The Application of Non-thermal Plasma-Catalysis in Fischer-Tropsch Synthesis at Very High Pressure: the Effect of Cobalt Loading

Byron B. Govender, Samuel A. Iwarere, and Deresh Ramjugernath

Abstract— **Fischer-Tropsch synthesis (FTS) was explored by combining a non-thermal plasma (NTP) with a 0 (blank), 2 or 6 wt%-Co/Al$_2$O$_3$ mullite catalyst at very high pressure (0.5 to 10 MPa) and at different treatment periods of 10 and 60 s. The 6 wt% Co catalyst system produced the highest methane, ethane, ethylene and propane yields at 2 MPa and 60 s, which were similar to the yields for the 2 wt% Co catalyst and 46, 96, 270 and 25 times higher than that of pure plasma.**

Index Terms— **Non-thermal plasma; High pressure; Arc discharge; Fischer-Tropsch synthesis; Cobalt catalyst.**

I. INTRODUCTION

Synthetic fuels produced via Fischer-Tropsch synthesis (FTS) is becoming a more competitive alternative to oil-derived fuels [1] due to the decreasing oil supply and greater need for energy security.

Non thermal plasma (NTP) reactors applied in FTS may provide a viable alternative to conventional processes owing to the rapid reactions (nanoseconds to minutes) promoted by the active NTP species at ambient temperature, and the minimal space and maintenance required by the technology. These technological features have recently incentivized the investigation of FTS using a non-thermal arc discharge, where C_1-C_3 hydrocarbons were synthesized at high pressure (P > 1 MPa) without a catalyst present (referred to herein as pure plasma FTS) [2, 3]. In order to improve the hydrocarbon product yields and reduce energy consumption, a Co-based catalyst was introduced into the arc discharge reactor in this work.

Historically, plasma-catalytic applications at atmospheric pressure have generally improved the process performance compared to the sum of the individual pure plasma (no catalyst) and pure catalysis (no plasma) processes [4].

With the expectation of similar plasma-catalytic synergistic effects leading to improved FTS performance,

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the influence of pressure (0.5 to 10 MPa) on the hydrocarbon yields and energy consumption were investigated for both pure plasma and plasma-catalytic FTS at high pressure (0.5 to 10 MPa). For plasma-catalysis, an industrially representative 0 (blank), 2 or 6 wt%-Co/Al$_2$O$_3$ mullite catalyst was introduced into the arc discharge reactor in order to determine the effect of cobalt loading on FTS performance.

II. EXPERIMENTAL SECTION

A. Arc discharge reactor

Syngas was prepared by mixing H$_2$ (99.999 mol%) and CO (99.999 mol%) to achieve a H$_2$/CO ratio of 2.2:1. The syngas mixture, containing 15 ppm of methane as an impurity, was transferred to the arc discharge reactor (illustrated in Figure 1) at operating pressures between 0.5 and 10 MPa.
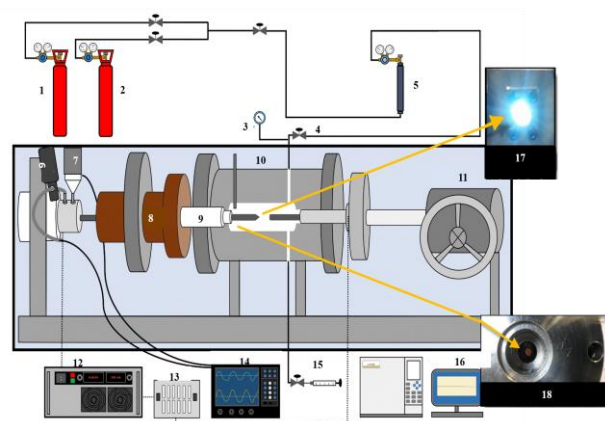

Fig. 1. Schematic of the high pressure arc discharge reactor used in this work. 1- Hydrogen Cylinder, 2- Carbon Monoxide Cylinder, 3- Pressure Transducer, 4- Reactor Inlet, 5- Mixing Cylinder, 6- Current Probe, 7- Voltage Probe, 8- Cathode Holder, 9- Electrical Insulator, 10- Thermocouple, 11- Anode Axial Positioning System, 12- HV DC Power Supply, 13- Resistors, 14- Digital Oscilloscope, 15- Reactor Sampling Port, 16- Gas Chromatograph, 17- Syngas arc discharge (axial view), 18- Co/Al$_2$O$_3$ coated mullite catalyst in reactor chamber (radial view).

Subsequent to reactor feeding, the mobile anode was moved towards the fixed cathode using an axial positioning system until contact of the electrodes was obtained. Direct contact of the electrodes was imperative in order to overcome the restrictions enforced by Paschen's Law under the low current (350 mA) and high pressure (0.5 to 10 MPa)

conditions. After electrode contact, the high voltage DC power supply, set at the supply current of 350 mA and offset voltage of 8 kV, was engaged. The mobile electrode was then retracted, immediately igniting an arc discharge between the electrodes. The inter-electrode gap was extended to 1 mm and the reaction proceeded for a treatment period of 10 or 60 s. After treatment, the power supply was switched off, leading to the instantaneous extinguishing of the arc discharge. The C_1 to C_3 hydrocarbon reaction products were withdrawn from the reactor via a sample point and were analysed off-line by a Shimadzu™ 2010 Plus.

B. Catalyst preparation

The industrially representative Co/Al_2O_3 was prepared by depositing $CoAl_2O_3$ on the surface of a pre-formed LINE-OX® porous (72 wt%-Al_2O_3/SiO_2) mullite substrate, fabricated by Ceradvance Engineering Ceramics (South Africa). The mullite substrate was designed to ensure that the fixed and mobile electrodes could axially contact each other within the annulus of the catalyst substrate whilst preventing direct contact of the electrodes/arc discharge with the catalyst inner surface, as illustrated in Figure 2.

Separate coating layers were obtained by firstly applying the γ-Al_2O_3 washcoating method described by Villegas et al. [5], and secondly, implementing the cobalt impregnation method used for monolithic FTS [6]. The prepared 0 (blank), 2 or 6 wt%-Co/5 wt%-γ-Al_2O_3 mullite catalyst was then inserted into the discharge chamber of the reactor.
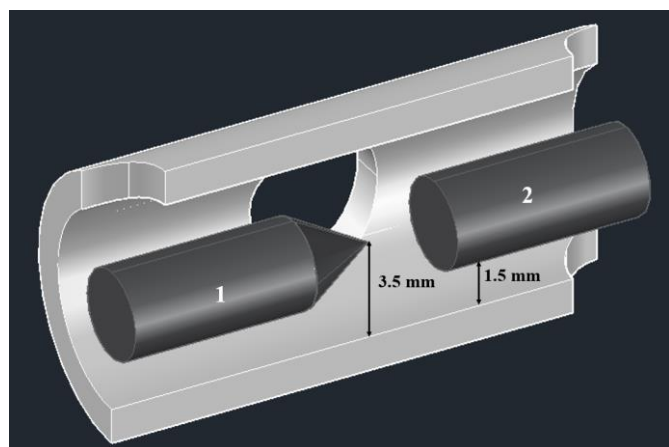

Fig. 2. Isometric cross sectional view of the LINE-OX® porous mullite substrate with electrodes. Note that 1 is the fixed cathode and 2 is the mobile anode.

III. RESULTS AND DISCUSSION

Pure plasma and plasma-catalytic FTS, using a 0 (blank), 2 and 6wt% Co/Al_2O_3 mullite catalysts, were investigated for varying operating 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 periods of 10 and 60 s. A full list of operating conditions are presented in table 1. The product yields and energy consumption for these four systems are presented in Figures 3 and 4 respectively.

The longer residence time of 60 s led to higher C_1-C_3 hydrocarbon yields for both the pure plasma and plasma-catalytic systems. Therefore, this discussion focuses on the 60 s study.

TABLE I
LIST OF OPERATING CONDITIONS USED IN PURE PLASMA AND PLASMA-CATALYTIC FTS

Operating Parameters	Pressure variation study [a]	
Discharge time (s)	10	60
Ignition current (mA)	350	350
Offset voltage (kV)	8	8
Electrode gap (mm)	1	1
Pressure (MPa)	0.5 - 10	0.5 - 10
H_2/CO ratio	2.2:1	2.2:1

[a] s = second, mA = milliampere, kV = kilovolt, mm = millimeter, MPa = megapascal.

The blank catalyst system (mullite coated with 0 wt%-Co/Al_2O_3) yielded the lowest hydrocarbon concentrations at all pressures investigated. The low yields were mainly attributed to the absence of active cobalt, needed to dissociate hydrogen for hydrogenation pathways [7] and the presence of strongly or irreversibly adsorbed CO [8]. As a result of the low hydrocarbon yields, the use of a γ-Al_2O_3-coated mullite catalyst without the active cobalt is not recommended in plasma-catalytic FTS.

The concentration-pressure trends for the 2 and 6 wt% Co catalysts at 60 s were more complex than the pure plasma and blank catalyst's behaviours in that the maximum hydrocarbons were obtained, in some cases, at 2 MPa. For the 2 wt% Co catalytic study at 60 s, the maximum paraffin yields (methane, ethane and propane) were observed at 10 MPa, with local maxima and the maximum ethylene obtained at 2 MPa. For the 6 wt% Co catalytic study at 60 s, the maximum methane and propane yields were achieved at 6 MPa (due to the arc discharge extinguishing before 60 s above 6 MPa, as a result of liquid water formation), whereas the maximum ethane, ethylene and propylene yields were obtained at 2 MPa.

A. Energy Consumption

In addition to the product yields, the energy consumption was evaluated from the rms voltage for the four systems, as indicated by the specific input energy (SIE) and specific required energy (SRE):

$$E(kJ) = V_{rms}I_{rms}\Delta t \qquad (1)$$

$$SIE(kJ/n_{syngas}) = \frac{E}{n_{syngas}} \qquad (2)$$

$$SRE(kJ/n_{CH4,produced}) = \frac{E}{n_{CH4,after} - n_{CH4,before}} \qquad (3)$$

Where V_{rms} and I_{rms} are the rms voltage and current; Δt is the discharge period of 10 or 60 s; E is the electrical energy supplied to ignite the arc discharge; n_{syngas} is the moles of syngas; and n_{CH4} represents the concentration of methane in the reactor pre and post-reaction.
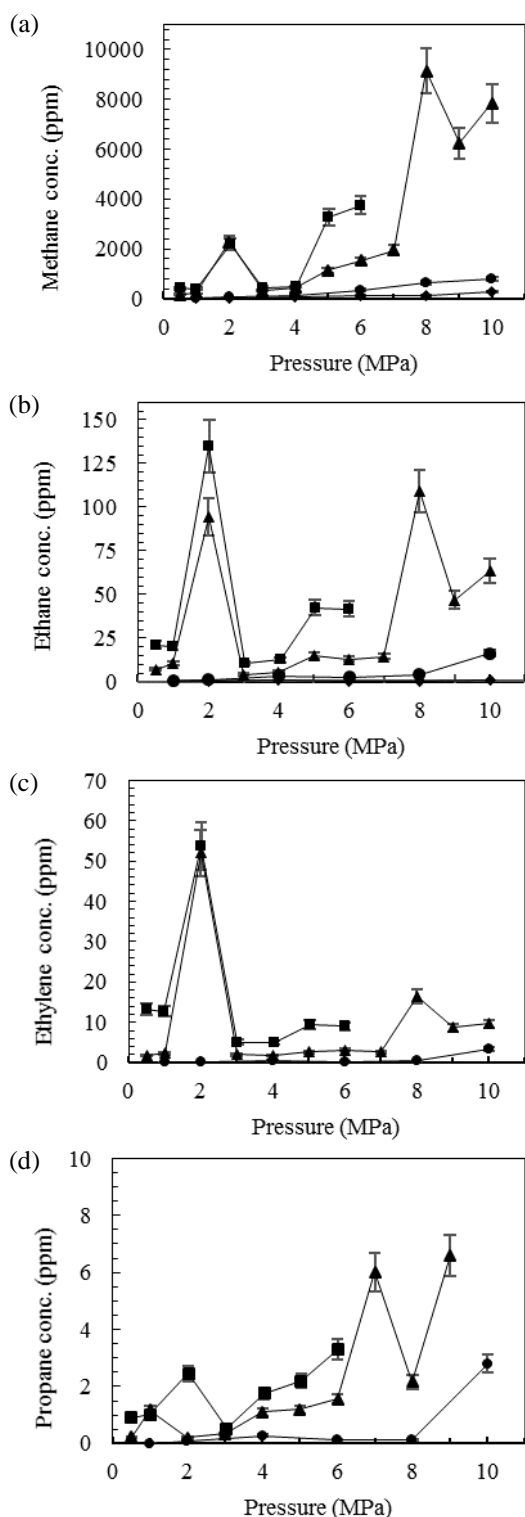
The decreasing trend of the SIE-pressure plots in Figure 4b for pure plasma and plasma-catalysis, which corresponds to the increasing concentration-pressure trends in Figure 3, suggests that more energy was expended on synthesis processes than bulk gas heating, with an opposite trend suggested at lower pressures.

The SRE-pressure plot trends in Figure 4c typically show that less energy was used to produce a mole of methane at higher pressures for the 60 s study, which when coupled with the plateauing voltage-pressure curves between 8 and 10 MPa (Figure 4a), indicate that higher energy efficiency was obtained at higher pressures. For the 60 s study at 2 MPa, the maximum C_2 yields for plasma-catalysis corresponded to a SRE value of 2148 $MJ/mol_{CH4,prod}$, which was ~18 times lower than pure plasma SRE value of 38 961 $MJ/mol_{CH4,prod}$.

Fig. 3. The influence of pressure on hydrocarbon concentration for plasma-catalytic FTS at a discharge time of 60 s; (a) methane, (b) ethane, (c) ethylene and (d) propane. **Legend:** ■ – 6 wt% Co; ▲ – 2 wt% Co; ● – pure plasma; ♦ – blank. **Operating conditions:** Syngas 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 ±11%.

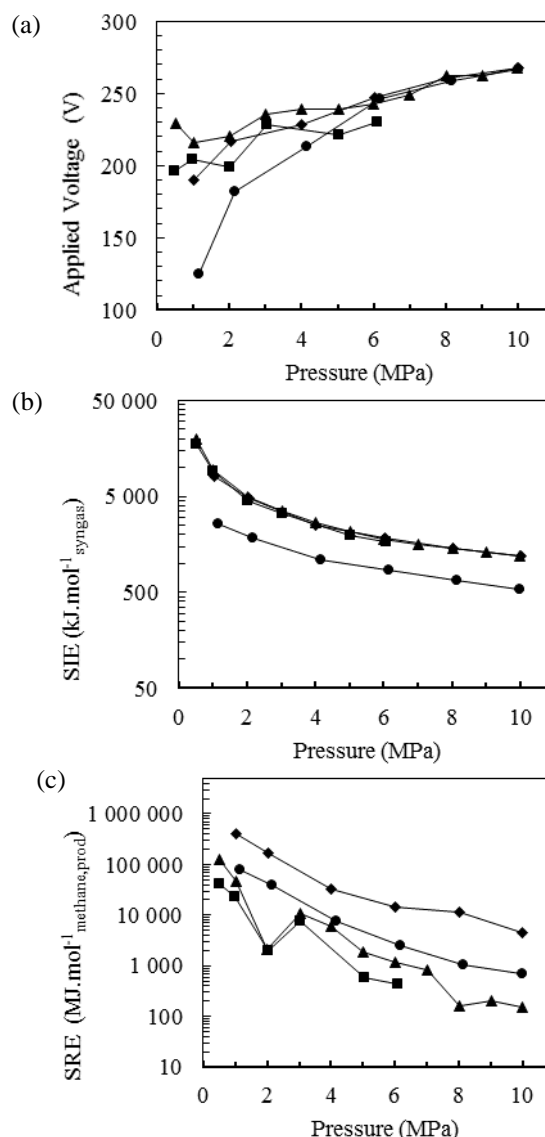Fig. 4. The influence of pressure on (a) applied voltage, (b) specific input energy (kJ/mol$_{syngas}$), and (c) specific required energy (MJ/mol$_{methane,prod}$) for pure plasma and plasma-catalytic FTS (NTP + blank, 2 or 6 wt% Co catalyst) at a discharge time of 60 s. **Legend:** ■ – 6 wt% Co; ▲ – 2 wt% Co; ♦ – blank; ● – pure plasma;. **Operating conditions:** Syngas (H$_2$/CO) ratio: 2.2:1; current: 350 mA; inter-electrode gap: 1 mm; wall temperature: 25°C.

For all the four systems investigated, the breakdown voltages required for syngas and ignition of an arc discharge increases with the operating pressures. The plasma-catalytic voltages differed from that of pure plasma, especially below 6 MPa, due to the lower bulk gas volume caused by the presence of the catalyst.

IV. CATALYST CHARACTERISATION

The SEM micrographs of the inner surfaces of the 6 wt% Co fresh and used catalysts, shown in Figure 5a, reveal larger cobalt clusters for the fresh (calcined/reduced) catalyst (a similar trend was seen for the fresh 2 wt% Co catalyst, not shown here).
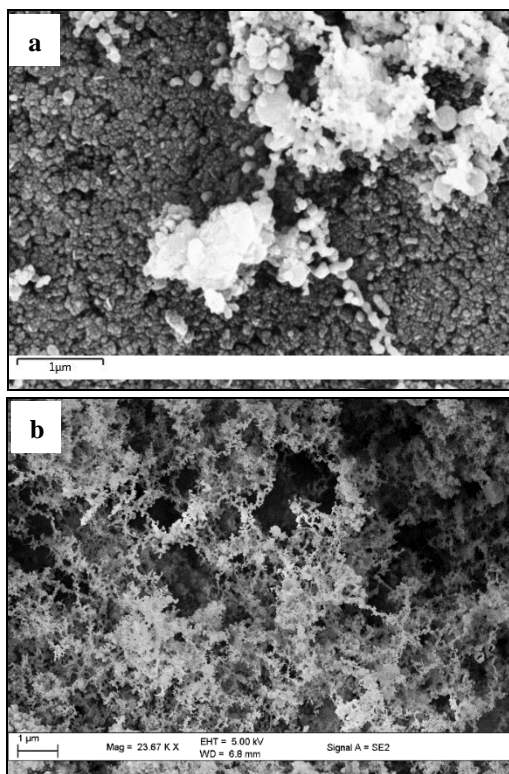

Fig. 5. SEM micrographs of 6 wt% Co catalysts; (a) fresh catalyst, (b) used catalyst.

In contrast, smaller and more highly dispersed clusters are visible on the used 6 wt% Co catalyst (Figure 5b). Greater cobalt dispersion for the used catalyst may have resulted from plasma-catalytic interactions coupled with the high operating pressures [9].

TEM analysis revealed the presence of carbon nanotubes (CNTs) on the used 6 wt% Co catalyst, as seen in Figure 6. This was not anticipated as CNTs are not produced in conventional FTS due to low temperature operation. Furthermore, the 6 wt% Co catalyst produced less carbon deposits near the electrode tips than the 2 wt% Co catalyst, resulting in a more stable arc discharge.
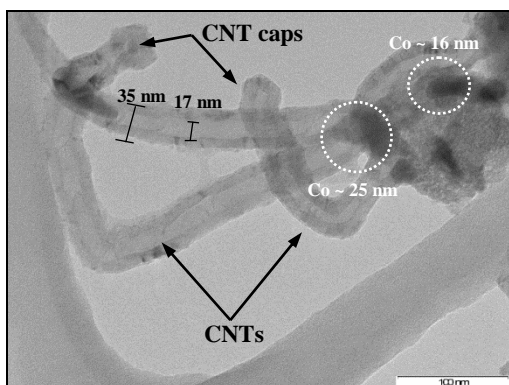

Fig. 6. TEM micrographs of carbon nanotubes (CNTs) detected on the used 6 wt%-Co/Al_2O_3 catalyst.

V. CONCLUSIONS

The hydrocarbon concentration-pressure results indicated that the highest cobalt loading of 6 wt% Co produced higher C_1-C_3 hydrocarbons yields than the other systems: 6 wt% Co > 2 wt% Co > pure plasma > blank. In addition to higher yields, the 6 wt% Co catalyst also led to higher olefinicity, improved C_2 and C_3 chain growth, and lower energy consumption (SRE), as well as exclusively synthesising propylene and carbon nanotubes.

The positive influence of the higher cobalt loading in plasma-catalytic FTS merits the investigation of loadings in the range of conventional FTS (10 and 40 wt%). Moreover, the effectiveness of plasma-catalysis in relation to pure plasma FTS, using the high pressure arc discharge reactor, provides an incentive to investigate other synthesis applications using this technology.

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