heteroatom removal operation for improving the productivity and selectivity of the laboratory scale plug-flow reactor.

2. The method of claim **1** wherein said measuring step includes the step of measuring the amounts of thiols, amines and alcohols in the effluents of each of said reactor stages.

3. The method of claim **1** further including the steps of:

saturating polynuclear aromatic molecules in the effluent of the said first laboratory scale reactor by feeding selected partial pressures of effluent from the last stage of said first multistage laboratory scale reactor and hydrogen to the inlet of the first reactor stage of a second multistage series-connected laboratory scale plug flow reactor in which each of the reactor stages of said second reactor includes a catalyst bed containing catalyst particles capable of catalyzing the saturation by hydrogen of such polynuclear aromatic molecules, said polynuclear aromatic molecule saturation process being implemented at a selected set of operating conditions of temperature, pressure, and reactant and reaction product flow rates, and the catalysts in the catalyst beds of the stages of said second laboratory scale reactor having selected sets of characteristics;

sampling the effluents of each of the reactor stages of said second multistage series-connected reactor;

measuring the concentration of products and byproducts of the catalytic reactions taking place in said second multistage series-connected reactor in the effluents of each of said reactor stages of said second multistage series connected reactor;

repeating steps (f) through (h) at different selected sets of said operating conditions, and/or at different selected sets of characteristics of the catalysts in the catalyst beds of said second laboratory scale reactor; and

using the results of said measurements obtained in one polynuclear aromatic molecule saturation operation to influence the selection of catalyst bed characteristics and operating parameters in a subsequent polynuclear aromatic molecule saturation operation for improving the productivity and selectivity of said second laboratory scale plug-flow reactor.

4. The method of claim **3** further including the steps of:

cleaving carbon-carbon bonds in cyclic molecules in the effluent of the said second laboratory scale reactor by feeding selected partial pressures of effluent from the last stage of said second multistage reactor and hydrogen to the inlet of the first reactor stage of a third multistage series-connected laboratory scale plug flow reactor in which each of the reactor stages includes a catalyst bed containing catalyst particles capable of catalyzing the cleaving by hydrogen of carbon-carbon bonds in cyclic molecules, said carbon-carbon bond cleaving process being implemented at a selected set of operating conditions of temperature, pressure, and reactant and reaction product flow rates, and the catalysts in the catalyst beds of the stages of said third laboratory scale reactor having selected sets of characteristics;

sampling the effluents of each of the reactor stages of said third multistage series-connected reactor;

measuring the concentration of products and byproducts of the catalytic reactions taking place in said third multistage series-connected reactor in the effluents of each of said reactor stages of said third multistage series connected reactor

repeating steps (k) through (m) at different selected sets of said operating conditions, and/or at different selected sets of characteristics of the catalysts in the catalyst beds of the stages of said third laboratory scale reactor; and

using the results of said measurements obtained in one carbon-carbon bond cleaving operation to influence the selection of catalyst bed characteristics and operating parameters in a subsequent carbon-carbon bond cleaving operation for improving the productivity and selectivity of the third laboratory scale plug-flow reactor.

5. The method of claim **4** further including the steps of:

saturating unsaturated molecules in the effluent of said third multistage laboratory scale reactor by feeding selected partial pressures of effluent from the last stage of said third laboratory scale reactor and hydrogen to the inlet of the first reactor stage of a fourth multistage series-connected laboratory scale plug flow reactor in which each of the reactor stages includes a catalyst bed containing catalyst particles capable of catalyzing the saturation by hydrogen of unsaturated molecules, said unsaturated molecule saturating process being implemented at a selected set of operating conditions of temperature, pressure, and reactant and reaction product flow rates, and the catalysts in the catalyst beds of the stages of said fourth laboratory scale reactor having selected sets of characteristics;

sampling the effluents of each of the reactor stages of said fourth multistage series-connected reactor; and

measuring the concentration of products and byproducts of the catalytic reactions taking place in said fourth multistage series-connected reactor in the effluents of each of said reactor stages of said fourth multistage series connected reactor

repeating steps (p) through (r) at different selected sets of said operating conditions, and/or at different selected sets of characteristics of the catalysts in the catalyst beds of the stages of said fourth laboratory scale reactor; and

using the results of said measurements obtained in one unsaturated molecule saturating operation to influence the selection of catalyst bed characteristics and operating parameters in a subsequent unsaturated molecule saturating operation for improving the productivity and selectivity of the fourth laboratory scale plug-flow reactor.

6. The method of claim **4** further including the steps of:

hydrocracking and isomerizing hydrocarbon molecules in the effluent of said third reactor by feeding selected partial pressures of effluent from the last stage of said third series-connected reactor and hydrogen to the inlet of the first reactor stage of a fourth multistage series-connected laboratory scale plug flow reactor in which each of the reactor stages includes a catalyst bed containing catalyst particles capable of catalyzing the hydrocracking and isomerization by hydrogen of hydrocarbon molecules, said hydrocracking and isomerization process being implemented at a selected set of operating conditions of temperature, pressure, and reactant and reaction product flow rates, and the catalysts in the catalyst beds of the stages of said fourth laboratory scale reactor having selected sets of characteristics;

sampling the effluents of each of the reactor stages of said fourth multistage series-connected reactor;

measuring the concentration of products and byproducts of the catalytic reactions taking place in said fourth multistage series-connected reactor in the effluents of each of said reactor stages of said fourth multistage series connected reactor;

repeating steps (u) through (w) at different selected sets of said operating conditions, and/or at different selected sets of characteristics of the catalysts in the catalyst beds of the stages of said fourth laboratory scale reactor; and

using the results of said measurements obtained in one hydrocracking and isomerization operation to influence the selection of catalyst bed characteristics and operating parameters in a subsequent hydrocracking and isomerization operation for improving the productivity and selectivity of the fourth laboratory scale plug-flow reactor.

7. The method of claim **5** further including the steps of:

hydrocracking and isomerizing hydrocarbon molecules in the effluent of said fourth reactor by feeding selected partial pressures of effluent from the last stage of said fourth multistage reactor and hydrogen to the inlet of the first reactor stage of a fifth multistage series-connected laboratory scale plug flow reactor in which each of the reactor stages includes a catalyst bed containing catalyst particles capable of catalyzing the hydrocracking and isomerization by hydrogen of hydrocarbon molecules, said hydrocracking and isomerization process being implemented at a selected set of operating conditions of temperature, pressure, and reactant and reaction product flow rates, and the catalysts in the catalyst beds of the stages of said fifth laboratory scale reactor having selected sets of characteristics;

sampling the effluents of each of the reactor stages of said fifth multistage series-connected reactor;

measuring the concentration of products and byproducts of the catalytic reactions taking place in said fifth multistage series-connected reactor in the effluents of each of said reactor stages of said fifth multistage series connected reactor;

repeating steps (z) through (bb) at different selected sets of said operating conditions, and/or at different selected sets of characteristics of the catalysts in the catalyst beds of the stages of said fifth laboratory scale reactor; and

using the results of said measurements obtained in one hydrocracking and isomerization operation to influence the selection of catalyst bed characteristics and operating parameters in a subsequent hydrocracking and isomerization operation for improving the productivity and selectivity of the fifth laboratory scale reactor.

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