CHAPTER TWO

Reviews on Chemistry of Fischer-Tropsch Synthesis

2.0 Introduction

It is envisaged that catalyst design for enhanced economy of the process can be pursued by tailoring the synthesis to high value chemicals. These objectives require detail insight of the reaction mechanism at the molecular level. Efforts for elucidating mechanism of FTS have come a long way, but general consensus on detail mechanism of FTS (and its sister process - methanol synthesis) are still under debates. FTS is a bottom-up process. The history of FTS mechanism dates back to its discovery and there have been a number of periodic reviews on the subject along the time line, yet it is very difficult to capture all reports on the subject. In order to identify platforms for molecular engineering of FTS, this section is a highlight on recent progress on mechanism of FTS. The scope of the review is limited to thermodynamics and stoichiometry; product distribution, kinetic expression.

2.1 FT Thermodynamics and Stoichiometry

Hydrocarbons formation from syngas is exothermic, it is driven by co-formation of water and/or carbon dioxide [42]. One of such reactions is, \(2H_2 + CO \rightarrow \frac{1}{3}C_3H_6 + H_2O, \Delta G^o_{(227^oC)} = -96\) kJmol\(^{-1}\). Release of heat increases with increasing chain length hence heat removal is a very important factor in reactor and process design. In practice, more than one reaction is possible on the catalyst surface in a FTS reactor. A list of likely reactions in an FT reactor is shown in Table 2.1. Thermodynamic product selectivity generally follows the order: alkanes > alkenes > alcohols, and the product distribution can vary significantly with catalyst type and reaction conditions. For simplicity the stoichiometry of FTS is often approximated as [43]:

\[ nCO + 2nH_2 \rightarrow - (CH_2)_n^- + nH_2O \Delta H_{R(227^oC)} = -165 \) kJ mole\(^{-1}\)

Stoichiometric requirement of the syngas feed for a FT process depends on operation mode and catalyst properties. When reactants are in stoichiometric balance, the relation, \(H_2/(2CO+3CO_2)\), known as Ribblett ratio, is unity [45]. It is generally believed that water gas shift (WGS) reaction have profound effect on the reaction stoichiometry. Co based catalysts generally exhibit low WGS activity, syngas of \(H_2/CO \approx 2\) is required. Fe based catalysts are generally WGS active, they can use \(H_2/CO \leq 2\), depending on reaction temperature.
Main reactions
1. Methane
   \[ \text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O} \]
2. Paraffins
   \[ (2n+1)\text{H}_2 + n\text{CO} \rightarrow C_n\text{H}_{2n+2} + 2n\text{H}_2\text{O} \]
3. Olefins
   \[ 2n\text{H}_2 + n\text{CO} \rightarrow C_n\text{H}_{2n} + n\text{H}_2\text{O} \]
4. Water gas shift (WGS) reaction
   \[ \text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \]

Side reactions
5. Alcohols
   \[ 2n\text{H}_2 + n\text{CO} \rightarrow C_n\text{H}_{2n+1} + n\text{H}_2\text{O} \]
6. Boudouard reaction
   \[ 2\text{CO} \rightarrow \text{C} + \text{CO}_2 \]

Catalyst modifications
7. Catalyst oxidation/reduction
   a. \[ \text{M}_x\text{O}_y + y\text{H}_2 \rightarrow y\text{H}_2\text{O} + x\text{M} \]
   b. \[ \text{M}_x\text{O}_y + y\text{CO} \rightarrow y\text{CO}_2 + x\text{M} \]
8. Bulk carbide formation
   \[ y\text{C} + x\text{M} \rightarrow \text{M}_x\text{C}_y \]

Table 2.1: Fischer–Tropsch synthesis reactions [44]

For high temperature (300-350 °C) operation mode, WGS proceed to equilibrium and can complement hydrocarbon. For instance, net reaction for hydrocarbon formation using syngas with \( \text{H}_2/\text{CO} = 1 \) can be given: \( 2\text{CO} + \text{H}_2 \rightarrow -\text{CH}_2- + \text{CO}_2 \). For low temperature (180-250 °C) operation mode, WGS proceed far less below equilibrium but significant CO\(_2\) formation can occur. Under this operation mode especially when using syngas of \( \text{H}_2/\text{CO} = 2 \), WGS activity is unwanted. This account in part for the preference of Co based catalysts for GTL plant. However, WGS is also considered a pre-requisite for hydrogenation of CO\(_2\), via the reverse reaction (rWGS) to CO before subsequent hydrogenation to hydrocarbon.

However, Ni et al. [46] have asserted that r-WGS is not an indispensable step for FTS using CO\(_2\). Fujiwara et al. [47] and Rongxian et al. [48] have also advanced that hydrogenation of CO\(_2\) using un-promoted and Zr promoted Fe-Zn FT catalyst indicate that hydrocarbon formation from CO\(_2\) precede largely via methanol intermediate. A common feature of the catalysts in the three reports is the presence of ZnFe\(_2\)O\(_4\) spinel phase. The same spinel phase is identified in the catalyst reported by Iglesia and co-workers [49]. The authors treat spinel phase as textural promoter which increases the surface of the catalyst. One of the qualities of their catalyst is lower CO\(_2\) formation. It appears that spinel is not only a textural promoter but also plays a role in the observed lower CO\(_2\) formation of the catalyst reported by Iglesia and co-workers. The above observation is particularly interesting from fundamental and applied studies and may open a new chapter in approaches to design of FT catalyst. Therefore, more fundamental studies are required for insights on the properties and FT activity of the spinel, ZnFe\(_2\)O\(_4\), and similar crystalline phases.
2.2 Fischer-Tropsch Synthesis Product Distribution

Syncrude is a spectrum of hydrocarbons ranging from C\textsubscript{1} to C\textsubscript{50-200}. Typical gas chromatogram of FTS products is a complex spectrum of products, characterised by notable degree of order with regard to class and size of the molecules or carbon number [50]. With cursory analysis of the chromatogram it is noticed that the mole fractions of the individual products in carbon number fractions declines exponentially with carbon number. This behaviour being typical of polymerisation reaction led to the description of FTS as a surface polymerisation reaction which proceeds via stepwise addition of a monomer carbon species and one termination constant for all products as shown in Scheme 2, X (where X may be CO, H\textsubscript{2}CO, HCOH, HCO, CHO, COH, C, CH, CH\textsubscript{2}).

![Scheme 2.1: FTS chain growth in classical ASF model](image)

Instead of tabular list or pictorial presentation of the products, a simple and unambiguous model will provide a quicker comparison of selectivity of catalysts and reaction conditions. Such a model may also provide indirect insights about mechanism of product formation. An empirical statistical product distribution model known as “Anderson-Schultz-Flory” (ASF) distribution law emerged for this purpose. Mathematical description of ASF law is illustrated in Equations 1 – 4. Similar to polymer product distribution, graphical description of FT as in Figure 2.1 or 2.2 become popular.

\[
m_n = (1-\alpha) \alpha^{n-1} \quad \text{.................... 1}
\]

\[
m_n = \frac{w_n}{n} = \frac{(1-\alpha)^2}{\alpha} \alpha^n \quad \text{.................... 2}
\]

Where

- \(n\) - carbon number of the product atom
- \(m_n\) - mole fraction of a hydrocarbon with chain length \(n\)
- \(\alpha\) - ASF chain growth probability

\[
\alpha = \frac{R_p}{R_p + R_t} \quad \text{.................... 3}
\]

\(R_p\) and \(R_t\) are the rate of propagation and termination,
For practical applications the ASF formula is mostly used in the logarithmic form:

$$\log \frac{w_n}{n} = n \log \alpha + \log \left( \frac{(1 - \alpha)^2}{\alpha} \right)$$

A semi-logarithm plot of product mole fraction as a function of carbon number should produce a straight line, and chain growth probability, $\alpha$, can readily obtain from the slope (Figure 2.3). As mentioned above the ASF distribution is based on the assumption that the chain growth probability is constant and saturated hydrocarbons are formed by stepwise addition of monomer to a growing chain.

Figure 2.1: Ideal ASF FT product selectivity as function of the chain growth probability factor $\alpha$

Figure 2.2: A typically theoretic FT synthesis distribution, $\alpha = 0.85$

Figure 2.3: Classical Anderson-Schulz-Flory distribution of all products
2.3 Deviations from ASF Distribution

Although a fair description of FTS products is obtained using ASF distribution law, there are significant deviations of FT product spectrum obtained from iron, cobalt, and ruthenium catalysts from the ASF distribution law [51-56]. The deviations are illustrated in Figure 2.4 and are as follows [57-59]:

- high molar methane content than predicted from ASF;
- an anomaly in C₂ with relatively low molar contents than in the ASF diagram and low olefin contents in the C₂ fraction;
- a curvature away from the ASF distribution at high carbon numbers;
- chain length dependency of olefin contents.

![Figure 2.4: Experimental FT product distribution in comparison to ASF distribution law](image)

While the deviations are generally attributed to occurrence of secondary reactions (hydrogenation, isomerization, \( \alpha \)-olefins reinsertion, and hydrogenolysis), van Dijk [60] draws attention to the point that FTS is not an ideal polymerization reaction assumed in the ASF model. He has pointed out that FTS differs from an ideal polymerization reaction because of the following: the monomer has to be formed in-situ on the catalyst surface from the reactants CO and H₂; the rates of surface reactions are chain length dependent and the primary products can undergo secondary reactions that influence the product distribution. In addition van Dijk has also opined that these three dissimilarities of FTS from ideal polymerization kinetics account for deviation of FTS product distribution from the ideal ASF distribution. He has drawn attention to the fact that erroneous product analyses can introduce
systematic deviations that may be mistaken for mechanistic phenomena, especially in non-steady state operations.

According to Dry [61], simple empirical rate equations may be sufficient for operation of pilot and commercial scale plants with a given catalyst. Moreover, general behaviour of Fischer-Tropsch catalysts at different process conditions are well known, details of Fischer-Tropsch mechanism is of little importance from process engineering perspectives. However, empirical rate equations give little or no insight into surface chemistry of the reaction. Surface chemistry of heterogeneous catalytic reactions is an essential tool for catalyst design and optimization. Accurate description and identification of adsorbed species on a catalyst surface are pre-requisites in gaining insights to its surface chemistry. In addition, detail profile of the products distribution is also essential for thorough kinetic analyses towards development of holistic reaction mechanisms and modelling. Detail description of FTS products is experimentally demanding and mathematically challenging. Experimentally, it is crucial to collect and analyse all the products (tail gas, water, oil, and wax), and search simple unambiguous model to describe the product distribution has been very challenging. In the subsequent sections, we examine proposed post ASF products distribution models and reaction mechanisms.

2.4 Post ASF product distribution models

Because of the highlighted limitations of ASF distribution law, there has been quest for more encompassing models to describe FTS products. The ASF model describes the entire product range by a single parameter, $\alpha$, the growth probability. Like ideal gas law, the beauty and the attraction of ASF model is its mathematical simplicity. However, it appears the single parameter, $\alpha$, is insufficient to describe the entire product range or the assumption of ASF that chain growth is independent of carbon number does not suffice in FTS. Approaches in post-ASF description of FT products are guided by this line of thoughts. The post ASF models to be discussed in next subsections are double-$\alpha$ model, olefin reinsertion models, chain-length-dependent desorption model [62-64].

2.4.1 Double-$\alpha$ model

Double-$\alpha$ model is based on the notion that there are more than one chain growth mechanisms on the surface of a FTS catalyst. Since FTS is considered as polymerization type reaction, having to
describe the FTS product spectrum with more than one \( \alpha \) values will introduce undue complexity, however, limiting the chain growth probability to two is considered a reasonable compromise. An illustration of double \( \alpha \) representation of FT product is shown is Figure 2.5. The double-\( \alpha \) model is a weighted sum of two ideal ASF product distributions as shown in Equation 5 below [65]:

\[
m_n = w_1 (1-\alpha_1) \alpha_1^{n-1} + w_2 (1-\alpha_2) \alpha_2^{n-1} \quad \text{......... 5}
\]

where \( \alpha_1 \) and \( \alpha_2 \) are chain growth probabilities.

Figure 2.5: A double \( \alpha \) representation of iron-catalysed LTFT product spectrum [66]

It becomes necessary to introduce another parameter, ‘breaking point’- a hypothetical carbon number value (not necessarily an integer), to delineate contributions of the chain growth probabilities, \( \alpha_1 \) and \( \alpha_2 \). The breaking point, designated as \( \mu \), has no physiochemical relevance, it is defined as the total mole fraction of hydrocarbons formed with growth probability \( \alpha_1 \) (Equation 6). Thus, the model is characterised by three independent parameters: \( \alpha_1, \alpha_2 \) and \( \mu \).

\[
\mu = \frac{w_1}{w_1 + w_2} \quad \text{......... 6}
\]

Where \( w_1 \) and \( w_2 \) are total mass from chain growths \( \alpha_1 \) and \( \alpha_2 \).

Detail quantitative analysis of FTS products is sine qua non to successful assessments of product distribution model and mechanistic studies. Accuracy of mass balance is particularly critical for using double-\( \alpha \) model for description FTS products. There have been significant advances in analytical techniques and procedures for providing reliable data for description of FTS product. Bertoncini et al. [67], reported application of combination of different types of gas chromatography techniques such as low resolution, high resolution and two-dimensional gas chromatography provide enhanced molecular characterization of FTS products. A detailed composition of olefin and
oxygenates by-products is reportedly achieved through magnified resolution associated with the high peak capacity provided by comprehensive two-dimensional gas chromatography. The authors claim that each of the three main class of FTS products (paraffin, olefin and oxygenates) present unique Anderson Schulz Flory (ASF) distributions. Westhuizen and associates [68] also reported that GC $\times$ GC provides more accurate quantitative data for evaluation of effects of reaction variables on the deviation of FT product distribution from ASF distribution law. Recent studies by Pour and co-workers on the effect reaction variable on FTS products description by double-$\alpha$ model indicate that the bent deviations from ASF distribution law decreases with increasing H$_2$/CO ratio over Ru-promoted Co/Al$_2$O$_3$ and reducing particle size of Fe/Cu/La catalysts [69]. It is also shown that the bent deviation is enhanced with increasing order of basicity of the promoter (X = Ca, Mg, La) in Fe/Cu/X catalysts [70]. In contrast to double-$\alpha$ model, reports of Pour and associates [71] indicates that the bent deviation depend on reaction conditions and catalysts properties rather occurrence of more than one chain growth mechanisms. Also the model parameters in double $\alpha$ model are not independent as assumed; it is statistically more prone to errors [65]. A small variation in one parameter can easily be translated or propagated by the other parameter; this can lead into wide ranges of product distribution prediction. For example, the value of $\mu$ is depends on $\alpha_1$, thus, a small change in $\alpha_1$ will impact on the values of $\mu$, this will translate in variations in product selectivities. However, there have been claims of experimental evidences in support of two incompatible chain growth mechanisms in FTS [72]. Nevertheless, as shown in Figure 2.5, double-$\alpha$ model focuses on the bent shape deviation in the ASF distribution law at high carbon numbers. It offers no contribution to account for the other aspects of deviation from the ASF distribution law.

2.4.2 Re-adsorption models

Another group of post ASF distribution models are based on the premise that $\alpha$-olefins are the main primary product of FTS reaction. Main secondary reaction of the $\alpha$-olefins is hydrogenation to alkanes or re-adsorption into chain growth stream. Re-adsorbed $\alpha$-olefins can be re-inserted into a growing chain or initiate a new chain growth. The re-adsorption or re-insertion of $\alpha$-olefins is carbon number dependent. These secondary reactions account for chain length dependency of olefin selectivity and the bent curvature away from the ASF distribution at high carbon numbers. The
carbon number dependency is attributed to physical phenomena, namely: diffusivity, solubility and physisorption [50]. We examine these phenomena on one after the other.

### 2.4.2.1 Diffusion enhanced olefin readsorption model

Diffusion enhanced olefin re-adsorption model is advanced by Iglesia and co-workers [73]. These authors have explained that tendency of re-adsorption of α-olefin increases the slower it diffusion away from the surface of the catalyst. Diffusivity of α-olefin is a function of molecular size or carbon number, catalyst properties and reaction condition. Decreasing diffusivity increases residence time and tendency of re-adsorption of α-olefins. Hence, enhanced re-adsorption of α-olefins due diffusion limitation leads to increase in chain growth probability with increasing carbon number until a constant asymptotic value is reached for large hydrocarbon.

The authors also correlate reaction conditions and catalyst properties with re-adsorption of α-olefin. Low temperature, high pressure and low space velocity favour increase of residence time and re-adsorption of α-olefins which in turn promotes selectivity to heavy hydrocarbon. It is also added further that pores of catalyst bed are filled with liquid hydrocarbons produced during FTS; this condition highly restrict diffusion of α-olefins out of the pores of the catalysts. The authors have modified Scheme 2.1 by introduction of reversible olefin desorption-readsorption step to give Scheme 2.2. In a nutshell, this model proposes that chain growth is dependent on carbon number dependent and is favoured by inhibited diffusion enhanced re-adsorption of α-olefins.

![Scheme 2.2](image_url)

Scheme 2.2: Diffusion enhanced olefin readsorption model, a modified form of the classical ASF with the termination step addition of reversible olefin desorption-readsorption step [74]

Deviations of FTS products from ideal ASF distributions are explained in terms of carbon number dependent diffusion parameter, Φ in Equation 7.
\[ \Phi_n = \left( \frac{k_{r,n}}{D_n} \right) \left( \frac{L^2 \cdot \varepsilon \cdot \theta_{MC}}{R_p} \right) = \psi_n \cdot \chi \]  

Where
- \( k_{r,n} \) - first-order rate constant for olefin readsorption reaction
- \( D_n \) - effective diffusivity
- \( L \) - average radius of the catalyst pellets
- \( \theta_{MC} \) – metal dispersion or active site density
- \( \varepsilon \) - void fraction
- \( R_p \) - average pore radius of the metal oxide support

The first term of the equation, \( \psi_n \), reflects the molecular properties of olefins with \( n \) carbon atoms which leads to the observed effect of chain size on termination probability and olefin content, while the second term of equation, \( \chi \), depicts structural parameter of catalyst (considered a guide for rational FT catalyst design catalyst) [75].

Carbon number dependent diffusivity of \( \alpha \)-olefins is described by an empirical relation, \( D_n \propto e^{-0.3n} \), but the relation overestimates the diffusivity of the hydrocarbon. In addition the model is unable to account for experimentally observed exponential decreases of olefin/paraffin ratio as a function of carbon number [76-77]. Report of Shi and Davis [78] also shows that molecular diffusivity of hydrocarbon displayed lower dependency in the chain length. A recent report by Davis’s group also indicates that diffusion enhanced re-adsorption of olefins product is significant only for products with carbon number greater than 17, but chain length–dependent solubility in the liquid phase is the predominant cause of chain length dependencies of secondary reactions of \( \alpha \)-olefins [79].

2.4.2.2 Solubility enhanced re-adsorption olefin model

As mentioned in the diffusion enhanced model some authors are of the opinion that carbon number dependency of residence time of \( \alpha \)-olefins is due to their solubility in the liquid reaction product (wax) in the reactor or catalyst pores [80-83]. It is argued that solubility of olefins increases exponentially with carbon number and it has much stronger carbon number dependency compared to diffusivity. In solubility enhanced olefin re-adsorption model, catalyst pores or reactor filled with liquid/wax is considered an Eley-Rideal system in which interaction between the dissolved olefins and surface species on the catalyst is either diffusion or activation controlled. The interaction is considered activation controlled since experimental results have shown that diffusion alone does not sufficiently account for carbon number dependent re-adsorption of \( \alpha \)-olefins. Olefins re-adsorption
rate is considered to depend on concentration of activated complex which also depend on solubility in the liquid phase, thus, using activated complex theory, rate of \( \alpha \)-olefins re-adsorption is shown in Equation 8,

\[
k = \frac{k_c \gamma_O \gamma_S}{\gamma_{OS}} \quad \text{8}
\]

where, \( k_c \) is gas phase or ideal solution rate constant, \( \gamma_O, \gamma_S \) and \( \gamma_{OS} \), are activity coefficients of dissolved olefin, surface species and their activated complex.

When \( \gamma_{OS} < 1 \), then \( k_c > k \); the complex is more solvated than the reactants, then solubility enhances re-adsorption of \( \alpha \)-olefins and chain growth initiation. Thus, carbon number dependent re-adsorption of olefins will be kinetics controlled rather than by thermodynamics. Solubilities of the \( \alpha \)-olefins can be related to vapor–liquid equilibria characteristics of FTS systems. Although estimates can be obtained using Raoult’s or Henry’s law, Derevich and associates [84] have commented that such empirical methods may not be accurate enough but a rigorous calculation based on the use of state equations with appropriate mixing rules.

In summary, description of FT product distribution using solubility enhanced \( \alpha \)-olefin re-adsorption model is characterised by use many parameters and complicated expression. Moreover, the assumption has been challenged from thermodynamic point of view. At equilibrium activity/chemical potential of a substance is identical in liquid and gas phase; hence, reactivity/olefin re-adsorption rate should be independent of concentration/solubility in the liquid phase.

2.4.2.3 Physisorption enhanced re-adsorption olefin model

Influence of physisorption of olefins has also been suggested as important factor that could influence the rate of re-adsorption of \( \alpha \)-olefins. Generally, linear relationships are observed between logarithm of equilibrium adsorption parameters and carbon number. Carbon number dependent \( \alpha \)-olefin re-adsorption over ruthenium catalyst under FT condition has been described with Henry constant, \( H_n \alpha \) e\(^{1.2n}\). And carbon number dependency of physisorption for larger olefins has also been used to predict the increase of the chain growth probabilities with chain length [80,85].
2.4.2.4 Combined Solubility-physisorption enhanced α-olefin re-adsorption model

As highlighted in Section 2.4.2.1, limitations of diffusivity model has motivated proposals in support of solubility and physisorption to account for re-adsorption of α-olefins. These factors are physical phenomena with common molecular origin but are manifested at different conditions. But it is difficult to delineate which one is responsible for observed carbon number dependent enhancement of re-adsorption of α-olefins. However, Geerlings et al [85] have showed that the chain length dependent re-adsorption of α-olefins is weaker in the presence of a wax layer than on a wax free layer. They have attributed their observation to differences in effective of heat of desorption. They have explained that in the absence of a wax layer, the hydrocarbons desorb from a bare metal surface, whereas in the presence of a wax layer desorption takes place through a liquid phase. The authors believe that carbon number dependent re-adsorption of α-olefins originates from solubility and physisorption, rather than from inhibited diffusion. Hence, they introduce transition point between solubility and physisorption contributions to re-adsorption of α-olefins in terms of critical chain growth probability, $\alpha_c$ (defined as maximum $\alpha$ value below which wax formation can be avoided). The FTS conditions with chain growth probability below and above the critical value are referred to as dry and wet operations respectively. Low conversions, high temperatures and low pressures favour dry conditions. The reaction conditions are characterized by smaller chain growth probability than correlation factor, $\beta$ (which relates hydrocarbon vapor pressure with carbon number). From a large collection of experimental gas-liquid data, Equations 9 and 10 are obtained as empirical relation between temperature and vapour pressure of hydrocarbons [59].

$$P_i = P_o \beta^\alpha$$, where $P_o = 1.78382 \times 10^4$ kPa ..............9

$$\beta = \exp \left( -427.218 \left( \frac{1}{T} - 0.001029801 \right) \right)$$ ....................10

The vapour pressure is then related to enthalpy of desorption as follow:

$$P_i^\alpha = P_o \cdot e^{\frac{-E_{des}}{RT}}$$ .........................11

Where $\frac{E_{des}}{R}$ is effective enthalpy of desorption (or vaporisation) per –CH$_2$– unit.

$$\alpha_c = \beta = e^{\frac{-E_{des}}{RT}}$$ .........................12

At 498 K, the critical chain growth probability is $\alpha_c = 0.66$. At $\alpha > \alpha_c$ solubility becomes dominant factor and vice-versa.
With the recognition that physisorption is a transition state between the chemisorbed and the vapor or liquid phase hydrocarbons, Van der Laan and Beenackers [86] relates the gas phase pressure to carbon number dependent concentration of olefins on a catalyst surface (see Figure 2.6) and derived Equation 13 which combines solubility and physisorption contributions to re-adsorption of α-olefins in a single constant, c.

\[
\frac{CC_nH_{2n}}{P_{CnH_{2n}}} \alpha e^{c_n} \quad \text{.......................... 13}
\]

Numerator and denominator terms in RHS of Equation 13 are solubility and physisorption contributions respectively. The value of ‘c’ as obtained by regression analysis is = 0.29 ± 0.07.

Like diffusion model, solubility and physisorption models focus on bent deviation, Van der Laan and Beenackers [86] provide explanations for other identified deviations from ideal ASF law. The post ASF models discussed so far are distances away from the coveted simplicity of ASF law. We provide an appraisal of the re-adsorption models before we examine chain-length-dependent desorption model.

**Appraisal of carbon dependent re-adsorption of olefin models**

Two key components in the assumptions of olefin re-adsorption models diffusion model premise, ‘olefin re-adsorption’ and ‘chain initiation’. The models treat the first component as physical phenomenon but are silent on the second component. Perhaps it is an oversight or olefin re-adsorption which is assumed to be the rate limiting step in the consecutive elementary processes. Hence, limitations of the models may be traceable to this oversight. Despite leading to more
complex expressions, success of the models is comparable irrespective of their different mathematic
treatment; possibly because diffusion, solubility and physisorption are closely inter-related and it
may be difficult to completely delineate their effects in FTS reaction conditions.

In the diffusion model, carbon number dependent diffusivity in the liquid filled-catalyst pores.
Although the model is silent about influence of solubility, the model has indirectly incorporated
solubility. Yet, it appears that solubility or the condition of catalysts pores being filled with liquid is
a requisite to observe highly restricted diffusion of the olefins. According to classical law of
diffusion of gasses (Graham’s law of diffusion: at constant temperature and pressure, rate of
diffusion is inversely proportional to square root of molecular mass, expressed mathematically in
Equation 14), diffusivity decreases or residence time increases naturally increase with their
molecular mass.

\[
\text{Diffusivity} \propto \frac{1}{\sqrt{\text{Mol. mass}}}
\]

Figure 2.7 shows a plot of reciprocal of molecular mass of olefins as a measure of gas phase
diffusivity of olefins (from C_2 to C_{50}) as a function of their carbon number. The figure shows that
C_2 stands out having exceptional very high diffusivity compared to other olefins. Although
diffusivity falls steeply from after C_2, C_3-C_6 olefins also have very high diffusivity and C_7-C_{10}
olefins can also be said to have high diffusivity. After C_{10}, decrease of diffusive becomes gradual
and very gradual with increasing carbon number.

![Figure 2.7: Graham’s law diffusion illustration of diffusivity on carbon number of olefins](image)

\[
y = 0.114e^{-0.02x}, \quad R^2 = 0.868
\]
Comparison of shape/pattern of Figures 2.7 and 2.4 shows that except C₂ anomaly typical of FTS product selectivity pattern reflects the diffusivity pattern of the hydrocarbons. This may suggest that the commonly observed curvature away from the ASF distribution at high carbon numbers is due naturally restricted diffusivity of the FTS products (including olefins) and not their tendency to initiate chain growth after readsorption on the catalyst surface. It also suggests that other deviations of FTS product selectivity from ASF distribution law are most probably due to characteristic chemical behaviours of those constituent FTS products rather than due to physical behaviours as described in the olefin readsorption models. In general the olefins readsorption models are only able to describe the FTS product spectrum from C₃⁺. These are unable to predict C₁ and C₂ selectivities without introduction of special parameters. Perhaps a model with approach based on the intrinsic chemical behaviour of C₂ and C₁ will provide an all-encompassing single parameter that will sufficiently/satisfactorily describe the entire FTS product spectrum.

The above assertion is in line with findings of Schulz and Claeys [87]. These authors have conducted extensive studies on the kinetics of re-insertion α-olefins. α-olefins of carbon numbers C₂-C₁₁ are co-fed syngas in a gradient less stirred slurry reactor during FTS. Reported observations from the experiments are as follows:

- Added olefins undergo limited reinsertion but significant extent hydrogenation and isomerisation reactions.
- Reactivity and selectivity of olefin incorporation is not chain length dependent (with exception of ethene which is 10-25 times more reactive than other olefins).
- Conversion of the co-fed olefins except (C₂, ethene) have no effect on olefin/paraffin ratio.
- Reaction conditions have a strong effect on extent of reaction and selectivity of co-fed olefins (e.g. inhibition by CO and alkali in iron based FTS).
- Olefins with internal double bonds and paraffins do not participate in secondary chain growth.

Despite the above findings, especially exceptional chemical behaviour of ethene compared to other olefins, the authors have explained the deviation of FTS product spectrum from ASF distribution law in terms of mean reactor residence of a FT product. They proposed FT products in the reactor are in a convective cycle (Scheme 2.3). An FT product revolves between ternary phase (catalyst
surface, wax or liquid phase and gas phase) system. Preferential removal of a product from the convective cycle determines its mean reactor residence time; this in turn governs re-adsorption of an α-olefin and by extension the FT product spectrum. The mean reactor residence time of a product is expressed as:

\[ K_n = \frac{\rho_{\text{wax}(T)} \cdot RT}{\gamma_{n(T)} \cdot P_{n, \text{sat}}(T)} \]

Where \( \rho_{\text{wax}(T)} \) - density of wax at temperature T, \( \gamma_{n(T)} \) and \( P_{n, \text{sat}}(T) \) are activity coefficient and saturation pressure of component carbon number ‘n’.

**Scheme 2.3: Mean reactor residence time model [87]**

### 2.4.3 Chain-length-dependent desorption model

In contrast to assumption of olefins re-adsorption models, Kuiper and associates [80] have advanced that olefins need not desorb away from the active sites, that chain growth intermediates are physically and chemically attached to catalyst surface. And that typical curvature deviation from ASF distribution law is a primary characteristic of the FT product spectrum. Chain-length-dependent desorption model (Scheme 2.4) takes clue from the above assertion, the model considers deviation from ASF product distribution as due to chemical behaviour of intermediates prior to leaving the active site or catalyst surface [65]. The model takes a chemical approach to explain the deviation from ASF distribution. Assumptions are essentially the same with what has been proposed about two decades earlier by Wojciechowski and co-workers [54], that paraffins and olefins are primary products, each having characteristic termination rate but a common rate of propagation.
Contributions of proponent of chain-length-dependent desorption model consists of mathematical treatment, making it quantitative.

\[ C_n \rightarrow C_{n+1} \]

\[ 1 - \alpha_n \rightarrow \alpha_n \]

\[ C_n^* \rightarrow C_{n+1}^* \]

\[ \alpha_{n+1} \]

Scheme 2.4: Scheme used to derive the relationship between selectivities of consecutive carbon numbers [88]

Thus, the model parameters are chain growth, chain desorption and chain hydrogenation. Hydrogenation and desorption are considered chain termination steps, chain-growth probability as a function of the carbon number \((\alpha_n)\) is described in terms of rate constants, \(k\), of the three generic reactions as follows:

\[
\alpha_n = \frac{k_g}{k_g + k_h + k_d e^{-c n}} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots 16
\]

The ‘k symbols’ are catalyst properties, \(c\) is physical desorption constant of product (depending on process conditions - temperature and reactant partial pressures). The model states that competition between the three generic reactions rather than their absolute rates governs the product distribution. The chain hydrogenation and desorption are assumed to give paraffins and olefins respectively. The relative rates are defined as follows:

\[
T_p = \frac{k_h}{k_g}, \quad T_O = \frac{k_d}{k_g}
\]

Where \(k_h\), \(k_g\) & \(k_d\) are rate constant for the chain hydrogenation, chain growth & chain desorption respectively. Propensity to olefins relative to paraffins is given below:

\[
\frac{T_O}{T_p} = \frac{k_d}{k_h}
\]

Hence, olefin/paraffin ratio \((O/P)_n\) and chain growth probability as a function of the carbon number are then be expressed as follows:
\[
(O/P)_n = \frac{T_o e^{-cn}}{T_{ph}} \quad \text{..........................17}
\]

\[
\alpha_n = \frac{1}{1 + T_p + T_o e^{-cn}} \quad \text{..........................18}
\]

The only mathematical constraints in \(\alpha_n\) is that all three must assume positive values. Olefin/paraffin ratio will decrease exponentially with the carbon number, increasing pressure and decreasing temperature.

In previous models, prediction is limited to C\(_3^+\) fractions of the product spectrum. Desorption model treats C\(_1\) precursor like higher Cn surface species and can terminate via either hydrogenation or desorption without considering the mechanistic implication of desorption aspect. Methane formation rate is described satisfactorily, using parameter values that are obtained from higher Cn product fraction. To predict C\(_2\), the model is extended by invoking Dry’s hypothesis that observes negative deviation in the total C\(_2\) selectivity is due to the possibility of two active growth positions in C\(_2\) surface species. Equation 18 is revised by diving \(T_p\) and \(T_o\) by 2.

\[
\alpha_n = \frac{1}{1 + 0.5T_p + 0.5T_o e^{-k}} \quad \text{for } n = 2 \quad \text{..............19}
\]

With the revision, total C\(_2\) formation rate is predicted almost perfectly, but ethylene/ethane ratio is overestimated. This is attributed to high tendency of ethylene to undergo secondary hydrogenation to ethane. Despite the overestimate, the model is the first model that successfully captures nearly all the deviations from ASF distribution law without introducing additional parameters to predict C\(_1\) and C\(_2\) selectivities.

So far we have been examining descriptions of FTS product spectrum, from the humble start with ASF distribution law and its deficiencies, and post ASF models which are attempted to correct ASF deficiencies. The models constitute indirect or backdoor view of mechanism of FTS. To a first approximation, ability of such model to fully describe the product spectrum is an indication of correctness of its assumptions with respect to the reaction dynamics. However, a front door or investigation of the reaction mechanism from starting reactant is necessary for confirmation. This leads us to examining macro kinetics and mechanisms of FTS in the remaining sections.
2.5 Kinetics of FTS reaction

Accurate understanding of mechanism of a chemical reaction is not only a pre-requisite for developing physically realistic mathematical models for the reaction; it is also a crucial requirement for rational design of efficient catalyst [89]. Activity of FT catalysts depends on choice of active metal and preparation method. It is generally accepted that the order of specific activity of FT active metals follows the order: Ru > Ni > Co > Fe; only iron and cobalt are commercially viable. There appears preference for cobalt based catalysts in most new FT plants because of higher activity and stability of cobalt compared to iron. However, precursors of iron based catalysts are cheaper than those of cobalt. From process economy point of view, it is desirable to develop iron based catalysts of comparable activity and stability as cobalt based.

A macro kinetic study is a useful tool for gaining insight about reaction mechanism. For simple reactions, macro kinetic studies may provide sufficient information to decipher reaction mechanism, but it is usually insufficient to provide satisfactory details of about complex reactions. However, it can provide a starting platform for further probe of reaction mechanism using other tools (isotopic, spectroscopic, and theoretical) [89-91]. There are two common approaches in macro kinetic studies: deductive or inductive methods. Deductive approach often involves fitting experimental kinetic data with empirical or polynomial models. When the species (reactants, intermediates, products) involved in the reaction are not explicitly defined in FTS, this approach may be associated with many fitted parameters which give little or no insight about the reaction mechanism. Moreover, extrapolation of the rate equations outside the region where data is collected may lead to significant deviations. In inductive approach, rate equations are derived based on proposed mechanism, the equation that best fit the experimental data is adjudged the most probable mechanism. Since inductive approach is based on prior informed assumption or theories, it is expected that the kinetic expression which best fits the experimental data should be capable of predicting the reaction rate at all conditions. Absence of significant deviation of extrapolations from an equation is a proof of validity of the assumptions or theories upon which the equation has been derived.

Although FTS is generally considered polymerisation in nature, polymerisation kinetic expressions [92-94] are not directly applicable because in FTS, monomer species are formed in-situ on catalyst surface and more than one potential monomer is possible. At present, there is no clear consensus on
the expression for the kinetics of FT reaction over iron and cobalt based catalysts. Various equations proposed to describe the rate of FTS reaction over iron and cobalt based catalysts are shown in Tables 2.2 and 2.3. The rate expressions in Table 2.2 and 2.3 are of Langmuir-Hinshelwood-Hougen-Watson type models based on different assumption. Without recourse to the various assumptions, cursory mechanistic interpretations can be drawn from the expressions based on a general form of useful kinetic equation for multi-step heterogeneous catalytic reactions given by Susu [95].

\[
\text{rate} = A \frac{k_i \prod C_i^{\alpha_i} - \prod K_j \prod C_i^{\beta_i}}{1 + \sum K_i C_i^{\gamma_i}}
\]

Where \(i, j, k, \ldots\) - are sequential elementary steps
\(k_i\) and \(k_{-i}\) - rate constants of the forward and reversed of elementary step \(i\)
\(K_i, K_j, \ldots\) - are equilibrium constants of elementary steps \(i, j, \ldots\)
\(C_i\) - concentration of species involved in elementary step \(i\)
<table>
<thead>
<tr>
<th>Proponent(s)</th>
<th>Kinetic expression</th>
<th>Derivable mechanistic insight</th>
<th>n</th>
<th>Species involved in the rate determining step</th>
</tr>
</thead>
<tbody>
<tr>
<td>a. Anderson-Dry</td>
<td>$R_{FT} = A \frac{P_{H_2}P_{CO}}{P_{CO} + bP_{H_2O}}$</td>
<td>1</td>
<td></td>
<td>Undissociated H$_2$ or CO</td>
</tr>
<tr>
<td>b. Ledakowicz-Nettelhoff</td>
<td>$R_{FT} = A \frac{P_{H_2}P_{CO}}{P_{CO} + cP_{CO}}$</td>
<td>1</td>
<td></td>
<td>Undissociated H$_2$ or CO</td>
</tr>
<tr>
<td>c. Satterfield-Huff</td>
<td>$R_{FT} = A \frac{P_{H_2}P_{CO}}{P_{CO} + b(P_{H_2O}/P_{H_2})}$</td>
<td>1</td>
<td></td>
<td>Undissociated H$_2$ or CO</td>
</tr>
<tr>
<td>d. Van Berge</td>
<td>$R_{FT} = A \frac{P_{CO}P_{H_2}^\alpha}{P_{CO}P_{H_2}^\beta + bP_{H_2O} + cP_{CO}^2}$</td>
<td>1</td>
<td>Undissociated H$_2$ or CO</td>
<td></td>
</tr>
<tr>
<td></td>
<td>where $\beta = \text{maximum} \ (\alpha - 1, 0)$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>e. Van Steen</td>
<td>$R_{FT} = A \frac{\frac{P_{CO}}{P_{H_2}^{0.5}P_{CO}}}{P_{H_2O}^{0.5}}$</td>
<td>2</td>
<td>Partially dissociated H$_2$ and Undissociated CO</td>
<td></td>
</tr>
<tr>
<td>f. Botes et al.</td>
<td>$R_{FT} = A \frac{P_{H_2}^{0.5}P_{CO}}{(1 + k_{CO}P_{CO})^2}$</td>
<td>2</td>
<td>Dissociated H$_2$ and Undissociated CO</td>
<td></td>
</tr>
</tbody>
</table>

Table 2.2: Proposed kinetic expression for FTS over iron catalysts (adapted from ref 104)
<table>
<thead>
<tr>
<th>Proponent(s)</th>
<th>Kinetic expression</th>
<th>Derivable mechanistic insight</th>
</tr>
</thead>
<tbody>
<tr>
<td>a. Rautavuoma and Van der Baan</td>
<td>$R_{FT} = A \frac{P_{H_2}P_{CO}^{0.5}}{(1 + k_{CO}P_{CO}^{0.5})^3}$</td>
<td>3 Undissociated H$_2$ and Dissociated CO</td>
</tr>
<tr>
<td>b. Yates and Satterfield</td>
<td>$R_{FT} = A \frac{P_{H_2}P_{CO}}{(1 + k_{CO}P_{CO})^2}$</td>
<td>2 Undissociated H$_2$ and CO</td>
</tr>
<tr>
<td>c. Sarup and Wojciechowski</td>
<td>$R_{FT} = A \frac{P_{H_2}^{a}P_{CO}^{b}}{(1 + \sum k_i P_{H_2}^{c}P_{CO}^{d})^2}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Where a, b, c and d could assume various values, including fractions such as 0.25 and 0.75.</td>
<td></td>
</tr>
<tr>
<td>c(1).</td>
<td>$R_{FT} = A \frac{P_{H_2}^{0.5}P_{CO}}{(1 + k_{CO}P_{CO} + k_{H_2}P_{H_2}^{0.5})^2}$</td>
<td>2 Dissociated H$_2$ and Undissociated CO</td>
</tr>
<tr>
<td>c(2).</td>
<td>$R_{FT} = A \frac{P_{H_2}^{0.5}P_{CO}^{0.5}}{(1 + k_{CO}P_{CO}^{0.5} + k_{H_2}P_{H_2}^{0.5})^2}$</td>
<td>2 Dissociated H$_2$ and CO</td>
</tr>
<tr>
<td>d. Van Steen</td>
<td>$R_{FT} = A \frac{\frac{P_{H_2}^2}{P_{H_2}^{H_2O}}}{\left(1 + \frac{kP_{H_2}P_{CO}}{P_{H_2}^{H_2O}}\right)^2}$</td>
<td>2 Partially dissociated H$_2$ and Undissociated CO</td>
</tr>
<tr>
<td>e. Botes et al.</td>
<td>$R_{FT} = A \frac{P_{H_2}^{0.75}P_{CO}^{0.5}}{(1 + k_{CO}P_{CO}^{0.5})^2}$</td>
<td>2 Dissociated H$_2$ and CO</td>
</tr>
<tr>
<td></td>
<td>where $k_{CO} = k_{COH}P_{H_2}^{0.25} + k_{OH}P_{H_2}^{-0.25}$</td>
<td></td>
</tr>
</tbody>
</table>

Table 2.3: Proposed kinetic expression for FTS over cobalt catalysts (adapted ref 105)
The rate expression is derived using principle of microscopic reversibility and steady state approximation. The exponent ‘n’ in the denominator is a reflection of number of colliding reacting species in the rate determining step (n ≤ 2, n > 2 is statistically less likely). The numerator terms are governed by assumptions of the elementary steps. To make kinetic sense, the exponents α, β, & γ cannot assume arbitrary values. They are related to the number species that is involved in the elementary reactions (usually α, β, & γ ≤ 2). Kinetically, only positive integer values (1 or 2) are reasonable, but fractional values are also permitted as indication of dissociation of a reacting species. Since the rate expressions are usually reflection of rate determining step, mechanistic insights derivable from the rate expressions also presented in the respective Tables 2.2 and 2.3.

Comparison of the kinetic expressions in the Table 2.2 (except entry ‘f’) reveals that H₂O or CO₂ are considered as inhibition terms for FT reaction on iron catalysts. This has been a long held view, but recently this long held view is subjected to critical analyses and is found invalid. The proponents of the equation in entry ‘f’ (Table 2.2) have shown that the effect of H₂O on FTS reaction rate is not statistically significant. They have argued that there is no justification for inclusion of H₂O in the rate expression. These authors have demonstrated that their proposed rate expression (without H₂O and or CO₂ as inhibition terms) describes both historical and new kinetic data more accurately than those that have H₂O or CO₂ as inhibition terms [96]. Although there are opposing views on the effect of water pressure in cobalt based FTS, it is generally accepted that water does not influence FT rate over cobalt catalysts [97]. Hence, the rate expressions for cobalt catalysts contain no water term.

Arguments advanced in favoured entry ‘f’ (Table 2.2) appear sufficient as proof of validity of the derivable mechanistic insights from it. Over cobalt based catalysts, a straight conclusion cannot be reached. More information beyond what is derivable from macro kinetic studies is required. Moreover, further validation of the preliminary inference in the case of iron based catalysts is necessary. Such information is recently made available via theoretical and isotopic studies. Theoretical calculations indicate that hydrogen assisted CO
dissociation is more thermodynamically favoured over direct CO dissociated path [98]. Experimental data in support of this theoretical prompt is reported by Ojeda et al [99-100]. They demonstrate that hydrogen-assisted CO activation is the predominant kinetically-relevant step on Fe and Co catalysts at conditions typical of FTS practice. These authors show through theoretical calculation that H₂ dissociates readily over Fe and Co, and H-atoms are involved in the CO dissociation elementary steps (see Scheme 2.5).

Scheme 2.5: CO activation paths on Fe [blue] and Co [red]. The preferred H-assisted CO dissociation path is highlighted in blue. Values on the arrows refer to the individual barriers (in kJ mol⁻¹) for each elementary step. (adapted from ref 99)

This finding agrees with the mechanistic inference drawn from entry f (table 2.2) for iron based catalyst. However, over cobalt based catalyst, entry ‘c1’ (Table 3) is closest to the results of theoretical calculations and the same conclusion is drawn recently by Bukur and co-workers [101].

As shown above, it is only recently that the question about CO activation is resolved and it represents a major progress in the quest to unravel the mechanism of FTS. It engenders greater confidence in fitting macro kinetic data. However, mechanistic insights of macro kinetic studies do not extend to answering questions about identity of the monomer species and pathway of monomer coupling cannot be drawn from macro kinetic studies. In the next section we examine studies in these areas.
2.6 Mechanism of FTS

Unlike conventional polymerisation reactions where feed reactants are monomers, in FTS, monomers are first generated in-situ from the syngas feed (CO and H\textsubscript{2}) and it is generally accepted that hydrocarbons formation proceed in the following sequence: generation of the chain initiator; chain growth or propagation and chain growth termination or desorption. While complete description of mechanism of FTS will entails details atomic dynamics of the hydrocarbon formation sequence, it becomes rather more complicated with the inclusion of monomer formation step. A picture of the situation can be inferred from the perspective of Krische et al. [102-103], who has described FTS as hydrogen mediated catalytic reductive polymerization of carbon monoxide. They suggest that organometallic intermediates arising transiently in the course of catalytic hydrogenation of CO may be intercepted and re-routed to C-C coupling products. However, a number mechanism has been proposed, we examine only main rival mechanisms.

2.6.1 Rival mechanism

The identity of the monomer species involves is central for gaining a clear picture about product formation and selectivity in FTS. From Scheme 2.5, it can be seen that kinetically relevant path to chain initiator is similar on Fe and Co. However, chain growth can occur via oxygenated or deoxygenated surface species and views about FTS mechanism are along this divide. While our group highlights on proposed rival FTS mechanisms into oxygenated and deoxygenated surface species; we feel that ability to control or engineer catalyst surface to favour either of the possible chain growth species will provide leverage for controlling C-C coupling pathway and product distribution.

2.6.1.1 Oxygenated surface species

Here, the monomer is oxygen containing species which is partially hydrogenated or adsorbed CO species. Mechanisms under this group are summarized in Table 2.4 and scheme 2.6 [104].
### Table 2.4: Chain initiation and monomer formation via partial CO dissociation mechanisms

<table>
<thead>
<tr>
<th>Pathway</th>
<th>Chain initiation</th>
<th>Chain propagation</th>
<th>Chain termination</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO insertion or Hydroformylation</td>
<td>( m)-H or ( m)-R</td>
<td>CO insertion into ( m)-H or ( m)-R, followed by sequential hydrogenation and elimination of water</td>
<td>Hydrogenation to aldehydes or alcohols</td>
</tr>
<tr>
<td>Enol Mechanism</td>
<td>( m)=CHOH</td>
<td>Condensation of adjacent ( m)=CHOH, followed by elimination of water</td>
<td>Dehydration of alcohols to 1-alkenes</td>
</tr>
</tbody>
</table>

(a) Enol mechanism  
(b) CO insertion or Hydroformylation Mechanism

Scheme 2.6: Proposed Fischer-Tropsch synthesis mechanisms via oxygenates monomer formation and chain propagation [104-105]

### 2.6.1.2 Deoxygenated surface species

The mechanisms under this group are based on ‘carbide theory’, which presume CO is activated as surface carbide followed by sequentially hydrogenation to CH, \( \text{CH}_2 \), \( \text{CH}_3 \) and eventually \( \text{CH}_4 \) or to \( \text{C}_2 \), \( \text{CH} \equiv \text{CH}_2 \), etc. But \( \text{CH} \) or \( \text{CH}_2 \) is recognised as the chain initiators and propagators. The original carbide theory (Scheme 2.7) has undergone modifications in
the light of new experimental and theoretical studies. It is later re-named as carbene mechanisms. There are three mechanisms that are based on carbene intermediates and their main features are presented in Table 2.5 and Scheme 2.8.

![Scheme 2.7: Activation of CO on a metal surface giving surface carbide](image)

<table>
<thead>
<tr>
<th>Pathway</th>
<th>Chain initiation</th>
<th>Chain propagation</th>
<th>Chain termination</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkyl mechanism</td>
<td>m-CH₃ or m-CH₂⁻</td>
<td>CH₂</td>
<td>β-elimination to give 1-alkenes</td>
</tr>
<tr>
<td>Alkenyl mechanism</td>
<td>m-CH=CHR</td>
<td>CH₂ and sequential allyl-vinyl rearrangement step</td>
<td>β-elimination to give 1-alkenes</td>
</tr>
<tr>
<td>Alkylidene Mechanism</td>
<td>m=CH—CHR</td>
<td>CH and sequential H addition</td>
<td>β-elimination to give 1-alkenes</td>
</tr>
</tbody>
</table>

Table 2.5: Chain initiation and monomer formation via CO dissociation mechanisms

![Scheme 2.7](image)

(a) Alkyl mechanism

![Scheme 2.7](image)

(b) Alkenyl mechanism
For fundamental and application objectives it is desirable to unequivocally elucidate detail mechanism/pathway of FTS. Different monomer species are suggested in the selected rival mechanism. In fact, it has been commented that FTS does not have any close parallel in solution chemistry. According to Maitlis and Zanotti [106], there are as many views on the mechanism of interactions between the CO and H₂ leading the alkene and alkane products, as there have been workers on the topic. However, there appears to be convergences of opinions from old literature and recent findings in support of oxygenate species as more probable chain propagator. Next section is discussions and highlights of studies on C-C coupling pathways in FTS.

2.6.2 C-C coupling pathways on cobalt and iron catalysts
Next to resolve CO activation pathway is in question about the identity of the monomer species and coupling pathway. From Scheme 6 potential candidates are: HCO*, HCOH*, CH* and CH₂*. These surface species correspond to suggest monomers in CO insertion, enol, alkylidene, and alkenyl mechanism respectively. Screening of the candidates by expected primary product(s) based on proposed chain termination steps is less useful,
because in addition to high tendency of secondary reactions, two monomers can give same product. More convincing evidences are required to screen out the surface species and C-C coupling pathway or provide probabilities of their contributions to primary product formation. Recent findings appear to be are converging towards oxygenate mechanisms as the favoured route to hydrocarbon formation over iron (as well as cobalt) catalysts under FTS condition. Here, with a very brief historical perspective we examine findings from theoretical, isotopic and spectroscopic studies toward unravelling C-C coupling pathway in FTS.

2.6.2.1 Iron catalysts

In a short account on mechanisms FTS reaction on iron catalysts is compiled by Davis [105], carbide mechanism is credited to Fischer even though he pre-supposed oxygenate intermediates route for C-C coupling. Carbide mechanism enjoyed acceptance in the first fourteen years of discovery of FTS. The next thirty years (1940–70) marked reports on oxygenated (enol) mechanisms on iron catalysts based on isotopic studies. From 1970, attention shifted back to the carbide mechanism and it dominates discussions on FTS afterwards. Series of reports on isotopic studies by Davis and co-workers strongly support oxygenates intermediate route to hydrocarbons over iron catalysts [107-112]. They demonstrated that co-fed alcohols re-incorporate 50 – 100 times as much as alkenes counterpart at initiating chain growth over iron catalysts. Investigation conversion of alcohols over iron oxide and iron carbides catalysts by Wang and Davis [110] indicated that the substrates undergo dehydration, dehydrogenation and ketonisation (Tischenko condensation) for tertiary, secondary and primary alcohols respectively. Through $^{14}$C-tracer studies it is also shown that alcohol dehydration to olefin in FTS product spectrum is insignificant. Putting these observations together, Davis has advanced that chain initiation over iron catalysts is most probably via formate species formed from either CO or CO$_2$. But he has added that propagation steps involve the addition of CO (or a surface species derived from CO) to a growing chain. The proposed mechanism is illustrated in Scheme 2.9. It is essentially the same as CO insertion mechanism in Table 2.4 but with oxygenates species as initiator [107].
Scheme 2.9: Chain initiation and chain propagation in modified oxygenate mechanism by Davis [107]

A recent report by Durham et al. [113], also supports CO insertion mechanism on iron catalysts. These authors have carried out FTS over Fe-Zn based catalyst in supercritical hexane media. In addition to alcohols as observed by Davis and associates, these authors obtain aldehydes as product and have shown aldehydes can initiate chain growth. They have proposed that n-alkanes and aldehydes as primary products, olefins are formed as both primary and secondary products, while CH$_4$ and CO$_2$ as secondary products.

2.6.2.2 Cobalt catalysts

Unlike iron catalysts in which there are older literatures that provide indications of involvement of oxygenate intermediates route to hydrocarbons, similar records are very scanty for cobalt catalysts. However, according to account on oxygenates mechanism compiled by Davis [107], in the early 1950s and 60s, British researchers while studying hydroformylation have inferred that alcohols are the true primary products of the Fischer–Tropsch synthesis on both cobalt and iron catalysts. Wender and associates [114] have also proposed hydroformylation as hydrocarbon formation route in FT reaction. The next reports that indicate oxygenated intermediate route hydrocarbon formation on cobalt catalyst was about two decades later by Mims [115]. He has stressed that evidence from isotopic transient studies of FTS over cobalt catalysts have shown that methanol shares the same oxygenate intermediate with hydrocarbon products. However, at about the time of report of Mims [115] carbide mechanism has gained wide acceptance as hydrocarbon formation route over cobalt catalysts. The original carbide mechanism was succeeded by carbene
mechanisms, which are short-lived by new findings in favour of oxygenate intermediate pathway.

After Fischer, Craxford and Rideal contributed to carbide mechanism. Brady and Pettit are known for the experiments which brought methylene to the fore as monomer or intermediate in hydrocarbon chain growth. In honour of contributions by Biloen and Sachtler, the alkyl-methylene C-C coupling mechanism was renamed Fischer–Tropsch–Brady–Pettit–Biloen–Sachtler Mechanism [116-118]. This mechanism enjoyed wide acceptance for short time but later became disfavoured, because alkyl-methylene C-C coupling pathway is found to be energetically unfavourable. Later alkenyl mechanism is proposed by Maitlis et al.[119-120] based on the consideration that achieving C-C coupling is more energetically favourable between alkenyl - methylene than alkyl-methylene. The mechanism is hinged on the following:

- analyses of products of FT reactions with $^{13}$C labelled alkene;
- decomposition of a model di-nuclear complex bearing three or four C1 ligands, $[(\text{Cp}^*\text{Rh})_2(\text{CH}_2)_2(\text{Me})(L)]^+$ or $[(\text{Cp}^*\text{RhMe})_2(\text{CH}_2)_2]$ to give propene $\text{MeCH}=$CH$_2$ under oxidative (or thermal) conditions;
- experiments which showed that vinyl + methyl coupling proceed more readily than methyl + methyl over model organometallic compounds.

But validity of the above observations was challenged by researchers. Shi and Davis [121-122] pointed out that the $^{13}$C-data and other isotopic tracer data of Maitlis et al., were wrongly interpreted and did not provide direct evidence in support of surface bound vinyl intermediate as chain initiator. Ndlovu and associates [123] also pointed out that allyl–vinyl isomerisation/rearrangement step claim in alkenyl mechanism cannot be replicated. They reported that under thermal treatment only decomposition of $\text{Fe}\{[\eta^5-\text{C}_5\text{H}_5]\text{CO}_2\text{CH}_2\text{CH.CH}_2\}$ and $\text{Fe}\{[\eta^5-\text{C}_5\text{(CH}_3)_3\text{CO}]_2\text{CH}_2\text{CH.CH}_2\}$, iron counterpart of the di-nuclear Rh complex, take place. In hydrogen atmosphere, mere hydrogenation of the ligand or cleavage of the metal-carbon bond is observed, and no allyl–vinyl isomerisation. They conclude that if allyl and vinyl species exist under Fischer–Tropsch synthesis
conditions, such species would desorb or be hydrogenated to alkyl species. Hence, the premise or the whole alkenyl mechanism is not a plausible chain growth mechanism in FTS.

Experiments and theoretical calculations have shown that CH₂ is kinetically unstable, it readily decomposes to CH. Hence, Ciobica et al. [124], explored CH as plausible monomer for hydrocarbon formation during FTS. In what is known as alkylidene mechanism, he proposed that CH can be added to an alkylidene (RCH) or alkyl (CH₃ or RCH₂) and C-C coupling in each case is followed by hydrogenation. Theoretical evaluation of mechanism was carried out using Ru(0001) surface, using periodic *ab initio* calculations. The authors have reported that calculation of results shows that the two C-C coupling shares the same intermediate and can occur in parallel. Comparing the results obtained with Ru with similar result on different transition metals, the authors have added that the stronger the M–C bond, the more difficult it is to hydrogenate toward methanation, they have advanced C–C coupling transition state over Ru(0001) surface is lower than transition state for methanation. They conclude that O atom is removed as water and the C atom is partially hydrogenated and then will enter in the C–C coupling cycle. In a similar investigation, Liu and Hu¹³⁴ have reported that C-CH coupling has lowest activation energy among the possible CH₃ species on Ru. They have proposed C + CR mechanism for FTS (Figure 2.8).

![Figure 2.8: Revised carbide (carbene) mechanism, Liu and Hu [125]](image)

The above theoretical studies in support of C-CH coupling mechanism are based on Ru. Although Ru is the most active FTS metal, data of calculations on Ru alone is not sufficient
to generalise validity of the mechanism. Reports of Cheng and co-worker [126] may afford a more valid generalisation. These researchers investigated the reaction rates of all possible C\(_1\) + C\(_1\) coupling pathways on stepped Rh, Co, Ru, Fe, Re surfaces. Their calculations indicated structures of transition states are similar on the surface of the metals but have different coupling barriers. They confirmed that CH\(_2\) + CH\(_3\) coupling is the least preferred pathway on the five metal surfaces due low stability of the reacting species. Calculations of Cheng et al. indicated that CH\(_3\), RCH\(_2\) and RCH species are unstable as coupling partners of CH. They have submitted that C-CH and CH-CH coupling play dominant role in chain growth on the five metal surfaces. Indication of instability of CH\(_3\), RCH\(_2\) and RCH species raise questions on the validity of mechanism that based on the species.

According to Morgan et al. [127], formyl is an unstable intermediate on Ru. However, recent findings points in the direction of likelihood of oxygenate intermediates in C-C coupling over cobalt catalysts. Hydroformylation experiments on silica supported cobalt catalysts seem to be the trigger of attention on possibility of oxygenate intermediates in C-C coupling on cobalt catalyst. Tsubaki and associates [128-130] have shown that Co/SiO\(_2\) catalysts are very active and selective for the synthesis of alcohols and aldehydes from syngas and 1-hexene under mild reaction conditions. Promotion of the cobalt with small amount of noble metals is found to enhance the hydroformylation activity of the catalysts. It is also found that the use of methanol and ethanol as solvent improve oxygenates selectivities. Conventional homogeneous catalysis hydroformylation reactions are usually carried out at conditions more severe (higher T and P) than FTS. But these authors performed the hydroformylation reactions at conditions (pressure and temperature) typical of LTFT. The enhancement of oxygenates selectivity by use of solvents can be interpreted as having similar effect as supercritical fluid media in FTS by minimizing extent of hydrogenation and other secondary reactions of the primary products.

Thus, it appears that by extrapolation there is a strong tendency of presence of oxygenates intermediates on cobalt catalysts at FTS conditions. This inference is supported by the report of Sanchez-Escribano et al. [131] who have used IR spectroscopy to investigate the
conversion of syngas and methanol over Cu–ZnO–Al₂O₃, Ni–Al₂O₃ and Co–Al₂O₃ (methanol synthesis, methanation and Fischer Tropsch catalysts respectively). These authors have shown that data obtained at low pressure provide clear evidence of existence oxygenate intermediates or pathway (formates, possibly dioxymethylene, methoxy groups) on the three catalysts. They have suggested that oxygenated surface species may be involved in the chain growth to give C₂⁺ compounds over Co–Al₂O₃. And that the oxygenate mechanism most probably co-exist with the carbide mechanism.

Although, theoretical calculation seems to lack behind, nonetheless, it provides further leads towards recognition of oxygenates mechanism on cobalt catalysts. Experimental results motivated theoretical studies to revisiting FTS mechanism and exploring the possibility of oxygenates on cobalt catalysts. Cheng et al. [132], use DFT calculations to investigate the mechanism of the formation of aldehydes and alcohols on Co based FT catalyst. They have identified CHO species as favoured oxygenates intermediate and CO-insertion mechanism is suggested as likely route for formation of long-chain oxygenates. The calculation results leading to the conclusion by Cheng et al., is without consideration of pressure gap between surface science and heterogeneous catalysis. Inderwildi and co-worker [133] have attempted bridging the pressure gap by using microkinetic simulations. From DFT calculation and simulation results they have asserted that preferred route of CO activation on cobalt catalyst proceed via formyl species intermediate (CO → CHO → CH₂O → CH₂). They reason that since CH₂ is an unstable species, it is less probable as the chain monomer. However, formyl species is also found to have very short half-lives and may be difficult to observe experimentally and may likely be detectable at high pressure.

Other DFT calculations by Inderwildi et al. [133] and Zhuo et al. [134], have shown that CO insertion is the most probable C-C coupling route to hydrocarbons over cobalt. Zhuo et al. reported that TOF of CO consumption through CO insertion doubles that through formyl intermediate. In confirmation of results of calculations, a recent report provides evidence of oxygenate pathway to hydrocarbon formation on cobalt catalyst [134]. Contrary to the anticipation of Inderwildi and co-worker that about experimental detection of oxygenates...
intermediates on cobalt catalysts, in a similar manner as Sanchez-Escribano et al. [131] and Kollar et al. [135] provide evidence of stable oxygenates intermediates on cobalt catalysts using variable temperature in-situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and optical diffuse reflectance (DRS) to identify oxygenate intermediates on cobalt catalysts.

From the above highlights, theoretical and experimental results converged on likelihood of oxygenate intermediates route to hydrocarbons on iron and cobalt catalysts. The results are in favour of CO insertion as C-C coupling mechanism on the two catalyst types. Yet it may be too early to arrive at conclusions on the topic, more rigorous fundamental studies are required to provide decisive evidences. Meanwhile, it is also instructive to compare FTS with other related C-C coupling reactions of CO.

### 2.7 Related C-C coupling reactions of CO

Table 2.6 shows other C-C coupling of reaction of CO. The closest to FTS in terms of co-reactant and product is isosynthesis. The key difference between the two reactions is nature catalyst, hydrogenation metals and acid-base metal oxides for FTS and isosynthesis respectively. The metal catalysts can activate the reactants (H₂ & CO) more efficiently than the oxide catalysts. This may account for need of greater severe reaction condition for isosynthesis than FTS. By extension, limited chain growth and branching in isosynthesis may also have connection with lower efficiency of the oxide catalysts at activating one or both reactants compared to metal catalysts in FTS. With this comparison, we are inclined to suggest that mechanisms of hydrocarbon formation in the two reactions are most probably similar if not identical.

It is generally agreed that C-C coupling during isosynthesis over ZrO₂ involve carbonylation and Aldol condensation. The major chain growth step occurs through CO insertion into activated aldehyde or ketone, alternative chain growth also occurs via condensation between methoxide and a surface bound enolate. Resulting intermediates can undergo further C-C coupling or hydrogenated to alcohols. This can be followed by
hydrogenolysis or dehydration to the corresponding alkanes or alkenes respectively [136-139]. CO insertion requires Lewis acid site (metal or non-metal), while Aldol condensation is favoured by basic sites.

<table>
<thead>
<tr>
<th>CO reactions</th>
<th>Co-reactant</th>
<th>Catalyst</th>
<th>Reaction condition</th>
<th>Major primary product</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Temp. (°C)</td>
<td>Press. (bar)</td>
</tr>
<tr>
<td>FTS</td>
<td>H₂</td>
<td>Ru, Ni, Fe, Co</td>
<td>180 - 350</td>
<td>10 – 20</td>
</tr>
<tr>
<td>Isosynthesis</td>
<td>H₂</td>
<td>ThO₂, ZrO₂</td>
<td>375 – 475</td>
<td>30 - 60</td>
</tr>
<tr>
<td>Hydroformylation</td>
<td>Alkene, H₂</td>
<td>Rh, Co, Ni</td>
<td>40 - 200</td>
<td>10 - 100</td>
</tr>
<tr>
<td>Carbonylation</td>
<td>Alkyl cation precursors (alkene, alkanol, dialkylethers, alkylesters), aldehyde, acetals</td>
<td>Bronsted and Lewis acids, Rh, Co, Ni, Pd, Mo</td>
<td>0 – 50</td>
<td>1 - 100</td>
</tr>
</tbody>
</table>

Table 2.6: C-C coupling reactions of CO

It is worthy of note that Aldol condensation is recognised as termination step which accounts for branching and non-ASF product distribution in isosynthesis [140]. A similar non-ASF product distribution has been observed in FTS over base (Ca) promoted cobalt [141] and iron catalysts (unpublished result by this authors), in each case of product selectivities, wax selectivity decreases and shifted to mainly middle distillate fraction. This may be a preliminary evidence in support of earlier suggestion that pathway to hydrocarbons in FTS and isosynthesis are similar. Similar non-ASF product distribution is therefore expected in potassium promoted FTS catalyst (especially iron based catalysts), however, there has not been report of such cases. Group I & II metals are usually employed in form of oxides hydroxides or carbonates as promoters in FTS catalysts. The compounds of Group I metals are more basic but water soluble than corresponding Group II metal compounds. Water is a co-product in FTS and at the reaction condition the Group I metal
promoters have tendency is being leached out by water from the catalyst. Hence, their effect on product selectivity may be short-lived and less noticeable.

Carbonylation and hydroformylation are essentially CO insertion C-C coupling reactions, differences but them consist in co-reactant to CO and post CO insertion reaction. In hydroformylation, activated hydrogen atom is added to π-coordinated alkene followed by CO insertion, then desorption of product as aldehyde, all the reaction step take place on a single metal centre [142]. Whereas in carbonylation, activation of the reactant occur on different sites, CO on Lewis acid centre (metal or non-metal) and alkyl species is adsorbed as conjugate base to a Bronsted acid site. After insertion of CO into the alkyl, the resulting produce acyl cation intermediate can be desorbed as carboxylic acid or esters by reaction with alcohol, ether [143-147] or water (Koch reaction) [148-149]. Traditionally, the two homogeneous catalysis reactions carried out in liquid phase which require high pressure to achieve substantial CO dissolution in the liquid medium. Heterogenisation of the processes can permit operations at pressures ranges used in FTS [150-153]. Although presence of hydrogen is indicated to promote carbonylation over metal catalyst 154-155], hydrogen assisted CO activation is not essential for initiation but product desorption is critical to continuity of catalytic cycle in carbonylation or hydroformylation.

From the above discussion we can draw that C-C coupling in carbonylation and hydroformylation involve acidic site (Lewis and/or Bronsted) CO insertion into electrophilic carbon species. This is similar to CO insertion reaction in isosynthesis discussed earlier. However, contrary to need for desorption step for continuity of catalytic cycle in carbonylation or hydroformylation, the coupled intermediate in isosynthesis remains at the active site for further chain propagation. Desorption can take place via another type (Aldol) of C-C coupling reaction as proposed. And product distribution is a function of relative rates of CO insertion and Aldol C-C coupling reactions. As suggested earlier that C-C coupling in isosynthesis and FTS are most likely similar, then, by extrapolation of ASF and non-ASF product distribution observed in Ca promoted catalyst can be accounted for by relative rates of CO insertion and Aldol C-C coupling reactions.
The reaction rates are function of respective site densities. Typical FTS catalysts are made up acidic sites species (active metals – Ru, Ni, Co, Fe; supports – SiO$_2$, Al$_2$O$_3$, TiO$_2$; promoters – Ru, Pt, Pd, ZrO$_2$, MnO, etc). These species favours CO insertion C-C chain growth, and absence of strong basic site to promote Aldol coupling leads to ASF production distribution. Non-ASF product distribution observed for the Ca promoted catalysts can be attributed to presence of strong basic site in substantial amount to compete favouring Aldol coupling to compete with CO insertion route. The comparison and explanations in this section are untested hypothesis, but they are suggestions for fundamental studies on the subject.

2.8 Deductions

FTS is a key technology to hydrocarbon from non-petroleum carbonaceous resources. In its early history, commercial FTS process was driven by political decisions, but motivations for the reaction now are environment concerns and economics. Strive at further improving the economics require among other things molecular engineering. This demands detail insight into chemistry of FTS. In it ninety years history, FTS has been an active area of research and tremendous efforts has been expended on elucidation of details of the reaction. Although commendable progress has been made over the years, clarifications on the chemistry of FTS are still necessary. FTS is generally considered as polymerisation type reactions involving: chain initiation, propagation and termination steps. Exact details of FTS polymerisation steps are not fully clear at present.

Proposed macro kinetics expressions and product distribution models are explored for clues about details of elementary steps involved in FTS. There is high level of certainty with findings about pathway of chain initiation step as involving hydrogen assisted CO activation. Except desorption model, proposed FTS product distribution models attribute olefin/paraffin ratio and curvature away from the ASF distribution at high carbon numbers to re-adsorption of primary olefins product. These models in themself are unable to account for C$_1$ and C$_2$ selectivities. However, desorption model captures all the observed deviations from ASF law. There appears more reaction types than the assumed hydrogenation and
desorption as chain termination step in the models. Investigations are needed into the intermediates and the elementary steps to paraffin and olefin products. These details will contribute to the goal of unravelling the full mechanism of FTS. There are increasing reports of evidences in support of CO insertion as C-C coupling mechanism and oxygenate intermediate pathways to hydrocarbon on both iron and cobalt catalyst.

However, more fundamental studies are necessary for more details and clearer picture. FTS is compared with other C-C coupling reactions of CO. Similarity of isosynthesis to FTS suggests the same C-C coupling mechanisms in the two reactions. These pathways are promoted by different site types (electrophilic and nucleophilic for CO insertion and Aldol condensation respectively), and relative densities of the sites can influence product distribution. Thus, it can be said that catalytic units for molecular manipulations of FTS are hydrogenation, electrophilic and nucleophilic sites. Hydrogenation property is critical to high activity, electrophilicity and nucleophilicity influence product distribution. Electrophilicity have been investigated, nucleophilicity is less recognised and combinations of the three are yet to be explored for possibilities.