

Claims.

1. A process for steam reforming a hydrocarbon feedstock containing one or more nitrogen compounds, comprising passing a mixture of the hydrocarbon feedstock and steam through a catalyst bed consisting of one or more nickel steam reforming catalysts disposed within a plurality of externally heated tubes in a tubular steam reformer, wherein each tube has an inlet to which the mixture of hydrocarbon and steam is fed, an outlet from which a reformed gas containing hydrogen, carbon monoxide, carbon dioxide, steam, ammonia and methane is recovered, and the steam reforming catalyst at least at the outlet of the tubes is a particulate eggshell steam reforming catalyst comprising 2.5 to 9.5% by weight nickel, expressed as NiO, wherein the nickel is provided in a layer at the surface of the catalyst and the thickness of layer is in the range of 100 to 1000µm.
2. A process according to claim 1, wherein the nickel is provided in a layer at the surface of the catalyst and the thickness of layer is in the range of 100 to 800 µm, preferably 100 to 600 µm.
3. A process according to claim 1 or claim 2, wherein the nickel is supported on a shaped particulate catalyst support comprising alumina, titania or zirconia or an alkaline earth metal aluminate, preferably one or more calcium aluminate compounds and/or magnesium aluminate.
4. A process according to any one of claims 1 to 3, wherein the nickel content of the eggshell catalyst, expressed as NiO, is in the range 2.5 to 5.5% by weight.
5. A process according to any one of claims 1 to 4, wherein the hydrocarbon feedstock comprises methane and is preferably a pre-reformed gas, an associated gas or natural gas, more preferably natural gas.
6. A process according to any one of claims 1 to 5, wherein the hydrocarbon feedstock is compressed to a pressure in the range 10 to 100 bar abs, preferably 15 to 80 bar abs, more preferably 20 to 50 bar abs.
7. A process according to any one of claims 1 to 6, wherein the one or more nitrogen compounds comprises nitrogen gas, N₂.
8. A process according to claim 7, wherein the nitrogen gas content of the hydrocarbon feedstock is in the range of 0.1 to 25% by volume or 0.5 to 25% by volume, preferably 1 to 10% by volume, more preferably 1 to 5% by volume.

9. A process according to any one of claims 1 to 8, wherein the mixture of hydrocarbon feedstock and steam has a steam to carbon ratio in the range 1.8:1 to 5:1, preferably 2.5:1 to 3.5:1, more preferably 2.8:1 to 3.2:1.
10. A process according to any one of claims 1 to 9 wherein the mixture of hydrocarbon feedstock and steam is fed to the inlets of the tubes at an inlet temperature in the range 300 to 650°C, preferably 450 to 650°C.
11. A process according to any one of claims 1 to 10, wherein the tubular steam reformer contains a plurality of tubes through which the mixture of the hydrocarbon feedstock and steam is passed, and to which heat is transferred by means of a hot gas comprising a combustion gas or a synthesis gas, flowing around the tubes.
12. A process according to any one of claims 1 to 11, wherein the catalyst bed consists of one, two, three or more layers of steam reforming catalyst wherein in each case the layer of steam reforming catalyst adjacent the outlets of the tubes is the eggshell nickel catalyst.
13. A process according to claim 12, wherein there are two or more layers of steam reforming catalyst within the tubes and the eggshell catalyst layer comprises 95% to 5% of the volume of the bed, preferably 80% to 20% of the volume of the bed, more preferably 75% to 25% of the volume of the bed.
14. A process according to any one of claims 1 to 13, wherein the methane content of the reformed gas is less than 15% by volume on a dry gas basis, preferably less than 10% by volume on a dry gas basis, more preferably less than 5% by volume on a dry gas basis.
15. A process according to any one of claims 1 to 14, wherein the ammonia content of the reformed gas is below 200ppmv on a dry gas basis, preferably below 100ppmv, more preferably below 50ppmv, most preferably below 10ppmv on a dry gas basis.
16. A process according to any one of claims 1 to 15, wherein the process further comprises cooling the reformed gas to below the dew point to condense steam and separating the liquid condensate to form a synthesis gas from the reformed gas.
17. A process according to claim 16, wherein the ammonia content of the liquid condensate is below 400 mg/Litre, preferably below 200 mg/Litre, more preferably below 100mg/Litre, most preferably below 20mg/Litre.
18. A process according to claim 16 or claim 17, wherein at least a portion of the condensate is recycled and used to generate steam used in the steam reforming process.

19. The use of an eggshell steam reforming catalyst comprising 2.5 to 9.5% by weight nickel, expressed as NiO, wherein the nickel is provided in a layer at the surface of the catalyst and the thickness of layer is in the range of 100 to 1000 μ m, for suppression of ammonia formation during catalytic steam reforming of a nitrogen containing hydrocarbon feedstock.