CARBON MONOXIDE PRODUCTION FROM CO_2 USING DC PLASMA JETS

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Abstract

Carbon dioxide is treated with low-voltage plasma to produce CO, in atmospheric pressure streams of gas which may include air. Nitrogen plasma produced conversion varying linearly with CO_2 concentration in presence of oxygen, and much higher conversions in its absence; water vapour in the processed gas had a marked positive effect on the CO production. Argon plasma produced negligible decomposition in the same gas mixtures. The energy used was approximately 10 MJ/mole CO, comparing favourably with other reported plasma experiments.

Introduction

Under the Climate Change Convention of the UN the U.S.A., the European Union and Japan, which together contribute 40 % of the world carbon dioxide emissions from burning fossil fuels, are all required to reduce their CO_2 emissions to 1990 levels by the year 2000. Also there is increasing pressure internationally to introduce UN-monitored carbon-tax to control the emission of CO_2.

Technologies for separation of CO_2 from gases and for sequestration of the enriched or pure CO_2 are frequently reviewed in literature, (for instance [1,2]). The separation processes are in a mature state of development for petrochemical and ammonia synthesis streams, where the CO_2 content is relatively low, but underdeveloped in the context of flue gas from conventional combustion, when it comprises say 5% concentration. Sequestration can in principle follow separation or concentration but equally there is an incentive to research use of the CO_2 as chemical feedstock, either directly (as in e.g. catalytic combination of CO_2 and H_2 [3,4]), or indirectly after conversion of the CO_2 to CO. The current work with

plasma has been done with this latter route in mind, within a programme of experiments in desulphurisation and de-NO_x [5].

In the 8th Symposium of this series, Tanaka and Gao [6] reported the yields at equilibrium of CO from low pressures of CO_2 by the use of electric discharge (1 to 2 kV, 6 to 12 mA). The maximum conversion achieved in their circulated batch reactor system was 0.6 (expressed as 1 - partl. press. CO_2 at equilm./partl. press. CO_2 initially). It can be estimated that the expenditure of energy per mole of CO_2 was of the order 70 MJ/mole CO., (for "Run 5", equilibrium conversion = 25%, total pressure = 50 Torr). In the 11th Symposium, experiments at atmospheric pressure were reported [7] with expenditures in the range 10-40 MJ/mole CO.

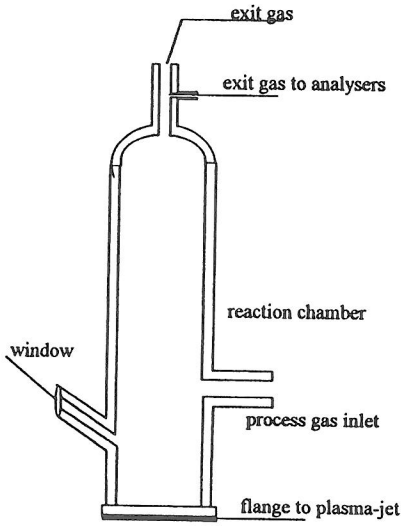

Figure 1 Flow reactor

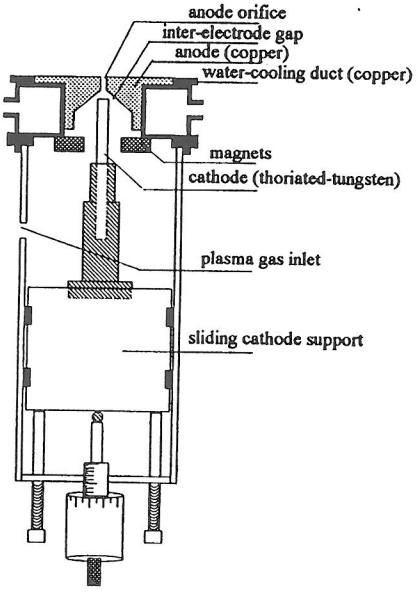

Figure 2 Plasma-jet

Experiments

The experiments consist of laboratory bench scale tests with a continuous flow reactor in which a "process gas mixture" is subjected to a stream of products from the plasma-jet. The process products are analysed at the reactor outlet. The process gas mixtures ranged from pure carbon dioxide at a flow rate of 5 - 45 litre/min. to carbon dioxide premixed (in the range 4% to 11%) with nitrogen or with nitrogen/air mixtures such that oxygen is in the range of 0% to 13% and the total flow rate is 45 litre/min. The gas was flowed to the reactor at either room temperature or at 150°C after preheating in an oven. The experiments with water vapour were carried out by injecting liquid water at a rate of 60 - 300 ml h^{-1} into gases heated to 150°C.
The reactor (see Figure 1) consists of an upright cylinder of stainless steel, diameter 55 mm. and height 260 mm. (approximately 600 ml. volume capacity) mounted above and sealed to the plasma-jet device. The stream of products leaves through a 12 mm. quartz glass inner tube mounted vertically with its inlet at 20 mm. above the plasma-jet. The inner tube has the purpose of constraining the process gas to flow near the plasma arc.

The plasma-jet used (designed by F.J. Weinberg and collaborators, [8]) is shown in Figure 2. A square cut cathode made of thoriated tungsten is surrounded by a water cooled copper anode, with a ring shaped magnet around the tip of the cathode. The interaction with the magnetic field rotates the DC arc and helps to minimise anode erosion. The rate of arc rotation depends on the inter-electrode gap and arc current as well as the magnetic field and gas swirl induced by tangential injection. The voltage current characteristics of the arc used in this study depend on the nature of the gas supply (and its flow rate) but they share with previous experimental devices a trend of falling voltage with increasing current. In the present experiments, argon plasma was operated with 20 volts and 15 amps current and nitrogen plasma with 60 volts and 20 amps current. The flow rate of feed gas to the plasma-jet was 22 litre/min. An inter electrode gap of 250 μm (see figure 2) was employed for both argon and nitrogen plasma and the diameter of the anode aperture was 2 mm.

While testing the operability of the jet in the reactor, no tendency to blow out the jet was found even with low (subsonic) plasma gas feed velocities. Subsonic operation was more economical in power and hence was normally used. The process gas had no discernible effects on the materials of the electrodes, having minimal contact with them due to the outward flow of plasma products. It has been shown by LIF visualisation [9] that such jets project hot pockets of gas of size of the order 2 mm. These pockets containing radicals and excited species, which survive up to distances of order 5mm, are envisaged to be sources of active species diffusing into the process gas.

The exit stream, at temperatures between 90° and 240°C, was passed through a water cooler and into analysers for CO ("Testo Term 342-1"), for NO_x ("Thermoelectron"), and for O_2, NO_x, and SO_2 ("Landcom 3200").

Results

(a) As shown in Figure 3, the nitrogen plasma produced considerable concentrations of CO in gases containing CO_2. The yield is linear with the CO_2 feed concentration in the absence of oxygen (amounting to about 1% conversion); in the absence of oxygen the yield of CO was considerably higher, ranging from 940 to 1230 vpm over the same range of CO_2 concentration (4% to 11%).

(b) (i) increasing the temperature of the process gas from room temperature to 150°C increased the amount of CO production in oxygen-free gas containing 11% CO_2 from 1230 vpm to 1700 vpm.

(ii) The addition of water vapour (12%) to gases containing 11% CO_2 increased the CO production increased sharply, to over 4000 vpm (the limit of the analyser used).

(c) The nitrogen plasma in pure CO_2 gas (feed at room temperature) also produced CO in concentrations in excess of 4000 vpm.

(d) In experiments with argon plasma a very small amount of CO was produced in gases containing 0 - 11% of CO_2 in air or nitrogen. The presence or absence of oxygen made no difference to the yield of CO, invariably less than 10 vpm.

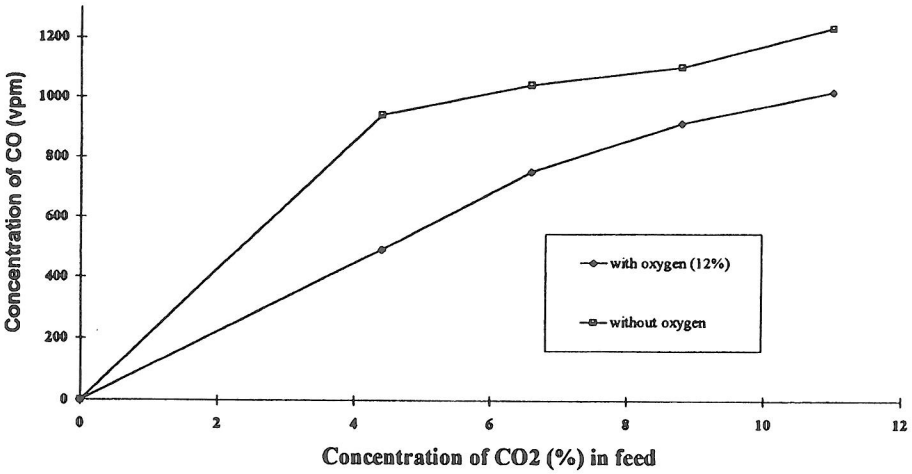

Figure 3. Carbon monoxide production with and without oxygen in the system

Discussion

In this work the amount of CO produced by N_2 plasma (by decomposition of CO_2) was much higher than that of NO, given similar concentrations of the precursors CO_2 and O_2.

With argon as the plasma gas the yield of CO was insignificant, whereas this plasma was able to produce NO even in the presence of CO_2

These results may be interpreted as follows:

(a) excited nitrogen molecules are dissociating the CO_2.

$N_2^* + CO_2 = CO + O + N_2$ 1 [10]

apparently in effective competition against the process which forms NO:

$N_2^* + O_2 = 2O + N_2$ 2_a [11]

$O + N_2 = NO + N$ 2_b [12]

Any of the electronically excited states of N_2 produced by the plasma would have energy exceeding the dissociation energy of CO_2 (530 kJ/mole [13]). There is evidence [10] that the $B^3\pi_g$ state (718 kJ/mole [14]) is more effective in reaction 1 above than the $A^3\Sigma_u^+$ state (598 kJ/mole [14]).

(b) The absence of CO production using the argon plasma can be attributed to its products carrying insufficient energy either to dissociate CO_2 directly , or to excite N_2^* even to its lowest excited state and thus to enable reaction 1. In contrast, the substantial production of NO with this plasma suggests that the argon carried enough energy to dissociate O_2 (490 kJ/mole) directly in reaction 2_a.

The enhancement of decomposition of CO_2 by water vapour in the process gas indicates that neither the "shift " reaction nor the reaction $OH + CO = CO_2 + H$ is effectively acting contrary to CO production. Water vapour may well be absorbing and transferring radiated energy from the arc; excited states of water may be effective in reactions analogous to reaction 1.

The experiments suggest that use of plasma may be envisaged for circumstances such as in a stream of separated CO_2 from whatever source, or in exhaust gas from oxygen-based combustion, especially in the schemes with re-circulated CO_2 in the combustor [1]. In flue gas from conventional air-based combustion, the design would have to allow for a raised NO concentration. The energy usage in this plasma treatment of gas at ambient pressure with low voltage and high current is of the order 10-20 MJ/ mol CO produced, at least as favourable as in the batch systems referred to above [6,7].

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