



## Synthesis and evaluation of pelletized Co/Al<sub>2</sub>O<sub>3</sub> catalyst for synthetic crude oil production via Fischer-Tropsch process

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### ABSTRACT

The global energy crisis, exacerbated by the depletion of fossil resources and the impacts of climate change, underscores the urgent need for a transition to renewable energy systems. The Fischer-Tropsch process presents a viable solution for producing synthetic fuels by converting syngas (H<sub>2</sub> and CO) into longer-chain hydrocarbons, suitable for various fuels and chemical products. This study focuses on the synthesis of an efficient and cost-effective catalyst, evaluating its performance in a Fischer-Tropsch reaction within a continuous-flow reactor aiming a process integration within hydrogen-rich gas production. In this study, a 20% Co/Al<sub>2</sub>O<sub>3</sub> catalyst was synthesized via the impregnation method and evaluated in Fischer-Tropsch synthesis to produce synthetic crude oil. Characterization confirmed successful impregnation of the active phase, with minimal alteration to the material's morphology following thermal treatment. The reaction tests demonstrated an average CO conversion rate exceeding 80%. The liquid fraction analysis revealed a significant presence of aliphatic hydrocarbons, primarily in the C<sub>16</sub> to C<sub>26</sub> range.

**Keywords:** Fischer-Tropsch; heterogeneous catalysts; hydrogen; synthetic crude-oil;

### INTRODUCTION

The global energy crisis, driven by the depletion of fossil resources and intensified by climate change, necessitates an urgent transition to renewable energy systems. The shift to renewable energy is crucial for achieving a sustainable future with reduced environmental impact, as outlined in the goal 7 of the 2030 Agenda for Sustainable Development of United Nations. This goal serves as a guide for global efforts to address the climatic, environmental, and social challenges of the 21st century [1].

Thus, technologies for low-carbon synthetic fuels production, are favored due to their ability to integrate with existing infrastructures, allowing for a gradual replacement of the energy matrix across various energy-demanding sectors, besides being crucial for mitigating climate change [2]. The Fischer-Tropsch process is a promising technology for producing synthetic fuels by converting syngas (H<sub>2</sub> and CO) into longer-chain hydrocarbons, which can be used to produce various fuels and chemical products [3].



Syngas production is currently dominated by fossil sources all over the world, but countries like Brazil have significant renewable energy potential on account its agro-industrial capacity, combining renewable resources with increasingly efficient processes [4]. This combination points to an increasingly promising scenario for both the control of processes inherent to the Fischer-Tropsch reaction and the research on catalyst materials, which are essential for the synthesis of synthetic crude oil [5]. Thus, the present study aims to synthesize an efficient and cost-effective catalyst and evaluate its performance in a Fischer-Tropsch reaction within a continuous-flow reactor. The reaction conditions will be based on literature precedents, with the goal of integrating this process into systems that produce hydrogen-rich renewable syngas.

## MATERIALS AND METHODS

### Catalyst synthesis and characterization

To the 20wt% Co/Al<sub>2</sub>O<sub>3</sub> synthesis the impregnation method was applied. For that, 50g of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O was dissolved in 150 mL of ultrapure water, followed by the addition of 40 g of pelletized Al<sub>2</sub>O<sub>3</sub> spheres (3 mm, Sigma-Aldrich). The solution was kept under constant stirring (100 RPM) for 2 hours and the excess water was removed in a rotary evaporator under vacuum (60°C). Thereon, the catalytic precursor was dried overnight at 110 °C in an oven and subsequently calcined at 600 °C for 6 hours in atmospheric air.

The fresh catalyst was characterized by scanning electron microscope equipped with energy dispersive spectrometer (SEM-EDS), X-ray fluorescence (XRF), thermogravimetric analysis (TGA) and N<sub>2</sub> adsorption/desorption isotherms analysis at –196 °C.

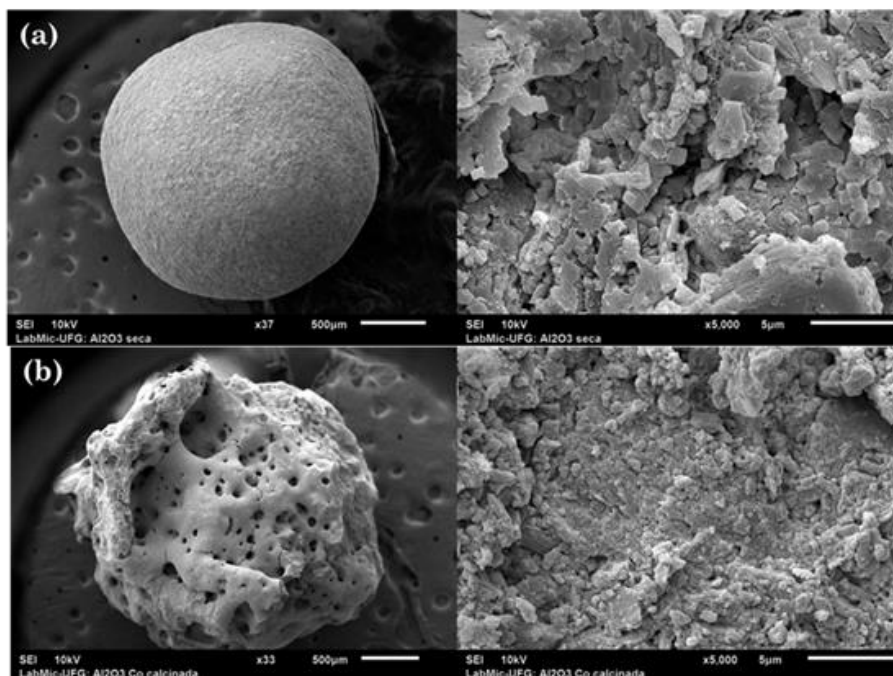
### Fischer-Tropsch synthesis

A long-term test (48 hours) was conducted in a continuous flow reactor (Parr Instruments) loaded with 15g of fresh catalyst that was subsequently reduced in an H<sub>2</sub> atmosphere. The internal reactor temperature was set to 200°C, the system pressure was set to 20 bar, and the chosen feed flow rates were 15, 30 and 15 mL/min to H<sub>2</sub>, CO, and N<sub>2</sub>, respectively. During the reaction test, gaseous fractions were collected from the outlet line in gasometric ampoules and subsequently analyzed via gas chromatography coupled with TCD and FID detectors (GC-TCD/FID) to evaluate the CO conversion. At the end of the experimental test, the liquid fraction of the product formed was collected from the phase separator and subjected to chemical characterization by gas chromatography coupled with mass spectrometry (GC-MS).

## RESULTS AND DISCUSSION

The catalyst produced was characterized by SEM-EDS for morphological evaluation, as shown in **Fig. 1**. The alumina used as the metallic support exhibited a regular, spherical surface prior to metal impregnation. In contrast, after impregnation and calcination, the catalyst displayed an irregular surface with prominent cavities.

The results of the textural properties of the materials are presented in **Table 1**. The modification of the material's structure through the impregnation and calcination process is evidenced by the reduction in specific surface area and the increase in pore diameter on the surface.



**Figure 1.** SEM images of (a) catalytic support  $\text{Al}_2\text{O}_3$  and (b) calcined catalyst  $\text{Co}/\text{Al}_2\text{O}_3$

The analysis of the isotherms for both materials demonstrated that the impregnation of the active phase did not alter the mesoporous nature of the material, characterized by the presence of pores with rigid agglomerates and a uniformly spherical appearance.

**Table 1.** Textural properties of catalyst and support

	Specific Surface Area ( $\text{m}^2/\text{g}$ )	Pore Volume ( $\text{cm}^3/\text{g}$ )	Average pore diameter ( $\text{\AA}$ )
$\text{Al}_2\text{O}_3$	128,28	0,41	10,26
$\text{Co}/\text{Al}_2\text{O}_3$	8,93	0,27	64,76

The XRF results indicate the presence of the major composition of oxides in support and catalyst synthesized, as detailed in **Table 2**. The mass percentage represented by the loss on ignition (LOI) of the samples may indicate the presence of binding materials in the catalytic support, as well as moisture and other impurities. The catalytic support shows a higher LOI fraction, which is consistent with a 16% mass loss observed in TGA analysis related to moisture or water content. The prepared catalyst exhibited CoO weighty percentage of 24.25%, which means the cobalt content of approximately 19.07 wt%. This result suggests that the metal impregnation on the catalytic support is satisfactory and close to the theoretical nominal value (20 wt%), demonstrating that this is a simple, rapid, and efficient method for synthesizing heterogeneous catalysts.

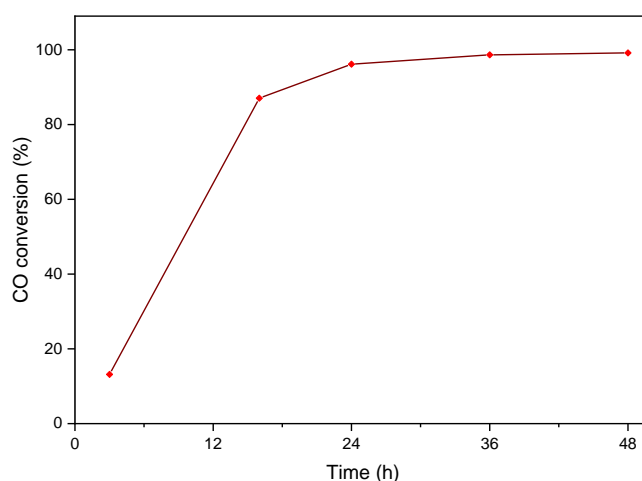


**Table 2.** Chemical composition of major oxides analyzed

	Dry Al <sub>2</sub> O <sub>3</sub> (%)	Calcined Co/Al <sub>2</sub> O <sub>3</sub> (%)
Al <sub>2</sub> O <sub>3</sub>	91,38	71,72
CoO	<LQ*	24,25
LOI**	8,94	4,01

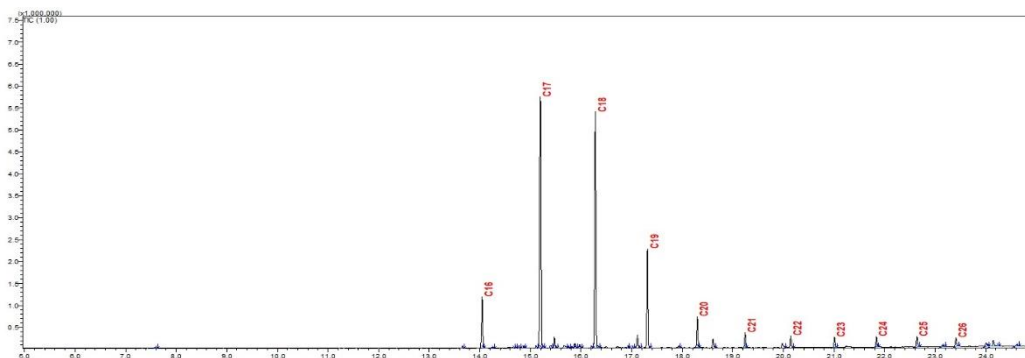
(\*) below the limit of quantification; (\*\*) = LOI at 1000°C.

**Fig. 2** presents the CO conversion graph over time, provided from the GC-TCD/FID analysis of outlet gas stream of FT reactor. It is observed that CO conversion tends to increase over time, reaching over 80% within the first 16 hours and stabilizing at values above 97% after 24 hours of testing. From this point onward, the CO conversion remained stable for the remaining 24 hours of the experiment. Some compounds also identified in the gaseous products included CO<sub>2</sub> and CH<sub>4</sub>.



**Figure 2.** CO conversion over time for the FT reaction.

Upon completion of the test, the entire liquid sample accumulated in the reactor's phase separator was collected and separated by decantation under refrigeration to isolate possible fractions of water, oils, and waxes. The oily phase was the major fraction and was subjected to GC-MS analysis under a gradual temperature ramp for the qualitative characterization of the formed compounds, as shown in **Fig. 3**.



**Figure 3.** GC-MS results for synthetic crude oil sample.



The results demonstrated the remarkable production of aliphatic hydrocarbons with carbon chains ranging from C<sub>16</sub> to C<sub>26</sub>, compounds of significant interest in fuel synthesis. Despite this promising outcome, further investigations are required regarding catalytic stability and product yield, as well as the evaluation of using renewable syngas as a feedstock for the process.

## CONCLUSION

The results showed that the impregnation method of the catalytic precursor on pelletized Al<sub>2</sub>O<sub>3</sub> support was satisfactory, as indicated by the material's morphological characterization and the resulting chemical composition. This clearly suggests that the method is an important approach for rapid and low-complexity syntheses. Furthermore, the experimental evaluation of the catalyst under bench-scale conditions in a continuous flow reactor demonstrated activity for the formation of synthetic crude oil with aliphatic carbon chains between C<sub>16</sub> and C<sub>26</sub> via Fischer-Tropsch synthesis. This outcome is promising, as it indicates the potential to integrate advanced technologies to produce new sustainable energy matrices. However, significant progress is still needed in improving efficiency, the potential integration with alternative renewable hydrogen production technologies, and the feasibility of industrial-scale application—critical goals for advancing new sustainable technologies in the context of energy transition.

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