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Characteristics of Petroleum Coke

CANMET has been involved in work to utilize a wide range of fuels by both conventional and novel combustion technology for several decades. In the last ten years petroleum cokes and fluidized bed combustion have received increasing attention by CANMET.

Petroleum cokes are byproducts of petroleum refining processes which employ carbon rejection to achieve the desired H/C ratio in the refined products. Heavy feedstocks such as heavy oil and tar sand bitumen produce more coke than light crudes. Although the cokes so produced are high heating value fuels they are often stockpiled or simply treated as a waste stream for three reasons.

First, they are relatively unreactive, both in terms of the petrographic structure of the carbon in the coke and the absence of volatiles which normally enhance the reactivity of coal. This means that these fuels can present severe difficulties for conventional coal burning technology such as pulverized coal fired boilers.

Second, such cokes often contain significant amounts of sulphur (6% or more). This means that they may be environmentally unattractive unless expensive flue gas cleanup is employed.

Third, some petroleum cokes contain significant amounts of heavy metals such as nickel and vanadium. These can contribute to severe corrosion in conventional boilers.

Fluidized Bed Boilers

Fluidized boilers have intrinsic advantages over conventional combustion equipment in combatting the aforementioned problems. At its simplest a fluidized bed combustor (FBC) consists of a bed of granular material, typically limestone, sand or powdered rock, in a chamber with a perforated bottom or distributor plate. When air is forced through the distributor at sufficient velocity, typically 0.6 m/s the particles in the bed lift and separate and behave very much like a boiling liquid. Thus the bed surface remains horizontal if the bed is tipped and a light object will float on the surface while a heavy one will sink; hence the name fluidized bed. Ancillary equipment brings the bed up to the ignition temperature of the fuel, introduces the fuel and removes excess bed solids (see Figure 1).

As the fuel is only 1 to 2% of the bed by weight at any time, FBC is insensitive to fuel type. Also because the fluidizing velocities are typically less than in conventional coal combustion equipment by an order of magnitude or more, the residence time of fuel in the FBC is far greater and this permits relatively unreactive fuels such as petroleum coke a much better chance to burn efficiently.

The violent turbulent motion of the bed results in very good mixing and gas/solids contact. This leads to very uniform temperature distribution in the bed and very high heat transfer rates. As a result, for the same thermal output, FBC boilers can be made smaller than pulverized fuel boilers. Additional benefits of the good mixing are that combustion can occur at much lower average temperatures, typically 750°C to 950°C, compared with greater than 1300°C for conventional boilers. At these low temperatures coal ash does not soften, slag or agglomerate and nitrogen oxide (NO_x) formation from the air does not occur; NO_x emissions are therefore low.

A further benefit of FBC for petroleum cokes appears to be that the heavy metals which could cause corrosion do not appear to be mobilized. Current research suggests that metals such as nickel and vanadium stay fixed with the ash or bed material and are not available to cause boiler damage.

Another very important feature of fluidized bed boilers is their ability to burn high sulphur fuels, such as many petroleum cokes, with low sulphur dioxide (SO_2) emissions. This is achieved by using limestone or dolomite as the bed material where it reacts with the SO_2 gas to form calcium sulphate, an inert insoluble solid. It has been amply demonstrated that FBC boilers can burn the highest sulphur-containing petroleum cokes in an environmentally benign manner.

Recently a new type of fluidized bed was introduced, the circulating fluidized bed or CFB. This operates with a combination of finer bed material, typically 200-400 m, and higher fluidizing velocities (up to 10 m/s cf. with a maximum of 3 m/s for FBC). CFB have superior turndown ratios to FBC which means they are likely to be superior for thermal power applications. Also because they operate with an entrained bed and a hot cyclone to maintain bed inventories they can achieve longer retention times hence superior combustion efficiencies. This is especially important with petroleum cokes like Syncrude coke which is both relatively unreactive and fine (mean size about 200 m) and therefore tends to elutriate from FBC systems before combustion is complete. A schematic of a CFB system is provided in Figure 2. Canada's first industrial size (20 MWe) CFB boiler is being built at Chatham, New Brunswick under the auspices of EMR and the New Brunswick Electrical Power Commission.

Petroleum Coke Research

The first FBC research in Canada was carried out using coke from the Suncor oil sands extraction plant (formerly the Great Canadian Oil Sands extraction plant). The plant produces a byproduct coke by a delayed coking process which is used as fuel to generate the plant's process steam requirements. However, the coke is a relatively unreactive fuel and the pulverized fired, anthracite-type boilers in which it is burnt experience a significant carry-over of unburnt carbon. Moreover, the coke has a high sulphur content, which in the absence of stack gas scrubbers, results in substantial emissions of SO_2 to the atmosphere.

Work was carried out on this fuel using a pilot scale FBC rig at CANMET's Energy Research Laboratories (ERL). It was shown that Suncor could be burnt with combustion efficiencies above 96% and reduction of SO_2 emissions by 80% or more by using limestone at the rate of .5 kg of limestone per kg of fuel. (This corresponds to a Ca/S molar ratio of 3:1 or a utilization of 27% of the calcium.) Although these trials were fairly limited they did demonstrate that Suncor could be burnt with high efficiency and acceptable sulphur capture in a FBC boiler.

Following this work interest in Syncrude coke developed at CANMET. This coke is produced by Canada's largest oil sands extraction plant. This plant upgrades the extracted bitumen by means of fluid coking, and the byproduct coke, being both high in sulphur, and relatively unreactive, is unsuitable for combustion by conventional combustion. Consequently, the fuel is stockpiled at the rate of 2000 metric t/d though in principle it could supply up to 15% of the plant's steam raising requirements. The fuel has other features; its ash is relatively high in the potentially corrosive element vanadium and the material is relatively fine (mean size about 200 μm and typically 98% less than 2 mm). Because of the fine size, it was anticipated that the coke would present problems for FBC technology.

In 1981, CANMET sent 18 tons of the byproduct coke to the Hans Ahlstrom Laboratory in Finland for some CFB tests, because at that time no CFB facilities existed in Canada. The results obtained from the limited test series were remarkably good. Combustion efficiencies from 95 to 99% were achieved and sulphur capture above 90% was achieved with a calcium to sulphur molar ratio of 1.7 to 2.1. This represents a calcium utilization of 43 to 53%; nearly twice as good as the results achieved in the earlier trials with Suncor coke.

Subsequently it was decided to carry out further pilot scale trials using bubbling FBC reactors at ERL and at Queen's University under contract. These results showed that reasonable combustion efficiencies, in the high nineties, can be achieved by operating at combustion temperatures from 950°C to 1050°C. Acceptable sulphur capture up to 90% with Ca/S ratios of 2 to 3 or 30 to 45% utilization of the calcium was also possible.

However, the maximum fluidizing velocity that could be used was less than 1.5 m/s. At higher velocities the coke is massively elutriated from the bubbling bed and performance both in terms of combustion efficiency and sulphur capture dramatically deteriorates. This means that the high volumetric heat release rates and turndown ratios required for industrial steam raising cannot be achieved by bubbling FBC for this particular fuel and CFB will be the preferred technology for any industrial steam raising plant utilizing Syncrude coke.

As a result of this test work a further series of trials with Ahlstrom CFB equipment was initiated. These trials are far more extensive and have been carried out with the Athabasca limestone that will be utilized in conjunction with any industrial use of this fuel. The results of these trials, which were completed in early 1986, will provide the data necessary to optimize the design of any large-scale CFB actually built.

Further trials are also being carried out utilizing a bench scale CFB at CANMET's Mineral Science Laboratories to further study the fate of heavy metals, particularly vanadium in CFB combustion of Syncrude coke. In addition the possibility of commercially extracting the vandium in the ash is being investigated. Results from this work should be available before the end of 1987.

CANMET continues to maintain an interest in utilizing petroleum cokes and other difficult to burn fuels. For example, trials will soon be underway using a low sulphur delayed, anode grade coke from Saskatchewan and it is likely in the future that other such fuels will be investigated in order to utilize such resources and help optimize plant efficiency.

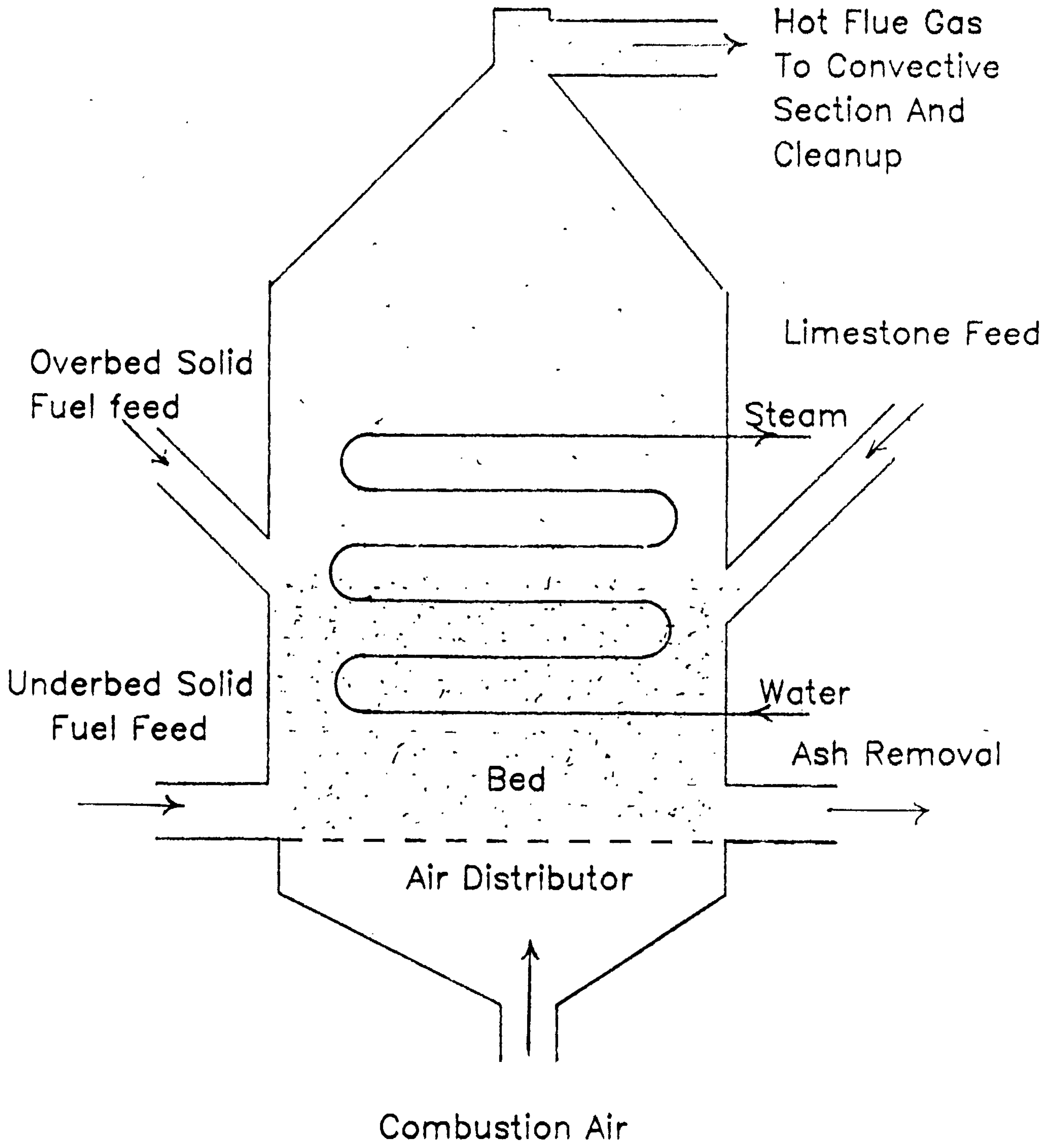

Fig. 1 Schematic Of A Fluidized Bed Combustor

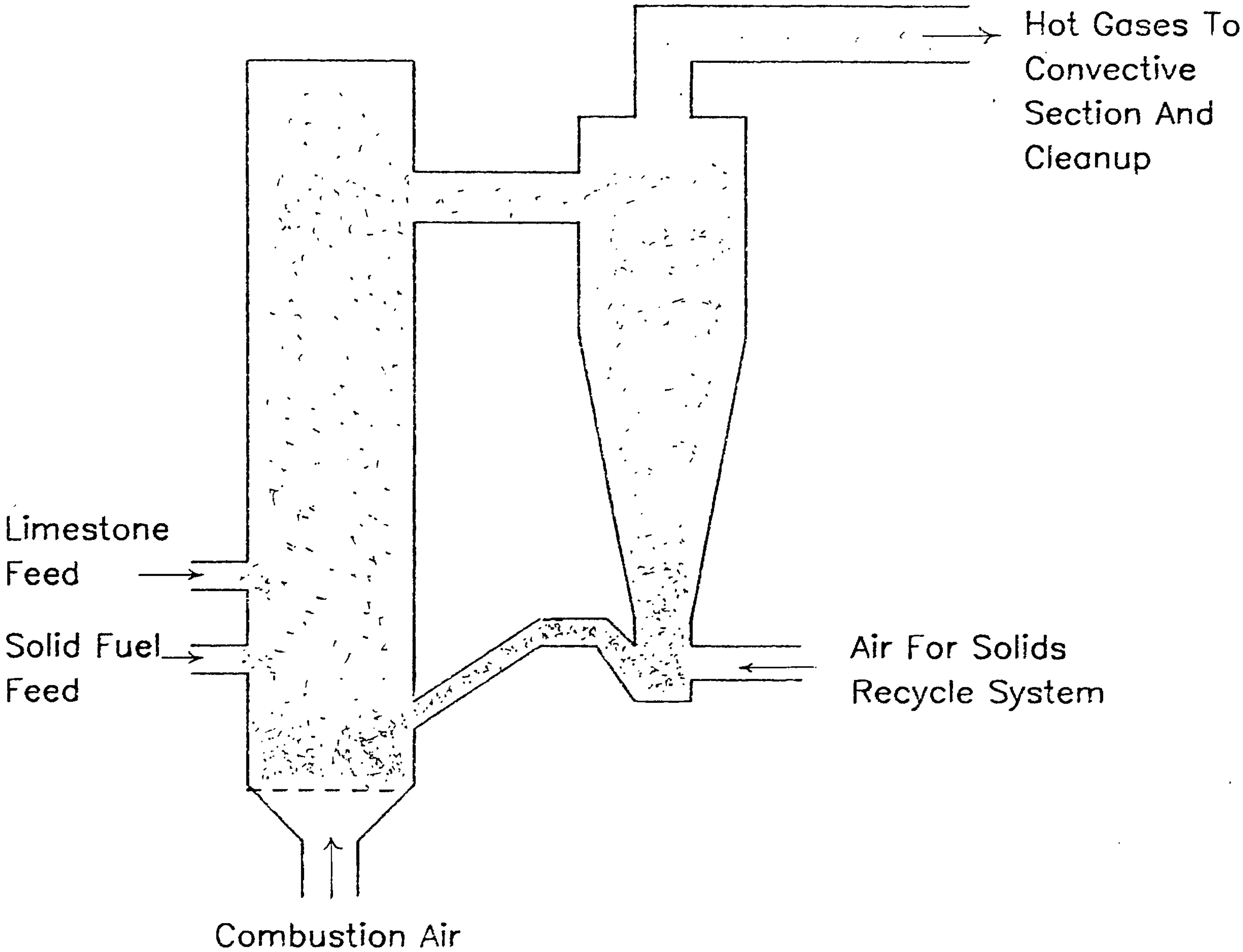

Fig 2 Schematic Of A Circulating Fluidized Combustor