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Compact heat exchange reactor for synthesis of mixed alcohols

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ABSTRACT

Stainless steel compact heat exchanger reactor with 66 mL catalyst loading was built and tested for synthesis of mixed alcohols. Compared to the fixed bed reactor, the compact heat exchanger reactor have much better heat and mass transfer due to the small particle sizes and miniaturized channels. Development of $NiMo_2C$ catalyst for synthesis of mixed alcohols is also reported. The compact reactor demonstrated two to four times process intensification.

1. Introduction

With industrialization spreading all over the world, we are facing a dilemma: on one hand, world population is increasing exponentially, so does the consumption of electricity and transportation fuels; on the other hand the depleting of natural resources and generating environmental hazards caused by the industrialization is worsening at a greater rate. Currently, majority of energy is supplied by fossil fuels, i.e. petroleum, coal and natural gas. Traditionally, petroleum is the source of transportation fuels, while coal and natural gas are for heat and electricity generation. Direct burning of coal for heat and electricity generation is the major source of air pollution such as SO_x, NO_x, Hg and particulate matters, and releases triple tonnage of CO_2. However, coal is the most abundant fossil fuel resources and readily available at low cost to the most parts of the world. Developing more efficient and environmental benign clean coal is of vital importance for the well-being of mankind and the future of the planet.

Coal can be gasified into synthesis gas, a mixture of H_2 and CO, with all the pollutants captured including CO_2. Synthesis gas can then be converted into hydrocarbons and oxygenates for use as fuels and chemicals via various catalytic processes, i.e. coal-to-liquids (CTL) processes. Similarly, natural gas can be reformed into synthesis gas and then catalytically converted into liquid fuels and chemicals via gas-to-liquids (GTL) processes. Major catalytic synthesis processes are the Fischer–Tropsch synthesis [1], synthesis of methanol, and synthesis of higher alcohols which is the combination of the above two reactions. Large scale CTL conversion is being employed in South Africa (Fischer–Tropsch) and in China (methanol and Fischer–Tropsch) via this indirect synthesis gas route [1–4]. In addition to coal, other solid waste materials such as agriculture wastes, forestry wastes, municipal solid wastes and alike can also be gasified into synthesis gas and then converted into fuels and chemicals. Since the seasonal and limited supply of such waste materials, the conversion plant from those alternate feedstock differ from the large coal- and gas-based plants. The flexibility of scaling up and down according to the availability of feed supply is necessary. In some cases, because of the limited and seasonal supply of the feedstock, such a plant would need to be movable. Similarly, for small gas fields in remote locations, stranded gas, flare gas, land-fill and digester gas-like applications with limited supply of methane, conversion to fuels and chemicals require modular, portable small scale plants.

1.1. Synthesis of mixed alcohol

While FT and methanol synthesis have been practiced at commercial scale, synthesis of higher alcohols is relatively new and undeveloped. Higher alcohols, and also referred to as mixed alcohols are C1–C6 alcohols which could be blended into gasoline as octane booster and oxygenate additives [5–7]. Mixed alcohols are more compatible with gasoline than ethanol which is currently blended at 10% in most US gasoline stations. Synthesis of mixed alcohols has not been commercialized, mainly due to lack of catalysts with desirable activity and selectivity [8]. Synthesis of mixed alcohols is a combination of alcohol formation and carbon–carbon

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chain growth. Catalyst design should consider both these functions [9,10]. Actually, the catalyst development of mixed alcohols was derived from the catalysts for synthesis of methanol, the modified methanol synthesis catalysts [11,12] or modified Fischer–Tropsch synthesis catalysts [13]. MoS_2 based catalyst developed by Dow [14–16] is one of the most promising catalysts since it is highly selective to alcohols with good yields. However, this catalyst contains sulfur and sulfur compounds are needed to maintain the catalyst activity and selectivity [17,18]. So the product of the MoS_2 catalyzed reactions contains sulfur component which need to be removed for use as gasoline blend [18]. It has been reported that other molybdenum compounds such as molybdenum carbide, nitrite, boride, phosphide are active for mixed alcohols synthesis. Particularly, Mo_2C based catalyst with promoters have high activity and selectivity to C2+ alcohols. Indeed, over the past ten years or so, Western Research Institute has developed a $NiMo_2C$ catalyst with high activity and selectivity for mixed alcohol synthesis [19]. One of the main advantage of mixed alcohol synthesis over FT synthesis is that final product does not require further upgrading and can be marketed as a fungible product as a blending stock for gasoline.

1.2. Development of synthesis gas conversion reactor technologies

Synthesis gas conversion reactions are highly exothermic. Heat removal is an important factor to consider when designing a synthesis gas conversion reactor. The commercial reactors for large-scale plants are: multitubular boiling water reactors such as those used by Shell [20] in Bintulu and Pearl GTL, slurry bubble column reactors [21] as used by Sasol, SynFuel China in GTL and CTL plants, and fluidized bed reactors as used by Sasol for high temperature Fischer–Tropsch Synthesis. All these designs are not feasible for small and portable synthesis gas conversion plants.

1.3. Microchannel reactors

Microchannel reactors provide significant benefits by enhancing heat and mass transfer. The integration of microreactor with heat exchangers could improve the yields and selectivity for highly exothermic/endothermic reactions, showing great process intensification properties. As stated by Tonkovich et al. [22], microchannel reactors has a parallel flow paths of 100–1000 μm in width and aspect ratio between 1:1 and 100:1. The distance between heat source and heat sink is greatly reduced.

Burns et al. [23] examined the fluid dynamics of narrow channel reactor, showing rapid mass transfer between phases can be achieved over a range of flow rates and viscosities. He also tested the nitration of benzene, in which rapid mass transfer is required to lower by-product formation. He indicated the channel size between 30 and 300 μm could achieve good mixing in 1–10 s. Losey et al. [24] examined the mass transfer property of the microchannel device by using the model reaction of cyclohexene hydrogenation and found the activity was nearly 2 orders of magnitude higher than the conventional fixed bed reactor.

Martin et al. [25] reported a micro-fabrication method by diffusion bonding patterned shims for natural gas reforming. The reactor channel dimension was 250 μm × 5000 μm with an aspect ratio of 20. The heat for reforming was provided by methane combustion. The pattern of the shims can be made by photochemical, electrochemical, laser or stamping. It could apply to copper, aluminum, stainless steel and alloys. After diffusion bonding, the reactor becomes monolithic and it is vacuum-tight. The reactor they made could be used at temperatures up to 900 °C.

Many reactions have been tested in microchannel reactors such as water gas shift [22], steam reforming [25], partial oxidation [26–28], Fischer Tropsch synthesis [29,30], synthesis of methanol [31], methane oxidative coupling [32], photocatalysis [33], catalytic combustion [34] and as a bioreactor [35]. These are just a few examples and the applications are spreading quickly.

The catalyst loading for the microchannel reactor is generally by applying a coating, similar to the washcoating of monolith catalysts in automobile exhaust gas treatment. This method of loading has very good heat transfer because the catalyst is closer to the walls. Although the microchannel reactors are excellent and have great advantages regarding heat and mass transfer, the catalyst loading is generally lower than a fixed bed reactor per volume. Another problem of this kind of loading is that the catalyst and the reactor is one unit. If for some reason the catalyst is deactivated, it could not be replaced easily. To overcome this problem, minichannel reactor has been developed.

1.4. Minichannel and micropacked reactor

Minichannel compact reactor is the larger version of the microchannel reactor. It has a similar structure as the microchannel reactor with larger channel sizes for catalyst packing. Since the enlarged channel sizes, the heat and mass transfer property is not as good as the microchannel reactor. However, it is much better than the commercial multitubular reactor in a number of aspects: small channel dimensions, small catalyst particle sizes. The heat transfer pass length is only a few millimeter, which is less than 1/10 of the multitubular reactor currently employed in the synthesis gas conversion (GTL and CTL) plants. The "pellet" size of catalyst for the minichannel reactor is similar to the slurry bubble column reactor; however, because the catalyst is present as a fixed-bed the minichannel reactor does not have the catalyst attrition and product–catalyst separation problems. Smaller catalyst pellet size greatly improves the mass transfer for synthesis gas conversion reactions.

1.5. Compact heat exchange reactor

Chart Energy and Chemicals developed a compact heat exchange reactor (CHER). There are two product lines (ShimTec® and FinTec®) of the minichannel reactor based on the heat exchanger technology. The ShimTec® line is based on the thin shims with patterns designed for process and heat transfer fluid. Stacks of such shims are diffusion bonded by heat and pressure. Complex channel system could be designed and manufactured with this method. ShimTec® is more suitable to niche processes such as fine chemicals and pharmaceuticals. FinTec® line is produced by fin-plate structure. The channels are formed by corrugated metal sheets and then bonded by diffusion bonding which can withstand high temperature and pressure. The construction materials could be copper, aluminum, stainless steel, and nickel alloys. A prototype 66 mL CHER based on Chart FinTec® was installed and operated by WRI. A 30-time scale-up to 2 L catalyst loading was also completed at WRI. In this paper, we will report the development of mixed alcohol synthesis catalyst and the operation of prototype CHERs.

2. Experimental

2.1. Catalyst preparation

Catalyst precursors used for preparation of the Ni/Mo_2C catalysts are a variety of Ni and Mo sources including nickel oxide, nickel nitrate, nickel acetate, $NiMoO_4$, MoO_3, ammonium molybdate, all in powder state. We have experimented with physical mixing, precipitation, impregnation and alike to obtain the right formula of catalyst composition. Carburization of the mixtures was performed via Temperature Programmed Reduction (TPR) using gaseous mixtures such as H_2/CH_4, H_2/C_2H_6 with 20% carbon atoms. Carburization process was carried out in quartz reactors, a tubular