

Article

Utilization of Iron Foam as Structured Catalyst for Fischer–Tropsch Synthesis

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Abstract

This work focuses on the fabrication, characterization, and performance of a structured iron catalyst to produce hydrocarbons by the Fischer–Tropsch synthesis (FTS). The structured catalyst enhances the heat and mass transfer and provides a larger surface area and lower pressure drop. Iron-based structured catalysts indicate more activity in lower H₂/CO ratios and improve carbon conversion as compared to other metals. These catalysts were manufactured using the sponge replication method (powder metallurgy). The performance of the structured iron catalyst was assessed in a fixed-bed reactor under industrially relevant conditions (250 °C and 20 bar). The feed gas was a synthetic syngas with a H₂/CO ratio of 1.2, simulating a bio-syngas derived from lignocellulosic biomass gasification. Notably, the best result was reached under these conditions, obtaining a CO conversion of 84.8% and a CH₄ selectivity of 10.4%, where the catalyst exhibited a superior catalytic activity and selectivity toward desired hydrocarbon products, including light olefins and long-chain paraffins. The resulting structured catalyst reached a one-pass CO conversion of 84.8% with a 10.4% selectivity to CH₄ compared to a traditionally produced catalyst, for which the conversion was 18% and the selectivity was 19%, respectively. The results indicate that the developed structured iron catalyst holds considerable potential for efficient and sustainable hydrocarbon production, mainly C10–C20 (diesel-range hydrocarbons), via Fischer–Tropsch synthesis. The catalyst's excellent performance and improved stability and selectivity offer promising prospects for its application in commercial-scale hydrocarbon synthesis processes.

Keywords: biomass to liquids; Fischer–Tropsch synthesis; structured catalyst; biofuels; syngas



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1. Introduction

The transportation sector accounts for approximately 16% of the world's energy consumption and more than a third of CO₂ emissions from end-use sectors [1–4]. However, due to the urgent need to reduce carbon emissions and promote sustainable mobility, there is a growing interest in developing low-carbon intensity fuels [5–8]. The combustion of fossil fuels leads to the emission of greenhouse gases, which cause climate change and raise global concerns. Thus, alternative processes for producing renewable energy have been developed to meet the growing demand for energy [9]. One promising approach is the biomass-to-liquid (BTL) processes, which convert lignocellulosic biomass into liquid fuels

via thermochemical reactions [10–13]. Bio-syngas could represent a suitable option as a synthetic fuel to replace non-renewable and fossil fuels.

One of the most well-known BTL routes involves using the syngas produced from biomass gasification. This syngas can then be converted into hydrogen, methanol, or synthetic fuels through different catalytic processes [14,15]. The Fischer–Tropsch synthesis (FTS) is often used to convert syngas into liquid fuels [16–18], and it has been widely utilized as a sustainable process for synthetic liquid fuel production [9]. The main operational conditions that influence the gas conversion and product distribution are the temperature (200–350 °C), pressure (10–40 bar), and H_2/CO ratio, which can vary depending on the syngas resource [18]. It has also been reported that temperatures of 220–350 °C and pressures of 15–40 bar are optimum FTS process conditions [9]. FTS involves hydrogenating carbon monoxide to produce hydrocarbons which is usually done using heterogeneous, solid metallic catalysts [19,20]. Cobalt and iron are the two most commonly used catalysts for FTS due to their commercial viability. The former is known for having an activity level four times higher than iron, but it can only be used within a very narrow temperature range (from 220 to 250 °C) and syngas composition ($H_2:CO$ ratio of 2 to 2.5) [1,21,22]. However, the syngas produced from biomass is often hydrogen-deficient, so obtaining a suitable syngas for FTS is challenging. Iron promotes the water–gas shift (WGS) reaction that occurs simultaneously with the main reaction and is preferred for a lower H_2/CO ratio, which is typical of biomass-derived syngas [23]. It has been reported that iron-based catalysts are suitable for a low H_2/CO ratio syngas and emphasize the role of promoters on the WGS activity [24]. Using an iron catalyst in a CO_2 -containing syngas FTS resulted in an 82–85% CO conversion and up to 74% selectivity toward C_5+ hydrocarbons under a low H_2/CO ratio [25]. Using iron catalysts, it has been found that decreasing the H_2/CO ratio from 2 to 1.2 significantly improves the olefin selectivity, reduces methane formation, and increases the CO conversion by up to 85% [26]. Additionally, iron has a higher thermal resistivity than cobalt and is more abundant, making it more economical for large-scale industrial applications. This difference is reflected in global market prices (Co: USD 35,000/ton vs. Fe: USD 120/ton). Therefore, considering iron as a BTL catalyst is an interesting alternative, as emphasized in [1,9]. The reactor design is another key factor in the efficiency and product distribution of the FTS process. The Slurry Bubble Column Reactor (SBCR) has been used mainly on a commercial scale by companies such as Shell and Sasol. While fixed-bed reactors are more common at lab and pilot-scale systems due to their simplicity and easier operation [27,28]. Furthermore, FTS presents challenges that must be addressed. The reaction is exothermic, so careful temperature control is required to optimize the production of the desired hydrocarbons [29,30]. CO_2 -rich syngas activation is reported to affect the iron carbide formation and product selectivity by improving the production of valuable products such as C_5+ and limiting the formation of undesired products such as CH_4 and C_2 – C_4 [31]. Additionally, side reactions, such as methanation and WGS reactions, can affect the overall efficiency of the process [32]. Furthermore, supported catalysts used for FTS may experience problems related to mass and heat transfer, such as internal mass transfer limitations and high pressure drops [27,33,34].

To address these issues, structured catalysts are being explored as an alternative to traditional supported catalysts. These catalysts are pre-shaped ceramic or metallic substrates that offer improved heat and mass transfer, reduced pressure drops, and larger geometric surface areas [35]. Structured catalysts have shown promising results in environmental catalysis applications, such as reducing nitrogen oxides in power plant emissions and controlling car exhaust emissions.

Several studies have demonstrated the feasibility of performing Fischer–Tropsch synthesis (FTS) using structural catalysts, including monoliths and foams [36–44]. However,

the active phase of these catalysts is often cobalt supported on a ceramic, which can negatively impact the bio-syngas conversion to biofuels due to the low thermal conductivity and low activity at low H_2/CO ratios. Plus, Fe-based structure catalysts demonstrated an improvement in terms of carbon conversion in the FTS-based method, using biomass-derived syngas as the feed gas [45]. Adding promoters such as Si, Al, and Zn to the iron-based catalyst for FTS is reported to have a notable effect on the catalyst's textural properties, reduction, carburization, activity, and selectivity. The structural modification was found to increase the extent of the reduction and CO carburization, specifically in the CO_2 -rich feed. The modified structure with Zn was found to increase CO conversion up to 33.69% and decreased the methane content to 8.5%. However, the catalyst structure using the Si additive indicated a low CO conversion and a high methane selectivity. Thus, the structural modification for iron-based catalysts used in FTS should benefit from a high carburization ability and high oxidation resistance to be suitable for CO_2 -rich syngas derived from biomass [24]. It has been reported that using structured catalysts, metallic foams such as Co/Cu_{foam} , indicated a higher activity and selectivity for C_5+ compared to $Co/Al_2O_3-SiO_2$, which is often used as a reference catalyst. Metal foam structures improve the thermal activity, which leads to chain propagation improvements and the suppression of methane formation [36]. To our knowledge, few studies have focused on Fe-based catalysts [46], hence, the general goal of this work is to design and evaluate iron-based structural catalysts for converting bio-syngas into renewable liquid fuels. Specifically, this study aims to investigate the feasibility of using a structured iron-based catalyst in the form of a metallic foam for Fischer–Tropsch synthesis (FTS) under hydrogen-deficient conditions, which are typical of biomass-derived syngas. This study aims to address key challenges associated with conventional powder catalysts, such as poor heat and mass transfer, a low selectivity to heavier hydrocarbons, and limited suitability for low H_2/CO ratios, by synthesizing and evaluating an Fe foam catalyst in a fixed-bed reactor. This study will determine if the open-cell metallic structure improves the catalyst's performance and selectivity.

2. Materials and Methods

2.1. Catalyst Preparation and Characterization

2.1.1. Catalyst Preparation

The structured catalyst used in this study was iron foam manufactured using the sponge replication method with a polyurethane (PU) foam as the template. Iron (composition: 95% Fe, 2% Fe_2O_3 , 200 mesh, Fisher Scientific (Alfa Aesar), Ottawa, ON, Canada) was used as the metallic precursor. The template used to generate the structure was a PU foam typically used as an air filter, with a pore count of 50 pores per linear inch (PPI) and a void fraction of approximately 95% that was bought at the local hardware store. The foam was 14 cm thick and cut into a disk with a diameter of 24 mm. The sponge replication method started with a slurry of the metallic precursor. A polymeric solution serves as the slurry's solvent. The components were sodium carboxymethyl cellulose (1% wt., M_w 700,000, Sigma-Aldrich, Oakville, ON, Canada), which increased viscosity; polyvinyl alcohol (6% wt., low molecular weight, Alfa Aesar), which served as a binder between the powder and template; and alginic acid sodium salt (0.5% wt., low viscosity, Alfa Aesar), which served as a dispersant. The components were selected based on their wide application in ceramic and metallic foam replication methodologies to be compatible with water-based systems, burnout facility, and uniform coating formation on polymer structure as reported in similar studies on Fe-based foam synthesis [47]. To prepare the polymeric solution, distilled water was heated to 80 °C. Then, CMC was added, and the solution was stirred at 300 rpm until homogenized using a magnetic stirrer. Then, the tem-

perature was reduced to 50 °C. Polyvinyl alcohol was added, and, once dissolved, sodium alginate was added [48,49]. Once a homogeneous solution was obtained, the temperature was reduced to 22 °C, after which, iron powder (60% wt.) was added. The metallic slurry was stirred manually, and to coat the template, the PU foam was left to soak in the slurry for 30 min. Then, the foam was removed from the slurry, drained, and pressed between two sheets of absorbent paper to remove excess slurry [47,48,50]. The foams were left to dry overnight at room temperature. Finally, the dry-coated foam was sintered to obtain the metallic structure. The heating ramp used for sintering went as follows: 5 °C/min up to 375 °C, followed by a 30 min plateau to burn the PU template. Then, it was heated at 10 °C/min up to 1200 °C, followed by a 2 h isotherm. The heating ramp was carefully selected to control PU decomposition to ensure structural integrity [51].

2.1.2. Catalyst Characterization

The microstructure of the cross-sections of the Fe foams was characterized by scanning electron microscopy (SEM—FEG—EDS, Hitachi S-4700, Hitachi High-Tech Corporation, Tokyo, Japan). The foam was cleaned in an ultrasonic bath and blow-dried to ensure that the loose particles were removed from the surface. A two-dimensional cross-sectional image of the foam was captured and post-processed to determine the strut size of the final structure, in addition to the grain size and shape of the final structure.

The void fraction of the foam was measured using Equation (1), where ρ_s [g/cm³] is the iron density, and ρ_b is the foam's bulk density, measured by the Buoyancy Method.

$$\varepsilon = 1 - \frac{\rho_b}{\rho_s} \quad (1)$$

The catalyst's specific surface area was measured by nitrogen physisorption (ASAP 2020, Micromeritics, Norcross, Georgia) based on ASTM D3663 [52]. To perform the measurement, a piece of iron foam was placed on the sampling cell and outgassed overnight. Then, a 3-point N₂ BET (Brunauer–Emmett–Teller) isotherm was measured at −196 °C.

XRD (X-ray diffraction) analysis was performed to identify the metal phase in the catalyst following the ASTM D3906 standard method [53]. The catalyst sample was manually ground in an agate mortar until a grain size of ≤ 45 μm was obtained. Then, the sample was placed in an XRD spectrophotometer (X-per Pro MPD, Panalytical, Almelo, the Netherlands), where the analysis was performed from 14° to 100° for 2 θ . Cu radiation was used as an X-ray source generated at 40 kV and 10 mA. Scans were taken with a 2 θ step size of 0.04°, and a counting time of 1.0 s was used to obtain the diffractogram. The MDI JADE software package (version 9.3) was used to determine the phase composition in the samples with the Rietveld analysis.

Catalyst reducibility was determined by TPR (temperature-programmed reduction) analysis. The experiment was conducted in a 1/2" tubular quartz fixed-bed reactor, and the gas samples were analyzed using a GC equipped with a TCD. The reduction gas mixture of 10% H₂/N₂ was made to flow across 300 mg of the Fe foam under gradually increasing temperature (10 °C·min^{−1}) from 196 °C to 970 °C, resulting in a qualitative co-relationship between reduction rate and temperature.

2.2. Catalyst Test

The Fe foams were stacked inside the reactor to form a catalytic bed approximately 50 to 70 mm high. Each cylinder was 24 mm in diameter and 14 mm in height. The weight of the catalyst in each test was approximately 30 g unless otherwise specified. The catalyst was reduced in situ with a mixture of 70% hydrogen and 30% nitrogen, both with a purity of 99%, at atmospheric pressure. Three reduction temperatures were tested—250 °C, 325 °C,

and 400 °C—to evaluate the stepwise activation behavior of the Fe foam catalysts. These temperatures are related to the reduction sequence from Fe_2O_3 to Fe^0 , and the carbonization occurred above 300 °C. The temperatures below 300 °C led to reduction without much carbide formation, while 325 °C is reported as an optimum temperature to form FeCx without extra sintering [54]. Additionally, 400 °C was selected to investigate whether deeper reduction could further improve activity. After reduction, the reactor was cooled by flowing the same gas mixture through it. Once the desired reaction temperature of 250 °C was reached, the gas mixture was switched to the desired syngas composition, and the reactor was pressurized to 20 bars. Figure 1 shows a schematic of the reactor and the peripheral components used in this study. The gases (carbon monoxide, hydrogen, and nitrogen) came from compressed gas cylinders. Electronic mass flow controllers (one for each gas) fed the gases to the reactor, ensuring a fixed composition for each experimental run. Before entering the reactor, the gases passed through a static mixer. The reactor's outlet leads to a gas–liquid separator. A backpressure regulator was installed at the end of the piping system to maintain a stable operating pressure throughout the experiment. Non-condensable gas samples were collected for gas chromatography (GC) analysis, and the remaining gas was purged to the ventilation system under atmospheric conditions. The liquid product, consisting of water and hydrocarbons, was collected in a trap beneath the reactor.

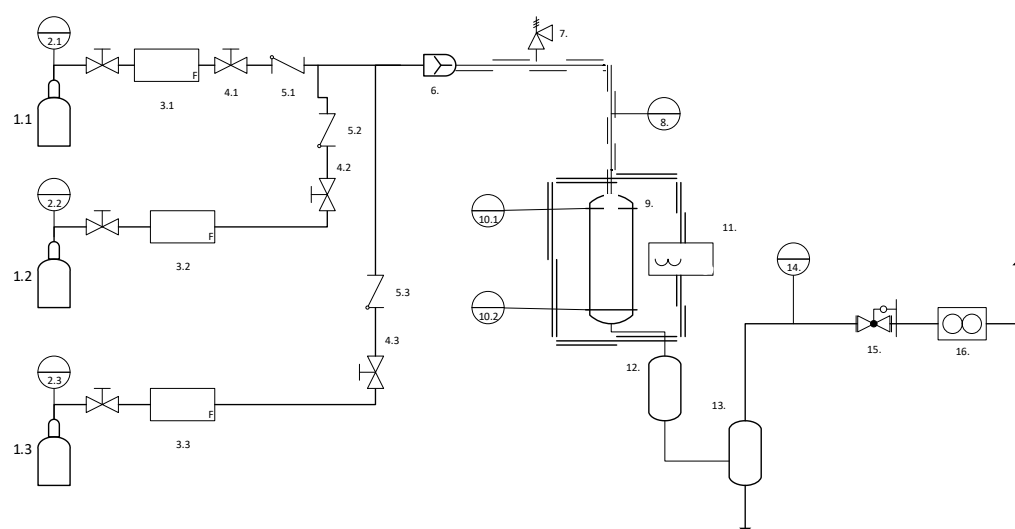


Figure 1. Simplified flow diagram for Fisher-Tropsch reactor and peripheral components. 1.1–1.3 Gas cylinders; 2.1–2.3 pressure regulators; 3.1–3.3, mass flow controllers (F); 4.1–4.3 valves; 5.1–5.3 check valve; 6. pressure gauge; 7. relief valve; 8. bypass valve; 9. tube and shell catalytic reactor; 10.1–10.2 temperature sensors; 11. oven; 12. separation column (hot trap); 13. separation column (cold trap); 14. pressure gauge; 15. backpressure regulator; and 16. gas flow counter.

The reactor was a stainless steel 316 tube with an internal diameter of 26 mm and a height of 500 mm and it was heated by a clamshell oven. In this process, the tail gas was not recirculated to the reactor, and no inert compounds were accumulated. The reactor does not have a cooling system and was equipped with two thermocouples that measured the temperature at the top and bottom of the catalytic bed [1]. A stainless steel mesh was placed before and after the catalytic bed to maintain the catalyst position. The gas effluent composition was determined by gas chromatography (GC) analysis using a Bruker Scion 456-GC equipped with two columns, a Molsieve (13X, 80/100 mesh, 1.5 m × 1/8 in. IS) and a Hayesep (N, 80/100 mesh, 0.5 m × 1/8 in. IS), as well as a TCD and an FID. The program used to process the data was Compass CDS with external standards (ASTM D1946 and ASTM D2163 [55,56]). The catalyst's performance was determined based on CO

conversion (X_{CO}), as well as CO_2 and CH_4 selectivity (S_{CH_4} , S_{CO_2} , and $S_{C_{5+}}$, respectively) using Equations (2)–(4).

$$X_{CO} = \left(1 - \frac{F_{CO,out}}{F_{CO,in}}\right) \cdot 100 \quad (2)$$

$$S_{CH_4} = \left(\frac{F_{CH_4,out}}{F_{CO,in} - F_{CO,out}}\right) \cdot 100 \quad (3)$$

$$S_{CO_2} = \left(\frac{F_{CO_2,out}}{F_{CO,in} - F_{CO,out}}\right) \cdot 100 \quad (4)$$

The conversion was calculated based on the product gas analysis for CO , H_2 , CO_2 , and CH_4 , where F indicates molar flow rate [$mol \cdot min^{-1}$].

2.3. Product Characterization

There are two liquid products for FTS: an aqueous phase and an organic phase. To characterize these products, their density and pH were measured. The organic phase was analyzed using an Leco Truspec Micro elemental analyzer as well as using GC-MS based on the ASTM D6730 method [57] using an Agilent 5975 Series MSD coupled to an Agilent 7820A GC (Santa Clara, CA, USA). The GC was equipped with a J&W DB-5MS (nonpolar phenyl arylene polymer) column measuring $15\text{ m} \times 0.25\text{ mm} \times 0.25\text{ }\mu\text{m}$. The autoinjector (Agilent ALS, Santa Clara, CA, USA) operated in 10:1 split mode at $300\text{ }^\circ\text{C}$, and helium served as the carrier gas at a flow rate of 1.2 mL/min . One microliter of the sample was injected. The oven temperature was held at $50\text{ }^\circ\text{C}$ for one minute, then heated to $300\text{ }^\circ\text{C}$ at a rate of $10\text{ }^\circ\text{C}$ per minute. The temperature of $300\text{ }^\circ\text{C}$ was held for 1 min. The aqueous phase was centrifuged and sterile-filtered using a $0.22\text{ }\mu\text{m}$ Chromspec membrane filter. Then, it was analyzed by HPLC based on ASTM D5501 [58] using an Agilent 1100 Series HPLC system (Santa Clara, CA, USA) equipped with a Rezex ROA-Organic Acid H^+ (8%) $300 \times 7.8\text{ mm}$ Phenomenex column. The mobile phase was $2.5\text{ mM H}_2\text{SO}_4$ at a flow rate of 0.6 mL/min . The column temperature was $65\text{ }^\circ\text{C}$ and three calibration curves were made for each compound of interest: ethanol, formic acid, and acetic acid.

3. Results

3.1. Catalyst Properties

Figure 2 shows a photograph of the iron metal structure obtained using the sponge replication method. The replicated metal foams closely resemble the original polyurethane (PU) structure used as template. However, the structure lost a large amount of the void fraction since the excess slurry agglomerated and could not drain from the cells before the binder dried. As shown in Figure 3, clogging occurred in the cells during the coating stage. Consequently, the metallic structure had a substantially reduced permeability, which could be related to the reduction in the void fraction from 0.95 (reported by the manufacturer) to 0.67. This value was calculated using Equation (1) with the bulk density of the metallic foam, $\rho_b = 1154\text{ g/cm}^3$ (measured by the volumetric displacement method), and the iron density, $\rho_s = 7874\text{ g/cm}^3$. Applying a higher pressure (approximately 5–10 kPa) to drain the slurry resulted in around 40% fewer closed cells [1]. Although the higher pressure helps remove the extra slurry and prevents pore blockage, extreme pressure makes the foams much more brittle and can break when packed in the reactor. This is consistent with literature, which reports that optimized draining can influence the foam porosity and stability [59].

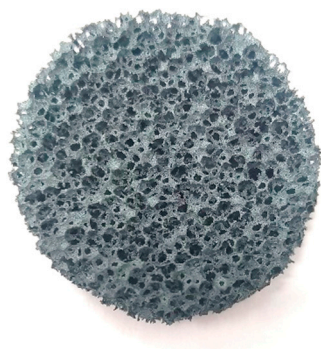


Figure 2. Iron foam as obtained by the sponge replication method.

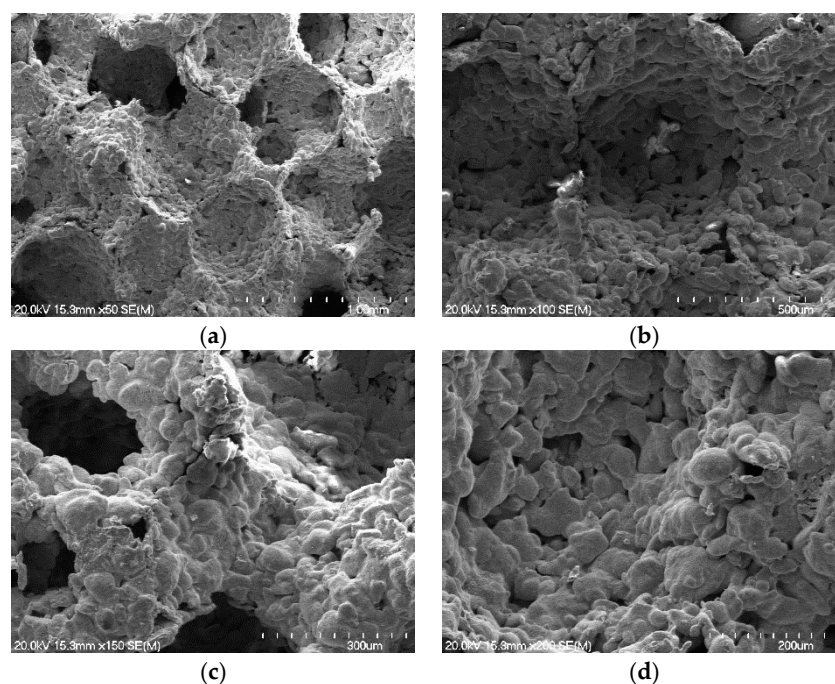


Figure 3. Micrographs of the sintered foams fabricated by the sponge replication method. The template used was PU foams (50 PPI), and the metallic precursor was the iron powder (mesh 200), where (a) the general aspect of the iron foam, (b) the cell-size view, (c) the strut view, and (d) the high magnification of the surface microstructure.

The area measured by the nitrogen adsorption was $3 \text{ m}^2 \cdot \text{g}^{-1}$, which is consistent with reported values for open-cell metal foams that have been sintered without the use of high-surface-area supports [60–64]. The catalyst's low surface area compared to powder catalysts ($20\text{--}80 \text{ m}^2 \cdot \text{g}^{-1}$) is offset by the high volume-to-area ratio achievable with a three-dimensional cellular structure, such as open-cell foams [60,64–66]. Additionally, higher rates of mass and heat transfer are achieved with a greater tortuosity in the catalytic bed.

The three-dimensional shape of the foam provides a high tortuosity and avoids clogging problems (and high pressure drop) through the reactor due to its open structure, which limits the liquid retention caused by the wax adsorption on the catalyst surface [61–64]. The open, metallic cellular structure that dissipates heat more effectively, acts as a thermal conductor, and reduces hot spots. Therefore, the Fe foam structure makes the catalyst less prone to sintering [65,67,68]. This has also been indicated in microfibrinous metal beds used in the FTS process and resulted in a better thermal gradient ($<5^\circ\text{C}$) compared to packed-bed systems ($>50^\circ\text{C}$) [59]. Figure 4 shows the XRD patterns of the Fe foam, which represents the iron phase before the reaction is essentially composed of Fe_2O_3 . It demonstrates Fe_2O_3 diffraction peaks, which confirms that the sintering preserved the hematite phase prior to

the reduction. The absence of the Fe_3O_4 (35.4°) and metallic iron (44.7°) peaks indicates that no reduction occurred during the sintering process. This is because the sintering occurred at 1200°C , and the hematite is thermally stable under oxidizing conditions. Similar trends have also been reported after sintering iron-based catalysts in air [66].

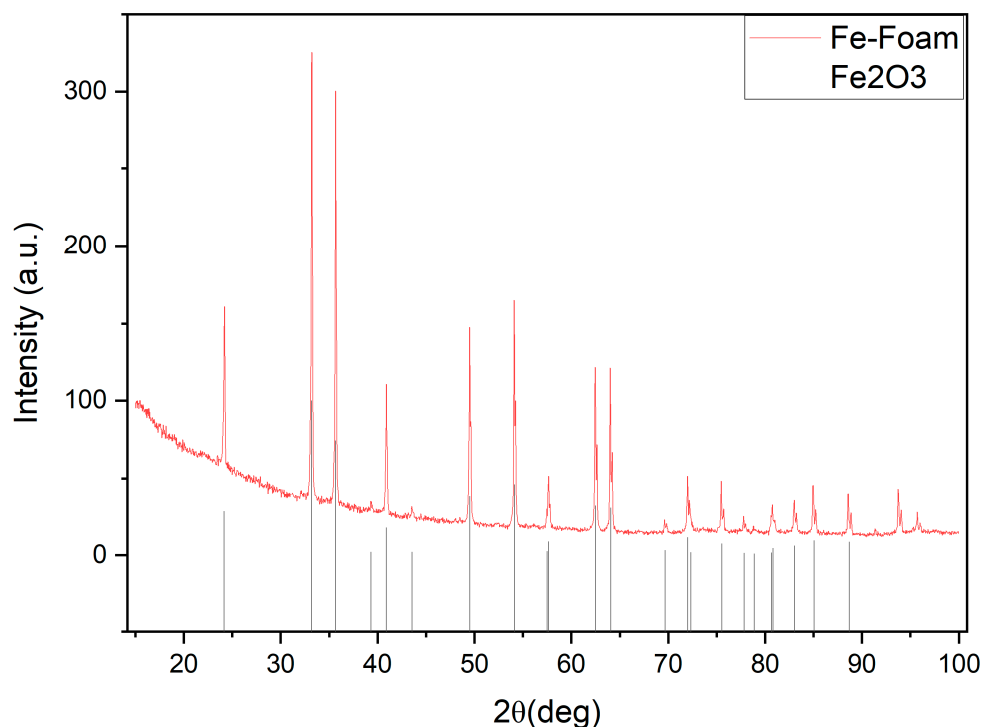


Figure 4. X-ray diffraction (XRD) pattern of Fe foam shown In red is the sample, while in gray is the reported match using the JADE software database.

A TPR analysis was used to characterize the catalyst and Figure 5 shows that the catalyst reduction occurs in four stages within the studied temperature range. The reduction begins at 230°C . The first significant H_2 uptake occurs around 315°C , which corresponds to the reduction of Fe_2O_3 to Fe_3O_4 . The relatively high H_2 consumption of the $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$ step suggests that a large fraction of Fe_2O_3 is present on the surface of the catalyst structure, as indicated by the XRD analysis [1]. The XRD and TPR combination indicates how the $\text{Fe}_3\text{O}_4/\text{Fe}_2\text{O}_3$ variation affects thereducibility and activity. It has been demonstrated that a higher Fe_2O_3 surface content enhances the hydrogen consumption in early TPR stages [69]. This justifies the inference that the high early H_2 uptake points to a surface-rich Fe_2O_3 structure. The next reduction step, $\text{Fe}_3\text{O}_4 \rightarrow \text{FeO}$, was observed at 600°C after which a third hydrogen uptake occurred around 820°C , where FeO is reduced to Fe^0 . A study on TPR profiles of $\text{Fe}/\text{Cu}/\text{K}/\text{Al}_2\text{O}_3$ showed similar multiple reduction steps, $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{FeO} \rightarrow \text{Fe}^0$ [54]. The hydrogen concentration increased to 7% at 900°C and shows that another H_2 uptake occurred close to 970°C , which may be associated with the reduction of the Fe carbide [70–72]. The high temperature H_2 uptake observation could be linked to the carbide transformation and Fe carbide formation [73].

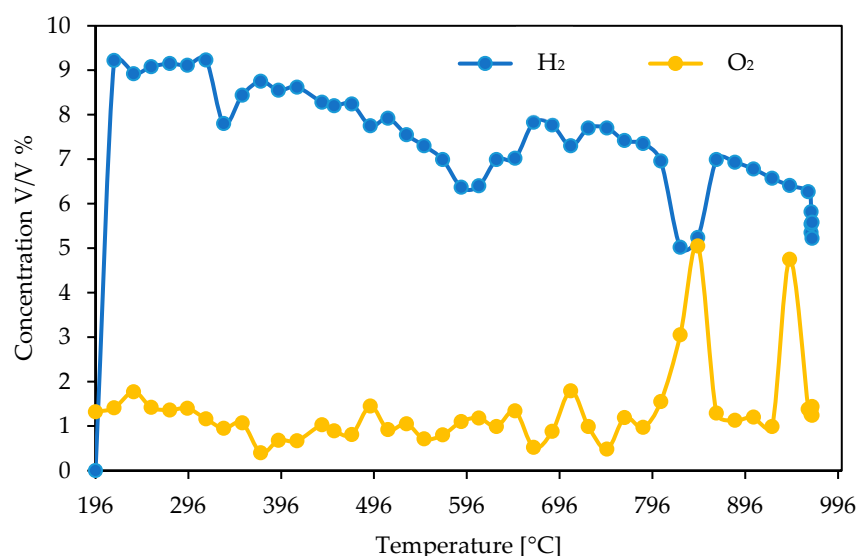


Figure 5. H₂ and O₂ evolution for the temperature program thermal treatment of the Fe foam heated to 970 °C at a heating rate of 10 °C·min^{−1} using a 100 mL/min flow of 10% H₂:N₂.

3.2. Catalytic Performance

The catalytic performance of the Fe foams was evaluated in a fixed-bed reactor for the FTS, and a precipitated catalyst with a similar grain size to the Fe foams was used as reference. To prove the concept, the first set of tests on the Fe foams' capacity as a catalyst for FTS was carried out under conditions more commonly reported in literature (250 °C, 20 bar, and a H₂/CO ratio of 2). Under these conditions, the intrinsic activity of the iron sites resulted in a CO conversion of 18–21% [28,30,74–77]. Both the Fe powder and the Fe foam were reduced in situ under a H₂ flow at 250 °C for 4 h prior to the FTS test. The reactions were carried out at 250 °C with a total pressure of 20 bar, an H₂/CO ratio of 2, and a CO flow of 100 mL/min, corresponding to a gas hourly space velocity (GHSV) of 1200 h^{−1}. Table 1 shows the performance of the two catalysts after 48 h of operation.

Table 1. Comparisons of the conversion and selectivity for Fe foams with the powder Fe/Al₂O₃ catalyst. Conditions: 250 °C, 20 bar, H₂/CO = 2, WHSV = 1200 h^{−1}, and ToS = 48 h.

Run	Catalyst	X _{CO}	S _{CO2}	S _{CH4+}	S _{C3+}
1	Fe powder	17.8	6.0	19.0	74.9
	Fe foam	10.1	7.5	4.57	87.9
2	Fe powder	16.3	6.5	14.0	78.5
	Fe foam	9.6	10.8	10.8	89.1

The low conversion rate was attributed to the short residence time, which resulted from the high void fraction of the foams. Despite the lower conversion as compared to the Fe powder catalysts, the foams resulted in more than 87% selectivity toward C₃+ hydrocarbons, as shown in Table 1, indicating their potential for diesel-range hydrocarbon production [78]. Nevertheless, these results demonstrate the feasibility of using Fe foams as a catalyst for Fischer–Tropsch synthesis, provided that the optimal porosity and WHSV conditions are identified [79,80].

For the second set of tests, the residence time was increased and the catalyst reduction temperature was varied to determine its influence on the catalyst reducibility and the generation of CO hydrogenation sites. The reduction temperatures used were 250 °C, 325 °C, and 400 °C. The other operating conditions were as follows: a catalyst weight of 30 g; a reaction temperature of 250 °C; a pressure of 20 bar; a CO flow of 135 mL/min,

corresponding to a WHSV of 600 h^{-1} ; a syngas ratio ($\text{H}_2:\text{CO}$) of 2; and a time-on-stream of 48 h. Table 2 presents the results of these reactions. It has been reported in literature that a higher reduction temperature favors Fe activation and surface dispersion. However, it can change the selectivity and cause sintering in extreme conditions [81].

Table 2. Conversion and selectivity for Fe foams using different reduction temperatures. Conditions: 250°C , 20 bar, $\text{H}_2:\text{CO} = 2$, WHSV = 600 h^{-1} , and ToS = 48 h.

Temp. Red ($^\circ\text{C}$)	X_{CO}	S_{CO_2}	S_{CH_4}	$S_{\text{C}+}$
400	15.2	4.2	10.1	85.7
325	36.2	18.6	14.7	66.6
250	16.1	3.5	9.7	86.8

For the next set of tests, the syngas ratios were modified since iron can be used for hydrogen-deficient as well as hydrogen-rich syngas. Table 3 shows the performance indicators for Fe foams under the following reaction conditions: a catalyst weight of 30 g; a reduction temperature of 325°C ; a reaction temperature of 250°C ; a pressure of 20 bar; a flow rate of 300 mL/min ; a time-on-stream of 48 h; and different syngas ratio from 1.2 to 2.5, as presented in Table 3 below.

Table 3. Conversion and selectivity for Fe foams at different syngas ratios (1.2–2.5). Conditions: 250°C , 20 bar, WHSV = 600 h^{-1} , and ToS = 48 h.

H_2/CO	X_{CO}	S_{CO_2}	S_{CH_4}	$S_{\text{C}+}$
1.2	84.8	26.2	10.4	63.4
1.6	37.1	10.2	16.7	73.2
2	36.2	18.6	14.7	66.6
2.5	19.9	11.1	18.9	70.0

Figure 6 shows a second run of the reaction with the highest performance ($\text{H}_2/\text{CO} = 1.2$, CO conversion of 84.8%, and CH_4 selectivity of 10.4%), where the reaction was tracked every two hours after reaching the steady state; however, abrupt changes in the performance indicators could not be perceived.

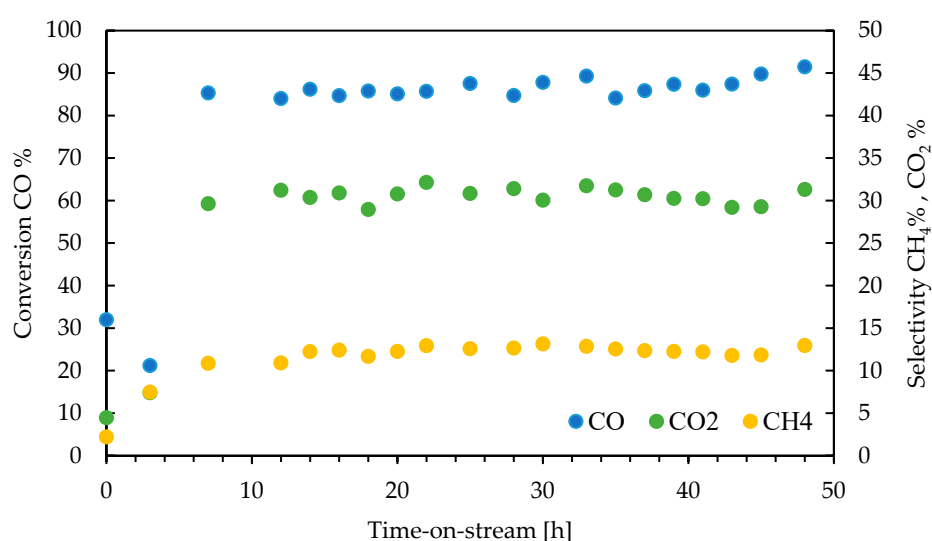


Figure 6. The CO conversion and CH_4 and CO_2 selectivity as a function of the time-on-stream for FTS using the Fe foam as a catalyst. Reaction conditions: $\text{H}_2/\text{CO} = 1.2$, 250°C , 20 bar, WHSV = 600 h^{-1} , and ToS = 48 h.

Figure 7 shows the liquid products obtained from the FTS reaction with different $H_2:CO$ ratios. It is evident that the Fe foam activity increased for the FTS and WGS. The aqueous by-product phase contained oxygenated compounds that, with the water, could potentially be used as an added-value residue [82].

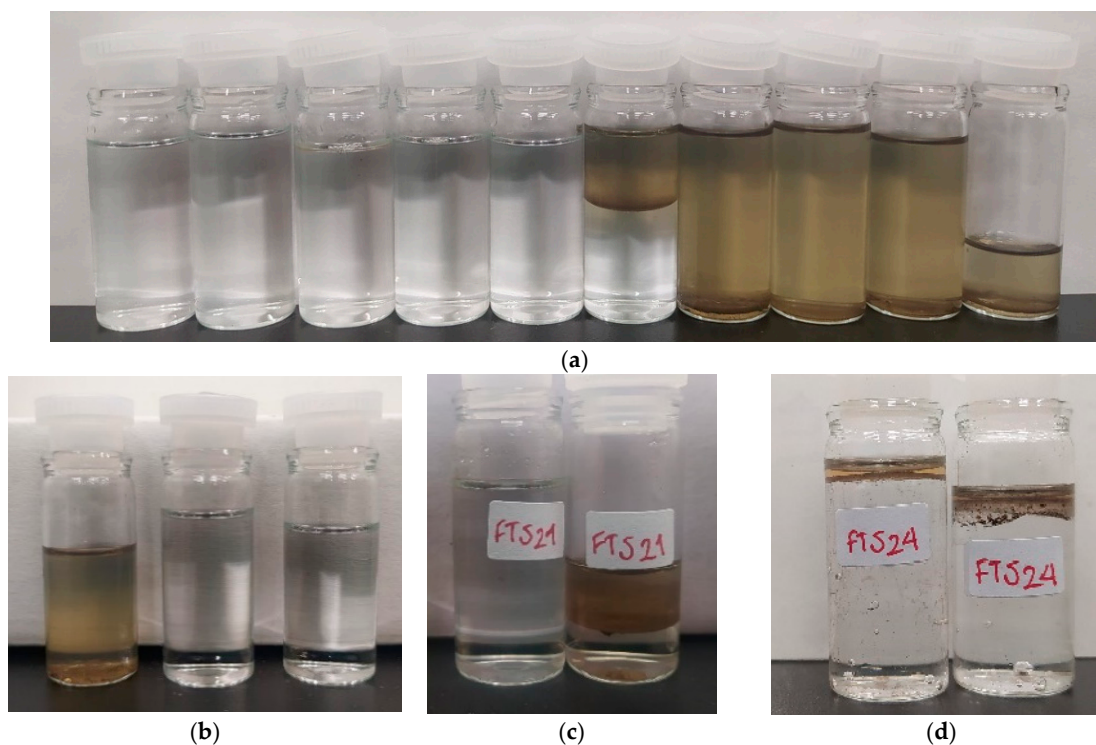


Figure 7. Liquid products of FTS using Fe foam as catalyst. (a) $H_2/CO = 1.2$; (b) $H_2/CO = 1.6$; (c) $H_2/CO = 2.0$; and (d) $H_2/CO = 2.5$. Reaction conditions: 250 °C, 20 bar, WHSV = 600 h^{-1} , and ToS = 48 h.

3.3. Product Analysis

To characterize the liquid products of the FTS process, the density and pH were measured as well as and carried out an elemental analysis of the oil phase. The oxygenates present in the water phase were identified by high-performance liquid chromatography (HPLC), and the hydrocarbon content in the organic phase was determined by a gas chromatography-mass-mass spectrometry (GC-MS) analysis. These analysis were performed for experiments with the lowest $H_2:CO$ ratios (1.2 and 1.6).

Table 4 shows the density and pH values of the water and hydrocarbon produced from the FTS reaction using hydrogen-deficient syngas. The density of the oil phase indicated that these products are in the gasoline/diesel range. Meanwhile, the pH suggested that the aqueous phase contains a significant amount of oxygenates. This was confirmed by the HPLC analysis of the samples which are summarized in Table 5. It has been reported that a low H_2/CO ratio improves the oxygenate formation through the WGS, and CO-derived intermediates can react with water to generate acetic acid and ethanol [83].

Table 4. The density and pH of liquid products of FTS using the Fe foam as a catalyst.

H_2/CO	1.2		1.6	
Phase	Aqueous	Oil	Aqueous	Oil
Density [$g \cdot mL^{-1}$]	0.992	0.750	0.988	0.772
pH	3.56	--	3.49	--
Viscosity [cSt]	--	1.28	--	1.37

Table 5. Ethanol and acetic acid content in the aqueous phase of FTS using Fe foam as catalyst and hydrogen-deficient syngas.

Oxygenate	Amount [mg·kg ^{−1}]	
	H ₂ :CO = 1.2	H ₂ :CO = 1.6
Ethanol	19,796.6	10,480.9
Acetic acid	2418.1	1330.5

Table 6 presents the result of the elemental analysis of the oil phase. The C/H ratio is consistent with the linear hydrocarbon compounds [84].

Table 6. Elemental analysis for the organic phase of FTS products using Fe foam as a catalyst and hydrogen-deficient syngas.

H ₂ /CO	1.2	1.6
C	62.4	69.6
H	10.8	12.5
O	26.7	17.8

According to Table 5, ethanol and acetic acid were the dominant components in the aqueous phase, which aligns with the partial oxidation at a low H₂/CO ratio [66]. The elemental analysis of the oil phase presented in Table 6 indicates a decreasing oxygen content at higher H₂/CO ratios, demonstrating the purity of the hydrocarbon.

The GC-MS analysis was carried out to identify the hydrocarbons. The GC-MS was run in TIC mode. Chromatograms and MS data were acquired simultaneously. The observed retention time and fragmentation pattern of each analyte were then compared to those of the diesel fuel obtained from a local gas station.

Figure 8 shows the chromatogram of the sample. Panel (a) corresponds to the organic sample with a syngas ratio of 1.2, and panel (b) corresponds to the organic sample with a syngas ratio of 1.6, while panel (c) shows the diesel standard. Relative ions and their abundance were verified using the instrument databases, NIST 23 (National Institute of Standards and Technology, version 2023), for compound identification [85]. The Fischer-Tropsch synthesis is not suited for internal standard since the components are either reaction products of the FTS that are reactive under process conditions or interfere with the signal of one or more products, making the interpretation of the GC-MS chromatogram complex. Nevertheless, diesel hydrocarbons typically contain 12–20 carbon atoms which provided a product range to target. Thus, the objective of this study was to determine whether the organic samples produced in this work contained paraffins within that range. Ultimately, it has been demonstrated that GC-MS was utilized to characterize FTS products by verifying the C12–C20 paraffins in the liquid. This approach aligns with the GC-MS product analysis in FTS studies, focusing on diesel could be in the hydrocarbon range [28,86].

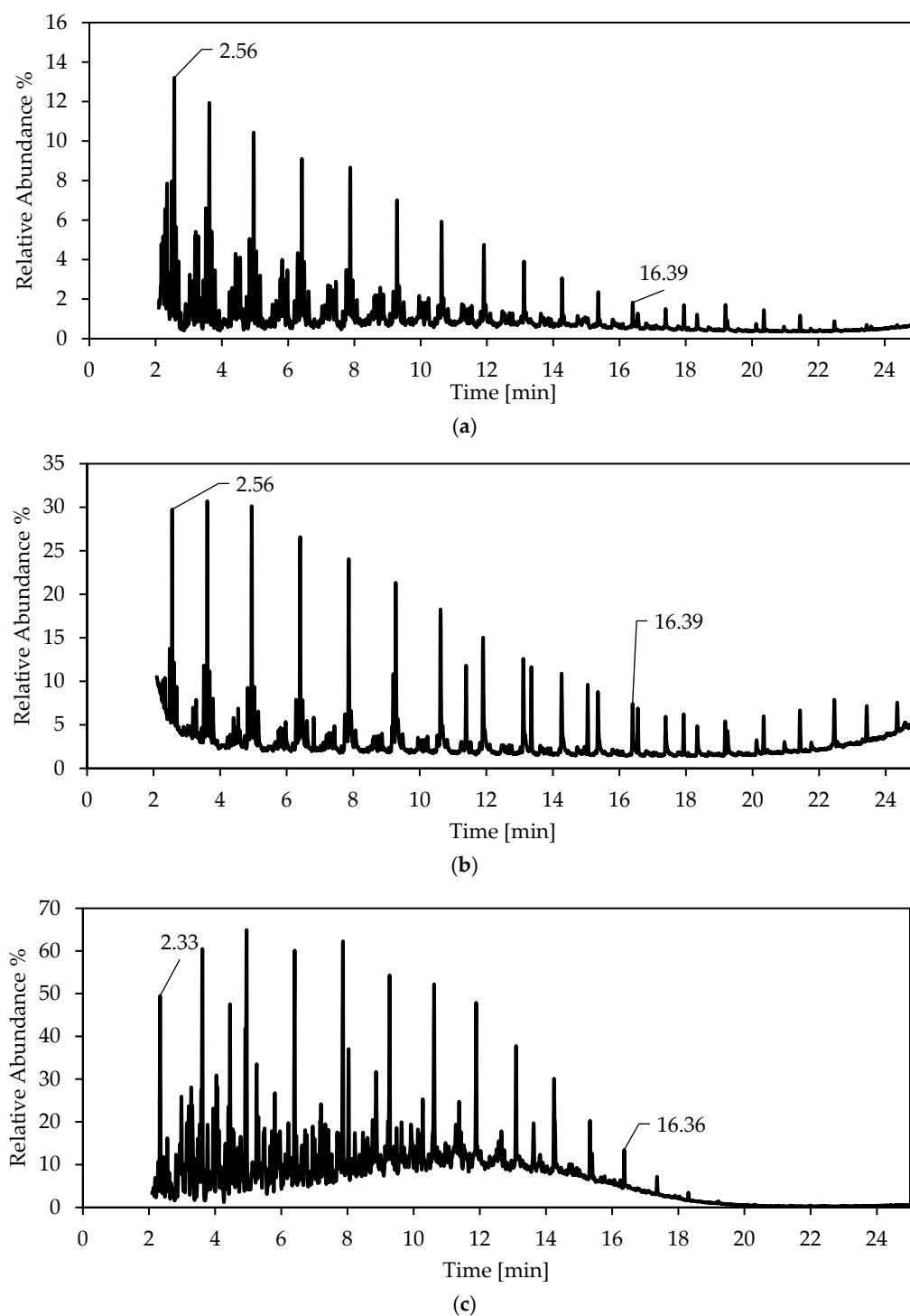


Figure 8. Chromatogram in TIC mode for organic samples of FTS using Fe foams and hydrogen-deficient syngas. (a) $H_2:CO = 1.2$, (b) $H_2:CO = 1.6$, and (c) diesel standard. Reaction conditions: 250 °C, 20 bar, WHSV = 600 h^{−1}, and ToS = 48 h.

4. Discussion

As shown in Section 3.2, the composition of the catalyst's bulk phase changed significantly with the reduction in the temperature, which in turn affected the catalytic activity. Increasing the reduction temperature from 250 to 325 °C improved CO conversion from 16.1% to 36.2%. It also increased the active metallic phase for FTS reactions and reduced the number of surface defects due to sintering. However, more research would be needed to fully understand these phenomena, optimize sintering protocols, and investigate promoters

such as Cu and K to stabilize the FeCx [78]. The particle size and reduction conditions influenced the formation and stability of Fe carbides, which are crucial for the FTS activity. Additionally, sintering at high temperatures decreased the Turnover Frequency (TOF), which could alter the selectivity. Iron foams lack promoters that would inhibit the sintering of oxide precursors or favor the nucleation of iron carbide crystals. From 330 °C to 600 °C, a reducibility peak could be observed, which can be attributed to the reduction of Fe₂O₃ to Fe₃O₄ (see Figure 5). Fe₃O₄ is the iron phase with a lower catalytic activity for FTS due to its size, as evidenced by its low catalytic activity (15% CO conversion) in this work.

At a lower reduction temperature of 325 °C, the CO binding sites were less likely to undergo sintering and thus, the catalyst activity is higher for all the reactions involved in the process. Since these are competing reactions, a higher conversion means a lower selectivity toward long-chain hydrocarbons and increased CO₂ and CH₄ production. The conversion increases by 5% when the reduction temperature was fixed at 250 °C, while the WHSV was decreased. The baseline for further experiments was set at 325 °C and at WHSV 600 h^{−1} because these conditions showed the best performance for the Fe foam so far. Decreasing the WHSV from 1200 h^{−1} to 600 h^{−1} increased the CO conversion mainly since it provided more residence time for the gas–catalyst interaction [59]. A comparison between Tables 1 and 2 showed that increasing the residence time positively affected the activity. It has been reported that a higher residence time improves C₂+ yields in Fe-based catalytic systems and is a key factor in the chain growth process. This supports the CO conversion improvement at lower WHSV [87].

As shown in Table 3, Fe foams can be used over a wide range of H₂/CO ratios, including those found in synthesis gas streams produced from biomass. These streams often have low H₂/CO ratios and produce more olefinic products with a lower CH₄ selectivity than Co-based catalysts. Fe foams achieved higher conversions than tailor-made catalysts in a single pass with a typical bio-syngas composition [18,27,77]. Another study confirmed that Fe catalysts demonstrated suitable activity in low H₂/CO ratios, a common feature for syngas produced from biomass [88]. The excellent performance of Fe foams as FTS catalysts is due to the uniform dispersion of the active components (FeCx and Fe₂O₃) on the catalytic bed, which was made possible by the open cellular structure of the catalyst. It has also been reported that structured Fe catalysts have distinct porosities and thermal properties [89]. Fe foams showed a better CO conversion and C₅+ selectivity because of their better heat dissipation and open geometry, which led to less mass transfer limitations and preserved active FeCx [31], resulting in better carbonization and product selectivity. The conversion and selectivity, as a function of the ToS, present stable behavior after around 8 h of testing for all experiments.

The liquid product characterization is presented in Section 3.3, while Figure 8 shows the GC-MS chromatograms of the combustible products, which are mainly n-paraffins and α-olefins. In addition to these primary products, minor peaks of other reaction products, including internal olefins, branched alkanes, and linear alcohols, are present, though in relatively small amounts. The peak with the highest intensity ranges from C₁₀ (RT = 2.5) to C₂₁ (RT = 16.3). The similarity of panels (a) and (b) to panel (c) indicates that the hydrocarbons obtained through FTS using iron foams fall within the diesel range. It has been verified that using iron-based catalysts in FTS reactions can result in C₁₀–C₂₀ n-paraffin production under controlled conditions [90].

5. Conclusions

This study evaluated the feasibility of using a structured iron catalyst for Fischer–Tropsch synthesis (FTS) using a synthesis gas (syngas) feedstock representative of those derived from biomass. The iron foam catalyst was synthesized and tested under different

reaction conditions. The results demonstrated the catalyst's activity across different feed compositions and residence times. The maximum CO conversion achieved was 84.8% at a H₂/CO ratio of 1.2, with a low CH₄ selectivity (10.4%) and a C₃+ selectivity reaching up to 89%. These results confirmed its strong performance under hydrogen-deficient conditions.

Compared to a conventional powder catalyst, the structured iron foam exhibited improved temperature control, enhanced activity, and reduced methane formation. These advantages stem from its open cellular geometry, which promotes efficient mass transfer due to the increased tortuosity and excellent thermal conductivity, minimizing hot spots across the catalyst bed. Despite its relatively low BET surface area (3 m²/g), the foam structure enabled the effective gas–solid contact and high catalytic efficiency. The characterization via the TPR and XRD confirmed that the reduction at 325 °C facilitated the FeC_x formation without significant sintering, which correlated with the increased catalytic performance.

Using structured Fe catalysts also enhanced the single-pass conversion, which could simplify the process design and enable smaller reactor volumes. Maintaining a controlled WHSV is critical for performance and highlights its importance for scaling up processes from the laboratory to pilot or even industrial level.

6. Future Overview

Future work should focus on developing synthesis and activation protocols that inhibit the sintering of oxide precursors and favor the nucleation of small iron carbide crystals in structured catalysts. This would allow for the direct comparison of turnover rates of FTS on iron and cobalt catalysts with similar crystal sizes.

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