



# Energieia

## Catalytic Membrane Reactor for Conversion of Syngas to Liquid Hydrocarbons

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### INTRODUCTION

The recent rise in crude oil price forces us to look for alternative energy sources. The most sensible direction of this search is natural gas upgrading to liquid hydrocarbons via a mixture of carbon monoxide and hydrogen (syngas). Hydrogenation of CO to liquid hydrocarbons has been known since 1923 as Fischer-Tropsch synthesis (FTS). Great R&D efforts have been made all over the world to develop the commercially effective Fischer-Tropsch process since that time. Despite these efforts, even now there are only two industrial plants converting natural gas to liquid fuels and chemicals – in Binthulu (Malaysia) by Shell and in Mossel Bay (South Africa) by Sasol. Successful pilot testing was reported also by Exxon, Syntroleum, BP, Rentech and by some other companies. However these technologies have not been realized at the industrial scale. The stumbling block of the Fischer-Tropsch synthesis R&D is finding the optimal reactor arrangement.

### Why is reactor choice so difficult for Fischer-Tropsch synthesis?

Fischer-Tropsch synthesis is a complicated exothermal *three-phase* process. Therefore, the reacting molecules of the gas phase have to dissolve in the phase of liquid products before contacting the surface of the solid catalyst particles. Also, the products should evaporate to

the gas phase in order to ‘quit’ the catalyst bed. The mass-transport within the flooded catalyst particle is four orders of magnitude slower than that in the case of a two phase process, due to lower diffusivities in the liquid phase. These and some other specific features of FTS make crucial the following requirements to the FTS reactor:

- (1) isothermal catalyst bed (temperature drop,  $\Delta T$ , less than 10 K);
- (2) high concentration of the catalytically active substance in the reactor volume;
- (3) high gas-liquid interface surface area (at least  $20 \text{ cm}^2 / \text{cm}^3$ );
- (4) small effective size of catalyst grains (preferably, less than 50  $\mu\text{m}$ );
- (5) low pressure drop.

These requirements seem to be common for any Fischer-Tropsch process regardless of the raw material source or product market.

The Industrial Sasol Slurry Phase Distillate (SPD) process uses slurry bed reactors, whose design satisfies the demands (1) and (3)-(5) described above. However the catalyst concentration in the reactor volume is rather low due to the conflict between the loading of a particular particulate matter in the slurry and the effective dynamic viscosity of the latter, which promotes coalescence of gas bubbles and a decrease in gas hold-up in the slurry. The interphase mass-transfer in the bubble slurry reactors strongly diminishes when the catalyst

loading is above 20-25 wt %. As a result, the space-time yield of hydrocarbons is low and the dimensions of industrial apparatuses are huge: the Sasol SPD reactor operating at 20 bar with productivity of 2500 barrels per day is 22 m in height and 5 m in diameter.

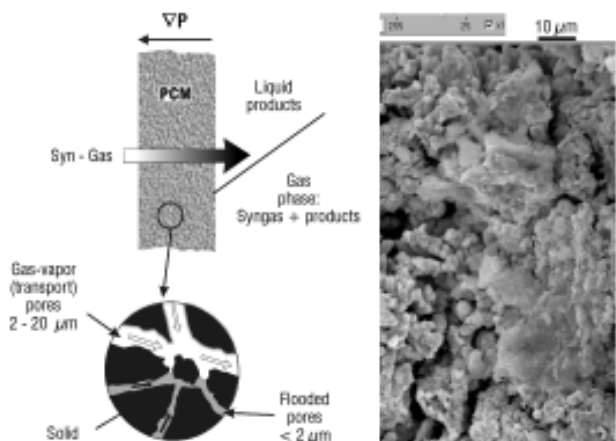
The fixed catalyst bed is much denser, but the conflict between the reasonable hydraulic resistance (large catalyst grains needed) and low diffusion constraints (small catalyst grains needed) results in even worse process performance. This contraposition can be resolved using the “egg-shell” catalysts with a low concentration of the active component with respect to the entire particle volume.

The solution of this knotty problem of trade between high concentration of the active component and diffusion limitations was suggested by using the heat-conductive plug-through contactor membranes (PCM).

### Plausible alternative: the catalytic membrane reactor using PCM membranes

The PCM is a three-component mixture of a catalytically active substance, pore-producing agent and reinforcing agent with a high-heat conductivity, which is sintered and reduced in  $\text{H}_2$  after mixing. Finally, the PCM is a strong three-modal porous structure, which is permeated by the syngas (**Figure 1**). The pores with the effective radius above 2-3 mm are almost gas-filled and are responsible for the gas permeation. These pores we will further denote as the “transport pores.” The smaller pores are flooded with liquid products due to capillary forces and are not permeable. The narrowest pores (effective radius less than 0.5 mm) are located inside the catalyst particles and the mass transfer within these pores is accounted for by the molecular diffusion.

## Catalytic Membrane Reactor for Conversion, (cont.)



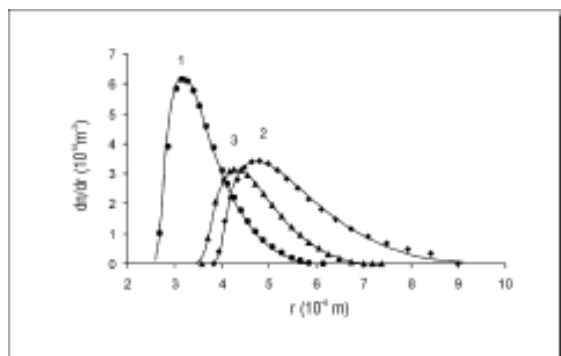
**Figure 1. The scheme of Fischer-Tropsch synthesis in the PCM membrane reactor and a typical SEM image of PCM.**

**Figure 2** shows the estimated distributions of the transport pores by size for three selected cylindrical PCM with diameters of 17 mm at GSHV of 1800 hr<sup>-1</sup>. Transport pores are distributed between 2 and 10 mm in radius and the concentration of transport pores is about 10<sup>9</sup> per m<sup>2</sup> of the membrane cross-section. The operational conditions and the wetting extent of the membrane have a significant impact on the permeability of each pore. Increasing the wetting extent or decreasing the gas flow through the membrane causes lower permeability of membrane and concentration of the transport pores.

The catalyst loading in the PCM is high (0.8-1.0 g<sub>cat</sub> cm<sup>-3</sup>) and approaches that of the fixed catalyst bed.

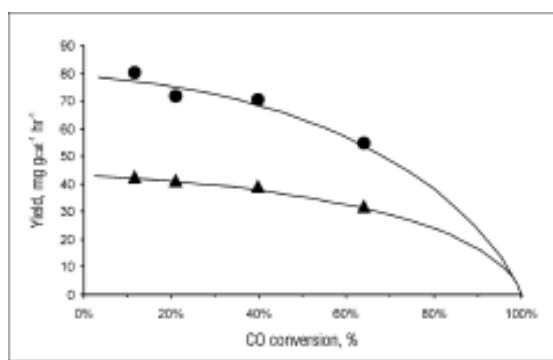
### Well developed pore structure: mild mass-transfer constraints

The intense convective mass-transfer within transport pores, high specific area of these pores (which can be



**Figure 2. The density functions of the transport pore size distributions for three selected cylindrical PCM membranes, PCM diameter, 17 mm.**

roughly considered as the specific gas-liquid interface area) and small distances between two adjacent transport pores (which is a good estimation for the effective diffusion length) weaken the mass-transfer constraints. By varying the preparation conditions and the PCM composition, it is possible to change the pore-size distribution of the membrane and so change the performance of the PCM in Fischer-Tropsch synthesis. The width of the transport pores' distribution impacts the gas-flow bypass and the extensiveness of the



**Figure 3. The impact of the CO conversion extent on the productivity of the FTS synthesis over PCM-Cyl-3 at 483 K, 0.1 MPa. Circles - total hydrocarbons yield; triangles - C<sub>5+</sub> yield.**

stagnation zones. Therefore, the productivity is favored at narrow distribution of the pores by size. The concentration of transport pores affects the mean distance between two adjacent transport pores, and so the intraparticle diffusion constrains can be weakened by increasing the transport pores' concentration. This is a

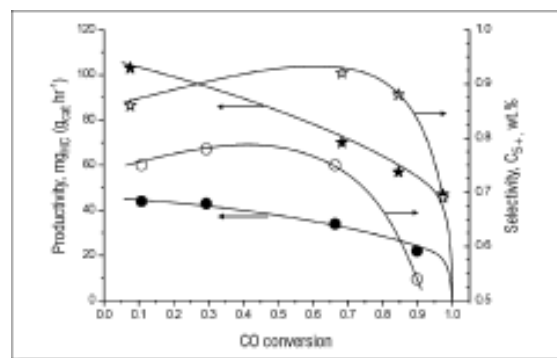
key to the improvement of the process selectivity with respect both to the heavy hydrocarbons and olefins. After taking into account these correlations, it becomes evident that the most efficient PCM membrane should have a high concentration of the transport pores having similar size. For example, the performance of the PCM-Cyl-1 and PCM-Cyl-3 (curves 1, 3 in **Figure 2**) is much better than that of the PCM-Cyl-2 (curve 2 in **Figure 2**).

**Figure 3** shows the PCM performance in the Fischer-Tropsch synthesis at 483 K, 0.1 MPa, H<sub>2</sub>:CO = 2, 10 % of N<sub>2</sub> as a function of the CO conversion extent. PCM-Cyl-3 membrane is chosen as an example. Taking into account the high catalyst loading (0.85 g cm<sup>-3</sup> for the PCM under discussion), one can see that even at 1 bar the PCM membrane provides the space-time yield of liquid hydrocarbons close to that of the slurry bed reactor operating at 20 bars. At that value of the ASF distribution parameter  $\alpha$  for the fraction of C<sub>10+</sub> is above 0.85. Increasing the pressure evidently improves the productivity and selectivity of the

Fischer-Tropsch process over PCM membranes. **Figure 4** presents the data of the 42-mm membrane PCM42-2 at 0.1, 0.6 MPa.

### Physical properties: high heat-conductivity and strength

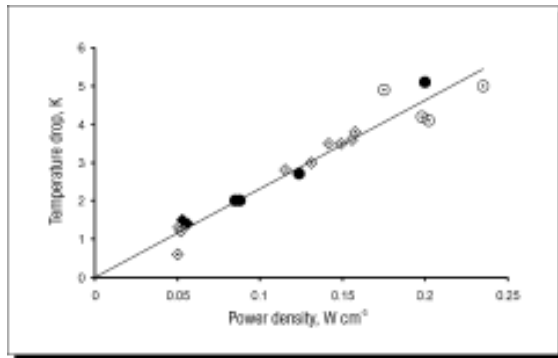
PCM can combine high permeability (above 20 mDarcy), high mechanical strength (above 20 kg cm<sup>-2</sup>) and high heat-conductivity. **Figure 5** gives the experimental dependence of the



**Figure 4. The impact the process pressure on the productivity and C<sub>5+</sub> selectivity of the FTS synthesis at 483 K over PCM with dia. 42 mm. Circles - at 0.1 MPa; stars - at 0.6 MPa.**

temperature drop over the cylindrical PCM membrane with the diameter of 42 mm versus the density of the heat release during the Fischer-Tropsch synthesis. Here the heat power that evolved during the reaction was calculated from the experimental data on the process productivity and selectivity. Temperature was measured in the PCM center and in the gas phase

## Catalytic Membrane Reactor for Conversion, (cont.)



**Figure 5. The experimental data on the temperature drop over the cylindrical PCMs with diameter of 42 mm in the FTS at 483 K, 0.1 - 1.6 MPa; diamonds - sample PCM42-1; circles - sample PCM42-2; solid symbols - syngas flow is directed radially from outside inwards; hollow ones - flow is directed from inside outwards.**

near the outer surface of the PCM. The rough estimation made in consideration of the uniform distribution of the heat sources within the membrane gives the value of PCM heat conductivity of about  $4.4 \text{ W (m K)}^{-1}$ . This value is close to the values of  $3.5\text{-}5 \text{ W (m K)}^{-1}$ , which were over PCM estimated earlier from the experimental data on the PCM electroconductivity by the Wiedemann-Franz equation and it is more than 10 times higher than the effective heat-conductivity of the fixed bed Fischer-Tropsch reactor. So, one can expect a rather flat temperature profile along the PCM membrane in the FTS reactor.

### Other advantages of the catalytic membrane reactor

In addition to the above mentioned advantages (high space-time yield, high selectivity, high heat-conductivity) the PCM reactor design is free from many disadvantages of the existing reactor types such as separation problems, backmixing, necessity of huge height (horizontal orientation is preferable for the PCM) and can be scaled up easily.

### Summary

Plug-through catalytically-active contactor membranes can combine high permeability ( $> 20 \text{ mDarcy}$ ), high mechanical strength ( $> 20 \text{ kg cm}^{-2}$ ) and high heat-conductivity ( $> 4 \text{ W(m K)}^{-1}$ ). Therefore, it provides isothermicity and low pressure drop. The intense mass-transfer within transport pores, high specific area of these pores (gas-liquid interface area) and small

distances between two adjacent transport pores (effective diffusion length) weaken the mass-transfer constraints. Using the PCM one can achieve high space time yield of hydrocarbons ( $60\text{-}70 \text{ kg (m}^3 \text{ hr)}^{-1}$  at 0.1 MPa,  $210^\circ\text{C}$  and upto  $100 \text{ kg (m}^3 \text{ hr)}^{-1}$  at 0.6 MPa,  $210^\circ\text{C}$ ) and high selectivity towards heavy hydrocarbons ( $\alpha > 0.85$ ,  $\text{C}_{5+}$  up to 0.9) and olefins (propene:propane ratio of 6-10).

These advantages allow supposing the effective usage the PCM catalytic membrane reactors in Fischer-Tropsch synthesis. Also the same approach could be efficient for some other multiphase catalytic processes, like hydrogenation of the unsaturated fatty acids.

## ACKNOWLEDGEMENTS

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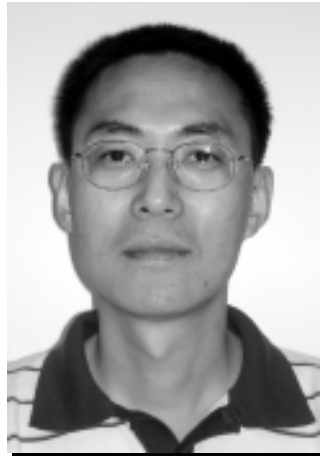
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## Two New Researchers Join

### **CAER**

The CAER recently added two distinguished new researchers to our staff. Both have many years of experience in energy research and will complement the efforts of other staff by broadening CAER's scope of expertise.



#### **Dr. Kunlei Liu**

comes to us with extensive academic and industrial training in clean combustion technology and emissions control research. He received a Ph.D., from the Thermoenergy Engineering Research Institute, Southeast University in Nanjing, PRC in 1993. His experience since then includes 14 years of research and project development; 11 years of industrial service and consulting; and 5 years of teaching. He has been the principal investigator on 15 projects and holds 1 patent.



#### **Mr. Philip Zacarias**

will be working in the Environmental and Coal Technologies Group, where he will contribute to research with his broad expertise in concrete. He is a scientist, originally from Canada, where he has worked largely in research and development of cement additives and concrete admixtures. He has initiated and managed programs related to fly ash, slag and cementitious materials.



### **JIM HOWER**

#### ***was presented with the Society of Organic Petrology's Distinguished Service Award***

at the 22nd annual meeting, which was held in Louisville, Kentucky. The award honors his role as Vice-President (1988-89), President-elect (1992-93) and President of the Society (1993-94), as well as his "behind the scenes" contributions.



## REFOCUSING *On Energy*

Sharing thoughts about the energy scene as we are entering a new year and reflecting on the year gone by, there are somber as well as exciting components. It has been a long while since energy received so much attention. The contributing factors that joined forces to sharpen the focus are varied in origin.

There was the squeeze between crude oil supply and demand. This was aggravated by the continuing war in Iraq; the impressive growth rates and energy demands by the blossoming economies of China and India; the prospect of having reached a peak in global oil supplies (or at least being relatively close to such a peak); the shrinking domestic supply of oil in the US; and superimposed on these considerations were geo-political uncertainties regarding some of the supplying countries.

Furthermore, the US experienced devastating hurricanes that caused havoc with oil and natural gas rigs, the refineries, harbors, and distribution systems and caused the loss of lives, including some of the staff that operated essential oil and gas facilities.

These are sobering and serious occurrences and ones which were largely unforeseen. Their combined impact on the price and availability of oil and oil-derived products in the US is unprecedented. It also affected the petrochemical industry in a big way. Add to that the rising natural gas prices which continued an upward price trend due to lack of supply and we see why energy is again being discussed in the daily media.

On a more positive note, one sees the interest in pushing for a greater diversity of energy sources and for methods and regulations to promote energy conservation and efficiency. Although that might be a concern for those in the coal industry, we must recognize that the nation's total energy consumption is so vast that there is a place for many players and with the expected growth rates in energy needs, we should not limit development opportunities to generate alternatives. Although subsidies are available to stimulate alternatives, it could be expected that

market forces will prevail in the long run. We must also accept that the market forces include clients' willingness to pay more for energy which they perceive as "clean." This is demonstrated by cases where utility customers actually pay more for "green power."

The greatest price crunch in 2005 was experienced with oil and natural gas but coal has also continued on an upward cost curve although at a less dramatic level. Since it is still the cheapest energy source, it is again considered as a source for domestic transportation fuels. Déjà vu! The new federal Energy Policy Act which came into force in August has a number of promising provisions to encourage new clean coal facilities by means of loan guarantees and other incentives. There is an authorization (not yet an appropriation) of \$85 million for developing clean coal technologies for liquid fuels production using Illinois basin coal in the energy policy. The Act stipulates that this is to be done at the universities of Purdue, Southern Illinois and at CAER. A memorandum of understanding among these three institutions is already in place and plans are well underway to define the scope and extent of the joint activities with the aim of getting appropriations soon. Besides this activity, which can potentially benefit CAER in a meaningful way, there is great interest in CTL (coal to liquids) technology in at least eight states. The military has made it known that they are interested in CTL as a source of jet fuels and it will be exciting to see how these intentions work out.

It might be a while before the federal money could be available to expand our CAER R&D in CTL, but in the meantime each of the three state governments involved has provided initial funding to assist in putting an appropriation proposal together. We appreciate the interest that the Commonwealth of Kentucky is taking in the CAER expertise in the CTL area which fits in very well with the Kentucky Comprehensive Energy Strategy that was released in February 2005. This Strategy covers a wide range of energy initiatives and CAER is

positioned to respond to a number of the topics emphasized in the Strategy.

A review such as this one cannot do justice to the large number of success stories which we can tell to boast about the achievements of our staff and colleagues. The success rate with project awards was again very good and in spite of tight financial times, we managed to expand our activities. This was also confirmed by the favorable Five Year Unit Review which was conducted by an external team with input from our Advisory Board. The suggestions from the review team, specifically to provide a more visible and comprehensive strategy, is already being addressed by CAER.

Looking forward, I am optimistic and excited about the challenging circumstances we experience and how we at CAER can contribute to providing solutions to real problems. I wish to thank all our stakeholders, which include a loyal and dedicated staff,

diligent students, an enthusiastic Advisory Board, our creative Faculty Associates, the supportive UK Administration as well as our willing industrial and federal sponsors for their faith in us and their ongoing support.

May we experience a blessed Christmas season and success in 2006.



ARI GEERTSEMA  
*Director*

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