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Partial oxidation of ethanol using a non-equilibrium plasma

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ABSTRACT

Partial oxidation of ethanol with air was carried out in a pulsed discharge plasma reactor at low temperature and atmospheric pressure. Effects of O_2:ethanol ratio, ethanol flow rate, and discharge current were investigated. H_2 and CO are the major products (>86%). Increases of O_2:ethanol ratio promote CO formation at the expense of C_2 hydrocarbons. H_2 selectivity and H_2 + CO selectivity are maximized at O_2:ethanol ratios of 0.3 and 0.5, respectively. Increases of feed flow rate accompanied by current increases allow the reactor to operate with high throughput. The LHV energy efficiency is increased with increasing feed flow rate, reaching 85% at high ethanol flow rates, conditions that also increase throughput. In contrast to catalytic and homogenous reactions, not all O_2 is consumed at high O_2:ethanol ratio for the low temperature plasma reaction. A radical reaction pathway of H abstraction from −OH and the α-H in ethanol to form CH_3CHO followed by C−C scission is proposed. The produced hydrogen rich gas can be potentially used in fuel cells and engines.

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Introduction

Hydrogen is a clean energy carrier with a high heating value per unit mass (120 kJ/g, based on lower heating value (LHV)). Production of hydrogen from renewable bio-mass derived ethanol provides an essentially CO_2 neutral energy production route [1]. Hydrogen for small scale applications, for example, fuel cells and internal combustion (IC) engines, requires compactness, fast response, high durability for frequent startup–shutdown cycles and low cost. Large scale catalytic hydrogen production has been successfully operating in industry for many decades. However, it is difficult to meet these requirements when the operating scale is reduced to small distributed production systems.
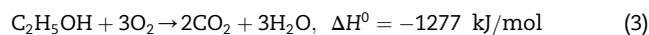
Alternately, a non-equilibrium (or non-thermal/cold) plasma could be a potential candidate for this kind of application. A plasma is defined as an ionized gas, which exists widely in the universe. The abundant highly energetic electrons, ions and radicals in plasmas can activate even the most stable molecules, for example, methane. Thus, radical reactions easily take place in plasmas. A non-equilibrium (or

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non-thermal/cold) plasma is a kind of plasma that has high electron temperatures (as high as 10 eV) with low bulk phase temperature [2–4]. A simple way to generate a non-equilibrium plasma is applying high voltage electricity to a gas to initiate discharge. There are a number of types of low temperature plasmas, and these can transition to thermal plasmas with sufficiently high energy input. The non-equilibrium plasma reaction has the advantage of low temperature thus providing non-equilibrium selectivity control to minimize over oxidation. They also have a rapid response to transient operation and avoid the use of expensive catalysts (and catalyst deactivation). Therefore, increasing attention has been paid to utilizing these plasma reactions for hydrogen production from hydrocarbons and oxygenated organics [5–14], particularly from biomass derived ethanol [15–27].

Compared to strongly endothermic steam reforming of ethanol (1), stoichiometric partial oxidation of ethanol (2) is a weakly endothermic reaction. Therefore, partial oxidation of ethanol can be carried out at higher space velocity than steam reforming. However, the highly exothermic total combustion of ethanol (3) can not be completely avoided for catalytic (or homogeneous) reactions that must be carried out at high temperatures [1,28–30]. Limited O_2 is provided and is completely consumed in that reaction, in order to prevent total combustion. Hot spots in the catalyst bed require both highly stable catalysts and reactor materials that are resistant to high temperatures.

$$C_2H_5OH + H_2O \rightarrow 2CO + 4H_2, \quad \Delta H^0 = 256 \text{ kJ/mol} \tag{1}$$

$$C_2H_5OH + 0.5O_2 \rightarrow 2CO + 3H_2, \quad \Delta H^0 = 14 \text{ kJ/mol} \tag{2}$$

$$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O, \quad \Delta H^0 = -1277 \text{ kJ/mol} \tag{3}$$

Bromberg et al. have reported partial oxidation of ethanol using a plasma [31]. However, their operation was carried out at high temperatures (650–850 °C), resulting in similar behavior as in the catalytic case; e.g. that all O_2 is consumed to control selectivity. Recently, several works studied partial oxidation of ethanol using plasmas briefly at similar high temperatures [32–35], with emphasis on reactor design, kinetic simulations [34,35], and combined steam reforming and partial oxidations [32–34]. The systematic study of ethanol partial oxidation using plasma at relatively low temperature without the influence of other parameters such as water addition was rare. In particular, detailed analysis of the product distributions, which is important for real applications, was less addressed.

In this work, partial oxidation of ethanol using a direct current (DC) pulsed plasma reactor has been conducted at low temperatures and atmospheric pressure. Several operational parameters (O_2:ethanol ratio, feed flow rate, discharge current) have been systematically investigated to obtain parameters that control product distributions and a possible chemical kinetic significant reaction path is deduced.

Experimental

The plasma used in this work is a DC pulsed discharge (corona) plasma, which has been described in previous work [14,25,26]. Briefly, the reactor configuration is point (anode) to plate (cathode), with a discharge gap of 15 mm (Fig. 1). A slight modification of the anode electrode was made in this work to allow both gases (air) and liquid (ethanol) to flow through it separately and become vaporized at the tip of the anode before entering the plasma reaction zone. The oxygen source was dry air, which was controlled by a mass flow controller. The liquid ethanol (EtOH, >99.5%) was fed using a calibrated high performance liquid chromatograph (HPLC) pump. The plasma reaction was initiated at room temperature. The temperature in the plasma zone reached 300–220 °C in few seconds due to the heat generated by the plasma, with the hottest place to be the tip of anode [14,25,26,36]. The heat produced on the anode effectively transferred to liquid ethanol and vaporized it when it flowed through the thin needle inside the anode [14,25,26]. This design utilizes plasma generated heat, avoiding additional energy input to preheat ethanol. In turn, ethanol cools the anode and thus retards erosion of the anode [14,25]. Ethanol was converted into synthesis gas rich gases in the plasma zone. The resulting reformates left the reactor through the porous cathode, passed an ice-water trap, and were analyzed by an online AGC 400 gas chromatograph (GC, Carle). The GC is equipped with a thermal conductivity detector (TCD), five columns and a hydrogen transfer system (HTS) hydrogen analysis system. This is capable of separating permanent gases (H_2, CO_2, CO, N_2, O_2) and hydrocarbons (up to C_6). The condensed liquid effluent in the trap was analyzed using a QP2010s GC-MS (Shimadzu), equipped with an Innowax capillary column. The major component of the liquid was unreacted ethanol, with trace amounts of acetaldehyde, acetone and 1,1-diethoxy ethane. NO_x were not observed by an online mass spectrometer (MKS).

The electric signal for the plasma was generated by a pulse generator (HP 8011A), and magnified by a high voltage amplifier (Trek, 20/20C). The discharge was monitored by an oscilloscope (Lecroy, wave surfer 422). The discharge current was set in the amplifier. Higher current led to a higher pulse rate and higher input power. For a typical run, the discharge current was set at 7 mA. After the discharge was initiated at a certain value of discharge current, the voltage and pulse rate was slightly affected by the feed flow rate and feed
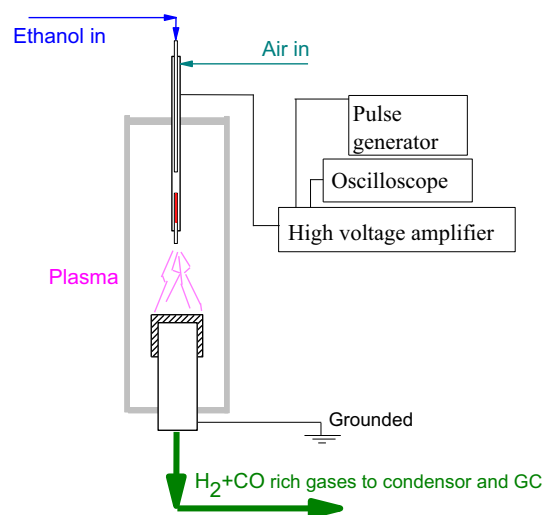

Fig. 1 – Schematic representation of the plasma reactor.