

CHAPTER 4

VERIFICATION OF REACTION RATE EQUATIONS

4.1 OVERVIEW

This chapter deals with the kinetics of the Fischer-Tropsch (FT) and Water-Gas-Shift (WGS) reactions of the ChemFT catalyst. Literature considered to be relevant to the topic of iron catalyst kinetics is reviewed and published rate equations evaluated for use with the ChemFT catalyst. The experimental program and process followed to gather the necessary reaction data is discussed together with the methodology behind the way in which the data was processed. This chapter will propose rate equations for both the FT and WGS reaction rates that will be valid in the typical operating conditions associated with the process.

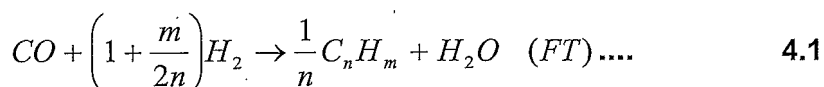
A large amount of literature is available on the topic of FT catalysts and their associated rate equations. Known rate equations have evolved from simple first order rate equations to complex equations which accommodate a wide range of operating conditions and catalyst behaviours. Rate equations are either empirically formulated or derived by making use of the Langmuir-Hinshelwood-Hougen-Watson (LHHW) adsorption theory. The formulation will normally be derived from assuming one of the proposed mechanisms for the FT reaction, i.e. the carbide theory, enolic theory or the direct insertion theory. Further improvement of the derived equations would depend on assumptions such as the degree in which the various reactants or products inhibit the observed reaction rate. It would appear throughout the literature that the researchers approximate the FT synthesis as a pair of simultaneous series-parallel reactions of the FT reaction and the WGS reaction. Generally small amounts of oxygenated products, primarily alcohols, and the CO_2 formed by the Boudouard reaction are neglected.

The application of the FT synthesis as a chemical production process with the primary aim of producing alcohols and olefins would thus pose a situation where the now large amounts of oxygenated products, in the form of alcohols, could make traditional FT equation inadequate if neglected. This investigation will thus evaluate published rate equations for applicability to such a scenario and propose rate equations for both the FT and WGS reaction rates.

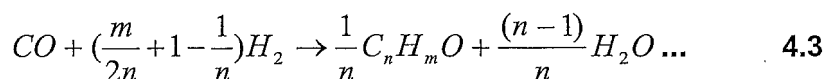
4.2 LITERATURE SURVEY ON THE KINETICS OF THE FISCHER-TROPSCH SYNTHESIS

4.2.1 The Fischer-Tropsch synthesis

It is generally accepted throughout the literature that the Fischer-Tropsch synthesis (FTS) can be approximated as a combination of simultaneous series-parallel reactions for the FT reaction and the WGS reaction for catalysts with WGS activity such as Fe based catalysts (Nettelhoff *et al*, 1985; Zimmerman and Bukur, 1990; Lox and Froment, 1993 and Van der Laan, 1999):



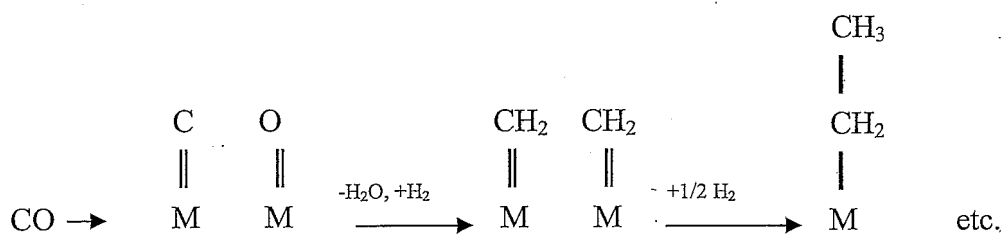
where n is the average carbon chain length of the hydrocarbon product and m is the average number of hydrogen atoms per hydrocarbon molecule. Both n and m vary with the catalyst and process conditions. Water is generally believed to be the primary by-product of the FT synthesis, and CO_2 is produced by the WGS (Dry *et al.*, 1972). The WGS is particularly important over potassium promoted iron catalysts (such as the ChemFT catalyst), which can have significant shift activity (Zimmerman and Bukur, 1990). The generally small amount of oxygenated products, primarily alcohols, and the CO_2 formed by the Boudouard reaction is neglected in the scheme of equation (4.1) and (4.2). It seems therefore that in the application of the FT synthesis as a ChemFT production process with the primary aim of producing alcohols, the so-called side reaction (equation 4.3), will have to be taken into account and this is assessed in this study.



4.2.2 Mechanism of FT synthesis

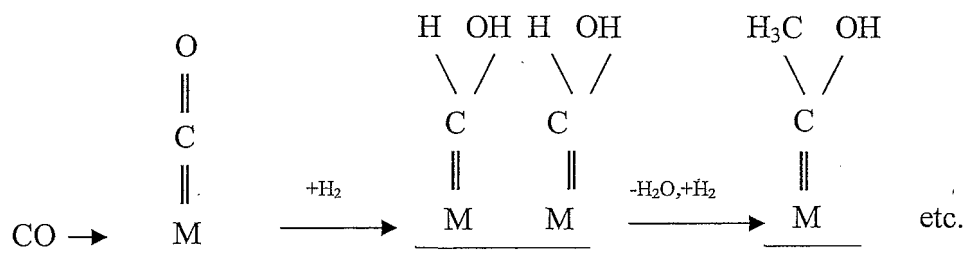
A number of papers in literature deal with the proposed mechanisms of the FT synthesis. The wide range of products and the diversity thereof resulted in the proposal of several different mechanisms (Dry, 1981). Mechanisms proposed principally on the basis of studies using heterogeneous catalyst systems, can be divided into three general theories (Masters, 1979; Huff and Satterfield, 1984; Xiaoding *et al.*, 1987; Davis, 2001). The three general theories postulated are:

- a) **The Carbide mechanism theory:** This mechanism was proposed by Fischer and Tropsch in 1926, but was later refined by Craxford and Rideal (1939). The original carbide mechanism of Craxford and Rideal can't explain the formation of oxygenated products. According to this mechanism CO dissociates and forms a surface metal carbide. The intermediate reacts to form a methylene group that polymerises into a hydrocarbon chain.



It was eventually recognised that the carbide mechanism was inconsistent with thermodynamic data for the formation of hydrocarbons by hydrogenation of the carbide at the temperatures used for the synthesis reaction (Davis, 2001).

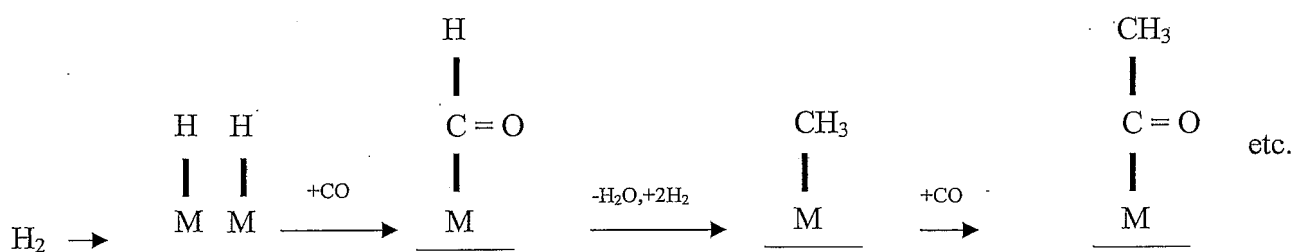
- b) **Enolic mechanism theory:** The objections concerning the Carbide theory and its inability to explain the formation of oxygenates led to the postulation of the Enolic mechanism in the 1950's (Storch *et al.*, 1951). HCOH – species forms the building blocks for chain growth according to this mechanism. This would thus entail that adsorbed CO is hydrogenated to hydroxylated species. Chain growth will occur by condensation with water elimination.



Results from work done by Emmett in the early 1970's (Davis, 2001) using ^{14}C -tracer studies provided strong support for the enol mechanism. Labelled alcohol or alkene added together with the synthesis gas showed that the added alkene or the alcohol was able to serve to initiate chain growth. This work was done at atmospheric pressure. Raje and Davis (1996)

showed that work done at medium pressure synthesis and slurry phase reaction conditions produced results that were in agreement with those obtained at atmospheric pressure.

- c) **Direct insertion mechanism theory:** Sternberg and Wender first postulated this mechanism in 1959. The mechanism entails that after formation of a metal hydride, CO is co-ordinated to the metal surface and inserted into the metal-H bond to initiate the reaction. Longer chain products are produced by the repetitive direct insertion of a CO ligand into the metal-C bond.



Literature is in agreement that there is less evidence to support this mechanism than for the other two. Denny and Whan (1978) report that the initiation step of this mechanism is particularly controversial.

Dry (1981) raised the question whether or not the above mentioned mechanisms are really different, or if they are simply variations of the same mechanism. Dry continues to propose a unified mechanism that incorporates all the key intermediate species of the carbide, enolic and direct CO insertion mechanisms.

4.2.3 FT reaction rate equations

Van der Laan and Beenackers (1999) recently performed a thorough literature search on the kinetics and selectivity of the FT synthesis. They concluded that the rate equations presented for the synthesis gas consumption do not present a uniform approach. Table 4.1 gives an overview of the iron related rate equations to be found in literature, where r_{FT} refers to the rate of hydrocarbon product formation. The table is setup to show the chronological development of the FT rate equation.

Table 4.1: Literature proposed FT reaction rate equations for iron-based catalysts.

Rate equations	Reference
(FT1) $r_{FT} = k_{FT} P_{H_2}$	Anderson (1956), Dry (1976), Zimmerman & Bukur (1990)
(FT2) $r_{FT} = k_{FT} P_{H_2}^{\gamma} P_{CO}^{\lambda}$	Bub & Baerns (1980)
(FT3) $r_{FT} = \frac{k_{FT} P_{H_2} P_{CO}}{P_{CO} + a P_{H_2O}}$	Anderson (1956), Dry (1976), Atwood & Bennett (1979), Zimmerman & Bukur (1990), Shen <i>et al.</i> (1994)
(FT4) $r_{FT} = \frac{k_{FT} P_{H_2}^2 P_{CO}}{P_{CO} P_{H_2} + a P_{H_2O}}$	Huff & Satterfield (1984), Deckwer <i>et al.</i> (1986), Whitters <i>et al.</i> (1990), Shen <i>et al.</i> (1994)
(FT5) $r_{FT} = \frac{k_{FT} P_{H_2}^2 P_{CO}}{1 + a P_{CO} P_{H_2}^2}$	Anderson (1956)
(FT6) $r_{FT} = \frac{k_{FT} P_{H_2} P_{CO}}{P_{CO} + a P_{CO_2}}$	Ledakowicz <i>et al.</i> (1985), Nettelhoff <i>et al.</i> (1985), Deckwer <i>et al.</i> (1986), Zimmerman & Bukur (1990)
(FT7) $r_{FT} = \frac{k_{FT} P_{H_2} P_{CO}}{P_{CO} + a P_{H_2O} + b P_{CO_2}}$	Ledakowicz <i>et al.</i> (1985), Nettelhoff <i>et al.</i> (1985), Zimmerman & Bukur (1990)
(FT8) $r_{FT} = \frac{k_{FT} P_{H_2}^{\gamma} P_{CO}}{P_{CO} + a P_{H_2O} + b P_{CO_2}}$	Van Berge (1991)

Equation FT1 shows a first order dependence of the FT reaction rate on hydrogen partial pressure. This first order rate equation indicates that rate inhibition by H_2O and CO_2 are negligible, a condition reported to hold only up to $H_2 + CO$ conversions of 60 % (Anderson, 1956). Activation energies of 84 – 87 kJ/mol were reported for precipitated iron catalysts, while Dry *et al.* (1972) reported 70 kJ/mol for a fused, promoted iron catalyst following this first order rate equation.

Bub and Baerns (1980) used the power law rate equation FT2 to describe kinetics of a Fe/Mn precipitated pelletised catalyst in a Berty reactor. The equation was used to describe the rates of formation of the individual hydrocarbons. Negative powers were reported for the CO partial pressure term, with activation energies varying from 35 to 60 kJ/mol for C_1 to C_4 hydrocarbons.

Anderson (1956) proposed rate equation FT3 which included water inhibition, which can occur at higher conversions (> 60 %). This same equation was also derived by Dry (1976) from the

enol/carbide combined mechanism, which assumed that the hydrogenation of chemisorbed CO was the rate determining step and that CO and water adsorbed much more strongly than either H₂ or CO₂. This rate equation was used by Atwood and Bennett (1979) for a fused nitrated ammonia synthesis catalyst ($E_A = 85$ kJ/mol), Shen *et al.* (1994) for a precipitated commercial Fe/Cu/K catalyst ($E_A = 56$ kJ/mol) and by Zimmerman and Bukur (1990) for a Fe/K/Cu catalyst in a slurry reactor. Rate equation Anderson (1956) proposed FT5 at the same time of his proposed rate equation FT3. Equation FT5 shows a very strong relation for hydrogen as a term within the denominator of the equation. Very little application of this equation can however be found in the literature. Investigating equation FT3, Huff and Satterfield (1984) observed hydrogen dependence. A linear decrease in the adsorption parameter “ a ” in equation FT3 with hydrogen pressure was seen. This observation was incorporated into the FT3 equation, thereby modifying it to equation FT4.

Equation FT4 was obtained via two different mechanisms, namely the carbide mechanism, using the hydrogenation of surface carbon as the rate-determining step and an enol/carbide mechanism, with the hydrogenation of surface enol as the rate-determining step. Huff and Satterfield (1984) developed equation FT4 from data obtained with a CSTR that indicated the inhibiting effect of CO and H₂O quantitatively.

Zimmerman and Bukur (1990) points out that equation FT3 and FT4 have the same form if the constant “ a ” in FT3 depends on the hydrogen partial pressure, i.e. $a_{FT3} = a_{FT4}/P_{H_2}$. Although this was done on a fused iron catalyst, Deckwer *et al.* (1986) used equation FT4 to describe the kinetics of a potassium-promoted precipitated iron catalyst in the slurry phase. It was however observed that this equation was not able to describe the results at low H₂/CO feed ratios, due to high water-gas shift activity. Whithers *et al.* (1990) verified equation FT4 and showed that a cobalt catalyst had low activity for the WGS reaction and that it performed poorly when CO rich feeds were used. Shen *et al.* (1994) obtained the same activation energy for their data than that obtained with FT3.

The large adsorption coefficient of water relative to that of CO and CO₂ generally means that inhibition by CO₂ is not as strong as inhibition by water. Inhibition by water in slurry reactors is further enhanced by its solubility in typical slurry reactor waxes (Zimmerman and Bukur, 1990). CO₂ inhibition may however become important when a large fraction of the water produced from the FT synthesis reaction is converted to CO₂. This may be the case with an iron catalyst having

a high water gas shift activity and/or when low H_2/CO feed ratios are employed. Ledakowicz *et al.* (1985), Nettelhoff *et al.* (1985) and Deckwer *et al.* (1986) reported a rate equation (FT6) that incorporates inhibition by CO_2 . This rate equation can be derived from the enol mechanism with hydrogenation of surface CO as the rate-determining step. It was assumed that CO and CO_2 were the only gaseous species to adsorb significantly on the catalyst surface. Ledakowicz *et al.* used this rate equation to describe the kinetic behaviour of a Fe/K catalyst with high WGS activity. The FT activation energy was determined as 103 kJ/mol. Deckwer *et al.* reported similar activation energy (105 kJ/mol) when using this rate equation for a precipitated iron catalyst in a slurry reactor.

FT7 proposed by Ledakowicz *et al.* (1985) is a general rate equation that accounts for inhibition by both water and CO_2 . This rate equation can thus be used for catalysts with low WGS activity (water concentrations high), as well as for catalysts with high shift activity which show inhibition by CO_2 . It must be noticed that the WGS may approach equilibrium in some situations. Based on all the above research work, Zimmerman and Bukur (1990) reported some conclusions: (1) water inhibits the rate more strongly than CO_2 , CO_2 inhibition is overshadowed by water inhibition, except when most of the product water is consumed by the WGS; and (2) all of the proposed FT rate equations reduced to first order in hydrogen partial pressure at low conversions.

Van Berge (1991) started his investigation into iron kinetics by showing that equation FT8 can be used as a general iron rate equation, of which FT3, FT4 and FT6 are special cases. Investigating the kinetics of the standard Arge catalyst showed that CO_2 inhibition is not significant and CO_2 term in the denominator was thus cancelled out, while a value of 0.5 was obtained for the power of the hydrogen partial pressure term.

Notable from the abovementioned rate equations is the absence of a unity term 1 within the denominators (except for FT 5). Such a term would normally be expected when a LHHW approach is used, but the researches neglected this term (Ledakowicz *et al.*, 1985 and Nettlehof *et al.*, 1985).

4.2.4 WGS reaction rate equations

Van der Laan and Beenackers (1999) concluded in their recent literature survey that only a few studies reported the WGS kinetics of iron catalysts under FT synthesis conditions. Some

equations to be found in literature are summarised in Table 4.2. Equations listed were derived from a number of mechanisms proposed for the WGS reaction.

Van der Laan (1999) points out that single studies of the WGS reaction over supported metals suggest the appearance of formate species. These formate species can be formed by the reaction between either a hydroxy species or water and CO either in the gas phase or in the adsorbed state. The hydroxy intermediate can be formed by the dissociation of water ($H_2O + 2\Phi_2 \leftrightarrow OH\Phi_2 + H\Phi_2$, where Φ_2 is the WGS catalytic site). The formate intermediate can be reduced to either adsorbed or gaseous dioxide. Rethwisch and Dumesic (1986) suggested that the WGS reaction over unsupported magnetite proceeds via a direct oxidation mechanism, while all supported iron catalysts operate via a mechanism with formate species due to limited change of oxidation state of the iron cations.

Table 4.2: Literature proposed WGS reaction rate equations for iron-based catalysts

Rate equations	Reference
(WGS1) $r_{WGS} = k_{WGS} (P_{H_2O} P_{CO} - \frac{P_{CO_2} P_{H_2}}{K_p})$	Zimmerman & Bukur (1990)
(WGS2) $r_{WGS} = k_{WGS} P_{CO}$	Dry (1976), Feimer <i>et al.</i> (1981), Zimmerman & Bukur (1990)
(WGS3) $r_{WGS} = \frac{k_{WGS} (P_{H_2O} P_{CO} - P_{CO_2} P_{H_2}^{1/2} / K_p)}{(1 + a' P_{H_2O} / P_{H_2}^{1/2})^2}$	Lox & Froment (1993)
(WGS4) $r_{WGS} = \frac{k_{WGS} (P_{H_2O} P_{CO} - P_{CO_2} P_{H_2} / K_p)}{P_{CO} P_{H_2} + a' P_{H_2O}}$	Huff & Satterfield (1984), Zimmerman & Bukur (1990), Shen <i>et al.</i> (1994)
(WGS5) $r_{WGS} = \frac{k_{WGS} (P_{H_2O} P_{CO} - P_{CO_2} P_{H_2} / K_p)}{P_{CO} + a' P_{H_2O} + b' P_{CO_2}}$	Zimmerman & Bukur (1990), Shen <i>et al.</i> (1994)
(WGS6) $r_{WGS} = k_{WGS} (P_{CO} - \frac{P_{CO_2} P_{H_2}}{K_p P_{H_2O}})$	Singh <i>et al.</i> (1979), Van Berge (1991)
(WGS7) $r_{WGS} = k_{WGS} (P_{CO} \left[\frac{P_{H_2O}}{P_{H_2}} \right]^{\frac{1}{2}} - \frac{P_{CO_2}}{K_p} \left[\frac{P_{H_2}}{P_{H_2O}} \right]^{\frac{1}{2}})$	Temkin & Kul'kova (1949)
(WGS8) $r_{WGS} = \frac{k_{WGS} (P_{H_2O} P_{CO} - P_{CO_2} P_{H_2} / K_p)}{(1 + a' P_{CO} + b' P_{H_2O})^2}$	Van der Laan (2000)

k_{WGS} = WGS reaction rate constant

The WGS2 equation was reported by Dry (1976) for conditions where the water partial pressure is high relative to CO and CO₂ or when water is strongly adsorbed and the reverse WGS reaction becomes negligible (reaction is far from equilibrium). Feimer *et al.* (1981) used this equation on a precipitated Fe/Cu/K catalyst with activation energy of 124 kJ/mol.

Zimmerman and Bukur (1990) tested a number of the rate equations to their experimental WGS rates. Some of their rate equations contain the same functional form (Table 4.2 equations WGS4 and WGS5) of the denominator as used in their rate equations of the FT synthesis (Table 4.1 equations FT4 and FT7). This implies that the reaction takes place on the same catalytic sites as the FT and the adsorption constants should thus be the same. They do however admit that although the equations did fit their WGS kinetics, they were very empirical and that a need for additional work in this area exists. Shen *et al.* (1994) assumed that the FT and WGS reactions proceeded on the same catalytic sites, thereby choosing the WGS adsorption constants of WGS4 and WGS5 equal to that of the FT equations. Activation energies for k_w in WGS4 and WGS5 of 88 and 125 kJ/mol respectively were calculated.

Lox and Froment (1993) discriminated between rival Langmuir-Hinshelwood-Hougen-Watson (LHHW) rate equations for the kinetics on a commercial Ruhrchemie (LP33/81) precipitated iron catalyst. The WGS3 equation was identified as the optimal equation. The rate-determining step was taken as the reaction between the adsorbed CO and adsorbed hydroxyl species resulting from the dissociation of water. As it is generally assumed that for supported iron catalysts magnetite is the most active phase for the WGS while the FT reactions proceed on iron carbide, the authors also assumed their WGS reaction to proceed on a different catalytic site than the FT synthesis.

Van der Laan (1999) assuming the elementary reactions shown in Table 4.3 derived equation WGS8 on the basis of the formate mechanism. Equation number 5 in Table 4.3, which is the reaction between the adsorbed water and CO, was assumed to be the rate-determining step. Other assumptions made to derive the LHHW rate equation, were:

- Steady state for the adsorbed species.
- One rate-determining step in the sequence of elementary reactions and over the complete range of experimental conditions.
- Surface concentrations of intermediate species are negligible.
- Active sites for the WGS (Φ_2) are different than the sites for the hydrocarbon forming reactions.
- Rate-determining step is a dual-site elementary reaction between two adsorbed species.

- Adsorption of reactants and desorption of products are at equilibrium.

The adsorption of H_2 and CO_2 are assumed to be negligible relative to CO and H_2O , thus giving the following mass balance of the catalytic sites: $\theta_{\Phi_2} + \theta_{H_2O\Phi_2} + \theta_{CO\Phi_2} = 1$

Table 4.3: Elementary reactions for the WGS reaction

Equation number	Elementary reaction
1	$CO + \Phi_2 \leftrightarrow CO\Phi_2$
2	$CO_2 + \Phi_2 \leftrightarrow CO_2\Phi_2$
3	$H_2O + \Phi_2 \leftrightarrow H_2O\Phi_2$
4	$H_2 + 2\Phi_2 \leftrightarrow 2H\Phi_2$
5	$CO\Phi_2 + H_2O\Phi_2 \leftrightarrow HCOO\Phi_2 + H\Phi_2$
6	$HCOO\Phi_2 + \Phi_2 \leftrightarrow H\Phi_2 + CO_2\Phi_2$

The temperature dependency of the equilibrium constant of the WGS reaction, K_p , can be calculated by the relation:

$$K_p = 0.0102 * EXP\left(\frac{4730}{T}\right) \dots 4.4$$

4.3 EXPERIMENTAL

4.3.1 Experimental conditions

4.3.1.1 Catalyst used for evaluation of rate equations

ChemFT catalyst identified as OLE 116 was used for this kinetic investigation. This catalyst is the one discussed in Chapter 2, which was subjected to a calcination step at $450^\circ C$ for a period of 16 hours. The catalyst characteristics are discussed in Chapter 2. The catalyst is a spray dried precipitated Fe-based catalyst promoted with Mn, Zn, Cu, K and SiO_2 . The catalyst particle size used was between $38 \mu m$ and $150 \mu m$.

4.3.1.2 Reduction / conditioning of catalyst

Reduction was done in-situ under hydrogen. A 6000 ml(n)/gcat/h hydrogen flow together with 10 % Ar was used for a period of 16 hours at 20 bar(g), 240°C and 450 rpm stirring speed. After the 16-hour period the temperature was decreased to 200°C and the hydrogen flow replaced by the required synthesis gas flow. After an hour of synthesis gas flow the temperature and pressure were adjusted to the desired conditions.

4.3.1.3 Synthesis conditions

Sixteen reactor experiments were performed to collect experimental data used for the investigation involving the determination of the kinetics. Experiments 1 to 5 were conducted to supply reaction data at different temperature and pressure points, while experiments 6 to 16 were planned with the aim of providing data points as the result of different H₂:CO:CO₂ feed ratios.

a) Effect of temperature and pressure(Experiments 1 to 5)

20 g (unreduced mass) of catalyst was used. Synthesis condition followed the reduction procedure described under Section 4.3.1.2. Experimental conditions are showed in Table 4.4.

Table 4.4: Experimental program for kinetic investigation – Experiments 1 to 5

	Pressure Bar(g)	Temperature °C	APG GHSV (ml/gcat/h)		Feed Vol %	Feed H ₂ /CO
Experiment 1	45	240	4500	APG Ar	90 10	2.00
Experiment 2	45	230	3500	APG Ar	90 10	2.00
Experiment 3	45	220	4500	APG Ar	90 10	2.00
Experiment 4	27.5	240	3000	APG Ar	90 10	2.00
Experiment 5	27.5	220	3000	APG Ar	90 10	2.00

b) Effect of feed composition (Experiments 6 to 16):

20 g (unreduced mass) of catalyst was used. Synthesis condition followed the reduction procedure described under 4.3.1.2. Experimental conditions as shown in Table 4.5 were used.

Table 4.5: Experimental program for kinetic investigation – Experiments 6 to 16

Condition	Pressure Bar(g)	Temperature °C	APG GHSV (ml/gcat/h)		Feed Vol %	Feed H ₂ /CO	Feed H ₂ /CO ₂
Experiment 6 Ref 1	50	240	5200	H ₂ CO Ar CH ₄	48.29 24.14 16.74 10.82	2.00	-
Experiment 7 Add H ₂	50	240	5200	H ₂ CO Ar CH ₄	52.48 24.14 12.56 10.82	2.17	-
Experiment 8 Add H ₂	50	240	5200	H ₂ CO Ar CH ₄	60.85 24.14 4.19 10.82	2.52	-
Experiment 9 Ref 1	50	240	5200			2.00	-
Experiment 10 Add CO	50	240	5200	H ₂ CO Ar CH ₄	48.29 28.33 12.56 10.82	1.70	-
Experiment 11 Add CO	50	240	5200	H ₂ CO Ar CH ₄	48.29 32.51 8.37 10.82	1.49	-
Experiment 12 Ref 1	50	240	5200			2.00	-
Experiment 13 Ref 2	25	240	3450	H ₂ CO Ar CH ₄	48.33 24.16 16.68 10.83	2.00	-
Experiment 14 Add CO ₂	25	240	3450	H ₂ CO CO ₂ Ar CH ₄	48.33 24.16 12.51 4.17 10.83	2.00	3.86
Experiment 15 Add CO ₂	25	240	3450 Add CO ₂	H ₂ CO CO ₂ Ar CH ₄	48.33 24.16 4.17 12.51 10.83	2.00	11.59
Experiment 16 Ref 2	25	240	3450			2.00	-

The reactor pressure was set at 50 bar(g) for the majority of the conditions, but a pressure of 25 bar(g) had to be used for the investigation regarding the addition of CO₂ due to the cylinder supply pressure restriction. The experimental conditions were set up in such a way that the APG GHSV was kept constant at the value estimated for the particular pressure, while Ar and additionally added H₂ or CO or CO₂ totalled 20 volume percent of the APG flow.

This experimental plan theoretically entailed that H₂:CO ratios from about 1.5 to 2.5 were obtained as well as H₂:CO₂ conditions varying from no CO₂ fed to ratios of 11.5 and 3.8.

Reference conditions were added in between the different conditions to make the correction of data due to deactivation possible if needed. Care was taken to ensure that the catalyst activity has stabilised before any data points were collected.

The catalyst activity time curve for a typical Sasol commercial Fe catalyst is shown in Figure 4.1. This figure indicates that the data stabilises after about 72 hours. Data points reported will thus be of periods longer than 72 hours.

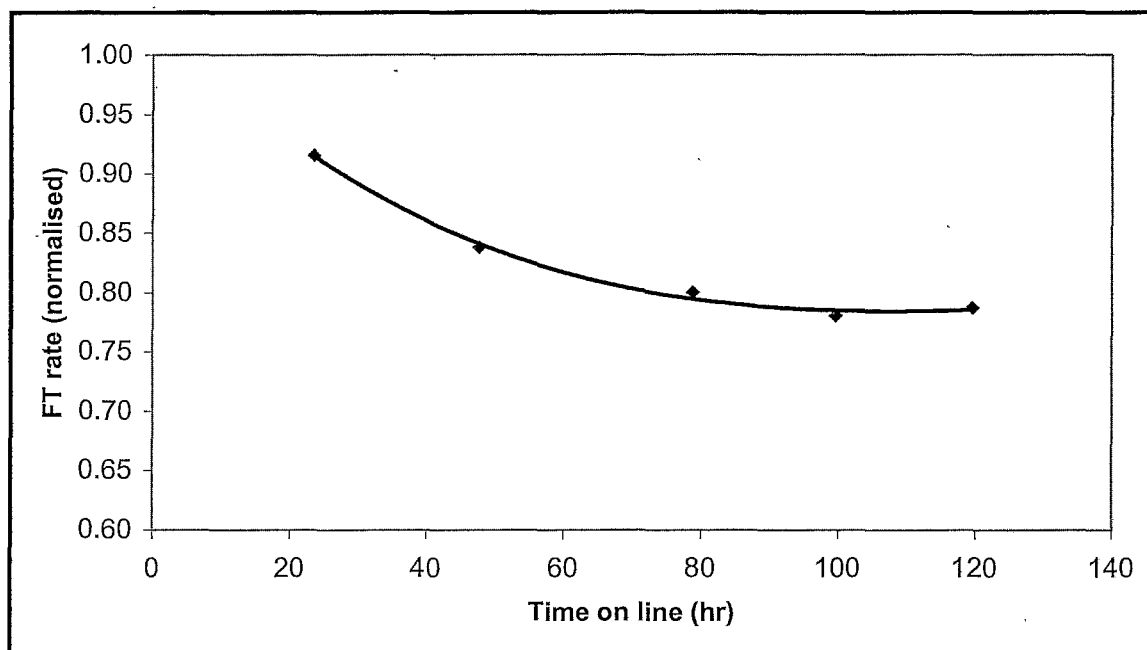


Figure 4.1: Typical time curve for Sasol commercial Fe catalyst

4.4 DATA PROCESSING

4.4.1 Molar flow calculations

The approach followed for the processing of the data of the kinetic investigation differs slightly from that discussed in Chapter 2. The main difference is in the way in which the calculations account for oxygenates present as alcohols and the handling thereof. Some aspects will thus be repeated for the sake of giving a logical explanation of the process.

Permanent gas (H_2 , CO, CH_4 and CO_2) conversion or formation could be determined by making use of the GC ampoule technique as reported by Harms (1996). The results from the TCD can be

used to calculate the absolute flow rates of the permanent gases entering and leaving the reactor, with the assistance of an internal inert reference gas such as argon. With this the Fischer-Tropsch and Water Gas Shift reaction rates and the synthesis gas space velocity can be calculated. The following relationship is used to calculate the molar flow rate of component “i” as a function of known and measurable quantities:

$$n_i^T = \left(\frac{A_i^{TCD} P_i^C n_{Ar}^T}{A_{Ar}^{TCD} P_{Ar}^C} \right) / \left(\frac{A_i^{TCD,C}}{A_{Ar}^{TCD,C}} \right) \quad \dots 4.5$$

With: n_i^T = total molar flow of component i, mol/s
 A_i^{TCD} = peak area of component i in the TCD spectra,
 P_i^C = quantity of i in the reference gas, mole percentage
 A_{Ar}^{TCD} = peak area of Argon in the TCD spectra,
 P_{Ar}^C = quantity of Argon in the reference gas, mole percentage
 $A_i^{TCD,C}$ = TCD peak area of component i in the reference gas,
 $A_{Ar}^{TCD,C}$ = TCD peak area of Argon in the reference gas,
 n_{Ar}^T = molar flow rate of Argon, mol/s.

With the above mentioned permanent gases calculated it was possible to use a carbon balance in determining the total amount of hydrocarbons (C_{2+}) formed. By setting up a carbon balance, an estimate of the C_{2+} hydrocarbon molar flow will be:

$$n_{HC^{2+}}^{T,OUT} = \frac{(n_{CO}^{T,IN} - n_{CO}^{T,OUT}) - (n_{CO_2}^{T,OUT} - n_{CO_2}^{T,IN}) - (n_{CH_4}^{T,OUT} - n_{CH_4}^{T,IN})}{\text{average carbon number } C_2 +} \quad \dots 4.6$$

with

$n_i^{T,OUT}$ = total out flow of component “i”, mol/s

$n_i^{T,IN}$ = total in flow of component “i”, mol/s

The average carbon number for the C_{2+} hydrocarbon products was calculated from the total product distribution. This number included the alcohol, olefin and paraffin contribution. The average carbon number for the olefins and paraffins products was calculated as 4 and that of the alcohol product as 1.4. From the product distribution a distribution of 70 mass % olefins and paraffins to 30 mass % alcohols was calculated. This ratio was used to calculate the average carbon number (C_{2+}) to be 3.22.

TCD analyses cannot directly measure water as well as the volatile hydrocarbons and oxygenates (Harms, 1996). Traditionally used equations to calculate water flows assume that the contribution of the volatile oxygenates to the product stream is negligible and therefore the water flow rate is calculated via an oxygen balance:

$$n_{H_2O}^{T,OUT} = n_{CO}^{T,IN} - n_{CO}^{T,OUT} - 2 \cdot (n_{CO_2}^{T,OUT} - n_{CO_2}^{T,IN}) \dots 4.7$$

From the amount of oxygenates analysed it was clear that such an assumption would be incorrect for the ChemFT catalyst. Oxygenates would therefore be accounted for in both the oxygen and carbon balance, resulting in over-estimation of products. A different approach was thus followed in determining the water product.

Humidity measurements of the reactor tailgas leaving the product knock-out vessels together with mass flow measurements thereof, indicated that 99 mass % of the water product is knocked out and drained at the experimental conditions. This measurement agrees very well with calculations performed from an Aspen simulation, which also showed 99 % (mass) of water to be knocked out at the operating conditions. The water product collected was corrected for the 1 % that leaves the process via the tailgas. With the aid of water analyses for the alcohol content thereof it was possible to determine the actual water mass of the water product drained. This mass was used as the water product flow during partial pressure and other calculations. The oxygenate (alcohol) content determined from the analyses were already accounted for via the carbon balance (equation 4.6). Permanent gases together with the Ar tracer accounted for the total inlet flow of the reactor, while the reactor outlet flow consisted of the calculated water and hydrocarbon flows together with the permanent gas flows calculated. Reactor partial pressures could be estimated using the relationship between the specific gas component, total reactor pressure and reactor total outlet flow (CSTR – implies that outlet stream composition equals reactor composition).

4.4.2 Fischer-Tropsch reaction rate calculation

The Fischer-Tropsch reaction rate was calculated by excluding the CO converted to CO₂ via the WGS reaction. Thus, r_{FT} as mole of CO converted to FT products/gcat/s:

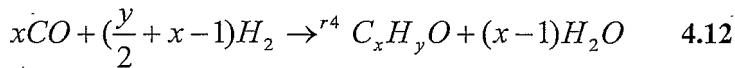
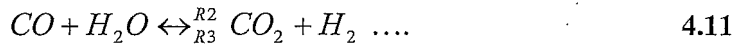
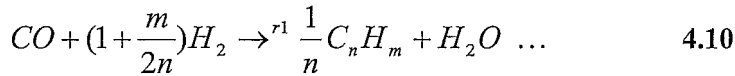
$$r_{FT} = \frac{CO_{IN} - CO_{OUT} - (CO_{2OUT} - CO_{2IN})}{Mass\ unreduced\ catalyst} \dots \quad 4.8$$

Nettelhoff *et al.* (1985) and Van Berge (1994) showed that the FT rate could practically be expressed as:

$$r_{FT} = \frac{-r_{CO+H_2}}{(M.(2 + \frac{m}{2}))} \dots \quad 4.9$$

where m refers to the stoichiometric coefficient of the hydrogen from the hydrocarbon product formed in the generalised reaction equation (see equation 4.1) and M is the mass of unreduced catalyst. A conclusion reached from the process of deriving equation 4.9, is that the CO + H₂ conversion rate depends only on the synthesis reaction and is independent of the extent of the shift reaction. The generalised reaction equation used does however assume that oxygen consumption due to the formation of oxygenates (alcohols, acids, etc.) is negligible.

The derivation that follows (equations 4.10 to 4.18) is an attempt at showing that the same conclusion regarding the shift reaction can be reached, when a generalised FT alcohol formation reaction (equation 4.12) is to be included in the process.



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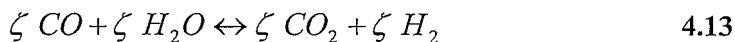
n = average carbon chain length for olefins + paraffin products

m = average number of hydrogen atoms per hydrocarbon (olefins+paraffins) molecule

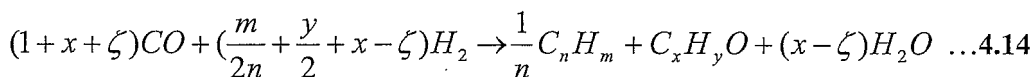
x = average carbon chain length for alcohol products

y = average number of hydrogen atoms per alcohol molecule

if ζ is the fraction of H₂O converted by the WGS reaction:



The overall balance would be:



following that

$$r = \frac{\phi_{CO}}{M.(1+x+\zeta)}, \dots \quad 4.15$$

and

$$r = \frac{\phi_{H_2}}{M.(\frac{m}{2n} + \frac{y}{2} + x - \zeta)} \dots \quad 4.16$$

$$r = \frac{1}{M} \left(\frac{\Lambda_{C_nH_m}}{n} + \Lambda_{C_xH_yO} \right) \dots \quad 4.17$$

with $\dot{O}_i$ = mol of component i converted per second

Λ_i = mol of component i formed per second

M = mass of unreduced catalyst

The synthesis gas conversion rate can thus be derived as:

$$\begin{aligned} r_{CO+H_2} &= \phi_{CO} + \phi_{H_2} \\ &= r.M(1+x+\zeta) + r.M\left(\frac{m}{2n} + \frac{y}{2} + x - \zeta\right) \\ &= (1+x+\zeta)\left(\frac{\Lambda_{C_nH_m}}{n} + \Lambda_{C_xH_yO}\right) + \left(\frac{m}{2n} + \frac{y}{2} + x - \zeta\right)\left(\frac{\Lambda_{C_nH_m}}{n} + \Lambda_{C_xH_yO}\right) \quad 4.18 \\ &= \left(\frac{1}{n} + \frac{2x}{n} + \frac{m}{2n^2} + \frac{y}{2n}\right).\Lambda_{C_nH_m} + \left(1 + 2x + \frac{m}{2n} + \frac{y}{2}\right).\Lambda_{C_xH_yO} \end{aligned}$$

This implies that the CO+H₂ conversion rate depends only on synthesis reactions and is independent of the extent of the shift reaction.

4.4.3 WGS reaction rate calculation

The WGS reaction rate was calculated by using a CO₂ balance. Thus the mol CO₂ formed via the WGS reaction per mass of catalyst per time unit is:

$$r_{WGS} = \frac{CO_{2,OUT} - CO_{2,IN}}{Mass \text{ unreduced catalyst}} \dots \quad 4.19$$

The temperature dependency of the equilibrium constant of the WGS reaction, K_p , was calculated by the relation:

$$K_p = 0.0102 * EXP\left(\frac{4730}{T}\right) \dots \quad 4.20$$

4.4.4 Reaction rate equation discrimination and evaluation

The approach followed for the evaluation of the literature rate equations was as follows.

- FT and WGS rate equations were solved separately. Similar kinetic parameters for the same FT and WGS rate equation denominator would indicate the need to re-evaluate such equations via simultaneous solving methods. Separate solving of the FT and WGS rate equations was also done by Zimmerman and Bukur (1990).
- Experimental data from experiments performed at different temperatures (Experiments 1 to 5, Appendix 8, Table A.8.1) were used to evaluate the reaction constant together with any adsorption parameters associated with the relevant rate equation. The experimental data used here was obtained from similar H₂:CO feed ratios.

Equation parameters were calculated by minimising the objective function χ^2 of equation 4.21 (Van der Laan, 1999) with the Microsoft Excel solver function. The Excel solver makes use of the generalised reduced gradient (GRG2) non-linear optimisation code, while linear and integer problems use the simplex method with bounds on the variables, and the branch-and-bound method.

$$\chi^2 = \sum_i \frac{(r_i^{\text{exp}} - r_i^{\text{mod}})^2}{\sigma_i^2} \dots \quad 4.21$$

where σ_i^2 is the relative variance of the experimental selectivities and r_i is the FT or WGS reaction rate. The experimental inaccuracies were taken as:

$$\sigma_i^2 = 0.05 r_i^{\text{exp}} \quad 4.22$$

Parameter values estimated is thus considered to have a 95 % accuracy, which takes experimental error into account.

- The activation energy associated with the specific reaction was calculated through the Arrhenius equation for the temperature dependence of a reaction rate constant (k_{FT} or k_{WGS}).

$$k(T) = A e^{(-E/RT)} \dots \quad 4.23$$

By taking the natural logarithm of equation 4.23, it can be seen that a plot of $(\ln k)$ versus $(1/T)$ should be a straight line whose slope is proportional to the activation energy (see equation 4.24):

$$\ln k = \ln A - \frac{E}{R} \left(\frac{1}{T} \right) \dots \quad 4.24$$

- With the activation energy known, the kinetic constant k_o (see equation 4.25) was solved while also recalculating any adsorption constants present. This step was done by making use of the data of the $H_2:CO:CO_2$ ratio investigation (Experiments 6 to 16, Appendix 8, Table A.8.2).

$$k = k_o \cdot \exp\left(\frac{-E}{RT}\right) \quad 4.25$$

- Different equations were compared by calculating the relative variance of the rate equation (Bartlett, 1937):

$$S_{rel} = \left(\sum_i^f \left(\frac{r_i^{exp} - r_i^{mod}}{r_i^{exp}} \right)^2 \cdot \frac{1}{f - e} \right)^{\frac{1}{2}} * 100 \dots 4.26$$

with f = the number of data points included, and

e = the number of optimised parameters

where a zero value will constitute a perfect prediction by the equation.

- The rate equations were ranked according to the relative variance calculated and the best FT and WGS rate equations were identified. These two equations were compared to see if they indicated the need for simultaneous optimisation or re-evaluation.
- New equations were derived to enhance the identified equations.

Zimmerman and Bukur (1990) who evaluated rate equations using slurry reactor data used a non-linear least square regression method, NLIN, for parameter estimates. The normalised root mean square error (RMSE) was used as indication of how well the kinetics predicted the reaction rate. Lox and Froment (1993) used data from a tubular reactor to evaluate kinetic parameters. The authors used the integral method of kinetic analysis. Kinetic parameters were estimated with the Marquardt non-linear regression algorithm. Rate equations were discriminated by looking at the goodness of fit via the F-test on the residual sum of squares at the 95 % confidence level. The t-test was applied to see if parameters were significantly different from zero.

4.5 EXPERIMENTAL RESULTS

The processed experimental data from Experiments 1 to 16 are summarised in Appendix 8. Processed data was checked for potential catalyst deactivation by plotting the calculated FT rate as a function of time on line. Figure 4.2 shows such a plot obtained when using data from Experiments 6 to 16. It can be seen from this Figure 4.2 that little deactivation occurred over the experimental period when comparing the different reference conditions. The low values towards the end of the experiment represent the low pressure points. No correction was thus made for potential deactivation when the data was used for the kinetic investigation.

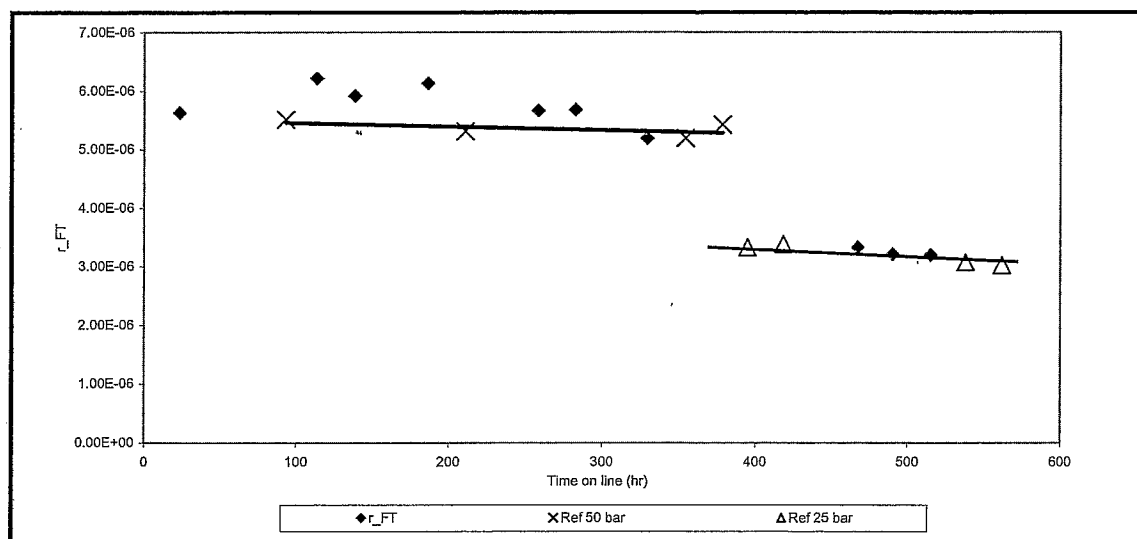


Figure 4.2: Data integrity of Experiments 6 to 16

4.6 REACTION RATE EQUATION DISCRIMINATION AND EVALUATION

4.6.1 FT reaction rate equation-evaluation

The procedure described under Section 4.4.4 was followed to evaluate all the rate equations mentioned in Table 4.1. Table 4.6 summarises the results obtained for the different rate equations. The equations were ranked according to their relative variance as calculated with equation 4.26. Shown in Table 4.6, for the equations with the smallest relative variance, are the number of data points “ f ” used for the parameter estimation as well as the number of parameters estimated “ e ” once the activation energy was estimated via the Arrhenius equation.

Literature equations for the FT reaction rate do describe the kinetics of the ChemFT catalyst reasonable well. The best four equations all show a very strong dependence on the hydrogen partial pressure, which agrees with literature observations for low conversion catalysts.

The best ranked equation is equation (FT8) as proposed by Van Berge (1991), but the b-term solved to a value of zero, resulting in an equation similar to the number 2 ranked equation (Anderson – FT3). Both can again be reduced to the number 4 (FT1) (and 3 – FT2 although empirical) equation. The Van Berge equation is an empirical rate equation based on the theoretical Anderson equation, thus the similarity between the two. Taking the experimental error of around 5 % into account, the two equations describe the data equally well as can be seen from the very similar kinetic parameters obtained.

Activation energies range from about 65 to 80 kJ/mol, which compares well with published values of 70 to 150 kJ/mol (Satterfield, 1984). Values from the best 3 equations indicate an activation energy of around 80 kJ/mol. Figure 4.3 show the Arrhenius plot for the activation energy determined from equation FT8 with data of Experiments 1 to 5, while Figure 4.4 shows the parity plot of the best equation (FT8) identified (Data of Experiments 6 to 16).

Table 4.6: FT reaction rate equation-evaluation results

Rate equations	Parameters estimated	E_{FT} (kJ/mol)	S_{rel}	Rank
(FT1) $r_{FT} = k_{FT} P_{H_2}$	$k_o^* = 1.2 \pm 0.06$ mol/gcat/s/bar	65 ± 3.25	8.02 f=18 e=2	4
(FT2) $r_{FT} = k_{FT} P_{H_2}^\gamma P_{CO}^\lambda$	$k_o = 18.2 \pm 0.91$ mol/gcat/s/bar ^($\gamma+\lambda$) $\gamma = 0.8$ $\lambda = 0.1$	75 ± 3.75	5.29 f=18 e=4	3
(FT3) $r_{FT} = \frac{k_{FT} P_{H_2} P_{CO}}{P_{CO} + a P_{H_2O}}$	$k_o = 50.5 \pm 2.52$ mol/gcat/s/bar $a = 0.70 \pm 0.04$	80 ± 4.00	5.22 f=18 e=3	2
(FT4) $r_{FT} = \frac{k_{FT} P_{H_2}^2 P_{CO}}{P_{CO} P_{H_2} + a P_{H_2O}}$	$k_o = 1.2 \pm 0.06$ mol/gcat/s/bar $a = 0.24 \pm 0.01$	65 ± 3.25	8.35	5
(FT5) $r_{FT} = \frac{k_{FT} P_{H_2}^2 P_{CO}}{1 + a P_{CO} P_{H_2}^2}$			31.34	8
(FT6) $r_{FT} = \frac{k_{FT} P_{H_2} P_{CO}}{P_{CO} + a P_{CO_2}}$			12.01	6
(FT7) $r_{FT} = \frac{k_{FT} P_{H_2} P_{CO}}{P_{CO} + a P_{H_2O} + b P_{CO_2}}$			22.72	7
(FT8) $r_{FT} = \frac{k_{FT} P_{H_2}^\gamma P_{CO}}{P_{CO} + a P_{H_2O} + b P_{CO_2}}$	$k_o = 49.72 \pm 2.49$ mol/gcat/s/bar ^{γ} $a = 0.25 \pm 0.01$ $b = 0$ $\gamma = 0.8$	78 ± 3.90	4.66 f=18 e=5	1

*see equation 4.25

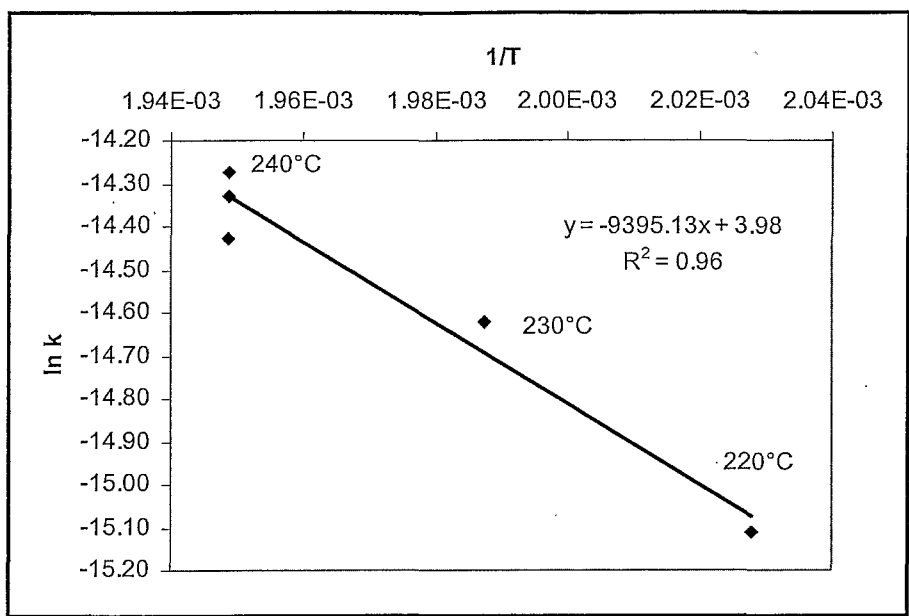


Figure 4.3: Arrhenius plot of equation FT8 activation energy calculation

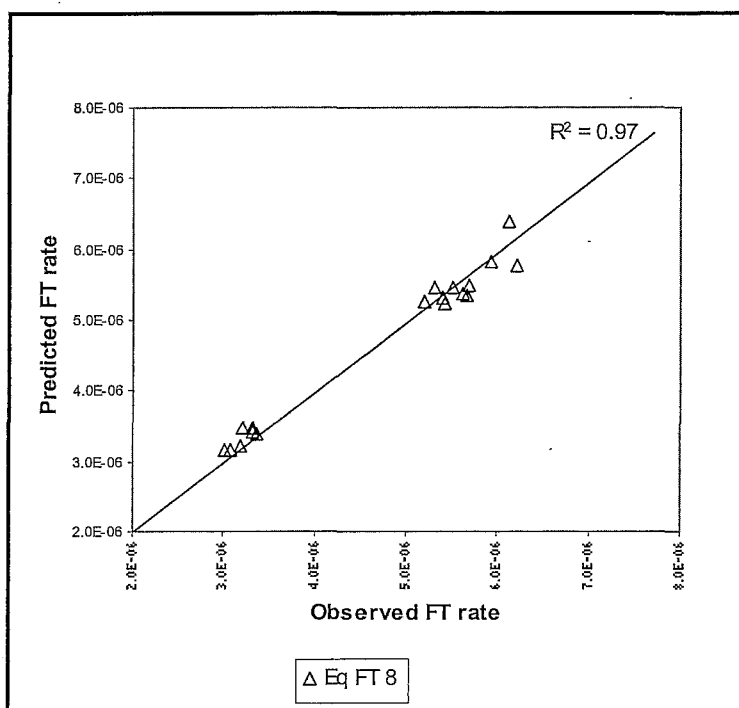


Figure 4.4: Parity plot of FT reaction rate equation FT8

4.6.2 WGS reaction rate equation-evaluation

The same procedure as that of the FT rate equation evaluation was followed to evaluate all the WGS rate equations proposed in Table 4.2. The results are shown in Table 4.7 together with the ranking according to relative variance. Estimated parameter values are shown for the three equations with the smallest relative variance. The results show that the WGS rate equations available from literature do not describe the data as well as those proposed for the FT kinetics, with much larger relative variance values. An activation energy value of 77 kJ was calculated for the best equation. The best rate equation is equation WGS8 reported by Van der Laan (2000), which is a LHHW derived equation. From the parity plot shown in Figure 4.5, it can be seen that the rate equation show a very poor fit for the lower WGS rates. These points correspond to the data points obtained at the lower pressure (25 bar(g)) when CO₂ was introduced into the system.

Values estimated for the various adsorption parameters do not show a correlation with those obtained during the FT rate equation parameter evaluation. It therefore appears that the two reactions take place on different catalytic sites and it is therefore not necessary to solve them simultaneously.

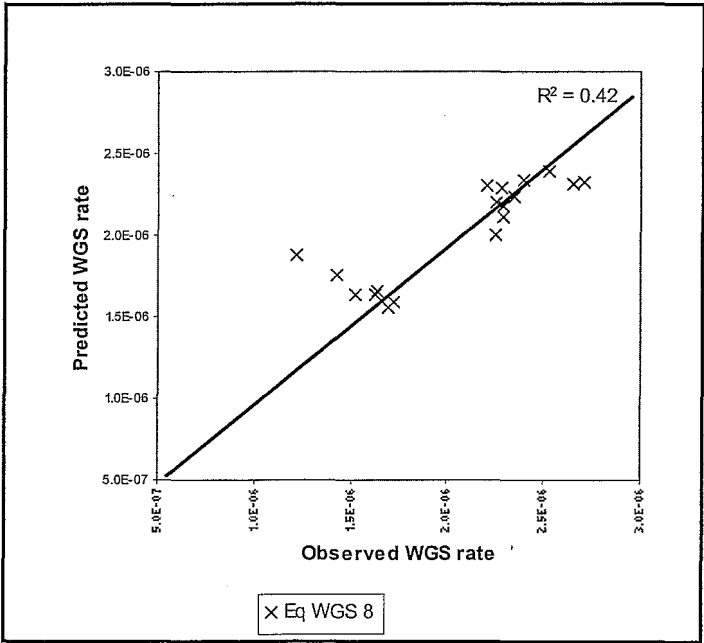


Figure 4.5: Parity plot of WGS reaction rate equation WGS8

Table 4.7: WGS reaction rate equation-evaluation results

Rate equations	Parameters estimated	E _{WGS} (kJ/mol)	S _{rel}	Rank
(WGS1) $r_{WGS} = k_{WGS} (P_{H_2O} P_{CO} - \frac{P_{CO_2} P_{H_2}}{K_p})$			57.82	8
(WGS2) $r_{WGS} = k_{WGS} P_{CO}$			35.94	4
(WGS3) $r_{WGS} = \frac{k_{WGS} (P_{H_2O} P_{CO} - P_{CO_2} P_{H_2}^{1/2} / K_p)}{(1 + a' P_{H_2O} / P_{H_2}^{1/2})^2}$	$k_o' = (1.99 \pm 0.10)E+7$ mol/gcat/s/(bar ^{1.5}) $a' = 1.08 \pm 0.05$		49.79	7
(WGS4) $r_{WGS} = \frac{k_{WGS} (P_{H_2O} P_{CO} - P_{CO_2} P_{H_2} / K_p)}{P_{CO} P_{H_2} + a' P_{H_2O}}$	$k_o' = 226.7 \pm 11.34$ mol/gcat/s $a' = 4.50 \pm 0.23$	69 ± 3.45	22.22 f=18 e=3	2
(WGS5) $r_{WGS} = \frac{k_{WGS} (P_{H_2O} P_{CO} - P_{CO_2} P_{H_2} / K_p)}{P_{CO} + a' P_{H_2O} + b' P_{CO_2}}$	$k_o' = 8241 \pm 412$ mol/gcat/s/bar $a' = 1.85 \pm 0.09$ $b' = 0$	95 ± 4.75	30.93 f=18 e=4	3
(WGS6) $r_{WGS} = k_{WGS} (P_{CO} - \frac{P_{CO_2} P_{H_2}}{K_p P_{H_2O}})$			37.27	5
(WGS7) $r_{WGS} = k_{WGS} (P_{CO} \left[\frac{P_{H_2O}}{P_{H_2}} \right]^{\frac{1}{2}} - \frac{P_{CO_2}}{K_p} \left[\frac{P_{H_2}}{P_{H_2O}} \right]^{\frac{1}{2}})$			43.93	6
(WGS8) $r_{WGS} = \frac{k_{WGS} (P_{H_2O} P_{CO} - P_{CO_2} P_{H_2} / K_p)}{(1 + a' P_{CO} + b' P_{H_2O})^2}$	$k_o' = 1136 \pm 56.80$ mol/gcat/s/bar ² $a' = 0.90 \pm 0.05$ $b' = 1.39 \pm 0.07$	77 ± 3.85	17.56 f=18 e=4	1

The WGS equilibrium constant K_p (see equation 4.20) calculated at a specific temperature can be compared to the observed ratio

$$\frac{P_{CO_2} P_{H_2}}{P_{CO} P_{H_2O}} \dots 4.27$$

under synthesis conditions to get a measure / indication of the catalyst activity towards the WGS reaction. Figure 4.6 shows the collective graph for all three experiments. Figure 4.6 indicates that the WGS reaction is still far from equilibrium at the temperature range investigated.

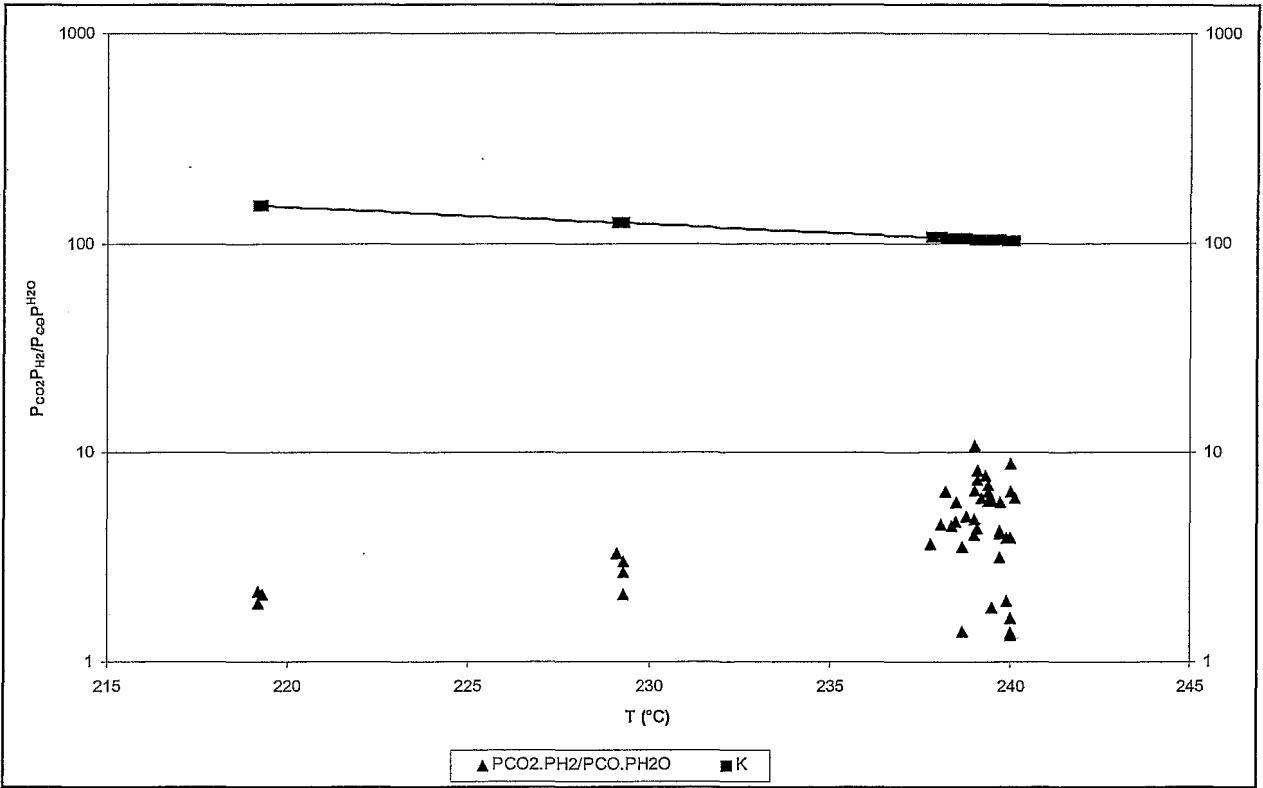
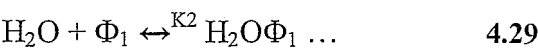
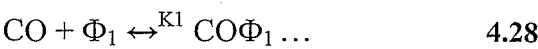


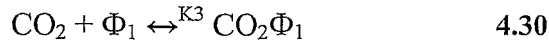
Figure 4.6: Equilibrium of WGS reaction

4.6.3 FT rate equation development

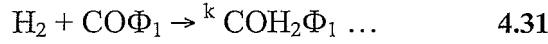
Van Berge’s general equation (FT8) proved to be the best equation to describe the ChemFT FT kinetics. This equation easily simplifies to the theoretical one of Anderson and Dry (FT3), which gave very similar results. The general equation is a generalisation of the equation proposed by Ledakowicz *et al.* (1985) and Nettelhof *et al.* (1985), i.e. equation FT7.

The general equation can be derived using the enolic complex theory, by way of LHHW equations (Nettelhoff *et al.*, 1985). The derivation of the equation takes the adsorption of CO, H₂O and CO₂ onto the active FT catalyst sites (Φ_1) into account:





In accordance with the enolic complex theory the hydrogenation of chemisorbed CO to a reactive and condensable C₁ species represents the rate-limiting step:



Thus

$$r_{FT} = kP_{H_2}\theta_{\text{CO}\Phi_1} \dots \quad 4.32$$

If one presents the balance of catalytic sites for FT synthesis:

$$\theta_{\Phi_1} + \theta_{\text{CO}\Phi_1} + \theta_{\text{H}_2\text{O}\Phi_1} + \theta_{\text{CO}_2\Phi_1} = 1 \dots \quad 4.33$$

It follows from substitution of the surface fraction of CO into equation 3.32, that:

$$r_{FT} = \frac{k_{FT}P_{H_2}P_{CO}}{1 + aP_{CO} + bP_{H_2O} + cP_{CO_2}} \dots \quad 4.34$$

The denominator of equation 4.34 accounts for the effect of competitive adsorption between different reacting species. This term can be simplified by assuming different adsorption strengths and coverage. Dry (1996) reasons that CO and H₂O adsorb much stronger than CO₂ and H₂ onto the iron surface. This together with the assumption that the surface is almost completely covered by CO and H₂O and thereby implying that the vacant sites would not have an influence on the reaction rate, would reduce equation 4.34 to the form of FT3:

$$r_{FT} = \frac{kP_{H_2}P_{CO}}{P_{CO} + aP_{H_2O}} \dots \text{FT3}$$

It can be argued that since equation FT3 can readily be converted to a two-dimensional linear form, the simplifying assumptions were possibly necessary to allow for parameter determination from experimental data by means of graphical methods at a time when computational ability was not as advanced as presently (Botes, 2001).

From literature it does however seem that the above discussed simplifying assumptions are used without real motivation. The “1” appearing in the denominator of equation 4.34, which relates to the vacant catalytic sites, is simply neglected to get to the known format of the equations (Ledakowicz *et al.*, 1985 and Nettlehof *et al.*, 1985).

From a scientific point of view this procedure will be valid if the constants a, b and c have significantly large values. This will be true if the catalyst surface is practically completely

covered with CO, H₂O and CO₂, so that the number of vacant sites is small compared to the occupied sites. Table 4.8 compares some literature denominator constant values and operating conditions for a denominator of the form, “ $P_{CO} + aP_{H_2O}$ ” (such as for FT3), at the minimum and maximum reactor conditions reported.

Table 4.8: Literature denominator constants and operating values for FT rate equations

Reference:	P _{CO} (bar)	a	P _{H2O} (bar)	P _{CO} + aP _{H₂O}
Zimmerman and Bukur (1990)	2.20	4.50	0.50	4.45
	8.10	4.50	2.70	20.25
	5.30	0.33	0.17	5.36
	12.00	0.33	1.17	12.39
Van Berge (1991)	0.93	1.63	0.33	1.47
	7.21	1.63	2.02	10.50
Nettlehof <i>et al.</i> (1985)	12.10	4.51	3.12	26.17
Atwood and Bennet (1979)	12.10	0.028	3.12	12.19

From Table 4.8 it can be seen that if the denominator term is increased by adding the vacant site “1” term, the denominator value might change between 4 and 68 % for the experimental conditions reported. This indicates that the accuracy of the final reaction rate equations might be jeopardised if simplification of the equations is done without substantial justification. Dry (1981) relates the extent to which olefins and oxygenated molecules emerge from the reactor to be dependent on the availability of vacant catalyst sites, which is in turn dependent on the degree of CO conversion.

In view of the above it cannot be theoretically correct to use a rate equation which does not account for the effect of vacant sites in the adsorption term where the primary aim of the catalyst is to produce olefins and alcohols. The following form of the general equations would seem more appropriate:

$$r_{FT} = \frac{k_o \cdot e^{(-E_{FT} / RT)} \cdot P_{H_2}^{\gamma} P_{CO}}{1 + aP_{CO} + bP_{H_2O} + cP_{CO_2}} \quad \text{...FT 8a}$$

This approach can also be followed for the best-suited rate equations from Table 4.6, namely FT3, FT4 and FT6. Taking the effect of the vacant sites into account results in the following equations:

$$r_{FT} = \frac{k_o \cdot e^{(-E_{FT}/RT)} \cdot P_{H_2} P_{CO}}{1 + aP_{CO} + bP_{H_2O}} \dots \text{FT3a}$$

$$r_{FT} = \frac{k_o \cdot e^{(-E_{FT}/RT)} \cdot P_{H_2}^2 P_{CO}}{1 + aP_{CO}P_{H_2} + bP_{H_2O}} \dots \text{FT4a}$$

$$r_{FT} = \frac{k_o \cdot e^{(-E_{FT}/RT)} \cdot P_{H_2} P_{CO}}{1 + aP_{CO} + cP_{CO_2}} \dots \text{FT6a}$$

Equations FT3a, FT4a, FT6a and FT8a were evaluated in the way previously described for equations FT1 to FT8. Results are shown in Table 4.9 and compared to the equations without the vacant site term. The criterion of relative variance (see equation 4.26) penalises the introduction of additional parameters. Despite the introduction of an extra parameter the new equations have a similar degree of compliance and in the case of FT8a it is a slight improvement on FT8. This is also shown by the reported R^2 -values, which is an indication of the goodness of fit of the data (1 being a perfect fit), not taking into account the different numbers of optimised parameters.

Figure 4.7 shows the parity plot obtained using FT8a. Noteworthy is that in the case of equations FT4a, FT6a and FT8a the water and CO_2 partial pressure terms solves to zero. This observation suggests that the vacant sites on the catalyst surface (and CO adsorption), and not the competitive adsorption of water or CO_2 had an inhibiting effect on the reaction rate. Inclusion of the vacant site term thus provided a rate equation, which results in a slight improvement over those without such term. The kinetic parameter value is such that for the CO partial pressures used during this investigation (3 to about 12 bar(g)), the partial pressure term is not justifying the omission of the “1” term within the denominator. The kinetic parameter value obtained compares very well with those observed in literature investigations (see Table 4.8), which would suggest similar FT catalytic surface properties.

Equation FT8a will be used as the equation of choice for data obtained with the ChemFT catalyst as it suggest a more accurate theoretical base than published equations:

$$r_{FT} = \frac{k_o \cdot e^{(-E_{FT}/RT)} \cdot P_{H_2}^\gamma P_{CO}}{1 + aP_{CO}} \dots \text{FT8a}$$

with: $k_o = 58.84 \pm 2.94 \text{ mol/gcat/s/bar}^{A+1}$

$E_A = 77 \pm 4 \text{ kJ/mol}$

$a = 1.09 \pm 0.05,$

$\gamma = 0.7$

Table 4.9: Modified FT reaction rate equation-evaluation results

Rate equations	Parameters estimated	E_{FT} (kJ/mol)	S_{rel}	R^2
(FT3) $r_{FT} = \frac{k_o \cdot e^{(-E_{FT}/RT)} \cdot P_{H_2} P_{CO}}{P_{CO} + aP_{H_2O}}$	$K_o = 50.5 \pm 2.52$ mol/gcat/s/bar $a = 0.70 \pm 0.04$	80 ± 4.00	5.22 f=18 e=3	0.968
(FT3a) $r_{FT} = \frac{k_o \cdot e^{(-E_{FT}/RT)} \cdot P_{H_2} P_{CO}}{1 + aP_{CO} + bP_{H_2O}}$	$K_o = 1880.1 \pm 94$ mol/gcat/s/bar $a = 14.64 \pm 0.73$ $b = 9.14 \pm 0.45$	84 ± 4.20	5.41 f=18 e=4	0.970
(FT4) $r_{FT} = \frac{k_o \cdot e^{(-E_{FT}/RT)} \cdot P_{H_2}^2 P_{CO}}{P_{CO} P_{H_2} + aP_{H_2O}}$	$K_o = 1.2 \pm 0.06$ mol/gcat/s/bar $a = 0.24 \pm 0.01$	65 ± 3.25	8.35 f=18 e=3	0.938
(FT4a) $r_{FT} = \frac{k_o \cdot e^{(-E_{FT}/RT)} \cdot P_{H_2}^2 P_{CO}}{1 + aP_{CO} P_{H_2} + bP_{H_2O}}$	$K_o = 3.36 \pm 0.17$ mol/gcat/s/bar $a = 0.73 \pm 0.04$ $b = 0$	61 ± 3.05	8.62 f=18 e=4	0.937
(FT6) $r_{FT} = \frac{k_o \cdot e^{(-E_{FT}/RT)} \cdot P_{H_2} P_{CO}}{P_{CO} + aP_{CO_2}}$	$K_o = 3158.1 \pm 157.91$ mol/gcat/s/bar $a = 0.63 \pm 0.03$	98 ± 4.90	12.01 f=18 e=3	0.920
(FT6a) $r_{FT} = \frac{k_o \cdot e^{(-E_{FT}/RT)} \cdot P_{H_2} P_{CO}}{1 + aP_{CO} + bP_{CO_2}}$	$K_o = 8299.6 \pm 414$ mol/gcat/s/bar $a = 1.01 \pm 0.05$ $b = 0$	102 ± 5.1	13.561 f=18 e=4	0.920
(FT8) $r_{FT} = \frac{k_o \cdot e^{(-E_{FT}/RT)} \cdot P_{H_2}^\gamma P_{CO}}{P_{CO} + aP_{H_2O} + bP_{CO_2}}$	$K_o = 49.72 \pm 2.49$ mol/gcat/s/bar ^A $a = 0.25 \pm 0.01$ $b = 0$ $\gamma = 0.8$	78 ± 3.90	4.66 f=18 e=5	0.971
(FT8a) $r_{FT} = \frac{k_o \cdot e^{(-E_{FT}/RT)} \cdot P_{H_2}^\gamma P_{CO}}{1 + aP_{CO} + bP_{H_2O} + cP_{CO_2}}$	$K_o = 58.84 \pm 2.94$ mol/gcat/s/bar ^{A+1} $a = 1.09 \pm 0.05$ $b = 0$ $c = 0$ $\gamma = 0.7$	77 ± 3.85	4.56 f=18 e=6	0.979

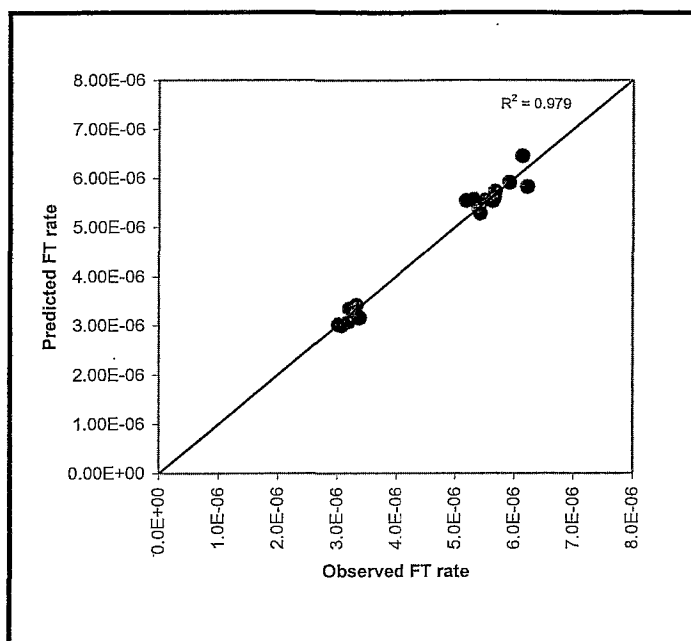


Figure 4.7: Parity plot for the proposed ChemFT – FT rate equation FT8a

Literature reports on various other approaches to finding the best FT rate equations. Lox and Froment (1993) followed an approach of determining the rate-limiting step of their network of reactions by applying the criteria related to the growth probability factor (growth parameter) and data obtained from a tubular reactor (Lox and Froment, 1993a). The reactions were based on the carbide mechanism. Using Langmuir-Hinshelwood-Hougen-Watson rate equations it was possible to predict rate equations for both the paraffin and olefin products.

Another approach can be to use reaction rate equations developed for methanol-higher alcohol synthesis catalysts. Such systems do however involve a complex variety of intermediates and products, with the product distribution and reaction network specific of the catalytic system used (Beretta *et al.*, 1998). These systems most often use some sort of modified methanol catalyst, consisting of Cu with Zn and/or Co promotion (Xiaoding *et al.*, 1987). Such processes also show a high selectivity towards methanol (above 90 %). Reaction rate equations can be developed from reactions assumed to be part of the reacting system. Such reaction sets were reported amongst others by Breman *et al.* (1994), Beretta *et al.* (1998) and Majocchi *et al.* (1998). These reaction sets require a large amount of data for accurate evaluation of the different parameters. The use of methanol-higher alcohol synthesis kinetics, which accounts for the partial pressure effects of the different products in a set of equations, necessitates very detailed product analyses. The approach followed with the investigation reported in this investigation resulted in a FT rate equation seen as an “easy-to-handle” mathematical tool necessitating minimal product analyses.

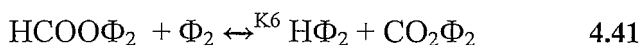
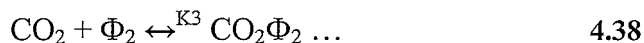
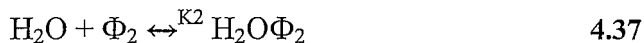
4.6.4 WGS rate equation development

Data from Experiment 6-16 show that between 30 and 35 % of the CO converted in the reaction process is converted to CO₂. This result indicates that a large fraction of the water produced by the FT process, is converted to CO₂. Ledakowicz (1985) observed FT inhibition due to competitive adsorption of CO and CO₂. The FT equation development / evaluation of Sections 4.6.1 and 4.6.3 did however not show CO₂ to be an inhibiting factor. This might not be true for the WGS reaction. Although the WGS reaction was shown to be far from equilibrium (Figure 4.6), CO₂ can potentially inhibit the WGS reaction. This might also indicate support for the idea that the FT and WGS reactions progress on different catalyst sites.

The best-fit WGS equation (WGS8) can be re-derived making the assumption that CO₂ adsorption is not negligible. The same assumptions was used as those of Van der Laan (1999) discussed under Section 4.2.3, except that the balance of the catalytic sites was changed to account for CO₂ adsorption, i.e.:

$$\theta_{\Phi_2} + \theta_{H_2O\Phi_2} + \theta_{CO\Phi_2} + \theta_{CO_2\Phi_2} = 1 \quad 4.35$$

With the following elementary reactions:



Assume that the reaction between the adsorbed water and CO is the rate-determining step (equation 4.40) and that surface concentrations of intermediate species are negligible. The catalytic site balance of equation 4.35 holds thus true. The following equation can then be derived by making use of the LHHW technique:

$$r_{WGS} = \frac{k_w(P_{H_2O}P_{CO} - P_{CO_2}P_{H_2} / K_p)}{(1 + aP_{CO} + bP_{H_2O} + cP_{CO_2})^2} \quad 4.42$$

Re-evaluation of the WGS kinetic data using equation 4.42 results in the parameter values reported in Table 4.10. This equation shows a much-improved fit to those discussed under Section 4.6.2. This is also evident in the parity plot shown in Figure 4.8.

Table 4.10: Proposed ChemFT – WGS reaction rate equation

Rate equation	Parameters estimated	E_{WGS} (kJ/mol)	S_{rel}
(WGS9) $r_{WGS} = \frac{k_o' \cdot e^{(-E_{WGS}/RT)} \cdot (P_{H_2O} P_{CO} - P_{CO_2} P_{H_2} / K_p)}{(1 + a' P_{CO} + b' P_{H_2O} + c' P_{CO_2})^2}$	$k_o' = 419.2 \pm 20.9$ kmol/gcat/s/bar ² $a' = 0.98 \pm 0.05$ $b' = 1.19 \pm 0.06$ $c' = 0.54 \pm 0.03$	101 ± 5	9.51

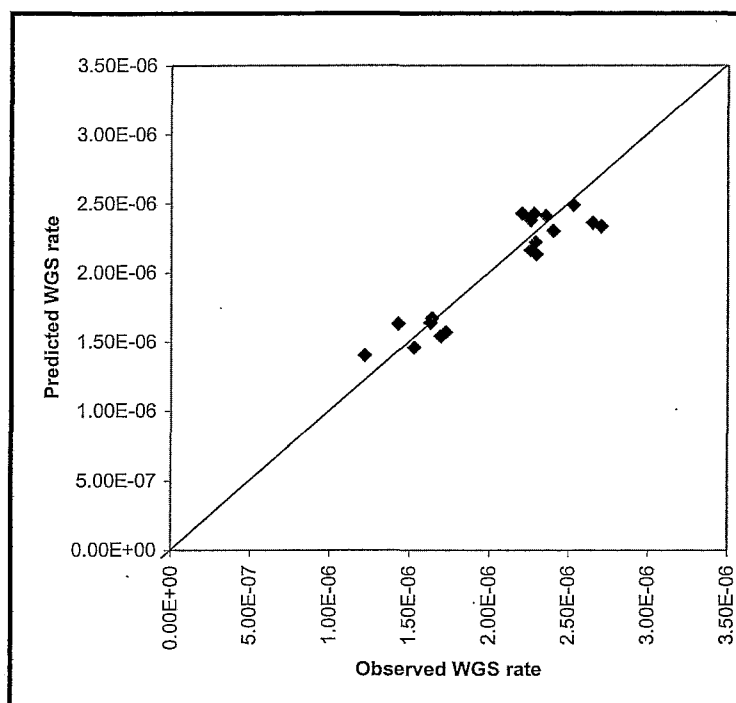


Figure 4.8: Parity plot for the proposed ChemFT – WGS rate equation (WGS9)

Although the proposed FT (FT8a) and WGS (WGS9) equations have the same basic form, they have different adsorption coefficients with “b” and “c” equal to zero for the FT rate equation. The FT equation does not seem to be inhibited by CO₂, while a definite improvement could be seen when incorporating the CO₂ term into the WGS equation. The WGS5 equation, which also has a CO₂ term in the denominator did not describe the data well, in fact the CO₂ term reduced to a zero term. It would thus seem the improvement when using WGS9 is not only due the CO₂ term on its own, but rather due to the whole group of terms – possessing a catalytic vacant site “1” term together with taking the square of the denominator.

Simultaneous solving of the parameters of the FT and WGS rate equations will be necessary if the reactions were taking place on the same catalytic sites. Such a case will see the FT and WGS rate equations having the same denominator with exactly the same adsorption constants. This will not be true for this particular case, as the two denominators are made up of different adsorption terms. Lox and Froment (1993) followed a similar approach where they evaluated the FT and WGS derived equations separately before solving the best rate equations simultaneously. The authors concluded that all the elementary hydrocarbon formation reactions are single-site reactions, while CO₂ formation via the WGS reaction is rate-limited by the formation of the formate surface intermediate, which involves two sites. The rate equation proposed by Lox and Froment (1993) assumed different active sites for the WGS reaction and for the reactions leading to the formation of hydrocarbons.

Not much literature is available for conclusive arguments on the possibility of the FT and WGS reactions sharing the same catalytic sites. Zimmerman and Bukur (1990) did evaluate FT and WGS equations with the same denominator, but concluded that they were not able to derive reliable rate equations, as their WGS results were largely empirical.

4.7 CONCLUSIONS

This chapter has shown that existing Fe catalyst rate equations do describe the FT kinetics of the ChemFT catalyst fairly well, but the WGS equations fall short of fully describing the kinetics. The improved FT reaction rate equation proposed within this study is the result of modifying a general FT rate equation by incorporating a term within the denominator, which accounts for vacant catalyst sites. The proposed FT rate equation is felt to have a more theoretically correct base in the current application than those obtained from literature.

The WGS reaction rate equation was derived by incorporating the presence of CO₂ adsorption on the catalyst active sites, into the final equation, thereby accounting for any rate inhibiting caused by the presence thereof. Activation energies calculated for both reactions fall well within those reported in literature, are also high enough to show that the influence of mass transfer is minimal.

Evaluation of the FT rate equations, showed that the best-suited equations were all based on the hydrogen dependency and can thus easily simplify to a first order equation for the dependence on hydrogen partial pressure. This observation is in line with literature reports of hydrogen

dependence at lower conversion levels. The final proposed rate equation suggests that the vacant sites on the catalyst surface (and CO adsorption), and not the competitive adsorption of water or CO₂ has an inhibiting effect on the reaction rate.

WGS reaction kinetics is a function of water, CO and CO₂ inhibition. The proposed rate equation takes all of these into account. The presence of different terms and adsorption coefficient values in the FT and WGS rate equation denominators, give strong support towards proving that the two reactions occur on different catalytic sites.

The proposed rate equations are adequate for use in the current ChemFT reactor operating regimes. It is however recommended re-evaluating the equations and the constants thereof when conditions fall outside that reported in this work or if any new promoters are added (or current ones eliminated) in the catalyst preparation formula.

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