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(54) **Process for the hydrogenation of solid carbonaceous fuses.**

(57) Solid carbonaceous fuels may be hydrogenated to form either gaseous or liquid products by subjecting a mixture of said fuel and a hydrogen-containing transport gas to hydrogenation conditions in the presence of a hydrogenating gas under entrained flow conditions, wherein the reaction mixture is circulated around an endless path and a portion of the reaction products are continuously withdrawn.

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The invention relates to the hydrogenation of solid carbonaceous fuels and in particular to a process for the manufacture of hydrocarbon-containing fuel gases and/or hydrocarbon liquids from solid carbonaceous fuels by reaction with hydrogen-containing gas in an entrained flow system.

It is known that solid carbonaceous fuels such as coals, coal chars and lignites will react exothermically with hydrogen when heated under pressure. Once initiated, this exothermic reaction is self-sustaining in an adiabatic reactor. Reaction rates increase with both temperature and pressure and rates high enough for commercial application are obtained at temperatures above 700°C and pressures above 25 bars. Depending on the nature of the solid fuel, the design of the reactor and such conditions as hydrogen partial pressure, temperature and residence time within the reactor, the hydrocarbon products range from a gas which is mostly methane, at high temperatures and long residence times, to the mixtures produced at lower temperatures and shorter residence times from which substantial quantities of hydrocarbon liquids may be condensed.

Coals and coal-like substances, as is well-known, are not homogeneous. Some part of their constituent matter reacts more readily with hydrogen than does the remainder; consequently hydrogenation generally leaves a residue which

requires more severe conditions for further reaction. Nevertheless, rapid reaction of a large part of the carbon in such fuels can be achieved and is facilitated if the fuel is in a finely divided state and is brought quickly to reaction temperature. For this and other reasons, suspension gasifiers (i.e. fluidised and entrained flow systems), which provide intensive gas-solids contacting, have been favoured in developing the technology to exploit coal hydrogenation. These gasifiers operate at high temperatures and pressures with gas residence times ranging from a few seconds to fractions of a second.

In fluidised gasifiers, recirculation of solids within the bed leads to good thermal stability, allowing reaction to be initiated with relatively little reactants preheat and thus enabling the preheat to be determined solely by overall thermal balance considerations. Superficial velocities, typically 0.03-1.5mls sec^{-1}, are low compared with 4.5 mls sec^{-1} or more in entrained flow systems, however, and this limits the ability of fluidised gasifiers to exploit the rapid reaction rates and achieve high gasifier throughputs. Fluidised gasifiers also impose a limit on the proportion of very small material in the feed size range in order to avoid excessive carry-over of fines.

There is no such limitation with entrained flow gasifiers; indeed, very small particles are a positive

advantage in terms of gasification rates. Very high specific reactor throughputs are characteristic of entrained flow systems and loadings of up to 13.5kg m^{-2} sec. $^{-1}$ have been reported in the literature, which may be compared with 1.35kg m^{-2} sec^{-1} for fixed bed and 2.7kg m^{-2} sec^{-1} for fluidised bed gasifiers. In addition to giving a high volumetric throughput, the use of high linear velocities allows reactors to be of relatively small diameter. The attraction of this feature to a designer is not only that smaller reactors are less costly but that they pose less severe mechanical design problems. Design and scale-up are conceptually easier than with fluidised beds and the simpler fluid mechanics of entrained flow systems gives greater potential turndown flexibility. At their present stage of development, however, entrained flow systems have certain short comings in comparison with fluidised beds in that co-current flow of reactants does not permit internal heat exchange between products and incoming reactants. In consequence, higher preheat temperatures are required to initiate reaction and gas outlet temperatures are comparatively high.

Much of the development work undertaken to exploit coal hydrogenation has been directed towards the production of high Btu gas, with emphasis in recent years on the manufacture of substitute natural gas (SNG). The Rockwell International Corporation has been prominent in developing entrained flow technology and a paper to the I.G.T. 10th

Synthetic Pipeline Gas Symposium, Chicago, October 1978 (The Rockwell Advanced SNG Gasifier by J. Friedman, L.P. Combs and J. Silverman) summarised their work. In this paper the authors state that the reactants, pulverised coal and hydrogen-rich gas, must be heated to temperatures of approximately 760°C or higher to initiate reaction. Caking coals cannot be heated above about 200 °C without causing severe problems with agglomeration and devolatilisation. Therefore, the coal is injected into the reactor at low temperature and then heated by rapid mixing with injected hot hydrogen. Requisite heat is supplied by preheating the gaseous hydrogen to a substantially higher injection temperature than the mixed reactants temperature required to initiate sustained hydrogenation. Substantially more hydrogen is fed to the reactor than is consumed in the hydrogenation reaction. Excess hydrogen is needed to favour methane synthesis and to supply the coal-heating function. Conventional heat exchangers can be used to preheat the hydrogen to about 815°C and the final increment of heat is provided by partial oxidation with a small amount of injected oxygen.

Co-current flow of reactants in entrained flow gasifiers is the cause of some disadvantageous features, the elimination of which would substantially improve process efficiency. One such feature, an obvious source of inefficiency, is the use of excess preheated hydrogen-

containing gas to heat the pulverised coal to initiate reaction. It is proposed that by reducing this excess, would lead to higher preheat temperatures. Another such feature is the injection of oxygen. But the need for oxygen injection arises because the preheat requirements generally exceed what is possible with conventional indirect heaters. Thus it is most probable that minimising the hydrogen provision would increase oxygen consumption, increasing the capital costs and fuel requirements of the oxygen production unit associated with the gasifier. Furthermore, partial combustion with oxygen leads to the formation of significant amounts of carbon oxides and, hence, a reduced degree of conversion of carbon to methane. Lower methane production results in reduced exothermicity of reaction and a consequent further increase in preheat requirement, exacerbating the disadvantage of increased oxygen consumption already mentioned. The object of the invention is to avoid the disadvantages which result from co-current flow of the reactants in entrained flow gasifiers.

Accordingly, the invention provides a continuous process for the hydrogenation of carbonaceous fuels wherein said fuel and a gas comprising hydrogen are continuously introduced into a thermally insulated reaction chamber so constructed as to define an endless path along which reactants and reaction products can circulate within the chamber and said fuel and said gas comprising hydrogen are

admixed and introduced in the form of at least one jet through orifice means into the reaction chamber to cause a substantial amount of an admixture of reactants and reaction products to circulate continuously around the said endless path characterised in that said fuel is solid particulate carbonaceous material transported in a stream of a hydrogen containing gas whose temperature is not greater than 200°C and wherein a portion of the reaction products is continuously withdrawn from the chamber, sufficient remaining in the chamber to permit adequate recirculation to support reaction of the fuel particles and produce a reaction product whose temperature is not less than 700°C.

The term 'reaction products' may include products of incomplete reaction and unreacted reactants. By recirculating the products of the exothermic reaction, operating temperatures in the reaction chamber may be maintained, without oxygen injection by employing only moderate preheat temperatures. Using a large reaction chamber having well insulated walls, so that the rate of loss of heat through the walls per unit internal volume of the reaction chamber is small, the temperature of said mixture of fuel and gas comprising hydrogen can be lower than that required to initiate and sustain reaction in a conventional entrained flow gasifier. Incoming reactants are then raised to a high enough temperature for reaction

to begin as they become mixed with hotter recycled products.

Furthermore, as the proportion of hydrogen-containing gas to solid carbonaceous fuel is reduced, the heat liberated by reaction of a given quantity of fuel can raise the temperature of the incoming reactants to a greater extent. Consequently, a lesser degree of reactants preheat suffices to initiate reaction. In contradistinction, greater preheat would be required with a conventional gasifier.

In the process of the invention it is unnecessary to use excess hydrogen-containing gas solely to introduce the preheat required to initiate reaction. In relation to conventional processes, therefore, the process of the invention has an improved thermal efficiency.

An additional advantage arises when it is desired to operate at relatively low outlet temperatures, for example when producing predominantly liquid products from coal. Conventional gasifiers can then be operated only over a restricted range of hydrogen/coal ratios because of conflicting requirements to reduce the degree of preheat but maintain the reaction initiation temperature. With the process of the invention it is possible to minimise the outlet temperature at lower hydrogen/fuel ratios than are accessible with conventional processes.

Hydrogen-containing gas suitable for use in the process may be provided by known methods, for example, by reacting hydrocarbons or carbonaceous materials with steam or with steam and oxygen to give mixtures of hydrogen and oxides of carbon. Known methods may then be used, if desired, to increase the hydrogen content of such mixtures. It is envisaged that incompletely reacted particles of solid fuel from the process of the invention itself may be so reacted to provide hydrogenating gas.

The proportion of hydrogen to be supplied in relation to the solid fuel will depend on the composition of the solid fuel, the composition of the hydrogenating gas, the nature of the products desired and the extent to which the solid fuel reacts but will generally lie within the range of weight ratios from 0.1:1 to 1:1.

When the process is to be used in the manufacture of SNG from coal and conditions are maintained such that the hydro-carbon products of reaction consist predominantly of methane it is preferred that the hydrogen/coal ratio should lie within the range from 0.2:1 to 0.5:1.

The stream of hydrogen-containing gas, transporting the particles of solid fuel into the reaction chamber may but need not be gently preheated up to a maximum temperature of 200°C. Above this temperature the effect of

heat on the particles of solid fuel is such as to make their transportation increasingly difficult and eventually impossible. On the other hand, limitations on the preheat temperature of the gas comprising hydrogen arise solely from the design criteria which govern the construction of fired heaters for operation at high pressure. It is a feature of the invention that the required preheat temperatures of the gas comprising hydrogen are comfortably within the capabilities of heaters which can be constructed using known, present day technology. That is to say, in general, that the preheat temperature need not exceed about 800°C and can be substantially lower. In the manufacture of SNG from coal, it is preferred that the gas comprising hydrogen should be preheated to a temperature within the range from 600° to 800°C.

The circulation of gas within the reaction chamber is caused by the transfer of momentum from the rapidly moving stream or streams of reactants entering the reaction chamber to the products already in the reaction chamber. The magnitude of the circulatory effect may be specified in terms of the recirculation ratio, that is to say, the ratio of the volume of gas circulating within the reaction chamber to the volume of gas withdrawn from the reaction chamber during one complete period of the circulatory motion.

Quite low recirculation ratios, in the region of 2:1, suffice to enable temperatures of the mixed reactants and products to be obtained which are well above the temperature at which the exothermic reaction is initiated. The use of higher recirculation ratios will lead to greater temperature uniformity within the reaction chamber and, consequently, will influence the nature of the reaction products. Whether it is desirable to use higher recirculation ratios will largely depend on what products the process is required to produce. In the manufacture of SNG from coal it is preferred that the recirculation ratio should lie within the range from 2:1 to 10:1.

The process of the invention, in the production of both gaseous and liquid products, is not pressure sensitive, although it is preferred that the process be carried out at pressures in excess of 5 bars.

For producing gaseous products eg. SNG precursors, it is preferred to operate at temperatures above 890°C with residence times normally in excess of 1 second. However, for liquid products, the reaction temperature is preferably between 800°C and 1000°C with a residence time ranging between 0.01 to 5 seconds depending upon both the reaction temperature and the nature of the carbonaceous fuel. Thus, for example, using a bituminous coal and a reaction temperature of 900°C, a typical residence time would be about 0.1 second.

Apparatus suitable for use in the process of the invention has been disclosed in our earlier British Patents 1031717 and 1074932. The reaction chamber advantageously comprises a generally cylindrical thermally insulated vessel having mounted coaxially within it a hollow cylindrical member, optionally taking the form of a venturi, which is shorter than the internal length of the vessel and which divides the interior of the reaction chamber into an inner region within the cylindrical member and an outer region of annular cross-section, the two regions being in communication with each other beyond the ends of the hollow cylindrical member to form the aforesaid endless path, and orifice means arranged to introduce the reactants at or close to one end of the vessel and axially towards the other end of the vessel. With this form of reaction chamber, the rapidly moving stream of reactants entering the reaction chamber passes along the inner region of the chamber, carrying reaction products already in the chamber along with it, and the moving body of gas and entrained particles then returns along the outer region of the chamber to the vicinity of the orifice means where it receives fresh impetus from the stream of reactants leaving the orifice means and starts a further cycle of the circulatory movement.

The transfer of heat from reaction products to

incoming reactants has been shown not to be greatly dependent on whether the circulating material does or does not contain incompletely reacted particles or solid fuel (char). This is a consequence of the high voids fraction of the dilute phase entrained flow system established within the reaction chamber. Even near the jet of incoming reactants, where the concentration of solid particles is greatest, the voids fraction will be above 95% and, of course, in the recycled reaction products it will be higher still. Optionally, therefore, provision may be made to separate and remove char at the end of the hollow cylindrical member remote from the jet and to recycle gaseous reaction products substantially free from solid particles. This option might be exercised to ensure that an adequate quantity of char is obtained, for example, to use in the manufacture of hydrogen-containing gas.

CLAIMS

A continuous process for the hydrogenation of carbonaceous fuels wherein said fuel and a gas comprising hydrogen are continuously introduced into a thermally insulated reaction chamber so constructed as to define an endless path along which reactants and reaction products can circulate within the chamber and said fuel and said gas comprising hydrogen are admixed and introduced in the form of at least one jet through orifice means into the reaction chamber to cause a substantial amount of an admixture of reactants and reaction products to circulate continuously around the said endless path characterised in that said fuel is solid particulate carbonaceous material transported in a stream of a hydrogen containing gas whose temperature is not greater than 200°C and wherein a portion of the reaction products is continuously withdrawn from the chamber, sufficient remaining in the chamber to permit adequate recirculation to support reaction of the fuel particles and produce a reaction product whose temperature is not less than 700°C.