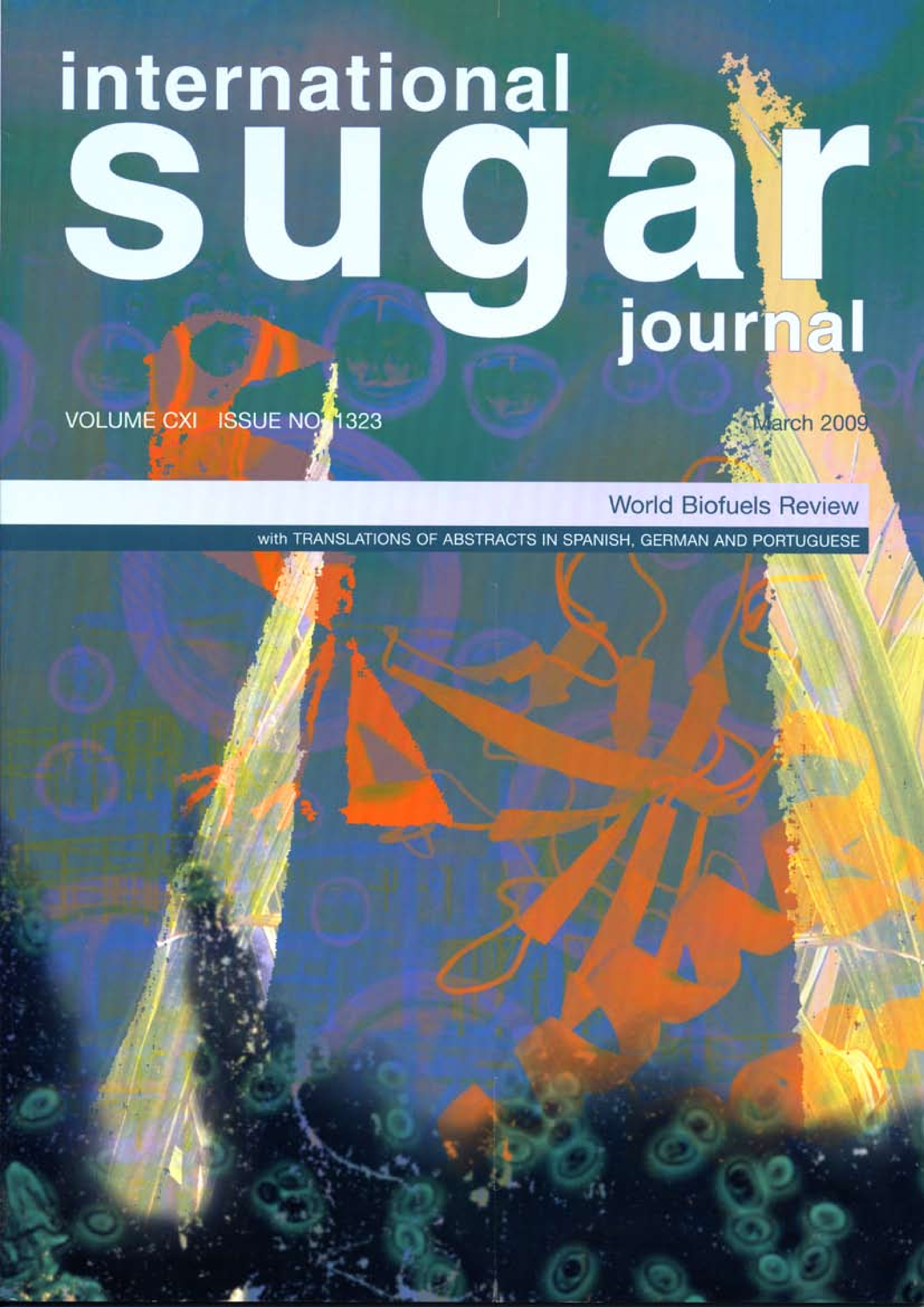
international sugar journal

VOLUME CXI ISSUE NO. 1323
March 2009

World Biofuels Review

with TRANSLATIONS OF ABSTRACTS IN SPANISH, GERMAN AND PORTUGUESE



Microchannel reactors are highly effective at processing cellulosic biofuels

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abstract

Of all the first generation biofuels (biofuels that are derived from food crops), sugar cane ethanol, produced by conventional fermentation and distillation processes, is one of the most attractive in terms of both productivity (litres of ethanol per hectare) and carbon footprint. However, these properties could be greatly enhanced and its environmental credentials could be improved by developing sugar biorefineries that incorporate microchannel reactors to support a Fischer-Tropsch-based biomass to liquid (BTL) process to co-produce sugar cane ethanol along with second generation liquid biofuels, such as diesel, from biomass residues. In addition, the excess heat generated from the BTL process could be used to drive the ethanol distillation, avoiding the need to burn other fuels or biomass residues.

Keywords: **biofuels, Fischer-Tropsch, microchannel reactors**

Los reactores de microcanales son altamente efectivos para procesar biocombustibles celulósicos

De todos los biocombustibles de primera generación (biocombustibles derivados de cultivos alimentarios), el etanol de caña de azúcar, producido por procesos de fermentación convencional y destilación, es uno de los más atractivos tanto por su productividad (litros de etanol por hectárea) como por la huella de carbono. No obstante, estas propiedades pueden ser intensificadas y sus credenciales ambientales mejoradas, desarrollando biorefinerias de azúcar que incorporen reactores de microcanales que sirvan de apoyo a un proceso de biomasa a líquido (BTL) basado sobre el método de Fisher-Tropsch para co-producir etanol de caña junto con biocombustibles líquidos de segunda generación, tales como biodiesel, a partir de residuos de biomasa. Además, el exceso de calor generado por el proceso BTL puede ser usado para impulsar la destilación de etanol, evitando la necesidad de quemar otros combustibles o residuos de biomasa.

Mikrokanal-Reaktoren sind hoch effektiv zur Verarbeitung cellulosehaltiger Biokraftstoffe

Von allen Biokraftstoffen der ersten Generation (Biokraftstoffe aus landwirtschaftlichen Ernteerzeugnissen) ist das durch konventionelle Gärungs- und Destillationsverfahren produzierte Zuckerrohr-Ethanol eines der attraktivsten Produkte – sowohl im Hinblick auf seine Produktivität (Liter Ethanol pro Hektar) als auch seine CO2-Bilanz. Diese Eigenschaften und seine Umweltfreundlichkeit könnten jedoch noch erheblich verbessert werden durch die Entwicklung von Zucker-Bioraffinerien, die ein Fischer-Tropsch-basiertes BTL-Verfahren (Biomasse zu Flüssigkeit) zur gemeinsamen Produktion von Zuckerrohrethanol und flüssigen Biokraftstoffen der zweiten Generation, z.B. Diesel aus Biomasseresten, unterstützen. Die überschüssige Wärme, die im BTL-Verfahren entsteht, könnte darüber hinaus dazu benutzt werden, die Ethanoldestillation anzutreiben, so dass die Notwendigkeit zur Verbrennung von anderen Kraftstoffen oder Biomasseresten entfallen würde.

Reatores de microcanais são altamente eficazes no processamento de biocombustíveis celulósicos

De todos os biocombustíveis de primeira geração (biocombustíveis derivados de culturas alimentares), o etanol de cana-de-açúcar, produzido pelos processos convencionais de fermentação e destilação, é um dos mais atraentes em termos tanto de produtividade (litros de etanol por hectare) e como rastro de carbono. No entanto, essas propriedades poderiam ser bastante reforçadas e as suas credenciais ambientais poderiam ser melhoradas através do desenvolvimento de biorefinarias de açúcar que incorporam reatores de microcanais para suportar o processo biomassa para líquido (BTL – do inglês, Biomass To Liquid) com base em Fischer-Tropsch para co-produzir etanol da cana-de-açúcar, juntamente com a segunda geração de biocombustível líquido, como diesel, a partir de resíduos de biomassa. Além disso, o excesso de calor gerado a partir do processo BTL poderia ser direcionado para impulsionar a destilação de etanol, evitando a necessidade de queimar outros combustíveis e resíduos de biomassa.

Introduction

Although the overall economics and environmental profile of cane sugar based ethanol production is superior to those of other first generation biofuels, [1] these characteristics could be greatly enhanced by adding a separate biomass to liquid (BTL) plant to standalone sugar refineries to process bagasse for biofuels production.

In such an integrated biorefinery, bagasse would be gasified and then converted by means of the Fischer-Tropsch (FT) reaction, to produce second generation biofuels. Because they are generated entirely from waste, such as crop residues, rather than using food crops, second generation biofuels overcome some of the environmental objections to the production of biofuels. The waste heat from the FT process would be used to drive the distillation step in ethanol production. In addition, methane and other smaller molecules not incorporated into biodiesel or other liquid second generation biofuel, could be burned to provide additional heat.

The Fischer Tropsch reaction

In the FT process, first developed by Franz Fischer and Hans Tropsch in Germany in the 1920s and 1930s to produce liquid fuel from coal, synthesis gas, composed of a mixture of carbon monoxide (CO) and hydrogen (H_2), is converted into various forms of liquid hydrocarbons by means of a catalyst at elevated temperatures and pressures. Because they do not contain aromatics or sulphur-containing contaminants, the liquid fuels produced are typically of higher quality and burn cleaner than petroleum-based diesel and jet fuels. This results in lower emissions of nitrogen oxides (NO_x) and harmful particulates.

In theory, any source of carbon can be used to generate synthesis gas. The FT reaction is already used to produce liquid fuels from natural gas (via GTL, or gas to liquid) on a large scale in Qatar, and is used in South Africa to generate liquid fuels from coal (via CTL, or coal to liquid). It can also be used to produce liquid fuel from biomass (via BTL, or biomass to liquid).

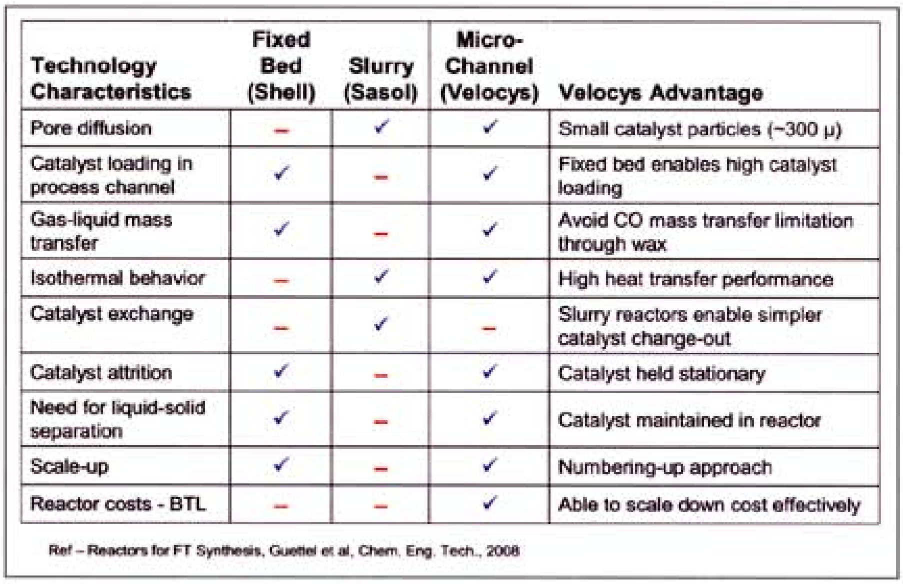
Although the BTL technology needed to produce second-generation biofuels exists, the FT technology used to produce it must be optimised in order to make the process viable from both environmental and commercial perspectives. Because biomass is not very dense it is uneconomical to transport it over long distances to production facilities. As a rule of thumb it takes one tonne of biomass to produce one barrel of liquid fuel. This means the facilities must be relatively small, producing on the order of just 500 - 2000 bbl/day, compared to 30,000 - 140,000 bbl/day for a GTL plant.

The presently available conventional technology for synthetic fuels does not scale down efficiently. Establishing BTL as a practical and economically feasible option, requires finding ways to intensify the BTL process. New reactor designs, such as microchannel reactors, combined with more efficient FT catalysts optimised for use in them are the key to successful BTL process intensification. To achieve this goal reactor designers and catalyst developers must work closely together.

FT reactor types

The main conventional reactor types used for the FT process include fixed bed and slurry bed reactors. Each has its drawbacks. Fixed bed reactors are comparable to the shell and tube heat exchangers that are common in the process industries. In these the catalyst, in the form of cylindrical pellets, is contained within 2.5 - 5 cm (1 - 2 inch) tubes that are oriented vertically within a large vessel. In the latest fixed bed FT reactors, these tubes are 2.5 cm (1 inch) in diameter and 12 m tall. The biggest challenge with conventional fixed bed FT reactors lies in controlling the temperature within the reactor

Figure 1. Comparison of the features of fixed bed, slurry and microchannel reactors



Technology Characteristics	Fixed Bed (Shell)	Slurry (Sasol)	Micro-Channel (Velocys)	Velocys Advantage
Pore diffusion	–	✓	✓	Small catalyst particles (~300 μ)
Catalyst loading in process channel	✓	–	✓	Fixed bed enables high catalyst loading
Gas-liquid mass transfer	✓	–	✓	Avoid CO mass transfer limitation through wax
Isothermal behavior	–	✓	✓	High heat transfer performance
Catalyst exchange	–	✓	–	Slurry reactors enable simpler catalyst change-out
Catalyst attrition	✓	–	✓	Catalyst held stationary
Need for liquid-solid separation	✓	–	✓	Catalyst maintained in reactor
Scale-up	✓	–	✓	Numbering-up approach
Reactor costs - BTL	–	–	✓	Able to scale down cost effectively

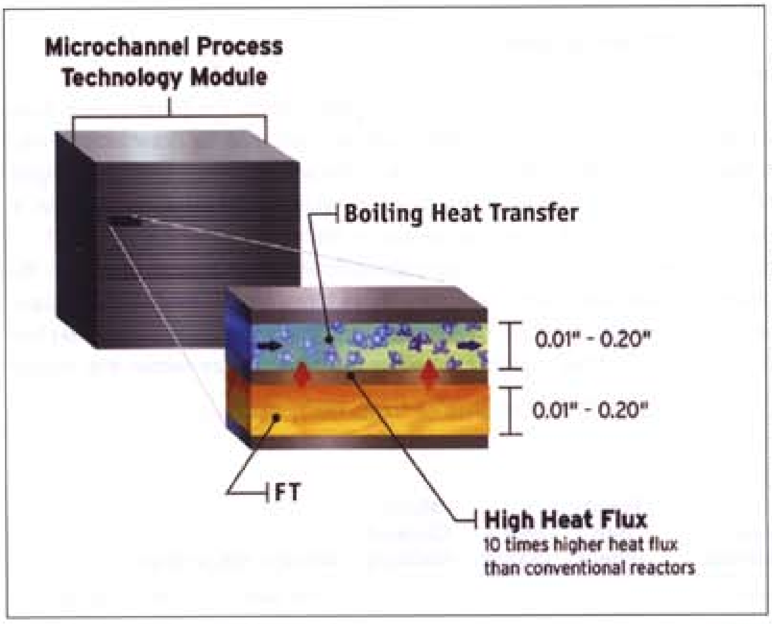
Ref – Reactors for FT Synthesis, Guettel et al, Chem. Eng. Tech., 2008

Table 1. Comparison of FT reactor features

	Microchannel FT technology	Conventional tubular reactor FT technology
Nature of catalyst bed	fixed	fixed
Reactor temperature	210-240°C	210-230°C
H:CO ratio	2.1	2.1
%CO conversion per pass	>70	45-60
Catalyst productivity ($kg_{prod}/kg_{cat}/h$)	1.53	0.05-0.09
Selectivity, %C_5+	78-82	81-94
Selectivity, %CH_4	<10	no information available
Alpha ratio	0.89–0.92	>0.9
Contact time, ms	<250	no information available
Catalyst life, years	not yet determined	2

(Data sources: Velocys test data and estimates from Nexant, Inc. [1])

Figure 2. In a microchannel reactor, a single reactor module consists of many hundreds of rows of microchannels each containing large numbers of parallel microchannels. The orientation and size of the channels within each row is determined by the application, adjacent rows of channels potentially having very different duties (diagram courtesy of Velocys)



tubes. Since the FT synthesis is exothermic and strongly affected by temperature, a hot spot can develop within the centre of the tube, resulting in a substantial drop in the catalyst performance. As a result, the performance of fixed bed reactors is limited by heat transfer.

In slurry bed reactors, the FT catalysts take the form of small particulates (~50 micron in diameter) that are suspended in the liquid wax produced by the reaction. The heat generated by the reaction is removed by coolant tubes that run throughout the reactor. The liquid slurry is quite efficient at heat removal; however, the liquid film surrounding the catalyst blocks the reactants (H_2 and CO) from quickly reaching the catalytic sites. This problem with mass transfer limits the performance and productivity of the slurry bed reactors. In addition, these slurry bed reactors can be more difficult to operate than fixed bed reactors. A particular problem associated with slurry bed reactors is the catalyst attrition caused when the catalyst particles collide against each other and the reactor walls.

In contrast the performance of microchannel reactors is not limited by either heat transfer or mass transfer (see figure 1 and table 1). As a result, they have the potential to offer improved performance in for FT processes.

Microchannel reactors: shrinking the hardware

Microchannel reactors are based on the use of microchannel process technology, a developing field of chemical processing that exploits rapid reaction rates by minimising heat and mass transport limitations. This is achieved by reducing dimensions of the reactor systems. In microchannel reactors the key process steps are carried out in parallel arrays of microchannels, each with typical dimensions in the range of 0.1 - 5 mm. (see figure 2). This modular structure offers many advantages when it comes to reducing the size and cost of the chemical processing hardware.

For a start, plant size is small - microchannel FT reactor assemblies have diameters of around just 1.5 m - and capital costs are relatively low compared to conventional reactor systems such as slurry beds. In addition, the modular structure means that maintenance and catalyst replacement can be carried out by replacing individual modules, rather than requiring the prolonged shutdown of the entire system.

The microchannel FT reactor design is also very flexible. For example, where increasing the size of conventional reactors normally requires plant designers to increase the size of each reactor unit, the modular structure of microchannel reactors means that increasing plant size to build demonstration or even commercial-sized plants can be done by 'numbering up'. This involves simply adding more reactors of the same proven dimensions, and thus greatly reduces the risks associated with scaling up in conventional reactors.

The modular structure also reduces the costs of installation. In large GTL plants scaling up typically involves a lot of fabrication in the field, which can be both expensive and time-consuming. In contrast, the microchannel reactors can be shop-fabricated, so microchannel-based plants can be constructed more quickly and easily - thus reducing set-up costs.

Breakthrough technology

When it comes to processing efficiency, microchannel process technology is looking like a breakthrough for a wide range of applications. These include the large number of chemical and process systems that involve thermal processing, ranging from ethane cracking to fuel processing catalytic processes, such as hydroprocessing; chemical reactions and production, for example, steam methane reforming and partial oxidations; separations, mixing and emulsification; catalytic processes; gas processing for operations such as hydrogen production; biological and medical applications; and integrated and multi-phase systems. In terms of small-scale distributed BTL production, microchannel reactors offer particular advantages (see table 2).

For example, because the structure and dynamics of microchannel reactors improves heat transfer between process fluids and channel walls, a signficantly more active catalyst can be used. As a result the BTL process is intensified. This intensification results in a greatly increased throughput per unit volume of the reactors.

Economies of small scale

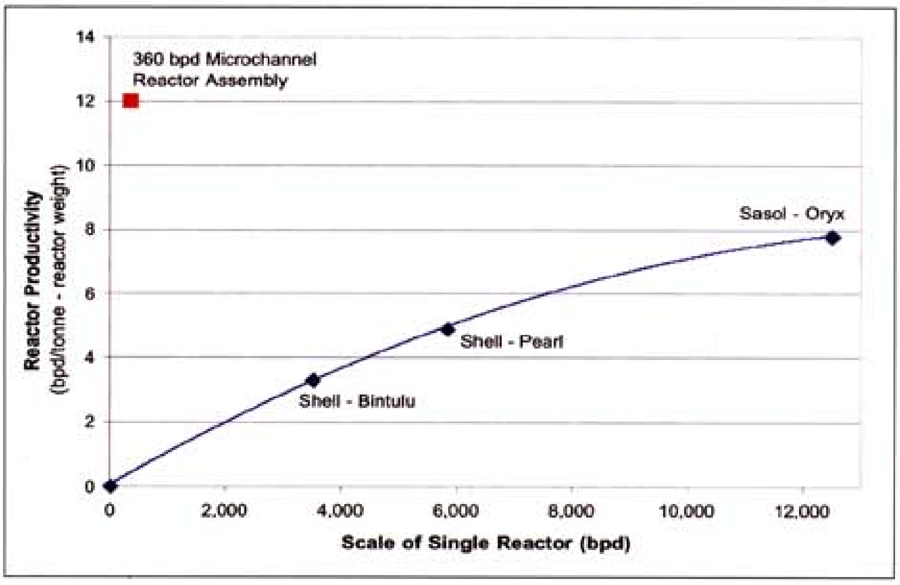
When it comes to second generation biofuels production, the ability to operate efficiently on the small scale is crucial. This is an area where microchannel reactors particularly shine. The secret of their performance success is down to the fact that the design of microchannel reactors enables efficient and precise temperature control, leading to higher throughput and conversion. Like the microelectronics technology that revolutionised the computer industry, microchannel technology shrinks processing hardware, while at the same time improving its performance. For example, while large conventional BTL plants would need to process biomass

Table 2. Microchannel advantages

The use of microchannel process technology offers a number of advantages in a range of energy and chemical processing applications. These include:[1]

- Improved heat transfer properties and higher energy efficiency. Microchannel has thin reaction channels which greatly improves heat and mass transfer. This allows optimal temperature control across the catalyst bed, which maximises catalyst activity and life.
- Smaller size and weight of reactors. Microchannel reactor assemblies are roughly 1.5m in diameter and sit horizontally. The small size and low profile are critical advantages for mobile and offshore installations. For comparison conventional FT reactors are situated vertically and can be more than 60m tall.
- Increased yields of target products. The improved heat transfer properties and higher energy efficiency offered by microchannel reactors leads to far higher reactor productivity, defined as barrels/day of FT product per tonne of reactor mass.
- Increased economies of scale. Microchannel FT realises economies of scale at a much smaller size (500 bpd) than conventional FT reactors (10,000 bpd) This increased economy of scale makes the use of microchannel reactors suitable for use for small-scale distributed BTL production. It also makes the use of microchannel reactors feasible for use for offshore gas to liquid (GTL) production.
- Lower feedstock and operating costs.
- The ability to optimise process conditions to an extent not achievable with conventional process techniques. This also makes it possible to make new products.
- Improved durability and serviceability.
- Improved inherent operating safety thanks to a reduction in the reactant residence time
- Improved corrosion protection
- For processing that involves coolants, reducing refrigerant charge by up to 50%
- Accelerated chemical process rates by 10 - 100 fold
- Amenable to the use of new, novel and more active catalysts
- Minimisation of production of emissions and undesirable by-products
- Lower overall capital costs

Figure 3. The productivity of small-scale microchannel reactors compared to large scale fixed bed FT reactors used by Shell in Malaysia and slurry reactors used by Sasol in South Africa



feedstocks of 10,000 tonnes/day in order to produce 10,000 barrels per day of fuel to be economically viable, small microchannel FT reactors can operate economically when processing just 500 - 2000 tonnes of waste per day.

Another great advantage of microchannel reactors is their capability to handle huge volumes of feedstock and their ability to produce high quality, energy-dense fuel from a wide variety of resources, including waste wood, energy crops and municipal solid waste. In terms of productivity (defined as barrels per day (bpd) of FT product per tonne of reactor mass (bpd/tonne)), microchannel FT reactors far outstrip their conventional cousins. For example, Velocys's microchannel FT reactor assembly, which has an output of 360 bpd, exhibits reactor productivities in the range of 12 bpd/tonne. In contrast Shell's Bintulu and Pearl GTL FT reactors with outputs ranging from 3500 – 6000 bpd have reactor productivities that range from around 3 to 5 bpd/tonne, and Sasol/QP's Oryx FT plant has a reactor with an output of more than 12,000 bpd, with a productivity of around 8 bpd/tonne (see figure 3).

This sterling performance is largely down to the process-intensified design, which results in massively enhanced heat and mass transfer capabilities (see table 3). Conventional reactor systems rely on the use of massive hardware to manage the heat in FT reactions and have relatively small heat transfer areas per volume of catalyst. In contrast, in microchannel reactors, each reactor block has thousands of thin process channels filled with FT catalyst which are interleaved with water-filled coolant channels. As a result they are able to dissipate the heat produced from the exothermic FT reaction much more quickly than conventional systems.

This makes them ideally suited for carrying out both highly exothermic catalytic reactions - such as FT synthesis - and highly endothermic reactions - such as methane reforming - in which heat must be efficiently transferred across reactor walls in order to maintain an optimal and uniform temperature to maximise the catalyst activity and prolong catalyst life. This allows microchannel reactors to operate at much higher conversions. Microchannel reactors exhibit conversion efficiencies in the range of 70% per pass. By comparison, conventional reactor systems typically operate at conversion efficiencies of only 50% per pass.

Catalysts: improved and optimised

In order for a catalyst to be used successfully on an industrial scale, it must be optimised for use

Table 3. Comparison of heat and mass transfer properties

	Microchannel reactors	Conventional reactors
Heat transfer (W/cm²)		
Convective	1-20	<1
Boiling	1-20	<1
Mass transfer (contact time in seconds)	0.001-0.3	1-10

Data source: reference[2]

Figure 4. Transmission electron microscope picture of the FT catalyst produced using the OMX method (photo courtesy of Oxford Catalysts)

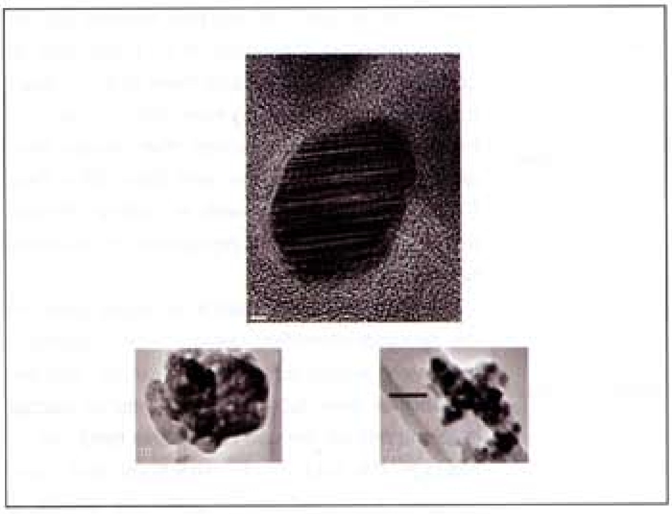
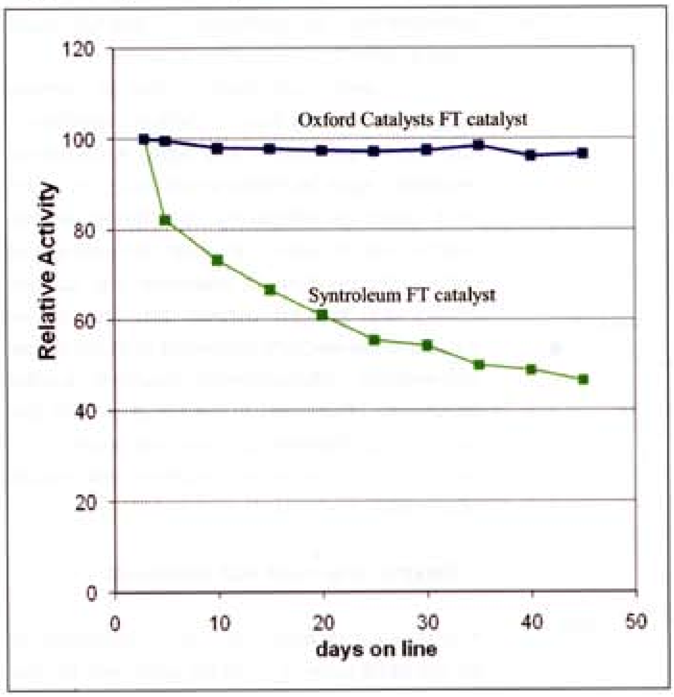


Figure 5. Comparison of deactivation rates between Oxford Catalysts new FT catalyst and a catalyst used in the Syntroleum FT process (data on this catalyst supplied by the FT process licensor, Syntroleum)



in the reactor used to carry out the process. For instance, in processes for highly exothermic reactions such as FT synthesis, or highly endothermic reactions such as steam methane reforming, and in high pressure processes such as hydrocracking, the catalysts used in conventional reactors typically incorporate large amounts of expensive precious and base metals. Because microchannel technology allows process reactors to be greatly reduced in size, a key advantage associated with the use of microreactors is to drive down the amounts, and therefore the costs, of metal alloys; structural supports, foundations and piping are also reduced compared to conventional processes.

Nevertheless, as with all catalytic reactions, to work effectively, the catalyst must be optimised for use in a specific process and reactor type. The level of catalyst activity is related to the surface area of the catalytic metals. This, in turn, is related to the crystal size of the catalytic metal, so producing catalysts with the optimal crystal size for a given application is a key goal for catalyst developers. The big challenge lies in achieving the right balance between catalyst activity and stability. If the crystal size is too large, the catalyst activity - and hence, conversion rates - will be reduced. If too small, the catalyst becomes unstable. The aim is always to produce a catalyst crystal size that is not too big, not too small, but just right.

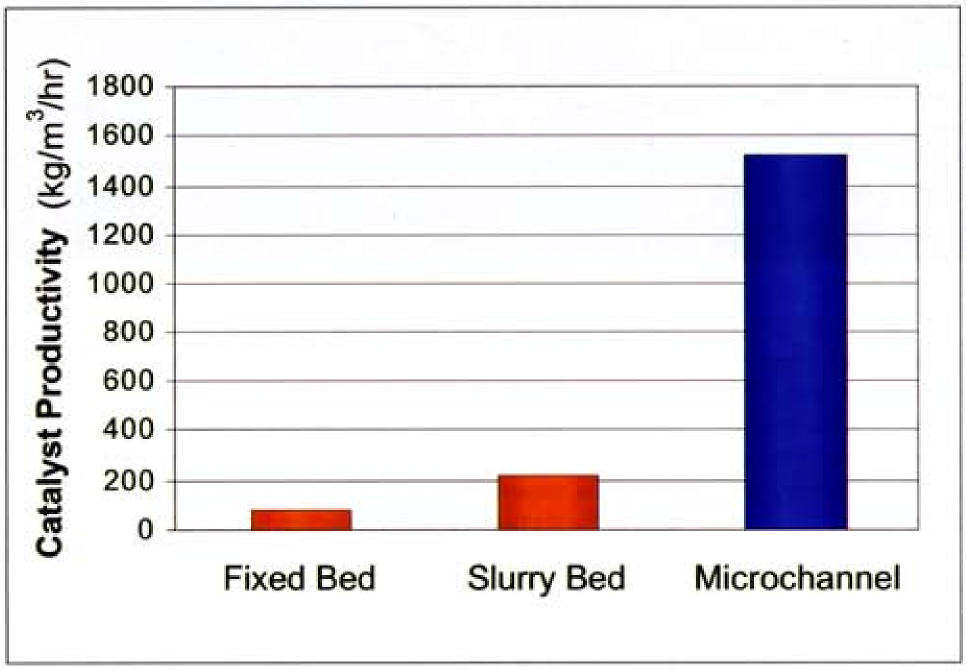
Taking advantage of the high conversion efficiencies offered by the use of microchannel reactors for BTL requires the right FT catalyst for the job. In order to boost conversion rates to an economic level, microchannel reactors require an FT catalyst with an exceptional level of activity. A new FT catalyst developed by Oxford Catalysts using the company's patented catalyst preparation method, organic matrix preparation (OMX), fits this bill exactly.

The OMX method

The OMX method combines the metal salt and an organic component to make a complex that effectively stabilises the metal. On calcination, combustion occurs that fixes the crystallites at this very small size. Since the calcination is quick, the metal crystallites do not have time to grow, and hence remain at the ideal size for these catalytic reactions. This is important because the improvements in catalyst performance are down to the fact that the OMX method produces crystallites in the 8-15 nanometre diameter range that exhibit a terraced surface (see figure 4). These are both features that enhance catalyst activity. OMX also produces fewer very small crystallites that could sinter at an early stage of operation. This results in greater catalyst stability. Less stable crystallites tend to deactivate quickly, reducing the activity of the catalysts.

The OMX method can be used to produce supported base metal catalysts for applications other than those produced for FT. Experiments carried out at Oxford Catalysts and independently elsewhere indicate that catalysts prepared via OMX perform better than catalysts containing the same metals, but prepared using standard methods such as mechanical milling, wet or dry impregnation, or via sol-gel or co-precipitation in a range of base metal catalysed reactions (see figure 5). Aside from their higher activity, the FT

Figure 6. Productivity of conventional FT catalysts in fixed bed and slurry reactors, compared to the productivity of the Oxford Catalyst FT catalyst in a microchannel reactor



catalysts produced using OMX have a longer life, and the need for precious metal promoters on the catalysts can be reduced, or in some cases, eliminated. while still retaining or even exceeding the benefits of traditional catalysts. Whilst the vast majority of base metal catalysts are not precious metal promoted, the benefits of the OMX technology in controlling and stabilising the metal crystallites are none the less apparent in OMX-produced catalysts for these catalyst formulations resulting in more active and more stable catalysts.

FT catalysts produced using OMX have been tested by a number of potential customers in powder form and work well at the lab scale. Oxford Catalysts are now working to scale up the OMX process to make it possible to supply formed catalysts in commercial quantities.

Optimised catalyst advantages

The new Oxford Catalyst FT catalyst allows operators of microchannel reactors to achieve productivities defined as kilograms of product per cubic metre of catalyst per hour ($kg/m^3/h$) that are orders of magnitude higher than for conventional systems (see Figure 6). For comparison, fixed bed reactors typically operate at catalyst productivities of $100 kg/m^3/h$, while slurry bed reactors operate at productivities of around $200 kg/m^3/h$. In contrast, a recent demonstration in a nominal 2 gallon per day microchannel reactor that operated for over 3000 hours using the new catalyst achieved productivities of over $1500 kg/m^3/h$.

The same catalyst will also be of great benefit for use in conventional FT systems, since another key feature of the catalyst is exceptional stability. This stability means that both microchannel reactors and conventional systems will be able to operate for longer without resorting to elevated temperatures - which accelerate the decay in catalyst activity - in order to maintain productivity.

Closer than you think

Although the FT reaction has been around for many years, there are just seven FT plants in operation worldwide, and these are used for producing liquid fuels, lubricant feedstocks and industrial waxes from coal or gas on a large scale. Taking advantage of FT to produce environmentally friendly and sustainable second generation biofuels, economically, and on a small distributed scale, presents new challenges. Some experts believe that we may have to wait as long as 5 - 10 years before commercial production of second generation biofuels becomes viable. But we believe that by working closely together to optimise and intensify the FT process, catalyst developers and microreactor designers could ensure that the distributed production of second generation biofuels becomes both a viable economic reality and a practical way to reduce carbon emissions, much sooner.

Endnote

[1] One of the main conclusions from the November 2008 report by Ralph Sims *et al* from the International Energy Agency "From 1st-2nd Generation Biofuel Technologies: An overview of current industry and RD&D activities" is that that while the 1st generation technologies for producing biofuels from simple feedstocks such as cereal grains, oil seeds are questionable purely from the view of "their ability to achieve targets for oil-product substitution, climate change mitigation, and economic growth", the only exception is, cane-based ethanol which "appears to meet many of the acceptable criteria".

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