Low Temperature Plasma Reforming of Hydrocarbon Fuels Into Hydrogen and Carbon Suboxide for Energy Generation Without CO$_2$ Emission

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Min Heon, Vadym N. Mochalin, and Yury Gogotsi

Abstract—An alternative process of extracting energy from fossil fuels (coal, biomass, hydrocarbons, etc.) without the emission of CO$_2$ is possible with nonequilibrium plasma. Apart from CO$_2$ and CO, there exists carbon suboxide ($C_3O_2$)—a solid carbon oxide, which can be polymerized to form chemically and thermodynamically stable substances. This article describes a novel process of extracting the energy from fossil fuels without the emission of CO$_2$ while producing hydrogen and carbon suboxide (a reddish, brown polymer), an important constituent of organic fertilizers. This approach has the capability of avoiding drawbacks associated with combustion of fossil fuels, such as CO$_2$ emission. The conversion processes of a hydrocarbon feedstock (n-butane) and characterization of the byproduct of the conversion process with energy dispersive X-ray spectroscopy are discussed. Thermodynamic calculation of energy efficiencies of conversion of readily available hydrocarbon feedstocks such as biomass, natural gas, and low quality coal ( lignite and peat) into hydrogen and carbon suboxide is also discussed. Thermodynamic results calculated show energy efficiency of up to 78% for producing carbon suboxide from various hydrocarbon feedstocks when compared to energy efficiency of producing syngas (100%).

Index Terms—Butane, carbon suboxide, coal, dielectric barrier discharge, partial oxidation.

I. INTRODUCTION

A MAJOR problem associated with modern energy production from fossil fuels is high CO$_2$ emissions, which is linked to global climate change also known as global warming. The transition from thermal power plants to nuclear energy would ensure a significant decrease in CO$_2$ emissions. In Europe, the total amount of electricity produced by nuclear power plants reaches 80% in France, 60% in Belgium and 43% in Sweden (14% of the world’s total electricity is produced by nuclear power plants) [1]. Nuclear accidents at the Chernobyl nuclear power plant, Ukraine (April 1986), and Fukushima nuclear power plant, Japan (March 2011), called into question not only further developments in nuclear energy, but its viability as a primary source of safe and clean energy. It turns out the current security measures cannot eliminate the possibility of a nuclear accident, which can result in the spread of radioactive substances across national borders. Taking all these facts into account, there is an ongoing debate over the direction of the development of the power industry. One option is the transition to thermal power stations running on fuels (such as peat, lignite, and human wastes) with low energy content (10–25 MJ/kg). World reserves of lignite coal and sub-bituminous coal make up more than half of all coal reserves in the world. Another energy source that can replace nuclear power is natural gas; the world’s gas reserves are 1754 trillion cubic meters (2006). It is estimated that there are also about 900 trillion cubic meters of “unconventional” gas such as shale gas, of which 180 trillion cubic meters may be recoverable [2]. The third source of energy is biomass. Biofuels are gaining increased public and scientific attention, driven by factors such as oil price and the need for increased energy security.

Three different methods of extracting chemical energy from a biomass feedstock are shown in Fig. 1. The direct combustion of biomass approach results in release of the most significant amount of energy as well as water and CO$_2$, but this process has a low efficiency—about 26% [3]. Another method of energy extraction from biomass is via reforming reactions (e.g., steam, dry CO$_2$ or partial oxidation reactions), which results in the production of syngas (combination of hydrogen and CO). Syngas can be subsequently burned releasing a significant amount of energy but this process also results in the eventual release of CO$_2$. Direct combustion and reforming of biomass both result in production of significant quantities of CO$_2$, a greenhouse gas. This drawback necessitates the adoption of expensive carbon sequestration methods (construction of underground storages for CO$_2$ chemical binding with amines, etc.) which can cost as much as $1800 per ton of carbon for 2.3 × 10^6$ tons of carbon [4]. A third possible method of extracting energy from biomass is the partial oxidation reaction which results in the production of hydrogen and solid ($C_3O_2$)$_n$ [poly(carbon suboxide)].

This novel route, which involves the production of hydrogen and solid carbon suboxide from a hydrocarbon feedstock without CO$_2$ emission, is demonstrated in this paper. This

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approach was first suggested by Fridman et al. [5] and was based mainly on thermodynamic assumptions. Although this approach may result in less energy release in comparison to direct combustion and reforming reactions, it avoids the release of CO\(_2\) in the atmosphere. An added advantage to this approach is its byproduct—solid poly (carbon suboxide) (C\(_3\)O\(_2\))\(_n\), major building block of organic soil fertilizers. The aim of this paper is to demonstrate, through experiments, the possibility of producing condensed carbon suboxide from a hydrocarbon feedstock using dielectric barrier discharge (DBD) plasma and also calculate the energy efficiency of hydrogen and solid carbon suboxide production from different feedstocks via thermodynamic calculations. Carbon suboxide (C\(_3\)O\(_2\)) is a fouling-smelling lachrymatory nontoxic gas. It has linear symmetric structure that can be represented as O = C = C = C = O. The suboxide monomer is stable at −78 °C; at 25 °C it polymerizes to form a highly colored solid material with a polycyclic six-member lactone structure. Carbon suboxide is typically produced by thermal dehyration of malonic acid CH\(_2\)(COOH)\(_2\) in the presence of P\(_2\)O\(_10\) (a drying agent) [5, 6]. Carbon suboxide is the anhydride of malonic acid, and it slowly reacts with water to produce malonic acid. It can be stored at a pressure of a few Torr, but under standard conditions C\(_3\)O\(_2\) forms a yellow, red, or brown polymer (C\(_3\)O\(_2\))\(_n\) (ruby-red above 100 °C, violet at 400 °C, and it decomposes into carbon at 500 °C) [5]-[8]. The energy of formation for gas-phase carbon suboxide C\(_3\)O\(_2\) was reported to be between −97.6 kJ/mol [9] and −95.4 kJ/mol [10]. The energy of formation for liquid polymerized carbon (C\(_3\)O\(_2\))\(_n\) is −100 kJ per one mole of carbon, and the energy of formation for solid polymerized carbon suboxide (C\(_3\)O\(_2\))\(_n\) is above −112 kJ per one mole of carbon [11]-[13]. (C\(_3\)O\(_2\))\(_n\) is a building block of humic substances, a main component of organic fertilizers [5, 14].

II. THERMODYNAMICS OF CARBON SUBOXIDE

An important aspect of transitioning to new energy sources or new technologies for extracting energy from fuels is the energy cost involved and the advantages they have over preceding technologies. The thermodynamic aspect of producing energy (hydrogen) and suboxide from different types of hydrocarbon fuel is described in detail below. First, the general formula for calculating energy efficiency is derived, followed by the results of thermodynamic calculation for different types of fuel considered. The efficiency of hydrocarbon conversion resulting in solid carbon suboxide and hydrogen is measured with respect to the efficiency of producing syngas (particularly CO) from reforming reaction of a hydrocarbon feedstock. In this regard, the efficiency (%) of producing solid carbon suboxide is derived as a percentage of the efficiency of producing syngas (assuming the efficiency of producing syngas is 100%). In solid state, carbon suboxide can be in form of (C\(_3\)O\(_2\))\(_n\) and also in the form of monomers with carbon to oxygen ratio, (C/O), 1 < (C/O) < (3/2). The general formula for polymerized carbon suboxide can be written as

\[
(C_{1-x}O_x)_n.
\]

Here, coefficients \(x\) and \(1-x\) represent proportional amounts of atoms of oxygen and atoms of carbon in mole monomers \((C_{1-x}O_x)_n\), respectively. Coefficient \(x\) lies in the limits: 0.4 ≤ \(x\) < 0.5, where \(x = 0.4\) corresponds to C\(_{0.6}\)O\(_{0.4}\) \(\equiv\) C\(_3\)O\(_2\) (tricarbon dioxide). Since energy of formation for solid carbon suboxide is known only for tricarbon dioxide, energy of formation for a mole of monomers (1) can be approximated by the linear formula

\[
E_x = a^*x + b
\]

where \(E_x\) represents the energy of formation, and \(a\) and \(b\) are constants. Assuming that energy of formation for pure carbon \((x = 0)\) equals 0, then constant \(b = 0\). Also, since the energy of formation per one mole of monomers C\(_1\)O\(_{2/3}\) is −112 kJ, therefore the energy of formation for monomers C\(_{0.6}\)O\(_{0.4}\) equals \(E_{0.4} = -112^* (1 - 0.4) = -67.2\) kJ. Substituting \(E_{0.4}\) in (2) allows calculating coefficient \(a\)

\[
a = \frac{112 \times (1 - 0.4)}{0.4} = 168 \quad E_x = 168x.
\]

Biofuels such as oil, wood, peat, lignite (type of coal), and natural gas consist mainly of carbon, hydrogen, and oxygen.
(95–98%). Therefore, the chemical formula for biofuel can be expressed in the form

$$C_{\alpha}H_{\beta}O_{\gamma}$$  
(4)

where $\alpha$, $\beta$, and $\gamma$ represent the ratios of molecules of carbon, oxygen, and hydrogen in biofuel, and it can be assumed that $\alpha + \beta + \gamma = 1$. Also, hydrogen, oxygen, and carbon in fuels can be expressed in weight percentage

$$C_wH_wO_w.$$  
(5)

It can be assumed again that $C_w + H_w + O_w = 1$. Formulas expressing values $\alpha$, $\beta$, $\gamma$ with respect to $C_wH_wO_w$ can be further written as

$$\alpha = \frac{C_w}{C_w + O_w + H_w}, \quad \beta = \frac{H_w}{C_w + O_w + H_w}, \quad \gamma = \frac{O_w}{C_w + O_w + H_w}.$$  
(6)

The formula expressing the heating value ($HV$) of hydrocarbon fuel in kJ per mole of monomers (4) with respect to heating value in kJ per kilogram is

$$HV_{\text{mol}} = 10^{-3}(12\alpha + 16\beta + \gamma)HV_w.$$  
(7)

Calculating the theoretical heating value of partial oxidation of biofuel (4) to suboxide and hydrogen gives

$$C_{\alpha}H_{\beta}O_{\gamma} + \frac{1}{2} \left( \frac{\alpha x}{1 - x} - \beta \right) O_2 = C_{1-x}O_x + \gamma \frac{1}{2} H_2.$$  
(8.1)

$$\gamma \frac{1}{2} H_2 + \frac{\gamma}{4} O_2 = \gamma \frac{1}{2} H_2O.$$  
(8.2)

Reaction (8.1) represents the conversion of the fuel into solid carbon suboxide and hydrogen, while reaction (8.2) represents the combustion of hydrogen. The heating value of carbon suboxide ($HV_{\text{sub}}$) can be expressed as

$$HV_{\text{sub}} = \text{Energy of formation}(C_{\alpha}H_{\beta}O_{\gamma})$$

$$- \text{Energy of formation} \left( \alpha \cdot CO + \gamma \frac{1}{2} H_2O \right).$$  
(9)

$$C_{\alpha}O_{\beta}H_{\gamma} + \frac{1}{2} \left( \frac{\alpha - \beta}{1 - x} \right) O_2 = \alpha CO + \gamma \frac{1}{2} H_2.$$  
(10.1)

$$\gamma \frac{1}{2} H_2 + \frac{\gamma}{4} O_2 = \gamma \frac{1}{2} H_2O.$$  
(10.2)

$$\alpha CO + \gamma \frac{1}{2} O_2 = \alpha CO_2.$$  
(10.3)

Equation (10.1) describes the production of carbon monoxide and hydrogen from biofuel (4). Equation (10.2) and (10.3) correspond to the subsequent combustion of CO and $H_2$ produced from conversion of biofuel. The energy released in reaction (10.1) is small. For methane, energy released in (10.1) equals 35.6 kJ per mole of carbon, which is only 4% of the full energy of combustion. For cellulose and lignite ($C_{0.44}O_{1.00}H_{0.80}$), reaction (10.1) is endothermic, it demands an additional 9.5 kJ per mole of carbon for cellulose and 31 kJ per mole for lignite. This shows that the energy released in reaction (10.1) is insignificant and can be neglected. Therefore, the heating value of CO ($HV_{CO}$) derived from (10.1–10.3) is stated as

$$HV_{CO} = \text{Energy of formation}(\alpha \cdot CO).$$  

$$- \text{Energy of formation} \left( \alpha \cdot CO_2 + \gamma \frac{1}{2} H_2O \right).$$  
(11)

Energy efficiency of producing solid carbon suboxide and hydrogen from a hydrocarbon is defined by the ratio of heating value of carbon suboxide (9) and that of carbon monoxide (11)

$$EF_{\text{sub}} = \frac{HV_{\text{sub}}}{HV_{CO}}.$$  
(12)

For a variety of fuels, the heating values are known, but the energies of formation are unknown. In such instances, the energy of formation of a hydrocarbon fuel can be calculated from the fuel’s composition and heating value

$$\text{Energy of formation}(C_{\alpha}H_{\beta}O_{\gamma}) = \text{Energy of formation}$$

$$\times \left( \alpha \cdot CO + \gamma \frac{1}{2} H_2O \right) + HV(C_{\alpha}H_{\beta}O_{\gamma}).$$  
(13)

### A. Thermodynamic Calculation of the Efficiency of Hydrogen and Carbon Suboxide Production

The difficulty associated with the calculation of the energy efficiency of hydrogen production from biofuels lies in the fact that the formation enthalpy is not known for many biofuels. Therefore, the use of the formulas obtained from extrapolating experimental data becomes essential for the calculation of energy efficiency. In Table I, the energy efficiency of hydrogen and solid carbon suboxide production with respect to the production of hydrogen and CO gas from methane, n-butane, and cellulose is presented for different contents of oxygen in the monomer $C_{1-x}O_x$. Energies of formation were obtained from the National Institute of Standards and Technology, Chemical Kinetics Database [15]. In Table I, $x = 0.4$ corresponds to $C_{3}O_{2}$, $x = 0.5$ corresponds to monomer CO ($x$ can be less than 0.5, but in this calculation, we have chosen $x = 0.5$). In Table II, the energy efficiency of hydrogen and carbon suboxide production with respect to the production of hydrogen...
and CO gas from wood, sunflower oil, and castor oil are presented for different values of oxygen atoms in the monomer \( C_{1-x}O_x \). For these calculations, energies of formation were obtained from [16].

Table III presents the energy efficiency of hydrogen and suboxide production with respect to the production of hydrogen and CO gas from biofuels and peat. For these energy efficiency calculations, formula from [17] was used

\[
HV_w = 10^3(-0.763 + 30.1C_w + 52.5H_w + 6.40O_w) \quad [\text{KJ/Kg}]
\]

This is the best approximation of experimental data for different concentrations of hydrogen \( H_w \), oxygen \( O_w \), and carbon \( C_w \) for biofuel. In the calculations, \( H_w = 0.06 \). It should be noted that heating value of peat is variable; it depends on moisture, composition, and ash content. Biofuels and peat are categorized together due to the similarity in the composition and properties of dry peat and biofuels.

Fig. 2 and Table IV present the energy efficiency of hydrogen and solid carbon suboxide production with respect to the production of hydrogen and CO gas from coal. It should be noted that heating value of lignite changes in wide limits from 10 MJ/kg to 20 MJ/kg and for peat, the heating value depends on humidity and coal composition. Heating value calculations [18] were based on the following:

\[
HV_w = 10^3(34.01C_w + 131.96H_w - 11.83O_w) \quad [\text{KJ/Kg}]
\]  
(Dry, Without Ash).  
(15)

Results from thermodynamic calculations show that the energy efficiency of producing hydrogen and solid carbon suboxide can be up to 78% of energy efficiency of syngas production (depending on the type of hydrocarbon feedstock). The decrease in energy efficiency is compensated for by the elimination of \( CO_2 \) emissions and production of two valuable products: hydrogen and carbon suboxide (a major component of organic fertilizers).

### III. EXPERIMENTAL SETUP

Gliding arc plasma, arc discharge, and DBD are three atmospheric pressure plasma discharges considered for the carbon suboxide \( (C_3O_2) \) formation from plasma-assisted hydrocarbon oxidation reaction. Arc discharge and gliding arc discharge proved to be ineffective in the formation of carbon suboxide due to the high heat generation by these discharges. A nonequilibrium plasma discharge (DBD) is better suited for low-temperature gaseous hydrocarbon oxidation reactions due to its low-temperature and low-power requirement. Low-temperature plasma-assisted oxidation of hydrocarbon was conducted in a DBD reactor with \( n \)-butane \( (C_4H_{10}) \) as the hydrocarbon feedstock mixed with air. The DBD reactor, Fig. 3, consists of a 1.22 m long quartz tube with 22 mm internal diameter. The quartz tube functions as a dielectric barrier. Inside the
Fig. 3. Schematic of the experimental setup for the formation of carbon suboxide from hydrocarbon oxidation reaction.

Fig. 4. Voltage (left) and current (right) characteristics of the plasma discharge, data points taken from a 500-MHz Tektronix digital phosphor oscilloscope.

quartz tube is an 80 cm long stainless steel electrode that serves as the high-voltage electrode. The high-voltage electrode was held in place inside the quartz tube with the aid of a silicone stopper at the inlet of the quartz tube and a ceramic holder at the inner center of the reactor. The uniform distance between the high-voltage electrode and the quartz inner wall will ensure the uniformity of the propagation of the plasma discharge from the high-voltage electrode to the inner wall of the quartz tube. A copper mesh is wrapped around the outer surface of the quartz tube to align with the stainless steel electrode, spanning 40 cm in length. The copper mesh serves as the ground electrode. n-Butane gas and air were mixed before entering the DBD reactor. The gas mixture was delivered to the reactor via 1/4" tubes and fed directly into the reactor through an aperture within the stainless steel electrodes. Butane and air flow rates were each controlled with Omega FMA-2605A series mass flow controllers according to the desired oxygen to carbon ratio.

A variable alternating current (AC) power supply was used to generate the DBD plasma. The power supply has an operational frequency of 50 Hz–1.66 kHz and a maximum peak-to-peak voltage range of 20 kV–34 kV. Typical voltage and current waveforms of the plasma discharge are shown in Fig. 4. A 500-MHz Tektronix digital phosphor oscilloscope is connected to the electrodes to monitor and evaluate the electrical characteristics of the plasma power. In order to obtain the total DBD power, integration of the voltage and current was conducted using the formula stated below and the parameters obtained from the oscilloscope. The average DBD power was calculated to be 80 W. The DBD power is calculated with the expression (16)

$$P = \frac{1}{T} \int_{0}^{T} u \times i \times dt = \frac{\sum_{n=0}^{n=m} (u_n \times i_n)}{m}.$$  

(16)

$P$: DBD power, $u$: applied voltage, $i$: total current; $m$: the number of sample points, $T$: sampling time.

The butane oxidation chemical reaction to form hydrogen and carbon suboxide is given by

$$3C_4H_{10} + 4O_2 \rightarrow 4 C_3O_2 + 15 H_2.$$  

(17)
The cylindrical DBD reactor was placed in a temperature controlled Carbolite STF 16/610 furnace. In order to accelerate the rate of deposition of solid products produced from the plasma-assisted oxidation of $n$-butane ($C_4H_{10}$), a water-cooled heat exchanger made from 1/16” copper tubing wound into a spiral shape was inserted inside the post-plasma region of the DBD reactor. Typical experiments involve the treatment of $n$-butane and air mixture with DBD for 150 min after which $n$-butane and air flows are shut off and the deposit dried up in the reactor via the heat from the furnace at 150 °C (Table V).

DBD is a nonthermal plasma discharge, which is strongly nonequilibrium at atmospheric pressure. DBD generates atomic and molecular species, free radicals, and electrons with mean kinetic energy of 1–10 eV [7]. DBD already has a wide range of applications which include ozone generation, thin film deposition [19], [20], polymer treatment [21], [22], pollution treatment [23], exhaust gas cleaning (from CO, NOx, SO2 and volatile organic compounds) [24], medical applications [7], [21], [25], in CO2 lasers [26], plasma-assisted combustion [7]. The DBDs have been extensively discussed in [27]–[29] As a result of a dielectric barrier between the high-voltage and ground electrodes, the DBD requires AC for its operation.

The current passing through the dielectric is limited by factors such as the dielectric thickness, dielectric constant, and the time derivative of the applied voltage $dU/dt$. High electric fields are required to propagate current through the gas. The current passing through the dielectric is limited by factors such as the dielectric thickness, dielectric constant, and the time derivative of the applied voltage $dU/dt$. High electric fields are required to propagate current through the gas.

The gas phase reaction and surface reaction mechanisms are presented in Tables VI and VII where $n$-butane is represented by RH, R is $C_2H_9$ and $R'$ is $C_3H_6$ (propylene). At low temperatures, initial stages of oxidation of saturated hydrocarbons (alkanes) start with the dissociation of oxygen. Atomic oxygen reacts forming an alkyl radical and a hydroxyl radical. Hydroxyl radical then eliminates a hydrogen atom from RH, forming water and an alkyl radical. The alkyl radical will typically react quickly with oxygen forming a peroxy radical [30]–[32].

<table>
<thead>
<tr>
<th>TABLE V</th>
<th>PARAMETERS AND CONDITIONS OF PARTIAL OXIDATION OF $n$-BUTANE EXPERIMENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas</td>
<td>$n$-Butane, Air</td>
</tr>
<tr>
<td>Total Flow rate</td>
<td>1.2 L/min</td>
</tr>
<tr>
<td>Temperature</td>
<td>150°C - 400°C</td>
</tr>
<tr>
<td>Oxygen : Carbon ratio</td>
<td>0.4-0.9</td>
</tr>
<tr>
<td>Discharge Power</td>
<td>80 Watts</td>
</tr>
</tbody>
</table>

The surface reaction mechanism for low-temperature $n$-butane oxidation has not been fully investigated, but a possible reaction mechanism is presented in Table VII. At appropriate temperatures, the peroxy radical decomposes into HCO$^-$ and propylene releasing water. HCO$^-$ combines to form $C_2O$ and $H_2O$ [7]. $C_2O$ monomer is formed by the reaction of $C_2O$ with CO [33].

<table>
<thead>
<tr>
<th>TABLE VI</th>
<th>GAS PHASE REACTION MECHANISM FOR LOW-TEMPERATURE $n$-BUTANE OXIDATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>$e + O_2$</td>
<td>$\rightarrow O + O + e$</td>
</tr>
<tr>
<td>$O + RH$</td>
<td>$\rightarrow R^+ + OH^-$</td>
</tr>
<tr>
<td>$OH^+ + RH$</td>
<td>$\rightarrow R^+ + H_2O$</td>
</tr>
<tr>
<td>$R^+ + O_2$</td>
<td>$\rightarrow R^O_2$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>TABLE VII</th>
<th>POSSIBLE SURFACE REACTION MECHANISM</th>
</tr>
</thead>
<tbody>
<tr>
<td>$RO_2$</td>
<td>$\rightarrow HCO^- + H_2O + R'$</td>
</tr>
<tr>
<td>$HCO^- + HCO^-$</td>
<td>$\rightarrow C_2O + H_2O$</td>
</tr>
<tr>
<td>$C_2O + CO$</td>
<td>$\rightarrow C_2O_2$</td>
</tr>
</tbody>
</table>

IV. RESULTS AND DISCUSSIONS

The low-temperature oxidation experiments were conducted in the DBD plasma reactor with $n$-butane ($C_4H_{10}$) and air as the reacting gases. The experiments were conducted at atmospheric pressure. The temperature around the external region of the DBD reactor was constantly monitored with the aid of thermocouples connected to temperature readers. Glass slides (19 mm × 19 mm × 0.5 mm) were placed within the post plasma region of the DBD reactor to collect solid deposits for analyses and characterization.

Solid deposits start to form within moments of $n$-butane-air reaction in the presence of plasma as shown in Fig. 5. The deposits formed within the post plasma region of the reactor usually appear reddish brown at temperatures between 150 °C–400 °C and black at temperatures greater than 500 °C. The reddish–brown deposits collected after 150 min of plasma treatment at low temperatures (150 °C–400 °C) appear wax-like and sticky. This is attributed to some water produced during the butane—oxidation reaction. The gas produced at the post plasma region of the DBD reactor as well as the reddish brown deposits had a pungent smell and induced lacrimation. The reddish brown deposits collected on the glass slides inside the reactor were dried (using the heat from a furnace) and analyzed for its atomic composition via energy-dispersive X-ray spectroscopy (EDX).

A. Characterization

The characterization of the deposits obtained from the DBD reactor was carried out with Zeiss Supra 50VP Scanning Electron Microscope with EDX. This is an analytical technique used for the elemental analysis. EDX works by detecting characteristic X-rays that are produced by a sample placed in
Fig. 5. Initial stage of carbon suboxide formation in the DBD reactor (left) and the later stage of gradual carbon suboxide formation along the walls of the DBD reactor (right).

Fig. 6. SEM image (left) and EDX spectrum (right) of deposit formed from plasma-assisted butane oxidation. The pink square in the SEM image represents the region on the sample where EDX signals were collected. The EDX spectrum shows the peaks of carbon, oxygen, and nitrogen.

TABLE VIII

<table>
<thead>
<tr>
<th>Element</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>53.69</td>
<td>50.55</td>
<td>51.43</td>
<td>51.64</td>
<td>52.7</td>
<td>51.74</td>
</tr>
<tr>
<td>N</td>
<td>12.77</td>
<td>15.78</td>
<td>14.18</td>
<td>10.61</td>
<td>14.66</td>
<td>14.65</td>
</tr>
<tr>
<td>O</td>
<td>33.54</td>
<td>33.67</td>
<td>34.39</td>
<td>35.41</td>
<td>32.51</td>
<td>33.61</td>
</tr>
<tr>
<td>C:O ratio</td>
<td>1.60</td>
<td>1.50</td>
<td>1.50</td>
<td>1.46</td>
<td>1.62</td>
<td>1.54</td>
</tr>
</tbody>
</table>

an electron beam [34]. In addition to visualization, SEM is capable of providing information such as surface topography and composition of the sample.

B. Procedure

To ensure the accuracy of the characterization results, a sample of caprolactam (C₆H₁₁NO) was tested first. The carbon:oxygen atomic ratio for caprolactam came out to be 5.5 6:5:1, confirming the accuracy of the EDX analysis. Elemental analysis tests were carried out on the solid deposit samples collected during the plasma-assisted n-butane oxidation experiments [Fig. 6(b)]. The carbon:oxygen ratio of the sample analyzed was in the range 1.5 1.8:1 (Table VIII) and this ratio corresponds to carbon suboxide C₃O₂ (Carbon: Oxygen = 1.5). The SEM image of the characterized sample is shown in Fig. 6(a).

Table VIII shows the analyses of a sample produced at Oxygen: Carbon = 0.42, 200 °C, 80 W, and 1.2 L/min. Six different spots of the sample have been analyzed by EDX and based on the results, the average C:O ratio is at 1.54. This result supports the assumption that the polymerized deposit has the atomic ratio close to carbon suboxide (C₃O₂)ₙ. Carbon suboxide (C₃O₂)ₙ has a carbon to oxygen ratio of 1.5 (exactly). From further analyses, greater carbon:oxygen ratios were observed with increasing temperature. With the low flow rates of gases in our experiments, hydrogen yield was extremely low, making analysis of the gas phase difficult.
Further work should be focused on establishing the optimal regimes for carbon suboxide and hydrogen production using different hydrocarbon feedstocks at different O/C ratios, temperature, plasma power, and reagents flow rates. The future work will also include more detailed analysis of the gas phase products of the \( n \)-butane oxidation reaction.

V. CONCLUSION

Thermodynamic calculations show that it is possible to attain relatively high energy efficiency of conversion of abundant, low quality energy feedstock such as lignite, peat, and biofuels into hydrogen and carbon suboxide. The highlighted approach suggests a major shift of the paradigm of hydrocarbon feedstock as an energy source. It allows a substantial portion of energy to be released in the form of hydrogen, or eventually electricity, together with simultaneous bonding of carbon into solid polymerized carbon suboxide that can be used to produce organic fertilizers. Decrease in energy efficiency, when compared to synthesis gas production is compensated by the elimination of \( \text{CO}_2 \) emissions and production of two valuable products: hydrogen and carbon suboxide. Experimental testing of nonthermal plasma reforming of \( n \)-butane in DBD reactor confirms carbon suboxide production. Elemental analysis (carried out with EDX spectroscopy) of the produced deposits suggests that C:O ratio in the analyzed sample is close to 1.5 and this corresponds to the C:O ratio in carbon suboxide \( (\text{C}_2\text{O}_3)_n \). The thermodynamic calculations show the efficiency of converting hydrocarbon feedstock such as low quality coal (lignite and peat) into carbon suboxide and hydrogen. The thermodynamic conversion efficiency was calculated to be as high as 78% with respect to the efficiency of converting the same hydrocarbon feedstock into hydrogen and carbon monoxide. The experimental results have demonstrated the possibility of producing carbon suboxide from a hydrocarbon feedstock—\( n \)-butane.

REFERENCES

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