Experimental study of methanol synthesis in a microchannel reactor

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Introduction/ Industrial Significance

Existence of around 25% (ca 1500 TCF) of the proven world's natural gas reserves in remote areas far from shore calls for developing new technologies which enable conversion into transportable fuels and chemicals. Research on microchannel reactors for chemical conversion of natural gas to methanol and Fischer-Tropsch (FT) products are examples of current efforts of energy companies in order to utilize these resources.

Since methanol synthesis is an exothermic reaction limited by thermodynamic equilibrium, there is always a trade-off between kinetics and thermodynamics. Calculations show that the rate of heat transfer between reactor and reaction media is lower than the intrinsic rate of reaction [1]. Hence theoretically, operating at contact times down to 100 milliseconds in a specific reactor design with high surface to volume ratio should result in better heat transfer, isothermal conditions and finally higher productivity and catalyst stability.

This research evaluates preliminary performance of an Integrated Micro Packed Bed Reactor- Heat Exchanger (IMPBRHE) for methanol synthesis reaction as compared to a non-isothermal fixed bed reactor (FBR). In order to fully evaluate IMPBRHE performance, assessment if possible external diffusion limitation was included in this study.

Materials and methods

Both home made (HMC) and commercial (CC) $Cu/ZnO/Al_2O_3$ catalysts have been used. The home made catalyst was prepared by coprecipitation resulting in 172 m^2/gr specific surface area. The stainless steel IMPBRHE made by Forschungszentrum Karlsruhe (FZK), consists of eight parallel channels with width of less than 1 mm and each reaction channel being sandwiched between two cross flow oil channels which serve as cooling media for heat removal. A high temperature oil circulator (Julabo HT30) was used to maintain the reaction at desired temperature. Temperatures were measured on the surface of the outer channel wall. The stainless steel FBR was ½" nominal size in diameter. Bed temperature was measured using a moveable thermocouple along the axis. The FBR wall temperature was kept constant by an electrical furnace. The catalyst was crushed down to 50-120 μm particles and packed in the reaction channels. Premixed synthesis gas containing H_2:CO:CO_2:N_2 in ratio 65:25:5:5 on vol.% basis was used. The reaction temperature and pressure were 255 ºC and 80 bars respectively, unless otherwise mentioned. Online feed and product gases analysis was performed by gas chromatography (Agilent 6890), while the liquid products were collected and analyzed offline. The FBR wall temperature was set in order to achieve a maximum bed temperature of 255 ºC at different gas flow rates. Depending on the flow rates, an exotherm of 6 to 20 ºC was observed. The IMPBRHE was operated at 255 ºC with an exotherm of maximum 2 ºC over the whole range of gas flows.

Results and discussion

Table1 shows comparison between isothermal IMPBRHE and non-isothermal FBR for contact times (bed volume to gas flow at normal conditions) down to 120 milliseconds. At high contact times FBR shows higher conversion, since the gas cools down along the reactor and this improves equilibrium conversion, while at contact times lower than 300 milliseconds, IMPBRHE tends to show considerably higher conversions. This is due to higher capability of heat removal at high flows where the total heat released in the reactor is higher (up to 25 times).The commercial catalyst was also tested in IMPBRHE, showing an even higher activity while the reactor remains essentially isothermal. These results indicate promising performance of microchannel reactors at high space velocities.

Table 1: Contact time study, comparison between two reactors

Contact time, milliseconds	120	160	240	325	480	800	1600
CO%., FBR, HMC	7.5	11.5	22.0	29.5	39.1	52.2	67.4
CO %., IMPBRHE, HMC	12.9	22.8	25.2	26.5	28.9	32.7	34.3
CO%, IMPBRHE, CC	22.1	24.1	-	32.8	39.0	42.6	50.1

The external mass transfer limitation was also checked in IMPBRHE at 50 bars pressure. Since the flow is laminar, velocity change is not a viable method for this purpose [2]. Helium as an inert gas was added to feed gas to change the molecular diffusivity, while the partial pressure and space velocity of reactants were kept constant. Dilution with Helium up to 90 bars results in reduced CO and CO_2 diffusivities in the gas mixture by approximately 25%. Table 2 shows the conversion level in IMPBRHE before and after dilution. Reduced conversion is an indication of external diffusion limitation in the system.

Table 2: External mass transfer check in IMPBRHE

Average Bed Temp. ºC	200	220	240	255	265
CO% at 50 bars, no dilution	47.3	38.4	26.3	21.4	18.6
CO% at 90 bars, Helium dilution	31.8	22.6	16.6	13.8	14.9

Acknowledgement:
This publication forms a part of the Remote Gas project, performed under the strategic Norwegian Research program Petromaks. The authors acknowledge the partners; StatoilHydro, UOP, Bayerngas Norge, Aker Solutions, DNV and the Research Council of Norway (168223/S30) for support.

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