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The Effect of Cobalt Catalyst Loading at Very High Pressure Plasma-Catalysis in Fischer-Tropsch Synthesis

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Abstract: The influence of different catalyst cobalt loadings on the C₁–C₃ hydrocarbon product yields and energy consumption in plasma-catalytic Fischer-Tropsch synthesis (FTS) was investigated from the standpoint of various reactor operating conditions: pressure (0.5 to 10 MPa), current (250 to 450 mA) and inter-electrode gap (0.5 to 2 mm). This was accomplished by introducing a mullite substrate, coated with 2 wt%-Co/5 wt%-Al₂O₃, 6 wt%-Co/5 wt%-Al₂O₃ or 0 wt%-Co/5 wt%-Al₂O₃ (blank catalyst), into a recently developed high pressure arc discharge reactor. The blank catalyst was ineffective in synthesizing hydrocarbons. Between the blank catalyst, 2 wt%, and the 6 wt% Co catalyst, the 6 wt% improved C₁–C₃ hydrocarbon production at all conditions, with higher yields and relatively lower energy consumption at (i) 10 MPa at 10 s, and 2 MPa at 60 s, for the pressure variation study; (ii) 250 mA for the current variation study; and (iii) 2 mm for the inter-electrode gap variation study. The inter-electrode gap of 2 mm, using the 6 wt% Co catalyst, led to the overall highest methane, ethane, ethylene, propane and propylene yields of 22 424, 517, 101, 79 and 19 ppm, respectively, compared to 40 ppm of methane and <1 ppm of C₁–C₃ hydrocarbons for the blank catalyst, while consuming 660 times less energy for the production of a mole of methane. Furthermore, the 6 wt% Co catalyst produced carbon nanotubes (CNTs), detected via transmission electron microscopy (TEM). In addition, scanning electron microscopy (SEM), energy dispersive x-ray spectroscopy (EDX) and x-ray diffraction (XRD) showed that the cobalt catalyst was modified by plasma treatment.

Keywords: arc discharge; cobalt catalyst; Fischer-Tropsch synthesis; high pressure; non-thermal plasma

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1. Introduction

Non-thermal plasma (NTP) has typically been restricted to ignition at low current ($I < 1$ A) and atmospheric pressure ($P \sim 1$ MPa) by electric discharges, such as the dielectric barrier discharge (DBD) and corona discharge. However, within the last decade, researchers such as Fulcheri and co-workers [1] have developed an electrical arc discharge reactor which enables NTP generation at low current ($I < 1$ A) and very high pressure ($P > 1$ MPa). The high pressure environment combined with the active plasma species have thus far been harnessed to undertake organic synthesis, namely hydrocarbon (Fischer-Tropsch) synthesis [2,3], dry reforming of methane [4] and fluorocarbon synthesis [5].

Fischer-Tropsch synthesis (FTS) is a well-established process which involves the hydrogenation of carbon monoxide ($\text{CO} + \text{H}_2$) to produce synthetic hydrocarbon fuels on an industrial scale. It is a process that provides a competitive alternative to oil-derived fuels [1], considering the declining oil reserves, fluctuating oil prices and increasing energy demand. Thus, there is an increase in investment in FTS technology especially in the area of gas-to-liquid (GTL) and biomass-to-liquid (BTL) production. This is an indication that FTS technology is poised to play a significant role in the global energy mix in the upcoming decades. However, the cost associated with a large volume reaction vessel and the high temperature required for the process has led researchers to investigate the design

of a micro-channel reactor as an alternative method. This new approach is considered to potentially reduce the limitations associated with mass and heat transfer within the reactor.

Plasma-based FTS technologies could provide a viable alternative to conventional processes as a result of the rapid reactions promoted by plasma species (milliseconds to minutes), and a reduction in space and maintenance required by the technology. Thus, few authors [2–4] in recent times have explored the use of pure plasma FTS (no catalyst) for the production of gaseous C_1 – C_3 hydrocarbons using the arc discharge reactor at current < 1 A. However, only a few experimental results are available in the literature for plasma-catalytic reactions applied in FTS at pressures above atmospheric conditions [6–9]. Therefore, the present study investigated the effect of catalyst loading (Co/ Al_2O_3) mullite catalyst incorporated into the arc discharge for FTS.

Researchers have recently reported on the performance of cobalt catalysts pretreated with glow-discharge plasma in FTS at atmospheric pressure, with the pretreated catalyst shown to improve carbon monoxide (CO) conversion and methane selectivity [10]. Aluha et al. [11] followed the approach of inducted suspension plasma technology to synthesize nano-catalysts, and nanometric C-supported catalysts (cobalt and iron) for application in FTS [12]. Although Aluha et al. [13,14] reported that plasma-synthesized catalysts were shown to have active catalytic species for FTS when Co-based and modified Co-Fe catalysts are used, Chu et al. [10] indicated that the selectivity of plasma-synthesized catalysts to longer-chain hydrocarbons (C_{5+}) is similar to those prepared through conventional techniques.

Contrary to the report by Chu et al. [10] on C_{5+} hydrocarbons, a recent review by Aluha et al. [15] covering some of the research carried out in the last four decades since the introduction of plasma techniques for catalyst synthesis highlighted that Co/C catalyst at 493 K, 2 MPa, and $3600\text{ cm}^3\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ gas hourly space velocity improved selectivity towards the longer-chain hydrocarbons.

Therefore, the present study contributes to the body of scientific knowledge in the field of catalysts at pressures $\gg 1$ MPa for FTS using a blank catalyst, containing no cobalt (0 wt%-Co/ Al_2O_3), and a 6 wt%-Co/ Al_2O_3 catalyst, and comparing the results to those previously reported in literature [9] to further determine the influence of low cobalt loadings on plasma-catalytic FTS. Furthermore, the hydrocarbon product yields and energy consumption were compared for varying operating parameters: pressure (0.5–10 MPa), ignition current (250–450 mA) and inter-electrode gap (0.5–2 mm).

2. Results and Discussion

The study compares a blank, 2 wt% Co catalyst and 6 wt% Co catalysts in order to determine the contribution of different cobalt loadings to the plasma-catalytic synergistic effect. These cobalt loadings were compared using the hydrocarbon product yields and energy consumption of these systems under the scope of three varying operating parameters: pressure, ignition current and inter-electrode gap.

Trace quantities (ppm levels) of C_1 – C_3 gaseous hydrocarbons were produced in the arc discharge reactor for both the blank, 2 wt%, and 6 wt% Co catalyst systems. This was because the arc discharge active volume was estimated to be more than 10,000 times lower than the total volume of the reactor containing the catalyst ($\sim 1.2\text{ cm}^3$). The large reactor/discharge volume ratio meant that C_1 – C_3 hydrocarbons, produced within the active arc volume, were mixed with the bulk volume of unreacted syngas ($CO + H_2$), leading to dilution of the reaction products ($< 3\text{ mol}\%$). The hydrocarbons yields were in the general order: C_1 (methane) $\gg C_2$ (ethane + ethylene) $> C_3$ (propane + propylene). These products were similar to those previously reported for pure plasma FTS [3].

2.1. Pressure Variation Study

2.1.1. The Influence of Pressure on FTS Product Yields

Plasma-catalytic FTS was undertaken for varying pressures between 0.5 and 10 MPa, at a fixed current of 350 mA and inter-electrode gap of 1 mm, and at different discharge times of 10 s and 60 s. A full list of operating conditions for the three parametric studies are

presented in Table 1. Prior to comparing the different cobalt loadings of 0 wt% Co (blank), 2 wt% Co, and 6 wt% Co in Section 2 wt% and 6 wt% Co Catalyst, the blank catalyst was firstly compared to the pure plasma study.

Table 1. List of operating conditions used in pure plasma and plasma-catalytic FTS.

Operating Parameters	Pressure Variation Study		Current Variation Study	Electrode Gap Variation Study
Discharge time (s)	10	60	60	60
Ignition current (mA)	350	350	250, 300, 350, 400, 450	350
Ignition voltage (kV)	8	8	8	8
Electrode gap (mm)	1	1	1	0.5, 1.0, 1.5, 2.0
Pressure (MPa)	0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10	0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10	2	2
H ₂ /CO ratio	2.2:1	2.2:1	2.2:1	2.2:1

The background: Highlights the key parameter ranges.

Blank Catalyst

A blank catalyst (mullite substrate coated with 5 wt%- γ -Al₂O₃), without cobalt, was tested as a control study in order to determine the contribution of different cobalt loadings on the γ -Al₂O₃-coated mullite in plasma-catalysis. The studies using the blank and cobalt loaded catalysts were directly comparable as all preparation parameters were maintained.

The concentration versus pressure plots at 10 s and 60 s for the blank catalyst and the pure plasma systems are shown in Figure 1a,b. The concentration curves for methane (Figure 1a) diverged from 1 MPa onwards compared to 4 MPa for pure plasma. This was probably due to the improvement in bulk gas circulation at lower pressures, caused by the catalyst reducing the reactor volume by approximately 54%.

Figure 1. The influence of pressure on the hydrocarbon concentration for plasma-catalytic FTS (NTP + Blank catalyst) at discharge times of 10 and 60 s; (a) methane and (b) ethane. Legend: □—Pure plasma (60 s); △—Pure plasma (10 s); ■—Blank (60 s); ▲—Blank (10 s). Operating conditions: Syngas (H₂/CO) ratio: 2.2:1; current: 350 mA; inter-electrode gap: 1 mm; wall temperature: 25 °C. Error bars (vertical): Expanded experimental hydrocarbon concentration uncertainty of $\pm 11\%$.

Similarly, to the pure plasma study, the pressure range of 4 to 8 MPa for the blank catalyst was less effective for chain growth promotion as compared to 8 to 10 MPa. The qualitative trend for the blank catalyst was analogous to that of pure plasma; however, its methane concentrations were lower for the pressure range studied: at 10 MPa and 60 s, the

methane concentration for the blank catalyst (269 ppm) was ~2.9 times lower than that for pure plasma (772 ppm).

Lower methane yields for the blank catalyst may infer lower CO conversions, and thus a decrease in methylene monomer production (CH_x)-the building blocks required for chain growth. Monomer reduction, in turn, may have been responsible for lower C_2 – C_3 hydrocarbon yields than pure plasma, as seen by the low ethane concentrations (<1 ppm) throughout the pressure range studied (Figure 1b). Furthermore, particularly low ethylene yields (<0.1 ppm) were detected (not shown in Figure 1), and C_3 hydrocarbons were not synthesized (or may have been present below the gas chromatograph detection limit).

The blank catalyst was not anticipated to improve hydrocarbon production as cobalt is the active catalytic material in conventional FTS. Al_2O_3 , however, has been shown to possess good catalytic activity linked to its acid/base surface properties and metal oxygen bond strength [16–19], which allows this refractory material to stimulate numerous acid catalyzed reactions [18,20]. Accordingly, it is possible that a decrease in FTS activity was due to the adsorptive properties of γ - Al_2O_3 . The pressure drop (ΔP_{drop}) immediately after the discharge period of 60 s was assumed to be an indicator of catalytic adsorption.

In pure plasma FTS, at 10 MPa and 10 s, the operating pressure minutely increased by 0.01 MPa ($-\Delta P_{\text{drop}}$). This increase suggests that the extension of the inter-electrode gap from 0 mm (before reaction, $t < 0$ s) to 1 mm (at the start of reaction, $t = 0$ s) had an insignificant effect on the reactor volume and the related pressure drop. However, for pure plasma at 10 MPa and at a longer discharge time of 60 s, the operating pressure, instead of increasing, decreased by 0.07 MPa, probably due to an increase in the C_1 – C_3 hydrocarbon yields, which possessed lower partial pressures than the H_2 and CO reactants

An identical decreasing pressure trend was seen for the blank catalyst at 10 MPa, where the ΔP drop values of 0.16 and 0.3 MPa at 10 and 60 s, respectively, were more than 16 and 4 times higher than the pure plasma values. However, the higher ΔP drop values for the blank catalyst were not due to lower partial pressure products (as in pure plasma FTS), as considerably lower hydrocarbon yields were obtained for the blank catalyst compared to pure plasma. Therefore, it is plausible to ascribe the decrease in operating pressure to CO adsorption on the blank catalyst (probably in the molecular, radical or vibrationally excited states), followed by surface reactions to form carbonaceous species. This was a reasonable reaction pathway as carbon deposits (in the form of graphite) were detected via x-ray diffraction (discussed in Section 2.4.4) on the blank, 2 and 6 wt% Co catalysts.

The adsorption properties of both γ - Al_2O_3 and mullite (72 wt% $\text{Al}_2\text{O}_3/\text{SiO}_2$) were considered to be responsible for CO adsorption and its effects on synthesis. Cabrejas Manchado et al. [19] indicated that CO was more strongly adsorbed on γ - Al_2O_3 than hydrogen (present as a reactant in this work) and oxygen. This occurs through CO possessing both a weak carbonyl bond, which is easily converted into formate, as well as a low activation energy, which can lead to high surface coverage (up to 90%) and possibly irreversible adsorption.

CO adsorption in the present study may have been further augmented by the thermal activation of the blank catalyst by the arc discharge, possibly generating radicals and vibrationally excited CO species that could be more readily adsorbed than ground state CO molecules.

It was shown in atmospheric pressure plasma-catalytic processes, namely dry reforming of methane and volatile organic compounds (VOCs) treatment, that the active plasma species can electrically modify the chemisorption properties of porous catalyst materials, including Al_2O_3 [21,22]. In addition, porous Al_2O_3 was indicated to increase the concentration (or pre-concentrate) of plasma species on the catalyst surface, resulting in a longer residence time in the discharge region [23]. The mentioned properties of Al_2O_3 could increase the collisional activity and promote additional surface reaction pathways [24,25], which in this work may have been translated to improved CO adsorption and inhibited hydrocarbon chain growth.

Hydrocarbon synthesis and chain growth would have also been impeded, apart from CO adsorption, by the absence of active cobalt. In classical catalysis, it has been suggested that

hydrogen dissociates on a catalytically active metal and spills over onto the catalyst support, generating a hydrogen reservoir for synthesis processes [26,27], which would be deficient in the blank catalytic experiments owing to the absence of catalytically active cobalt.

It is therefore plausible to ascribe the low CO conversion, low methane yields, and the detection of carbonaceous (graphite) species, to both the strongly /irreversibly adsorbed CO and the shortage of adsorbed hydrogen (needed for precursor (CH_x) hydrogenation). In addition, silica and alumina, present in mullite, could have contributed to the low C_2 and C_3 hydrocarbon yields, and possibly graphite production, as silica-alumina have been recognized to catalyze cracking reactions, which are promoted by low concentrations of water [18]. These conditions, existing during experimentation (including the detection of water, discussed later), may have caused the catalytic cracking of ethylene, which is readily susceptible to cracking [28].

The oxidative properties of Al_2O_3 could have also contributed to the low hydrocarbon concentrations. In plasma-catalytic VOCs treatment, aromatic compounds were oxidized to CO, CO_2 , and other hydrocarbons. Oxidation was facilitated by short-lived active species, such as atomic oxygen, being adsorbed in the catalyst pores [23,24,29]. In plasma-catalytic dry reforming of methane, methane was oxidized to CO by combining a dielectric barrier discharge (DBD) and a $\gamma\text{-Al}_2\text{O}_3$ catalyst [30].

Due to the oxidative ability of Al_2O_3 , the hydrocarbons produced in the arc discharge core, having similar yields to that of pure plasma FTS, may have been oxidized by excited oxygen species and oxygen radicals within the Al_2O_3 pores to produce CO and/or CO_2 . This reaction pathway, however, was difficult to support as an increase in the CO concentration and the formation of CO_2 by oxidation, if at all active, were too minute to detect by the calibrated gas chromatograph.

The reaction schemes mentioned in this section for the blank catalyst, namely CO chemisorption, arise from the presence of Al_2O_3 and mullite hydrogen shortage, owing to the absence of active cobalt as well as hydrocarbon cracking and hydrocarbon oxidation, may have been responsible for lower $\text{C}_1\text{--C}_3$ hydrocarbon yields and higher energy consumption for both the current and inter-electrode gap variation studies when compared to previous study on the pure plasma FTS by Govender et al. [9]. Overall, the blank catalyst's experiment involving current and interelectrode gap variation studies showed lower yields than the pure plasma experiments previously reported in the literature [9].

2.1.1.2. wt% and 6 wt% Co Catalyst

In Section Blank Catalyst, it was shown that the blank catalyst produced lower yields than pure plasma [6] at all pressures. However, in this section, the influence of cobalt loadings 2 wt% Co catalyst and 6 wt% Co catalyst are discussed.

For the 6 wt% Co catalyst, the arc discharge was unstable above 6 MPa. This instability led to extinguishing of the arc discharge before completion of the 60 s treatment period, which contrasted with the blank and 2 wt% Co catalyst experiments, where the arc discharge was stable at all pressures investigated (1 to 10 MPa) and at both discharge periods of 10 s and 60 s. After arc termination, instantaneous re-striking of the arc was practically impossible as cathode/anode contact was required for ignition under the low current and high pressure conditions as governed by Paschen's law.

The instability and extinguishing of the arc for the 6 wt% catalyst was due to the production of high water yields. Higher yields were produced due to an increase in CO dissociation (implying a higher availability of oxygen for water formation), which was promoted to a greater degree by the higher 6 wt% Co loading compared to the lower (2 wt% Co) catalyst loading. It was the condensation of the relatively large quantities of water (seen visually as liquid droplets on the sight glass and verified using a GC-MS), which was the source of the arc extinguishing. Condensation did not occur for the lower 2 wt% Co loading, i.e., lower water concentrations remained in the vapor phase.

Moreover, the arc extinguished more rapidly at higher pressures: ~30 s at 7 MPa, and ~12 s at 10 MPa. At 10 MPa and ~12 s (shown in Figure 2a–e), the methane, ethane,

ethylene, propane and propylene concentrations were 32,598 (3.2 mol%), 268, 61, 51 and 30 ppm, respectively.

Figure 2. The influence of pressure on hydrocarbon concentration for plasma-catalytic FTS (NTP + 2 or 6 wt% Co catalyst) at discharge times of 10 and 60 s; (a) methane, (b) ethane, (c) ethylene, (d) propane and (e) propylene. Legend: ■—6 wt% Co (60 s); ▲—6 wt% Co (10 s); □—2 wt% Co (60 s); △—2 wt% Co (10 s); ◆—6 wt % Co (arc extinguished < 60 s). Operating conditions: Syngas (H_2/CO) ratio: 2.2:1; current: 350 mA; inter-electrode gap: 1 mm; wall temperature: 25 °C. Error bars (vertical): Expanded experimental hydrocarbon concentration uncertainty of $\pm 11\%$.

Although these were the maximum yields obtained for all systems investigated in this study, extinguishing of the arc discouraged experimentation at 10 MPa. During arc termination, the arc unhinged from its anodic root and jumped to the ceramic insulator (that securely held the cathode). Arc jumping 'burnt' the insulation material, as shown in Scheme 1, which could not be used again as it prevented ignition of the arc in subsequent experimentation: the arc continued to jump to the cathode insulator, instead of the anode, and was immediately extinguished. Consequently, a replacement insulator was required.

Scheme 1. Image depicting the cathode ceramic insulator (supplied by Ceradvance Engineering Ceramics), which was 'burnt' during the 6 wt% Co catalytic experiments at 60 s and between 7–10 MPa.

Due to these experimental constraints and to prevent instrumentation damage, the pressure range was restricted to 1–6 MPa at 60 s for the 6 wt% Co catalyst. At 10 s, however, the arc was stable from 0.5 to 10 MPa due to lower water concentrations as a result of the shorter discharge time.

The 6 wt% Co catalyst produced higher hydrocarbon concentrations than the 2 wt% Co catalyst at both 10 and 60 s, as shown in the concentration-pressure plots in Figure 2a–e. At 2 MPa and 60 s, both the 2 and 6 wt% Co catalysts shared a similar trend, in that a sharp increase occurred for all hydrocarbon yields.

In contrast to the other systems, where 60 s led to higher yields than 10 s throughout the pressure range, the 6 wt% Co catalyst displayed a reverse trend at 0.5, 1, 3 and 4 MPa. At these pressures, the C₁ to C₃ hydrocarbon yields at 60 s were significantly lower than that at 10 s, implying that within the additional 50 s, secondary reactions, namely cracking or hydrogenolysis could have occurred, thus decreasing the methane, ethane, ethylene and propane concentrations.

Apart from secondary reactions, which seem more influential for the 10 s study (discussed in detail later in this section), higher water yields (higher CO conversion) at the longer residence time of 60 s (and at 3 and 4 MPa) could have reduced methane production. The rationale behind this trend in conventional FTS is that water is competitive with methane for hydrogen, particularly with increasing CO conversion (longer residence time) [30–34].

For the 10 s study, where the arc was stable up to 10 MPa, the methane, propane and propylene yields typically increased with increasing pressure, specifically between 8 and 10 MPa. However, the ethane concentration decreased from 57 ppm at 1 MPa to 26 ppm at 4 MPa, and increased to 57 ppm at 10 MPa. Similarly, the ethylene concentration sharply decreased from 39 ppm at 1 MPa to 6 ppm at 4 MPa, and decreased slightly up to 10 MPa. This 6 wt% Co catalyst's ethylene trend differed from the other systems at 10 s, where the ethylene yield generally increased at higher pressures.

The decreasing trend of the ethylene (olefin) yields at 10 s, and the C₁ to C₃ hydrocarbon yields at 0.5, 1, 3 and 4 MPa, at 60 s, may all be explained by the literature.

In conventional FTS, using cobalt catalysts, the primary olefin yields decreased due to readsorption onto the catalyst surface. The readsorbed olefins, depending on the operating conditions (temperature, pressure and residence time), were then subject to secondary reactions: hydrogenation to paraffins, reinsertion into growing chains, hydrogenolysis, cracking and isomerization [28,35]. Hydrogenation to paraffins (causing chain termination) was shown to be dominant at 0.1 MPa (atmospheric pressure), whereas reinsertion into growing chains was dominant at 1 and 2 MPa (a typical FTS operating pressure) [36–39].

In this study, there may have been the secondary reinsertion of ethylene into C_3 hydrocarbon chains, especially for the 10 s study, which could be indicated by the decrease in ethylene yields and increase in propane and propylene yields with increasing pressure. This could have led to the maximum ethylene yields being obtained at lower pressures of 1 MPa at 10 s, and 2 MPa at 60 s.

Furthermore, high methane yields between 8 and 10 MPa, could have arisen from the hydrogenolysis of readsorbed ethylene (and other olefins)—a dominant secondary reaction above 550 K (277 °C) in conventional FTS, which leads to a significant increase in methane selectivity with increasing CO conversion (longer residence time) [40,41]. This reaction temperature was attainable at between 8 and 10 MPa due to greater plasma heating. On the contrary, the reaction temperature could have been considerably lowered by the active plasma species (pre-dissociated H_2 and CO reactants) [42–55].

Amongst the olefins, ethylene, in particular, was highly susceptible to readsorption and secondary reactions due to its high surface mobility and low activation energy barrier [28]. Besides these secondary reactions, Bodke et al. [56] suggested that the micro-pores on washcoated catalysts could trap and decompose ethylene to form graphite, which was likely to occur in this study as graphite and carbon nanotubes (grown from graphite precursors) were observed on the catalyst surface using diagnostic tools (discussed in Sections 2.4.3 and 2.4.4).

So far, it has been shown that ethane, ethylene and propane were produced at all pressures for both discharge periods. However, propylene was only produced between 4 and 10 MPa at 10 s (Figure 2e), indicating that chain growth was directly influenced by pressure. In addition, propylene was only produced for the 60 s study (Figure 2e) at 2 and 6 MPa (maximum pressure for a stable arc), which was in agreement with the high ethane, ethylene and propane yields at these two pressures. At 60 s, the absence of propylene at 4 and 5 MPa and its low yield at 6 MPa compared to the 10 s study, infers that propylene cracking occurred during the additional 50 s. Similarly, in conventional FTS, longer residence times decreased olefinicity (olefin to paraffin ratio) as a result of olefin readsorption and reinsertion into growing chains [57]. Alternatively, readsorbed propylene may have been hydrogenated to paraffins, especially propane, which marginally increased by ~1 ppm from 4 to 6 MPa (Figure 2d). Furthermore, propylene, synthesized by the 6 wt% Co catalyst and not by the 2 wt% Co catalyst, suggests that the higher cobalt loading favored chain growth as in conventional FTS [58].

In addition, carbon deposition occurred for both plasma-catalytic systems. Carbon deposits were seen at the apex of the cathode tip for the 6 wt% Co catalyst compared to carbon coating the entire cathode tip for the 2 wt% Co catalyst (as shown in Scheme 2). These observations reiterate that the 6 wt% Co catalyst was more selectively focused on synthesizing chain growth monomers (CH_x), whereas the 2 wt% Co catalyst formed more C-C chains.

2.1.2. The Influence of Pressure on Energy Consumption

In addition to product yields, energy was an important factor for comparing the plasma-catalytic FTS performance. The energy consumption indicators, specific input energy (SIE) and specific required energy (SRE), were determined from the input voltage and current, as described in Section 3.1.3.

The current was fixed at 350 mA for the pressure study, while the voltage required for arc ignition (set at an ignition voltage of 8 kV), was self-adjusted by the power supply. The

average (self-adjusted) voltage, determined using Equation (5) in Section 3.1.3, is presented as a function of pressure in Figure 3a–b.

Scheme 2. Carbon deposits observed on the cathode's 60° conical tip for the (a) 2 wt% and (b) 6 wt% Co catalytic systems.

Figure 3. The influence of pressure on average voltage for plasma-catalytic FTS (NTP + Blank, 2 or 6 wt% Co catalyst) at discharge times of (a) 60 s and (b) 10 s. Legend: ■—6 wt% Co; ▲—2 wt% Co; △—Blank. Operating conditions: Syngas (H_2/CO) ratio: 2.2:1; current: 350 mA; inter-electrode gap: 1 mm; wall temperature: 25 °C. Error bars (vertical): Expanded experimental hydrocarbon concentration uncertainty of $\pm 11\%$.

The voltage-pressure plots show an increasing for all systems investigated, characteristic of the voltage behaviour using a similar arc discharge reactor [1,3]. At higher pressures (generating a hotter arc), greater convective heat losses were encountered, which required higher voltages for maintaining the higher arc temperature, and thus sustaining the arc. The blank, 2 and 6 wt% Co catalytic systems required relatively similar supply voltages (power) throughout the pressure range. These trends reveal the positive influence of depositing cobalt on the mullite substrate and the contribution of a higher cobalt loading, as the 6 wt% Co catalyst produced greater hydrocarbon yields than the 2 wt% Co and blank catalysts despite using similar supply voltages.

The input voltage (power) caused the bulk gas temperature to fluctuate during the treatment period. The change in the bulk gas temperature (ΔT), shown in Figure 4, is the difference between the maximum and initial temperatures recorded during the 60 s treatment period.

Figure 4. The temperature increase (ΔT) as a function of operating pressure for plasma-catalytic FTS (NTP + Blank, 2 or 6 wt% Co catalyst) at a discharge time of 60 s (N.B. the discharge time for the 6 wt% Co catalyst at 10 MPa was ~12 s). Legend: $\square$ —6 wt% Co; $\blacksquare$ —2 wt% Co; $\blacksquare$ —Blank. Operating conditions: Syngas (H_2/CO) ratio: 2.2:1; current: 350 mA; inter-electrode gap: 1 mm; wall temperature: 25 °C.

For instance, at 6 MPa, the blank, 6 and 2 wt% Co catalytic systems' ΔT values were 7.1, 5.3 and 3.6 °C respectively. These ΔT -pressure trends show that the catalyst heating (assuming that the catalyst surface temperature is a direct function of the bulk gas temperature), decreased in the order: Blank > 6 wt% Co > 2 wt% Co. The 6 wt% Co catalyst was heated to a greater extent than the 2 wt% Co catalyst, inferring greater thermal activation. This higher catalyst temperature in conjunction with the larger catalytic cobalt sites (a result of higher cobalt loading), probably led to the highest hydrocarbon yields being produced by the 6 wt% Co catalyst (as shown in Figure 2).

The blank catalyst, in contrast, encountered a higher degree of heating than the 2 and 6 wt% Co catalysts, but produced the lowest hydrocarbon yields. As discussed in Section Blank Catalyst, lower yields for the blank catalyst were due to the absence of cobalt, the active catalytic component for synthesis, and the presence of $\gamma-Al_2O_3$ and mullite, which may have induced alternate reaction pathways including the stimulation of CO chemisorption and carbonaceous species.

Specific Input Energy (SIE)

The SIE (kJ/mol syngas)-pressure plots for pure plasma and plasma-catalysis are shown in Figure 5. Higher SIE values and lower hydrocarbon product yields at lower pressures suggest that more energy was spent on bulk gas heating instead of hydrocarbon synthesis. In contrast, at higher pressures, reverse trends are observed—lower SIE values and higher yields, suggesting that energy was more selectively focused on hydrocarbon synthesis.

Specific Required Energy (SRE)

The general trend of the SRE (MJ/mol methane, prod)-pressure plots, shown in Figure 6, shows that the energy required to produce a mole of methane decreased with increasing pressure for both the 10 and 60 s studies. This SRE trend and the plateauing voltage-pressure plots between 8 and 10 MPa (Figure 1) suggest that higher pressures led to higher energy efficiency.

Figure 5. Specific input energy (kJ/mol_{syngas}) as a function of pressure for plasma-catalytic FTS (NTP + Blank, 2 or 6 wt% Co catalyst) at discharge times of 10 and 60 s. Legend: ■—6 wt% Co (60 s); ▲—2 wt% Co (60 s); ●—Blank (60 s); □—6 wt% Co (10 s); △—2 wt% Co (10 s); ○—Blank (10 s). Operating conditions: Syngas (H₂/CO) ratio: 2.2:1; current: 350 mA; inter-electrode gap: 1 mm; wall temperature: 25 °C.

Figure 6. Specific required energy (MJ/mol_{methane, prod}) as a function of pressure for plasma-catalytic FTS (NTP + Blank, 2 or 6 wt% Co catalyst) at discharge time of 10 and 60 s. Legend: ■—6 wt% Co (60 s); ▲—2 wt% Co (60 s); ●—Blank (60 s); □—6 wt% Co (10 s); △—2 wt% Co (10 s); ○—Blank (10 s). Operating conditions: Syngas (H₂/CO) ratio: 2.2:1; current: 350 mA; inter-electrode gap: 1 mm; wall temperature: 25 °C.

2.1.3. Optimum Conditions

In Section 2.1.1, the effects of pressure on hydrocarbon yields for the blank, 2 wt%, and 6 wt% Co catalysts were discussed with a focus on the reaction pathways and discharge phenomena. This section provides a quantitative comparison of product yields and specific required energy (SRE) for the blank, 2 and 6 wt% Co catalysts at 10 and 60 s, as shown in Table 2.

Table 2. Hydrocarbon concentrations and specific required energy (SRE) values for the blank, 2 and 6 wt% Co catalyst systems investigated for the pressure variation study at discharge times of 10 and 60 s. (Syngas (H₂/CO) ratio: 2.2:1; current: 350 mA; inter-electrode gap: 1 mm; wall temperature: 25 °C; expanded experimental hydrocarbon concentration uncertainty: ±11%).

Product	Conc. (ppm) at 10 s						Conc. (ppm) at 60 s					
	Blank		2 wt% Co		6 wt% Co		Blank		2 wt% Co		6 wt% Co	
	1 MPa	10 MPa	1 MPa	10 MPa	1 MPa	10 MPa	2 MPa	10 MPa	2 MPa	10 MPa	2 MPa	6 MPa
Methane	14	60	68	2428	1526	5200	31	269	2266	7836	2194	3749
<i>C₂ hydrocarbons</i>												
Ethane	0.4	0.2	2.8	19	57	57	0.8	0.8	95	64	135	42
Ethylene	0.05	0.1	0.7	1.6	39	5	0.1	0.1	52	9.6	54	9.0
<i>C₃ hydrocarbons</i>												
Propane	0.0	0.0	0.1	4.5	1.3	11.7	0.0	0.1	1.2	6.6	2.5	3.3
Propylene	0.0	0.0	0.0	0.0	0.0	4.8	0.0	0.0	0.0	0.0	4.3	2.4
<i>Product ratio</i>												
Methane/ ethane	32	308	24	125	27	92	39	317	24	123	16	89
Ethane/ ethylene	8.7	2.4	4.0	12.2	1.5	11.5	11.1	10.9	1.8	6.6	2.5	4.7
<i>Specific required energy (MJ/mol_{CH₄, produced})</i>												
	99,179	3375	23,666	84	950	38	167,334	4432	2148	152	1991	448

Highlighted values mark the key findings.

At 2 MPa and 60 s, the 6 wt% Co catalyst's methane, ethane, ethylene and propane concentrations of 2194, 135, 54 and 2.5 ppm, respectively, were similar to the yields of 2266, 95, 52, 1.2 ppm for the 2 wt% Co catalyst, with a distinct increase of 1.4 and 2 for ethane and propane. Moreover, these 6 wt% Co catalyst's methane, ethane, ethylene and propane yields were 77, 170 and 755 (no C₃ hydrocarbons produced) times higher, respectively, than that of pure plasma.

For the 10 s study, the 6 wt% Co catalyst was considered the optimal system in regard to chain growth and product yields, as it produced the highest C₃ hydrocarbons at 10 MPa. At 10 MPa and 10 s, the 6 wt% Co catalyst's methane, ethane, ethylene and propane concentrations of 5200, 57, 5 and ~12 ppm, respectively, were 2, 3, 3 and 2 times higher than that of the 2 wt% Co catalyst and 86, 289 and 60 (no C₃ hydrocarbons produced) times higher, respectively, than that the blank catalyst.

Another indicator of chain growth is the methane/ethane ratio listed in Table 2. This ratio of the two main products reveals the pressure at which there was a minimum methane yield—the least desired product in conventional FTS. The methane/ethane ratio at 1 MPa and 10 s for the blank catalyst, 2 and 6 wt% Co catalyst systems of 32, 24 and 27, respectively, were 10, 5 and 3 times lower than that at 10 MPa. The higher methane/ethane ratios at 10 MPa were probably caused by higher arc temperatures (increasing with pressure) promoting methanation. Furthermore, the lowest ratios were achieved by the 2 and 6 wt% Co catalysts, suggesting the promotion of chain growth.

Furthermore, at 10 s study and 10 MPa, the minimum SIE and SRE values and the maximum C₁–C₃ hydrocarbon yields coincide for all systems, which is therefore considered as the optimum operating pressure. At 10 MPa and 10 s, the 6 wt% Co catalyst was the most energy efficient system as evaluated from its SRE value of 38 MJ/molCH₄, prod (Table 2), which was ~2.2 times lower than 2 wt% Co catalyst (84 MJ/molCH₄, prod) and 89 times lower than the blank catalyst (3375 MJ/molCH₄, prod).

The longer discharge time of 60 s generally led to higher C₁–C₃ hydrocarbon concentrations (as seen in Table 2), which agreed with conventional FTS trends [59,60]. At 60 s, the most favourable pressure for chain growth using the 6 wt% Co catalyst was 2 MPa, where the maximum ethane, ethylene and propylene yields were attained.

Similarly, to the 10 s study, a lower pressure led to a lower methane/ethane ratio for the 60 s study (as shown in Table 2); in this instance, 2 MPa. The methane/ethane ratio at 2 MPa for the blank catalyst, 2 and 6 wt% Co catalysts systems of 39, 24 and 16, respectively, were 8, 5 and 5.6 times lower than the ratios at 10 MPa. The ethane/ethylene

ratio (representing the olefin/paraffin ratio commonly used as a performance indicator in conventional FTS), was also relatively low at 2 MPa for the 2 and 6 wt% Co catalysts. This latter ratio indicates that 2 MPa promoted olefin formation-desired in conventional FTS. Chain growth was also improved by the higher cobalt loading of 6 wt%, which produced the maximum C₃ hydrocarbons at 2 MPa.

These maximum C₂ and C₃ yields produced at 60 s and 2 MPa by the 6 wt% Co catalyst corresponded to a SRE value of 1991 MJ/molCH_{4,prod}, which was 84 times lower than the blank catalyst's SRE value of 167 334 MJ/molCH_{4,prod}. However, the minimum SRE value for the 6 wt% Co catalyst was obtained at 6 MPa (448 MJ/molmethane, prod). Since the main objective at this exploratory phase of FTS research is to improve product yields and chain growth, a trade-off between these factors and energy consumption favors 2 MPa as the optimum pressure for the 60 s study.

2.2. Current Variation Study

2.2.1. The Influence of Current on FTS Products Yields

For the current variation study, the current was varied between 250 and 450 mA while fixing the other operating parameters: discharge time of 60 s, inter-electrode gap of 1 mm and pressure of 2 MPa. The pressure was fixed at 2 MPa as this lower pressure generated a stable arc discharge at lower currents (<350 mA). 2 MPa was also considered to be the optimum pressure for the pressure variation study: producing the maximum C₂–C₃ hydrocarbon yields and the lowest methane/ethane and ethane/ethylene ratios.

The blank catalyst's C₁–C₃ yields slightly decreased between 250 and 350 mA and remained relatively constant between 350 and 450 mA, as shown in Figure 7. This general trend of decreasing yields with increasing current is indicative of an increase in the thermal nature of the plasma, where electrons are less selectively focused on plasma-chemical reactions and more directed towards bulk gas heating i.e., the bulk gas for the blank catalyst system was heated above the initial room temperature (ΔT) by 5.21 °C at 250 mA and 6.25 °C at 450 mA.

The 6 wt% Co catalyst led to dramatic improvements in the C₁–C₃ hydrocarbon concentrations (Figure 7). In contrast to the blank and 2 wt% Co catalysts, which produced an arc discharge between 250 and 450 mA, the 6 wt% Co catalyst discharge behaviour was more complex: a glow-like discharge or arc-to-glow transition discharge (emitting a dim orange light at the cathode tip) was formed at 250 and 300 mA, whereas an arc discharge (seen as a luminous blue/white arc column) was formed at 350, 400 and 450 mA.

The glow-to-arc transition (GAT) [61] is a widely studied phenomena for glow discharges, caused by the instability of the glow discharge at near and beyond atmospheric pressure [62]. However, in this work, an inverse transition occurred—an arc-to-glow transition, in which the arc traverses further away from thermal equilibrium towards the more non-equilibrium glow region at lower currents (250 and 300 mA). The occurrence of GAT in glow discharges was stated to occur by either increasing the current at a fixed pressure or increasing the pressure at a fixed current [63]. Once again, the inverse of this trend was applicable here, i.e., decreasing the current (from 350 mA, used in the pressure variation study, to 250 and 300 mA, used in the current variations study), at a constant pressure of 2 MPa, led to an arc-to-glow transition. Since this transitional phase was not observed for the blank and 2 wt% Co catalyst systems, it is therefore attributed to plasma-catalytic interactions arising from the higher cobalt loading of 6 wt%, which is most likely to have modified the electrical characteristics of the non-thermal plasma as proposed by van Durme et al. [64] and other authors [65,66].

Figure 7. The influence of current on hydrocarbon concentration for plasma-catalytic FTS (NTP + Blank, 2 or 6 wt% Co catalyst) at a discharge time of 60 s; (a) methane, (b) ethane, (c) ethylene and (d) propane/propylene. Legend: ■—6 wt% Co; △—2 wt% Co; ▲—Blank; X—6 wt% Co (propylene). Operating conditions: Syngas (H_2/CO) ratio: 2.2:1; pressure: 2 MPa; inter-electrode gap: 1 mm; wall temperature: 25 °C. Error bars (vertical): Expanded experimental hydrocarbon concentration uncertainty of $\pm 11\%$.

In the 6 wt% Co catalyst study, the maximum methane (17,729 ppm), ethane (282 ppm), ethylene (59 ppm), propane (58 ppm) and propylene (10 ppm) concentrations were attained at the lowest operating pressure of 250 mA (glow-like or arc-to-glow discharge region). These were approximately 8, 2, 1, 24 and 2.4 times higher, respectively, than the concentrations obtained in the arc discharge region at 350 mA, which was due to the volumetric behaviour (greater treatment volume) of the glow-like discharge. This transitional region also favored C_3 hydrocarbon production, especially propane at 250 mA and propylene at 250 and 300 mA. In addition, propylene was only detected for the 6 wt% Co catalytic system, again suggesting that the higher Co loading of 6 wt% promoted chain growth.

The contribution of a higher cobalt loading was also clearly seen in that the maximum methane, ethane, ethylene and propane concentrations, obtained for the 6 wt% Co catalyst at 250 mA, were 9.6, 3.4, 1.6 and 85 times higher, respectively, than the 2 wt% Co catalyst's concentrations of 1852, 82, 38 and 0.7 ppm (at 250 mA), and 457, 232 and 456 (C_3 hydrocarbons not produced) times higher, respectively, than the blank catalyst's concentrations of 39, 1.2 and 0.1 ppm (at 250 mA).

2.2.2. The Influence of Current on Energy Consumption

According to the rms voltage-current plots in Figure 8, all systems required higher supply voltages at lower currents for sustaining the arc discharge, with all plasma-catalysis systems requiring similar voltages. These plots conformed to the voltage-current behaviour of typical non-thermal arc discharge generated at high pressure [1,3,67].

Figure 8. The influence of current on average voltage for plasma-catalytic FTS (NTP + Blank, 2 or 6 wt% Co catalyst) at a discharge time of 60 s. Legend: ■—6 wt% Co; △—2 wt% Co; ▲—Blank. Operating conditions: Syngas (H_2/CO) ratio: 2.2:1; pressure: 2 MPa; inter-electrode gap: 1 mm; wall temperature: 25 °C.

The increase in current with decreasing voltage also increased the electric field energy and specific input energy (SIE) as shown in Figure 9. The more energetic field at higher currents could have produced a more thermal-natured plasma that was less selectively focused on synthesis processes, indicated by lower hydrocarbon yields at higher currents as presented in the concentration-current plots in Figure 7a–d.

Figure 9. Specific input energy (kJ/mol_{syngas}) as a function of current for plasma-catalytic FTS (NTP + Blank, 2 or 6 wt% Co catalyst) at a discharge time of 60 s. Legend: ■—6 wt% Co; △—2 wt% Co; ▲—Blank. Operating conditions: Syngas (H_2/CO) ratio: 2.2:1; pressure: 2 MPa; inter-electrode gap: 1 mm; wall temperature: 25 °C.

The specific required energy (SRE)-current plots, presented in Figure 10, show a significant increase for the 6 wt% Co catalyst from 232 MJ/molmethane, prod at 250 mA (glow-like or arc-to-glow discharge) to 3002 MJ/molmethane, prod at 450 mA (arc discharge). This result reveals the energy intensive behaviour of a discharge traversing from a glow to an arc region i.e., from a less to more thermal state. In this glow-to arc transition region for the 6 wt% Co catalyst, the SRE values at 250 and 300 mA were 10 and 8.7 times lower, respectively, than that of the 2 wt% Co catalyst and 485 and 339 times lower, respectively, than that of the blank catalyst. This was due to the 2 wt% Co catalyst's discharge remaining as an arc at all currents studied. The transition of the glow-like discharge for the 6 wt% Co catalytic system to a stable arc between 350 and 450 mA is also reflected by its SRE values mirroring those of the 2 wt% Co catalyst at these currents.

Figure 10. Specific required energy (MJ/molmethane, prod) as a function of current for plasma-catalytic FTS (NTP + Blank, 2 or 6 wt% Co catalyst) at a discharge time of 60 s. Legend: ■—6 wt% Co; △—2 wt% Co; ▲—Blank. Operating conditions: Syngas (H_2/CO) ratio: 2.2:1; pressure: 2 MPa; inter-electrode gap: 1 mm; wall temperature: 25 °C.

Furthermore, the difference between the arc-to-glow transitional and stable arc states for the 6 wt% Co catalyst was also observed from the arc's stability, which is described by the voltage error (determined using equations 6 and 7 in Section 3.1.3). The voltage errors for the 6 wt% Co catalyst were approximately 9 and 6% at 250 and 300 mA (arc-to-glow transitional region), respectively, compared to 1.7% at 350 mA (stable arc region). The average voltage errors for the blank and 2 wt% Co catalysts, in contrast, were both ~0 and 1.9% at 250 mA and 300 mA (stable arc region), respectively. These values were much lower than the 6 wt% Co catalyst's errors, verifying the instability of the arc-to-glow region, and, in turn, demonstrating the more pronounced influence of the higher cobalt loading of 6 wt% on the electrical properties of the discharge.

2.3. Inter-Electrode Gap Variation Study

2.3.1. The Influence of Inter-Electrode Gap on FTS Products Yields

The final parameter studied, the inter-electrode gap, was varied from 0.5 to 2 mm at fixed operating conditions: pressure of 2 MPa, current of 350 mA, and discharge period of 60 s. These fixed conditions led to a stable arc discharge and were also the optimum conditions in the pressure variation study. The hydrocarbon yields generally increased with increasing inter-electrode gap as shown in Figure 11.

Figure 11. The influence of inter-electrode gap on hydrocarbon concentration for plasma-catalytic FTS (NTP + Blank, 2 or 6 wt% Co catalyst) at a discharge time of 60 s; (a) methane, (b) ethane, (c) ethylene and (d) propane/propylene. Legend: ■—6 wt% Co; △—2 wt% Co; ▲—Blank; X—6 wt% Co (propylene). Operating conditions: Syngas (H_2/CO) ratio: 2.2:1; pressure: 2 MPa; current: 350 mA; wall temperature: 25 °C. Error bars (vertical): Expanded experimental hydrocarbon concentration uncertainty of $\pm 11\%$.

A wider inter-electrode gap produced a longer arc column, thus treating a greater volume of syngas. An increase in the discharge gap (volume) for plasma-catalysis also inferred an increase in the catalytic surface area exposed to the discharge, translating to a larger overall reaction volume for plasma-catalysis. This was observed for the 6 wt% Co catalyst, where the methane (22,424 ppm), ethane (517 ppm), ethylene (101 ppm), propane (79 ppm) and propylene (19 ppm) concentrations at an inter-electrode gap of 2 mm were approximately 22, 10, 6, 26 and 5 times higher, respectively, than the concentrations at 0.5 mm. These results show that a fourfold increase in the discharge gap (0.5 to 2 mm) produced a significantly greater reaction volume (arc discharge volume + catalyst surface area exposed to the discharge).

Although the blank catalyst had a similar reaction volume to the 2 and 6 wt% Co catalyst systems, its yields were considerably lower. For example, at the widest discharge gap of 2 mm, the methane (22,424 ppm), ethane (517 ppm), ethylene (101 ppm) and propane (79 ppm) concentrations for the 6 wt% Co catalyst were 558, 543, 436 and 2 453 times higher, respectively, than that of the blank catalyst (40, 0.95, 0.23 and 0.03 ppm—values not provided in Figure 11).

The hydrocarbon yields for the 6 wt% Co catalyst were generally higher than those of the 2 wt% Co catalyst for most discharge gaps studied. However, a reverse trend was

observed for methane, ethane and ethylene at 0.5 mm, which was especially apparent for ethylene between 1 and 2 mm. The lower ethylene yields for the 6 wt% Co catalyst between the 1 and 2 mm discharge gaps may have resulted from these larger arc discharge volumes causing an elevation of the catalyst surface temperature. The catalyst temperature is related to the bulk gas temperature, which increased (ΔT) during the 60 s treatment by 3.3, 5.0, 12.5 and 25.4 °C at 0.5, 1, 1.5 and 2 mm respectively.

The higher bulk gas/catalyst temperatures probably promoted ethylene readsorption, followed by secondary reactions, such as hydrogenation to ethane, or reinsertion into propane or propylene chains (reaction pathways discussed in the pressure variation study in Section 2 wt% and 6 wt% Co Catalyst). These reaction phenomena, describing the lower ethylene yields at 1 and 2 mm for the 6 wt% Co catalyst, were verified at 2 mm. At this inter-electrode gap, the ethane (517 ppm) and propane (79 ppm) concentrations were 1.5 and 4 times higher, respectively, than that of the 2 wt% Co catalyst. In addition, the higher cobalt loading led to the exclusive production of propylene (not detected for the 2 wt% Co catalyst system).

Furthermore, ethylene secondary reactions in the 6 wt% Co catalyst study appear to be more predominant at wider inter-electrode gaps than at higher pressures, as discussed in the pressure variation study in Section 2 wt% and 6 wt% Co Catalyst.

2.3.2. The Influence of Inter-Electrode Gap on Energy Consumption

The average voltage increased with increasing inter-electrode gap as shown in Figure 12. Higher voltages are typically required for sustaining the arc discharge at wider discharge gaps. This is due to the higher electrical resistivity (higher energy requirement) of the longer arc column, which is further from non-equilibrium than the near-electrode border zones [1,68]. Hence, for arc generation for the 6 wt% Co catalytic system, 268 V was required at 2 mm (longer arc column), whereas 157 V was required at 0.5 mm (shorter arc column).

Figure 12. The influence of inter-electrode gap on rms voltage for plasma-catalytic FTS (NTP + Blank, 2 or 6 wt% Co catalyst) at a discharge time of 60 s. Legend: ■—6 wt% Co; △—2 wt% Co; ▲—Blank. Operating conditions: Syngas (H_2/CO) ratio: 2.2:1; pressure: 2 MPa; current: 350 mA; wall temperature: 25 °C.

The voltage behaviour of the varying arc column width is also reflected by the specific input energy (SIE) values shown in Figure 13. The higher SIE values suggest that wider discharge gaps (longer arc columns), produced a more energy intensive (exhibited by greater bulk gas heating), and less non-equilibrium plasma.

Figure 13. Specific input energy (kJ/mol_{syngas}) as a function of inter-electrode gap for plasma-catalytic FTS (NTP + Blank, 2 or 6 wt% Co catalyst) at a discharge time of 60 s. Legend: ■—6 wt% Co; △—2 wt% Co; ▲—Blank. Operating conditions: Syngas (H₂/CO) ratio: 2.2:1; pressure: 2 MPa; current: 350 mA; wall temperature: 25 °C.

The specific required energy (SRE) values, presented in Figure 14, significantly decreased between 0.5 and 2 mm for the 2 and 6 wt% Co catalysts, revealing 1.5 to 2 mm as the optimum inter-electrode gap range in regard to energy efficiency and hydrocarbon yields. At 2 mm, the similar SRE values for the 2 wt% (224 MJ/mol_{methane, prod}) and 6 wt% (265 MJ/mol_{methane, prod}) Co catalysts were approximately 778 and 660 times lower, respectively, than that of blank catalyst (174 451 MJ/mol_{methane, prod}).

Figure 14. Specific required energy (MJ/mol_{methane, prod}) as a function of inter-electrode gap for plasma-catalytic FTS (NTP + Blank, 2 or 6 wt% Co catalyst) at a discharge time of 60 s. Legend: ■—6 wt% Co; △—2 wt% Co; ▲—Blank. Operating conditions: Syngas (H₂/CO) ratio: 2.2:1; pressure: 2 MPa; current: 350 mA; wall temperature: 25 °C.

Although the SRE value for the 2 and 6 wt% Co catalysts were similar at 1.5 and 2 mm, the 6 wt% Co catalyst produced significantly higher quantities of C_1 – C_3 paraffins and propylene (not detected for the other systems) in this discharge gap range. This catalyst, once again, is shown to be the most favourable for promoting chain growth. However, if higher ethylene concentrations were desired, then the 2 wt% Co catalyst operating between 1.5 and 2 mm would be preferred.

2.4. Catalyst Characterisation

The effects of plasma on the surface properties of the different cobalt loaded catalyst were assessed using various catalyst characterization tools, namely scanning electron microscopy (SEM), energy dispersive x-ray (EDX), transmission electron microscopy (TEM) and x-ray diffraction (XRD). These diagnostic tools and their experimental methods are described in this section.

2.4.1. Scanning Electron Microscopy (SEM)

The SEM micrographs, presented in Figure 15, depict the distinction between the coating layer and mullite substrate for the blank, 2 and 6 wt% Co catalysts. The coating layer thicknesses, measured at 20 different sites on the blank, 2 and 6 wt% Co catalysts, ranged between 21–49 μm , 34–67 μm , and 41–75 μm , respectively, with average coating thicknesses of 37, 49 and 51 μm .

Figure 15. SEM images of catalyst coating thickness; (a) blank, (b) 2 wt% Co, (c) 6 wt% Co.

The average coating thicknesses increased with increasing cobalt loading, which coincides with the increasing C_1 – C_3 hydrocarbon yields is discussed in Sections 3.1–3.3. Bakhtiari et al. [69] observed a similar trend using a monolithic reactor (pure catalysis). They found that an increase in the coating thickness with cobalt loading, increasing from 15 to 33 wt%, improved the C_{5+} selectivity. The coating thickness, although an important design factor for continuous monolith reactors-in which the diffusion length (governed by the coating thickness), directly affects the mass transfer limitations [69]-is not a significant factor for the batch process in this work.

In addition to the coating thickness, SEM was also used to analyze the surface characteristics of the catalyst i.e., the cylindrical inner surface exposed to the arc discharge. A micrograph of the fresh uncoated mullite (without γ - Al_2O_3 and Co) is shown in Figure 16a. In contrast, γ - Al_2O_3 clusters are clearly visible on the fresh blank catalyst (without Co) in Figure 16b.

Figure 16. SEM micrographs of catalysts; (a) uncoated mullite (no γ - Al_2O_3 and Co), (b) blank catalyst.

The SEM micrographs of inner surface of the 2 and 6 wt% Co catalysts, shown in Figures 17 and 18, respectively, show a vast difference between the fresh and used cobalt catalysts. Large cobalt clusters are visible on both the fresh (calcined/reduced) 2 wt% Co catalyst (Figure 17a) and 6 wt% Co catalyst (Figure 18a,b). In contrast, smaller and more highly dispersed clusters are seen on the used 2 wt% Co catalyst (Figure 17b) and 6 wt% Co catalyst (Figure 18c,d).

Figure 17. SEM micrographs of 2 wt% Co catalysts; (a) fresh catalyst, (b) used catalyst.

Figure 18. SEM micrographs of 6 wt% Co catalysts; (a,b) fresh catalyst, (c,d) used catalyst.

In conventional FTS, for a Co/SiO₂, an increase in cobalt dispersion—to a higher degree than that caused by H₂ activation—occurred due to an increase in the operating pressure from 2 to 4 MPa [70]. Higher pressures were suggested to promote CO chemisorption, causing cobalt cluster segregation and a larger catalytic surface area.

Therefore, higher operating pressures (0.5–10 MPa) than that in conventional FTS, combined with the pre-dissociated CO plasma species, are factors that were probably responsible for the high cobalt dispersion shown in Figures 17b and 18c,d. In addition, the reduction of unreduced Co oxides to form smaller Co metal particles, a phenomenon reported in several plasma-catalytic studies [71–74], may also explain the smaller particle sizes of the used catalysts.

Furthermore, the different cluster sizes for the used 6 wt% Co catalyst, shown in Figure 18c,d, were due to the different areas of the catalyst being exposed to varying discharge intensities, i.e., non-uniform plasma-heating of the catalyst surface. The smaller and more modified clusters seen in Figure 18d, suggest that this portion of the catalyst was located in closer proximity to the arc discharge (directly above the upward curved arc column). This is the most thermally intense region of the discharge, probably leading to hotspot formation, a phenomenon observed in the plasma-catalytic literature [66]. Furthermore, these catalyst's areas closest to the active arc core were likely to contribute the most to hydrocarbon production.

2.4.2. Energy Dispersive X-ray (EDX)

SEM-EDX dot mapping images revealing the major elemental components (Co, Al and Si) on the inner surfaces—exposed to plasma—of the used 2 and 6 wt% Co catalysts, are presented in Figures 19 and 20, respectively. These images show that the cobalt particles

were uniformly distributed on both used catalyst surfaces, which was enhanced by plasma treatment as shown in SEM (Section 2.4.1) and TEM (Section 2.4.3) analysis. The images and intensity plots also verify that approximately three times more cobalt was present in the 6 wt% Co catalyst.

Figure 19. EDX dot mapping analysis of the surface of a used 2 wt% Co catalyst.

Figure 20. EDX dot mapping analysis of the surface of a used 6 wt% Co catalyst.

2.4.3. Transmission Electron Microscopy (TEM)

Particle Size Distribution

The 2 and 6 wt% Co catalysts produced significantly higher product yields and a wider product distribution than the blank catalyst, which clearly indicates the contribution of cobalt in plasma-catalytic FTS. In order to better understand the influence of cobalt loading on plasma-catalytic interactions, the cobalt particle size analysis and particle distribution were examined using transmission electron microscopy (TEM).

A TEM micrograph of the blank catalyst (mullite coated with only γ - Al_2O_3) is shown in Figure 21a. Compared to the lighter γ - Al_2O_3 and mullite ($\text{Al}_2\text{O}_3/\text{SiO}_2$) particles seen in Figure 21a, the darker cobalt clusters, are clearly visible for the 2 wt% Co catalyst (Figure 21b) and 6 wt% Co catalyst (Figure 21c), as highlighted by the white dashed circles.

Figure 21. TEM micrographs of used catalysts; (a) blank, (b) 2 wt% Co, (c) 6 wt% Co. (N.B. Examples of cobalt clusters are encircled by white dashed rings).

The cobalt particle size distribution, presented in Figure 22, was determined by measuring the approximate particle sizes of 100 cobalt clusters for both the 2 and 6 wt% Co catalysts using the iTEM image analysis software. The size of the 6 wt% Co particles spanned 6 to 57 nm with 84% of the particles in the range of 6 to 25 nm. The size of the 2 wt% Co particles spanned 2 to 35 nm with 95% of the particles in the range of 2 to 19 nm. Based on this data, the average particle sizes for the 2 and 6 wt% Co catalysts were estimated to be 10 and 19 nm, respectively.

Figure 22. Particle size histogram of the 2 wt% (■) and 6 wt% (■) cobalt catalysts.

Tavasoli et al. [58] showed that an increase in the cobalt loading (from 8 to 40 wt%) on an Al_2O_3 support, caused a higher deposition onto the same support surface, resulting in the agglomeration of cobalt crystal particles, thus forming larger clusters. Larger clusters were associated with weaker metal-support interactions, resulting in improved reducibility [75,76], and thus generating more active sites (a larger catalytic surface area) for FTS reactions. It was also reported that larger clusters may reduce steric hindrance for dissociative adsorption of CO [58], which could promote chain growth monomer formation.

The effects of a higher cobalt loading on the FTS performance factors in this work are in agreement with the literature mentioned above [58,75,76]. That is, the larger cobalt particles of the 6 wt% Co catalyst corresponded to higher C_1 – C_3 hydrocarbon yields. It also improved chain growth, as indicated by propylene production, which was absent for the blank and 2 wt% Co catalysts studies.

In addition to the cobalt particle sizes, TEM also revealed the presence of carbonaceous species on the 6 wt% Co catalyst in the form of carbon nanotubes (CNTs), as shown in Figure 23. This was an unexpected finding as CNTs are not synthesized in conventional FTS due to low temperature operation. The only known connection between CNTs and conventional FTS in the literature is the use of CNTs as catalyst supports [77–86].

CNT synthesis in this work is suggested to occur through similar mechanisms to that in thermal chemical vapor deposition (CVD) and/or plasma enhanced chemical vapor deposition (PECVD), as there seem to be some similarities between these processes and their products.

Figure 23. TEM micrographs of carbon nanotubes (CNTs) detected on the used catalyst; (a–d) 6 wt% Co.

Firstly, CNTs may be formed from several carbon precursors: carbon monoxide, methane, ethylene, acetylene, benzene and xylene [87–89]. Carbon monoxide was the obvious carbon precursor in this work, with prospective contributions from the C1–C3 hydrocarbon products. Secondly, CNT growth usually occurs via precursor decomposition on the catalyst surface at high temperatures [90]. Here, precursor decomposition could have been induced by CVD and/or PECVD routes: molecular CO and hydrocarbons decomposed on the cobalt surface between 600 and 1200 °C, which is similar to thermal CVD (less likely due to the high temperature requirements), or PECVD (where carbon-plasma, pre-dissociated CO, was deposited on the cobalt surface at temperatures as low as 120 °C) [89,91].

The PECVD route for CNT synthesis was more likely to occur due to the ability of the active plasma species to reduce the temperature requirement by lowering the activation barrier, a phenomena reported in other plasma-catalytic applications [78,79]. However, the CNTs structure resembled the “curly” or “spaghetti-like” structure of CVD-CNTs [88,89], as opposed to the vertically aligned assembly of PECVD-CNTs [89,91]. In addition, CNTs may have been modified during the grinding of the 6 wt% Co catalyst into powder (the form required for TEM analysis); however, the effect of grinding on these nano-sized structures are not known. Therefore, a precise CNT mechanism cannot be deciphered at this exploratory stage of experimentation.

Furthermore, the appearance of these CNTs resembled that of multi-walled CNTs (MWCNTs) [87,92]. The MWCNTs had inner diameters between 12–17 nm and outer diameters between 36–38 nm, visually measured from the TEM images in Figure 26 using the iTEM software. The dimensions were in the general MWCNT diameter range of 2 to 100 nm [93], with the tubes diameters increasing proportionally with the catalyst particle

size, a relationship reported in the PECVD literature [88] i.e., larger catalyst particles formed CNTs with larger tube diameters, vice versa. The average diameters of at least 10 nm for the cobalt particles in this study, corresponded to the range (of tens of nanometers) reported in the literature for MWCNTs. In contrast, a few nanometers (≤ 3 nm) were reported for single-walled CNTs (SWCNTs) [60,94]. Furthermore, the lower temperature range of 600 to 900 °C for MWCNT synthesis was more likely to occur than the range of 900 to 1200 °C for SWCNT synthesis [60].

In regard to the growth mechanism, it appears that a MWCNT originated at the surface of a cobalt cluster (firmly rooted to the γ -Al₂O₃/mullite support), and as it grew, protruded away from the cobalt cluster. This growth process conforms to the base-growth mechanism, which occurs due to the strong interaction between Co and γ -Al₂O₃. In contrast, moderate interactions between Co and TiO₂, and weak interactions between Co and SiO₂ [31]-other oxide supports used in FTS-would probably be described by the tip-growth mechanism. In this mechanism, the graphitic cylinder evolves between the metal and support, pushing the metal upwards.

2.4.4. X-ray Diffraction (XRD)

A powder XRD apparatus equipped with a cobalt radiation source was used to classify the molecular compounds comprising the blank, 2 and 6 wt% Co catalysts. The catalyst spectra, shown in Figure 24a, were identified by comparison to reference peak patterns (Figure 24b). The reference peaks were sourced from the HighScore Plus database, which listed potential compound matches and their order of probability. The highest reference peak in each reference spectra in Figure 24b, corresponds to 100% intensity, with the outstanding peaks having relative intensities.

Figure 24. XRD plots of (a) catalyst peaks and (b) reference peak patterns.

The reference peak patterns show that mullite and alumina are the dominant components of the blank, 2 and 6 wt% Co catalysts, as these patterns matched the catalyst spectra with the highest probability. Furthermore, the 2 and 6 wt% Co catalysts' spectra for mullite and alumina display relatively similar peak intensities, but the mullite/alumina peaks at

62°, 63°, 67°, 71°, 76°, 79°, 81°, 84° and 89° for the blank catalyst have a slightly higher intensity, which is probably due to more mullite and alumina being present in the absence of cobalt. Moreover, the prominence of mullite and alumina might have also swamped the detection of cobalt for the Co-loaded catalysts.

In addition to mullite and alumina, graphite (more specifically graphite 2H [95]) was detected in all three catalysts. The graphite reference peaks at ~31°, 49°, 59° and 71° intersect those of mullite, with the graphite peak at 71° closely corresponding to alumina, thus making it difficult to distinguish graphite. However, the peak at 52° (highlighted by the dashed line), absent in alumina and mullite, suggests that graphite was formed on all three catalysts.

The deposition of graphite on the catalysts may be confirmed by it being a precursor in the synthesis of carbon nanotubes (CNTs), which were detected using TEM (discussed Section 2.4.3) i.e., CNTs are fundamentally cylindrical graphene sheets, where graphene is a single layer of graphite. Graphite formation may be further verified by the intersection of temperatures required to synthesize these carbonaceous compounds: graphite forms above 400 °C [96–100], whereas CNT growth occurs above 600 °C by thermal CVD and above 120 °C by PECVD [60,89,91]. These high temperatures, 400 to 600 °C, usually lead to surface carbon being converted into more stable carbon species that possess a lower affinity for hydrogenation [100].

2.4.5. Carbon Deposition on Electrodes

In addition to the catalyst surface, carbon deposits were also seen on the cathode and anode surfaces for the 2 wt% Co catalyst system, as shown in Scheme 2 in Section 2 wt% and 6 wt% Co Catalyst. These deposits were seen to destructively interfere with the arc stability. Apart from visual observation, the stability was also evaluated based on the voltage errors (signifying voltage fluctuations) [1], as discussed in Section 3.1.3. The voltage errors for the blank catalyst, 2 and 6 wt% Co catalysts systems were 1.2, 2.9 and 1.4% respectively.

The 2 wt% Co catalyst exhibited the highest voltage error (highest arc fluctuation), confirming that the carbonaceous species on the electrodes had a negative influence on the arc stability. The arc fluctuation/deformation probably occurred by the arc unhinging from the anodic root, jumping, and re-hinging onto the electrically conductive [101] carbon species, which were coated on the electrodes. Furthermore, these arc jumps, caused by the carbon species, led to the arc interacting with the internal reactor components, which was problematic as it hindered the operability and performance of the arc reactor. These findings, in addition to higher yields and lower energy consumption, favors the application of the 6 wt% Co catalyst in plasma-catalytic FTS, and necessitates the investigation of higher cobalt loadings [58].

3. Materials and Methods

3.1. Arc discharge Reactor

3.1.1. Reactor Set-Up

Fischer-Tropsch synthesis was explored using a tip-to-plane arc discharge (batch) reactor previously reported by Fulcheri et al. [1] and Iwarere et al. [3] with capability to operate at low current and high pressure (up to 20 MPa). A schematic illustrating the process flow of the reactor and its peripheral equipment are illustrated in Figure 25.

The reactor was equipped with two axially-positioned tungsten electrodes. The stationary cathode was fixed in position by a ceramic holder, fabricated by Ceradvance Engineering Ceramics, Pretoria, South Africa. The mobile anode was moved using a hand wheel, enabling an adjustable inter-electrode gap. This was an innovative feature of the reactor, as contact of the electrodes (inter-electrode gap = 0 mm) minimized the electrical resistance of the high pressure gas, thus enabling the ignition of an arc discharge, and ultimately circumventing the high pressure limitations prescribed by Paschen's law [68,102–104].

The electrodes and electrode holders were fitted with O-rings, ensuring a leak tight discharge chamber. The arc discharge could be viewed via two face-to-face borosilicate Pyrex™ sight glasses, Sophia Antipolis, France. The reactor was equipped with a thermocouple for measuring the bulk gas temperature, which was positioned at around 8.5 to 9 mm away from the conical tip of the cathode (the origin of arc discharge). The reactor operating pressure was measured by a WIKA E-10 flameproof pressure transmitter (0–25 MPa) (WIKA Instruments Pty Ltd., Durban, South Africa). Due to the high temperature arc, the room temperature bulk gas was regulated using a water-cooled cooling jacket.

Figure 25. Schematic of the high pressure arc discharge reactor used in this study [9].

A high voltage DC power supply (Technix-SR-15-R-10,000 model, Technix, Créteil, France) was used to ignite the discharge between the electrodes. The cathode was attached to the negative polarity and the anode to the neutral point of the power supply, which had a maximum supply voltage of 10 kV and current of 500 mA. The operator could pre-set the current, whereas the power supply automatically self-adjusted the voltage. As a safety precaution, two 1 kΩ resistors were inserted in series between the power supply and reactor in order to limit the supply current. A similar power supply and its electrical design were previously described by Fulcheri et al. [1].

Apart from the reactor and power supply, the equipment setup incorporated peripheral equipment, which included a syngas mixing vessel and reactor feed system, a products sampling port, and control and data (temperature, pressure, voltage and current) acquisition tools (as illustrated in Figure 25).

3.1.2. Reactor Experimental Procedure

The H₂ and CO reactant gases (both 99.999 mol% purity), acquired from Afrox (Durban, South Africa), were mixed to form syngas with a H₂/CO ratio of 2.2:1. Composition analysis using a Shimadzu 2010 Plus gas chromatograph (Kyoto, Japan), prior to experiments, showed that only methane (up to 15 ppm) was present as an impurity in the syngas. Before every experiment, the reactor was purged with helium and evacuated using an Edwards vacuum pump in order to remove product impurities from previous experiments.

After purging, the syngas mixture was delivered to the reactor at the desired operating pressure (between 0.5 and 10 MPa). The mobile electrode (anode) was then moved along an axial axis, using a positioning system, until it contacted the fixed electrode (cathode).

Electrode continuity was confirmed by a multimeter. Direct tip-to-plane contact of the electrodes was compulsory in order to reduce the gas resistivity and overcome the restrictions enforced by Paschen's Law under the low current (≤ 450 mA) and high pressure (≥ 1 MPa) operating conditions.

Subsequent to electrode contact, the high voltage DC power supply was switched on. The power supply was pre-set to the required supply current (between 250 and 450 mA) and ignition voltage (8 kV). Once the power supply was activated, the mobile anode was immediately retracted from the fixed cathode, instantaneously forming a luminous arc discharge. The anode was retracted until an inter-electrode gap of 1 mm (between the electrodes) was acquired. The discharge was maintained at this electrode gap, at which syngas treatment proceeded for a pre-determined period of either 10 or 60 s. After this discharge period, the power supply was switched off, instantaneously extinguishing the arc discharge. As a safety measure, an insulated copper wire was utilized to transmit residual charge from the arc discharge reactor to ground.

Thereafter, the products were sampled from the reactor and analyzed off-line using a Shimadzu 2010 Plus Gas Chromatograph (Kyoto, Japan). The GC was fitted with a thermal conductivity detector (TCD), calibrated to detect CO and H₂, and a flame ionization detector (FID), calibrated to detect C₁ to C₃ hydrocarbons using the same GC operating parameters previously reported in literature [9]. A standard method in literature [9] was followed to determine the hydrocarbon product concentrations via the following equations:

$$n_i(\text{mols}) = (\text{GC Calibration slope})_i \times (\text{GC peak area})_i \quad (1)$$

$$C_i(\text{ppm}) = \left(\frac{n_i}{\sum_{i=1}^{\text{tot}} n_i + n_{\text{CO}} + n_{\text{H}_2}} \right) \times 1,000,000 \text{ ppm} \quad (2)$$

$$C_{i,\text{prod}}(\text{ppm}) = C_{i,\text{final}} - C_{i,\text{initial}} \quad (3)$$

where i represents the C₁–C₃ hydrocarbon species, C_i denotes the concentration of species i present in the gas mixture prior to and after reaction, and $C_{i,\text{prod}}$ is the concentration of species i produced by the reaction.

The expanded experimental uncertainty (U) of $\pm 11\%$ for $C_{i,\text{prod}}$ was evaluated from the uncertainty contributions of two major error sources: sample measurement (u_{rep}) and GC calibration (u_{calib}).

$$U(\text{ppm}) = f(u_{\text{rep}}, u_{\text{calib}}) \approx \pm 11\% \quad (4)$$

The expanded uncertainties are signified by the vertical error bars in the concentration versus operating parameter (pressure, current or inter-electrode gap) plots.

3.1.3. Reactor Energy Analysis

The electrical energy efficiency for plasma-catalytic FTS, in conjunction with product yields, were used to determine the optimal operating conditions. The energy efficiency of each system was assessed from the current and voltage. A current of 350 mA was used for the pressure and inter-electrode variation studies, but was varied for the current study. The ignition voltage was fixed at 8 kV for all parametric studies. The voltage, much higher than the breakdown voltage, was set as a precautionary measure in the event of a voltage surge.

The constant-current direct current (DC) power supply automatically self-adjusted the voltage between the electrodes throughout the discharge period. This maintained the current at its original setpoint. The varying voltage signal (consisting of up to 10,000 and 60,000 voltage values at 10 and 60 s respectively) were recorded using a digital oscilloscope. These voltage signal values were used to calculate the average voltage using Equation (5) (also applicable to the average current (I_{avg})).

$$V_{\text{avg}} = \sum_{i=1}^n \frac{V_{\text{exp}}}{n} \quad (5)$$

where V_{avg} is the voltage attained from the oscilloscope response data, and n is the number of voltage value between 10,000 and 60,000 at 10 and 60 s respectively.

Furthermore, the average voltage and voltage signal, comprised of 60,000 voltage values for the 60 s study, were used to determine the voltage error (V_{err} (%)) for each operating parameter setpoint (pressure, current and inter-electrode), using equations 6 and 7. The average voltage error, describing the fluctuations in the voltage signal, was used to assess the arc stability.

$$\sigma_V = \sqrt{\frac{\sum_1^n |V - V_{avg}|^2}{n}} \quad (6)$$

$$V_{err}(\%) = (\sigma_V / V_{avg}) \times 100\% \quad (7)$$

where V is the voltage attained from the oscilloscope response data, n refers to 60,000 voltage values for the 60 s study, V_{avg} is the rms voltage, and σ_V is the standard deviation error.

The average voltage (V_{avg}), representative of the gas breakdown voltage when the electrodes were in contact (for negligible gas resistivity), was used with the average current to determine the energy consumption. Energy was evaluated in the form of the specific input energy (SIE), input energy required per mole of syngas, and the specific required energy (SRE), energy required to produce a mole of methane (the main synthesis product) as previously reported in the literature [9].

$$E \text{ (kJ)} = V_{avg} I_{avg} \Delta t \quad (8)$$

$$SIE \text{ (kJ/n}_{syngas}) = \frac{E}{n_{syngas}}, \text{ where } n_{syngas} = \frac{PV_{reactor}}{RT} \quad (9)$$

$$SIE \left(\text{kJ/n}_{CH_4,produced} \right) = \frac{E}{n_{CH_4,after} - n_{CH_4,before}} \quad (10)$$

where V_{avg} and I_{avg} denote the average voltage and current, respectively; Δt is the discharge period of 10 or 60 s; E is the electrical energy delivered by the power supply to ignite the arc discharge; n_{syngas} is the moles of syngas, which is a function of the universal gas constant (R), syngas volume ($V_{reactor}$), pressure (P), and (room) temperature (T); and finally, n_{CH_4} is the concentration of methane in the reactor before and after the discharge period.

All the plasma-catalytic FTS processes utilized the experimental apparatus and procedure discussed above. The preparation and configuration of the catalyst within the reactor are discussed in Section 3.2.

3.2. Catalyst Preparation

3.2.1. Catalyst Design and Configuration

A Co/ Al_2O_3 catalyst, representative of an industrial Fischer-Tropsch synthesis (FTS) catalyst, was used in plasma-catalytic FTS. Due to several factors, namely the high temperature (10,000 to 20,000 K) of the arc discharge [105] (contrasting with its ambient bulk gas), the low reactor volume (2.56 cm^3), and a labyrinth of internal reactor components (electrodes and electrode insulators), the catalyst could not be inserted into the reactor according to the conventional plasma-catalytic (DBD or corona discharge) methods. In these atmospheric pressure discharge reactors, a catalyst, prepared in various forms [55,64,106,107], is usually inserted into the reactor via two different configurations, namely, in plasma-catalysis (IPC) [23,49,108–112] or post-plasma catalysis (PPC) [23,109,110].

In lieu of the complexities of the arc discharge reactor, an alternate catalyst configuration was implemented. The reactor catalyst configuration utilized in the gliding arc discharge reactor [113,114], in which active cobalt is coated onto a ceramic substrate and positioned near (but not directly contacting) the discharge, was adapted for this work. This configuration was combined with the catalyst preparation method used for preparing monolithic catalysts [69,115–122].

The combination of these methods resulted in a catalyst consisting of a pre-formed LINE-OX[®] (CERadvance Engineering Ceramics Pty Ltd., Pretoria, South Africa) porous mullite (sintered 72 wt%-Al₂O₃/SiO₂) ceramic substrate, coated with γ -Al₂O₃ (high surface area support) and cobalt (active FTS material).

The mullite substrate design, illustrated in Figure 26, enabled the mobile anode to axially move and freely contact the fixed cathode within the annulus of the catalyst whilst preventing direct contact of the electrodes and arc discharge with the catalyst's inner surface, as illustrated in Figure 27. This was achieved due to a sufficient clearance of approximately 1.5 mm between the catalyst's inner surface and electrodes' outer surfaces, and approximately 3.5 mm between the catalyst's inner surface and cathode tip (where the arc originated). Other design factors were also considered: firstly, the catalyst substrate fitted precisely into the reactor chamber due to an outer diameter of ~12 mm (dimensions shown in Figure 26), which also provided adequate radial support at high pressures (0.5 to 10 MPa); secondly, face-to-face perforations of 5 mm, aligned with the two circular sight glasses of the reactor, permitting visualization of the arc discharge; and finally, three 2.5 mm semi-circular cut-outs (wedges) at the boundaries of the substrate, housing the thermocouple line, and reactor inlet and outlet (sampling) lines.

Figure 26. SW Isometric view of the LINE-OX[®] porous mullite substrate.

Figure 27. Isometric cross-sectional view of the LINE-OX[®] porous mullite substrate with electrodes.

Mullite was considered as a more suitable substrate material for this application (instead of the commonly used cordierite), due to its excellent thermo-physical properties (listed in Table 3): thermal stability [123], mechanical strength [123], porous structure, electrical resistivity [124], and the availability of oxygen vacancies [125]. Mullite as a catalyst support, has been used in limited applications [126–128].

Table 3. Thermo-mechanical properties of mullite supplied by Ceradance Engineering Ceramics.

Mechanical		Thermal	
Alumina content	72 wt%	Max. temperature	1400 °C
Other constituents	Silica (bound)	Thermal conductivity	5 Wm ^{−1} K ^{−1}
Bulk density	2.7–2.8 g/cm ³	Thermal expansion:	
Porosity	15%	at 400 °C	4.68 × 10 ^{−6} °C ^{−1}
Water absorption	6–8%	at 800 °C	5.54 × 10 ^{−6} °C ^{−1}
Modulus of rupture	100 MPa	at 1000 °C	5.88 × 10 ^{−6} °C ^{−1}
Modulus of elasticity	140 GPa	-	-

3.2.2. Catalyst Preparation Procedure

Al₂O₃ and Cobalt were coated in succession onto the surface of a pre-formed LINE-OX[®] porous mullite substrate, manufactured by Ceradance Engineering Ceramics (Pretoria, South Africa). Successive coatings, as opposed to coating a mixture of Co/Al₂O₃, was shown to produce higher conversions and C₅₊ selectivity in classical FTS using a monolithic reactor [69].

The γ-Al₂O₃ was coated using the washcoating method developed by Villegas et al. [129]. Thereafter, cobalt was deposited using the preparation technique for coating monoliths in FTS [69,115,118,119,121,130]. Both methods were modified for this application.

For the first coating layer, the γ-Al₂O₃ powder (3 µm average particle size procured from Alpha-Aesar, Haverhill, Massachusetts, United States) was added to water to form a slurry (Al₂O₃/H₂O = 25 wt%). Nitric acid (HNO₃/Al₂O₃ = 2.2 mol.g^{−1}) was added to assist alumina dispersion. The slurry was mixed for 15 h at room temperature using a magnetic stirrer. A mullite substrate was dipped vertically into the slurry for 15 min. After this immersion period, compressed air was utilized to remove the excess slurry. The alumina-coated substrate was dried in a static furnace for 15 min at 600 °C. Finally, the substrate was weighed. The coating procedure (dipping and drying) was repeated until a 5 wt% γ-Al₂O₃ washcoat was obtained. The 5 wt% γ-Al₂O₃ coated onto mullite (and not containing cobalt), was referred to as the blank catalyst. The blank was used as a control study to determine the contribution of cobalt loading in plasma-catalytic FTS.

For the cobalt-based catalyst, the alumina-coated mullite substrate was dipped for 15 min in a cobalt nitrate hexahydrate Co(NO₃)₂·6H₂O solution (procured from Sigma Aldrich[®], Johannesburg, South Africa). The excess solution was removed using compressed air. The cobalt-dip-coated substrate was dried in an oven at 120 °C for up to 60 min and weighed. This was followed by calcination of the substrate in air at 450 °C for 4 h, and ex-situ reduction at 350 °C for 3 h using 30 mL.min^{−1} of pure hydrogen. Thereafter, the catalyst was immediately weighed and configured in the discharge chamber of the reactor. The final catalyst was comprised of 6 wt%-Co/5wt%-γ-Al₂O₃.

The blank, 2 wt%, and 6 wt% Co catalysts were retained in the reactor chamber for the entire duration of the pressure, current and inter-electrode gap variation investigations (exceeding 40 experiments). Thereafter, the pressure variation study was repeated at various pressures, especially at 2 MPa, thus ensuring experimental repeatability. The experimental repeatability indicates a relatively stable catalyst in the short-term—an expected benefit of this non-thermal plasma system is a shorter reaction time than conventional FTS. However, further research is required to confirm long-term catalyst stability.

3.3. Catalyst Characterisation

Scanning electron microscopy (SEM), energy dispersive x-ray (EDX), transmission electron microscopy (TEM) and x-ray diffraction (XRD) were used to characterize the 6 wt% Co/5 wt%-Al₂O₃ mullite catalyst.

For SEM imaging, the coated mullite substrate was fragmented into smaller pieces that were able to fit onto the SEM stage. Prior to analysis, the fragments were gold coated using a Quorum Tech Q150RES sputter coater (Quorum Technologies, East Sussex, UK). The catalyst was imaged using a Zeiss Ultra Plus FEG instrument (Carl Zeiss AG, Oberkochen, Germany) combined with the SmartSEM image capture software. Images were captured at a maximum magnification of 30 000. Elemental analysis was undertaken by coupling SEM with an EDX instrument—an Oxford X-Max 80mm SDD instrument (Oxford Instruments, High Wycombe, United Kingdom) with Aztec analysis software.

The mullite coated substrate was milled into a fine powder for TEM analysis. The powder was mixed with ethanol to form a solution, which was then sonicated. The sonicated solution was dispersed onto an Agar 200 mesh copper grid for analysis by a JEOL JEM-1010 TEM instrument (JEOL Ltd., Tokyo, Japan). A final powdered catalyst sample was analysed using a Panalytical Empyrean x-ray powder diffractometer (XRD) fitted with a Co-K α radiation source (Malvern Panalytical technologies, Worcestershire, United Kingdom).

4. Conclusions

In this work, the influences of different cobalt loadings on the product yields and energy consumption for plasma-catalytic Fischer Tropsch synthesis (FTS) were explored. The blank, 2 wt%, and 6 wt% Co catalyst systems produced C₁–C₃ hydrocarbons, with yields in the order: methane >> ethane > ethylene > propane. The product concentration results indicated that the highest cobalt loading of 6 wt% achieved higher C₁–C₃ hydrocarbons yields than the other systems: 6 wt% Co > 2 wt% Co > blank. In addition to higher yields, the 6 wt% Co also led to higher olefinicity, improved C₂ and C₃ chain growth, higher energy efficiencies (lower specific required energy (SRE)), and exclusively produced propylene and carbon nanotubes (detected using transmission electron microscopy (TEM)). Furthermore, TEM and scanning electron microscopy (SEM) showed that the 6 wt% Co catalyst provided a larger active cobalt surface area for synthesis, hence the higher yields. These findings suggest that syngas, apart from reacting in the arc core, also reacted on the 6 wt% Co catalyst surface. These catalytic surface reactions may have occurred via various reaction schemes: (i) the plasma (species) thermally activated the catalyst (without external heating), encouraging the adsorption of H₂ and CO ground state molecules and/or (ii) plasma-dissociated CO (in the form of radicals and vibrationally-excited CO) interacted with the catalyst at lower temperatures than that required in conventional FTS.

In contrast to the 2 wt% and 6 wt% cobalt-based catalysts, the blank catalyst led to significantly lower C₁–C₃ hydrocarbon yields than the other systems, which was related to the absence of cobalt and presence of Al₂O₃ and mullite in the catalyst leading to alternate reaction pathways. Due to providing the largest treatment volume, the inter-electrode gap of 2 mm was the most effective operating parameter for improving FTS performance, trailed by current and pressure. At a gap of 2 mm, using the 6 wt% Co catalyst—a combination that produced the highest yields in this work, the methane, ethane, ethylene and propane yields of 22 424 (2.24 mol%), 517, 101 and 79 ppm, respectively, were 1.5, 1.5, 0.8 and 4 times greater than the 2 wt% Co catalyst yields, and 558, 543, 436 and 2 453 times greater than the blank catalyst yields. Additionally, at 2 mm, the 6 wt% Co catalyst (SRE = 265 MJ/molmethane, prod) used marginally higher energy than the 2 wt% Co catalyst (SRE = 224 MJ/molmethane, prod), but ~660 times less energy to produce a mole of methane than the blank catalyst (SRE = 174 451 MJ/molmethane, prod).

Overall, the 6 wt% Co catalyst, the most effective catalyst, produced the highest yields and consumed relatively less energy at the following conditions: (i) 1 MPa and 10 MPa, the latter pressure being the most favourable for C₂ hydrocarbon production,

for the pressure variation study at 10 s (0.5 to 10 MPa); 2 MPa (most favourable for C₂ hydrocarbon production) for the pressure variation study at 60 s (0.5 to 10 MPa); (ii) 250 mA for the current variation study (250 to 450 mA), due to this lower current generating a more non-equilibrium plasma; and (iii) the widest discharge gap of 2 mm for the inter-electrode gap variation study (0.5 to 2 mm), as this gap produced the greatest discharge volume, which, in turn, interacted with a larger fractional area of the catalyst.

This study revealed the positive influence of tripling the cobalt loading (from 2 to 6 wt%) on plasma-catalytic FTS, and provided evidence as to why the use of a mullite substrate coated with only γ -Al₂O₃ is not recommended for plasma-catalytic FTS. This merit the investigation of higher loadings in the range of conventional FTS, which is typically between 10 and 40 wt% [58].

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