

**STRUCTURED CATALYST BED AND  
METHOD FOR CONVERSION OF FEED  
MATERIALS TO CHEMICAL PRODUCTS  
AND LIQUID FUELS**

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FIELD OF THE INVENTION

The present invention relates generally to methods for conversion of syngas feed materials to conversion products. More particularly, the invention relates to a monolithic-type structured catalyst, reactor, and method for synthesis of chemical products and liquid fuels that provide improved product selectivity, reactor throughput, and temperature control.

BACKGROUND OF THE INVENTION

Fischer-Tropsch synthesis is a surface-catalyzed polymerization process that uses  $\text{CH}_x$  monomers, formed by hydrogenation of adsorbed CO, to produce hydrocarbons with a broad range of chain lengths and functionality. Total product yield decreases exponentially with chain length, forming a so-called Anderson-Shultz-Flory (ASF) distribution. A Schulz-Flory distribution is a distribution of compounds that is expressed by the Schulz-Flory "alpha" value. The Schulz-Flory distribution value ( $W_i$ ) represents the probability of making the next higher carbon number from a given carbon number, as given by Equation [1]:

$$W_i = (1 - \alpha)^{2i} \alpha^{(i-1)} \quad [1]$$

Here, (i) represents carbon number; ( $\alpha$ ) is the Schulz-Flory distribution factor (so-called "alpha" number), which represents the ratio of the rate of chain propagation to the rate of chain propagation plus the rate of chain termination; and ( $W_i$ ) represents the weight fraction of product of carbon number (i). Alpha numbers above about 0.9 are, in general, representative of wax-producing processes. The higher the alpha number—as it approaches 1.0—the more selective a process is for producing wax molecules. The term "wax molecule" refers to solid hydrocarbons with a straight chain carbon length greater than 28. Because ASF distributions are unselective toward middle distillates for all possible chain growth probabilities, enhancing yields to obtain products in the middle distillates range remains a great challenge. During the last two decades, efforts have been made to shift the ASF distribution to a narrow range. These efforts include, e.g., conventional upgrading, interconversion of alkanes via alkane methathesis (interconversion), and incorporation of membrane and reactive distillation into the design of FTS reactors.

Gas-to-liquid conversion such as Fischer-Tropsch (FT) type of synthesis is needed for production of liquid fuels and/or chemical feedstock from a variety of renewable energy and hydrocarbon sources in addition to fossil fuels. New and/or improved catalyst and reactor technologies are needed. FTS is a three-phase (gas-solid-liquid) reaction process, wherein hydrodynamic and mass transfer effects are very important. Even though reactants are in the gas phase, the pores of catalysts are filled with liquid products. Diffusion rates in the liquid phase are typically five orders of magnitude slower than in the gas phase, and even slow reactions may be diffusion limited in the liquid phase. With increasing transport limitations, the selectivity to  $\text{C}_5^+$  will go through a maxi-

imum. The  $\text{C}_5^+$  selectivity will increase as a result of the longer olefin residence times. On the other hand, increasing transport limitations will eventually result in CO depletion since hydrogen diffusion rate is much faster than that of CO, resulting in enhanced hydrogenations and lower selectivity to  $\text{C}_5^+$ . In addition, in conventional FTS, even if  $\text{C}_5^+$  may be maximized, it is still necessary to upgrade/hydrocrack wax ( $\text{C}_{30}^+$ ) in order to obtain valuable middle distillates. Implications from all these research findings are possibilities of optimizing mass transport limitations, which will reduce the chance of re-adsorption of olefins, therefore leading to a desired product chain length distribution and enhanced overall reaction rate within intra-pellet of catalyst particles.

Another important problem for gas-to-liquid conversion is formation of methane from syngas. Formation of methane is highly undesirable. Syngas is wasted as a result of methane formation. Methane is refractory compound. The methane byproduct has to be recycled back to the upstream of the syngas production process unit, such as gasification or steam-reforming reactor, to be cracked back into syngas. The resulting gas stream has to go through the gas clean-up and conditioning process steps. Thus, reprocessing or reusing of the methane byproduct is associated significant capital and operation costs. The other problem with formation of methane by product is generation of excessive amount of heat, which makes difficult to control the reaction temperature. Temperature control for gas-liquid conversion is critical, since the reactions involved are highly exothermic. Temperature control can be easily lost if reaction heat is not effectively removed from the catalyst. Without effective temperature control, desired gas-liquid conversion reactions can fail. The greater the reaction heat that is generated, the hotter the catalyst surface becomes, and ultimately, the faster the process reactions occur. Ultimately, uncontrolled reactions result in auto-catalytic reactions that generally produce methane gas and (solid state) coke.

Physical phases in an FT reactor are complex and can include gas, liquid hydrocarbon, water, and solid catalyst. Mass transfer is considered to be a very important factor that affects both activity and selectivity. Even though the syngas feed is in the gas phase, catalyst pores may be filled with liquid products. Diffusion rate in the liquid phase is typically 4 to 5 orders of magnitude slower than in the gas phase. Some reactions are also slow due to limited diffusion in the liquid phase. Impact of mass transport on reaction activity thus can be readily understood. However, impact of mass transport on product distribution has not been clearly elucidated due to complex reaction kinetics. Since the FT reaction is highly exothermic, heat transfer is also critical to product selectivity.

Catalyst pellet-loaded fixed-bed and fine catalyst particle-dispersed slurry reactors are often used to conduct FTS reactions. In a fixed bed, catalytic materials can be deposited in a thin outer layer of the catalyst pellet (i.e., "egg-shell" catalysts) to mitigate the pore-diffusion mass transport and selectivity problems. However, external mass and heat transfer, and hydrodynamics are difficult to control in pellet-loaded beds due to random stacking of individual particles and non-uniform contacting of catalyst surface/liquid product/gas reactants. For example, liquid products can be readily trapped among inter-particle voids due to capillary forces, resulting in only a fraction of the external surface of the catalyst pellet becoming accessible to gas reactants. In addition, point-to-point contact in packed pellet beds results in poor thermal conductivity for dissipation of reaction heat. In a slurry reactor, in principle, pore-diffusion mass and heat transfer and related activity and selectivity problems can be mitigated by using small catalyst particles. However, there are several