Executive Summary

Introduction

With the development of more efficient catalysts, it has become possible to increase the rates of synthesis reactions several fold[1]. However, catalyst and reactor technologies need to work in concert in order to be able to take advantage of higher catalyst reactivity. In some respects, reactor technology lags behind the potential increases in conversion efficiency promised by the development of ever more active catalysts. *A propos* of this, there are examples of catalytic reactor systems, in commercial application, where exothermic heat generation in the catalytic reactor system limits process efficiencies, for example, achieving equilibrium conversion efficiencies. The initial impetus for design of a new reactor technology came out of the desire to further develop technology for the production of dimethyl ether. In particular, the initial impetus was driven by the desire to develop of an efficient single-stage syngas to DME conversion technology.

Slurry Reactors

It was recognised that slurry reactor technologies could potentially allow for improved process optimisation for exothermic conversions, such as the reactions involved in the direct conversion of syngas to DME. However, it was also recognised that there were several deficiencies associated with current slurry reactor technologies, as well as single-stage DME catalyst technologies. Syngas conversion processes in slurry reactors are multiphase systems requiring a number of mass and energy transfer steps to occur before reaction can proceed. Typically, the following steps occur:

1. Transport of reactants and energy from the gas phase to the bulk liquid fluid of the catalyst containing slurry medium (typically an inert hydrocarbon liquid);
2. Transport of reactants and energy from the bulk fluid up to external surface of the catalyst,
3. Transport of reactants and energy from the external surface into the pores of the catalyst,
4. Adsorption, chemical reaction, and desorption of products at catalytic sites within the catalyst,
5. Transport of products and energy from the catalyst interior to the external surface of the pellet,
6. Transport of products and energy into the bulk fluid, and
7. Transfer of products and from the bulk fluid.

When employing a bifunctional DME catalyst, step 4 above involves a plurality of chemical reactions (e.g. methanol synthesis, water gas shift, methanol dehydration) leading to an extra degree of system complexity.

Slurry reactors are used in a variety of chemical, petrochemical, biochemical, and environmental processes, including hydrogenation, hydroprocessing, oxidation, chlorination, hydroformylation, cell growth, and bioremediation. **Figure I** below illustrates a slurry bubble column reactor for the conversion of syngas to DME.

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[1] Sadettin S. Ozturk, Yatish T. Shah, “Coal Liquefaction: Investigation of Reactor Performance, Role of Catalysts and PCT Properties. I-C Methanol Synthesis Process,” Chemical and Petroleum Engineering Department, University of Pittsburgh, Technical Progress Report – 1985, I-210 – I-211

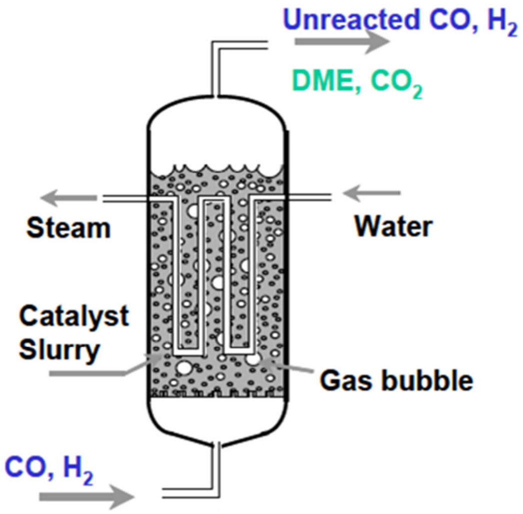

Figure I: *Slurry Bubble Column Reactor*

A "conventional" catalytic slurry reactor is usually described as a three-phase bubble column in which the fine solid catalyst particles are held in suspension in a liquid phase by bubbling gas phase reactants. Reaction heat is absorbed by the large-heat-capacity liquid. For highly exothermic reactions, cooling coils can be provided in the reaction zone. Broadly, bubble column slurry reactors have been considered to have the following advantageous properties:

- Simple construction and potentially lower capital required for a large-scale slurry reactor;
- Excellent temperature control;
- Rapid mixing, which facilitates efficient heat transfer and, thus, isothermal operation;
- Moderately good interphase mass transfer with low energy output;
- Lower pore-diffusional resistance, due to the small size of catalyst particles typically used;
- Feasibility for large capacity;
- Low pressure loss that saves considerably on compression costs; and
- Online removal and addition of catalyst.

Moreover, the use of a relatively rapidly deactivating catalyst (such as the majority of DME catalyst that have been developed to date) can be achieved through use of a slurry system where catalyst change-out refreshment is relatively easily accomplished, whereas with a fixed-bed system this is not possible to accomplish while maintaining the reactor system online.

DME

DME is a unique energy carrier molecule that can have a place in the current fossil-fuel reliant world as an energy carrier (e.g. municipal gas, diesel substitute, turbine fuel, etc), as a "hub chemical" (an intermediate in chemical processing), as well as hold a position as a "future fuel" beyond a fossil-fuel based world. DME has the potential to address concerns such as: energy security, energy conservation, and the environment. DME can be produced from coal, natural gas, biomass, and any other carbonaceous materials through gasification. The infrastructure of DME is less cost intensive than that for other alternative fuels because DME can use the existing LPG and natural gas infrastructures for transport and storage (with some modifications). DME can typically be prepared in one of the following two ways from synthesis gas (syngas):

- Syngas is converted to methanol, which is subsequently dehydrated to form DME (the two stage process); and
- Syngas is converted directly to DME in a single reactor (the single stage process).

The most common, currently employed, commercial technology for the preparation of DME is the two stage process. The single stage process has been demonstrated by JFE and Air Products. JFE's technology used a slurry bubble column reactor as did the LPDME Process demonstrated by Air Products. Ambre Energy Limited, and its subsidiaries, has been involved in the development of a novel DME reactor technology since May 2007. Single stage syngas to DME synthesis takes advantage of synergies in the reaction pathways. Final product formation is favored due to thermodynamic equilibrium limitations being overcome through products acting as reagents in subsequent reactions.

(a) $2CO + 4H_2 \leftrightarrow 2CH_3OH$ $\Delta H = -181$ kJ (MeOH synthesis)
(b) $2CH_3OH \leftrightarrow CH_3OCH_3 + H_2O$ $\Delta H = -23$ kJ (MeOH dehydration)
(c) $H_2O + CO \leftrightarrow H_2 + CO_2$ $\Delta H = -41$ kJ (WGS)

Overall Reaction: $3CO + 3H_2 \rightarrow CH_3OCH_3 + CO_2$ $\Delta HT = -245$ kJ

As shown in **FigureII** below, at syngas ratios of H_2:CO, 1:1 there is an equilibrium maximum for the conversion of syngas to DME with an approximately 90% conversion efficiency achievable.

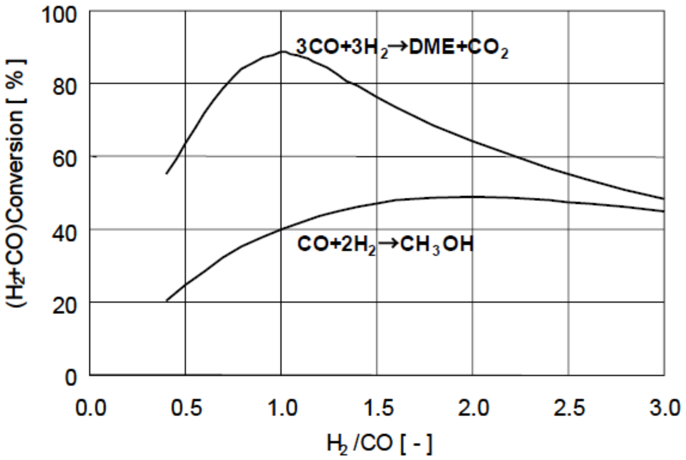

Figure II: *Equilibrium Conversion, 260°C, 5MPa*[2]

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[2] Yotaro Ohno, Hiroshi Yagi, Norio Inoue, Keiichi Okuyama, Seiji Aoki, "Slurry phase DME direct synthesis technology -100 tons/day demonstration plant operation and scale up study", *Studies in Surface Science and Catalysis*, **2007**; *167*, 403-408

The single-stage syngas to DME catalyst is designed to have two different specific activities, with a third activity also inherent. The two specific activities are: (1) Methanol Synthesis and (2) Methanol Dehydration. The third activity is water gas shift.

The Helical Channel Reactor (HCR)

Figure III below illustrates an expanded view of the helical channel gas plenum and sparge-zone. Referring to **Figure III**, pressurized syngas is forced into the helical channel through a gas plenum. The gas plenum is in communication with the reactor wall, which is itself a micro-porous tube (sintered steel tube). There is a pressure drop across this reactor wall with process conditions adjusted to achieve the correct reactor system pressure. The pressure drop is a function of the porosity of the reactor wall and is one of many design considerations. The micropores generate a micro-bubble stream. The micro-bubble stream is continually sheared by the action of the catalyst and mineral oil containing slurry, which is forced around the helical channel at high velocity by a pump in the slurry circuit. Mass transfer properties are improved by the generation of micro-bubbles by this shearing action. Moreover, inducement of secondary flows in the channel means that the number of collisions between small gas bubbles and catalyst particles contained in the slurry are increased. The sparge zone portion of the reactor is specifically for introduction of syngas into the slurry stream. Connected to the sparge zone is a reaction or residence time zone (not shown in **Figure III**), which is essentially a continuation of the helical channel without addition of further syngas. As such, the residence time zone can simply be in the form of a helical tube. This tube may be of variable length, pitch, helix diameter and channel cross-sectional area.

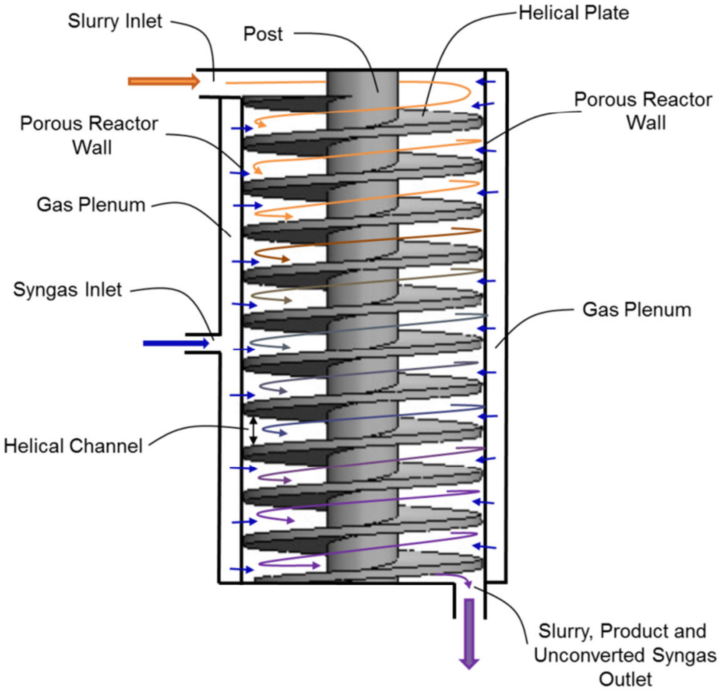

Figure III: *Helical Channel Reactor*

The liquid/slurry flowing through the helical channel or coiled tube is subjected to a secondary flow induced by an imbalance between the centrifugal forces due to curvature and the cross-stream pressure gradient due to viscous forces. Further, the pitch between the coil rings is responsible for a torsion effect.

These effects generate turbulent flow and show the high energy dissipated in the slurry mass, which induces dispersion and mixing of the reactants and catalyst particles, and heat exchange. The secondary flow can be described by the Dean number and the torsion effect can be described by the Germano number. These numbers provide fluid-dynamic characterization for coil flow reactors and make possible the determination of proper scale-up factors for design and fabrication of larger reactors having the same fluid-dynamic conditions which were optimized at laboratory scale.

HCR Design

The HCR test unit that was installed and tested at WRI was designed through a joint venture between Ambre Energy, WRI, and Jantra. The plant design was completed at WRI, all system modeling and plant design support was provided by Ambre Energy. Jantra provided the necessary operational conditions, including pipe velocity calculations for optimizing secondary and tertiary mixing in the reactor.

The desired operational parameters of the HCR test system are detailed in the following table.

Table A: *Test unit design conditions*

Parameter	Units	Minimum	Maximum
Slurry Flow Rate	kg/min	6	30
Reactor Temperature	^{o}C	230	250
System Pressure	barg	35	50

The sparge zone of the reactor is designed to effectively combine the syngas and catalyst slurry at high velocity. Syngas is introduced to the catalyst slurry through a sintered stainless steel sparger, while the slurry is passed through the inside of the sparger, through a helical channel, at high velocity. The combination of the high velocity slurry along with the micro-porosity of the sparger, results in very fine syngas bubbles in the slurry in the reactor. As with any slurry-based reactor, finer reactant gas bubbles result in an increase in reaction rate.

In the HCR reactor, the length of capillaries of the porous wall is small compared to the diameter of the reactor. Hence, we can assume that gas flow into a single capillary tube is equal to the gas flow into the bubble. When gas starts flowing through the capillary, it passes at a constant flow condition, raising the pressure inside the bubble linearly.[3]

The following images show the sparge zone of the reactor, and the internal structure of the reactor.

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[3] Lehr F., Millies M., and Mewes D., "Bubble-Size Distributions and Flow Fields in Bubble Columns", *AIChE Journal*, **2002**, 48(11), 2426 - 2443.

Figure IV: *Helical Channel Reactor*

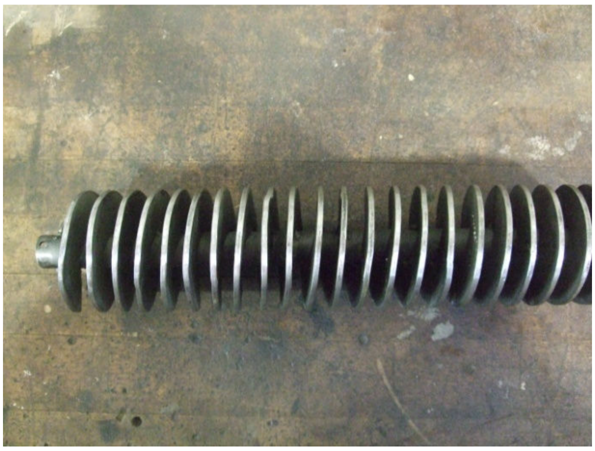

Figure VI: *Reactor Helical Channel*

Figure V: *Reactor Helical Channel Installed in Sintered Stainless Sparger*

Reaction Zone

The residence time zone of the reactor is designed to maintain intimate contact between catalyst and syngas over a longer time period than is available in the main reactor. For the test HCR unit, the default residence time zone was constructed out of 80-feet of tightly coiled stainless steel tubing. However, this could be modified by increasing or decreasing the length, changing the helix diameter and changing the helix pitch. In addition to increasing the reactor residence time, the tight coiling of the stainless steel tubing increases fluid mixing due to the formation of primary and secondary vortices.

The liquid/slurry flowing through the helical channel or coiled tube is subjected to a secondary flow induced by an imbalance between the centrifugal forces due to curvature and the cross-stream pressure gradient due to viscous forces. Further, the pitch between the coil rings is responsible for a torsion effect. These effects generate turbulent flow and show the high energy dissipated in the slurry mass, which induces efficient dispersion and mixing of the reactants and catalyst particles, and a very efficient heat exchange. The secondary flows are, for a wide range of conditions, manifested by two or more counter-rotating vortices (shown in the following figure) commonly called “Dean vortices” or “recirculation cells”.

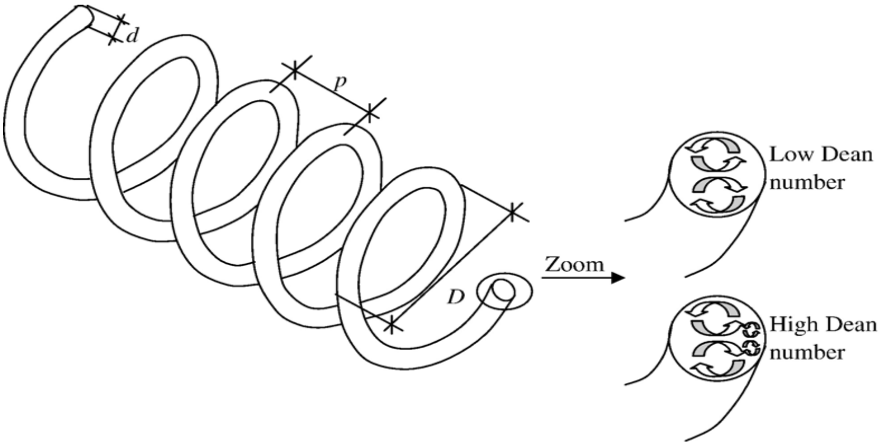

Figure VII: *Secondary flow in coiled Pipe*

The following image shows the installed coiled tubing used as the reaction zone during HCR testing.

Figure VIII: *Installed Reaction Zone*

Reactor Sizing and Flow Rates

In the typical helical channel reactor application, the centrifugal force with Reynolds numbers being in the range of 25,000 to 50,000, results in numerous small bubbles/droplets sparged and sheared from the reactor porous surface. These bubbles generally tend to move toward the inner surface of the channel, but are subjected to the overwhelming action of the strongly turbulent constrained flow. In this way, the turbulent flow causes intensive contact between bubble/droplet reactants and catalyst particles.

Based on the sparge zone calculations, the desired gas flow rate is 0.1 to 0.3 m/s. The maximum syngas supply for the given installation is in the 120-135 SLPM range. Given these constraints, the desired reactor size is easily calculated. The critical reactor dimensions are given in the following table:

Table B: *Critical Reactor Parameters*

Spare Zone Height	300 mm
Sparge Diameter	65 mm
Helical Cross Sectional Area	325 mm^2
Helical Turns	20
Reactor Volume	0.75 L
Slurry Flow Rate	6 to 30 kg/min
Reynolds Number Through Reactor	10,000[*] to 40,000
Residence Time in Reactor	1 to 5 s
Residence Time in Reactor and Reaction Zone	3.5 to 15 s

[*] Lower Reynolds number than ideal for low flow rate. This allows for increased data analysis

Reactor Channel Cross-sectional Area and Shape

For ease of construction, the cross-sectional shape of the HCR was designed to mimic the shape of a screw conveyor screw. This design allowed for construction utilizing off the shelf materials, and most closely matched the calculated parameters of the helical coil channel analyzed during the design phase.

Figure IX: *Close-up of constructed helical coil channel*

Slurry Pump

The critical piece of equipment for operation of the HCR is the slurry pump. The pump must be capable of operating at full system pressure, provide the required flow and energy to overcome system pressure losses, and stand up to the wear of pumping an abrasive slurry material. Due to these constraints, a magnetic-drive two-stage turbine pump was selected. The pump was ordered from and provided by Warrender LTD based in Wood Dale Illinois.

Disengagement Chamber

The disengagement chamber serves several purposes for the HCR system. During startup, the chamber must allow the addition of measured quantities of slurry oil and catalyst. Once in operation, the disengagement chamber must allow for the separation of slurry from un-reacted syngas and vapor-phase product. To accomplish these goals, calculations were undertaken to determine the bubble rise velocity of vapor-phase constituents in the slurry material. Based on these calculations, a minimum residence time of 5 minutes was needed.

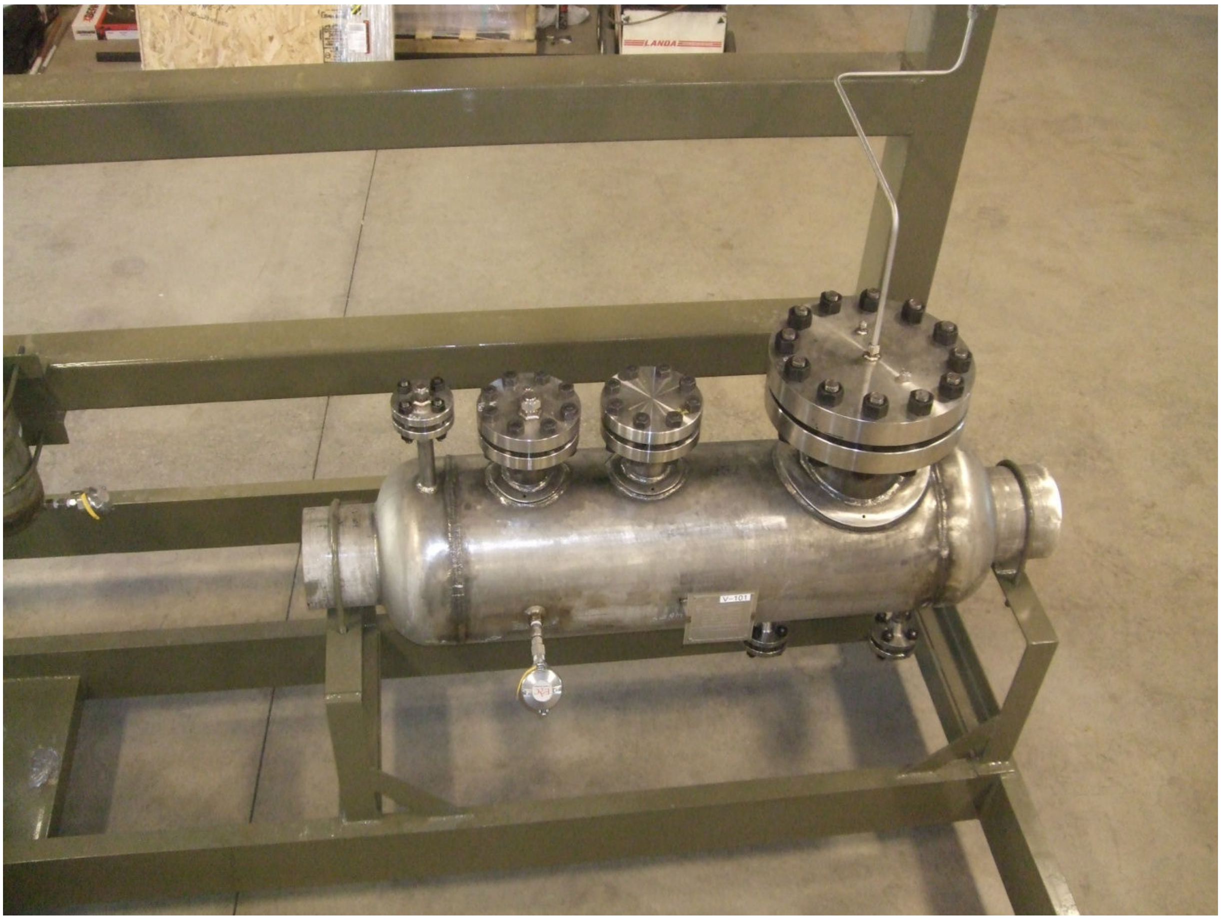

Figure X: *Picture of disengagement chamber*

Summary of Results, Remaining Work and Process Limitations

The pilot-scale HCR system showed very promising results during the project period. At its peak, a single pass conversion to methanol of 28.5% was observed with a catalyst loading of only 3% by weight. This conversion is approaching 60% of equilibrium with a very low residence time and catalyst loading. A summary of results for methanol synthesis catalyst in the HCR system is provided in **Table C** below.

Table C: *Methanol Synthesis Results Summary*

Test #	Catalyst loading, wt%	CO conversion to MeOH, %	MeOH purity in product (range), %
1	1	3.00	92.9 – 98.0
2	1	2.27	91.8 – 97.1
3	1	2.15	92.9 – 97.3
4	3	28.5	92.7 – 98.1
5	3	21.7	92.4 – 98.2
6	3	20.3	93.6 – 98.0

The results obtained for the proprietary DME catalyst were unexpected, particularly in light of the success achieved using methanol synthesis catalyst. However, the description of catalytic reactions carried out in the helical channel reactor (HCR) is very complicated. This complication is related not only to Dean vortices resulting from oil carrier flow along a curved tube, but also due to presence of catalysts and reactants, both dissolved in oil and/or existing in a separate gas phase. Further complications arise from the multiple catalytic reactions that need to occur in the system (methanol synthesis, methanol dehydration and water gas shift).

The most plausible theory so far proposed is that the low conversion to DME was caused by a slow transport of reactants between two catalytic components through the oil carrier phase under applied mixing conditions. This can potentially be overcome by modifications to the catalyst structure. A summary of results for the DME synthesis catalyst in the HCR system is provided in **Table D** below.

Table D: *DME Synthesis Results Summary*

Test #	Catalyst loading, %	C conversion to DME, %
1	1.5	0.75
2	1.5	0.4
3	1.5	0.34
4	3	1.92
5	7.5	1.92

Given the overall promising nature of the results, future research into the HCR system is warranted. Several research angles have been identified for inclusion when future project funding is obtained.

Remaining Work – Slurry Parameters

Due to constraints in time and equipment, only a narrow regime of slurry flow rate and catalyst loading was tested. During future testing, when a more robust slurry pump is available, several additional slurry rates and concentrations will be tested. Single pass conversion of 28.5% was observed with a minimal loading of 3% by weight. Higher catalyst concentrations will be used until the system shows no increased activity with the addition of extra catalyst. Based on early results, it may be possible to approach equilibrium conversion levels given the correct catalyst loading and slurry flow rate. Slurry flow rate will also be adjusted throughout a broader range. This will clarify the mass transfer effects of laminar vs. fully turbulent flow throughout the reactor and reaction zones.

Remaining Work – Disengagement Chamber

Throughout the course of testing the HCR system, the disengagement chamber proved to be significantly larger than necessary for the system size. This had several effects on the system that could be improved with a re-design of the disengagement chamber. First, due to the large chamber size, a minimum of 50 kg heat transfer oil was necessary to maintain slurry pump suction. Given the large inventory of oil needed, significant quantities of catalyst were also necessary to achieve the desired catalyst loading levels. In addition to the large catalyst inventory, the thermal mass of the oil and catalyst extended the period needed for heating and cooling during a run. A smaller disengagement chamber would allow for faster process changes including startup and shut down time. For proper specification of a commercial unit, a disengagement chamber of appropriate size will have to be determined, allowing for a maximum productivity with the minimum catalyst inventory necessary.

Remaining Work – Reaction Zone Coil Alterations
During future work, the reaction zone coils will be altered to determine the effect of altered coil diameter and pitch on the reaction efficiency. These alterations to the coil diameter and pitch will alter the balance of centrifugal and torsional forces in the reaction coils. Work will also be completed to optimize the total length, and thus residence time, in the reaction zone coils. Coil length will be added and removed during testing to determine the optimal balance between reaction efficiency and pressure drop for the system. This additional data will allow for the optimization of the reactor system.

Remaining Work – Reactor Size Modifications
Finally, additional work needs to be performed to test the limits of size and aspect ratio for the main reactor in the system. Reactor efficiency, during scale up, will be a critical design parameter for any commercial application of the technology. During future testing, the reactor dimensions will be altered to change the aspect ratio of the helical channel. Namely, the outer diameter of the reactor will be increased significantly while maintaining the same reactor volume. This increase in outer diameter, with a concurrent increase in the inner reactor diameter, will allow the simulated testing of larger reactor systems by altering the aspect ratio of the slurry/syngas interface.

Limitations
Additional engineering work will be necessary before commercial implementation of the HCR technology. The major barrier to long-term operation of the process is system wear due to high-velocity, high-abrasiveness process fluid. This flow of catalyst-laden slurry throughout the system leads to abrasive wear on all of the slurry circuit process plumbing and equipment. As this is a pressure and temperature rated system, wear rates and maintenance schedules will be critical for commercial system operation.

The main piece of equipment affected by abrasive wear is the slurry pump. On the pilot-scale system installed at WRI, there were very few pump manufacturers that could provide a pump that would handle all of the process conditions. Even the pump supplied by Warrender experienced significant wear to the pump internals during testing.For a successful commercial implementation, a process pump will have to be chosen. Given the conditions, this pump will either have to come from the petrochemical industry, or be developed by an industrial equipment manufacturer.

Conclusions
Broadly, with the completion of this report, the objectives set out in the funding application have been met. There were some delays, initially with the reactor design package and then in respect of the pilot skid manufacture. In respect of the latter, on 13 July 2012 a design package was released to the selected fabrication company, and a preliminary quote received from them on 27 July 2012, with a final quote

received on 6 August, 2012 An estimated delivery on the final quotation was 26 October 2012. On 17 August 2012 a purchase order for construction of skid delivered to the selected manufacturer. Partial delivery of the skid was received on 25 March 2013 with final delivery of the order not made until 8 April 2013. This signified the most significant delay to the project. Nevertheless, the reactor skid was successfully installed into the WRI synthesis facility and commissioned.

During early stage of most new technology developments, process optimization is an ongoing activity that can take considerable time. Whilst some preliminary process optimization investigations were made into the effects of flow rates on the system, the amount of work required in this respect was beyond the scope, budget and time limitations of this project.

As proposed in the funding application, the project resulted in the design, construction and testing of a novel reactor capable of liquid fuel synthesis via multiple catalytic routes. The reactor was designed and tested at the pilot scale, and integrated with WRI's liquid-fuel synthesis facility. The overarching goal for the project was a "proof of concept" test of the novel reactor system. That is, determination of the technical feasibility of the proposed reactor concept. This was a successful outcome of the project. Initial technical proof of concept allows that the reactor system has demonstrated sufficient technical feasibility to warrant further investigation.