Conversion of Biomass-derived Syngas to DME and Transportation Fuels Using a Microchannel Reactor

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Introduction
Biomass feedstocks, such as agriculture and forestry residues, play an important role in developing alternatives to fossil fuels. Biomass gasification process provides feedstock (syngas) that can be used as building blocks for transportation fuels and chemical intermediates. However, an obstacle to economically producing these valuable products from biomass syngas has been associated with the decentralized nature of biomass operations. In another word, biomass feedstocks are distributed, and are not economic to centralize. The scale of the distributed biomass gasification plants is at least an order of magnitude smaller than that of the conventional fossil fuel based gas-to-liquid (GTL) technologies. We have developed an enabling technology for direct synthesis of dimethylether (DME) and Fischer-Tropsch products from biomass syngas, based on the microchannel reactor technology recently developed at PNNL [1]. In this paper, a catalytic microchannel reactor was used to demonstrate the significantly improved productivity by minimizing heat and mass transfer limitations in this three phase reaction system. In F-T synthesis, we have developed a unique structured catalyst suitable for the deployment in microchannel reactor applications. By tailoring the mass transfer limitations, we have demonstrated that this engineered catalyst produces hydrocarbons with narrower carbon distributions (mainly less than C30) than a conventional particulate catalyst at similar conversion and methane selectivity. Also demonstrated in microchannel reactor was the enhanced productivity in DME synthesis through a factor of six heat transfer enhancement over a conventional slurry reactor.

Materials and Methods
A hybrid catalyst system, consisting of methanol synthesis catalyst, F51-8PPT (Kataco Corporation) and dehydration catalysts, ZSM-5 zeolite or acidic Al2O3 was placed in microchannel reactor. F-T catalysts were synthesized using five sequential impregnations to obtain final formulated catalyst with 30wt%Co and 4.5wt%Re on alumina. The synthesized powder catalyst has a surface area of 60m²/g and pore volume of 0.14 cm³/g. An engineered catalyst was prepared by washcoating the aforementioned catalyst on an aluminum monolithic substrate.

Results and Discussion
As shown in Figure 1, pressure exhibited a positive effect on DME formation. A sharp increase in CO conversion is observed when pressure is increased from 1.0 to 3.8 MPa. The phenomenon observed in the study of pressure effect appears different from what has been reported in the literature. In a review paper, Wender [2] indicated that, in DME synthesis, CO conversion increased with pressure but started to level off at 2 MPa, beyond which the impact of pressure on CO conversion was not significant. Because the source of syngas, especially the type of reactor configuration, and the loading of two functionally independent catalysts are closely interrelated, the performance of DME synthesis in a microchannel reactor could be different from conventional fixed-bed or slurry reactors. Ng et al. compared the difference between a slurry reactor and a fixed-bed reactor and discussed the complexity of reaction variables that influence DME formation [3]. It may be possible that back mixing is minimized in microchannel reactor as compared to other type of reactor configuration. In F-T Synthesis, the diffusion resistance was tailored by changing the coating thickness of catalytic materials on the engineered substrate. In a typical example, an engineered monolith with a catalyst coating thickness of 15µm was compared with powder catalysts of 45µm diameter. Both catalysts have similar Co loading (30wt%) and Co/Re ratio (21). Their performances were evaluated in the microchannel reactor under identical WHSV (weight hourly space velocity) with H2/CO=2 at 250°C. The product distribution and methane selectivities for both forms of catalysts are compared in Figure 2. Under the similar methane selectivity (about 10%), the engineered monolith catalyst exhibits a unique narrower product distribution.

Significance
When microchannel reactor is used in F-T synthesis, majority of the synthesis products falls into the gasoline and diesel range. This unique product distribution, in turn, has positive impact on process economics since a milder or no hydrocracker will be required in downstream product processing. It is also demonstrated in DME synthesis that microchannel reactor can achieve higher space time yield and faster heat removal rate than commercial slurry reactor.

References

Figure 1. Effect of pressure and H2/CO ratio on DME formation
Figure 2. Tailoring the FT product distributions. H2/CO=2, 250°C, similar WHSV (3.73 gCO/gcat/hr)