

DEVELOPMENT AND TESTING OF COMPACT HEAT EXCHANGE REACTORS (CHER) FOR SYNTHESIS OF LIQUID FUELS

FINAL REPORT

June 15, 2014

Prepared for

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Advanced Conversion Technologies Task Force**

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EXECUTIVE SUMMARY

Western Research Institute teamed with Chart Energy and Fuels to conduct research for the development of a novel compact reactor - Compact Heat Exchange Reactor (CHER). The CHER is based on the concept of heat exchangers in which the process channels are packed with catalysts. CHER has high heat transfer rate due to its high surface area and miniature channel sizes. The CHERs developed at WRI are constructed of stainless steel material built utilizing the Chart Fintec® technology. They can operate at high temperatures and pressures. The CHERs have been tested with several synthesis conversion reactions, such as methanol synthesis, DME synthesis, Fischer-Tropsch synthesis and mixed alcohol synthesis. Synthesis gas conversion is a common route for indirect liquefaction of coal, natural gas and biomass. Synthesis gas conversion is highly exothermic and reaction heat removal is critical for reactor design. Although large scale gas-to-liquid (GTL) and coal-to-liquid (CTL) processes have been commercialized, small scale GTL and biomass to liquid (BTL) are still not economically viable, partly due to a lack of suitable reactor technologies that are cost effective and resistant to variations in the feedstock supply. CHER is essentially a high temperature and high pressure heat exchanger with the process channels open for catalyst loading. CHER is a fixed bed reactor with multiple miniature channels holding catalysts particles sized at 100-200 micrometers. The heat exchange surface area of the CHER is hundreds of times greater than a traditional fixed bed reactor. CHER has excellent heat and mass transfer properties, resulting in significant process intensification. CHER is modular and easy to scale up or down according to the feed supply or the product market by simply adding or removing modules.

A prototype stainless steel CHER was fabricated for testing the performance of the concept. The reactor was 1 foot long with 30 channels which are divided into three rows interlaced with four layers of heat exchange media. Figure 1 below shows the channel view of the prototype CHER. The effective capacity of catalyst loading of the reactor is 66 ml. The maximum design temperature and pressure are 400°C and 1750 psi. This prototype has been tested at temperatures up to 350°C and pressures as high as 1500 psi.

Appropriately sized catalyst particles are packed into the openings of the channels. The reaction temperature is regulated by a heat-transfer oil (Therminol 72) system at a rate of 1 gpm. Four thermocouples were used to monitor the temperature distribution in the reactor channels. The operational temperature profile measurement indicated a uniform temperature distribution across the entire reactor. The reaction system is controlled by a customized PLC-DAQ-HMI system designed and built by the WRI team which includes automatic computer control of the reaction parameters, data logging and interlocked safety features allowing the reactor system to run 24/7 with or without an onsite operator.



Figure 1: **Channel view of the prototype CHER**

Several synthesis conversion reactions have been carried out with the prototype CHER, including the synthesis of methanol, DME, Fischer-Tropsch liquids, and mixed alcohols. During operation, the temperature control of the CHER was excellent, and the reactor system showed a significant process intensification as compared to a standard fixed-bed reactor. Uniform Catalyst loading is crucially important for optimum CHER performance, and the pressure drop across each channel should be balanced to avoid syngas channeling through a small number of channels. Catalyst loading techniques have been developed over the course of testing, and multi-layered loadings are possible with the reactor system. This allows the flexibility to process multi-step synthesis reactions in series in the same reactor.

Synthesis of methanol was conducted with two commercial catalysts, i.e. MK121 from Topsoe and MegMax 800 from Sud Chemie. Both catalysts yielded excellent performance, showing process intensification of about 4-times as compared to a conventional fixed-bed reactor, and 10-times when compared to a conventional quench reactor. Net effect of such an excellent reactor performance is that for achieving a given production rate, catalyst loading and reactor size are reduced such that overall cost of the technology is reduced.

The CHER was also tested for DME synthesis. The synthesis of DME is more exothermic and less equilibrium restricted than the synthesis of methanol due to the tandem methanol dehydration reaction. Several reactions are involved in DME synthesis:

Synthesis of methanol: $2\text{H}_2 + \text{CO} = \text{CH}_3\text{OH}$

Methanol dehydration: $2\text{CH}_3\text{OH} = \text{CH}_3\text{OCH}_3 + \text{H}_2\text{O}$

Water gas shift reaction: $\text{CO} + \text{H}_2\text{O} = \text{H}_2 + \text{CO}_2$

The overall reaction: $3\text{H}_2 + 3\text{CO} = \text{CH}_3\text{OCH}_3 + \text{CO}_2$

The ideal H_2/CO ratio is 1:1, and CO_2 is the preferred oxygen sink since high concentrations of H_2O cause hydrothermal deactivation of the catalyst. One step DME synthesis catalyst is a combination of methanol synthesis catalyst and an acid catalyst for dehydration. The

balance of the methanol synthesis and dehydration functions of the multifunctional catalyst is crucial for a good DME synthesis activity. Three tests of the prototype CHER for DME synthesis were performed using a proprietary WRI catalyst blend. One test was performed with a full catalyst loading, with the other two tests performed with partial loadings. The full loading test lasted 200 hours continuously under remote monitoring and unattended operation. The catalyst showed good activity and selectivity. It reached equilibrium at 500°F and 700 1/h space velocity. The STY of DME peaked at about 480 to 500F. The optimal H₂/CO ratio was about 1:1, which is in agreement with the overall reaction pathways described above.

Fischer-Tropsch synthesis is highly exothermic since all oxygen is striped off the hydrocarbon product. A one-month long run of a highly productive Fischer-Tropsch catalyst was carried out in the prototype CHER and established the superior heat transfer characteristics of the reactor. The run was continuous and in the most part autonomous under pc-based controls. The test established the reactor and equipment capabilities in highly exothermic synthesis reactions. The pressure drop across the reactor was about 3-4 psi with 0.2 mm catalyst pellet size. Again, about 10 time process intensification was confirmed when compared to a standard fixed-bed reactor.

Synthesis of mixed alcohols is similarly more exothermic than synthesis of methanol and DME. The molybdenum based catalysts used for the synthesis reaction require high temperature and pressure. Slurry column type reactors are not viable because of the significant loss of the dispersion media due to cracking at reaction temperature. Compared to other synthesis reactions, the synthesis of mixed alcohols requires narrow temperature range, usually less than 5°C to get the optimal yield and selectivity. Lower temperatures hinder the conversion and yield, while higher temperatures produce more undesirable hydrocarbons. Such a narrow operational temperature regime make CHER an ideal choice for synthesis of mixed alcohols. To demonstrate the superior performance of the reactor, one test was carried out with the prototype CHER with a supported NiMo₂C catalyst. The catalyst is active at 500 °F, 1400 psi. CO conversion reached about 40% and an alcohol yield of 0.120 g/gcat/h at low SV (2365 1/h) was achieved. The space time yield of alcohols increases with temperature and space velocity. It reached about 0.75 g/gcat/h (0.95g/ml/h) at 585 °F and 17000 1/h. These synthesis productivities for mixed alcohols are not possible in standard fixed bed or slurry reactors. This could be attributed to the excellent heat and mass transfer properties of the CHER. In the alcohol product, about 75% is C₂+ alcohols and only a quarter of the fraction is methanol. This product is an excellent gasoline blending stock.



Figure 2: Channel view of pilot CHER

Based on successful operation of the prototype CHER, we scaled up the reactor to 2L catalyst loading capacity, which is 30 time scale-up from the prototype (see picture above). This reactor, pilot CHER, is two feet long, 7 rows of process channels interlaced with 8 heat transfer layers. Each row is composed of 30 channels. Two CHERs were fabricated for flexibility. However, the design pressure of the two reactors is different. High-pressure reactor used CL1500 flanges in which the design temperature and pressure are 750F and 1750 psi, separately. For reducing the cost and the reactor weight, the low-pressure reactor used CL900 flanges which reduce the design temperature and pressure slightly. The high-pressure reactor was further modified to accommodate five thermocouples to measure the temperature of the channels inside the reactor to provide further information of the reactor heat transfer performance. The pilot CHER is designed to be compatible with heat transfer oil system or steam heat transfer system for reaction temperature control. In our installation, we chose the oil system very similar to that employed at the prototype CHER.

The pilot CHER was simulated with Aspen plus for methanol synthesis, synthesis of ethanol, and Fischer-Tropsch synthesis for sizing the preheater and heating oil system. The max temperature of the hot oil system is 716 °F. The canned centrifugal pump can deliver 50 gpm of hot oil circulation which meets the heat management requirement of Fischer-Tropsch and mixed alcohols synthesis. During the course of this project, two tests of the pilot CHER have been carried out. The first test was a verification test which lasted for 14 hours. The second test was a more extensive longer duration operations, which included nitrogen and CO₂ dilution of the feed and recycle, divided into 7 distinct test periods. The second test lasted for about 100 hours. Both tests used a commercial methanol synthesis catalyst (MK121). Both tests were successful, and operation of the CHER was smooth and stable. Because of the limited supply of hydrogen and carbon monoxide, the space velocity used was not adequate for performing any tests without recycle. With recycle, almost all the synthesis gas was consumed and converted into methanol.

The tests revealed that the system was fully functional and ready for evaluating more exothermic reactions such as synthesis of DME, mixed alcohols, and Fischer-Tropsch reactions at the larger scale. With improved gas delivery system and interface the pilot CHER with natural gas reforming or coal gasification, the pilot CHER would be an excellent reactor in gas to liquid, coal to liquid and biomass to liquid processes.

In summary, we have designed, fabricated and installed a prototype CHER system and tested the performance and operation stability with synthesis of methanol, DME, mixed alcohols and Fischer-Tropsch synthesis. A month long term continuous test was completed with minimal supervision, and showed the reliability and stability of the system. The CHER showed excellent heat and mass transfer and process intensification of 3 to 10 times. The temperature variation across the reactor is minimal and the reaction essentially running at isothermal conditions. We have scaled up the CHER to a 2L catalyst loading pilot scale, which is a 30x scale up from the prototype CHER. The pilot CHER installation was complete. 100 hour test of methanol synthesis was carried out successfully. When recycle was employed, nearly complete synthesis gas conversion was reached with methanol selectivity over 99%.