CHARPTER III
SCHULZ-FLORY DISTRIBUTION

As indicated in the preceding chapter, in a large number of catalytic processes carbonaceous deposits are formed through polymerization on the surface of the catalysts. Along the way, the deposition intermediates propagate reaction chains of coke molecules, which are formed, and the sites are completely deactivated. The probability of chain growth of coke species is extremely valuable for understanding and modeling the coking process that relatively few studies. Recently, interest in the distribution of Fischer-Tropsch, polymerization reaction from insertion of carbon intermediate, products was a result of improvements of the analysis of all isomers and products which can not be described with the classical Anderson-Schulz-Flory (ASF) distribution. Hence, an application of the Schulz-Flory distribution for the probability study of chain growth of coke is significantly described in more detailed.

3.1 Schulz-Flory distribution theory

As reviewed in the published literature elsewhere [164-167], considerable work has been published concerning the Fischer-Tropsch (FT) reactions. The FT is a polymerization reaction with the following steps: reactant adsorption, chain initiation, chain growth, chain termination, product desorption and readsorption and further reaction. The FT synthesis product spectrum consists of a complex multicomponent mixture of linear and branched hydrocarbons and oxygenated products. Main products are linear paraffins and olefins. Fuels produced with the FT synthesis are of a high quality due to a very low aromaticity and zero sulfur content. Literature on the kinetics and selectivity of FT synthesis can be divided into two classes. Most studied aim at catalyst improvement and postulate empirical power-law kinetics for the CO and hydrogen conversion rates and a simple polymerization reaction following an Anderson-Schulz-Flory (ASF) distribution for the total hydrocarbon product yield. This distribution describes the entire product range by a single parameter, α, the probability of the addition of a carbon intermediate (monomer) to a chain.

This model was developed mathematically in more detail for quantitative description of product compositions. From detailed product composition data, it was suited as well to discriminate primary product compositions from those which were obscured by secondary reactions. It has already been used to determine the variation of kinetic constants of the elemental reactions linear growth, branching and formation of paraffins and olefins as a function of chain length, reaction parameters and catalysts properties for a few cases. Consequently, the composition of hydrocarbon product fraction, as a function of the carbon atoms in the hydrocarbon molecule, could be described via Schulz-Flory distribution. This distribution basically implies that the ratio between the rate of formation of hydrocarbons with n carbon atoms and the rate of formation of the hydrocarbon with n-1 carbon atoms is independent of number of carbon atoms in the molecule. This ratio is called the growth probability, in analogy with the terminology used in polymerization:

$$R_{Cn} / R_{Cn-1} = \alpha\ (T, P_{CO}, P_{H2}) \tag{1}$$

The mole fraction, M_n, of hydrocarbons with n carbon atoms in the total amount of hydrocarbons formed can then be calculated from,

$$M_n = R_{Cn} / \sum_i R_{Ci} \tag{2}$$

By substitution of (2) in (1) it follows that

$$M_n = \alpha^{n-1}\ (1-\alpha) \tag{3}$$

or, by taking the logarithm of both sides of (3)

$$\log (M_n) = n\log(\alpha) + \log((1-\alpha)/\alpha) \tag{4}$$

Which means that a plot of log (M_n) versus n should be linear.

Chain growth probabilities were calculated using a non-linear semi-logarithmic least square regression. The range of α is dependent on the reaction conditions and catalyst type. Typical ranges of α on Ru, Co and Fe of 0.85-0.95, 0.70-0.80 and 0.50-0.70 were reported respectively. The growing mechanism is shown in Figure 3.1. For a constant α (Figure 3.1a), the ASF equation does not distinguish between different product types. A semilogarithmic plot of the mole fraction against carbon number yields the well-known Schulz-Flory diagram (Figure 3.2a), where the slope of the straight line yields the chain growth probability α. In practice, a multicomponent product mixture is formed. Main products are paraffins and olefins. Dependent on process conditions and catalysts, oxygenated products (e.g. alcohols and aldehydes), branched hydrocarbons and β–olefins can be formed as well. The original Anderson-Schulz-Flory equation can be modified for the description of multicomponent FT products. Figure 3.1b shows the reaction scheme for this model; the Schulz-Flory diagram is presented in Figure 3.2b. Assuming all products to be formed from the same intermediate, a semilogarithmic plot of the mole fractions against carbon number shows straight parallel lines.
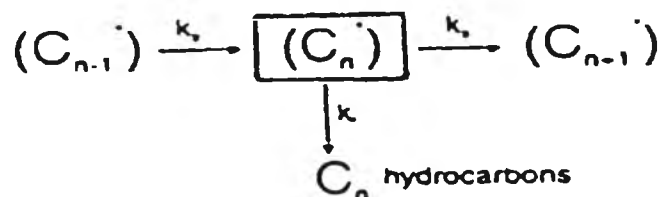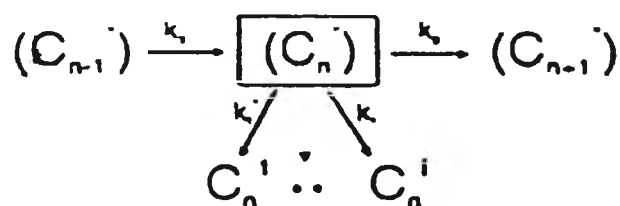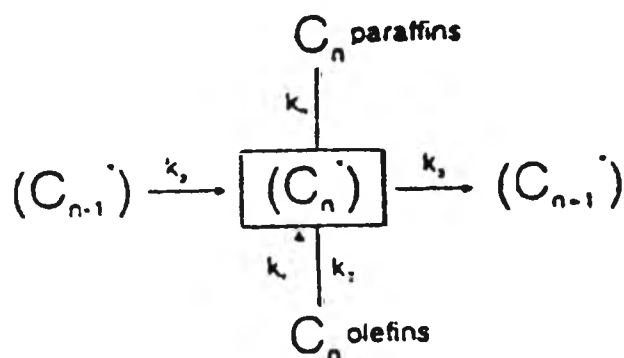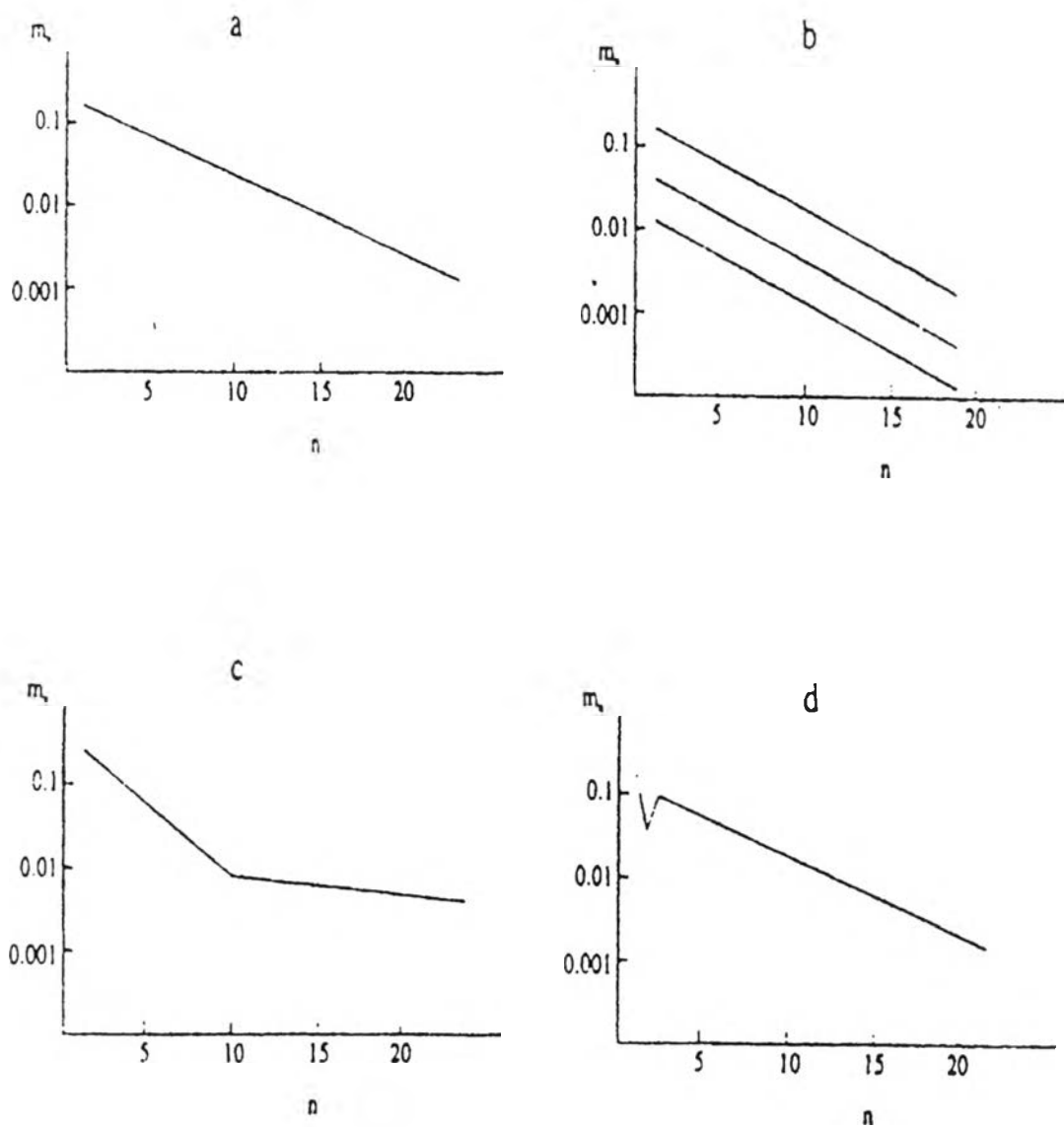
Figure 3.1 Reaction growth schemes for Fischer-Tropsch synthesis. (a) Classical SF model with one termination constant for all products; (b) multiple termination probabilities originating from single intermediate; (c) termination to paraffins and olefins [74]

Figure 3.2 Schematic product distribution graphs of the Fischer-Tropsch hydrocarbons. (a) Classical SF distribution of all product; (b) multiple termination probabilities yield several parallel straight distributions: (c) distribution graph with two different growth probabilities; (d) classical distribution with anomalllies at C_1 and C_2 products [167].

3.2 The previous study of the probability of chain growth

The process conditions as well as the catalyst influence on the product selectivity. The effect of temperature, partial pressures of H_2 and CO, time-on-stream, composition and reduction of the catalyst was discussed briefly. An increase of temperature resulted in a shift toward products with a lower carbon number on iron, ruthenium and cobalt catalysts. With increasing temperature, an increase of the olefin-to-paraffin ratio on potassium-promoted precipitated iron catalysts was observed, while a decrease of the olefin selectivity was present for unalkalized iron oxide powders.

Most studies showed that the product selectivity shifts to heavier products and to more oxygenates with increasing total pressure. Increasing H_2/CO ratios in the reactor resulted in lighter hydrocarbons and a lower olefin content. The influence of the space velocity of the synthesis gas (residence time) on the selectivity has been investigated. The increase of the olefin-to-paraffin ratio with increasing space velocity was observed on a polycrystalline cobalt foil. A commercial supported iron catalyst ($Fe/Cu/K/SiO_2$) was investigated and found that there was no effect of the space velocity on the molecular weight of the hydrocarbons. On the other hand, the TiO_2-supported ruthenium catalysts were observed an increase of the average molecular weight of the products with a decrease of the space velocity. The selectivity to methane and olefins decreased with a decrease of the space velocity, whereas the selectivity toward paraffins remains unchanged.

Deactivation of catalysts during the FT may affect the activity and selectivity to hydrocarbon products. An increase of the selectivity to oxygenate was reported after a period of 1300 h time-on-stream with a precipitated promoted iron catalyst. An increase of the methane selectivity and low-molecular-weight products was observed on iron catalysts. It was known that selectivity changes with time were caused by the formation of carbonaceous deposits on sites with potassium promoters. Deposits was removed from a fused iron catalyst by hydrogen treatment at temperatures higher than 350°C. Sintering of precipitated iron catalysts led to a reduction of the surface area from 300 m^2g^{-1} for a fresh catalyst to about 90 m^2g^{-1} for

a used catalyst. The effect of pretreatment conditions of promoted iron catalysts on the hydrocarbon selectivity and activity was studied. The hydrocarbon selectivity appeared to relate strongly on the pretreatment procedure. Low methane and C_2-C_4 selectivities and high diesel fuel and wax (C_{12+}) selectivities were observed at pretreatment with CO and CO/H_2.

Such a distribution is sometimes referred to as a double α and suggests that two independent chain growth mechanisms contribute to the overall distribution. Furthermore, there has been renewed interest in the deviation of FT products from the FT distribution. The deviation became pronounce only for the mole fraction hydrocarbons with more than ten carbon atoms. These results caused by accumulation of higher weight hydrocarbons that from the secondary mechanisms.

Three different proposals given for chain-length-dependent processes in the FTS influence the product distribution and results in a decreasing olefin-to-paraffin ratio.

1. n-Dependent diffusion limitations.

Both diffusion limitations of reactants to the catalytic sites and of products from the sites may occur. Slow removal of reactive products (e.g., α-olefins) due to a decrease of diffusion coefficients with increasing chain length can influence the FTS reaction rate and selectivity.

2. n-Dependent solubility in the FT wax

A greater solubility of larger hydrocarbons results in an increase of the residence time and higher readsorption rates.

3. n-Dependent physisorption strength

The effect of stronger physisorption for larger olefins to predict the increase of the chain growth probabilities with chain length was reported.

3.3 Comment on previous work

As described in the literature reviews on the chapters II and III, coke deposition occurs in the high temperature and low pressure of catalytic reaction on the surface of Pt-based catalyst, zeolite and other catalysts. The mechanism of coke formation was reviewed and different approaches to control coking were discussed. Ensemble size control produced by adsorbing controlled amounts of sulfur on the surface has been found to be very effective at controlling coking. An approach based on the prevention of carbide formation has also been shown to be extremely effective, although the exact mechanism of coke minimization is uncertain. Small amounts of tin reduce coking significantly. Indications exist that the use of rare earth oxides as supports can also reduce coking. Numerous species of carbon were observed to be deposited or formed on the surfaces of coked catalysts with a detailed analysis. The spectrum was broad, ranging from carbides or microcrystalline and amorphous species to highly aromatic/graphitic carbons. Different types of carbon, which were of detrimental or beneficial impact on the catalytic activity, had identified and characterized as reviewed in the literature. Mechanisms of coke formation have been studied with respect to the coke precursors as well as growth and termination reactions of polymerization reactions. Coke precursors can transform from the metal site to the support site. The morphology and crystalline order of catalytic carbons have been revealed by means of electron microscopic methods and was discussed from the thermodynamic point of view including the tubular growth on submicron catalytic particles. Details on the high industrial relevance of coking and on the various aspects of catalyst deactivation by coke formation were outlined with many factors such as time, temperature, etc. Some of the key parameters that govern the morphology, and thus the adhesion of carbonaceous species to the catalyst surface and the deactivation effect, include the presence of other catalytically relevant impurities in coke-forming processes, and the content of hydrogen. From the mechanism of coke formation, a polymerization of coke precursors was pronounced. The chain growth of coke is interesting to be investigated. At a precious information, FT reaction is also a polymerization and hydrocarbon products of this reaction are generated from addition of CH_2 intermediates. A detailed of FT synthesis was

recently determinate the probability of chain growth using the Schulz-Flory distribution. The higher probability of chain growth value means the higher chain growth and gives the higher molecules of products. Many factors affected the probability of chain growth. The increase of temperature and time reduced the chain growth. On the other hand, the addition of K and the increase of space velocity attained the chain growth of product. The increase of H_2 and CO shows a little effect on the chain growth. Accordingly, this is a good idea for the application of the Schulz-Flory distribution to the determination of the probability of chain growth of coke in order to well understand the coking mechanism.

From the above reviewed literature, coke can be divided into 2 types; one deposited on the metal and the other one deposited on the support. Many techniques of pioneering work are useful for guideline in the application of this research. The physically mixed catalyst of Pt/SiO_2 and Al_2O_3 represented the Pt/Al_2O_3 was used for considering coke on the metal and support. Furthermore, the earlier work did not study the probability of chain growth of coke, although the composition of coke was observed. Hence, Schulz-Flory distribution is a new development for investigation.