




Review

# Effect of Co-Feeding Inorganic and Organic Molecules in the Fe and Co Catalyzed Fischer–Tropsch Synthesis: A Review

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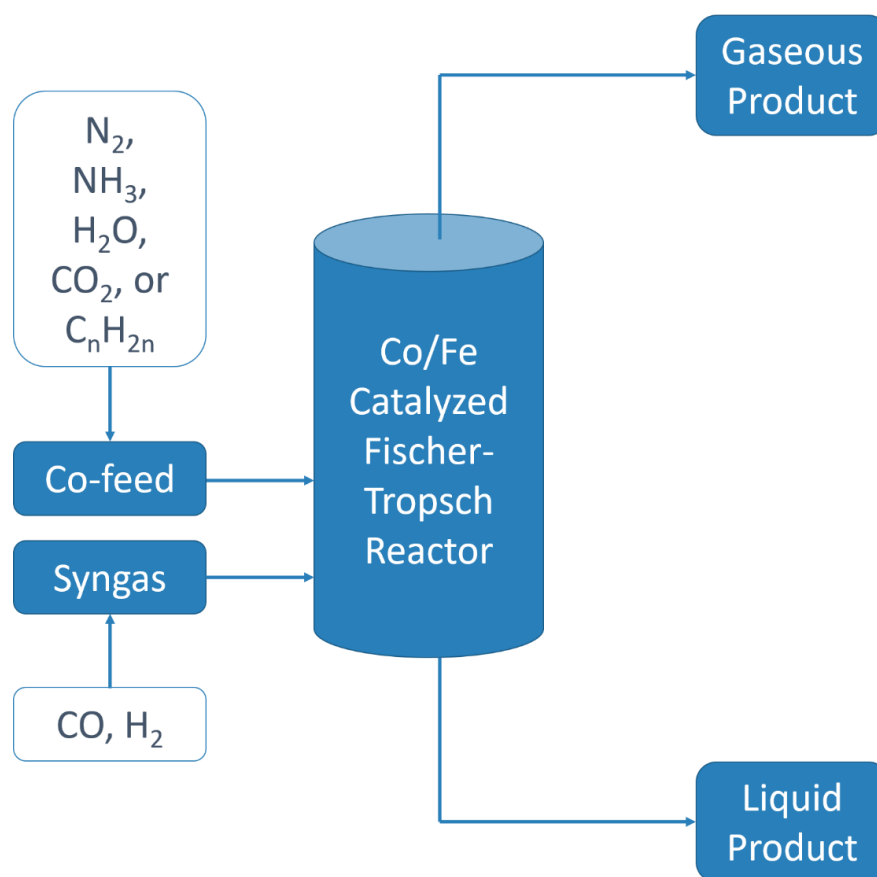


**Abstract:** This short review makes it clear that after 90 years, the Fischer–Tropsch synthesis (FTS) process is still not well understood. While it is agreed that it is primarily a polymerization process, giving rise to a distribution of mainly olefins and paraffins; the mechanism by which this occurs on catalysts is still a subject of much debate. Many of the FT features, such as deactivation, product distributions, kinetics and mechanism, and equilibrium aspects of the FT processes are still subjects of controversy, regardless of the progress that has been made so far. The effect of molecules co-feeding in FTS on these features is the main focus of this study. This review looks at some of these areas and tries to throw some light on aspects of FTS since the inception of the idea to date with emphasis and recommendation made based on nitrogen, water, ammonia, and olefins co-feeding case studies.

**Keywords:** Fischer–Tropsch product distribution; reaction mechanism; catalysis; process synthesis and design; catalyst deactivation

## 1. Introduction

The addition of molecules other than syngas in the reactor during Fischer–Tropsch synthesis (FTS) is considered co-feeding of that molecule to the FTS. These molecules, usually with lower molecular weights, could be water, organic or inorganic additives. For instance, there have been controversies about the co-feeding of water to the FT reactor. Several researchers have investigated the addition of water to elucidate the water effect on both activity and selectivity [1–4] on the catalyst deactivation [5–7], the kinetics and mechanism [8–10], and product distribution [3]. Due to the different views on the effect of water co-feeding in syngas during FTS, some authors have focused their studies on shedding light on the subject of positive effects of water co-feeding on the FT rate, which was observed for some, but not all, Co-based catalysts [9]. Reports on the negative effects of water on FT processes are also available [11]. It is worth noting that the FTS mechanism is not entirely clear, and the distribution of products does not typically follow a typical Anderson–Schulz–Flory (ASF) distribution. As such, various molecules have been used in the FT reactions in an attempt to better the understanding of the reaction mechanism and explain the deviations observed from the ASF distribution [12–14]. In particular, the additives that have been co-fed to syngas to investigate their effects on the mechanism and influence on product distribution in FTS include light olefins [14–17], alcohols [18,19], water [1,20–26], CO<sub>2</sub> [27–31], and many more, as illustrated in Figure 1.



**Figure 1.** Illustration of co-feeding components considered in this review.

Several researchers [32–34] have reported the effect of ammonia in syngas on the FT reaction. The authors studied the effect to explore possible phase changes of the Fe catalyst with change in time on the stream. What they also assessed was the deactivation mechanism of the Fe catalyst by poisoning during the FT reaction [32]. The effect of co-feeding ammonia on the conversion of syngas using traditional cobalt catalyst was investigated to probe the catalyst deactivation and ability to affect the selectivity of methane and C<sub>5+</sub> hydrocarbon formation [33]. Sango et al. [34] also reported the co-feeding of ammonia in different concentrations to a slurry phase, iron-based FT synthesis to study catalyst deactivation, methane selectivity, the chain growth probability, the olefin selectivity, and the FT reactions mechanisms. In a separate experimental study, controlled and verified quantities of hydrogen sulfide and ammonia were added into the feed gas. Hydrogen sulfide was employed to probe the impact of irreversible catalyst poisoning relative to the intrinsic deactivation profile, whereas ammonia co-feeding was done to quantify the impact of regenerable catalyst poisoning. The combined effects provided insight regarding catalyst deactivation and possibly prediction of time dependant catalyst performance during FTS [35].

In recent studies, the synthesis gas mainly obtained from the reforming of coal, biomass, and natural gas contains significant amounts of carbon dioxide (CO<sub>2</sub>) [36]. CO<sub>2</sub> removal from the synthesis gas is quite complex and expensive, hence, consequently, takes part in the FT catalytic activity [36]. A series of FTS experiments, which entail the co-feeding of CO<sub>2</sub> were conducted in a fixed bed reactor over a cobalt-based catalyst to investigate the catalyst deactivation, catalytic activity, and product selectivity and formation rates [28]. The influence of CO<sub>2</sub> content in the feed stream was shown to improve the product distribution toward valuable hydrocarbons and conversion rates [36]. CO<sub>2</sub> was added to the FT feed to investigate the CO conversion, chain growth probability, the products distribution, and FT reaction mechanisms [37,38]. Further investigations of the CO<sub>2</sub> influence in the

feed gas relate to the economy and sustainability developments of FT technology [29,39,40]. Still, on the cost-effectiveness of the FT system, it has been reported that the use of nitrogen-rich syngas could be a better approach than the classical processes where syngas is free of nitrogen [39,40]. Inert gases, such as nitrogen, have also been co-fed to the FT reactor. The effects of co-feeding nitrogen ( $N_2$ ) in the FTS in a fixed bed reactor over a Co/TiO<sub>2</sub> catalyst was investigated by Muleja et al. (2016) to elucidate the effect on the catalytic activity, selectivity, and the implication on the FTS kinetics [41]. Nitrogen-rich syngas was used to gain an understanding of its behavior in thermochemical catalytic conversion to gasoline range hydrocarbon [42]. As such, researchers [43] have recently proposed that when operating a cobalt-based FTS process, the olefin and paraffin formation rates should be considered separately. The reason being that the rates before, during, and after deactivation during FTS are comparatively inconclusive, for instance, in the studies by [41,43] the olefin formation rate was fairly constant over time, and in some cases even increased, while the paraffin formation rate dropped, indicating that the deactivation mainly affects the paraffin formation rate. This review is undertaken to summarize and consolidate the co-feeding work done so far and to try explaining findings in terms of controlling the catalytic activity, the selectivity of desired products, products distributions, understanding the mechanism, kinetics, and/or thermodynamics of the Fischer–Tropsch (FT) processes.

## 2. Co-Feeding in Fischer–Tropsch Synthesis

Syngas is a mixture of carbon monoxide (CO) and hydrogen ( $H_2$ ) often used as the feed to the FT process. As the feed in FTS is central to the process, a plethora of studies has been conducted on the feed composition and co-feeding of different molecules with the syngas for the FT reactions [39,44,45]. In terms of co-feeding, extensive investigations have been conducted, and some of the molecules that have been co-fed include water [1,11,45–48] additives, such as CO<sub>2</sub> [28,30,31,36,49,50], and hydrocarbons, such as olefins [51–56]. Although researchers [32–34,57] have published findings on nitrogen-containing compounds including ammonia, inorganic compounds, such as nitrogen gas, have not been reported on intensively. But to show the importance of co-feeding in FT reaction, already in the 1950s, scientists had investigated FT processes with both inorganic and organic compounds, to be exact CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>, and they have shown that the addition of these diluents poses a negative effect on FT reaction rate [58]. Some major co-feeding effect studies are summarized in Table 1.

The co-feeding of molecules to the syngas during FTS is important. However, each of these molecules has advantages and inconveniences. As such, the choice of one molecule over another additive is dictated by the aim of the study. For example, water is an inherently oxygen-containing by-product in the FTS. Oxygen atoms furnished by the CO in the feed are mainly removed as water in FT reactions. The water may negatively affect syngas conversion as it contributes to catalyst deactivation by oxidation. In addition, the products selectivity product distribution, and secondary reactions and catalyst longevity is also affected. [46]. It is, therefore, necessary to identify the aspect of the FT process that requires improvement to devise an appropriate experiment for the co-feeding of water into the syngas for FT reactions.

In FTS, high methane selectivities are generally not preferred as it is comparatively a low-value product than higher olefins and paraffins. Recycling the formed methane back to syngas would be complex and uneconomical, therefore, suppressing its formation would be key [46]. Most studies should, therefore, focus on reducing the production of methane while increasing heavy hydrocarbons formation.

The literature findings indicate that the effect of the co-feeds, whether organic or inorganic, are almost the same regardless of the operating condition or the catalyst used (See Table 1).

Inorganic co-feeds are often incorporated in FTS to enhance selectivity to higher hydrocarbons. In the case of N<sub>2</sub>, however, peer-reviewed publications indicate negative effects of the addition, as in the case of H<sub>2</sub>O and CO<sub>2</sub>. The inorganic feed H<sub>2</sub>O source affected catalyst durability; however, overall co-feed type differences in effects were significantly different with the likelihood of affecting the FTS performance upon feeding.

**Table 1.** Summary of some effects of the co-feeds used in Fischer–Tropsch synthesis (FTS). The Co-feeds are grouped as organic or inorganic.

Nature of Co-Feed	Co-Feed	Catalyst Used	Reaction Conditions	Effect in FTS	Amount Used	Ref
Inorganic Co-feeds	Water	Pt (0.5%)-15%Co/Al <sub>2</sub> O <sub>3</sub>	2.93 MPa, and H <sub>2</sub> /CO was 2.0.	Decreased CO conversion, permanent deactivation of the catalyst.	3–25 vol%	[6]
	Water	0.27%Ru-25%Co/Al <sub>2</sub> O <sub>3</sub> 25%Co/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	205–230 °C, 1.4–2.5 MPa, H <sub>2</sub> /CO = 1.0–2.5, and 3–16	Reduction in the CH <sub>4</sub> rate by 12% catalyst deactivation observed during the addition of water.	10 vol%	[10]
	CO <sub>2</sub>	Co/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	(H <sub>2</sub> /CO = 2), fixed-bed reactor; 220 °C, 20 bar, and SV (L/kg cat/h) = 2000.	Decrease in CO conversion and C <sub>5</sub> + selectivity partial oxidation of surface cobalt metal	20 vol%	[30]
	Nitrogen	Co/TiO <sub>2</sub>	220 °C; 60 (NTP)mL/min to 75 (NTP) mL/min; 20.85 bar abs 25.85 bar abs	Reduced selectivity to the undesired light hydrocarbons (mainly CH <sub>4</sub> )	28% N <sub>2</sub>	[41]
	Ammonia	100Fe/5.1Si/2.0Cu/3.0K	220–270 °C and 1.3 MPa using a 1-L slurry phase reactor.	Rapidly deactivation of catalyst simultaneously changed the product selectivities.	0.1–400 ppm	[32]
	Ammonia	iron-catalyst	250 °C, 75 mL NTP/min, H <sub>2</sub> :CO = 2 and 5 bar, respectively.	The selectivities toward nitrogen-containing compounds enhanced with increasing NH <sub>3</sub> content. Rates of formation of alcohols, aldehydes, and organic acids decreased	0–10 vol%	[59]
Organic co-feeds	Ethene	62 wt% cobalt oxide and was supported on kieselguhr	473 K and 110 kPa pressure.	The selectivity of the higher hydrocarbons was improved.	1% to 2%	[16]
	Ethanol addition	10% Co/TiO <sub>2</sub> catalyst	T = 220 °C, P = 8 bar, H <sub>2</sub> /CO = 2)	The selectivity to light products increased, as well as the olefin to paraffin ratio. A significant decrease in the catalyst activity.	2 vol% and 6 vol%)	[19]
	Small oxygenates	Iron catalysts. gas with a mol ratio H <sub>2</sub> :CO = 0.5	2.0 MPa; 543 K flow (VHSV = 1000)	Aldehydes suppress and entirely change normal synthesis behavior.	10 mol% dimethyl ether (DME). Diethyl ether (DEE) is 3.3 mol%. Acetaldehyde is 3 mol%	[44]
	1-olefins as additives	Co/ZrO <sub>2</sub> –SiO <sub>2</sub> bimodal catalyst	513 K, 1.0 MPa, W/F Syngas = 10 g – cat h/mol.	Resulted in an anti-Anderson–Schulz–Flory (anti-ASF) product distribution. 1-decene and 1-tetradecene mixed with the volume ratio of 1:1, showed the highest selectivity to jet-fuel-like hydrocarbons. Formation rates of CH <sub>4</sub> and CO <sub>2</sub> , as well as light hydrocarbons (C <sub>2</sub> –C <sub>4</sub> ), suppressed	20 mol%	[60]

### 3. Water Co-Feeding in FTS

Water is of particular interest because the FTS produces a significant volume of water [61]. Conventional and green processes rely on accurate accounts of products and by-products [62]. An account of all large quantities of produced material should be thoroughly conducted to ensure the integration of various scenarios happening at different levels [63]. This is crucial not only for the FT reaction but also for downstream processes [64–66]. Okoye-Chine et al. [67] recently proposed that phase of H<sub>2</sub>O impacts FT reaction in their report about the effect of water co-feeding on a cobalt-based FT catalyst. They have also proposed that the relationship between water affinity and/or resistance behavior of the supported catalyst affect the activity and selectivity, which could assist the explanation of the kinetic influence of H<sub>2</sub>O in FT reactions. Fratalocchi et al. [3] found that added water reduced the selectivity to CH<sub>4</sub> and alcohol and increased C<sub>25+</sub> hydrocarbon, olefin, and CO<sub>2</sub> selectivities, which they ascribed to the suppression of hydrogenation reactions by water. The decrease of the selectivity to methane was also observed with in situ experiments designed for laboratory X-ray diffractometers in the laboratory [68]. The ability to influence FT selectivity could be useful in the design of intensified processes, such as FT reactive distillation (RD) systems [69], which would enable streams to be directed to particular trays in an RD to achieve the desired product specification on that tray.

Iglesia et al. [70] have reported that water influences chain growth, selectivity, and depending on the catalyst, the co-feeding of water also affects the rate of the initial CO hydrogenation reaction. When the pressures of the reactants or the reactants conversions are low, the addition of water improves the FTS reaction productivity (rates and selectivity) of olefins and C<sub>5</sub>+ hydrocarbons. Furthermore, at low CO conversion, the effects of water co-feeding in FTS are influenced by the type of supports and lead to support effects. The pressure is one of the most critical operating conditions of the FT process. The feed partial pressure is equally important. The effect of water co-feeding stands to affect the performance of catalysts. Scientists [1] have studied the effect of water while changing the conversion and thereby, raising the partial pressure of water. They have also investigated the influence with the co-feeding of water to the feed gas. Upon increasing the water partial pressures, a shift from the ASF distribution was observed with the FTS total product distribution, the olefin reinsertion caused typical deviations, to a much narrower distribution. The sole C<sub>1</sub>-wise chain growth process cannot be explained by such mechanisms. As such, another product formation route which takes into consideration the combination of adjacent alkyl chains leading to paraffin (“reverse hydrogenolysis”), has, therefore, been suggested [2]. Certain features (physico-chemical properties) of the catalysts affect the catalytic activity behavior in an FT reactor. The reduction in the reaction rates was found when the water was co-fed with an inlet partial pressure ratio ( $P_{H_2O}/P_{H_2} = 0.4$ ) for the narrow-pore catalysts. Whereas, the reaction rates increased for the larger pores catalysts with the same water pressure. Overall, when the quantity of water added was equal to  $P_{H_2O}/P_{H_2} = 0.7$  at the reactor inlet, the reaction rates were suppressed, resulting in permanent deactivation. Furthermore, the addition of water improved the selectivity to C<sub>5+</sub> and decreased the selectivity to CH<sub>4</sub> selectivity for all type of catalysts. Hence, the pore characteristics appear to define the impact of water on the rates [23]. Bertole et al. [47] added water at partial pressures amounting to 8 bar to an FT functioning unsupported cobalt catalyst and managed to increase the reactivity of CO which was adsorbed on the surface without affecting the reactivity of the active surface of carbon intermediate. An increase in surface concentration was obtained for the monomeric carbon precursors leading to hydrocarbon formation [47]. The interaction of water with the catalysts differs in many ways. The effect of water with Co particle sizes, adsorbed species on the catalyst surface, in terms of secondary reactions, and diffusion in liquid-filled is reported in the literature [1]. The complexity of the effect of water on the product distribution has also been reported [3]. It has been revealed that water has both irreversible and reversible effects. The former becomes evident upon raising the concentration of co-fed water, and the latter is clearly visible, starting from small concentrations of co-fed water. These two effects result in the decline of the selectivity to the undesired CH<sub>4</sub> and alcohol while the selectivity to C<sub>25+</sub> hydrocarbon, olefin, and those for CO<sub>2</sub> increase. The authors concluded that these findings can be described by an assumption that water

suppresses hydrogenation reactions [3]. Another negative effect of co-feeding water to syngas is the deactivation of the catalysts. At high partial pressures, the presence of water deactivates unsupported cobalt catalysts. The deactivation of the catalyst is noticeable through the reduction of site activity of the catalyst and/or lower CO surface inventory. The treatment of the catalyst with hydrogen generally recovers site activity, and it does not affect surface inventory. The latter observation indicates that cobalt surface loss is due to sintering. This sintering process is prominently facilitated by high water partial pressure, such as >4 bar [47]. Claeys and van Steen [8] reported a noticeable increase in the formation rates of the product and significant changes in the selectivity to the FT product, in particular, lower methane selectivity and enhanced chain growth ensuing from the effect of water. The flow rate of the main reactants (CO and H<sub>2</sub>) is another FT operating process parameter that affects the performance of the FT processes. Li et al. [71,72] investigated the effects of adding water to the feed gas by changing the values of the space velocity. They found that the addition of water did not affect the CO conversion significantly at higher syngas space velocity values. At lower space velocity, the water co-feeding decreased the CO conversion; yet, the negative effect was reversible with the catalyst quickly recovering the activity obtained before the feeding of water. When the space velocity is low, the CO conversion is high, and researchers have found that the addition of water permanently deactivates the catalyst [71,72]. The quantity of water added to the syngas feed also plays a role in the catalytic activity. For example, it was found that co-feeding of small amounts of water slightly affects the CO conversion, but interestingly the effect was reversible. However, a large amount of added water which could equal the partial pressures  $P_{H_2O}/P_{CO} \sim 1$  in the feed permanently deactivated the catalyst. When the selectivity to CO<sub>2</sub> is higher, it indicated that cobalt oxide or another catalytic form of cobalt, such as cobalt aluminate, was formed in the presence of higher water partial pressure [11]. Dalai and Davis [46] reviewed the influence of water on the performances of numerous cobalt catalysts for FTS and confirmed that the effect of co-feeding water into an FT reactor is quite complicated. They found that the influence of water addition depends on various aspects, including the catalyst support and its nature, the Co metal loading, the promoters used with noble metals, and also the preparation procedure.

It is, therefore, generally accepted by researchers [1,9,11,45–48] that the effects of water on FTS are quite complex. Dalai and Davis [46] summarised the effects of water in FTS with three scenarios:

- (i) An oxidation process for the cobalt supported catalyst with the extent of oxidation being a function of features of the cobalt namely the crystallite size but also the ratio values of the reactor partial pressures of hydrogen and water ( $P_{H_2O}/P_{H_2}$ ).
- (ii) The average support pore diameter influences the water-co-feeding.
- (iii) The effects could be kinetic in particular the CO dissociation by direct interaction with co-adsorbed CO can be lowered with water co-feeding while the secondary hydrogenation of olefin products can be inhibited as a result of competitive adsorption of water [46].

On the other hand, Yan et al. used Fe-Pd/ZSM-5 catalyst (a bi-functional catalyst) which yielded relatively high activity and selectivity in producing liquid hydrocarbons when the FT reaction was carried out with nitrogen-rich syngas [73]. Conversely, Visconti and Mascellaro [74] co-fed nitrogen to the reactor, increasing the nitrogen content (23.5% to 45.1%) and kept the total pressure unchanged and found that the CO conversion dropped. It is most likely that the CO conversion decreased because the reactant partial pressures values declined when adjustment was made to maintain the total pressure while increasing the nitrogen content. Nevertheless, researchers who investigated the effect FTS with nitrogen-rich syngas have reported that such FT process is feasible because it could potentially be cost-effective [39,75–78]. The addition to the FTS of molecules, namely olefins, alcohols, carbon dioxide, water, and isotope markers, has contributed to a better understanding of the reaction mechanism. These same molecules were also used by researchers who were studying the deviations observed from the ASF distribution [12].



#### 4. Organic Co-Feeds

Small hydrocarbons are an important organic additive in FTS. The most commonly used co-feeds include acetylene ( $C_2H_2$ ), ethylene ( $C_2H_4$ ), ethane ( $C_2H_6$ ), propyne ( $C_3H_4$ ), propene ( $C_3H_6$ ), and propane ( $C_3H_8$ ). These hydrocarbons are needed for elucidating reaction mechanisms. These molecules exist in the gas-phase during the reaction and through a series of temperatures used in FTS.

For instance, the influence of low molecular weight olefins on FTS has been examined with the aim of either understanding the mechanism of chain growth or influencing the distribution of products formed [14]. Experiments conducted with co-feeding of ethene, 1-alkenes, and diazomethane as a source of surface methylene have been undertaken to strongly support the hypothesis of two independent mechanisms during FTS with the methylene insertion mechanism as one of them [13]. Furthermore, FT experiments with 1-alkene and ethane co-feeding in a reactor loaded with cobalt catalysts and iron catalysts were carried out to study the product distributions, chain growth probabilities, and different chain growth mechanisms [16,79,80]. In brief, olefins, alcohols or  $CO_2$  additives have all been co-fed to investigate the chain growth and mechanism during FTS [12,14,18,81], the ASF distribution [13], and the role of secondary reactions of olefins [15,17]. Specifically, olefins have been used as co-feeds in FT which resulted in enhancing the selectivity to hydrocarbons ( $C_8$ – $C_{16}$ ), while at the same time, the formation of light hydrocarbons, such as  $CH_4$  and  $CO_2$  was suppressed [60].

On the other hand, when additives, such as small 1-alkenes, alcohols, or  $CO_2$ , were co-fed into the FT reactor, they acted as chain initiators for the FTS. The probe-initiated and conventional FTS progress concurrently, with their separate products overlapping. It has been shown, overwhelmingly, that co-feeding additives do not contribute to chain growth, although when olefins and alcohols were added, their incorporation into FTS products was evident usually through chain initiation [12]. However, up to now, the effects and influences of the additives reported [12] on the overall FT product distributions and on the FT catalysts activity are yet to convince the majority of researchers universally. However, Sage and Burke [12] reported in their review that olefins adsorb on the catalyst surface influenced the overall FTS product distribution. As such, it could be assumed that co-feeding olefins might be useful for FTS to modify the catalyst surface. For example, the catalyst surface modification could be achieved by selectively binding to and/or inhibiting certain active sites favorable to chain growth of higher hydrocarbons, or reactions, such as secondary hydrogenation, to improve the overall FT efficiency and selectivity of the process [12].

Alkane, such as n-hexane, has also been co-fed into the FT reaction. The addition of this molecule to the FTS feed under realistic conditions will not result in supercritical FT conditions. However, such an addition will change the composition of the liquid phase in the FT reactor leading in a higher liquid flow rate and a greater diffusivity of reactants ( $H_2$  and  $CO$ ). Therefore, the effectiveness of the process was increased if the FTS is conducted under internal mass transport limiting conditions [82]. Patzlaff et al. [79] conducted experiments with 1-alkene and ethane co-feeding using cobalt and iron catalysts and revealed superimposed distributions with different chain growth probabilities resulted from different chain growth mechanisms. When alcohols were co-fed, the results showed reliance on the ratio of the two distributions on the reactant pressures while the promoter effect on iron catalysts also supported the hypothesis of the two mechanisms. They also suggested the CO insertion mechanism as the second approach that is exhibited by the higher growth probability of the resulting ASF distribution [13].

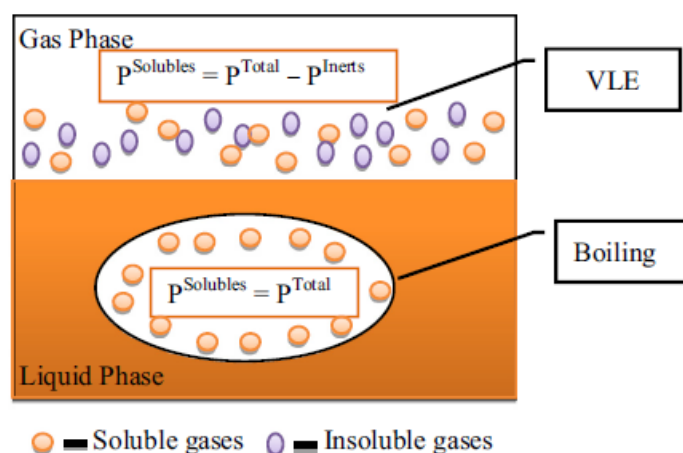
It is known that the FT synthesis is highly exothermic, which makes the heat removal and control of the reaction temperature critical steps since the damage of the catalyst at high temperatures decreases the conversion rate. Product selectivity also shifts with increasing temperature towards the production of more unwanted short-chain hydrocarbons, including methane [75]. FT processes are also categorized based on the temperature at which the operation is being carried out, and the products obtained differ. For example, the syncrude produced during high temperature (300–350 °C) Fischer–Tropsch (HTFT) synthesis has more light hydrocarbons, hence, is gaseous at reaction conditions; more than one product phase is formed on cooling. Low temperature (200–260 °C) Fischer–Tropsch (LTFT)

syncrude is acknowledged to be a two-phase mixture at reaction conditions, but at ambient conditions, the syncrude from LTFT synthesis consists of four different product phases: gaseous, organic liquid, organic solid (wax), and aqueous [83]. Medium temperature Fischer–Tropsch (MTFT) ranges from 270 to 300 °C, the product phases are similar to those of LTFT. Although FTS products are useful, it is usually more profitable to obtain fewer light hydrocarbons, such as methane and oxygenate products, which are often unwanted. It has been reported that the commercialization of the FT technology suffers from two of major limitations. These are limited selectivity for the main products since it produces a broad spectrum of products and catalyst deactivation, which leads to frequent replacement of the catalyst [39]. Cobalt-based catalysts are only used in LTFT processes as at the higher temperatures excess CH<sub>4</sub> is produced [84].

## 5. Effect of Nitrogen as a Co-Feed

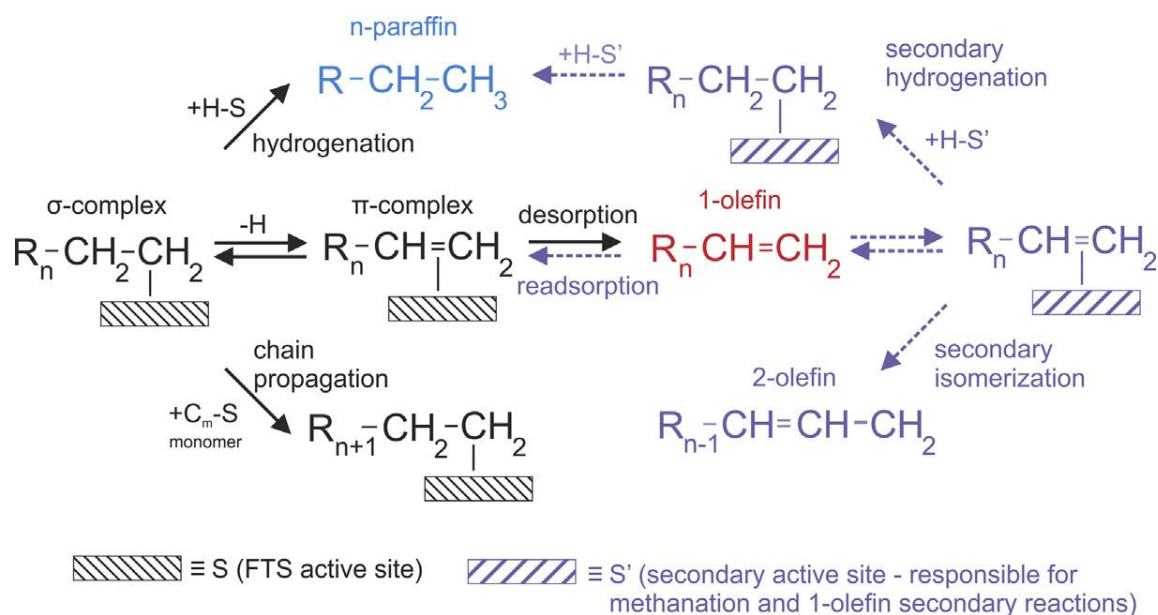
In addition to the contribution of cost reduction during syngas preparation, the presence of nitrogen in the syngas is significant for safety purpose, mass balance determination, and controlling the heat in the FT system. Jess and co-workers [77] suggested a process with nitrogen co-feeding to the syngas. They reported that the proposed process with syngas co-fed does not utilize a recycle loop, hence, skipping any build-up of nitrogen in the system. This configuration is probably cost-effective because a recycle compressor is not required. The presence of the syngas with nitrogen plays a significant role which removes substantial amounts of heat generated during the FT reaction [85]. Furthermore, researchers have reported that  $\alpha$ -olefins formation was enhanced by the two processes between FTS and N<sub>2</sub> purging. The improved result was achieved, when the liquid filled in pores of the catalyst purged with nitrogen, prompting the release of olefins from liquid to gas phase and minimizing its secondary reaction [86]. On the other hand, Jess et al. [75,77] and Xu et al. [78] separately conducted studies on the effect of nitrogen co-feeding in FT reactor and found that nitrogen only dilutes syngas. The presence of nitrogen in the reactor has little influence on the kinetics if the reactants (carbon monoxide and hydrogen) partial pressures are kept constant. However, Lu et al. [42] used feed composed of nitrogen-rich syngas in FTS and obtained more C<sub>10</sub> hydrocarbons and smaller amounts of C<sub>8</sub> hydrocarbons which were more when compared to FTS carried out with pure syngas. These results are different from the findings of Jess et al. [75] and Xu et al. [78]. Lu et al. [42] findings are partially in agreement with conclusions from Muleja et al. [41] studies. Muleja et al. [41] investigated the effect of nitrogen co-feeding to an FT reactor while maintaining the partial pressures of reactants and concluded that the selectivity to all light hydrocarbons decreased while the selectivity to C<sub>5+</sub> in mainly C<sub>5</sub>–C<sub>19</sub> fraction is enhanced. They [41], therefore, suggested such findings could not be explained by kinetics alone but compared the vapour–liquid equilibrium (VLE) and boiling effect and drew attention to the boiling phenomenon during FTS which is depicted in Figure 2.





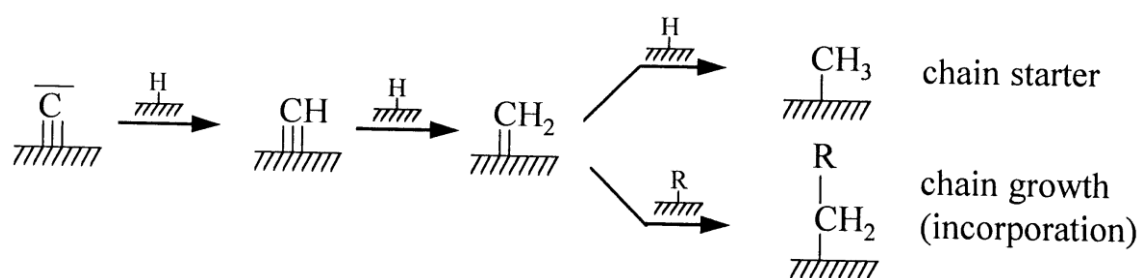
**Figure 2.** A schematic diagram for the comparison between the pressure in vapour–liquid equilibrium and boiling [41].  $p^{\text{Total}}$  is the total pressure of the system,  $p^{\text{Inerts}}$  are the total partial pressures of all the virtually insoluble gases, and  $p^{\text{Solubles}}$  is the total partial pressure of the soluble gases.

However, it is relatively agreed that FTS is a polymerization process leading to a distribution of mainly olefins and paraffins, although the mechanism by which this occurs on catalysts is still a subject of much debate. Todici et al. [87] reported well detailed schematic reactional representation of the FTS process as depicted in Figure 3.



**Figure 3.** Schematic representation of Fischer–Tropsch synthesis (FTS) (chain propagation, hydrogenation to n-paraffins, and desorption to 1-olefins) and 1-olefin secondary reaction (hydrogenation, isomerization, and readsorption) [87].

On the other hand, van Steen and Schulz [88] have simplified the scheme representing (Figure 4) the formation of chain initiators and insertion into the developing chains. This is what is used to show the growth of rate equations using the polymerization principle.



**Figure 4.** Simplified kinetic scheme of the successive hydrogenation of surface carbon yielding chain starters and incorporation into growing chains [88].

Furthermore, Muleja et al. [89] attempted to explain the effect of nitrogen co-feeding into the FT reactor with a reactive distillation mapping leading to the suggestion that further to kinetics, thermodynamic equilibrium and VLE should potentially be considered for FT processes modeling.

## 6. Concluding Remarks and Recommendations

Maximizing the yield of high-value product is a critical factor for the commercialization and successful implementation of the FT process. Coal or biomass gasification and natural gas reforming generally produce syngas that contains some short-chain hydrocarbons and impurities [90]. Some feed streams have contaminants that affect the FT reactor in various ways. The ability to integrate some contaminants, such as CO<sub>2</sub>, into the process design might be crucial to the success of a new design. Taking advantage of N<sub>2</sub> that is inherent in air could save capital installation costs in eliminating the need for cryogenic air separation units. The by-product water could be used to absorb the heat of reaction upon vaporization in an intensified unit, such as an FT reactive distillation system [91]. Since olefin readsorption has been demonstrated in an FT reactor [17,92–94], the light gas stream could be recycled to various trays in a reactive distillation column to influence product selectivity [95]. Insights gained from FT co-feeding studies are not only applicable to FTS but could also be extended to methanol-to-hydrocarbons synthesis and other hydrocarbons processing systems [96]. There are some ongoing ethylene co-feeding studies to try to understand the impact on olefin selectivity over Co-based catalysts [97]. Thus, insight from co-feeding studies leads to process synthesis and integration opportunities that were not envisaged by the researchers probing various phenomena.

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## References

1. Storsæter, S.; Borg, Ø.; Blekkan, E.A.; Holmen, A. Study of the effect of water on Fischer–Tropsch synthesis over supported cobalt catalysts. *J. Catal.* **2005**, *231*, 405–419. [\[CrossRef\]](#)
2. Claeys, M.; van Steen, E. On the effect of water during Fischer–Tropsch synthesis with a ruthenium catalyst. *Catal. Today* **2002**, *71*, 419–427. [\[CrossRef\]](#)
3. Fratalocchi, L.; Visconti, C.G.; Lietti, L.; Groppi, G.; Tronconi, E.; Roccaro, E.; Zennaro, R. On the performance of a Co-based catalyst supported on modified  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> during Fischer–Tropsch synthesis in the presence of co-fed water. *Catal. Sci. Technol.* **2016**, *6*, 6431–6440. [\[CrossRef\]](#)

4. Krishnamoorthy, S.; Tu, M.; Ojeda, M.P.; Pinna, D.; Iglesia, E. An investigation of the effects of water on rate and selectivity for the Fischer–Tropsch synthesis on cobalt-based catalysts. *J. Catal.* **2002**, *211*, 422–433. [\[CrossRef\]](#)
5. Sadeqzadeh, M.; Chambrey, S.; Piché, S.; Fongarland, P.; Luck, F.; Curulla-Ferré, D.; Khodakov, A.Y. Deactivation of a Co/Al<sub>2</sub>O<sub>3</sub> Fischer–Tropsch catalyst by water-induced sintering in slurry reactor: Modeling and experimental investigations. *Catal. Today* **2013**, *215*, 52–59. [\[CrossRef\]](#)
6. Li, J.; Davis, B.H. Effect of water on the catalytic properties of supported cobalt Fischer–Tropsch catalysts. In *Studies in Surface Science and Catalysis*; Elsevier: Amsterdam, The Netherlands, 2004; Volume 147, pp. 307–312.
7. Ma, W.; Jacobs, G.; Sparks, D.E.; Spicer, R.L.; Davis, B.H.; Klettlinger, J.L.; Yen, C.H. Fischer–Tropsch synthesis: Kinetics and water effect study over 25% Co/Al<sub>2</sub>O<sub>3</sub> catalysts. *Catal. Today* **2014**, *228*, 158–166. [\[CrossRef\]](#)
8. Rytter, E.; Borg, Ø.; Enger, B.C.; Holmen, A.  $\alpha$ -alumina as catalyst support in Co Fischer–Tropsch synthesis and the effect of added water; encompassing transient effects. *J. Catal.* **2019**, *373*, 13–24. [\[CrossRef\]](#)
9. Lögdberg, S.; Boutonnet, M.; Walmsley, J.C.; Järås, S.; Holmen, A.; Blekkan, E.A. Effect of water on the space-time yield of different supported cobalt catalysts during Fischer–Tropsch synthesis. *Appl. Catal. A Gen.* **2011**, *393*, 109–121. [\[CrossRef\]](#)
10. Ma, W.; Jacobs, G.; Das, T.K.; Masuku, C.M.; Kang, J.; Pendyala, V.R.R.; Yen, C.H. Fischer–Tropsch Synthesis: Kinetics and Water Effect on Methane Formation over 25% Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> Catalyst. *Ind. Eng. Chem. Res.* **2014**, *53*, 2157–2166. [\[CrossRef\]](#)
11. Li, J.; Zhan, X.; Zhang, Y.; Jacobs, G.; Das, T.; Davis, B.H. Fischer–Tropsch synthesis: Effect of water on the deactivation of Pt promoted Co/Al<sub>2</sub>O<sub>3</sub> catalysts. *Appl. Catal. A Gen.* **2002**, *228*, 203–212. [\[CrossRef\]](#)
12. Sage, V.; Burke, N. Use of probe molecules for Fischer–Tropsch mechanistic investigations: A short review. *Catal. Today* **2011**, *178*, 137–141. [\[CrossRef\]](#)
13. Gaube, J.; Klein, H.F. Studies on the reaction mechanism of the Fischer–Tropsch synthesis on iron and cobalt. *J. Mol. Catal. A Chem.* **2008**, *283*, 60–68. [\[CrossRef\]](#)
14. Jordan, D.S.; Bell, A.T. Influence of ethylene on the hydrogenation of carbon monoxide over ruthenium. *J. Phys. Chem.* **1986**, *90*, 4797–4805. [\[CrossRef\]](#)
15. Boelee, J.H.; Custers, J.M.G.; Van Der Wiele, K. Influence of reaction conditions on the effect of Co-feeding ethene in the Fischer–Tropsch synthesis on a fused-iron catalyst in the liquid phase. *Appl. Catal.* **1989**, *53*, 1–13. [\[CrossRef\]](#)
16. Adesina, A.A.; Hudgins, R.R.; Silveston, P.L. Effect of ethene addition during the Fischer–Tropsch reaction. *Appl. Catal.* **1990**, *62*, 295–308. [\[CrossRef\]](#)
17. Schulz, H.; Claeys, M. Reactions of  $\alpha$ -olefins of different chain length added during Fischer–Tropsch synthesis on a cobalt catalyst in a slurry reactor. *Appl. Catal. A Gen.* **1999**, *186*, 71–90. [\[CrossRef\]](#)
18. Kummer, J.T.; Emmett, P.H. Fischer–Tropsch synthesis mechanism studies. The addition of radioactive alcohols to the synthesis gas. *J. Am. Chem. Soc.* **1953**, *75*, 5177–5183. [\[CrossRef\]](#)
19. Jalama, K.; Coville, N.J.; Hildebrandt, D.; Glasser, D.; Jewell, L.L. Fischer–Tropsch synthesis over Co/TiO<sub>2</sub>: Effect of ethanol addition. *Fuel* **2007**, *86*, 73–80. [\[CrossRef\]](#)
20. Jacobs, G.; Patterson, P.M.; Das, T.K.; Luo, M.; Davis, B.H. Fischer–Tropsch synthesis: Effect of water on Co/Al<sub>2</sub>O<sub>3</sub> catalysts and XAFS characterization of reoxidation phenomena. *Appl. Catal. A Gen.* **2004**, *270*, 65–76. [\[CrossRef\]](#)
21. Rytter, E.; Borg, Ø.; Tsakoumis, N.E.; Holmen, A. Water as key to activity and selectivity in Co Fischer–Tropsch synthesis:  $\gamma$ -alumina based structure–performance relationships. *J. Catal.* **2018**, *365*, 334–343. [\[CrossRef\]](#)
22. Rytter, E.; Holmen, A. Perspectives on the effect of water in cobalt Fischer–Tropsch synthesis. *ACS Catal.* **2017**, *7*, 5321–5328. [\[CrossRef\]](#)
23. Borg, Ø.; Storsæter, S.; Eri, S.; Wigum, H.; Rytter, E.; Holmen, A. The effect of water on the activity and selectivity for  $\gamma$ -alumina supported cobalt Fischer–Tropsch catalysts with different pore sizes. *Catal. Lett.* **2006**, *107*, 95–102. [\[CrossRef\]](#)
24. Hibbitts, D.D.; Loveless, B.T.; Neurock, M.; Iglesia, E. Mechanistic role of water on the rate and selectivity of Fischer–Tropsch synthesis on ruthenium catalysts. *Angew. Chem. Int. Ed.* **2013**, *52*, 12273–12278. [\[CrossRef\]](#) [\[PubMed\]](#)
25. Yang, J.; Ma, W.; Chen, D.; Holmen, A.; Davis, B.H. Fischer–Tropsch synthesis: A review of the effect of CO conversion on methane selectivity. *Appl. Catal. A Gen.* **2014**, *470*, 250–260. [\[CrossRef\]](#)

26. Borg, Ø.; Yu, Z.; Chen, D.; Blekkan, E.A.; Rytter, E.; Holmen, A. The effect of water on the activity and selectivity for carbon nanofiber supported cobalt Fischer–Tropsch catalysts. *Top. Catal.* **2014**, *57*, 491–499. [[CrossRef](#)]
27. Sirikulbodee, P.; Ratana, T.; Sornchamni, T.; Phongaksorn, M.; Tungkamani, S. Catalytic performance of Iron-based catalyst in Fischer–Tropsch synthesis using CO<sub>2</sub> containing syngas. *Energy Procedia* **2017**, *138*, 998–1003. [[CrossRef](#)]
28. Yao, Y.; Liu, X.; Hildebrandt, D.; Glasser, D. The effect of CO<sub>2</sub> on a cobalt-based catalyst for low temperature Fischer–Tropsch synthesis. *Chem. Eng. J.* **2012**, *193*, 318–327. [[CrossRef](#)]
29. James, O.O.; Mesubi, A.M.; Ako, T.C.; Maity, S. Increasing carbon utilization in Fischer–Tropsch synthesis using H<sub>2</sub>-deficient or CO<sub>2</sub>-rich syngas feeds. *Fuel Process. Technol.* **2010**, *91*, 136–144. [[CrossRef](#)]
30. Kim, S.M.; Bae, J.W.; Lee, Y.J.; Jun, K.W. Effect of CO<sub>2</sub> in the feed stream on the deactivation of Co/γ-Al<sub>2</sub>O<sub>3</sub> Fischer–Tropsch catalyst. *Catal. Commun.* **2008**, *9*, 2269–2273. [[CrossRef](#)]
31. Yao, Y.; Hildebrandt, D.; Glasser, D.; Liu, X. Fischer–Tropsch synthesis using H<sub>2</sub>/CO/CO<sub>2</sub> syngas mixtures over a cobalt catalyst. *Ind. Eng. Chem. Res.* **2010**, *49*, 11061–11066. [[CrossRef](#)]
32. Ma, W.; Jacobs, G.; Sparks, D.E.; Pendyala, V.R.R.; Hopps, S.G.; Thomas, G.A.; Davis, B.H. Fischer–Tropsch synthesis: Effect of ammonia in syngas on the Fischer–Tropsch synthesis performance of a precipitated iron catalyst. *J. Catal.* **2015**, *326*, 149–160. [[CrossRef](#)]
33. Pendyala, V.R.R.; Gnanamani, M.K.; Jacobs, G.; Ma, W.; Shafer, W.D.; Davis, B.H. Fischer–Tropsch synthesis: Effect of ammonia impurities in syngas feed over a cobalt/alumina catalyst. *Appl. Catal. A Gen.* **2013**, *468*, 38–43. [[CrossRef](#)]
34. Sango, T.; Fischer, N.; Henkel, R.; Roessner, F.; van Steen, E.; Claeys, M. Formation of nitrogen containing compounds from ammonia co-fed to the Fischer–Tropsch synthesis. *Appl. Catal. A Gen.* **2015**, *502*, 150–156. [[CrossRef](#)]
35. Steynberg, A.P.; Deshmukh, S.R.; Robota, H.J. Fischer–Tropsch catalyst deactivation in commercial microchannel reactor operation. *Catal. Today* **2018**, *299*, 10–13. [[CrossRef](#)]
36. Díaz, J.A.; de la Osa, A.R.; Sánchez, P.; Romero, A.; Valverde, J.L. Influence of CO<sub>2</sub> co-feeding on Fischer–Tropsch fuels production over carbon nanofibers supported cobalt catalyst. *Catal. Commun.* **2014**, *44*, 57–61. [[CrossRef](#)]
37. Liao, P.Y.; Zhang, C.; Zhang, L.J.; Yang, Y.Z.; Zhong, L.S.; Wang, H.; Sun, Y.H. Effect of promoter and CO<sub>2</sub> content in the feed on the performance of CuFeZr catalyst in the synthesis of higher alcohol from syngas. *J. Fuel Chem. Technol.* **2017**, *45*, 547–555. [[CrossRef](#)]
38. Liu, Y.; Zhang, C.H.; Wang, Y.; Li, Y.; Hao, X.; Bai, L.; Li, Y.W. Effect of co-feeding carbon dioxide on Fischer–Tropsch synthesis over an iron–manganese catalyst in a spinning basket reactor. *Fuel Process. Technol.* **2008**, *89*, 234–241. [[CrossRef](#)]
39. Lu, Y.; Lee, T. Influence of the feed gas composition on the Fischer–Tropsch synthesis in commercial operations. *J. Nat. Gas Chem.* **2007**, *16*, 329–341. [[CrossRef](#)]
40. Daramola, M.O.; Matamela, K.; Sadare, O.O. Effect of CO<sub>2</sub> co-feeding on the conversion of syngas derived from waste to liquid fuel over a bi-functional Co/H-ZSM-5 catalyst. *J. Environ. Chem. Eng.* **2017**, *5*, 54–62. [[CrossRef](#)]
41. Muleja, A.A.; Yao, Y.; Glasser, D.; Hildebrandt, D. Effect of feeding nitrogen to a fixed bed Fischer–Tropsch reactor while keeping the partial pressures of reactants the same. *Chem. Eng. J.* **2016**, *293*, 151–160. [[CrossRef](#)]
42. Lu, Y.; Hu, J.; Han, J.; Yu, F. Synthesis of gasoline-range hydrocarbons from nitrogen-rich syngas over a Mo/HZSM-5 bi-functional catalyst. *J. Energy Inst.* **2016**, *89*, 782–792. [[CrossRef](#)]
43. Muleja, A.A.; Yao, Y.; Glasser, D.; Hildebrandt, D. Variation of the short-chain paraffin and olefin formation rates with time for a cobalt Fischer–Tropsch catalyst. *Ind. Eng. Chem. Res.* **2017**, *56*, 469–478. [[CrossRef](#)]
44. Snel, R.; Espinoza, R.L. Fischer–Tropsch synthesis on iron-based catalysts: The effect of co-feeding small oxygenates. *J. Mol. Catal.* **1989**, *54*, 213–223. [[CrossRef](#)]
45. Sarup, B.; Wojciechowski, B.W. The effect of time on stream and feed composition on the selectivity of a cobalt Fischer–Tropsch catalyst. *Can. J. Chem. Eng.* **1984**, *62*, 249–256. [[CrossRef](#)]
46. Dalai, A.K.; Davis, B.H. Fischer–Tropsch synthesis: A review of water effects on the performances of unsupported and supported Co catalysts. *Appl. Catal. A Gen.* **2008**, *348*, 1–15. [[CrossRef](#)]
47. Bertole, C.J.; Mims, C.A.; Kiss, G. The effect of water on the cobalt-catalyzed Fischer–Tropsch synthesis. *J. Catal.* **2002**, *210*, 84–96. [[CrossRef](#)]

48. Rothaemel, M.; Hanssen, K.F.; Blekkan, E.A.; Schanke, D.; Holmen, A. The effect of water on cobalt Fischer-Tropsch catalysts studied by steady-state isotopic transient kinetic analysis (SSITKA). *Catal. Today* **1997**, *38*, 79–84. [\[CrossRef\]](#)
49. Gnanamani, M.K.; Shafer, W.D.; Sparks, D.E.; Davis, B.H. Fischer-Tropsch synthesis: Effect of CO<sub>2</sub> containing syngas over Pt promoted Co/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and K-promoted Fe catalysts. *Catal. Commun.* **2011**, *12*, 936–939. [\[CrossRef\]](#)
50. Yao, Y.; Liu, X.; Hildebrandt, D.; Glasser, D. Fischer-Tropsch synthesis using H<sub>2</sub>/CO/CO<sub>2</sub> syngas mixtures: A comparison of paraffin to olefin ratios for iron and cobalt based catalysts. *Appl. Catal. A Gen.* **2012**, *433*, 58–68. [\[CrossRef\]](#)
51. Zhang, R.; Hao, X.; Li, Y. Investigation of acetylene addition to Fischer-Tropsch Synthesis. *Catal. Commun.* **2011**, *12*, 1146–1148. [\[CrossRef\]](#)
52. Kuipers, E.W.; Vinkenburg, I.H.; Oosterbeek, H. Chain length dependence of  $\alpha$ -olefin readsorption in Fischer-Tropsch synthesis. *J. Catal.* **1995**, *152*, 137–146. [\[CrossRef\]](#)
53. Iglesia, E.; Reyes, S.C.; Madon, R.J. Transport-enhanced  $\alpha$ -olefin readsorption pathways in Ru-catalyzed hydrocarbon synthesis. *J. Catal.* **1991**, *129*, 238–256. [\[CrossRef\]](#)
54. Snel, R.; Espinoza, R.L. Secondary reactions of primary products of the Fischer-Tropsch synthesis: Part 1. The role of ethene. *J. Mol. Catal.* **1987**, *43*, 237–247. [\[CrossRef\]](#)
55. Fan, L.; Fujimoto, K. Fischer-Tropsch synthesis in supercritical fluid: Characteristics and application. *Appl. Catal. A Gen.* **1999**, *186*, 343–354. [\[CrossRef\]](#)
56. Snel, R.; Espinoza, R.L. Secondary reactions of primary products of the fischer-tropsch synthesis: Part II. The role of propene. *J. Mol. Catal.* **1989**, *54*, 103–117. [\[CrossRef\]](#)
57. Henkel, R. The Influence of Ammonia on Fischer-Tropsch Synthesis and Formation of N-Containing Compounds. Ph.D. Thesis, Universität Oldenburg, Oldenburg, Germany, 2013.
58. Gibson, E.J.; Hall, C.C. Fischer-tropsch synthesis with cobalt catalysts. II. The effect of nitrogen, carbon dioxide and methane in the synthesis gas. *J. Appl. Chem.* **1954**, *4*, 464–468. [\[CrossRef\]](#)
59. Ordonsky, V.V.; Carvalho, A.; Legras, B.; Paul, S.; Virginie, M.; Sushkevich, V.L.; Khodakov, A.Y. Effects of co-feeding with nitrogen-containing compounds on the performance of supported cobalt and iron catalysts in Fischer-Tropsch synthesis. *Catal. Today* **2016**, *275*, 84–93. [\[CrossRef\]](#)
60. Li, J.; Yang, G.; Yoneyama, Y.; Vitidsant, T.; Tsubaki, N. Jet fuel synthesis via Fischer-Tropsch synthesis with varied 1-olefins as additives using Co/ZrO<sub>2</sub>-SiO<sub>2</sub> bimodal catalyst. *Fuel* **2016**, *171*, 159–166. [\[CrossRef\]](#)
61. Lu, X.; Zhu, X.; Masuku, C.M.; Hildebrandt, D.; Glasser, D. A study of the Fischer-Tropsch synthesis in a batch reactor: Rate, phase of water, and catalyst oxidation. *Energy Fuels* **2017**, *31*, 7405–7412. [\[CrossRef\]](#)
62. Seadira, T.; Sadanandam, G.; Ntho, T.A.; Lu, X.; Masuku, C.M.; Scurrrell, M. Hydrogen production from glycerol reforming: Conventional and green production. *Rev. Chem. Eng.* **2018**, *34*, 695–726. [\[CrossRef\]](#)
63. Masuku, C.M.; Biegler, L.T. Recent advances in gas-to-liquids process intensification with emphasis on reactive distillation. *Curr. Opin. Chem. Eng.* **2019**. [\[CrossRef\]](#)
64. Eze, P.C.; Masuku, C.M. Vapour-liquid equilibrium prediction for synthesis gas conversion using artificial neural networks. *S. Afr. J. Chem. Eng.* **2018**, *26*, 80–85. [\[CrossRef\]](#)
65. Eze, P.C.; Masuku, C.M. Supporting plots and tables on vapour-liquid equilibrium prediction for synthesis gas conversion using artificial neural networks. *Data Brief* **2018**, *21*, 1435–1444. [\[CrossRef\]](#) [\[PubMed\]](#)
66. Zhang, Y.; Masuku, C.M.; Biegler, L.T. Equation-oriented framework for optimal synthesis of integrated reactive distillation systems for Fischer-Tropsch processes. *Energy Fuels* **2018**, *32*, 7199–7209. [\[CrossRef\]](#)
67. Okoye-Chine, C.G.; Moyo, M.; Liu, X.; Hildebrandt, D. A critical review of the impact of water on cobalt-based catalysts in Fischer-Tropsch synthesis. *Fuel Process. Technol.* **2019**, *192*, 105–129. [\[CrossRef\]](#)
68. Fischer, N.; Clapham, B.; Feltes, T.; Claeys, M. Cobalt-based Fischer-Tropsch activity and selectivity as a function of crystallite size and water partial pressure. *ACS Catal.* **2014**, *5*, 113–121. [\[CrossRef\]](#)
69. Masuku, C.M.; Lu, X.; Hildebrandt, D.; Glasser, D. Reactive distillation in conventional Fischer-Tropsch reactors. *Fuel Process. Technol.* **2015**, *130*, 54–61. [\[CrossRef\]](#)
70. Iglesia, E. Design, synthesis, and use of cobalt-based Fischer-Tropsch synthesis catalysts. *Appl. Catal. A Gen.* **1997**, *161*, 59–78. [\[CrossRef\]](#)
71. Li, J.; Jacobs, G.; Das, T.; Davis, B.H. Fischer-Tropsch synthesis: Effect of water on the catalytic properties of a ruthenium promoted Co/TiO<sub>2</sub> catalyst. *Appl. Catal. A Gen.* **2002**, *233*, 255–262. [\[CrossRef\]](#)



72. Li, J.; Jacobs, G.; Das, T.; Zhang, Y.; Davis, B. Fischer–Tropsch synthesis: Effect of water on the catalytic properties of a Co/SiO<sub>2</sub> catalyst. *Appl. Catal. A Gen.* **2002**, *236*, 67–76. [\[CrossRef\]](#)
73. Yan, Q.; Yu, F.; Cai, Z.; Zhang, J. Catalytic upgrading nitrogen-rich wood syngas to liquid hydrocarbon mixture over a Fe–Pd/ZSM-5 catalyst. *Biomass Bioenergy* **2012**, *47*, 469–473. [\[CrossRef\]](#)
74. Visconti, C.G.; Mascellaro, M. Calculating the product yields and the vapor–liquid equilibrium in the low-temperature Fischer–Tropsch synthesis. *Catal. Today* **2013**, *214*, 61–73. [\[CrossRef\]](#)
75. Jess, A.; Popp, R.; Hedden, K. Fischer–Tropsch-synthesis with nitrogen-rich syngas: fundamentals and reactor design aspects. *Appl. Catal. A Gen.* **1999**, *186*, 321–342. [\[CrossRef\]](#)
76. Dai, X.; Yu, C. Characterization and catalytic performance of CeO<sub>2</sub>–Co/SiO<sub>2</sub> catalyst for Fischer–Tropsch synthesis using nitrogen-diluted synthesis gas over a laboratory scale fixed-bed reactor. *J. Nat. Gas Chem.* **2008**, *17*, 17–23. [\[CrossRef\]](#)
77. Jess, A.; Hedden, K.; Popp, R. Diesel Oil from Natural Gas by Fischer–Tropsch Synthesis Using Nitrogen-Rich Syngas. *Chem. Eng. Technol. Ind. Chem. Plant Equip. Process Eng. Biotechnol.* **2001**, *24*, 27–31. [\[CrossRef\]](#)
78. Xu, D.; Duan, H.; Li, W.; Xu, H. Investigation on the Fischer–Tropsch Synthesis with nitrogen-containing syngas over CoPtZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst. *Energy Fuels* **2006**, *20*, 955–958. [\[CrossRef\]](#)
79. Patzlaff, J.; Liu, Y.; Graffmann, C.; Gaube, J. Studies on product distributions of iron and cobalt catalyzed Fischer–Tropsch synthesis. *Appl. Catal. A Gen.* **1999**, *186*, 109–119. [\[CrossRef\]](#)
80. Patzlaff, J.; Liu, Y.; Graffmann, C.; Gaube, J. Interpretation and kinetic modeling of product distributions of cobalt catalyzed Fischer–Tropsch synthesis. *Catal. Today* **2002**, *71*, 381–394. [\[CrossRef\]](#)
81. Hanlon, R.T.; Satterfield, C.N. Reactions of selected 1-olefins and ethanol added during the Fischer–Tropsch synthesis. *Energy Fuels* **1988**, *2*, 196–204. [\[CrossRef\]](#)
82. Biquiza, L.D.; Claeys, M.; Van Steen, E. Thermodynamic and experimental aspects of ‘supercritical’ Fischer–Tropsch synthesis. *Fuel Process. Technol.* **2010**, *91*, 1250–1255. [\[CrossRef\]](#)
83. De Klerk, A. Fischer–Tropsch refining: Technology selection to match molecules. *Green Chem.* **2008**, *10*, 1249–1279. [\[CrossRef\]](#)
84. Dry, M.E. The fischer–tropsch process: 1950–2000. *Catal. Today* **2002**, *71*, 227–241. [\[CrossRef\]](#)
85. Jess, A.; Popp, R.; Hedden, K. From natural gas to liquid hydrocarbons. Pt. 4. Production of diesel oil and wax by Fischer–Tropsch–Synthesis using a nitrogen-rich synthesis gas-investigations on a semi-technical scale. *Erdoel Erdgas Kohle* **1997**, *113*, 531–540.
86. Shi, H.X.; Li, Z.K.; Liu, K.F.; Xiao, H.C.; Kong, F.H.; Zhang, J.; Chen, J.G. Enhanced formation of  $\alpha$ -olefins by the pulse process between Fischer–Tropsch synthesis and N<sub>2</sub> purging. *J. Fuel Chem. Technol.* **2016**, *44*, 822–829. [\[CrossRef\]](#)
87. Todici, B.; Ma, W.; Jacobs, G.; Davis, B.H.; Bukur, D.B. Effect of process conditions on the product distribution of Fischer–Tropsch synthesis over a Re-promoted cobalt-alumina catalyst using a stirred tank slurry reactor. *J. Catal.* **2014**, *311*, 325–338. [\[CrossRef\]](#)
88. Van Steen, E.; Schulz, H. Polymerisation kinetics of the Fischer–Tropsch CO hydrogenation using iron and cobalt based catalysts. *Appl. Catal. A Gen.* **1999**, *186*, 309–320. [\[CrossRef\]](#)
89. Muleja, A.A.; Yao, Y.; Glasser, D.; Hildebrandt, D. A study of Fischer–Tropsch synthesis: Product distribution of the light hydrocarbons. *Appl. Catal. A Gen.* **2016**, *517*, 217–226. [\[CrossRef\]](#)
90. Kapfunde, N.; Masuku, C.M.; Hildebrandt, D. Optimization of the thermal efficiency of a fixed-bed gasifier using computational fluid dynamics. In *Computer Aided Chemical Engineering*; Elsevier: Amsterdam, The Netherlands, 2018; Volume 44, pp. 1747–1752.
91. He, N.; Hu, Y.; Masuku, C.M.; Biegler, L.T. 110th Anniversary: Fischer–Tropsch Synthesis for Multiphase Product Recovery through Reactive Distillation. *Ind. Eng. Chem. Res.* **2019**, *58*, 13249–13259. [\[CrossRef\]](#)
92. Masuku, C.M.; Hildebrandt, D.; Glasser, D.; Davis, B.H. Steady-state attainment period for Fischer–Tropsch products. *Top. Catal.* **2014**, *57*, 582–587. [\[CrossRef\]](#)
93. McNab, A.I.; McCue, A.J.; Dionisi, D.; Anderson, J.A. Combined quantitative FTIR and online GC study of Fischer–Tropsch synthesis involving co-fed ethylene. *J. Catal.* **2018**, *362*, 10–17. [\[CrossRef\]](#)
94. Hutchings, G.J.; Copperthwaite, R.G.; van der Riet, M. Low methane selectivity using Co/MnO catalysts for the Fischer–Tropsch reaction: Effect of increasing pressure and Co-feeding ethene. *Top. Catal.* **1995**, *2*, 163–172. [\[CrossRef\]](#)



95. Zhang, Y.; Masuku, C.M.; Biegler, L.T. An MPCC Reactive Distillation Optimization Model for Multi-Objective Fischer–Tropsch Synthesis. In *Computer Aided Chemical Engineering*; Elsevier: Amsterdam, The Netherlands, 2019; Volume 46, pp. 451–456.
96. Ntelane, T.S.; Masuku, C.M.; Scurrrell, M.S. TPSR study: Effect of microwave radiation on the physicochemical properties of Fe/ZSM-5 in the methanol to hydrocarbons (MTH) process. *J. Porous Mater.* **2019**. [[CrossRef](#)]
97. Yang, J.; Ledesma Rodriguez, C.; Holmen, A.; Chen, D. Ethylene co-feeding effect on Fischer–Tropsch synthesis to olefin over Co based catalysts. In Proceedings of the American Chemical Society National Meeting & Expo, San Diego, CA, USA, 25–29 August 2019.



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