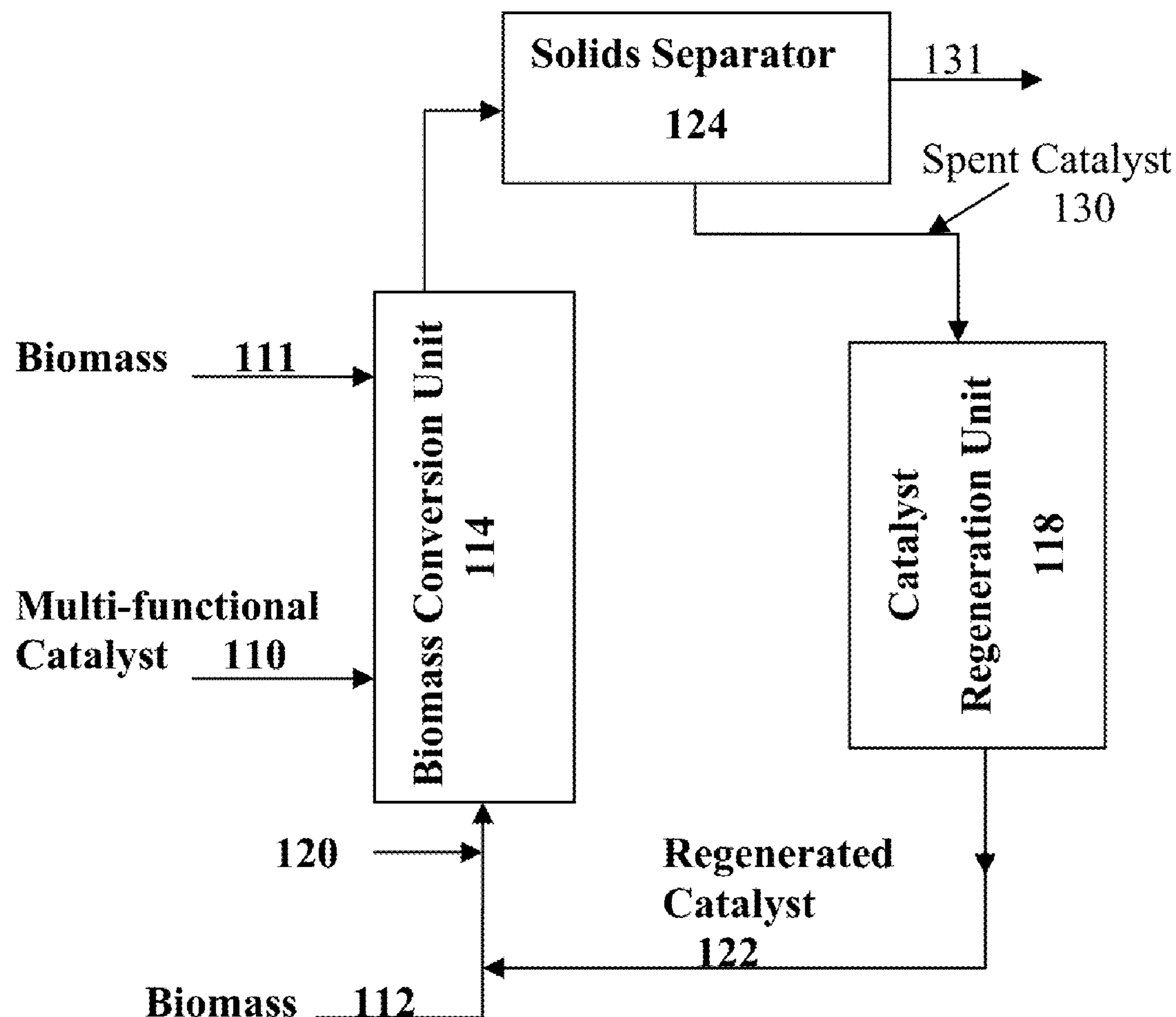


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(19) **United States**(12) **Patent Application Publication**
Ramirez Corredores et al.(10) **Pub. No.: US 2015/0247095 A1**(43) **Pub. Date: Sep. 3, 2015**(54) **METHOD OF BIOMASS CONVERSION
USING A MULTIFUNCTIONAL CATALYST
SYSTEM****Publication Classification**(51) **Int. Cl.**
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Zhou**, Houston, TX (US); **Rocio Banda**,
Houston, TX (US)(57) **ABSTRACT**

Solid biomass may be converted to hydrocarbons for use in renewable fuels uses by feeding biomass into a biomass conversion unit and pyrolyzing the biomass in the presence of a regenerated multi-functional catalyst. The regenerated multi-functional catalyst contains an acidic component, a basic component and a metallic component. The biomass is treated within the biomass conversion unit in at least two stages wherein at least one component of the regenerated multi-functional catalyst is fed into each of the stages.

(21) Appl. No.: **14/168,796**(22) Filed: **Jan. 30, 2014**

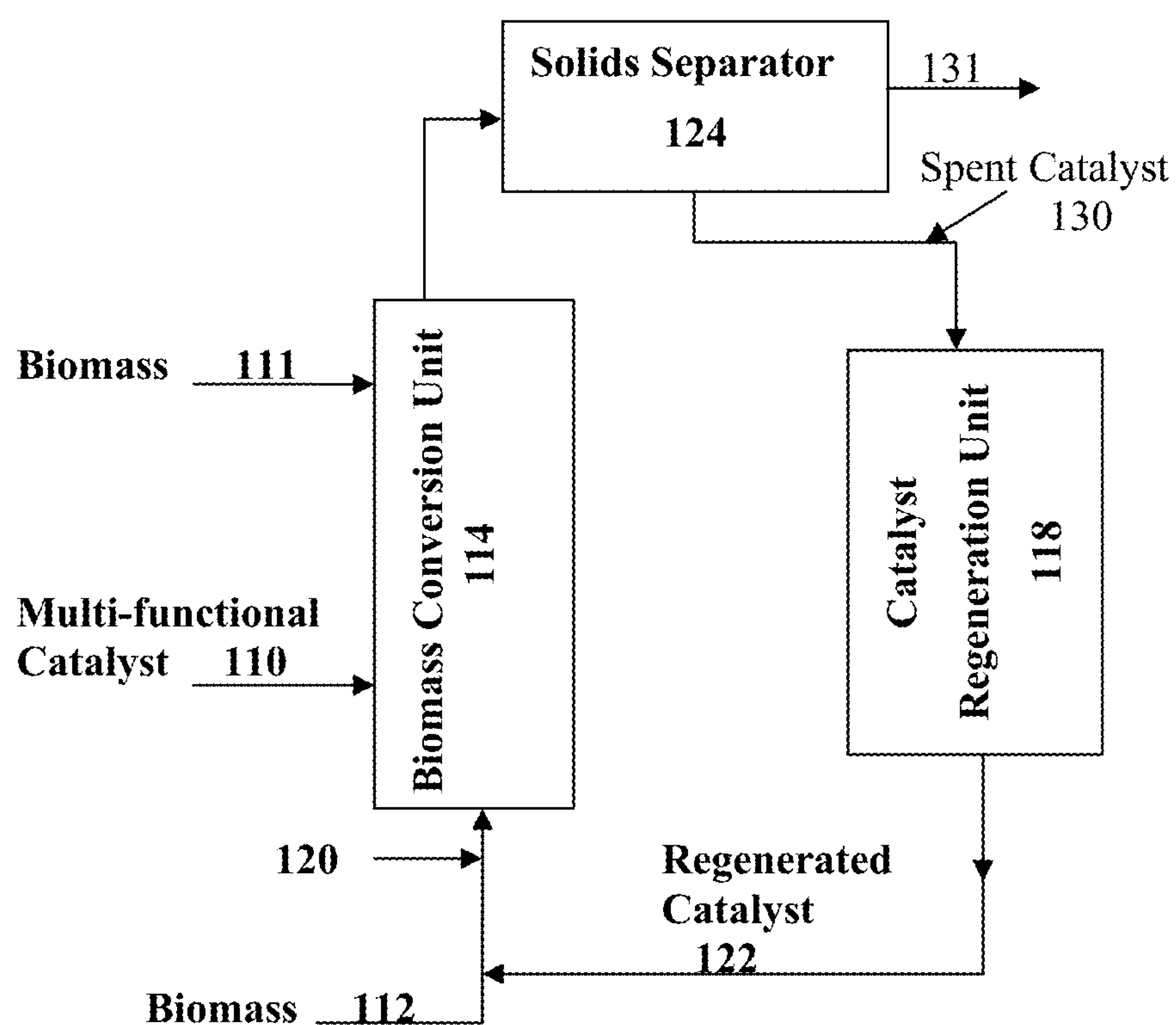


FIG. 1

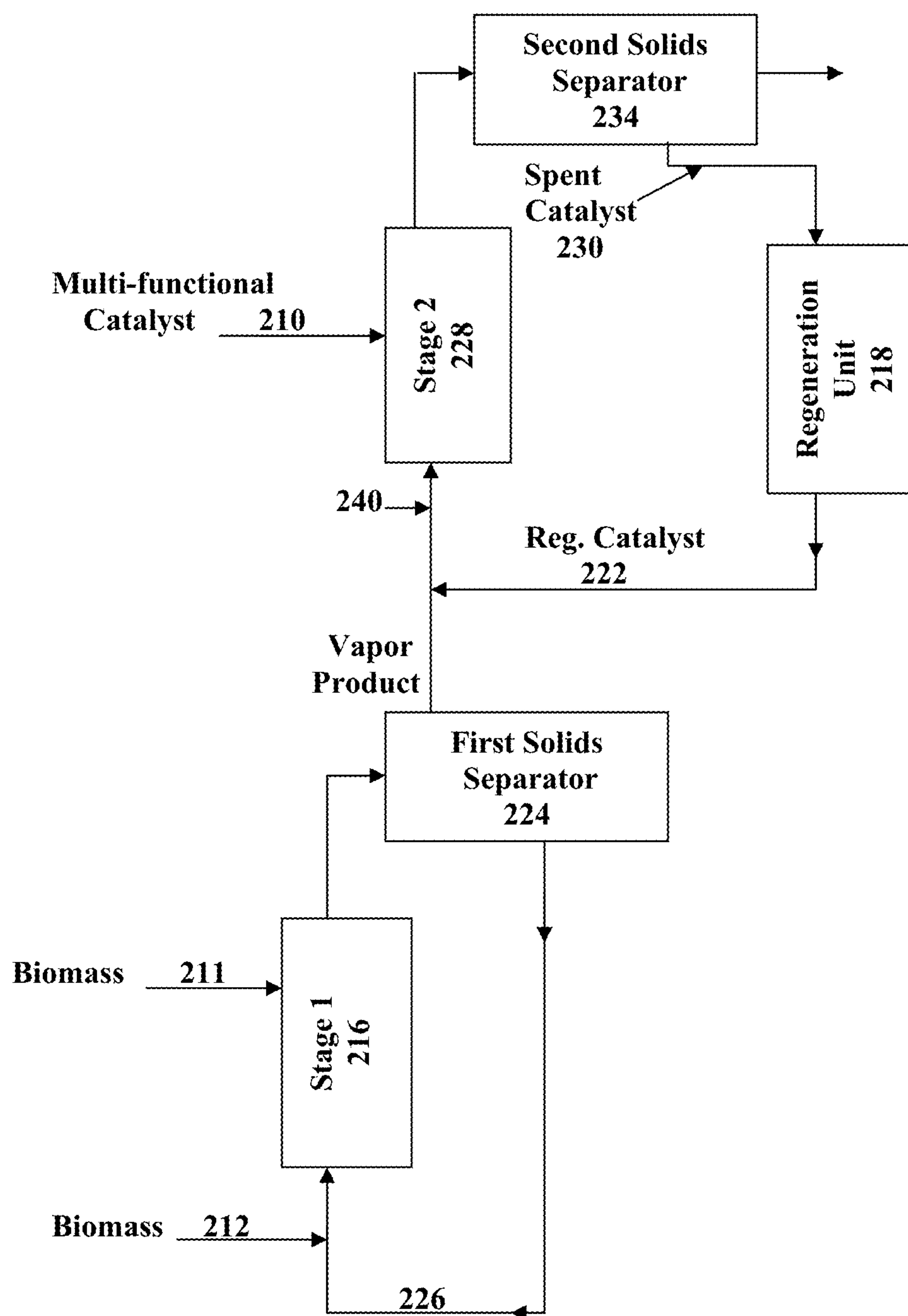


FIG. 2

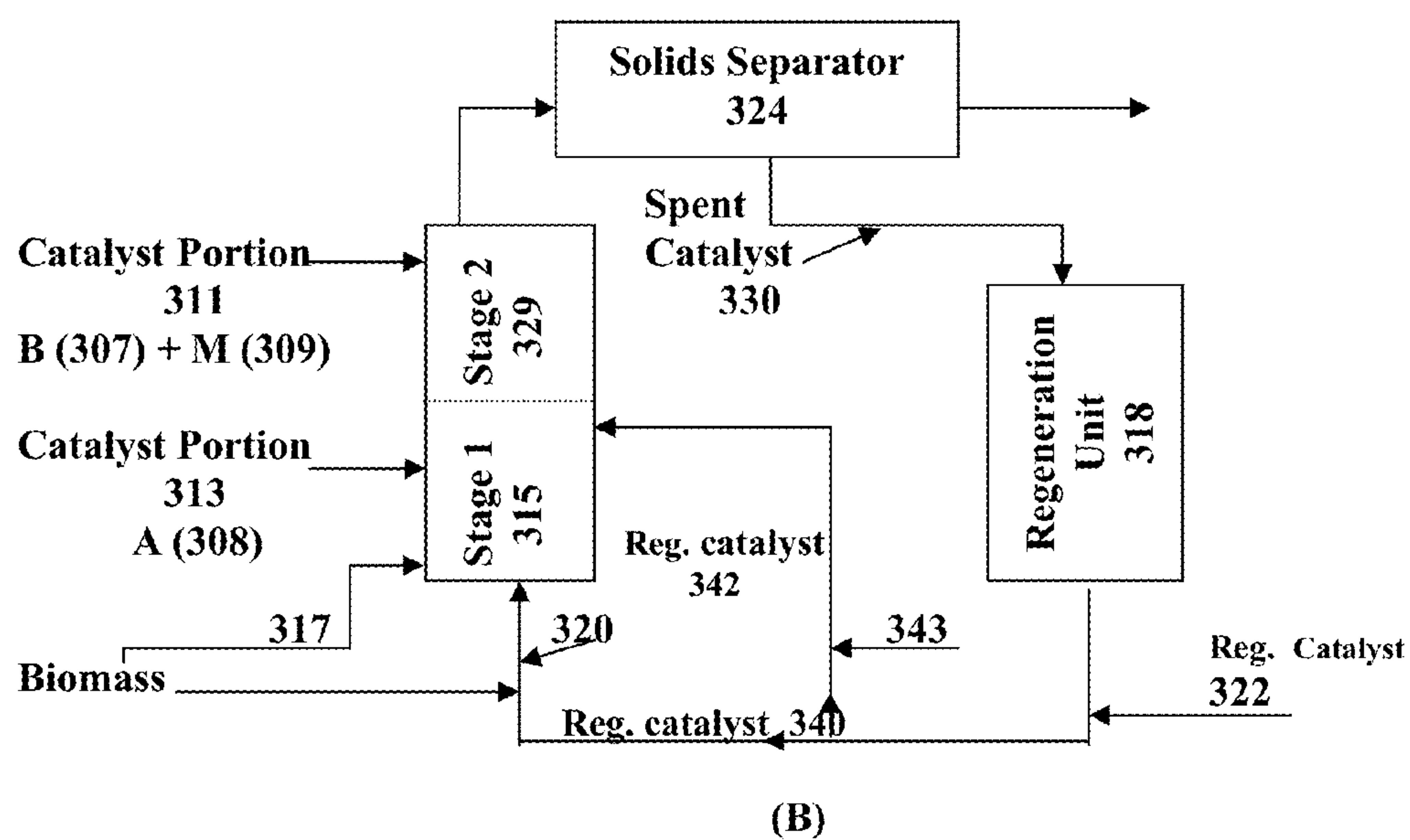
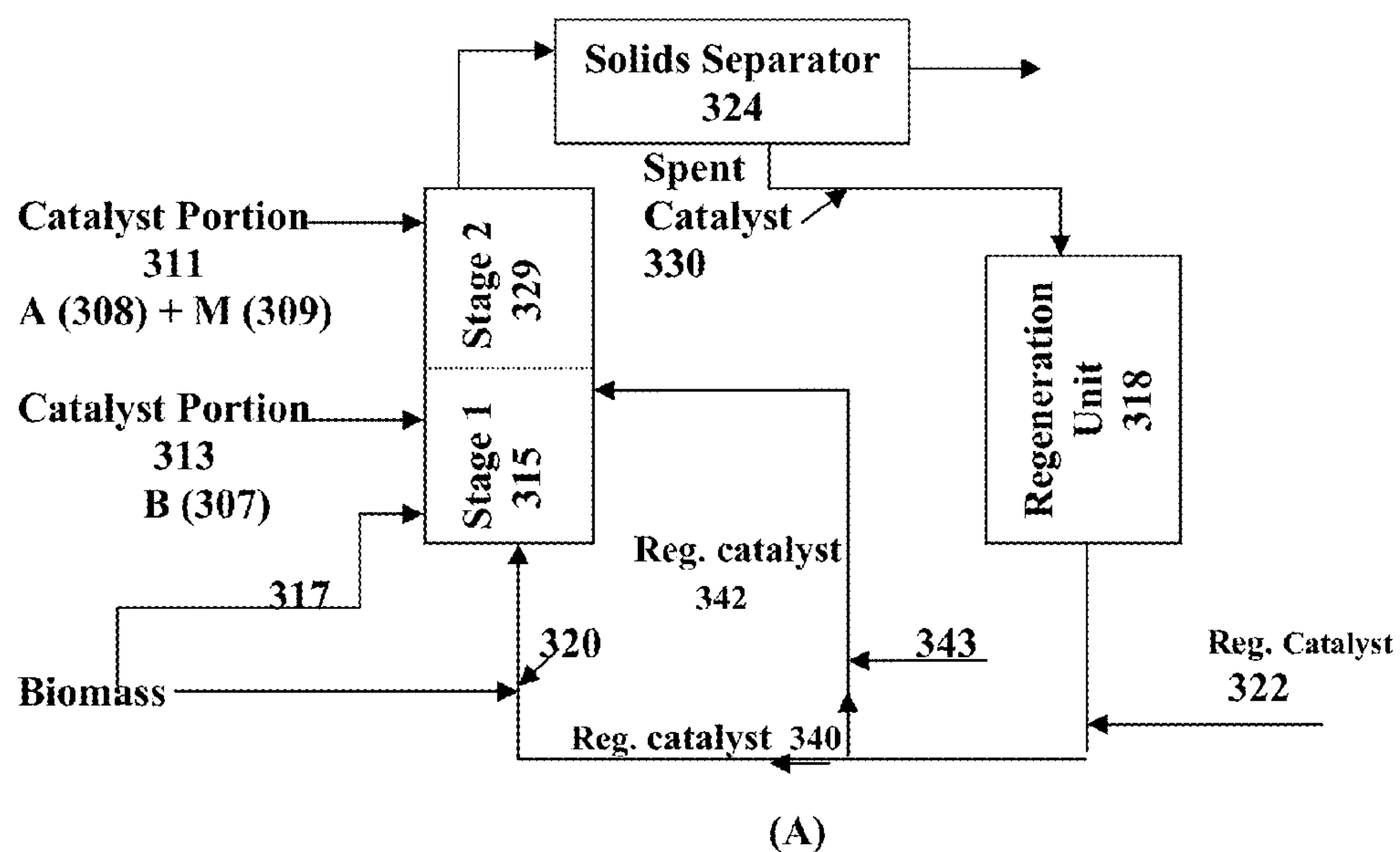
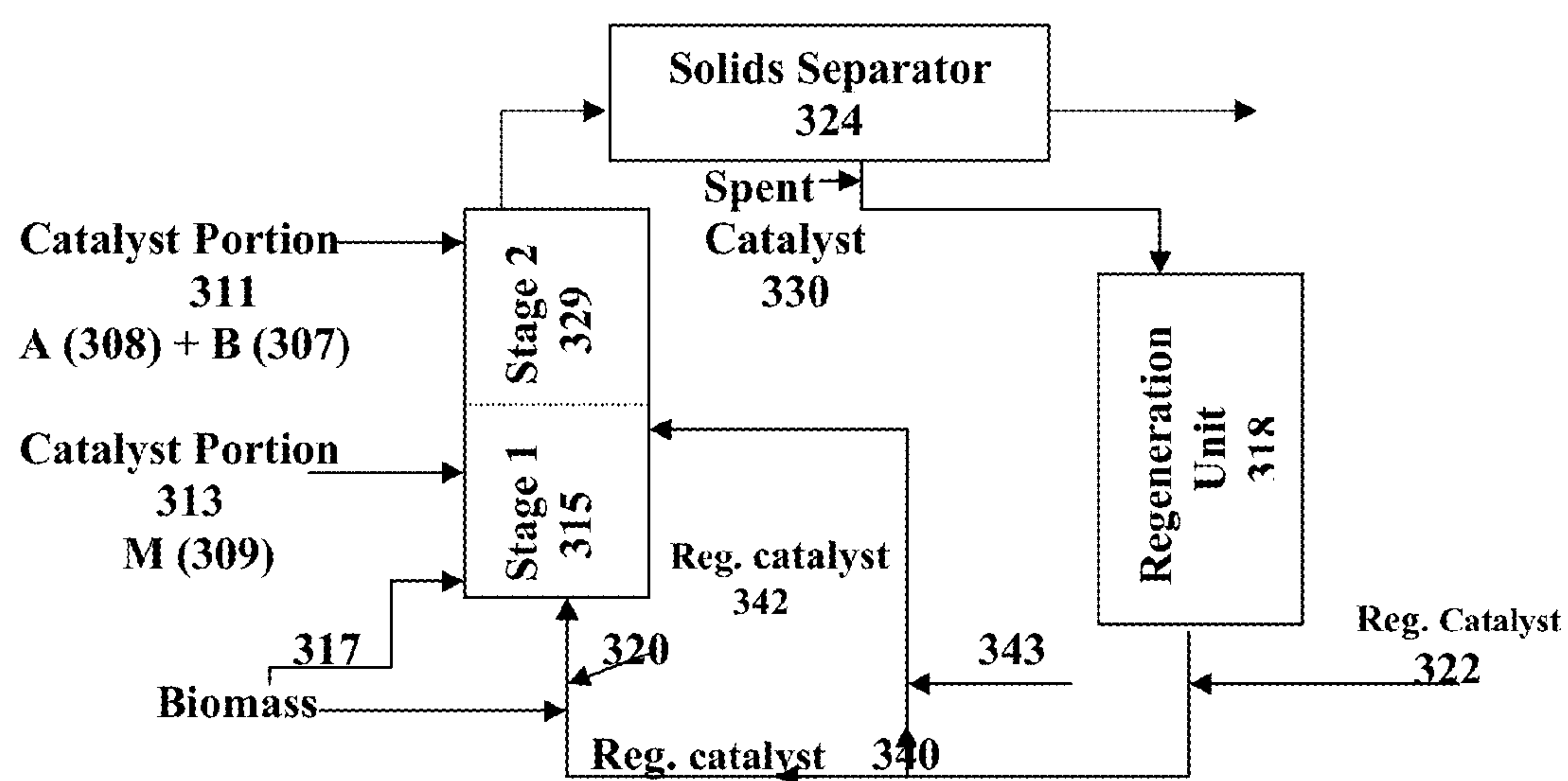
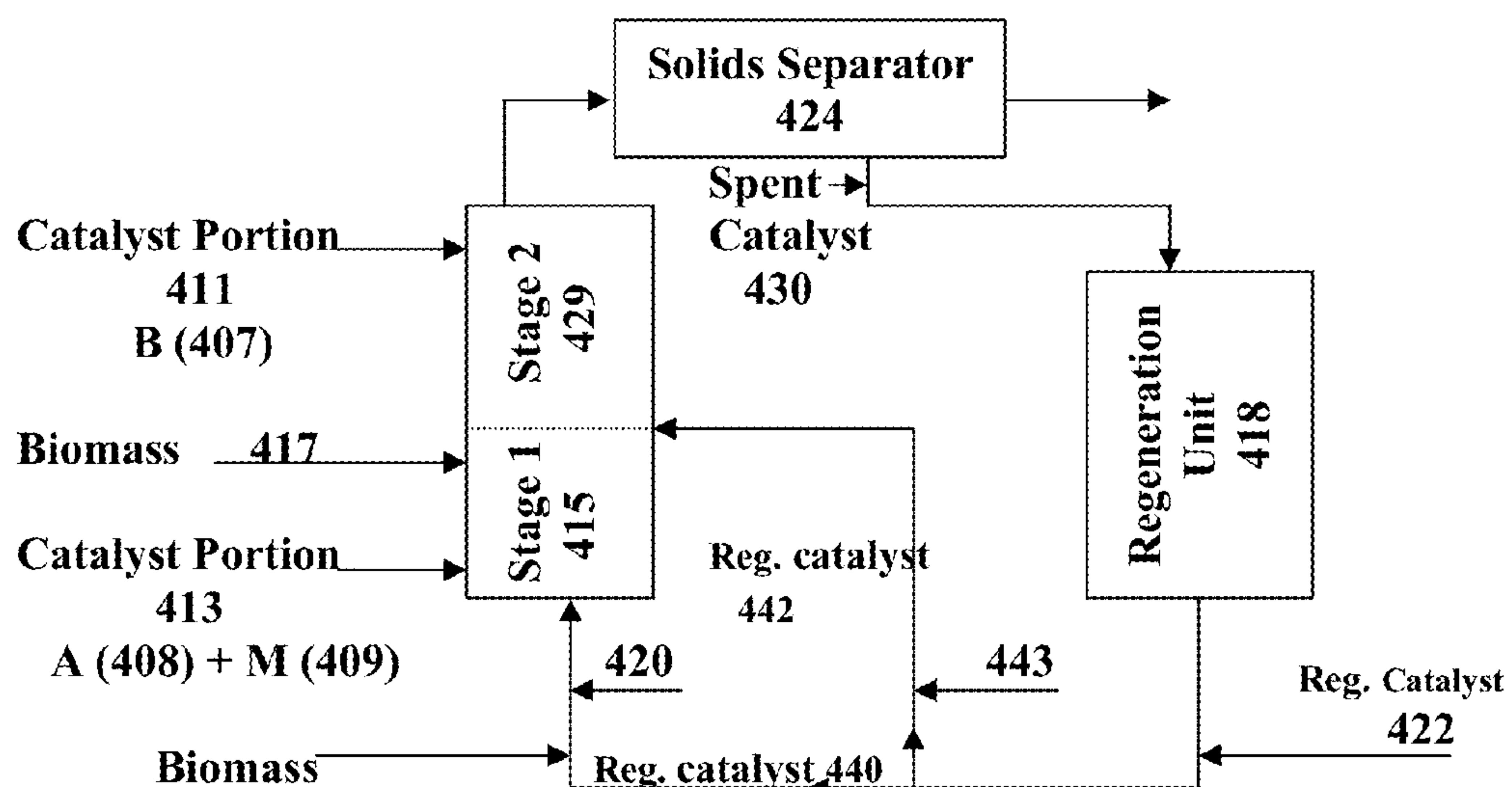


FIG. 3A & B

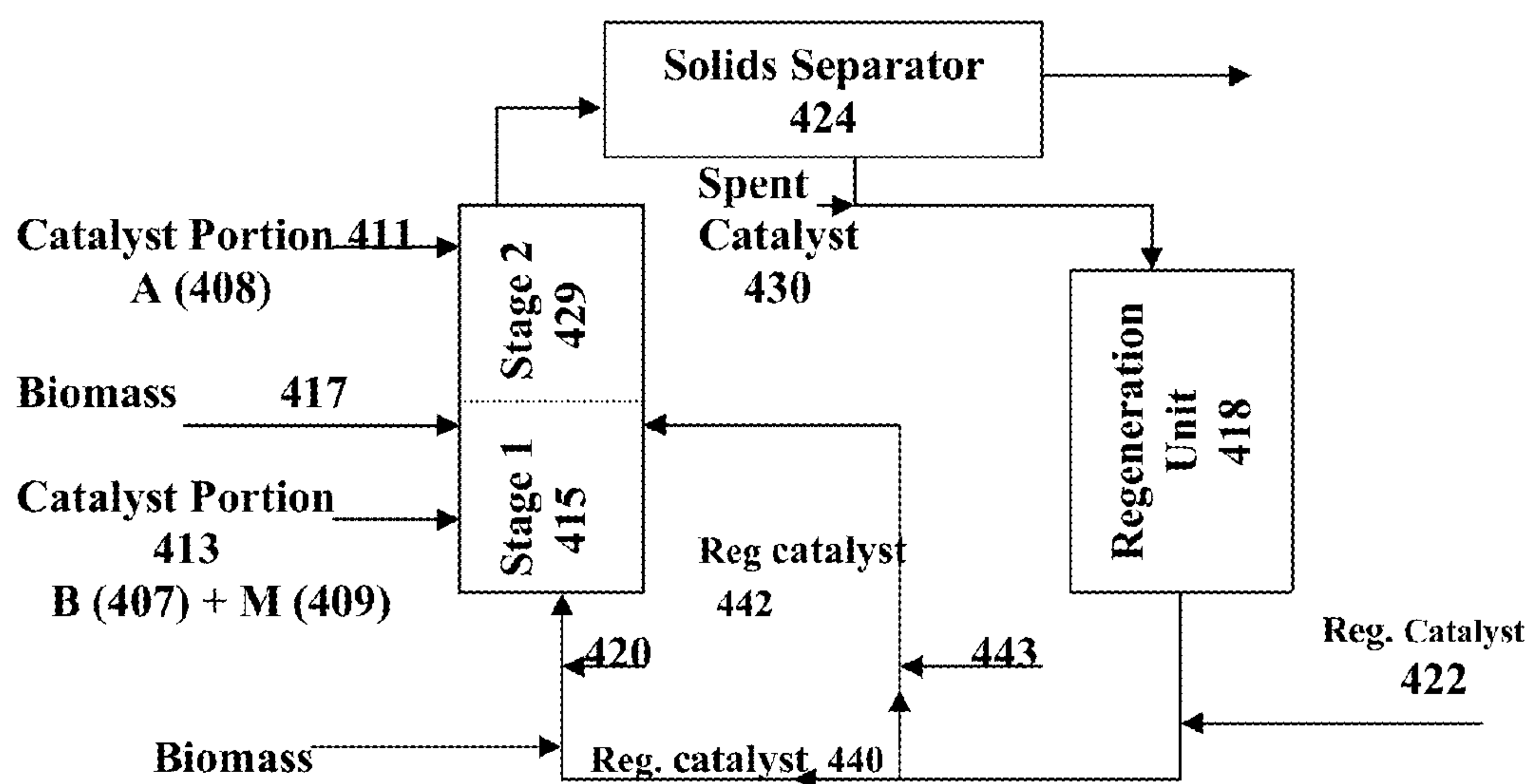


(C)

FIG. 3C

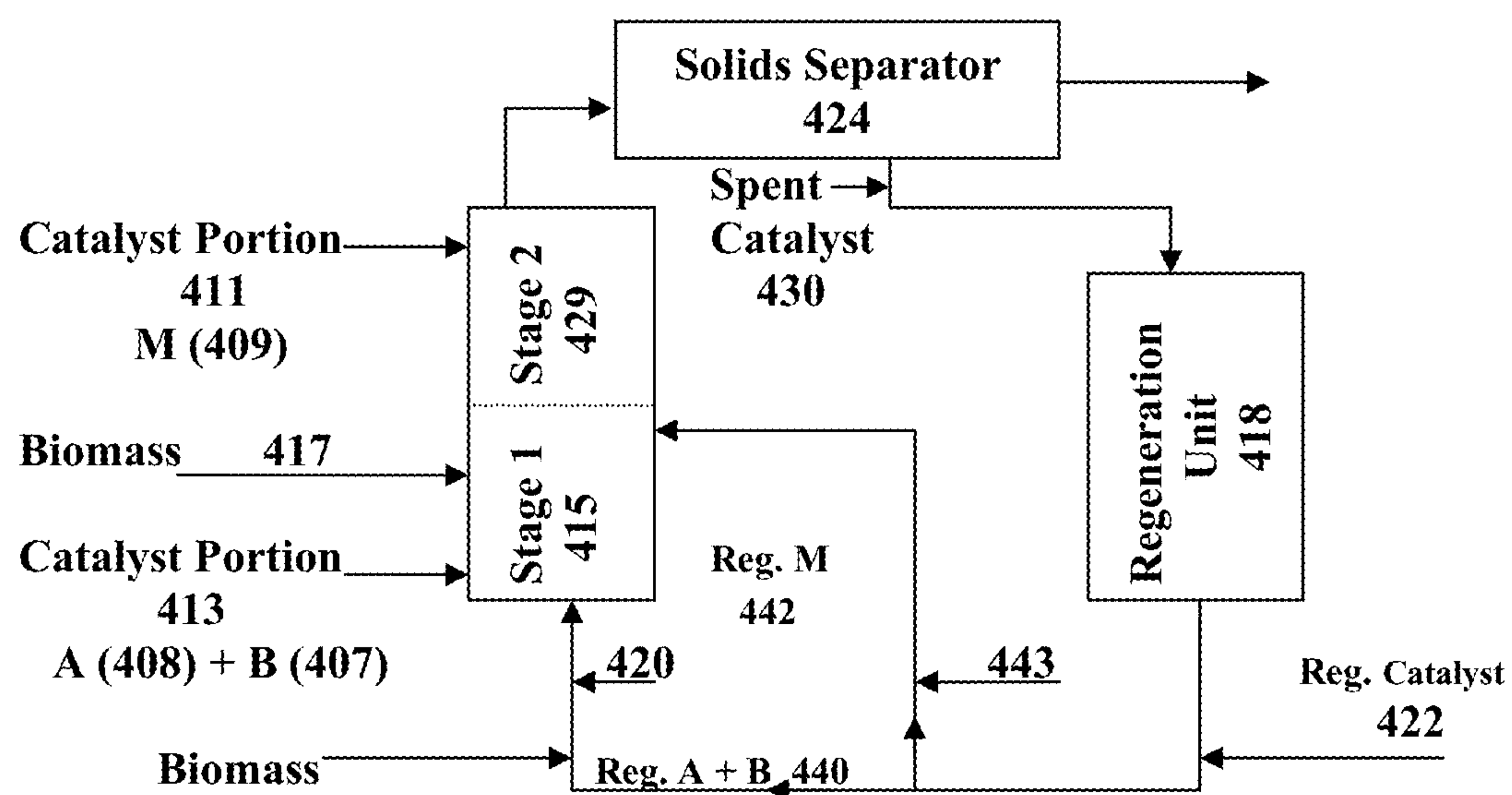


(A)



(B)

FIG. 4A & B



(C)

FIG. 4C

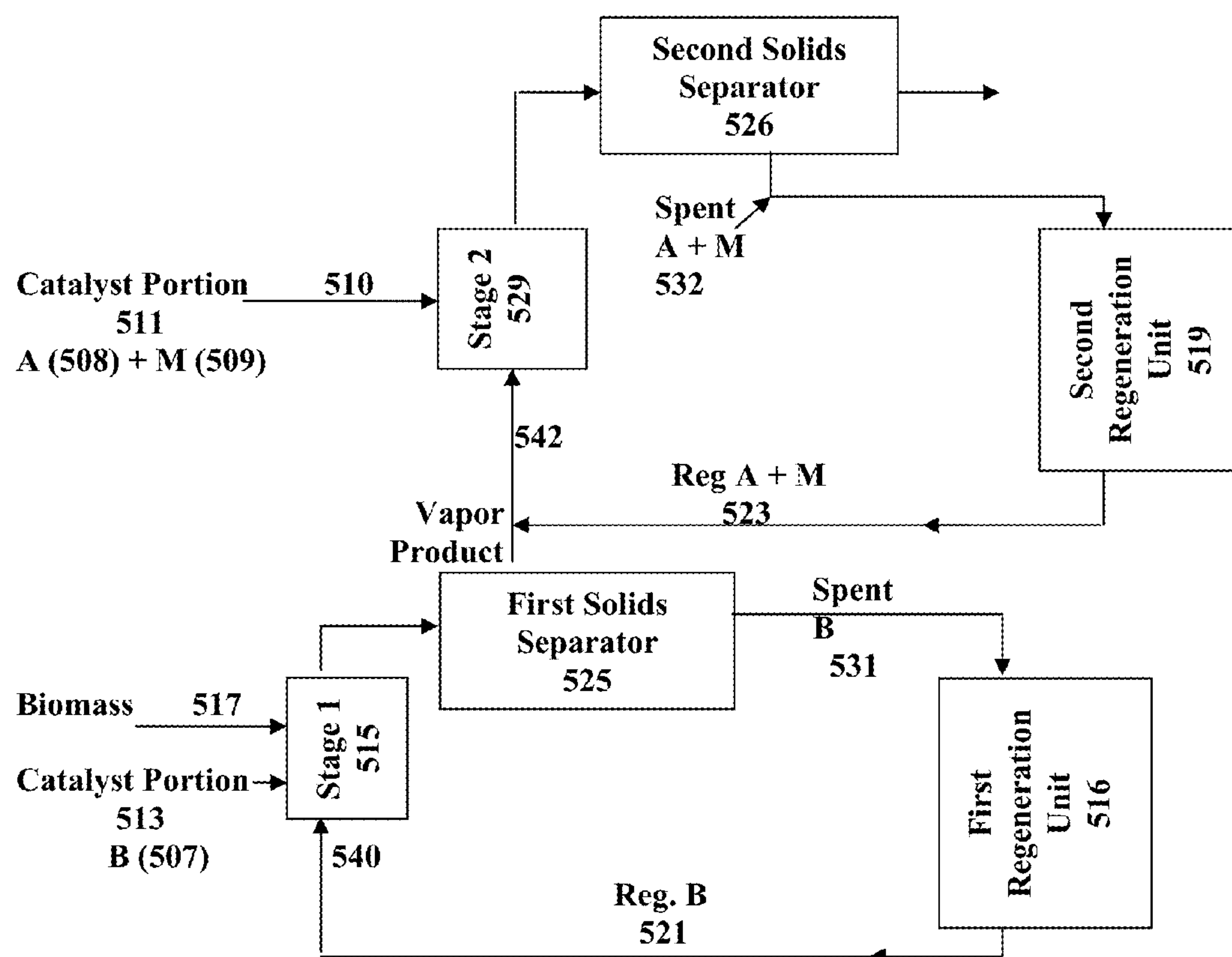


FIG. 5A

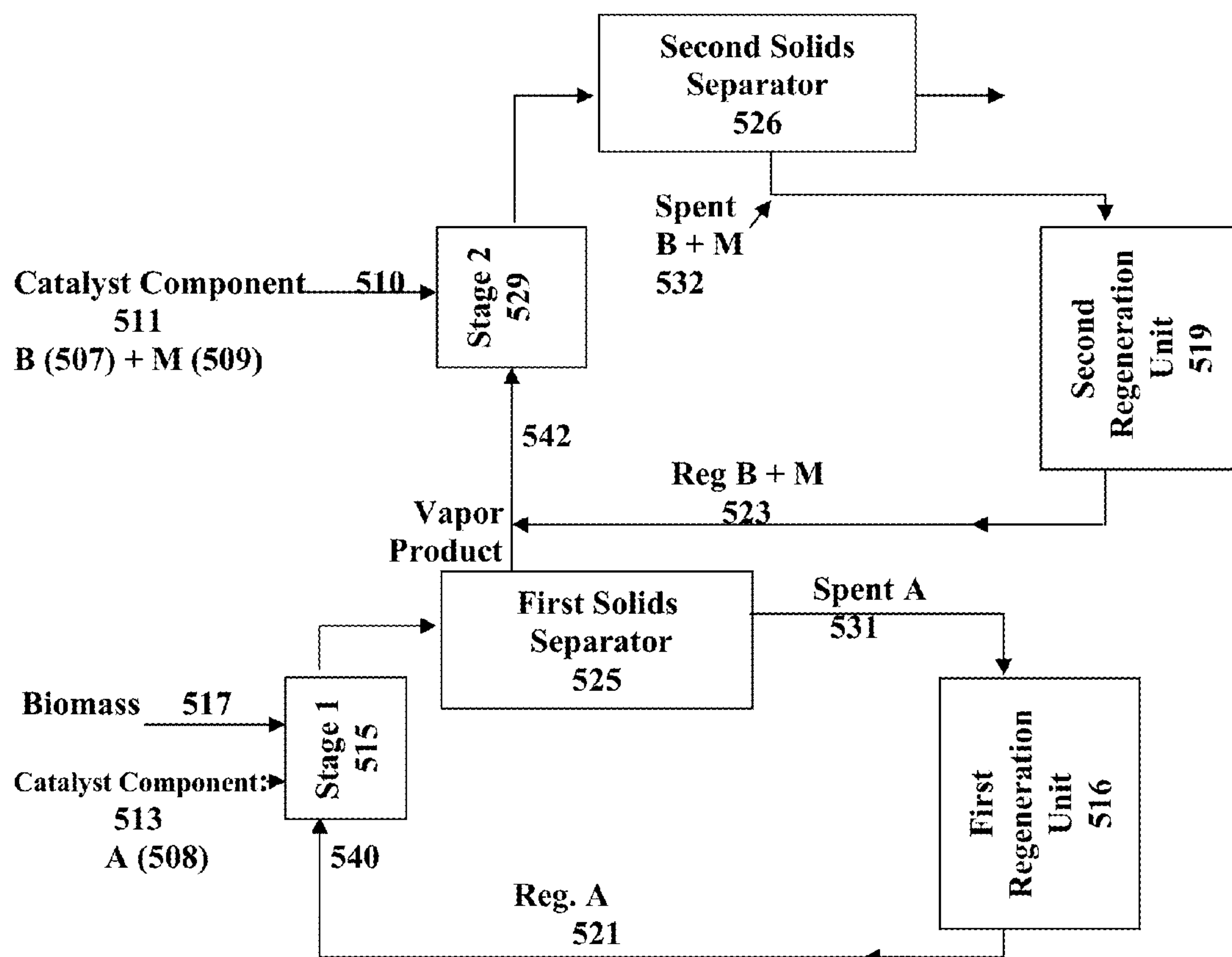


FIG. 5B

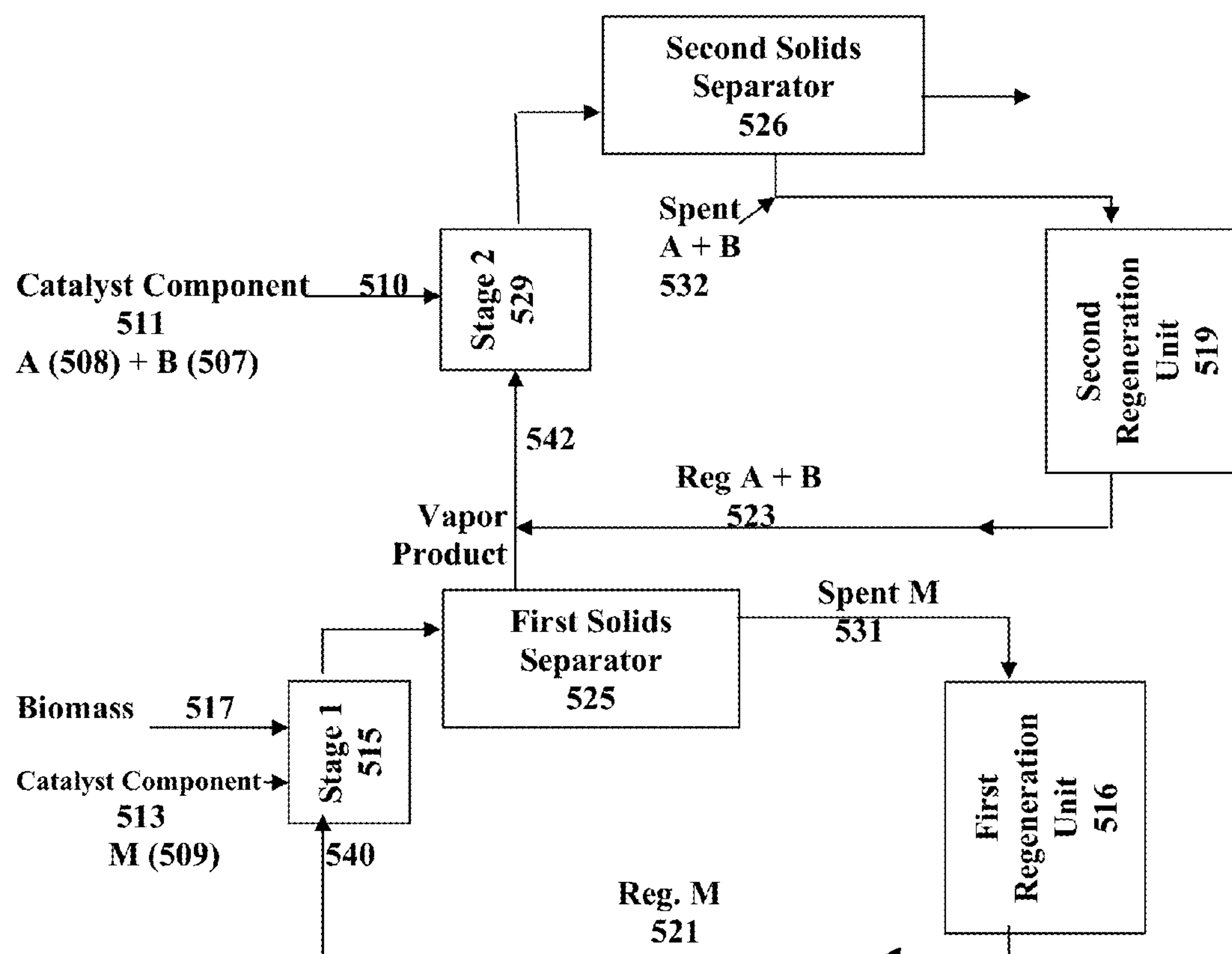


FIG. 5C

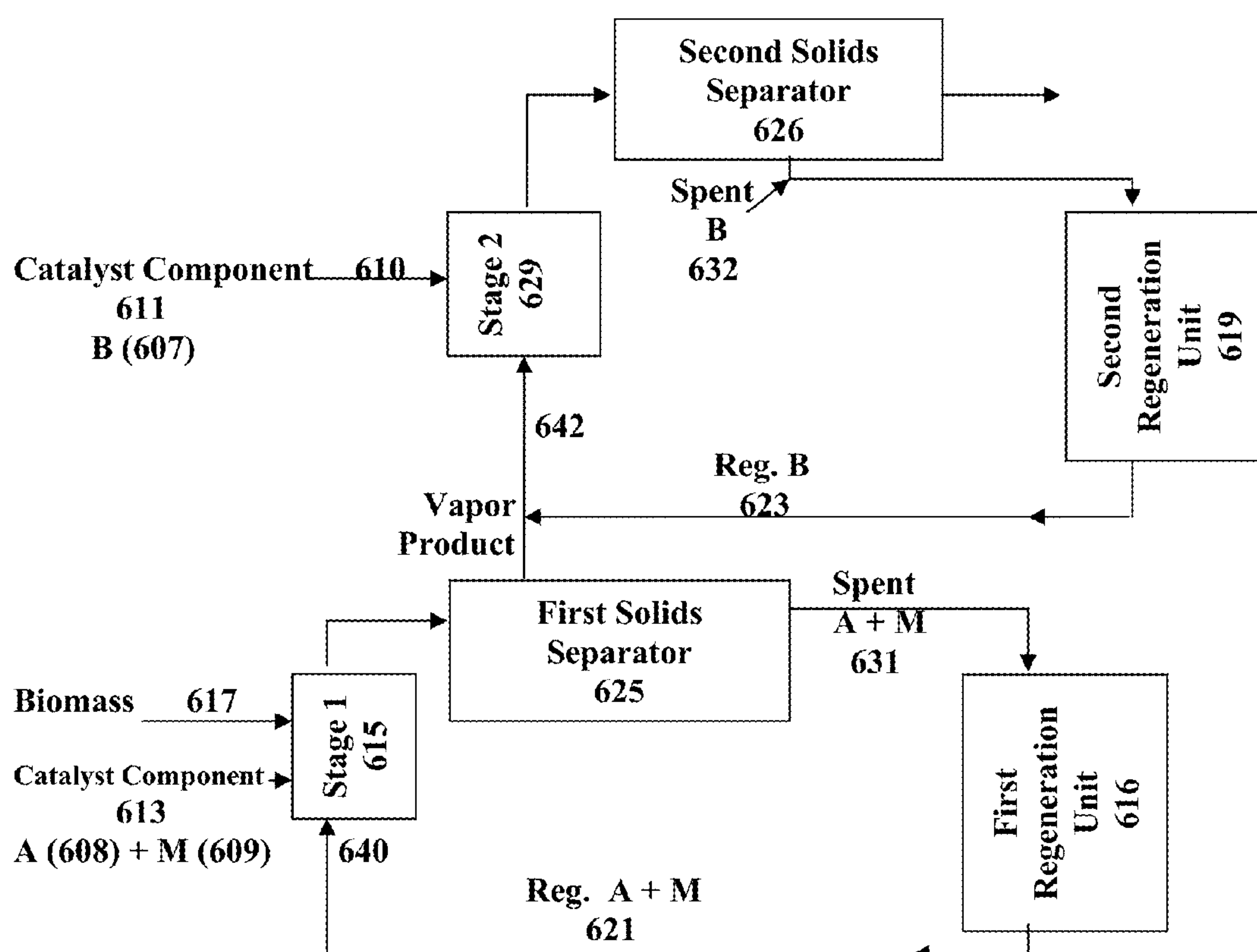


FIG. 6A

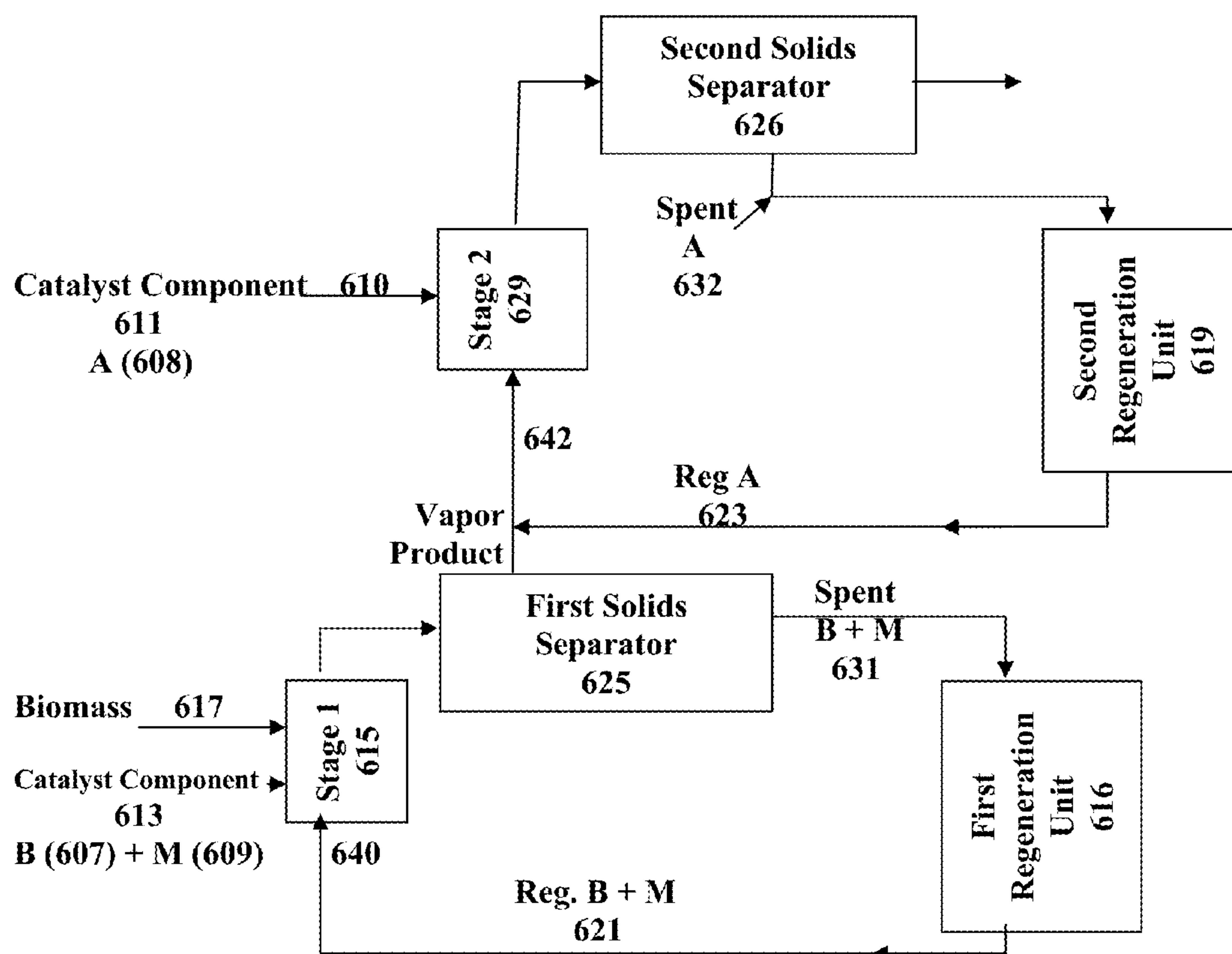


FIG. 6B

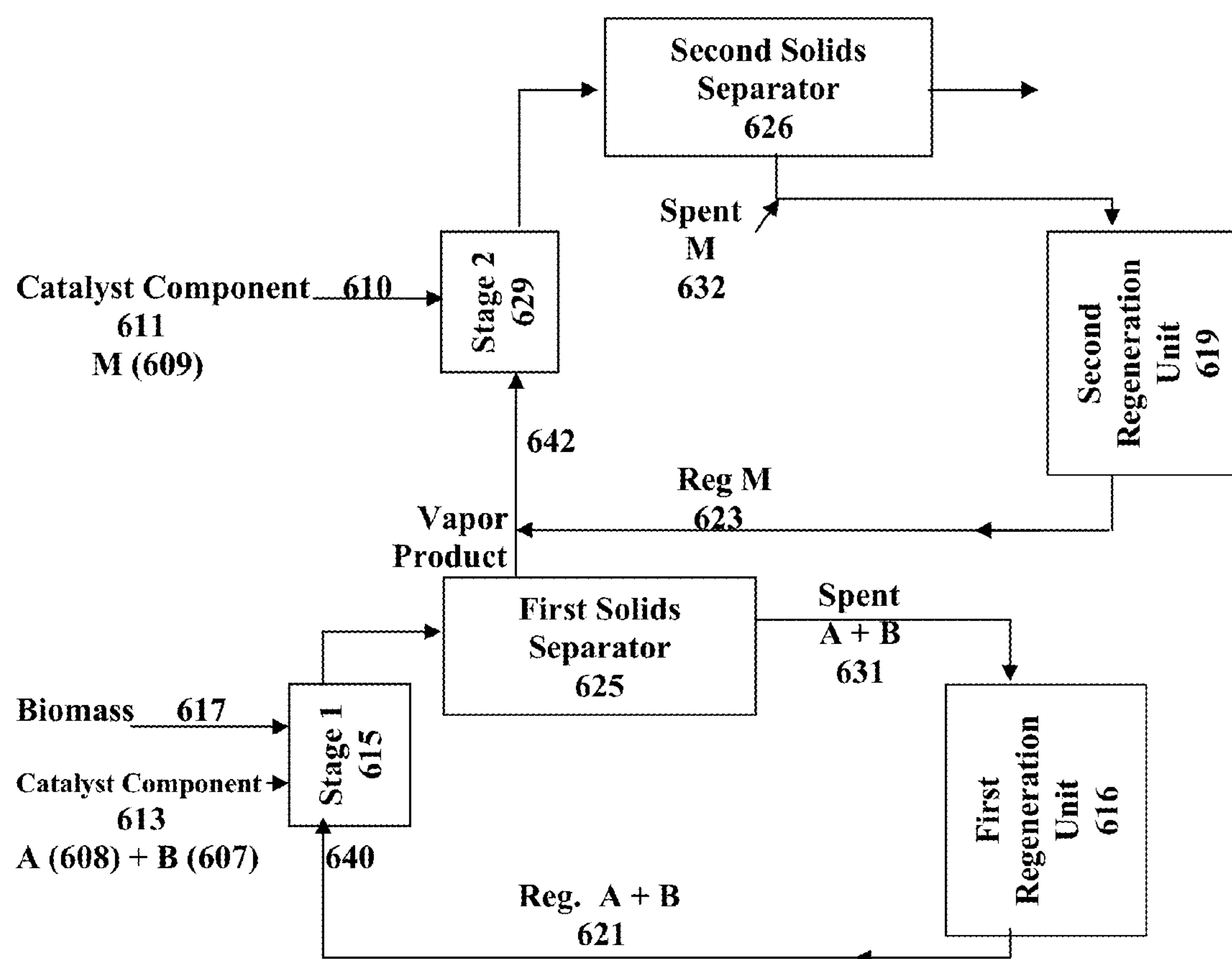
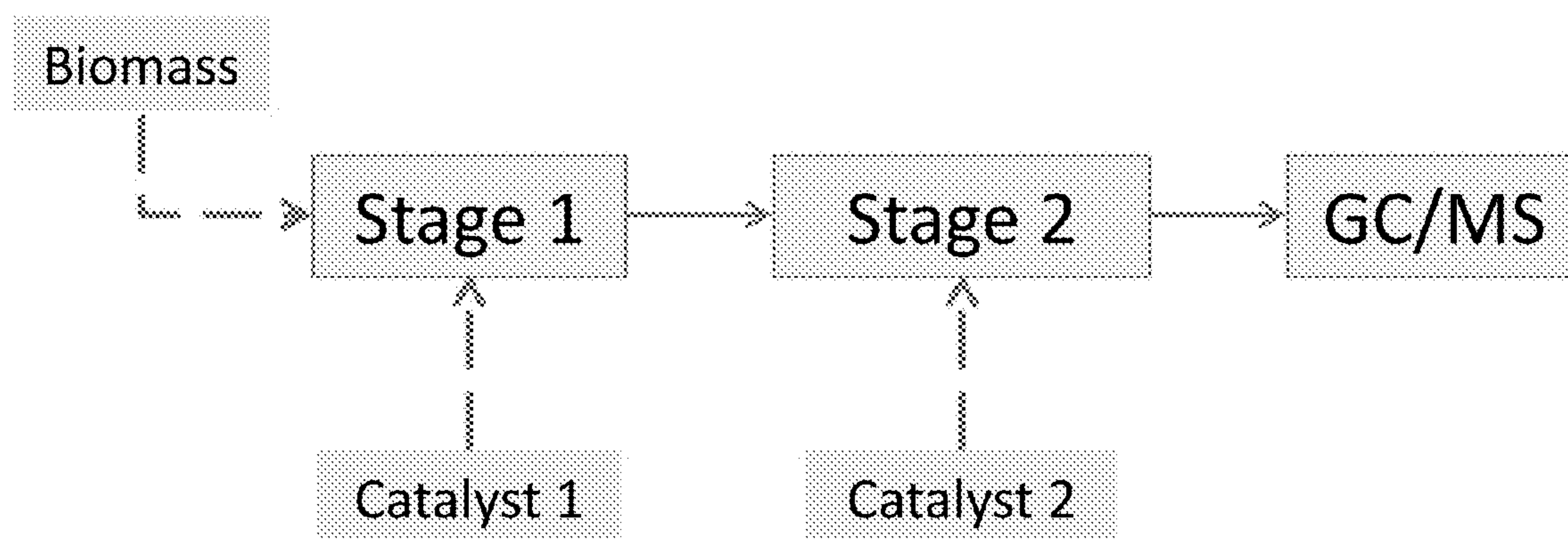


FIG. 6C

**FIG. 7**

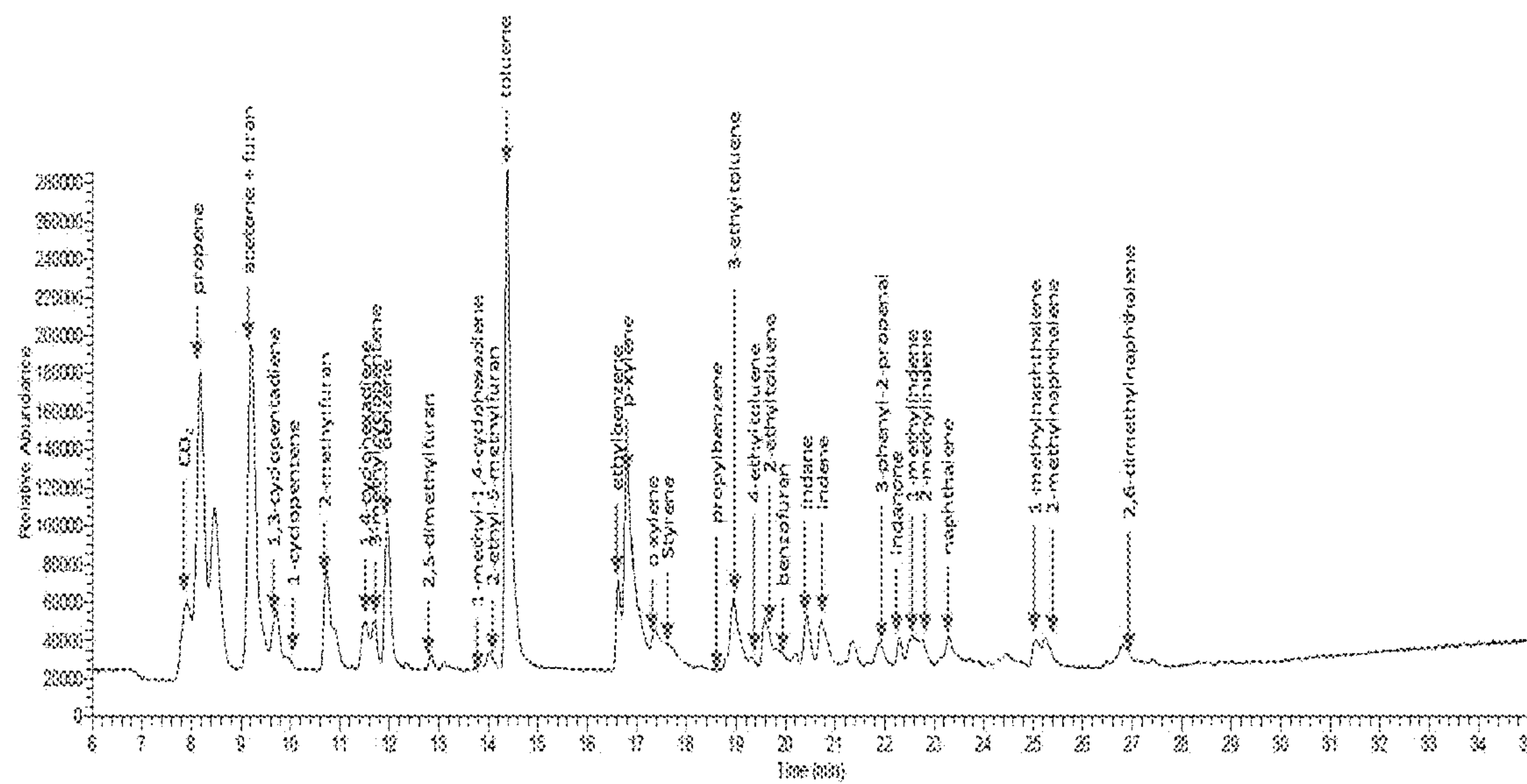
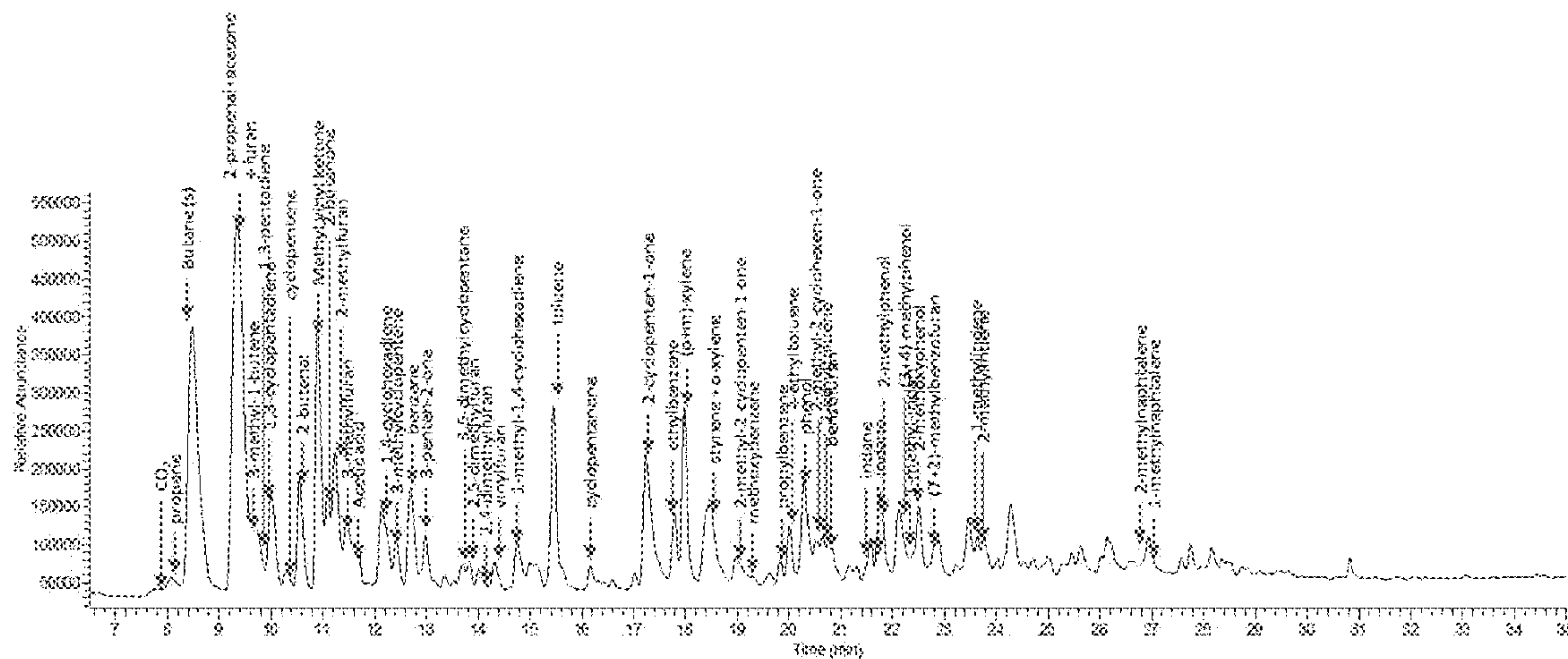


FIG. 8A



FIB. 8B

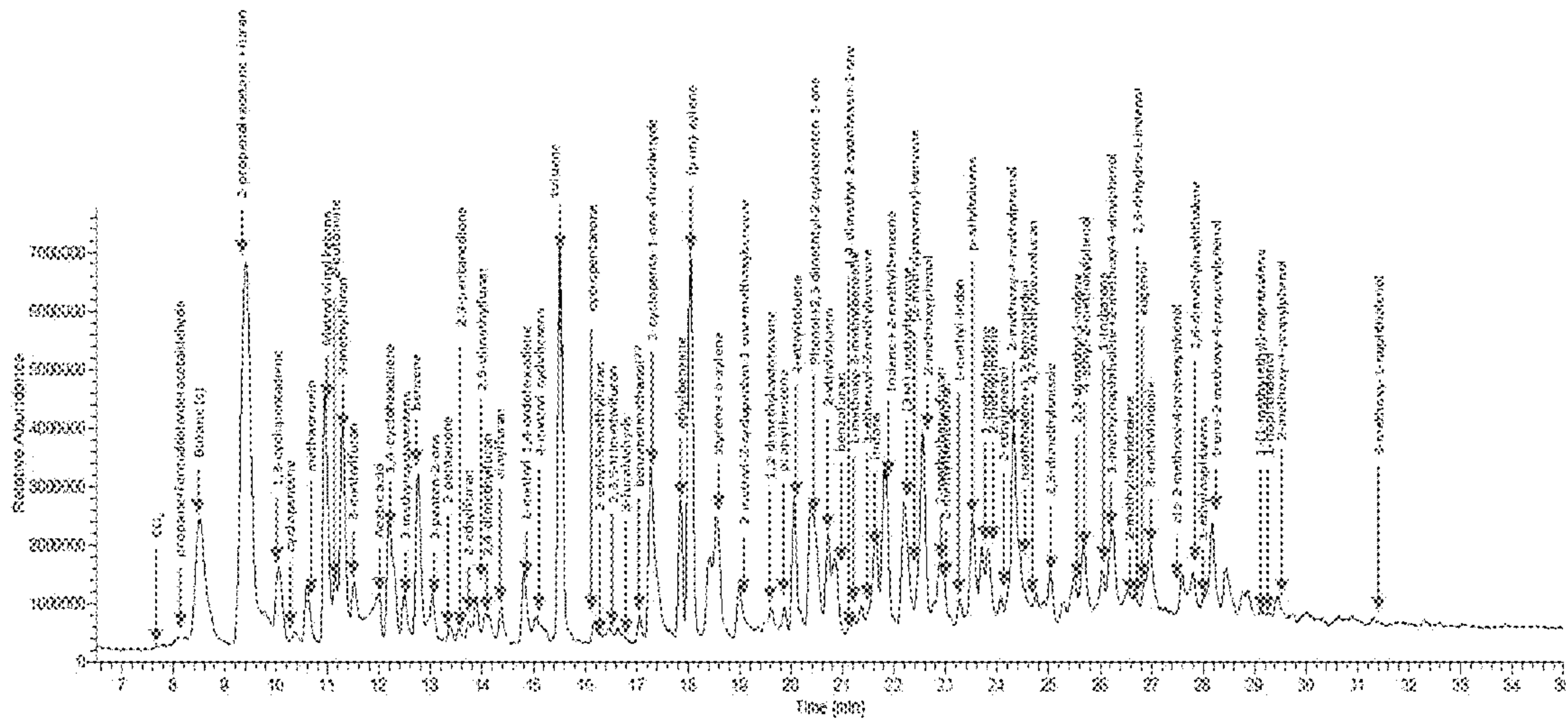


FIG. 8C

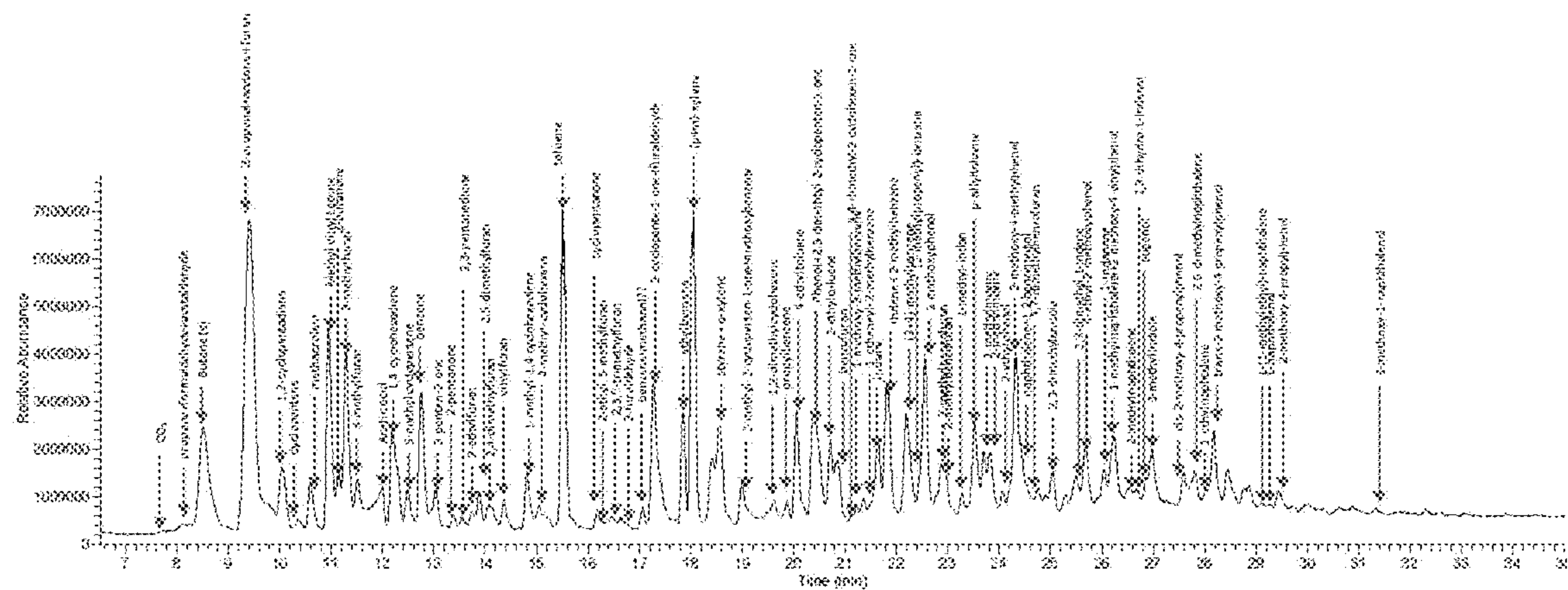


FIG. 8D

METHOD OF BIOMASS CONVERSION USING A MULTIFUNCTIONAL CATALYST SYSTEM

FIELD OF THE DISCLOSURE

[0001] The disclosure relates to a method of converting biomass to hydrocarbons using a multi-functional catalyst.

BACKGROUND OF THE DISCLOSURE

[0002] Renewable energy sources are a substitute for fossil fuels and provide a means of reducing dependence on petroleum oil. Renewable fuels include biofuels which may be produced by subjecting a biomass, such as a lignocellulosic biomass, to catalytic thermolysis processes, such as pyrolysis. This results in the conversion of the biomass into hydrocarbon containing feedstreams which are then used to produce biofuels. During catalytic pyrolysis, the lignocellulosic biomass is deoxygenated and depolymerized. Dehydration and dehydroxylation of the biomass are typically the principal reactions occurring during pyrolysis. In addition, carbonyl linkages within the biomass may be broken down into carbon monoxide by decarbonylation. Decarbonylation, which typically increases in catalytic pyrolysis, decreases the liquid yield by removing carbon bearing molecules with gaseous streams.

[0003] A water-gas shift (WGS) reaction might also occur during deoxygenation of the biomass wherein carbon dioxide and hydrogen are produced from the reaction of carbon monoxide and water, depending on catalyst and reaction conditions.

[0004] In light of the complexity of lignocellulosic biomasses, other reactions need to be promoted within the biomass conversion unit in order to enhance the efficiency of pyrolysis. Such reactions include decarboxylation, oligomerization, condensation, and cyclization.

[0005] Typically, a mono-functional catalyst (e.g., an acid catalyst) is used for the multiple reactions which occur in the biomass conversion unit. Alternatively, different mono-functional catalysts have been used for various purposes, such as to modulate cracking and enhance decarboxylation to maximize carbon dioxide (e.g., bases). The use of a mono-functional catalyst to tackle the complexity of pyrolysis decreases the efficiency of conversion of the biomass to hydrocarbons and shortens the life cycle of any catalyst used within the biomass conversion unit. While bi-functional catalysts have been explored, a method which enhances the processability of biomass feedstocks with multi-functional catalysts has not been reported.

[0006] It should be understood that the above-described discussion is provided for illustrative purposes only and is not intended to limit the scope or subject matter of the appended claims or those of any related patent application or patent. Thus, none of the appended claims or claims of any related application or patent should be limited by the above discussion or construed to address, include or exclude each or any of the above-cited features or disadvantages merely because of the mention thereof herein.

[0007] Accordingly, there exists a need for alternative methods for producing hydrocarbons by pyrolyzing a biomass feedstream in the presence of a multi-functional catalyst having one or more of the attributes or capabilities described or shown in, or as may be apparent from, the other portions of this patent.

SUMMARY OF THE DISCLOSURE

[0008] In an embodiment, the disclosure relates to a process of converting solid biomass to hydrocarbons by feeding into a biomass conversion unit at least a portion of a regenerated multi-functional catalyst. The regenerated multi-functional catalyst contains an acidic component, a basic component and a metallic component. The biomass is treated within the biomass conversion unit in at least two stages wherein at least a fresh portion of one component of the regenerated multi-functional catalyst is fed into each of the stages.

[0009] In another embodiment, the disclosure relates to a process of converting solid biomass to hydrocarbons in a two stage process. The process is conducted in the presence of at least a portion of a first regenerated catalyst and at least a portion of a second regenerated catalyst wherein the first regenerated catalyst or the second regenerated catalyst is a monofunctional catalyst and the other is a bifunctional catalyst. The combination of the monofunctional catalyst and the bifunctional catalyst contains an acidic component, a basic component and a metallic component. The bifunctional catalyst contains two of the components and the monofunctional catalyst contains the remaining component. Further, a first stage reactor has a first solids separator and a first regeneration unit and a second stage reactor has a second solids separator and a second regeneration unit. In the process, the solid biomass is subjected to catalytic pyrolysis in the first stage reactor unit. Spent catalyst and vapors are separated from the pyrolyzed biomass in the first solids separator. The separated vapor is then fed into the second stage reactor. The spent catalyst is fed into the first regeneration unit to render the first regenerated catalyst. The vapor phase is subjected to a second catalytic pyrolysis step in the second stage reactor. Spent catalyst separated from the pyrolyzed vapor phase in the second stage reactor is fed into the second regeneration unit to render the second regenerated catalyst. At least a portion of the first regenerated catalyst is fed into the first stage reactor and at least a portion of the second regenerated catalyst is fed into the second stage reactor. At least a fresh portion of one component of the regenerated multi-functional catalyst is fed into each of the stages.

[0010] In another embodiment, a process of converting solid biomass to hydrocarbons in at least two stages is disclosed. The biomass is subjected to pyrolysis in a first stage reactor in the absence of a catalyst. Vapors and solids are separated from the pyrolyzed biomass. The separated vapor is fed into a second reactor. The separated vapor is converted into hydrocarbons in the presence of a regenerated multi-functional catalyst in the second reactor. At least a fresh portion of the multi-functional catalyst is fed into the second stage. The multi-functional catalyst contains an acid component, a basic component and a metallic material.

[0011] In another embodiment, a process of converting solid biomass to hydrocarbons is disclosed wherein the biomass is first pyrolyzed in a biomass conversion unit in the absence of a catalyst. Solids and vapors are separated from the pyrolyzed product. At least a portion of a regenerated multi-functional catalyst is fed into a second reactor. The regenerated catalyst contains an acidic component, a basic component and a metallic component. The separated vapor is then pyrolyzed in the presence of at least a portion of the regenerated catalyst.

[0012] In another embodiment, a process of converting solid biomass to hydrocarbons is disclosed wherein a regenerated multi-functional catalyst comprising an acidic compo-

ment, a basic component and a metallic component is fed into a biomass conversion unit. The biomass is then pyrolyzed in the biomass conversion unit.

[0013] Accordingly, the present disclosure includes features and advantages which are believed to enable it to advance the conversion of biomass into hydrocarbons. Characteristics and advantages of the present disclosure described above and additional features and benefits will be readily apparent to those skilled in the art upon consideration of the following detailed description of various embodiments and referring to the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] The following figures are part of the present specification, included to demonstrate certain aspects of various embodiments of this disclosure and referenced in the detailed description herein:

[0015] FIG. 1 illustrates the process of converting solid biomass to hydrocarbons by feeding a regenerated multi-functional catalyst into a biomass conversion unit.

[0016] FIG. 2 illustrates a process of converting solid biomass to hydrocarbons in two stages wherein in the first stage a biomass feedstream is pyrolyzed in a first reactor in the absence of a catalyst and in the second stage a vapor phase (separated from the biomass in the first reactor) is subjected to pyrolysis in a second reactor in the presence of a regenerated multi-functional catalyst.

[0017] FIGS. 3A, 3B and 3C illustrate a process of converting solid biomass to hydrocarbons by feeding a regenerated multi-functional catalyst into a biomass conversion unit in two stages. A single component of a multi-functional catalyst is fed into the first stage of the biomass conversion unit and two components of the multi-functional catalyst are fed into the second stage.

[0018] FIGS. 4A, 4B and 4C illustrate a process of converting solid biomass to hydrocarbons by feeding a regenerated multi-functional catalyst into a biomass conversion unit in two stages. Two components of the multi-functional catalyst are fed into the first stage of the biomass conversion unit and one component of the multi-functional catalyst is fed into the second stage.

[0019] FIGS. 5A, 5B and 5C illustrate a process of converting solid biomass to hydrocarbons by feeding a regenerated multi-functional catalyst into a biomass conversion unit in two stages. A single component of a multi-functional catalyst is fed into a first reactor and two components of the multi-functional catalyst are fed into a second reactor. Both reactors have a solids separator and a catalyst regenerator.

[0020] FIGS. 6A, 6B and 6C illustrate a process of converting solid biomass to hydrocarbons by feeding a regenerated multi-functional catalyst into a biomass conversion unit in two stages. Two components of a multi-functional catalyst are fed into a first reactor and one component of the multi-functional catalyst is fed into a second reactor. Both reactors have a solids separator and a catalyst regenerator.

[0021] FIG. 7 is a representative reactor system which may be used to practice the process disclosed herein as illustrated in Example 1.

[0022] FIGS. 8A, 8B, 8C and 8D illustrate product distributions which may result from the disclosed process.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0023] Characteristics and advantages of the present disclosure and additional features and benefits will be readily apparent to those skilled in the art upon consideration of the following detailed description of exemplary embodiments of the present disclosure and referring to the accompanying figures. It should be understood that the description herein and appended drawings, being of example embodiments, are not intended to limit the claims of this patent or any patent or patent application claiming priority hereto. On the contrary, the intention is to cover all modifications, equivalents and alternatives falling within the spirit and scope of the claims. Many changes may be made to the particular embodiments and details disclosed herein without departing from such spirit and scope.

[0024] In showing and describing preferred embodiments in the appended figures, common or similar elements are referenced with like or identical reference numerals or are apparent from the figures and/or the description herein. The figures are not necessarily to scale and certain features and certain views of the figures may be shown exaggerated in scale or in schematic in the interest of clarity and conciseness.

[0025] As used herein and throughout various portions (and headings) of this patent application, the terms “disclosure”, “present disclosure” and variations thereof are not intended to mean every possible embodiment encompassed by this disclosure or any particular claim(s). Thus, the subject matter of each such reference should not be considered as necessary for, or part of, every embodiment hereof or of any particular claim(s) merely because of such reference.

[0026] Certain terms are used herein and in the appended claims to refer to particular components. As one skilled in the art will appreciate, different persons may refer to a component by different names. This document does not intend to distinguish between components that differ in name but not function. Also, the terms “including” and “comprising” are used herein and in the appended claims in an open-ended fashion, and thus should be interpreted to mean “including, but not limited to” Further, reference herein and in the appended claims to components and aspects in a singular tense does not necessarily limit the present disclosure or appended claims to only one such component or aspect, but should be interpreted generally to mean one or more, as may be suitable and desirable in each particular instance.

[0027] Preferred embodiments of the present disclosure thus offer advantages over the prior art and are well adapted to carry out one or more of the objects of this disclosure. However, the present disclosure does not require each of the components and acts described above and is in no way limited to the above-described embodiments or methods of operation. Any one or more of the above components, features and processes may be employed in any suitable configuration without inclusion of other such components, features and processes. Moreover, the present disclosure includes additional features, capabilities, functions, methods, uses and applications that have not been specifically addressed herein but are, or will become, apparent from the description herein, the appended drawings and claims.

[0028] The method disclosed herein uses a multi-functional catalyst. Such catalysts provide greater versatility than those mono-functional catalysts typically used to convert biomass into renewable fuels. Multi-functional catalysts are fur-

ther capable of maximizing liquid yield of produced hydrocarbons in a more cost effective manner.

[0029] The multi-functional catalyst used may have an acidic component, a basic component and a metallic component.

[0030] Prior to treatment of the biomass with the multi-functional catalyst, the biomass may be subjected to “thermal pyrolysis” wherein the feedstock is heated in the substantial absence of a catalyst in an atmosphere that is substantially free of oxygen. The atmosphere may be an inert gas, such as nitrogen. Alternatively, the atmosphere can comprise a reactive gas, such as hydrogen, carbon monoxide, steam, or a combination thereof.

[0031] Treatment of the biomass with the multi-functional catalyst may occur in one or more stages. By the process disclosed herein, the multi-functional catalyst may be regenerated in one or more stages.

[0032] When only a single stage is used, all of the components of the multi-functional catalyst may be simultaneously introduced into the biomass conversion unit. Regenerated multi-functional catalyst may thus be fed back into the biomass conversion unit. When a single stage is used, all of the components of the multi-functional catalyst may be combined in a single catalyst particle and fed into the reactor. Alternatively, different components of the catalyst system may be present in different particles.

[0033] When a single reactor is used, the first stage and the second stage may correspond to the lower and the upper zone or section of the reactor. In such instances, the two zones of the reactor may have different geometries. For example, the lower zone of the reactor may have a frustrum geometry and the second zone a cylindrical geometry. In some embodiments, the two stages or zones of the reactor may have different diameters. In the first stage, the particulate solid biomass material is thermally pyrolyzed, to form primary reaction products and in the second stage primary reaction products may be catalytically converted to secondary reaction products. The first stage and second stage of the single reactor are typically in fluid communication.

[0034] When multiple stages (i.e., more than one stage) are used to convert the biomass, different components of the catalyst may be introduced into different reactors. Thus, different regenerated components of the catalyst are fed back into different reactors. As an example, two or more of the components of the catalyst may be introduced into a first reactor (as one stage) and one or more other components of the catalyst may be introduced into a second reactor (as another stage). The components introduced into the first reactor may then be regenerated and fed back into the first reactor. The components introduced into the second reactor may be regenerated and fed back into the second reactor.

[0035] Further, multiple stages may be used wherein each stage has a reactor for one or more of the components of the catalyst. In an embodiment, there may be as many stages as there are components of the multi-functional catalyst. For instance, each of the multiple stages may have a single reactor for a single component such that each component of the multi-functional catalyst is introduced in a separate reactor. Thus, when regenerated, the single component may be fed back into its respective reactor.

[0036] In a preferred embodiment, the process is conducted in at least two reactors. For example, the process employs two reactors wherein at least one of the components is introduced into one reactor (a first stage) and the remaining components

are introduced into a second reactor (a second stage). Typically, solid particulate biomass material is converted thermally pyrolyzed in the first stage reactor to form primary reaction products and in the second stage reactor at least part of the primary reaction products are catalytically converted to secondary reaction products. The first stage and second stage reactors are in fluid communication. In a preferred embodiment, the second stage reactor is positioned above the first stage reactor.

[0037] The presence of the acidic component in the multi-functional catalyst preferred for use in the method disclosed herein accelerates deoxygenation of low molecular oxygenates which are produced in high amounts during the conversion of biomass. Exemplary oxygenates are alcohols, aldehydes, ketones, carboxylic acids, diols, ethers, esters, and the like. Those having an isolated carbonyl group include aldehydes and ketones like acetaldehyde, methyl vinyl ketone and ethyl vinyl ketone.

[0038] In a preferred embodiment, the acidic component of the multi-functional catalyst is zeolite ZSM-5. The presence of zeolite ZSM-5 promotes oligocyclization and/or aromatization of the bio-oil and/or pyrolysis oil compounds. As such, zeolite enables production of higher molecular weight hydrocarbons versus the low molecular weight (generally less than C₅) in bio-oil and/or pyrolysis oil produced during pyrolysis of a biomass in a biomass conversion unit.

[0039] Typically, amount of zeolite ZSM-5 in the multi-functional catalyst disclosed herein may be from about 5 to about 40 wt. %. (As used herein, the wt. % of a component of the multi-functional catalyst refers to the amount of the component based on all of the components in all of the stages.) Thus, for example, where different stages are used in the process, the amount of zeolite ZSM-5, based on the weight percent of all of the components of the multi-functional catalyst within the stages, is from about 5 to about 40 wt. %.

[0040] The multi-functional catalyst disclosed herein may also include zeolite USY. Zeolite USY promotes cracking of the biomass monomers, dimers and/or small oligomers. In a preferred embodiment, the amount of zeolite USY in the multi-functional catalyst is from about 5 to about 40 wt. %. When present, the weight ratio of Si:Al in zeolite USY is from about 5 to about 200, more typically from about 20 to about 100.

[0041] In another embodiment, L-zeolite may also be included with zeolite ZSM-5 and zeolite USY in the preferred multi-functional catalyst. When present, the amount of L-zeolite in the multi-functional catalyst is less than about 20 wt. %. L-zeolite may be used to promote aromatization of hydrocarbons produced during pyrolysis.

[0042] The ZSM-5 zeolite, zeolite USY and, optional, L-zeolite in the preferred multi-functional catalyst are included in their acid form and thus provide an acidic functionality to the multi-functional catalyst.

[0043] The presence of the metallic component in the multi-functional catalyst promotes the WGS reaction producing hydrogen in-situ and consequently minimizing hydrogen transfer reaction from the organic solid to the vapors. Reactants for the WGS reaction may be produced during catalytic pyrolysis, deoxygenation and cracking of the biomass. For instance, deoxygenation via decarbonylation and dehydroxylation produces carbon monoxide and water, respectively. In addition, the metallic component enhances dry reforming (DR) reaction between hydrocarbon moieties and carbon

dioxide to increase further the hydrogen content of the gas phase and suppress even more the hydrogen transfer from the organic solid to the vapors.

[0044] Suitable metallic components of the multi-functional catalyst include copper, nickel, chromium, tungsten, molybdenum, a metal carbide, a metal nitride, a metal sulfide or a mixture thereof. Suitable metal carbides include chromium carbide, molybdenum carbide and tungsten carbide as well as mixtures thereof. In a preferred embodiment, the metal carbide is molybdenum carbide.

[0045] In a preferred embodiment, the metallic component of the multi-functional catalyst is copper, nickel or a carbide of molybdenum and mixtures thereof. In another preferred embodiment, the metallic component is a blend of copper and molybdenum carbide or a blend of nickel and molybdenum carbide.

[0046] The basic component of the multi-functional catalyst typically enables decarboxylation of the biomass and thus assists in the removal of oxygen from the biomass. The material providing the basic functionality to the multi-functional catalyst is preferably an alkaline-exchanged zeolite, an alkaline earth-exchanged zeolite, basic zeolite, an alkaline earth metal oxide, cerium oxide, zirconium oxide, titanium dioxide, mixed oxides of alkaline earth metal oxides and combinations thereof and mixed oxides selected from the group of magnesia-alumina, magnesia-silica, titania-alumina, titania-silica, ceria-alumina, ceria-silica, zirconia-alumina, zirconia-silica and mixtures thereof and wherein the exchanged zeolite has from about 40 to about 75% of exchanged cationic sites. In a preferred embodiment, the exchanged zeolite has 50% exchanged cationic sites.

[0047] Where the basic material is an alkaline earth metal oxide, cerium oxide, zirconium oxide, titanium dioxide, mixed oxide of an alkaline earth metal oxide and combinations thereof or a mixed oxide selected from the group of magnesia-alumina, magnesia-silica, titania-alumina, titania-silica, ceria-alumina, ceria-silica, zirconia-alumina, zirconia-silica and mixtures thereof, the basic material may further serve to form a support or a matrix for the other components of the multi-functional catalyst. For instance, the basic material may be the support for the metallic component.

[0048] The multi-functional catalyst defined herein may also include a binder for agglomerating the different functional entities of the catalyst and facilitating molding and/or shaping of the components of the catalyst. When different stages are used in the process, the binder may present in one or more of the stages. Suitable binders include clay-based binders (such as kaolin-based binder), alumina based binders (such as aluminum chlorohydrate and aluminum nitrohydrates), silica based binders (such as silicic acid, polysilicic acid, silica gel and colloidal silica) as well as combinations of any of such binders. In a preferred embodiment, the binder is kaolin-based. When present, the amount of binder in the multi-functional catalyst is typically less than 50 wt. %, more typically less than 30 wt. %.

[0049] The multi-functional catalyst for use in the methods disclosed herein may also include a promoter. Suitable promoters include phosphates, silica, alumina and metallic promoters and mixtures thereof. In the multi-functional catalyst, phosphate is typically used to promote the catalytic effect of the acid component and to enhance the binding capabilities of the binding materials and is present in the stage where the acid component is present. Silica and/or alumina are typically used to promote the catalytic effect of the basic material and

is present in the stage where the basic material is present. A metallic promoter is typically used to impart either a bi-metallic functionality or to stabilize the metallic component and thus enhance the performance of the metal component of the multi-functional catalyst. The metallic promoter is typically present in the stage where the metallic component is present.

[0050] In a preferred embodiment, the multi-functional catalyst for use in the methods defined herein may contain from about 5 to about 40 wt. % zeolite ZSM-5; from about 5 to about 30 wt. % zeolite USY; from about 3 to about 15 wt. % of metallic material; and from about 5 to about 40 wt. % of basic material; the balance being the binder.

[0051] The methods disclosed herein are especially suitable for the treatment of lignocellulosic biomasses. Such biomasses contain carboxylic groups and ester-type bonds that can be decarboxylated, providing a suitable catalyst functionality is included. Said functionality is provided by the basic material component of the multi-functional catalyst. The enhanced formation of carbon dioxide from the decarboxylation reaction of biomass moieties further drives the dry reforming reactions promoted by the metallic component of the multifunctional catalyst.

[0052] In an embodiment, the biomass may be pre-treated with at least one component of the catalyst system. Such a pretreatment step can comprise impregnating a cellulosic biomass with a solution of a component of the catalyst system. For this embodiment of the process, it is desirable to use for the pretreatment one or more components of the multi-functional catalyst that is soluble in water and aqueous solvents, so that an inexpensive solvent system can be used in the pretreatment step. In an alternate embodiment of the process, pretreatment is carried out with one or more solid components of the multi-functional catalyst by mechanically treating the biomass in the presence of the catalyst component in particulate form. The mechanical treatment can comprise milling, grinding, kneading, or a combination thereof.

[0053] The biomass initially introduced into the reactor(s) may be in a solid or finely divided form or may be a liquid. In an embodiment, the water soluble content of the biomass is no greater than about 7 volume percent.

[0054] In an embodiment, the biomass particles can be fibrous biomass materials comprising cellulose. Examples of suitable cellulose-containing materials include algae, paper waste, and/or cotton linters. In one embodiment, the biomass particles can comprise a lignocellulosic material. Examples of suitable lignocellulosic materials include forestry waste such as wood chips, saw dust, pulping waste, and tree branches; agricultural waste such as corn stover, wheat straw, and bagasse; and/or energy crops such as eucalyptus, switch grass, miscanthus, coppice and fast-growing woods, such as willow and poplar.

[0055] In each of the reactors, the biomass may be subjected to any of a variety of conversion conditions. Such conversion conditions include those of fast pyrolysis, slow pyrolysis, liquefaction, catalytic gasification, thermocatalytic conversion, etc. Typically, the reactors are a fluidized bed reactor, a cyclone reactor, an ablative reactor, an auger reactor, a riser reactor, a trickle bed configuration, another bed regimen or a combination thereof. The reactors are typically fluid bed reactors wherein at least part of the thermocatalyst might be used as a heat carrier. When the reactor(s) are fluidized beds, the components of the catalyst should have a

shape and size to be readily fluidized. Preferred are components in the form of microspheres having a particle size in the range of 20 μm to 3000 μm .

[0056] A broad range of fluidization conditions might be used when more than one stage is desired. For instance, a two stage fluidized bed system might comprise two fluidized bed reactors coupled together with provisions for gas and/or materials transfer in between. Feasible combinations include circulating-circulating or bubbling-circulating or bubbling-bubbling type systems.

[0057] In the reactor, solid biomass particles may be agitated, for example, to reduce the size of particles. Agitation may be facilitated by a gas including one or more of steam, flue gas, carbon dioxide, carbon monoxide, hydrogen, and hydrocarbons such as methane. The agitator further be a mill (e.g., ball or hammer mill) or kneader or mixer.

[0058] Typically, the reactor(s) is operated at temperatures in excess of 250° C. In some conversion reactions, such as fast pyrolysis, where the biomass is exposed to short contact times and rapid heating, reaction temperatures may be as high as 1,000° C. Preferably, the reactor is maintained at a temperature in the range of from 250° C. to about 650° C., more typically preferably from 400° C. to 600° C.

[0059] FIG. 1 illustrates a single stage process wherein multi-functional catalyst 110 is shown as being introduced into biomass conversion unit 114. The biomass is thermocatalytically treated to render liquid products that spontaneously separate into an aqueous phase and an organic phase. Bio-oil (which is used to produce biofuel) consists of the organic phase. In addition to the removal of heavy materials and solids, water may be removed during the separation. The bio-oil, having the byproduct water, heavy materials and solids removed may then be introduced into a fractionator.

[0060] The multi-functional catalyst disclosed herein may be added as fresh catalyst to the biomass conversion unit. Alternatively, the multi-functional catalyst may be an equilibrium catalyst ("E-cat"), also referred to as regenerated catalyst. Such catalysts are produced by burning coke deposits and/or char from a spent catalyst in oxygen or an oxygen containing gas, such as air, in a catalyst regeneration unit or regenerator. All or a portion of the spent catalyst formed in the biomass conversion unit may be subjected to treatment in the regenerator.

[0061] Biomass conversion unit 114 may, for example, be a fluidized bed or a trickle bed configuration or another bed regimen. The biomass may be converted in a single stage to hydrocarbons (including bio-oil) in the biomass conversion unit. Undesirable heavy materials and solids may be separated from the pyrolyzed biomass in solids separator 124 and the solids, including spent catalyst 130, are then allowed to proceed to catalyst regeneration unit 118. (Suitable solid separators in the figures provided herein may be a cyclone, coalescer, gravity phase separator, liquid hydrocyclone, electrostatic desalter, etc.) The liquid portion 131 separated in solids separator 124 may then be further processed to render hydrocarbon distillates for use in renewable fuel production. In catalyst regeneration unit 118, spent catalyst 130 is regenerated. Regenerated catalyst is then introduced into biomass conversion unit 114. Solid biomass 112 may also be introduced with multi-functional regenerated catalyst 122 into biomass conversion unit 114 through line 120. During the process, fresh multi-functional catalyst may optionally be added into biomass conversion unit 114 in order to attain the desired activity of the catalyst within the reactor. Similarly,

lower activity regenerated catalyst may optionally be removed from the catalyst regeneration unit 118 in order to attain the desired activity of the catalyst within the reactor and keep solid hold-up in the unit.

[0062] FIG. 2 illustrates another embodiment wherein biomass is treated in two stages. In the first stage of the process, biomass may be fed through line 211 into a first stage (pyrolysis) reactor 216. As illustrated, undesirable heavy materials and solids may be separated from the pyrolyzed biomass in first solids separator 224. Typically, from about 90 to 95 weight percent of the solids are removed from the biomass in separator 224. In addition to the removal of heavy materials and solids, water may be removed during the separation. Remaining treated biomass, enriched with heavy materials and solids including the heat carrier separated from the pyrolyzed biomass in solids separator 224, is then fed via line 226 back into first stage (pyrolysis) reactor 216. Optionally and in order to keep solid hold-up in the unit, the treated biomass, enriched with heavy materials and produced biochar, may occasionally be removed from the separated solid stream prior to feeding the separated heat carrier via line 226 back into first stage (pyrolysis) reactor 216. Untreated biomass may further be fed through line 212 into first stage reactor 216 and admixed with the solids stream from line 226.

[0063] In the second stage, the pyrolysis products are upgraded in the presence of a multi-functional catalyst. As illustrated, the separated vapors from the pyrolyzed biomass, substantially free of solids separated in first solids separator 224 is introduced into a second stage reactor 228 through line 240. The vapor may include, in addition to liquid reaction products, the lift gas and gaseous reaction products such as carbon dioxide, carbon monoxide, and relatively minor amounts of hydrogen, methane, ethylene and other light hydrocarbons.

[0064] Multi-functional catalyst may be fed into second stage reactor 228 via line 210. The treated biomass from second stage reactor 228 may then be introduced into the second solids separator 234. Solids, including spent or contaminated catalyst 230, separated in the second solids separator 234 may then be fed into the catalyst regeneration unit 218. Within catalyst regeneration unit 218, regenerated catalyst or E-cat is produced by burning coke deposits from spent catalyst in oxygen or an oxygen containing gas, such as air. The bio-oil, having the byproduct water, heavy materials and solids removed in second solids separator 234 may be further processed. For instance, the bio-oil may be introduced into a fractionator for further processing to render boiling point equivalent fractions of renewable gasoline, renewable jet fuel, renewable diesel and/or renewable fuel oil. Multi-functional catalyst 222, regenerated in regeneration unit 218, may then be fed into second stage reactor 228 through line 240. During the process, fresh multi-functional catalyst may optionally be added into second stage reactor 228 in order to attain desired activity of the catalyst within the reactor. Similarly, lower activity regenerated catalyst may optionally be removed from catalyst regeneration unit 218 in order to attain the desired activity of the catalyst within the reactor and keep solid hold-up in the unit.

[0065] In FIG. 3A, a two stage process is illustrated wherein catalyst portion 313 comprising basic component 307 of the multi-functional catalyst is introduced in a first stage into first reactor 315. Biomass may be introduced directly into the first stage reactor 315 through line 317. In the second stage reactor 329, a catalyst portion 311 comprising

acid component **308** and metallic component **309** of the multi-functional catalyst are introduced. The pyrolyzed biomass from the second stage reactor **329** is treated in solids separator **324** such that solids including spent or contaminated catalyst **330** are separated from the pyrolyzed biomass. Liquids and vapors (including bio-oil) separated from the treated biomass in solids separator **324** may be further processed in order, for instance, to render boiling point equivalent fractions of renewable gasoline, renewable jet fuel, renewable diesel and/or renewable fuel oil.

[0066] Solids separated in solids separator **324** including spent or contaminated catalyst **330** may then be fed into catalyst regeneration unit **318** wherein at least a portion of coke deposits are burned from the spent catalyst in oxygen or an oxygen containing gas, such as air. At least a portion **340** of regenerated catalyst **322** containing acid component **308**, basic component **307** and metallic component **309** exiting the catalyst regeneration unit **318** may proceed via line **320** into first stage reactor **315** and/or at least another portion **342** of regenerated catalyst **322** proceeds via line **343** into second stage reactor **329**. Optionally, regenerated catalyst **322** from catalyst regeneration unit **318** may be divided such that stream **340** contain the regenerated basic component and stream **342** comprises regenerated acidic component and regenerated metallic component. A stream of fresh basic component **307** may be fed into first stage reactor **315** and a stream of fresh acidic component **308** and/or metallic component **309** may be fed into second stage reactor **329** as make-up component(s) in order to attain the desired activity of the catalyst components within each staged-reactor, as needed. Similarly, lower activity regenerated catalyst may optionally be removed from catalyst regeneration unit **318** in order to attain the desired activity of the catalyst within the reactor and keep solid hold-up in the unit. Untreated biomass may further be admixed with regenerated basic component and be fed into first stage reactor **315** through line **317**. In an alternative, illustrated in FIG. 3A, untreated biomass may be fed into line **320** where it is combined with the regenerated basic component.

[0067] In another embodiment, illustrated in FIG. 3B, a two stage process is illustrated as described in the paragraph above except catalyst portion **313** comprises acidic material **308** and is introduced into first stage reactor **315** and catalyst portion **311** comprises basic component **307** and metallic component **309** and is introduced into second stage reactor **329**. At least a portion **340** of regenerated catalyst **322** containing acid component **308**, basic component **307** and metallic component **309** exiting the catalyst regeneration unit **318** may proceed via line **320** into first stage reactor **315** and/or at least another portion **342** of regenerated catalyst **322** proceeds via line **343** into second stage reactor **329**. Optionally, regenerated catalyst **322** from catalyst regeneration unit **318** may be divided such that stream **340** comprises the regenerated acidic component and stream **342** comprises regenerated basic component and regenerated metallic component. A stream of fresh acidic component **308** may be fed into first stage reactor **315** and a stream of fresh basic component **307** and/or metallic component **309** may be fed into second stage reactor **329** as make-up component(s) in order to attain the desired activity of the catalyst components within the reactor, as needed. Similarly, lower activity regenerated catalyst may optionally be removed from catalyst regeneration unit **318** in order to attain the desired activity of the catalyst within the reactor and keep solid hold-up in the unit.

[0068] In FIG. 3C, a two stage process is illustrated as described in the paragraph above except catalyst portion **313** comprises metallic component **309** and is introduced into first stage reactor **315** and catalyst portion **311** comprises acidic component **308** and basic component **307** and is introduced into second stage reactor **329**. At least a portion **340** of regenerated catalyst **322** containing acid component **308**, basic component **307** and metallic component **309** exiting the catalyst regeneration unit **318** may proceed via line **320** into first stage reactor **315** and/or at least another portion **342** of regenerated catalyst **322** proceeds via line **343** into second stage reactor **329**. Optionally, regenerated catalyst **322** from catalyst regeneration unit **318** may be divided such that stream **340** contain regenerated the metallic component and stream **342** comprises regenerated acidic component and regenerated basic component. A stream of fresh metallic component **309** may be fed into first stage reactor **315** and a stream of fresh acidic component **308** and/or fresh basic component **307** may be fed into second stage reactor **329** as make-up component(s) in order to attain the desired activity of the catalyst components within the reactor, as needed. Similarly, lower activity regenerated catalyst may optionally be removed from catalyst regeneration unit **318** in order to attain the desired activity of the catalyst within the reactor and keep solid hold-up in the unit.

[0069] In FIG. 4A, a two stage process system is illustrated wherein catalyst portion **413** comprising acidic component **408** and metallic component **409** of the multi-functional catalyst are introduced into first stage reactor **415**. Biomass **412** may be introduced directly into first stage reactor **415** through line **417**. In the second stage reactor **429**, catalyst portion **411** comprising basic component **407** of the multi-functional catalyst is introduced. The pyrolyzed biomass from second stage reactor **429** is treated in solids separator **424** such that solids including spent or contaminated catalyst **430** are separated from the pyrolyzed biomass. Liquids and vapor (including bio-oil) separated from the treated biomass in solids separator **424** may be further processed. Spent or contaminated catalyst **430** may then be fed into catalyst regeneration unit **418** wherein at least a portion of coke deposits are burned from the spent catalyst in oxygen or an oxygen containing gas, such as air. The resulting regenerated catalyst **422** contains the acidic component, basic component and the metal component of the multi-functional catalyst as described herein. At least a portion **440** of regenerated catalyst **422** containing acid component **408**, basic component **407** and metallic component **409** exiting the catalyst regeneration unit **418** may proceed via line **420** into first stage reactor **415** and/or at least another portion **442** of regenerated catalyst **422** proceeds via line **443** into second stage reactor **429**. Optionally, regenerated catalyst **422** from catalyst regeneration unit **418** may be divided such that stream **440** contains the regenerated acidic component and the regenerated metallic component and stream **442** comprises the regenerated basic component. A stream of fresh acidic component **408** and/or fresh metallic component **409** may be fed into first stage reactor **415** and a stream of fresh basic component **407** may be fed into second stage reactor **429** as make-up component(s) in order to attain the desired activity of the catalyst components within the staged-reactor, as needed. Untreated biomass may further be admixed with regenerated acidic component and regenerated metallic component and be fed into first stage reactor **415** through line **417**. Similarly, lower activity regenerated catalyst may optionally be removed from catalyst

regeneration unit **418** in order to attain the desired activity of the catalyst within the reactor and keep solid hold-up in the unit. In an embodiment, untreated biomass may be fed into line **420** where it is combined with the regenerated acidic and metallic components.

[0070] In another embodiment, illustrated in FIG. 4B, a two stage reacting system is illustrated as described in the paragraph above except catalyst portion **413** comprises basic component **407** and metallic component **409** and is introduced into first stage reactor **415** and catalyst portion **411** comprises acidic component **408** and is introduced into second stage reactor **429**. At least a portion **440** of regenerated catalyst **422** containing acid component **408**, basic component **407** and metallic component **409** exiting the catalyst regeneration unit **418** may proceed via line **420** into first stage reactor **415** and/or at least another portion **442** of regenerated catalyst **422** proceeds via line **443** into second stage reactor **429**. Optionally, regenerated catalyst **422** from catalyst regeneration unit **418** may be divided such that stream **440** contain regenerated the basic component and regenerated metallic component, and stream **442** comprises regenerated acidic component. A stream of fresh basic component and/or metallic component may be fed into first stage reactor **415** and a stream of acid component **409** may be fed into second stage reactor **429** as make-up component(s) in order to attain the desired activity of the catalyst components within the reactor (s). Similarly, lower activity regenerated catalyst may optionally be removed from catalyst regeneration unit **318** in order to attain the desired activity of the catalyst within the reactor and keep solid hold-up in the unit.

[0071] In the embodiment illustrated in FIG. 4C, a two stage reacting system is illustrated as described in the paragraph above except catalyst portion **413** comprises basic component **407** and acidic component **408** and is introduced into first stage reactor **415** and catalyst portion **411** comprises metallic component **409**. At least a portion **440** of regenerated catalyst **422** containing acid component **408**, basic component **407** and metallic component **409** exiting the catalyst regeneration unit **418** may proceed via line **420** into first stage reactor **415** and/or at least another portion **442** of regenerated catalyst **422** proceeds via line **443** into second stage reactor **429**. Optionally, regenerated catalyst **422** from catalyst regeneration unit **418** may be divided such that stream **440** comprises the regenerated acidic component and regenerated basic component and stream **442** comprises regenerated metallic component. A stream of fresh acidic component and/or basic component may be fed into first stage reactor **415** and a stream of metallic component **409** may be fed into second stage reactor **429** as make-up component(s) in order to attain the desired activity of the catalyst components within the reactor(s). Similarly, lower activity regenerated catalyst may optionally be removed from catalyst regeneration unit **418** in order to attain the desired activity of the catalyst within the reactor and keep solid hold-up in the unit.

[0072] FIG. 5A illustrates a two stage pyrolysis system wherein catalyst component **513** comprising basic component **507** is fed into first stage reactor **515**. Biomass may be introduced directly into first stage reactor **515** through line **517**. After pyrolysis in first stage reactor **515**, the treated biomass may be fed into first solids separator **525** such that solids including spent or contaminated (basic) component **531** may be separated from the pyrolyzed biomass. Liquids and vapor (including bio-oil) are separated from the pyrolyzed biomass and are then fed into second stage reactor **529**.

[0073] Spent or contaminated component **531** from first solids separator **525** may then be fed into first catalyst regeneration unit **516** wherein at least a portion of coke deposits are burned from the spent component in oxygen or an oxygen containing gas, such as air. The resulting regenerated (basic) component **521** may then be fed through line **540** into first stage reactor **515**. Untreated biomass may further be admixed with the regenerated basic component and fed into first stage reactor **515** through line **540**. A stream of fresh component **507** may also be fed into first stage reactor **515** and/or admixed with the regenerated basic component **521** in order to attain the desired activity of the basic catalyst component within the reactor. Similarly, lower activity regenerated basic component may optionally be removed from catalyst regeneration unit **516** in order to attain the desired activity of the component within the reactor and keep solid hold-up in the unit.

[0074] The pyrolyzed liquids and vapors (including bio-oil) substantially free of solids separated in the first solids separator **525** are introduced as vapor into second stage reactor **529** through line **542**. Catalyst portion **511** comprising acidic component **508** and metallic component **509** is fed into second stage reactor **529** through line **510**. The pyrolyzed biomass from second stage reactor **529** may then be fed into second solids separator **526** where solid spent or contaminated component **532** (acid component and metallic component) are separated from the liquids and vapor. The liquids and vapor (including bio-oil) separated from the biomass in second solids separator **526** may be further processed to render hydrocarbon distillate for use in renewable fuels production.

[0075] Spent solids **532** may then be fed into second regeneration unit **519** wherein at least a portion of coke deposits are burned. The regenerated catalyst component **523** from second regeneration unit **519** enriched in regenerated acidic component and regenerated metallic component may then be fed via line **542** into second stage reactor **529**.

[0076] A stream of fresh acidic component and/or metallic component may be fed into second stage reactor **529** as needed as make-up component(s). The fresh component(s) may be added directly into the reactor and/or fed into line **542** and/or admixed with the regenerated component(s). Similarly, lower activity regenerated acidic and/or metallic components may optionally be removed from catalyst regeneration unit **519** in order to attain the desired activity of these components within the reactor and keep solid hold-up in the unit.

[0077] A similar process as described above and depicted in FIG. 5A is set forth in FIG. 5B. However, catalyst portion **513** is comprised of acidic component **508** and catalyst portion **511** is composed of basic component **507** and metallic component **509**. Thus, acidic component **508** is introduced into first stage reactor **515** and basic component **507** and metallic component **509** are fed into second stage reactor **529**. It is understood then that spent component **531** comprises the spent acidic component and spent component **532** comprises the spent basic and metallic components. In addition, it is understood that regenerated component **521** comprises regenerated acidic component **508** and regenerated portion **523** comprises regenerated basic component **507** and regenerated metallic component **509**. A stream of fresh acidic component **508** may also be fed into first stage reactor **515** and/or admixed with regenerated acidic component **521** in order to attain the desired activity of the acidic catalyst component

within the reactor. Similarly a stream of fresh basic component **507** and/or metallic component **509** may be fed into second stage reactor **529** and/or admixed with regenerated components **523** in order to attain the desired activity of the fresh basic component and metallic component within the reactor to keep solid hold-up in the unit. Lower activity regenerated acidic component may optionally be removed from first regeneration unit **516** and/or lower activity basic component **507** and/or metallic component **509** may be removed from second regeneration unit **519** in order to attain the desired activity of the catalyst component(s) in the stage 1 reactor **515** and second stage reactor **529** and keep solid(s) hold-up in the unit.

[0078] A similar process as described above depicted in FIG. **5A** is also set forth in FIG. **5C**. However, catalyst portion **513** is comprised of metallic component **509** and catalyst portion **511** is composed of acidic component **508** and basic component **507**. Thus, metallic component **509** is introduced into first stage reactor **515** and acidic component **508** and basic component **507** are fed into second stage reactor **529**. It is understood then that spent component **531** comprises the spent metallic component and spent component **532** comprises spent acidic and spent basic components. In addition, it is understood that regenerated component **521** comprises regenerated metallic component **509** and regenerated portion **523** comprises regenerated acidic component **508** and regenerated basic component **507**.

[0079] A stream of fresh metallic component **509** may be fed into first stage reactor **515** and/or admixed with regenerated component **521** in order to attain the desired activity of the fresh metallic component within the reactor to keep solid hold-up in the unit. Similarly a stream of acidic component **508** and/or basic component **507** may be fed into second stage reactor **529** and/or admixed with regenerated components **523** in order to attain the desired activity of the acidic component **508** and/or basic component **507** within the reactor to keep solid hold-up in the unit. Lower activity regenerated metallic component may optionally be removed from first regeneration unit **516** and/or lower activity acidic component **508** and/or basic component **507** may be removed from second regeneration unit **519** in order to attain the desired activity of the catalyst component(s) in the stage 1 reactor **515** and second stage reactor **529** and keep solid(s) hold-up in the unit.

[0080] In another embodiment, illustrated in FIG. **6A**, a two stage process is illustrated as described in the paragraphs above except catalyst portion **613** is comprised of acidic component **608** and metallic component **609** of the multi-functional catalyst and are introduced into first stage reactor **615**. The basic component **607** of the multi-functional catalyst is introduced as component **611** into the second reactor **629**. It is understood then that spent component **631** comprises the spent acidic component and metallic component and spent component **632** comprises the spent basic component. In addition, it is understood that regenerated component **621** comprises regenerated acidic component **608** and regenerated metallic component **609** and regenerated portion **623** comprises regenerated acidic component **607**.

[0081] A stream of fresh acidic component **608** and/or metallic component **609** may be fed into first stage reactor **615** and/or admixed with regenerated components **621** in order to attain the desired activity of the acidic component and/or metallic component within the reactor to keep solid hold-up in the unit. Similarly, a stream of basic component **607** may be fed into second stage reactor **629** and/or admixed

with regenerated components **623** in order to attain the desired activity of the basic component within the reactor. Lower activity regenerated acidic component and/or metallic component may optionally be removed from first regeneration unit **616** and/or lower activity basic component may be removed from second regeneration unit **619** in order to attain the desired activity of the catalyst component(s) in the stage 1 reactor **615** and second stage reactor **629** and keep solid(s) hold-up in the unit.

[0082] In FIG. **6B**, a two stage process is illustrated as set forth in FIG. **6A** above except catalyst portion **613** is comprised of basic component **607** and metallic component **609** and catalyst portion **611** is composed of acidic component **608**. The acidic component **608** of the multi-functional catalyst is introduced into second reactor **629**. It is understood then that spent component **631** comprises the spent basic component and metallic component and spent component **632** comprises the spent acidic component. In addition, it is understood that regenerated component **621** comprises regenerated basic component **607** and metallic component **609** and regenerated portion **623** comprises regenerated basic component **608**.

[0083] A stream of fresh basic component **607** and/or metallic component **609** may be fed into first stage reactor **615** and/or admixed with regenerated components **621** in order to attain the desired activity of the basic component and/or metallic component within the reactor to keep solid hold-up in the unit. Similarly, a stream of acidic component **608** may be fed into second stage reactor **629** and/or admixed with regenerated component **623** in order to attain the desired activity of the acidic component within the reactor. Lower activity regenerated basic component and/or metallic component may optionally be removed from first regeneration unit **616** and/or lower activity acidic component may be removed from second regeneration unit **619** in order to attain the desired activity of the catalyst component(s) in the stage 1 reactor **615** and second stage reactor **629** and keep solid(s) hold-up in the unit.

[0084] In FIG. **6C**, a two stage process is illustrated as set forth in FIG. **6A** above except catalyst portion **613** is comprised of basic component **607** and acidic component **608**. The metallic component **609** of the multi-functional catalyst is introduced in catalyst portion **611** into second reactor **629**. It is understood then that spent component **631** comprises the spent basic component and spent acidic component and spent component **632** comprises the spent metallic component. In addition, it is understood that regenerated component **621** comprises regenerated basic component **607** and regenerated acidic component **608** and regenerated portion **623** comprises regenerated metallic component **609**.

[0085] A stream of fresh acidic component **608** and/or basic component **607** may be fed into first stage reactor **615** and/or admixed with regenerated components **621** in order to attain the desired activity of the acidic component and/or basic component within the reactor to keep solid hold-up in the unit. Similarly, a stream of metallic component **609** may be fed into second stage reactor **629** and/or admixed with regenerated component **623** in order to attain the desired activity of the metallic component within the reactor. Lower activity regenerated acidic component and/or basic component may optionally be removed from first regeneration unit **616** and/or lower activity metallic component may be removed from second regeneration unit **619** in order to attain

the desired activity of the catalyst component(s) in the stage 1 reactor **615** and second stage reactor **629** and keep solid(s) hold-up in the unit.

[0086] All percentages set forth in the Examples are given in terms of weight units except as may otherwise be indicated.

Example 1

[0087] A reactor system as that shown in FIG. 7 was used to assess the capabilities of the different process configurations that employ the multi-functional catalyst of the present disclosure. Each stage was run at fixed bed mode. Stage 1 was set at 550° C. and Stage 2 was set at 450° C. The catalyst composition employed at each stage was adjusted to represent the ranges of the multi-functional catalyst of the present disclosure. Comparative experiments were run using the same proportions of catalyst components for each experiment, which were 20% ZSM-5+10% USY as the acid (A) component, 30% MgO—Al₂O₃ as the basic (B) component and 10% Mo₂C as the metal (M) component. Three consecutive experiments were executed for each configuration and the products were online analyzed by GC/MS. For the first run (Run 1), there was not any catalyst in the first stage and the catalyst of the second stage (Catalyst 2) was composed of the A component, the M component and the B component. In Run 2, the catalyst in the first stage (Catalyst 1) was composed by the B component and Catalyst 2 was composed of the A component and the M component. In Run 3, Catalyst 1 was composed by the B component and the M component; and Catalyst 2 was composed of the A component. And in Run 4, Catalyst 1 was composed by the B component and the M component; and Catalyst 2 was composed of the A component. As feed a sample of Southern Yellow Pine milled to a particle size below 1000 μm was used.

[0088] The Total Ion Chromatogram (TIC) of the products for each experiment was recorded and a representative TIC of each run is set forth in FIGS. 8A, B, C and D and summarized in Table 1.

TABLE 1

Run No.	Catalyst 1	Catalyst 2	Product TIC
1	None	A + B + M	FIG. 8A
2	B	A + M	FIG. 8B
3	A + B	M	FIG. 8C
4	B + M	A	FIG. 8D

This example demonstrates that the resulting product distribution from the same biomass can be tuned by changing the configuration and/or the catalyst composition of the multi-functional catalyst of the present disclosure, used at each stage. Consequently, there would be an optimum configuration and/or catalyst system for each type of biomass processed.

[0089] While exemplary embodiments of the disclosure have been shown and described, many variations, modifications and/or changes of the system, apparatus and methods of the present disclosure, such as in the components, details of construction and operation, arrangement of parts and/or methods of use, are possible, contemplated by the patent applicant(s), within the scope of the appended claims, and may be made and used by one of ordinary skill in the art without departing from the spirit or teachings of the disclosure and scope of appended claims. Thus, all matter herein set forth or shown in the accompanying drawings should be

interpreted as illustrative, and the scope of the disclosure and the appended claims should not be limited to the embodiments described and shown herein.

What is claimed is:

1. A process of converting solid biomass to hydrocarbons comprising feeding into a biomass conversion unit at least a portion of a regenerated catalyst in two stages wherein:

- (i) the regenerated catalyst comprises an acidic component, a basic component and a metallic component; and
- (ii) treatment of the biomass within the biomass conversion unit occurs in at least two stages; and
- (iii) at least one component of the regenerated catalyst is fed into each of the stages.

2. The process of claim 1, wherein treatment of the biomass within the biomass conversion unit occurs in two stages.

3. The process of claim 2, wherein at least a portion of the acidic component of the regenerated catalyst is fed into the biomass conversion unit during the first stage.

4. The process of claim 3, wherein at least a portion of the basic component and the metallic component of the regenerated catalyst are fed into the biomass conversion unit during the second stage.

5. The process of claim 4, wherein:

- a) fresh acidic component of the acidic component of the regenerated catalyst is further fed into the first stage;
- b) fresh basic component and/or metallic component of the basic component and/or metallic component of the regenerated catalyst is further fed into the second stage; or
- c) both (a) and (b).

6. The process of claim 1, wherein at least one of the following conditions prevail:

- a) the acidic component is a mixture of zeolite ZSM-5 and zeolite USY;
- b) the basic component is selected from the group consisting of alkaline-exchanged zeolite, alkaline earth-exchanged zeolite, basic zeolite, alkaline earth metal oxide, cerium oxide, zirconium oxide, titanium dioxide, mixed oxides of alkaline earth metal oxides and combinations thereof and mixed oxides selected from the group of magnesia-alumina, magnesia-silica, titania-alumina, titania-silica, ceria-alumina, ceria-silica, zirconia-alumina, zirconia-silica and mixtures thereof and wherein the exchanged zeolite has from about 40 to about 75% of exchanged cationic sites; or
- c) the metallic component is selected from the group consisting of Cu, Ni, Cr, W, Mo, a metal carbide, a metal nitride, a metal sulfide and mixtures thereof.

7. The process of claim 1, wherein the acidic component is a mixture of zeolite ZSM-5 and zeolite USY.

8. The process of claim 2, wherein a promoter is further fed into the first stage or the second stage or both the first stage and the second stage.

9. The process of claim 8, wherein at least one of the following conditions prevail:

- a) a phosphate promoter is further fed into the stage containing the acidic component of the catalyst;
- b) a silica promoter, an alumina promoter or both a silica and alumina promoter are further fed into the stage containing the basic component of the catalyst; or
- c) a metallic promoter is further fed into the stage containing the metallic component of the catalyst.

10. The process of claim **2**, wherein the basic component of the regenerated catalyst is fed into the biomass conversion unit during the first stage.

11. The process of claim **10**, wherein the acidic component and the metallic component of the regenerated catalyst are fed into the biomass conversion unit during the second stage.

12. The process of claim **11**, wherein:

- a) fresh basic component of the basic component of the regenerated catalyst is further fed into the first stage;
- b) fresh acidic component and/or metallic component of the acidic component and/or metallic component of the regenerated catalyst is further fed into the second stage; or
- c) both (a) and (b).

13. The process of claim **2**, wherein the metallic component of the regenerated catalyst is fed into the biomass conversion unit during the first stage.

14. The process of claim **13**, wherein the acidic component and the basic component of the regenerated catalyst are fed into the biomass conversion during the second stage.

15. The process of claim **14**, wherein:

- a) fresh metallic component of the metallic component of the regenerated catalyst is further fed into the first stage;
- b) fresh acidic component and/or basic component of the acidic component and/or basic component of the regenerated catalyst is further fed into the second stage; or
- c) both (a) and (b).

16. The process of claim **2**, wherein at least a portion of the acidic component and metallic component of the regenerated catalyst are fed into the biomass conversion unit during the first stage.

17. The process of claim **16**, wherein at least a portion of the basic component of the regenerated catalyst is fed into the biomass conversion unit during the second stage.

18. The process of claim **17**, wherein:

- a) fresh acidic component and/or metallic component of the acidic component and/or metallic component of the regenerated catalyst is further fed into the first stage;
- b) fresh basic component of the basic component of the regenerated catalyst is further fed into the second stage; or
- c) both (a) and (b).

19. The process of claim **2**, wherein at least a portion of the basic component and metallic component of the regenerated catalyst are fed into the biomass conversion unit during the first stage.

20. The process of claim **19**, wherein at least a portion of the acidic component of the regenerated catalyst is fed into the biomass conversion unit during the second stage.

21. The process of claim **20**, wherein:

- a) fresh basic component and/or metallic component of the basic and/or metallic component of the regenerated catalyst is further fed into the first stage;
- b) fresh acidic component of the acidic component of the regenerated catalyst is further fed into the second stage; or
- c) both (a) and (b).

22. The process of claim **2**, wherein at least a portion of the acidic component and basic component of the regenerated catalyst are fed into the biomass conversion unit during the first stage.

23. The process of claim **22**, wherein at least a portion of the metallic component of the regenerated catalyst is fed into the biomass conversion unit during the second stage.

24. The process of claim **23**, wherein:

- a) fresh acidic component and/or basic component of the acidic component and/or basic component of the regenerated catalyst is further fed into the first stage;
- b) fresh metallic component of the metallic component of the regenerated catalyst is further fed into the second stage; or
- c) both (a) and (b).

25. A process of converting solid biomass to hydrocarbons in two stages in the presence of at least a portion of a first regenerated catalyst and at least a portion of a second regenerated catalyst wherein the first regenerated catalyst or the second regenerated catalyst is a monofunctional catalyst and the other is a bifunctional catalyst, wherein:

- (i) the combination of the monofunctional catalyst and the bifunctional catalyst contains an acidic component, a basic component and a metallic component wherein the bifunctional catalyst contains two of the components and the monofunctional catalyst contains the remaining component;
- (ii) the first stage in a first reactor has a first solids separator and the second stage in a second reactor has a second solids separator; and
- (iii) the first reactor has a first regeneration unit and the second reactor has a second regeneration unit

the process comprising:

- a) subjecting the solid biomass to pyrolysis in the first reactor of the biomass conversion unit;
- b) separating spent catalyst and vapor from the pyrolyzed biomass in the first solids separator;
- c) feeding the separated vapor of step (b) into the second reactor and the spent catalyst into the first regeneration unit to render the first regenerated catalyst;
- d) subjecting the vapor phase in the second reactor to pyrolysis;
- e) feeding spent catalyst separated from the pyrolyzed vapor phase of step (d) into the second regeneration unit to render the second regenerated catalyst; and
- f) feeding into the first reactor at least a portion of the first regenerated catalyst and feeding into the second reactor at least a portion of the second regenerated catalyst.

26. The process of claim **25**, wherein at least a portion of the monofunctional catalyst is fed into the first reactor.

27. The process of claim **26**, wherein the monofunctional catalyst contains the acidic component and the bifunctional catalyst contains the basic component and the metallic component.

28. The process of claim **27**, wherein:

- a) fresh acidic component of the acidic component of the monofunctional catalyst is further fed into the first reactor;
- b) fresh basic component and/or metallic component of the basic component and/or metallic component of the bifunctional catalyst is further fed into the second reactor; or
- c) both (a) and (b).

29. The process of claim **25**, wherein the first stage or the second stage or both the first stage and the second stage further comprises a promoter.

30. The process of claim **29**, wherein at least one of the following conditions prevail:

- a) the stage comprising the acidic component further comprises a phosphate promoter;

- b) the basic component further comprises a silica promoter, an alumina promoter or both a silica promoter or an alumina promoter; or
 - c) the stage comprising the metallic component further comprises a metallic promoter.
- 31.** The process of claim **25**, wherein at least a portion of the basic component of the regenerated catalyst is fed into the biomass conversion unit during the first stage.
- 32.** The process of claim **31**, wherein at least a portion of the acidic component and the metallic component of the regenerated catalyst are fed into the second reactor.
- 33.** The process of claim **32**, wherein:
- a) fresh basic component of the basic component of the regenerated catalyst is further fed into the first reactor;
 - b) fresh acidic component and/or metallic component of the acidic component and/or metallic component of the regenerated catalyst is further fed into the second reactor; or
 - c) both (a) and (b).
- 34.** The process of claim **25**, wherein at least a portion of the metallic component of the regenerated catalyst is fed into the first reactor.
- 35.** The process of claim **34**, wherein at least a portion of the acidic component and the basic component of the regenerated catalyst are fed into the second reactor.
- 36.** The process of claim **35**, wherein:
- a) fresh metallic component of the metallic component of the regenerated catalyst is further fed into the first reactor;
 - b) fresh acidic component and/or basic component of the acidic component and/or basic component of the regenerated catalyst is further fed into the second reactor; or
 - c) both (a) and (b).
- 37.** The process of claim **25**, wherein at least a portion of the bi-functional catalyst is fed into the first reactor.
- 38.** The process of claim **37**, wherein at least a portion of the acidic component and metallic component of the regenerated catalyst are fed into the first reactor.
- 39.** The process of claim **38**, wherein at least a portion of the basic component of the regenerated catalyst is fed into the second reactor.
- 40.** The process of claim **39**, wherein:
- a) fresh acidic component and/or metallic component of the acidic component and/or metallic component of the regenerated catalyst is further fed into the first reactor;
 - b) fresh basic component of the basic component of the regenerated catalyst is further fed into the second stage; or
 - c) both (a) and (b).
- 41.** The process of claim **37**, wherein at least a portion of the basic component and metallic component of the regenerated catalyst are fed into the first reactor.
- 42.** The process of claim **41**, wherein at least a portion of the acidic component of the regenerated catalyst is fed into the second reactor.
- 43.** The process of claim **42**, wherein:
- a) fresh basic component and/or fresh metallic component of the basic component and/or metallic component of the regenerated catalyst is further fed into the first reactor;
 - b) fresh acidic component of the acidic component of the regenerated catalyst is further fed into the second reactor; or
 - c) both (a) and (b).

44. The process of claim **37**, wherein at least a portion of the acidic component and basic component of the regenerated catalyst are fed into the first reactor.

45. The process of claim **44**, wherein at least a portion of the metallic component of the regenerated catalyst is fed into the second reactor.

46. The process of claim **45**, wherein:

- a) fresh acidic component and/or fresh basic component of the acidic component and/or basic component of the regenerated catalyst is further fed into the first stage;
- b) fresh metallic component of the metallic component of the regenerated catalyst is further fed into the second stage; or
- c) both (a) and (b).

47. A process of converting solid biomass to hydrocarbons in at least two stages within a biomass conversion unit wherein at least one of the stages is conducted in the presence of at least a portion of a regenerated multi-functional catalyst comprising an acid component, a basic component and a metallic material, the process comprising:

- a) pyrolyzing the biomass in a first stage in a first reactor in the absence of a catalyst in a first stage; and
- b) separating vapor and solids from the pyrolyzed biomass;
- c) feeding the separated vapor into a second stage in a second reactor; and
- d) converting the separated vapor into hydrocarbons in the presence of the regenerated catalyst in a conversion unit.

48. The process of claim **47**, wherein at least one of the following conditions prevail:

- a) the acidic component of the regenerated catalyst is a mixture of zeolite ZSM-5 and zeolite USY;
- b) the basic component of the regenerated catalyst is selected from the group consisting of alkaline-exchanged zeolite, alkaline earth-exchanged zeolite, basic zeolite, alkaline earth metal oxide, cerium oxide, zirconium oxide, titanium dioxide, mixed oxides of alkaline earth metal oxides and combinations thereof and mixed oxides selected from the group of magnesia-alumina, magnesia-silica, titania-alumina, titania-silica, ceria-alumina, ceria-silica, zirconia-alumina, zirconia-silica and mixtures thereof and wherein the exchanged zeolite has from about 40 to about 75% of exchanged cationic sites; or
- c) the metallic component is selected from the group consisting of Cu, Ni, Cr, W, Mo, a metal carbide, a metal nitride, a metal sulfide and mixtures thereof.

49. A process of converting solid biomass to hydrocarbons in at least two stages comprising:

- a) pyrolyzing the biomass in a first stage in a first reactor in the absence of a catalyst;
- b) separating solids and vapor from the pyrolyzed product of step (a);
- c) feeding into a second stage in a second reactor at least a portion of a regenerated catalyst comprising an acidic component, a basic component and a metallic component; and
- d) pyrolyzing vapor separated in step (b) in the presence of at least a portion of the regenerated catalyst.

50. The process of claim **49**, wherein one or more components of the regenerated catalyst are fed into the second reactor and the remaining component(s) are fed into a third reactor.

51. The process of claim **49**, wherein at least one of the following conditions prevail:

- a) the acidic component is a mixture of zeolite ZSM-5 and zeolite USY;
- b) the basic component of the regenerated catalyst is selected from the group consisting of alkaline-exchanged zeolite, alkaline earth-exchanged zeolite, basic zeolite, alkaline earth metal oxide, cerium oxide, zirconium oxide, titanium dioxide, mixed oxides of alkaline earth metal oxides and combinations thereof and mixed oxides selected from the group of magnesia-alumina, magnesia-silica, titania-alumina, titania-silica, ceria-alumina, ceria-silica, zirconia-alumina, zirconia-silica and mixtures thereof and wherein the exchanged zeolite has from about 40 to about 75% of exchanged cationic sites; or
- c) the metallic component is selected from the group consisting of Cu, Ni, Cr, W, Mo, a metal carbide, a metal nitride, a metal sulfide and mixtures thereof.

52. The process of claim **50**, wherein at least a portion of the acidic component of the regenerated catalyst is fed into the second reactor and at least a portion of the basic component and the metallic component of the regenerated catalyst are fed into the third reactor.

53. The process of claim **50**, wherein at least a portion of the basic component of the regenerated catalyst is fed into the second reactor and at least a portion of the acidic component and the metallic component of the regenerated catalyst are fed into the third reactor.

54. The process of claim **50**, wherein at least a portion of the metallic component of the regenerated catalyst is fed into the second reactor and at least a portion of the acidic component and the basic component of the regenerated catalyst are fed into the biomass-vapors staged-conversion into the third reactor.

55. The process of claim **50**, wherein at least a portion of the acidic component and metallic component of the regenerated catalyst are fed into the second reactor and at least a portion of the basic component of the regenerated catalyst is fed into the third reactor.

56. The process of claim **50**, wherein at least a portion of the basic and metallic component of the regenerated catalyst are fed into the second reactor and at least a portion of the acidic component of the regenerated catalyst is fed into the third reactor.

57. The process of claim **50**, wherein at least a portion of the acidic component and basic component are fed into the second reactor and the metallic component of the regenerated catalyst is fed into the third reactor.

58. A process of converting solid biomass to hydrocarbons comprising the step of feeding into a biomass conversion unit at least a portion of a regenerated multi-functional catalyst comprising an acidic component, a basic component and a metallic component and pyrolyzing the biomass in the biomass conversion unit wherein at least one of the following conditions prevail:

- a) the regenerated multi-functional catalyst further comprises a binder;
- b) the acidic component is the combination of zeolite ZSM-5 and zeolite USY;
- c) the metallic component is selected from the group consisting of Cu, Ni, Cr, W, Mo, a metal carbide, a metal sulfide and mixtures thereof;
- d) the basic material is selected from the group consisting of alkaline-exchanged zeolite, alkaline earth-exchanged zeolite, basic zeolite, alkaline earth metal oxide, cerium oxide, zirconium oxide, titanium dioxide, mixed oxides of alkaline earth metal oxides and combinations thereof and mixed oxides selected from the group of magnesia-alumina, magnesia-silica, titania-alumina, titania-silica, ceria-alumina, ceria-silica, zirconia-alumina, zirconia-silica and mixtures thereof and wherein the exchanged zeolite has from about 40 to about 75% of exchanged cationic sites; or
- e) the multi-functional catalyst further contains at least one promoter.

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