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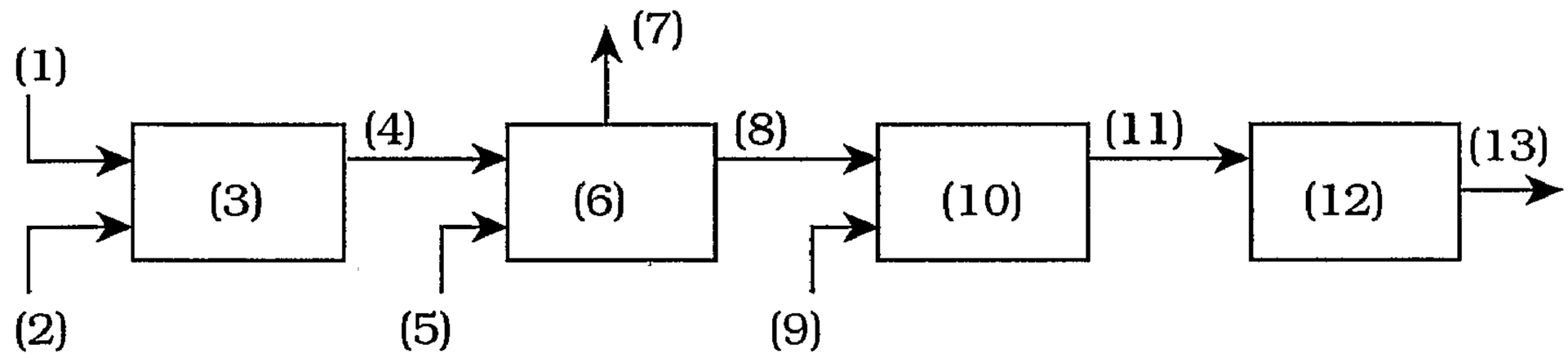
(54) Title: SELECTIVE NAPHTHA HYDRODESULFURIZATION WITH HIGH TEMPERATURE MERCAPTAN DECOMPOSITION



(57) Abrégé/Abstract:
A process for the selective hydrodesulfurization of olefinic naphtha streams containing a substantial amount of organically bound sulfur and olefins. The olefinic naphtha stream is selectively desulfurized in a first hydrodesulfurization reaction stage. This effluent stream is then contacted with a stripping agent in a H_2S removal zone, such as steam or an amine solution, to remove H_2S from the effluent stream, thereby reducing the H_2S partial pressure of the process stream. The process stream is then subjected to a second desulfurization reaction stage followed by a mercaptan decomposition stage to reduce the content of mercaptan sulfur in the final product stream. In a second embodiment, the effluent stream from the first hydrodesulfurization reaction stage, after being subjected to the H_2S removal zone, is fed directly to the mercaptan decomposition stage where total sulfur content and mercaptan sulfur content are reduced in the final product stream.

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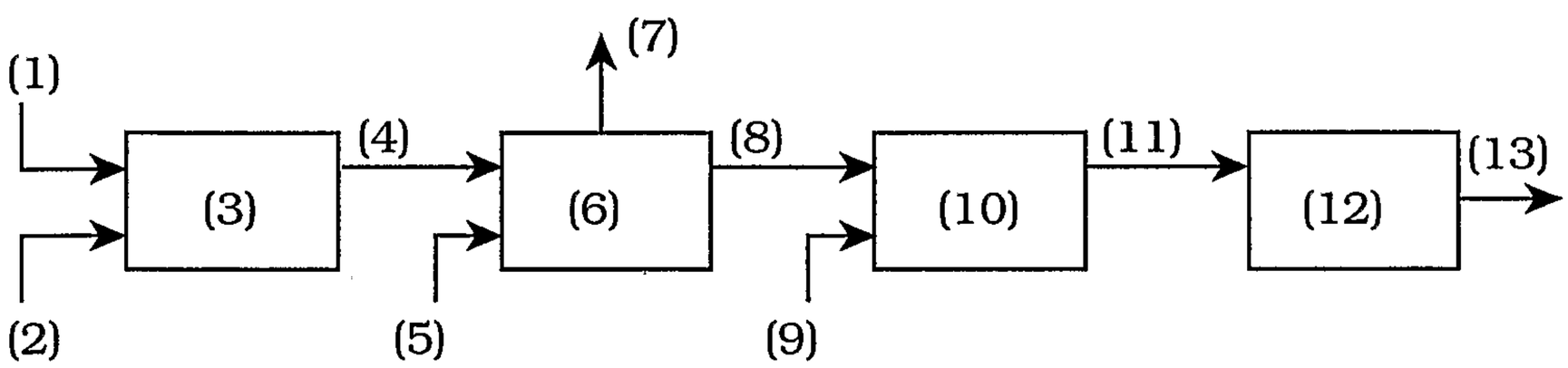
(54) Title: SELECTIVE NAPHTHA HYDRODESULFURIZATION WITH HIGH TEMPERATURE MERCAPTAN DECOMPOSITION



(57) Abstract: A process for the selective hydrodesulfurization of olefinic naphtha streams containing a substantial amount of organically bound sulfur and olefins. The olefinic naphtha stream is selectively desulfurized in a first hydrodesulfurization reaction stage. This effluent stream is then contacted with a stripping agent in a H_2S removal zone, such as steam or an amine solution, to remove H_2S from the effluent stream, thereby reducing the H_2S partial pressure of the process stream. The process stream is then subjected to a second desulfurization reaction stage followed by a mercaptan decomposition stage to reduce the content of mercaptan sulfur in the final product stream. In a second embodiment, the effluent stream from the first hydrodesulfurization reaction stage, after being subjected to the H_2S removal zone, is fed directly to the mercaptan decomposition stage where total sulfur content and mercaptan sulfur content are reduced in the final product stream.

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SELECTIVE NAPHTHA HYDRODESULFURIZATION WITH HIGH TEMPERATURE MERCAPTAN DECOMPOSITION

FIELD OF THE INVENTION

[0001] The present invention relates to a multistage process for the selective hydrodesulfurization and mercaptan removal of an olefinic naphtha stream containing a substantial amount of organically bound sulfur and olefins.

BACKGROUND OF THE INVENTION

[0002] Environmentally driven regulatory pressure concerning motor gasoline ("mogas") sulfur levels have resulted in the widespread production of less than 50 wppm sulfur mogas in 2004, and levels below 10 wppm are being considered for later years. In general, this will require deep desulfurization of refinery naphtha streams. The largest target of naphtha streams for such processes are those resulting from cracking operations, particularly those from a fluidized catalytic cracking unit which comprise a large volume of the available refinery blending stock as well as generally higher sulfur content than the "non-cracked" refinery naphtha streams. Naphthas from a fluidized catalytic cracking unit ("cat naphthas") typically contain substantial amounts of both sulfur and olefins. Deep desulfurization of cat naphtha requires improved technology to reduce sulfur levels without the severe loss of octane that accompanies the undesirable hydrogenation of olefins.

[0003] Hydrodesulfurization is one of the fundamental hydrotreating processes of refining and petrochemical industries. The removal of feed organically bound sulfur by conversion to hydrogen sulfide is typically achieved by reaction with hydrogen over non-noble metal sulfided supported and unsupported catalysts, especially those containing Co/Mo or Ni/Mo. This is usually achieved at fairly severe temperatures and pressures in order to meet product quality specifications, or to supply a desulfurized stream to a subsequent sulfur sensitive process.

[0004] Olefinic naphthas, such as cracked naphthas and coker naphthas, typically contain more than about 20 wt.% olefins. Conventional fresh hydrodesulfurization catalysts have both hydrogenation and desulfurization activity. Hydrodesulfurization of cracked naphthas using conventional naphtha desulfurization catalysts under conventional startup procedures and under conventional conditions required for sulfur removal, typically leads to an undesirable loss of olefins through hydrogenation. Since olefins are high octane components, it is desirable to retain the olefins rather than to hydrogenate them to saturated compounds that are typically lower in octane. This results in a lower grade fuel product that needs additional refining, such as isomerization, blending, etc., to produce higher octane fuels. Such additional refining, or course, adds significantly to production costs.

[0005] Selective hydrodesulfurization to remove organically bound sulfur, while minimizing hydrogenation of olefins and octane reduction by various techniques, such as selective catalysts and/or process conditions, has been described in the art. For example, a process referred to as SCANfining has been developed by ExxonMobil Corporation in which olefinic naphthas are selectively desulfurized with little loss in octane. U.S. Patent Nos. 5,985,136; 6,013,598; and 6,126,814, disclose various aspects of SCANfining. Although selective hydrodesulfurization processes have been developed to avoid significant olefin saturation and loss of octane, such processes have a tendency to liberate H_2S that reacts with retained olefins to form mercaptan sulfur by reversion.

[0006] As these refinery hydrodesulfurization catalytic processes are operated at greater severities to meet the lower sulfur specifications on products, the H_2S content in the process streams increases, resulting in higher saturation of olefins and reversion to mercaptan sulfur compounds in the products. Therefore, the industry has sought for methods to increase the desulfurization efficiency of

a process while reducing or eliminating the amount of reversion of mercaptan sulfur compounds in the final product.

[0007] Many refiners are considering combinations of available sulfur removal technologies in order to optimize economic objectives. As refiners have sought to minimize capital investment to meet low sulfur mogas objectives, technology providers have devised various strategies that include distillation of the cracked naphtha into various fractions that are best suited to individual sulfur removal technologies. While economics of such strategies may appear favorable compared to a single processing technology, the complexity of overall refinery operations is increased and successful mogas production is dependent upon numerous critical sulfur removal operations. Economically competitive sulfur removal strategies that minimize olefin saturation and minimize the production of mercaptan sulfur compounds in the products, as well as decrease the required capital investment and operational complexity will be favored by refiners.

[0008] Consequently, there is a need in the art for technology that will reduce the cost and complexity of hydrotreating olefinic naphthas to low levels of sulfur content while either reducing the amount of mercaptans formed or by providing an economical process to destroy the mercaptans that are formed as a resultant of the hydrotreating process. There is a need in the industry for a process to reduce these product mercaptan levels while meeting higher sulfur reduction specifications, minimizing the saturation of olefins, and reducing the loss of octane in the final product.

SUMMARY OF THE INVENTION

[0009] In accordance with the present invention, there is provided a process for hydrodesulfurizing olefinic naphtha feedstream and retaining a substantial amount of the olefins, which feedstream boils in the range of about 50°F (10°C) to about 450°F (232°C) and contains organically bound sulfur and an olefin content of at least about 5 wt.%, which process comprises:

a) hydrodesulfurizing the olefinic naphtha feedstream in a first reaction stage in the presence of a hydrogen-containing treat gas and a hydrodesulfurization catalyst, at first hydrodesulfurization reaction conditions including temperatures from about 450°F (232°C) to about 800°F (427°C), pressures of about 60 to about 800 psig, and hydrogen-containing treat gas rates of about 1000 to about 6000 standard cubic feet per barrel, to convert a portion of the elemental and organically bound sulfur in said olefinic naphtha feedstream to hydrogen sulfide to produce a first reactor effluent stream which has a reduced total sulfur content;

b) conducting said first reactor effluent stream to an H_2S removal zone wherein a stripping agent, such as steam or an amine solution, is utilized to remove substantially all of the H_2S from said first reactor effluent stream to produce a stripped effluent stream;

c) conducting said stripped effluent stream to a second reaction stage in the presence of a hydrogen-containing treat gas and a hydrodesulfurization catalyst, at second hydrodesulfurization reaction conditions including temperatures from about 450°F (232°C) to about 800°F (427°C), pressures of about 60 to about 800 psig, and hydrogen-containing treat gas rates of about 1000 to about 6000 standard cubic feet per barrel, to convert a potion of the remaining elemental and organically bound sulfur in said stripped effluent stream to hydrogen sulfide to produce a second reactor effluent stream which has a reduced total sulfur content; and

d) conducting said second reactor effluent stream to a mercaptan decomposition reaction stage in the presence a mercaptan decomposition catalyst, at reaction conditions including temperatures from about 500°F (260°C) to about 800°F (427°C), and pressures of about 60 to about 800 psig, to decompose at least a portion of the mercaptans to produce a mercaptan

decomposition reactor product with a lower mercaptan sulfur content than that of said second reactor effluent stream.

[0010] In a second embodiment of the present invention, there is provided a process for hydrodesulfurizing olefinic naphtha feedstream and retaining a substantial amount of the olefins, which feedstream boils in the range of about 50°F (10°C) to about 450°F (232°C) and contains organically bound sulfur and an olefin content of at least about 5 wt.%, which process comprises:

a) hydrodesulfurizing the olefinic naphtha feedstream in a first reaction stage in the presence of a hydrogen-containing treat gas and a hydrodesulfurization catalyst, at first hydrodesulfurization reaction conditions including temperatures from about 450°F (232°C) to about 800°F (427°C), pressures of about 60 to about 800 psig, and hydrogen-containing treat gas rates of about 1000 to about 6000 standard cubic feet per barrel, to convert a portion of the organically bound sulfur to hydrogen sulfide to produce a first reactor effluent stream which has a reduced total sulfur content;

b) conducting said first reactor effluent stream to an H_2S removal zone wherein a stripping agent, such as steam or an amine solution, is utilized to remove substantially all of the H_2S from said first reactor effluent stream to produce a stripped effluent stream;

c) conducting said stripped effluent stream to a mercaptan decomposition reaction stage in the presence of a hydrogen-containing treat gas and a mercaptan decomposition catalyst, at reaction conditions including temperatures from about 500°F (260°C) to about 800°F (427°C), pressures of about 60 to about 80 psig, and hydrogen-containing treat gas rates of about 1000 to about 6000 standard cubic feet per barrel, to convert at least a portion of the non-mercaptan organic and elemental sulfur compounds and decompose at least a portion of the mercaptans to produce a mercaptan decomposition reactor

product with a lower mercaptan sulfur content than that of said first reactor effluent stream.

[0011] In a preferred embodiment, the feedstreams to the hydrodesulfurization reactor and mercaptan decomposition stages will be in the vapor phase.

[0012] In another preferred embodiment, a portion of the hydrogen-containing treat gas to said first, second and mercaptan decomposition reaction stages is comprised of a portion of the gas removed from said first reactor effluent stream in said H_2S removal zone.

[0013] In still another preferred embodiment, the heat from at least a portion of said first reactor effluent is utilized to heat at least a portion of said olefinic naphtha feedstream prior to contact with said first reaction stage.

[0014] In still another preferred embodiment, the heat from at least a portion of said mercaptan decomposition reactor product is utilized to heat at least a portion of said olefinic naphtha feedstream prior to contact with said first reaction stage.

[0015] In still another preferred embodiment, the total sulfur content of said mercaptan decomposition reactor product stream is less than about 1 wt.% of the total sulfur content of said olefinic naphtha feedstream.

[0016] In still another preferred embodiment, the mercaptan sulfur content of said mercaptan decomposition reactor product stream is less than about 10 wt.% of the mercaptan sulfur content of said first reactor effluent stream.

BRIEF DESCRIPTION OF THE DRAWINGS

[0017] FIGURE 1 depicts a first preferred process scheme for practicing the present invention, wherein the olefinic naphtha feedstream is subjected to two hydrodesulfurization reaction stages with an intermediate H_2S removal step which is then followed by a final mercaptan decomposition reaction stage.

[0018] FIGURE 2 depicts a second preferred process scheme for practicing the present invention, wherein the olefinic naphtha feedstream is subjected to one hydrodesulfurization reaction stage followed by an H_2S removal step which is then followed by a final mercaptan decomposition reaction stage.

DETAILED DESCRIPTION OF THE INVENTION

[0019] Feedstocks suitable for use in the present invention are olefinic naphtha boiling range refinery streams that typically boil in the range of about 50°F (10°C) to about 450°F (232°C). The term "olefinic naphtha stream" as used herein are those naphtha streams having an olefin content of at least about 5 wt.%. Non-limiting examples of olefinic naphtha streams include fluid catalytic cracking unit naphtha (FCC catalytic naphtha or cat naphtha), steam cracked naphtha, and coker naphtha. Also included are blends of olefinic naphthas with non-olefinic naphthas as long as the blend has an olefin content of at least about 5 wt.%.

[0020] Olefinic naphtha refinery streams generally contain not only paraffins, naphthenes, and aromatics, but also unsaturates, such as open-chain and cyclic olefins, dienes, and cyclic hydrocarbons with olefinic side chains. The olefinic naphtha feedstock can contain an overall olefins concentration ranging as high as about 60 wt.%, more typically as high as about 50 wt.%, and most typically from about 5 wt.% to about 40 wt.%. The olefinic naphtha feedstock can also have a diene concentration up to about 15 wt.%, but more typically less than about 5 wt.% based on the total weight of the feedstock. High diene concentrations are undesirable since they can result in a gasoline product having poor stability and color. The sulfur content of the olefinic naphtha will generally range from about 300 wppm to about 7000 wppm, more typically from about 1000 wppm to about 6000 wppm, and most typically from about 1500 to about 5000 wppm. The sulfur will typically be present as organically bound sulfur. That is, as sulfur compounds such as simple aliphatic, naphthenic, and

aromatic mercaptans, sulfides, di- and polysulfides and the like. Other organically bound sulfur compounds include the class of heterocyclic sulfur compounds such as thiophene and its higher homologs and analogs. Nitrogen will also be present and will usually range from about 5 wppm to about 500 wppm.

[0021] As previously mentioned, it is highly desirable to remove sulfur from olefinic naphthas with as little olefin saturation as possible. It is also highly desirable to convert as much as possible of the organic sulfur species of the naphtha to hydrogen sulfide with as little mercaptan reversion as possible. The level of mercaptans in the product stream has been found to be directly proportional to the concentration of both hydrogen sulfide and olefinic species at the hydroconversion reactor outlet, and inversely related to the temperature at the reactor outlet.

[0022] Figure 1 is a simple flow scheme of the first preferred embodiment for practicing the present invention. Various ancillary equipment, such as compressors, pumps, heat exchangers and valves is not shown for simplicity reasons.

[0023] In this first embodiment, an olefinic naphtha feed (1) and a hydrogen-containing treat gas stream (2) are contacted with a catalyst in a first hydrodesulfurization reaction stage (3) that is preferably operated in selective hydrodesulfurization conditions that will vary as a function of the concentration and types of organically bound sulfur species of the feedstream. By "selective hydrodesulfurization" we mean that the hydrodesulfurization reaction stage is operated in a manner to achieve as high a level of sulfur removal as possible with as low a level of olefin saturation as possible. It is also operated to avoid as much mercaptan reversion as possible. Generally, hydrodesulfurization conditions for both of the hydrodesulfurization reaction stages include: temperatures from about 450°F (232°C) to about 800°F (427°C), preferably from

about 500°F (260°C) to about 675°F (357°C); pressures from about 60 to about 800 psig, preferably from about 200 to about 500 psig, more preferably from about 250 to about 400 psig; hydrogen feed rates of about 1000 to about 6000 standard cubic feet per barrel (scf/b), preferably from about 1000 to about 3000 scf/b; and liquid hourly space velocities of about 0.5 hr^{-1} to about 15 hr^{-1}, preferably from about 0.5 hr^{-1} to about 10 hr^{-1}, more preferably from about 1 hr^{-1} to about 5 hr^{-1}. It is preferred that the feedstream to the first and second reaction stages as well as the mercaptan destruction reaction stage be in the vapor stage when contacting the catalyst. The terms "hydrotreating" and "hydrodesulfurization" are sometimes used interchangeably herein.

[0024] This first hydrodesulfurization reaction stage can be comprised of one or more fixed bed reactors each of which can comprise one or more catalyst beds of the same, or different, hydrodesulfurization catalyst. Although other types of catalyst beds can be used, fixed beds are preferred. Non-limiting examples of such other types of catalyst beds that may be used in the practice of the present invention include fluidized beds, ebullating beds, slurry beds, and moving beds. Interstage cooling between reactors, or between catalyst beds in the same reactor, can be employed since some olefin saturation can take place, and olefin saturation as well as the desulfurization reaction are generally exothermic. A portion of the heat generated during hydrodesulfurization can be recovered by conventional techniques. Where this heat recovery option is not available, conventional cooling may be performed through cooling utilities such as cooling water or air, or by use of a hydrogen quench stream. In this manner, optimum reaction temperatures can be more easily maintained. It is preferred that the first hydrodesulfurization stage be configured in a manner and operated under hydrodesulfurization conditions such that from about 40% to 100%, more preferably from about 60% to about 95% of the total targeted sulfur removal is reached in the first hydrodesulfurization stage.

[0025] Preferred hydrotreating catalysts for use in both the first and second hydrodesulfurization reaction stages are those that are comprised of at least one Group VIII metal oxide, preferably an oxide of a metal selected from Fe, Co and Ni, more preferably selected from Co and/or Ni, and most preferably Co; and at least one Group VI metal oxide, preferably an oxide of a metal selected from Mo and W, more preferably Mo, on a high surface area support material, preferably alumina. Other suitable hydrotreating catalysts include zeolitic catalysts, as well as noble metal catalysts where the noble metal is selected from Pd and Pt. It is within the scope of the present invention that more than one type of hydrotreating catalyst be used in the same reaction vessel. The Group VIII metal oxide of the first hydrodesulfurization catalyst is typically present in an amount ranging from about 0.1 to about 20 wt.%, preferably from about 1 to about 12%. The Group VI metal oxide will typically be present in an amount ranging from about 1 to about 50 wt.%, preferably from about 2 to about 20 wt.%. All metal oxide weight percents are on support. By "on support" we mean that the percents are based on the weight of the support. For example, if the support were to weigh 100 g. then 20 wt.% Group VIII metal oxide would mean that 20 g. of Group VIII metal oxide is on the support.

[0026] Preferred catalysts for both the first and second hydrodesulfurization stage will also have a high degree of metal sulfide edge plane area as measured by the Oxygen Chemisorption Test as described in "Structure and Properties of Molybdenum Sulfide: Correlation of O2 Chemisorption with Hydrodesulfurization Activity," S.J. Tauster et al., Journal of Catalysis 63, pp. 515-519 (1980). The Oxygen Chemisorption Test involves edge-plane area measurements made wherein pulses of oxygen are added to a carrier gas stream and thus rapidly traverse the catalyst bed. For example, the oxygen chemisorption will be from about 800 to 2,800, preferably from about 1,000 to 2,200, and more preferably from about 1,200 to 2,000μmol oxygen/gram MoO_3.

[0027] The most preferred catalysts for the first and second hydrodesulfurization zone can be characterized by the properties: (a) a MoO_3 concentration of about 1 to 25 wt.%, preferably about 2 to 18 wt.%, and more preferably about 4 to 10 wt.%, and most preferably 4 to 8 wt.%, based on the total weight of the catalyst; (b) a CoO concentration of about 0.1 to 6 wt.%, preferably about 0.5 to 5.5 wt.%, and more preferably about 1 to 5 wt.%, also based on the total weight of the catalyst; (c) a Co/Mo atomic ratio of about 0.1 to about 1.0, preferably from about 0.20 to about 0.80, more preferably from about 0.25 to about 0.72; (d) a median pore diameter of about 60 Å to about 200 Å, preferably from about 75 Å to about 175 Å, and more preferably from about 80 Å to about 150 Å; (e) a MoO_3 surface concentration of about 0.5×10^{-4} to about 3×10^{-4} g MoO_3/m^2, preferably about 0.75×10^{-4} to about 2.5×10^{-4} g MoO_3/m^2, more preferably from about 1×10^{-4} to 2×10^{-4} g MoO_3/m^2; and (f) an average particle size diameter of less than 2.0 mm, preferably less than about 1.6 mm, more preferably less than about 1.4 mm, and most preferably as small as practical for a commercial hydrodesulfurization process unit.

[0028] The hydrodesulfurization catalysts used in the practice of the present invention are preferably supported catalysts. Any suitable refractory catalyst support material, preferably inorganic oxide support materials, can be used as supports for the catalyst of the present invention. Non-limiting examples of suitable support materials include: zeolites, alumina, silica, titania, calcium oxide, strontium oxide, barium oxide, carbons, zirconia, diatomaceous earth, lanthanide oxides including cerium oxide, lanthanum oxide, neodynium oxide, yttrium oxide, and praesodymium oxide; chromia, thorium oxide, urania, niobia, tantala, tin oxide, zinc oxide, and aluminum phosphate. Preferred are alumina, silica, and silica-alumina. More preferred is alumina. Magnesia can also be used for the catalysts with a high degree of metal sulfide edge plane area of the present invention. It is to be understood that the support material can also contain small amounts of contaminants, such as Fe, sulfates, silica, and various

metal oxides that can be introduced during the preparation of the support material. These contaminants are present in the raw materials used to prepare the support and will preferably be present in amounts less than about 1 wt.%, based on the total weight of the support. It is more preferred that the support material be substantially free of such contaminants. It is an embodiment of the present invention that about 0 to 5 wt.%, preferably from about 0.5 to 4 wt.%, and more preferably from about 1 to 3 wt.%, of an additive be present in the support, which additive is selected from the group consisting of phosphorus and metals or metal oxides from Group IA (alkali metals) of the Periodic Table of the Elements.

[0029] Returning now to the Figure 1 hereof, the total effluent product from the first hydrodesulfurization reaction stage (4) is conducted to an H_2S removal zone (6). In this zone, a stripping agent such as a steam or an amine solution (5) is contacted with the first reactor effluent to remove substantially all of the H_2S from the effluent stream (7). This H_2S removal zone operates at substantially the same pressure as the first hydrodesulfurization reaction stage pressure. The H_2S stripped product stream (8) from the H_2S removal zone and a hydrogen-containing treat gas (9) is then contacted with a catalyst in a second hydrodesulfurization reaction stage (10) that is also preferably operated at selective hydrodesulfurization conditions. Generally, the hydrodesulfurization conditions of the second stage reaction include similar temperature ranges, pressure ranges, treat gas ranges, liquid hourly space velocities ranges, catalyst properties, catalyst characteristics and catalyst compositions, reactor configurations, and heat recovery configurations as described for the first reaction stage above. The reactor effluent (11) from the second reaction stage is then contacted with a catalyst in a mercaptan decomposition reaction stage (12).

[0030] This mercaptan decomposition reaction stage can be comprised of one or more fixed bed reactors, each of which can comprise one or more catalyst beds of the same, or different, mercaptan decomposition catalyst. Although

other types of catalyst beds can be used, fixed beds are preferred. Non-limiting examples of such other types of catalyst beds that may be used in the practice of the present invention include fluidized beds, ebullating beds, slurry beds, and moving beds. The mercaptan decomposition catalysts suitable for use in this invention are those which contain a material that catalyzes the mercaptan reversal back to H_2S and olefins. Suitable mercaptan decomposition catalytic materials for this process include refractory metal oxides resistant to sulfur and hydrogen at high temperatures and which possess substantially no hydrogenation activity. Catalytic materials which possess substantially no hydrogenation activity are those which have virtually no tendency to promote the saturation or partial saturation of any non-saturated hydrocarbon molecules, such as aromatics and olefins, in a feedstream under mercaptan decomposition reaction stage conditions as disclosed in this invention. These catalytic materials specifically exclude catalysts containing metals, metal oxides, or metal sulfides of the Group V, VI, or VIII elements, including but not limited to V, Nb, Ta, Cr, Mo, W, Fe, Ru, Co, Rh, Ir, Ni, Pd, and Pt. Illustrative, but non-limiting, examples of suitable catalytic materials for the mercaptan decomposition reaction process of this invention include materials such as alumina, silica, both crystalline and amorphous silica-alumina, aluminum phosphates, titania, magnesium oxide, alkali and alkaline earth metal oxides, alkaline metal oxides, magnesium oxide supported on alumina, faujasite that has been ion exchanged with sodium to remove the acidity and ammonium ion treated aluminum phosphate.

[0031] Generally, the mercaptan decomposition reaction stage conditions include: temperatures from about 500°F (260°C) to about 800°F (427°C), preferably from about 550°F (288°C) to about 700°F (371°C); pressures from about 60 to about 800 psig, preferably from about 150 to about 500 psig; hydrogen feed rates of about 1000 to about 6000 standard cubic feet per barrel (scf/b), preferably from about 1000 to about 3000 scf/b; and liquid hourly space velocities of about 0.5 hr^{-1} to about 15 hr^{-1}, preferably from about 0.5 hr^{-1} to

about 10 hr^{-1}, more preferably from about 1 hr^{-1} to about 5 hr^{-1}. In this mercaptan decomposition reaction stage, organic and elemental sulfur compounds and mercaptan sulfur compounds are converted with a minimal amount of olefin saturation resulting in a final product stream (13) with properties of a reduced organic and elemental sulfur content, reduced mercaptan content and minimal octane reduction.

[0032] Figure 2 is a simple flow scheme depicting a second preferred embodiment for practicing the present invention. Again, various ancillary equipment, such as compressors, pumps, heat exchangers and valves are not shown for simplicity reasons.

[0033] In this second embodiment, an olefinic naphtha feed (1) and a hydrogen-containing treat gas stream (2) are contacted with a catalyst in a first hydrodesulfurization reaction stage (3) that is preferably operated in selective hydrodesulfurization conditions that will vary as a function of the concentration and types of organically bound sulfur species of the feedstream. Generally, the hydrodesulfurization conditions of the first reaction stage in Figure 2 utilizes similar temperature ranges, pressure ranges, treat gas ranges, liquid hourly space velocities ranges, catalyst properties, catalyst characteristics and catalyst compositions, reactor configurations, and heat recovery configurations as described for the first reaction stage in Figure 1, above. The total effluent product from the first hydrodesulfurization reaction stage (4) is conducted to an H_2S removal zone (6). In this zone, a compound such as a steam or an amine solution (5) is contacted with the first reactor effluent to substantially remove all of the H_2S from the effluent stream (7). This H_2S removal zone operates at substantially the same pressure as the first hydrodesulfurization reaction stage pressure. The H_2S stripped product stream (8) from the H_2S removal zone and a hydrogen-containing treat gas (9) is then contacted with a catalyst in a mercaptan decomposition reaction stage (10).

[0034] The mercaptan decomposition conditions of the mercaptan decomposition reaction stage in this configuration (see Figure 2) are the same as described for the mercaptan decomposition reaction stage in the first embodiment, above (see Figure 1 and associated detailed description). The mercaptan decomposition reaction conditions include similar temperature ranges, pressure ranges, treat gas ranges, liquid hourly space velocities ranges, catalyst properties, catalyst characteristics and catalyst compositions, reactor configurations, and heat recovery configurations as described for the mercaptan decomposition reaction conditions described in the first embodiment, above (see Figure 1 and associated detailed description). In this mercaptan decomposition reaction stage, organic and elemental sulfur compounds and mercaptan sulfur compounds are converted with a minimal amount of olefin saturation resulting in a final product stream (11) with properties of a reduced organic and elemental sulfur content, reduced mercaptan content and minimal octane reduction.

[0035] The following examples are presented to illustrate the invention.

Example 1

[0036] In this example, the process configuration utilized is shown in Figure 1. The hydrogen treat gas rates, shown as streams (2) and (9) in Figure 1, are 2,000 standard cubic feet per barrel (scf/b). The amount of H_2S removal in the H_2S reaction zone (6) is modeled utilizing an H_2S removal step to remove free and dissolved H_2S from the process stream at the first hydrodesulfurization reaction pressures (327 psig). Any stripping agent utilized in the art to facilitate H_2S removal, such as steam or an amine solution, can be utilized and is shown as stream (5). The H_2S or H_2S rich compound is then removed from the process via stream (7). The conditions and resulting product qualities are predicted based on a kinetic model developed from a pilot plant database are shown in Tables 1 and 2 below.

Table 1

	1st HDS Stage (3)	2nd HDS Stage (10)	Mercaptan Removal Stage (12)
Temperature (°F)	535	525	625
Pressure (psig)	327	327	327

Table 2

	Olefinic Feedstream (1)	First Reactor Effluent Stream (4)	Stripped Effluent Stream (8)	Second Reactor Effluent Stream (11)	Third Reactor Product Stream (13)
Sulfur (wppm)	1900	180	180	14	10
Mercaptan (wppm)	-	76	76	9	5
Bromine No. (cg/g)	67.0	55.6	55.6	44.3	44.0
RON	92.0	-	-	-	87.7
MON	80.0	-	-	-	78.5

This process will result in a total hydrodesulfurization of 99.5% with an overall RON loss of 4.3 and MON loss of 1.5. By comparison, a similar design utilizing two HDS reactors and no mercaptan removal would result in a RON loss of 5.0 and a MON loss of 1.8.

Example 2

[0037] In this example, the process configuration utilized is shown in Figure 2. The hydrogen treat gas rates, shown as streams (2) and (9) in Figure 2, are 2,000 standard cubic feet per barrel (scf/b). The amount of H_2S removal in the H_2S reaction zone (6) is modeled utilizing an H_2S removal step to remove free and dissolved H_2S from the process stream at the hydrodesulfurization reaction pressures (327 psig). Any stripping agent utilized in the art to facilitate H_2S removal, such as steam or an amine solution, can be utilized and is shown as stream (5). The H_2S or H_2S rich compound is then removed from the process via stream (7). The conditions and resulting product qualities are predicted based on a kinetic model developed from a pilot plant database are shown in Tables 3 and 4 below.

Table 3

	1st HDS Stage (3)	Mercaptan Removal Stage (12)
Temperature (°F)	535	625
Pressure (psig)	327	327

Table 4

	Olefinic Feedstream (1)	First Reactor Effluent Stream (4)	Stripped Effluent Stream (8)	Second Reactor Product Stream (11)
Sulfur (wppm)	1900	62	62	10
Mercaptan (wppm)	-	55	55	3
Bromine No. (cg/g)	67.0	46.3	46.3	46.3
RON	92.0	-	-	88.3
MON	80.0	-	-	78.7

This process will result in a total hydrodesulfurization of 99.5% with an overall RON loss of 3.7 and MON loss of 1.3. By comparison, a similar design utilizing two HDS reactors and no mercaptan removal would result in a RON loss of 5.0 and a MON loss of 1.8.

CLAIMS:

1. A process for hydrodesulfurizing an olefinic naphtha feedstream and retaining a substantial amount of the olefins, which feedstream boils in the range of 50°F (10°C) to 450°F (232°C) and contains organically bound sulfur and an olefin content of at least 5 wt. %, which process comprises:

a) hydrodesulfurizing said olefinic naphtha feedstream in a first reaction stage in the presence of a hydrogen-containing treat gas and a hydrodesulfurization catalyst, at first hydrodesulfurization reaction conditions including temperatures from 450°F (232°C) to 800°F (427°C), pressures of 60 to 800 psig, and hydrogen-containing treat gas rates of 1000 to 6000 standard cubic feet per barrel, to convert a portion of the elemental and organically bound sulfur in said olefinic naphtha feedstream to hydrogen sulfide to produce a first reactor effluent stream which has a total sulfur content lower than that of said olefinic naphtha feedstream;

b) conducting said first reactor effluent stream to an H_2S removal zone wherein a stripping agent is utilized to remove substantially all of the H_2S from said first reactor effluent stream to produce a stripped effluent stream;

c) conducting said stripped effluent stream to a second reaction stage in the presence of a hydrogen-containing treat gas and a hydrodesulfurization catalyst, at second hydrodesulfurization reaction conditions including temperatures from 450°F (232°C) to 800°F (427°C), pressures of 60 to 800 psig, and hydrogen-containing treat gas rates of 1000 to 6000 standard cubic feet per barrel, to convert at least a portion of the elemental and organically bound sulfur in said olefinic naphtha feedstream to hydrogen sulfide to produce a second reactor effluent stream which has a total sulfur content lower than that of said stripped effluent stream and some amount of mercaptan sulfur; and

d) conducting said second reactor effluent stream to a mercaptan decomposition reaction stage in the presence of a mercaptan decomposition catalyst, at mercaptan decomposition reaction conditions including temperatures from 550°F (288°C) to 700°F (371°C), and pressures of 150 to 500 psig, to decompose at least a portion of the mercaptan sulfur to produce a mercaptan decomposition reactor product

stream with a mercaptan sulfur content lower than that of said second reactor effluent stream;

wherein said second reactor effluent stream is in the vapor phase prior to contacting the mercaptan decomposition stage;

wherein the total sulfur content of said mercaptan decomposition reactor product stream is less than 1 wt % of the total sulfur content of said olefinic naphtha feedstream; and

wherein the mercaptan sulfur content of said mercaptan decomposition reactor product stream is less than 10 wt. % of the mercaptan sulfur content of said first reactor effluent stream.

2. The process of claim 1, wherein said olefinic naphtha feedstream is in the vapor phase prior to contacting said first reaction zone, and the stripped effluent stream is in the vapor phase prior to contacting said second reaction stage.

3. The process of claim 1, wherein said stripping agent is selected from the group consisting of steam and an amine solution.

4. The process of claim 1, wherein said hydrodesulfurization catalysts utilized in said first and second reaction stages are comprised of at least one Group VIII metal oxide and at least one Group VI metal oxide.

5. The process of claim 4, wherein said hydrodesulfurization catalysts utilized in said first and second reaction stages are comprised of at least one Group VIII metal oxide selected from Fe, Co and Ni, and at least one Group VI metal oxide, selected from Mo and W.

6. The process of claim 4, wherein said metal oxides are deposited on a high surface area support material.

7. The process of claim 6, wherein said high surface area support material is alumina.

8. The process of claim 1, wherein said mercaptan decomposition catalyst is comprised of a refractory metal oxide in an effective amount to catalyze the decomposition of said mercaptan sulfur resistant to H_2S.

9. The process of claim 8, wherein said mercaptan decomposition catalyst is comprised of materials selected from alumina, silica, silica-alumina, aluminum phosphates, titania, magnesium oxide, alkali and alkaline earth metal oxides, alkaline metal oxides, magnesium oxide, faujasite that has been ion exchanged with sodium to remove the acidity, and ammonium ion treated aluminum phosphate.

10. The process of claim 9, wherein said mercaptan decomposition catalyst is comprised of materials selected from alumina, silica, and silica-alumina.

11. The process of claim 10, wherein said mercaptan decomposition catalyst possesses substantially no hydrogenation activity.

12. The process of claim 1, wherein said first and second hydrodesulfurization reaction conditions include temperatures from 500°F (260°C) to 675°F (357°C), pressures of 200 to 500 psig, and hydrogen-containing treat gas rates of 1000 to 3000 standard cubic feet per barrel.

13. The process of claim 12, wherein said first and second hydrodesulfurization reaction conditions include pressures of 250 to 400 psig.

14. A process for hydrodesulfurizing an olefinic naphtha feedstream and retaining a substantial amount of the olefins, which feedstream boils in the range of 50°F (10°C) to

450°F (232°C) and contains organically bound sulfur and an olefin content of at least 5 wt. %, which process comprises:

a) hydrodesulfurizing said olefinic naphtha feedstream in a first reaction stage in the presence of a hydrogen-containing treat gas and a hydrodesulfurization catalyst, at first hydrodesulfurization reaction conditions including temperatures from 450°F (232°C) to 800°F (427°C), pressures of about 60 to 800 psig, and hydrogen-containing treat gas rates of 1000 to 6000 standard cubic feet per barrel, to convert at least a portion of the elemental and organically bound sulfur in said olefinic naphtha feedstream to hydrogen sulfide to produce a first reactor effluent stream which has a total sulfur content lower than that of said olefinic naphtha feedstream;

b) conducting said first reactor effluent stream to an H_2S removal zone wherein a stripping agent is utilized to remove substantially all of the H_2S from said first reactor effluent stream to produce a stripped effluent stream; and

c) conducting said stripped effluent stream to a mercaptan decomposition reaction stage in the presence of a hydrogen-containing treat gas and a mercaptan decomposition catalyst, at mercaptan decomposition reaction conditions including temperatures from 550°F (288°C) to 700°F (371°C), and pressures of 150 to 500 psig, and hydrogen-containing treat gas rates of 1000 to 6000 standard cubic feet per barrel to decompose at least a portion of the mercaptan sulfur and convert at least a portion of the elemental and organically bound sulfur to produce a mercaptan decomposition reactor product stream with a mercaptan sulfur content less than that of said first reactor effluent stream,

wherein said stripped effluent stream is in the vapor phase prior to contacting said mercaptan decomposition stage,

wherein the total sulfur content of said mercaptan decomposition reactor product stream is less than 1 wt % of the total sulfur content of said olefinic naphtha feedstream, and

wherein the mercaptan sulfur content of said mercaptan decomposition reactor product stream is less than 10 wt. % of the mercaptan sulfur content of said first reactor effluent stream.

15. The process of claim 14, wherein said olefinic naphtha feedstream is in the vapor phase prior to contacting said first reaction stage.

16. The process of claim 14, wherein said stripping agent is selected from the group consisting of steam and an amine solution.

17. The process of claim 14, wherein said hydrodesulfurization catalyst utilized in said first reaction stage is comprised of at least one Group VIII metal oxide and at least one Group VI metal oxide.

18. The process of claim 17, wherein said hydrodesulfurization catalyst utilized in said first reaction stage is comprised of at least one Group VIII metal oxide selected from Fe, Co and Ni, and at least one Group VI metal oxide, selected from Mo and W.

19. The process of claim 18, wherein said metal oxides are deposited on a high surface area support material.

20. The process of claim 19, wherein said high surface area support material is alumina.

21. The process of claim 14, wherein said mercaptan decomposition catalyst is comprised of a refractory metal oxide in an effective amount to catalyze the decomposition of said mercaptan sulfur resistant to H_2S.

22. The process of claim 21, wherein said mercaptan decomposition catalyst is comprised of materials selected from alumina, silica, silica-alumina, aluminum phosphates, titania, magnesium oxide, alkali and alkaline earth metal oxides, alkaline metal oxides, magnesium oxide, faujasite that has been ion exchanged with sodium to remove the acidity, and ammonium ion treated aluminum phosphate.

23. The process of claim 22, wherein said mercaptan decomposition catalyst is comprised of materials selected from alumina, silica, and silica-alumina.

24. The process of claim 23, wherein said mercaptan decomposition catalyst possesses substantially no hydrogenation activity.

25. The process of claim 14, wherein said first hydrodesulfurization reaction conditions include temperatures from 500°F (260°C) to 675°F (357°C), pressures of 200 to 500 psig, and hydrogen-containing treat gas rates of 1000 to 3000 standard cubic feet per barrel.

26. The process of claim 25, wherein said first hydrodesulfurization reaction conditions include pressures of 250 to 400 psig.

Figure 1

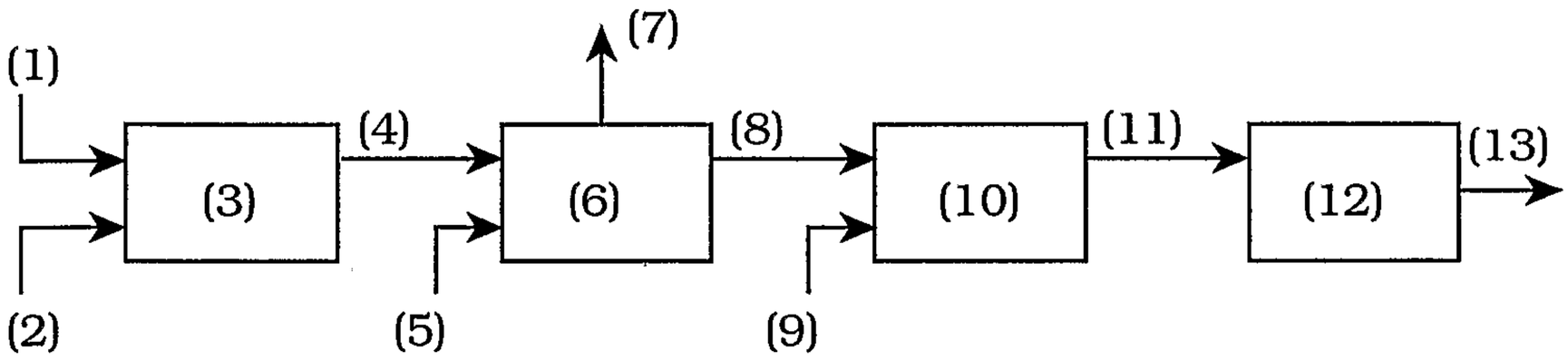
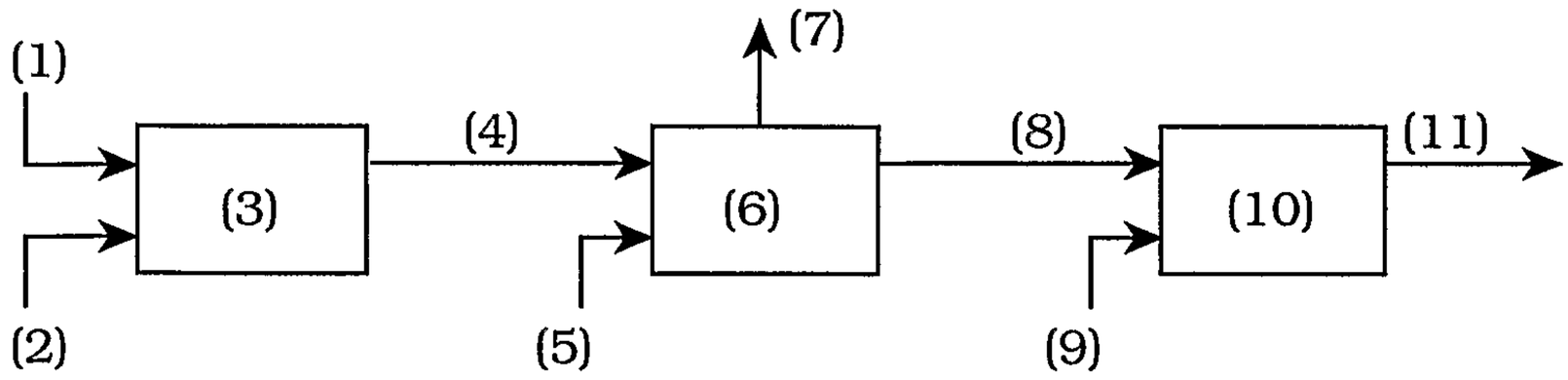
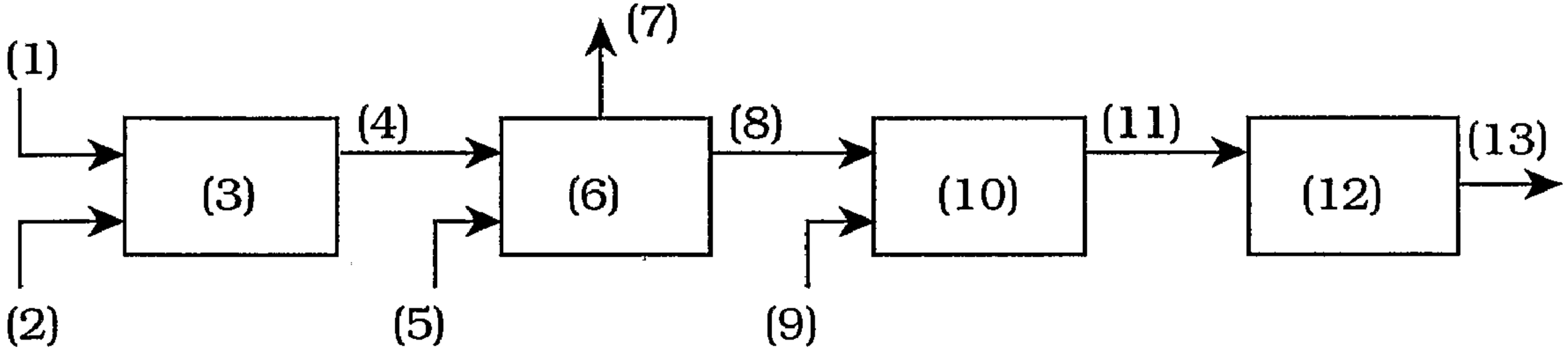


Figure 2

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