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(57) **Abrégé/Abstract:**

A slurry catalytic hydrocarbon synthesis process which employs a catalyst comprising a supported cobalt component achieves a short term catalyst half life or more than 10 days, by using a syngas feed which contains less than fifty parts per billion of a combined total amount of HCN and NH₃.



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<p>(54) Title: SLURRY HYDROCARBON SYNTHESIS PROCESS WITH INCREASED CATALYST LIFE</p> <p>(57) Abstract</p> <p>A slurry catalytic hydrocarbon synthesis process which employs a catalyst comprising a supported cobalt component achieves a short term catalyst half life or more than 10 days, by using a syngas feed which contains less than fifty parts per billion of a combined total amount of HCN and NH₃.</p>		

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SLURRY HYDROCARBON SYNTHESIS
PROCESS WITH INCREASED CATALYST LIFE

BACKGROUND OF THE DISCLOSURE

Field of the Invention

The invention relates to a hydrocarbon synthesis process with increased catalyst life. More particularly, the invention relates to a slurry catalytic hydrocarbon synthesis process employing a supported cobalt metal catalyst in which catalyst half life is increased by using a syngas feed containing less than fifty parts per billion of nitrogenous, catalyst deactivating species.

Background of the Invention

Slurry hydrocarbon synthesis (HCS) processes are known. In a slurry HCS process a synthesis gas (syngas) comprising a mixture of H₂ and CO is bubbled up as a third phase through a slurry in a reactor in which the slurry liquid comprises hydrocarbon products of the synthesis reaction and the dispersed, suspended solids comprise a suitable Fischer-Tropsch type hydrocarbon synthesis catalyst. Reactors which contain such a three phase slurry are sometimes referred to as "bubble columns", as is disclosed in U.S. Patent 5,348,982. Irrespective of whether the slurry reactor is operated as a dispersed or slumped bed, the mixing conditions in the slurry will typically be somewhere between the two theoretical conditions of plug flow and back mixed. It is also known that Fischer-Tropsch type catalysts useful for forming hydrocarbons from a syngas are rapidly, but reversibly deactivated by certain nitrogenous species in the syngas feed, particularly HCN and NH₃. Syngas made from hydrocarbon feedstocks which contain nitrogen (i.e., natural gas) or nitrogen containing compounds (i.e., resids, coal, shale, coke, tar sands, etc.) invariably contains

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HCN and NH₃ which contaminate the reactive slurry and deactivate the catalyst. Certain oxygenates and carbonaceous compounds which are formed in the slurry as by-products of the HCS reaction are also believed to cause rapid deactivation. Deactivation of such catalysts by HCN and NH₃ may be reversed and catalytic activity restored (rejuvenated) by contacting the deactivated catalyst with hydrogen or a hydrogen containing gas (rejuvenating gas). Deactivation of such catalysts by these species is reversible and catalytic activity is restored (the catalyst rejuvenated) by contacting the deactivated catalyst with hydrogen either continuously or intermittently as is disclosed, for example, in U.S. Patents 5,260,239; 5,268,344 and 5,283,216. While methods have been suggested for reducing the HCN and NH₃ content of syngas down to about 0.1 ppm (100 ppb) by catalytic hydrolysis (U.S. 4,769,224) and chemical scrubbing (U.S. 5,068,254), it has now been found that even as little as 100 vppb of a combined total of HCN and NH₃ in the syngas will result in a catalyst half life of only four days for the case of a supported Co metal catalyst in an HCS slurry. It has now been found that reducing the level of the HCN and NH₃ catalyst poisons in the syngas below 50 ppb produces increased catalyst life and requires less catalyst rejuvenation. A method for achieving such low levels has also been found and is disclosed in copending US Patent Nos. 6,063,349, 5,968,465 and 6,107,353.

SUMMARY OF THE INVENTION

The present invention relates to a slurry hydrocarbon synthesis (HCS) process employing a supported cobalt metal catalyst in which the short term catalyst half life is at least 10 days, preferably at least 30 and more preferably at least 40 or more days. By short term half life is meant that the catalytic activity caused by reversible deactivation of the catalyst is 50% that of fresh

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catalyst and that this loss is substantially restored (the catalyst rejuvenated) by contacting the deactivated catalyst with a rejuvenating gas comprising H₂. Catalyst activity is defined in terms of the CO conversion to hydrocarbons. Thus, if under a given set of HCS conditions fresh catalyst produces a CO conversion of 80 mole %, the catalyst half life is realized when the conversion drops to 40%, as a result of contact with the reversibly deactivating nitrogenous species in the synthesis gas (syngas) feed. By reversibly deactivating nitrogenous species is meant HCN, NH₃ and mixture thereof. It is also an embodiment of the process of the invention that the catalyst will have a long term half life of at least 100 days and preferably at least 200 days. It has been found that there is also an unrejuvenable catalyst activity loss which occurs over time, which cannot be restored by contacting the catalyst with H₂, but which can be restored by regeneration. The unrejuvenable, but regenerable loss in catalyst activity drops continuously, so that eventually the catalyst has a CO conversion activity at its long term half life only half or 50% of fresh catalyst and this long term activity loss cannot be restored (the catalytic activity cannot be rejuvenated) by contacting the deactivated catalyst with H₂ or a H₂ containing rejuvenating gas. Thus, by long term half life is meant the time it takes the catalyst to have only half the activity of fresh catalyst and that this activity loss, while reversible, is not restored by a rejuvenation process in which the deactivated catalyst is contacted with H₂ or an H₂ containing gas. Instead, the catalyst has to be separated from the slurry and regenerated by processes that include oxidation or burning, rereduction of the catalytic metal(s) and, optionally, passivation in CO and/or syngas. Thus, long term loss of catalyst activity in the context of the invention is regenerable, but not rejuvenable with H₂. Further, regenerable activity loss is different from irreversible catalyst activity loss due to, for example, sulfur poisoning, which requires catalyst replacement. The relatively long short term and long term catalyst life in the practice of the invention is achieved by using a syngas feed in which the total level of the catalyst deactivat-

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ing nitrogenous species HCN, NH₃ and mixture thereof is less than 50 vppb (volume parts per billion), preferably less than 20 vppb, and still more preferably less than 10 vppb. A slurry HCS catalyst useful in the practice of the invention comprises a catalytically active cobalt component dispersed and supported on a particulate inorganic refractory oxide carrier or support, and preferably as a thin catalytically active surface layer, ranging in thickness from about 5-200 microns. It is also preferred the catalyst have a productivity of at least 150 hr⁻¹ at 200°C, preferably at least 500 hr⁻¹ and more preferably at least 1000 hr⁻¹. By productivity is meant the standard volume of CO converted per volume of catalyst per hour. In a further embodiment, the catalyst employed in the process of the invention will have a methane selectivity of less than 10 mole % and preferably less than 5 mole %. This means that less than 10% of the CO converted is converted to methane. In one embodiment the catalyst comprises catalytically effective amounts of Co and one or more of Re, Ru, Fe, Ni, Th, Zr, Hf, U, Mg and La on a suitable inorganic support material, and preferably one which comprises one or more refractory metal oxides. Preferred supports for Co containing catalysts comprise titania and titania-silica composites, particularly when employing a slurry HCS process in which higher molecular weight, primarily paraffinic liquid hydrocarbon products are desired. Useful catalysts and their preparation are known and illustrative, but nonlimiting examples may be found, for example, in U.S. Patents 4,568,663; 4,663,305; 4,542,122; 4,621,072 and 5,545,674, with those disclosed in U.S. 5,545,674 being particularly preferred.

An HCS slurry process of the invention comprises reacting a syngas which contains HCN, HN₃ or mixture thereof in the presence of a solid, particulate HCS catalyst in a slurry which comprises the catalyst and gas bubbles in a hydrocarbon slurry liquid, at reaction conditions effective to produce hydrocarbons from the syngas, wherein the total amount of HCN, HN₃ or mixture

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thereof in the syngas is less than 50 vppb, preferably less than 20 vppb and more preferably less than 10 vppb to achieve a short term catalyst half life greater than 10 days, preferably greater than 30 days and more preferably greater than 40 days, and with a long term catalyst half life greater than 100 and preferably greater than 200 days. Those skilled in the art will appreciate the unusually large difference in catalyst half life resulting from a relatively small difference in concentration of the HCN and NH₃ catalyst deactivating species in the syngas feed. It was not known that the relatively small differences and extremely low concentrations of HCN and NH₃ in the syngas feed would make such a large difference in catalyst half life. The increased catalyst half life reduces catalyst rejuvenation requirements and concomitant hydrogen consumption, while maintaining good productivity and selectivity to liquid hydrocarbon products. The process of the invention has been demonstrated with a slurry HCS process in which the syngas is bubbled up through a three phase HCS slurry comprising the particulate catalyst and gas bubbles in a hydrocarbon slurry liquid, and in which the catalyst comprised a catalytically active cobalt component dispersed and supported on a particulate inorganic refractory oxide carrier or support, as a thin catalytically active surface layer which met the above requirements for productivity and methane make. This catalyst was of the type disclosed and claimed in the '674 patent referred to above.

A number of methods have been found to achieve the low concentration of the HCN to NH₃ in the syngas useful in the practice of the invention. These include catalytic hydrolysis of the HCN to NH₃, followed by scrubbing with water to dissolve out the NH₃ and, optionally, the use of guard beds containing one or more solid adsorbents, preferably acidic, to adsorb any HCN and NH₃ that may break through. This process is disclosed in US Patent 6,107,353 referred to above. Another method comprises cryogenic separation of nitrogen from natural gas used as a syngas

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feed, so that not enough nitrogen is present in the natural gas to produce the catalyst deactivating species in the syngas generating unit. In this process too, solid adsorbent beds will be placed between the syngas generation and the HCS reactor(s), in the event of a nitrogen break through upstream of the syngas generating unit and result in increasing the concentration of the catalyst deactivating species in the syngas. In a more specific embodiment of a slurry HCS process, the invention comprises reacting a synthesis gas comprising a mixture of H₂ and CO and containing HCN, NH₃ or mixture thereof, in the presence of a hydrocarbon synthesis catalyst in a slurry comprising said catalyst and gas bubbles in a hydrocarbon slurry liquid, under reaction conditions effective to form hydrocarbons from said syngas, said catalyst comprising a catalytically active cobalt component dispersed and supported on a particulate inorganic refractory oxide carrier or support, as a thin catalytically active surface layer, said catalyst having a productivity of at least 150 hr⁻¹ and less than 5 mole % methane make from said synthesis gas, and wherein the amount of said HCN, NH₃ or mixture thereof present in said gas is less than 50 vppb so as to achieve a short term catalyst half life of at least 10 days. The hydrocarbon slurry liquid comprises hydrocarbon products of the HCS reaction which are liquid at the reaction conditions and a portion is continuously or intermittently withdrawn from the slurry HCS reactor as long as the hydrocarbons are being produced. The hydrocarbon liquid withdrawn from the reactor comprises C₅₊, primarily paraffinic hydrocarbons and is typically upgraded into more valuable products by one or more conversion operations, or sold neat. As the HCS reaction progresses, the catalyst loses activity due to the presence of the HCN, NH₃ or mixture thereof in the syngas and must be either continuously or intermittently rejuvenated by bubbling H₂ or an H₂ containing gas up through the slurry in which it contacts the catalyst and at least partially, and preferably substantially completely, restores the catalytic activity, as is disclosed in the prior art referred

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to above and more preferably after all or at least a portion of the CO has been removed from the slurry.

DETAILED DESCRIPTION

In a Fischer-Tropsch slurry HCS process, a syngas comprising a mixture of H₂ and CO is bubbled up into a reactive slurry in which it is catalytically converted into hydrocarbons and preferably liquid hydrocarbons. The mole ratio of the hydrogen to the carbon monoxide may broadly range from about 0.5 to 4, but which is more typically within the range of from about 0.7 to 2.75 and preferably from about 0.7 to 2.5. The stoichiometric mole ratio for a Fischer-Tropsch HCS reaction is 2.0, but there are many reasons for using other than a stoichiometric ratio as those skilled in the art know and a discussion of which is beyond the scope of the present invention. In a slurry HCS process the mole ratio of the H₂ to CO is typically about 2.1/1. Slurry HCS process conditions vary somewhat depending on the catalyst and desired products. Typical conditions effective to form hydrocarbons comprising mostly C₅₊ paraffins, and preferably C₁₀₊ paraffins (e.g., C₅₊-C₂₀₀), in a slurry HCS process employing a catalyst comprising a supported cobalt component include, for example, temperatures, pressures and hourly gas space velocities in the range of from about 320-600⁰F, 80-600 psi and 100-40,000 V/hr/V, expressed as standard volumes of the gaseous CO and H₂ mixture (0⁰C, 1 atm) per hour per volume of catalyst, respectively. Slurry catalyst rejuvenation conditions of temperature and pressure are similar to those for hydrocarbon synthesis and are disclosed in the prior art. The syngas may be formed by various means, including contacting a hot carbonaceous material such as coke or coal, with steam, or from a feed comprising methane. A feed comprising methane is preferred for convenience, cleanliness and because it does not leave large quantities of ash to be handled and disposed of. The methane containing gas feed is obtained from natural gas

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or by burning coal, tar, liquid hydrocarbons and the like and is fed into a syngas generator. The production of syngas from methane by either partial oxidation, steam reforming or a combination thereof is well known as is disclosed, for example, in U.S. Patent 4,888,131. In many cases it is preferred to catalytically partially oxidize and steam reform the methane in a fluid bed syngas generating unit (FBSG) as is disclosed, for example, in U.S. Patents 4,888,131 and 5,160,456. Irrespective of the source of the methane, nitrogen or nitrogen containing compounds are present in the methane containing gas fed into the syngas generator, some of which are converted into NH_3 and HCN during the syngas formation. These will deactivate a Fischer-Tropsch HCS catalyst, particularly those comprising Co as the catalytic metal. As the prior art teaches, deactivation by these species is reversible and the catalyst can be rejuvenated by contacting it with hydrogen. This restoration of the catalytic activity of a reversibly deactivated catalyst is referred to as catalyst rejuvenation and is disclosed, for example, in the 5,260,239; 5,268,344 and 5,283,216 patents referred to above. It has also been found that both the short term and long term catalyst half life of a Co containing slurry HCS catalyst are unacceptably short unless the combined amount of the HCN and NH_3 present in the syngas being fed into an HCS reactor is less than 50 vppb, preferably less than 20 vppb and more preferably less than 10 vppb, so that the short term or H_2 rejuvenable catalyst half life will be at least 10 days, preferably at least 30 days and more preferably at least 40 days and for the long term catalyst half life to be at least 100 days and preferably at least 200 days. As mentioned above, with a Co metal containing HCS catalyst of the type disclosed and claimed in U.S. Patent 5,545,674 in a reactive HCS slurry, 100 vppb of a combined total of HCN and NH_3 present in the syngas results in the catalyst having a half life of only 4 days. By half life is meant that the overall activity of the catalyst body is reduced by 50% in 4 days. An activity level of 50% is totally unacceptable. It means that the productivity of the catalyst (and, concomitantly the reactor), measured in

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terms of CO conversion, is only 50% of what it should be in 4 days. A productivity level of at least 90% is desired. This means that in cyclic or batchwise rejuvenation, the reactor is taken off-line for one-quarter of each day to maintain the activity level at no less than about 90%, during which time the catalyst in the reactor is rejuvenated with hydrogen. As a practical matter, the reactor is off-line more than one-quarter of each day, due to the time it takes to purge out the syngas, pass in the hydrogen or hydrogen containing catalyst rejuvenating gas and then restart the HCS reaction. This results in a continuous average 25% loss of hydrocarbon production from the reactor, even with rejuvenation. Further, as the catalyst deactivates at otherwise constant conditions, the conversion level drops resulting in a decrease in liquid hydrocarbon make and a small increase in methane make. Alternatively, conversion can be held relatively constant despite the catalyst deactivation, by increasing the reactor temperature, but this results in a relatively large increase in methane make and consequent decrease in liquid product make. At a combined HCN and NH₃ level of about 20 vppb in the syngas, the catalyst half life is 20 days. This means that about every fourth day the catalyst has to be rejuvenated, using the same amount of time and hydrogenation for the rejuvenation as for the case above, yielding an average production loss of only about 6%. At about 40-50 vppb, it is about 15%. At a combined level of about 10-12 vppb, the catalyst half life is about 40 days and the catalyst has to be rejuvenated for one-quarter of a day only every 8 days, yielding a productivity loss of only about 3%. The catalyst half life is about 30 days when the combined amounts of HCN and NH₃ is about 13-17 vppb. In the case of a slurry HCS process, the catalyst in the slurry can be either continuously rejuvenated with the reactor remaining on-line using the methods disclosed in U.S. Patents 5,260,239 and 5,268,344. Nevertheless, the case of a catalyst half life of only 4 days will still consume five times more hydrogen rejuvenation gas than if the half life were 20 days, and ten times the amount required for a 40 day half life.

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While prior art methods have included catalytic hydrolysis and chemical scrubbing for reducing the synthesis gas HCN content to 0.01 vol% or 100 vppb, even 100 vppb of HCN in the syngas is an unacceptably high level. Further, HCN removal by alkaline scrubbing and with alkaline ferrous sulphate solutions is hampered by the presence of other acidic materials in the syngas, particularly CO₂. Washing with water which contains chemicals is further disadvantaged by process complexity, costly chemical consumption, and waste disposal demands. Also, while NH₃ is water soluble, HCN is not soluble enough in water to be able to remove it down to the low levels of less than 50 vppb, preferably less than 20 vppb and more preferably less than 10 vppb required to achieve reasonable levels of catalyst half life. Chemical scrubbing processes are not selective enough to remove the HCN down to these levels. Some prior art catalytic conversion processes have employed relatively low activity catalysts which require excessive catalyst volume and/or high processing temperatures. Other processes have employed sulfided catalysts which will leak out sulfur and irreversibly deactivate an HCS catalyst downstream. Processes which rely primarily or solely on adsorption to remove the HCN and NH₃ require impractically large quantities of adsorbent to achieve useful operating times to reduce the combined HCN and NH₃ concentration to the desired levels. The methods disclosed in the copending patent applications referred to above are preferred for achieving the low levels of HCN and NH₃ required for acceptable catalyst half life.

In a slurry HCS process according to the practice of the invention, liquid and gaseous hydrocarbon products are formed by contacting a syngas comprising a mixture of H₂ and CO with a Fischer-Tropsch type of HCS catalyst, under shifting or non-shifting conditions and preferably under non-shifting conditions in which little or no water gas shift reaction occurs,

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particularly when the catalytic metal comprises Co, Ru or mixture thereof. Suitable Fischer-Tropsch reaction types of catalyst comprise, for example, one or more Group VIII catalytic metals such as Fe, Ni, Co, Ru and Re. Particularly preferred in the practice of the invention is a catalyst in which the catalytic metal comprises a catalytically active cobalt component dispersed and supported on a particulate inorganic refractory oxide carrier or support, with the total thickness of the catalytically active layer in the range of from about 5-200 microns. For support particles of a diameter greater than these values, the metal will be impregnated as a thin surface layer no thicker than this range. For support particles smaller than the upper limit of this range, the catalytic metal may be either uniformly impregnated throughout the particles or deposited as a thin(er) surface layer. Paraffinic, C_{5+} hydrocarbon products are preferred and preferably more than 50% of the C_{5+} hydrocarbons will be paraffins. Preferably the catalyst will have a productivity in excess of 150 hr^{-1} at 200°C and exhibit a methane selectivity of less than 10%. More specifically and as set forth above, the catalyst comprises catalytically effective amounts of Co and one or more of Re, Ru, Fe, Ni, Th, Zr, Hf, U, Mg and La on a suitable inorganic support material, and preferably one which comprises one or more refractory metal oxides. Preferred supports for Co containing catalysts comprise titania and titania-silica composites, particularly when employing a slurry HCS process in which higher molecular weight, primarily C_{5+} paraffinic liquid hydrocarbon products are desired. Useful catalysts and their preparation are known and illustrative, but nonlimiting examples may be found, for example, in U.S. Patents 4,568,663; 4,663,305; 4,542,122; 4,621,072 and 5,545,674, with those disclosed in U.S. 5,545,674 being particularly preferred.

The hydrocarbons produced by an HCS process according to the invention are typically upgraded to more valuable products, by subjecting all or a portion of the C_{5+} hydrocarbons to fractionation and/or conversion. By conver-

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sion is meant one or more operations in which the molecular structure of at least a portion of the hydrocarbon is changed and includes both noncatalytic processing (e.g., steam cracking), and catalytic processing (e.g., catalytic cracking) in which a fraction is contacted with a suitable catalyst. If hydrogen is present as a reactant, such process steps are typically referred to as hydroconversion and include, for example, hydroisomerization, hydrocracking, hydrodewaxing, hydrorefining and the more severe hydrorefining referred to as hydrotreating, all conducted at conditions well known in the literature for hydroconversion of hydrocarbon feeds, including hydrocarbon feeds rich in paraffins. Illustrative, but nonlimiting examples of more valuable products formed by conversion include one or more of a synthetic crude oil, liquid fuel, olefins, solvents, lubricating, industrial or medicinal oil, waxy hydrocarbons, nitrogen and oxygen containing compounds, and the like. Liquid fuel includes one or more of motor gasoline, diesel fuel, jet fuel, and kerosene, while lubricating oil includes, for example, automotive, jet, turbine and metal working oils. Industrial oil includes well drilling fluids, agricultural oils, heat transfer fluids and the like.

It is understood that various other embodiments and modifications in the practice of the invention will be apparent to, and can be readily made by, those skilled in the art without departing from the scope and spirit of the invention described above. Accordingly, it is not intended that the scope of the claims appended hereto be limited to the exact description set forth above, but rather that the claims be construed as encompassing all of the features of patentable novelty which reside in the present invention, including all the features and embodiments which would be treated as equivalents thereof by those skilled in the art to which the invention pertains.

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CLAIMS:

1. A slurry hydrocarbon synthesis process for making liquid hydrocarbons from a synthesis gas mixture comprising H₂ and CO which contains HCN, NH₃ or mixture thereof, said process comprising reacting said gas in the presence of a hydrocarbon synthesis catalyst in a slurry comprising said catalyst and gas bubbles in a hydrocarbon slurry liquid, under reaction conditions effective to form hydrocarbons from said synthesis gas, at least a portion of which are liquid at said reaction conditions and wherein said slurry liquid comprises said liquid hydrocarbons, said catalyst having a productivity of at least 150 hr⁻¹ and comprising a catalytically active cobalt component on a particulate inorganic refractory oxide carrier, and wherein the total amount of said HCN, NH₃ or mixture thereof present in said synthesis gas is less than 50 vppb.
2. A process according to claim 1 wherein said hydrocarbon liquid produced by said reaction comprises C₅₊ hydrocarbons.
3. A process according to claim 2 wherein said catalytically active cobalt component of said catalyst is dispersed and supported on an inorganic refractory oxide support.
4. A process according to claim 3 wherein said catalyst has a methane selectivity of less than 5 mole %.
5. A process according to claim 4 wherein said catalytically active cobalt component is present on said support as a layer of from 2-200 microns thick.

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6. A process according to claim 4 wherein said total amount of said HCN, NH₃ or mixture thereof present in syngas is less than 20 vppb.
7. A process according to claim 6 wherein said catalyst has a long term half life of at least 100 days and a short term half life of at least 30 days.
8. A process according to claim 7 wherein said C₅₊ hydrocarbons comprise primarily paraffins.
9. A process according to claim 2 wherein at least a portion of said C₅₊ hydrocarbons are upgraded by one or more conversion operations to more valuable products.
10. A process according to claim 9 wherein said total amount of said HCN, NH₃ or mixture thereof present in gas is less than 10 vppb to achieve a short term catalyst half life of at least 40 days.