Anderson-Schulz-Flory Product Distribution - Can It Be Avoided For Fischer-Tropsch Synthesis?

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During the 1930s, Schulz and Flory developed equations for predicting the polymer molecular weight distribution for a mechanism that involved adding one monomer unit at one time. In the late 1940s, Herington and Bureau of Mines workers, notably Sol Weller and Robert Anderson, developed independently equations that described the product distribution for the lower molecular weight products from the Fischer-Tropsch synthesis. The distribution equations for FT products were developed without being aware of earlier equations derived by Schulz and Flory. These or similar distributions have been rediscovered and the conflicts among individuals this caused will be reviewed. Initially, analytical procedures limited accurate product measurements of carbon numbers less than about 15; today, the products can be accurately measured to carbon number 80 by gas chromatography, and even higher by some techniques. FT gradually was recognized as a polymerization reaction with the monomer being some C_1-species. A plot of the log of the moles of each carbon number products versus the carbon number provides a straight line whose slope is related to alpha, which is related to the termination and propagation probabilities for the surface reaction. Even with the limited carbon number distribution, it appeared that there were at least two product distributions, a low value for the lower carbon number products and a higher value for the higher carbon number products. This became known as the two-alpha distribution and a variety of mechanisms have been advanced to explain the phenomenon. These will be reviewed and contrasted. Investigators have also reported a different deviation where there was a dramatic negative deviation from the straight line at some carbon number so that only low molecular weight products were obtained (the so-called cut-off). These will be reviewed and the case will be made that they are due either to inappropriate analysis of products or to non-steady state conditions. Finally, the dramatic deviations that have been reported for operations at supercritical conditions will be described.