Fuel 158 (2015) 843–847

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

A novel method of production of ethanol by carbon dioxide with steam

Li Guo [a], Xiaoxun Ma [a,*], Yashen Xia [b,*], Xiaofeng Xiang [a], Xing Wu [a]

[a] School of Chemical Engineering, Northwest University, Xi'an, PR China
[b] HyChar Energy, LLC, Newton, MA 02466, USA

HIGHLIGHTS

- Negative ions of CO_2 and H_2O have been used for CO_2 reduction to produce ethanol.
- The CO_2 conversion could be about 16% at 1 atm and 105 °C.
- The molar yield of both ethanol and methanol could achieve 11.9% at 4 atm.
- The production of ethanol by negative-ion method could lead to energy storage.

ARTICLE INFO

Article history:
Received 23 February 2015
Received in revised form 4 June 2015
Accepted 5 June 2015
Available online 13 June 2015

Keywords:
CO_2 reduction
CO_2 utilization
Negative ion plasma
Negative corona discharge
Ethanol synthesis

ABSTRACT

Direct production of useful fuel from the emitted carbon dioxide has been one of major challenges in industries. We here report a novel approach in which ethanol could simply be synthesized under negative DC corona discharge at 1 atm and 105 °C. The experimental results have shown that CO_2 and H_2O could be reduced mainly into ethanol with yield of 4.7% without applying any metal catalyst. And with increase of total feeding pressure of gases, the yield appears to rise. The mechanism of electron attachment on those gaseous molecules creating accelerated anions might be the key of CO_2 and H_2O reduction reaction. This finding also implies that it might be feasible to use of negative corona discharge and CO_2 as only carbon source with steam as only source of hydrogen to produce energy-dense ethanol fuel, also possibly leading to electric energy storage.

1. Introduction

Carbon dioxide continues to attract significant interest mainly due to its wide emission [1–3] from industries. A major problem in the CO_2 reduction worldwide is the direct utilization of CO_2 for production of value-added production in industrial combustion facilities. The problem is attributed to inactivity of CO_2 with conventional technology. The primary cause of increasing CO_2 emission is the lack of cost-effective CO_2 capture and utilization technologies which could combine emitted CO_2 and off-peak electricity in combustion facilities to produce value-added product.

It would also be desirable' to produce fuel directly from emitted CO_2 as only carbon source or feedstock and renewable or off-peak electricity as energy input. One important challenge for environmental chemists is the synthesis of various products by CO_2.

Much research [4] has been focused on reducing CO_2 by conventional low-temperature non-equilibrium plasma process. However, existing methods have severe economic and technical limitations. Thus, despite extensive research efforts, there is no acceptable plasma method for reducing CO_2 to produce fuel.

Corona discharges have been used for nearly a century in many industrial applications. Corona discharges are typically generated in one of three ways, i.e., two-electrodes, positive-electrode-only and negative-electrode-only, to produce three kinds of plasmas as follows, respectively:

1. Normal plasma [5].
2. Positive ion plasma [6].
3. Negative ion plasma [7].

In the two-electrode corona method [5], there are two electrodes, one positive and one negative, to be used in a container with DC high electric voltage (+/−), to obtain a normal or neutral plasma, where the plasma may be described as an electrically neutral medium of unbound positive and negative particles (i.e. the overall charge of a plasma is roughly zero). In such a system [5], mixed gases could be activated to implement rapid complex reactions (for example reducing and then oxidizing rapidly), while maintaining an electrically neutral medium. Although

* Corresponding authors.
E-mail addresses: maxym@nwu.edu.cn (X. Ma), ceo@hychar.com (Y. Xia).

http://dx.doi.org/10.1016/j.fuel.2015.06.020
0016-2361/

two-electrode corona discharge had been widely utilized by other workers for CO_2 reduction, such normal plasma could only create an dynamic oxidation–reduction environment, potentially producing mixtures of trace organic compounds.

In a positive-electrode-only method [6], a positive electrode connected to a positive high voltage is placed in a reactor is used to produce a positive DC corona discharge. This creates a strong oxidizing environment to drive oxidation of molecules, e.g., oxidation of ozone from air.

In a negative-electrode-only method [7], one negative electrode is connected to a negative high voltage source and placed in a reactor to produce a negative DC corona discharge. This creates a strong reducing environment, where the plasma is not described as an electrically neutral medium of particles but as negatively charged one, which has a rather high energy (e.g., 4–5 eV) and the negatively-charged particles of CO_2 and H_2O or other electronegative gases can travel rather freely in very large space in a reactor for successful reduction, completely differently from the locally limited neutral-ions as the normal plasma utilized. We believe that one of possible or practical approaches for CO_2 conversion is that a strong reducing environment should be maintained. The fundamental properties of negative ions have been extensively studied [8–10]. Such negative corona discharge may create anionic gases, which could capture free electrons to form strong reducing agents for CO_2 conversion, differently from conventional low-temperature plasma technology which just create oxidizing-reducing at the same time. We have found that by using negative corona, useful products, e.g., urea [11] and tetraiodomethane [12] could be produced.

Furthermore, it is also significant to treat CO_2 and H_2O by negative corona discharge technology to examine if we could produce hydrocarbons by CO_2 and H_2O steam. It has been known [13] that in reduction of CO_2 and H_2O using normal microwave plasma technology, only trace amounts of methanol were obtained.

Ethanol or corn-made ethanol is currently a major component of the gasoline market, as the global demand for ethanol as fuel amounts to approximately 75 million tons/year. In fact, ethanol production was expected to continue to grow over many years. It would be desirable to produce ethanol directly by CO_2 which is emitted from industrial combustion as only carbon source or feedstock and off-peak or renewable electricity which may be used to create negative corona.

We here consider a reaction process of CO_2 and H_2O steam to produce ethanol as a reversal process of ethanol combustion as follows:

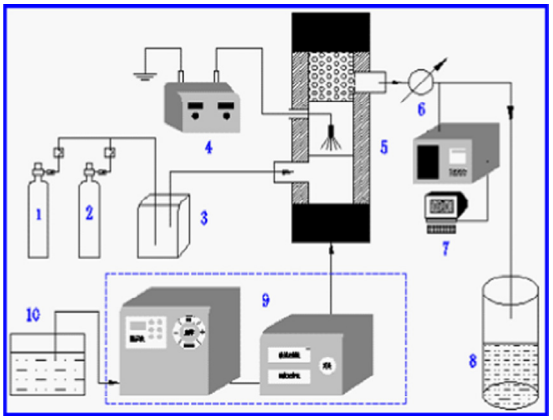
$$2CO_2 + 3H_2O \rightarrow C_2H_5OH + 3O_2 \quad (1)$$

The change of the standard Gibbs free energy at 25 °C and 1 atm, for reaction (1) is 1306.1 kJ, obviously not thermodynamically feasible at ambience, unless enough external energy input is given.

We here report the results of the reaction of CO_2 and H_2O steam under negative corona discharge at 105 °C, resulting in ethanol as a main product, also setting a potential for producing ethanol fuel in coal-fired power plants as energy storage.

2. Experimental

Experimental system is shown in Fig. 1. In the experiments, the reactor was purged by N_2 for 15 min. CO_2 (99.99%) from the gas cylinder were fed through a mass flowmeter, and drying and preheating zones, and H_2O vapor which is generated by an adjustable steam generator, entering the tubular reactor from the bottom. SJ-2000E negative power supply with voltage of −15 kV and current of 0–2 A was applied to the experiments. A half-wave rectifier unit was connected to the outlet of the power supply, so as to generate a stable negative DC high voltage. S49-33/MT mass-flowrate meter and D08-1D/ZM flowrate monitor were used. A GC/MS-QP2010 (SHIMADZU) gas chromatography/mass spectrometry instrument was connected to the outlet of the reactor. An AIC1000 anion detector was utilized for monitoring of concentrations of electronegative molecules in the outlet. A home-made Langmuir probe [14], which was calibrated by an AIC1000, also was used to verify the presence of negative ions around the stainless steel pins. As the AIC1000 anion detector is a major tool to verify and monitor the negative ions in the outlet of reactor, the probe as the secondary means for roughly monitoring proof of the negative ions presence around pins should be essentially valid although potential errors due to existence of reactive gases might exist [15]. A thermostar GSD320 mass spectrometer was connected to the outlet of the reactor. MC-1 steam generator, with a digital temperature control of an electric-powered heater and a digital flowrate monitor were utilized for the experiments.



1-CO_2, 2-N_2, 3-Buffer bottle, 4-Negative-ion generator, 5-Glass tube reactor, 6-Condenser, 7-Thermostar GSD320 mass spectrometer, 8- Cold trap flask, 9- Steam generator, 10- Tank

Fig. 1. Schematic diagram of experimental apparatus.

The reaction of negative ions of CO_2 and steam was carried by a tubular reactor, which was made of quartz-glass tube with buffer, negative ion generation and zones. The reactor has inner diameter of 55 mm and length of 400 mm. The electrode was made of stainless steel needles that contained twelve pins. And the sealing was made by Teflon material. Reaction device is shown in Fig. 1. During the experiment, the reactor was purged by N_2 for 0.5 h. CO_2 (99.99%) were fed from the gas cylinder, through a mass-flowrate meter, and buffer bottle, entering the tubular reactor from the entrance. Water vapor was created by an adjustable steam generator, flowing into the bottom of the first glass reactor, controlled by the steam flowrates and temperature. The glass tube between steam generator and the reactor was heated to at least about 105 °C. The reaction time was 1.5 h. The collected products were tested by gas chromatograph mass spectrometer. The gases from the outlet of reactor were tested by quadrupole mass spectrometer within the flowrate range of 0.05–0.30 L/min.

3. Results and discussion

Our experiment shows that, under negative corona discharge, when CO_2 gas was mixed with water vapor in the reactor, the liquid product as shown in Fig. 2A, were collected by condensation in a cold trap flask surrounded with circulating ice-cold water. In order to identify the compositions of the product, we used GC–