Title: USE OF MICROCHANNEL REACTORS IN COMBINATORIAL CHEMISTRY

Abstract: Methods for discovering optimum catalysts and/or reaction conditions for performing endo- or exothermic reactions, in particular gas-to-liquid reactions, are disclosed. A combinatorial approach is used to identify optimum catalysts and/or reaction conditions for performing the reactions. The reactions are performed in the channels of a microchannel reactor. These results can be used directly to optimize large scale reactions performed in a plurality of microchannel reactors, or can be correlated to useful catalysts and reaction conditions for use in large scale reactors by taking into consideration the heat transfer effects in the microchannel reactor and the large scale reactor. The method can advantageously be used to generate a database of combinations of catalyst systems and/or reaction conditions which provide various product streams, such that as market conditions vary and/or product requirements change, conditions suitable for forming desired products can be identified with little or no downtime. The catalysts can be evaluated using varied reaction conditions, which can provide a) a combinatorial library of product streams and a database including the combination of catalysts and reaction conditions to provide each product stream and/or b) the optimum combination of catalysts and reaction conditions for obtaining a desired product stream.
Use of Microchannel Reactors in Combinatorial Chemistry

Field of the Invention

This invention is generally in the area of the use of microchannel reactors and/or combinatorial chemistry to optimize the conditions for endo- and exothermic catalytic reactions.

Background of the Invention

Combinatorial chemistry is in widespread use in the pharmaceutical industry, where it is used to synthesize, purify and evaluate new drugs at a tremendously fast pace. In the field of pharmaceutical chemistry, the reactions are typically performed at a relatively small scale, since only a small amount of each drug is required for testing. Typically, only those drugs which are active in relevant bioassays are scaled up. The type of chemistry used to generate commercial quantities of the drugs is rarely the same as that used in small scale synthesis.

Combinatorial chemistry is also being used in petroleum chemistry. However, a major goal in petroleum chemistry is to optimize the reaction conditions and catalysts used for particular reactions rather than to synthesize, purify and evaluate a plurality of products. To have commercial significance, there must be a correlation between the results obtained on the small scale and those which might be obtained on a commercial scale.

One combinatorial chemistry approach used by Symyx to identify optimum catalysts for various reactions involves placing a plurality of catalysts on a metal plate, contacting the plate with a gaseous reactant, and analyzing the products obtained via GC/MS. This approach is limited because, at least for a number of exothermic and endothermic catalytic reactions, it is difficult to correlate the results obtained on this small scale with those obtained on a commercial scale. This limitation exists, in part, because the heat transfer obtained on such a small scale cannot reasonably be correlated with what would be observed in a large reactor.

Heat transfer effects are extremely relevant in exothermic and endothermic reactions. For example, Fischer-Tropsch synthesis, an
exothermic reaction, is very sensitive to heat transfer effects. A small scale
reaction which provides an acceptable product mixture may provide an
unacceptable level of methane production on scale-up due to heat transfer
effects. Accordingly, it is often difficult to extrapolate the results on small
scale endo- and exothermic reactions to commercial scale reactors.
However, it is also difficult to perform combinatorial chemistry using
commercial scale reactors.

It would be advantageous to provide devices and methods for
discovering optimum catalyst systems using combinatorial chemistry that take
the heat transfer effects on product distribution into consideration. The
present invention provides such devices and methods.

Summary of the Invention

The present invention is directed to devices and methods for
optimizing endo- and exothermic reactions, in particular, gas-to-liquid
reactions, using combinatorial chemistry. The devices include a
microchannel reactor that includes a plurality of channels. Some or all of
these channels are used to carry out the desired endo- or exothermic
reactions. The individual channels include individual catalysts or
combinations thereof, such that all or part of a combinatorial library of
catalysts can be evaluated. The devices can also include channels which are
used to provide heating and cooling, and/or heating and cooling can be
provided using other means.

The methods use a combinatorial approach to identify optimum
reaction conditions and catalysts or catalyst combinations for performing the
desired reactions and/or for providing a desired product. Preferred
exothermic reactions are gas-to-liquid reactions, in particular Fischer-Tropsch
synthesis, isosynthesis, olefin oligomerization, olefin polymerization, and
syngas generation by partial oxidation, methanol synthesis, oxidative
methane coupling to ethane and ethylene, methanol conversion to
hydrocarbons. Preferred endothermic reactions are catalytic cracking,
naphtha reforming, methane conversion to aromatics and steam reforming of
methane; steam reforming reaction of H₂O with CH₄ to make H₂ and CO, with
traces of CO₂; aromatization, the conversion of paraffins and olefins to
aromatics, and hydrocracking reactions. The products can include olefins
such as ethylene, iso-paraffins, aromatics and combinations thereof, and
preferably include iso-paraffins in the distillate fuel and/or lube base stock
ranges, and, more preferably, iso-paraffins in the jet or diesel range.

The methods involve obtaining a microchannel device that includes a
plurality of channels, placing an effective amount of a catalyst (or a catalyst
combination) from one or more catalyst libraries in a channel, repeating this
step as necessary with different channels and different catalysts, and
performing the desired reactions. The product streams are preferably
analyzed, for example by GC, HPLC and/or GC/MS. The reaction conditions,
catalysts, and analytical information regarding the product streams are
preferably stored in a database.

The information obtained in the combinatorial step can be applied
commercially in several ways. For example, a plurality of microchannel
reactors can be used in series and/or in parallel such that the chemistry can
be performed on a commercial scale in the plurality of microchannel reactors.
This is advantageous, since the reaction conditions and catalysts used in the
combinatorial step are directly applicable to the commercial scale chemistry.
Alternatively, the results obtained in the microchannel reactors can be
correlated to what would be obtained in a conventional large scale reactor.

The microchannel reactors are preferably in the form of a
microcomponent sheet architecture, for example a laminate with
microchannels. The sheet architecture may be a single laminate with a
plurality of separate microcomponent sections or the sheet architecture may
be a plurality of laminates with one or more microcomponent sections on
each laminate. The microcomponents include passive microcomponents, for
example micro flow paths, and active components including but not limited to
micropumps and microcompressors. In one embodiment, one type of
laminate receives chemical reactants, rejects chemical products and rejects
or receives heat to or from a second type of laminate.

The microcomponents or plurality of like microcomponents can
perform at least one unit operation. In one embodiment, a first laminate
having a plurality of like first microcomponents is combined with at least a
second laminate having a plurality of like second microcomponents. The
combination of at least two unit operations provides a system operation. For
example, a laminate containing a plurality of microchannel evaporators can
be combined with an insulating laminate and a laminate containing a plurality
of microchannel condensers, and connected to a compressor and expansion
valve to obtain a macroscale heat pump. The laminates can be used for
chemical processes such as chemical conversions and separations.

Heat transfer in the microchannel reactors is controllable, in part by
adjusting the heating/cooling through the microchannels, through the
individual laminate layers, and/or through the judicious choice of materials
used to prepare the reactors. Ideally, the heating and/or cooling provided by
the microchannel reactors can be made to approximate or at least be
correlated to that of a large scale (commercial) reactor. One way to provide
such a correlation is to place a commercially-known catalyst in one or more of
the channels, and adjust the reaction conditions/heating/cooling and other
factors such that the results can be correlated with the results obtained in the
large scale commercial reactors.

Whether the results obtained in the combinatorial step are used in a
plurality of microchannel reactors, or the chemistry is scaled up to a large
scale reactor, it may be advantageous to include the same catalyst in a
plurality of channels to verify that the results obtained are reasonably
consistent throughout the reactor.

The methods can advantageously be used to generate a database of
catalysts and, optionally, reaction conditions, which provide various product
streams. As market conditions vary and/or product requirements change,
conditions suitable for forming desired products can be identified with little or
no downtime using the methods described herein.

**Detailed Description of the Invention**

The present invention is directed to devices and methods for
optimizing endo- and exothermic reactions, in particular gas-to-liquid
reactions, using combinatorial chemistry. The devices include a
microchannel reactor with a plurality of channels, where a plurality of the
channels individually include catalysts selected from a library of catalysts.
Using the devices and methods described herein, a plurality of catalysts
and/or reaction conditions can be evaluated simultaneously.

Types of Reactions
The devices and methods can be used to evaluate and optimize
virtually any type of endo- or exothermic catalytic reaction. These types of
reactions are well known to those of skill in the art, and include most gas-to-
liquid reactions. Particularly preferred gas-to-liquid reactions include Fischer-
Tropsch synthesis, isosynthesis (conversion of syngas to methanol and
subsequent conversion of the methanol to higher molecular weight products),
olefin oligomerization, olefin polymerization, syngas generation by partial
oxidation or steam reforming of methane, methanol synthesis, higher alcohol
synthesis, oxidative coupling of methane, methane conversion to aromatics,
and light paraffin dehydrogenation. Other reactions which can be optimized
include hydroformylations, hydrocracking, isodewaxing, isomerizations,
dehydrogenations, olefin metathesis, polymerization, paraffin redistribution,
alkylbenzene redistribution, molecular redistribution, molecular averaging,
naphtha reforming, and catalytic oxidations of various sorts, including CO
oxidation, NOx reduction. Molecular averaging and redistribution is
described, for example, in U.S. Patent No. 3,699,035; U.S. Patent No.
3,914,330, the contents of which are hereby incorporated by reference.
Reactants

The reactants are typically low molecular weight gases, but can also include liquids. Examples include water, hydrogen gas, carbon monoxide, carbon dioxide, oxygen, syngas (a mixture of carbon monoxide and hydrogen gas), nitrogen oxides (NOx), methane, low molecular weight olefins and/or paraffins (typically including less than 6 carbon atoms), low molecular weight oxygenates such as methanol, ethanol, and dimethyl ether, and other reactive gases. Inert diluent gases may also be present.

The reactants can be reacted with the catalysts in any suitable ratio and amount, given the size of the channels and the desired conversions. The reactants preferably come from a common source, to ensure consistency between channels. A splitter can be used, for example, to direct the reactants to the plurality of channels.

Products

The products are typically light gases and hydrocarbons or oxygenates useful as naphtha, distillate fuels, lube oils, waxes, or as components in such products. The hydrocarbon products generally are olefins such as ethylene, n-paraffins, iso-paraffins, aromatics and combinations thereof, and preferably include iso-paraffins in the distillate fuel and/or lube base stock ranges, and, more preferably, iso-paraffins in the jet or diesel range.

Catalysts

Suitable catalysts for performing various reactions in the field of petroleum chemistry are well known to those of skill in the art. Catalyst libraries including such catalysts and combinations thereof can be readily prepared. Libraries include a plurality of catalysts, preferably at least 10 catalysts, more preferably at least 50 catalysts and most preferably at least 100 catalysts. Large numbers of catalysts can be evaluated, for example by using a plurality of microchannel reactors and/or by performing consecutive runs with a single microchannel reactor.

The amount of the catalyst used in the reaction depends on the size of the channel. Those of skill in the art can readily determine an appropriate
amount of catalyst for a particular channel in a microchannel reactor. In gas-
to-liquid reactions and a number of other endo- and exothermic reactions, the
catalysts tend to be zeolites, other molecular sieves such as borosilicates,
ELAPOs such as SAPOs, Fischer-Tropsch catalysts, and alkali or alkaline
earth promoted oxides for oxidative coupling of methane and other
dehydrogenation reactions, nickel or noble metal catalysts for syngas
generation, noble metal catalysts for CO and hydrocarbon oxidation,
platinum-based catalysts for naphtha reforming, copper-zinc and zinc-
chromium catalysts for methanol synthesis, metal-zeolite catalysts for
hydrocracking and hydroisomerization, USY zeolites for catalytic cracking.

Fischer-Tropsch Catalysts

Fischer-Tropsch catalysts contain a Group VIII transition metal on a
metal oxide support. The catalysts may also contain a noble metal
promoter(s) and/or crystalline molecular sieves. Certain catalysts are known
to provide chain growth probabilities that are relatively low to moderate, and
the product of the reaction includes a relatively high proportion of low
molecular (C_{2,8}) weight olefins and a relatively low proportion of high
molecular weight (C_{30+}) waxes. Certain other catalysts are known to provide
relatively high chain growth probabilities. Such catalysts are well known to
those of skill in the art and can be readily obtained and/or prepared.

Zeolites

Catalysts useful for isomerizing alpha olefins typically include one or
more zeolites and/or non-zeolitic molecular sieves. Those zeolites which are
relatively acidic tend to be more efficient than those which are relatively less
acidic.

The zeolites and/or molecular sieves are preferably large and/or
intermediate pore size zeolites, although zeolites with small pore sizes can be
included in the catalyst libraries. Examples of these catalysts, any and all of
which can be included in the catalyst libraries, are described, for example, in
U.S. Patent Nos. 3,546,102; 3,574,092; 3,679,575; 4,018,711; 4,104,320;
4,347,394; 4,370,224; 4,417,083; 4,434,311; 4,447,316 and 5,559,068.
Zeolite-containing catalysts, for example the zeolite mordenite, ZSM-type zeolites, zeolite L, Faujasites X and Y, and the zeolite omega, are preferably included into the catalyst libraries. L-zeolites and zeolites having an L-zeolite-type channel structure and size, such as ECR-2, which is described in U.S. Patent No. 4,552,731, and ECR-31, which is described in U.S. Patent No. 5,624,657 (Vaughan), are also preferably included in the libraries.

The composition of type L-zeolite expressed in terms of mole ratios of oxides may be represented by the following formula:

\[(0.9-1.3)M_{2/n}O:Al_{2}O_{3}(5.2-6.9)SiO_{2}:yH_{2}O\]

In the above, formula M represents a cation, n represents the valence of M, and y may be any value from 0 to about 9. Zeolite L, its X-ray diffraction pattern, its properties and method for its preparation are described in detail in, for example, U.S. Patent No. 3,216,789, the contents of which is hereby incorporated by reference. The actual formula may vary without changing the crystalline structure. For example, the mole ratio of silicon to aluminum (Si/Al) may vary from 1.0 to 3.5.

described in U.S. Patent No. 4,910,006. SSZ-31 is described in U.S. Patent No. 5,106,801. SSZ-33 is described in U.S. Patent No. 4,963,337. SSZ-35 is described in U.S. Patent No. 5,316,753. SSZ-37 is described in U.S. Patent No. 5,254,514. SSZ-41 is described in U.S. Patent No. 5,591,421. SSZ-42 is described in U.S. Serial No. 08/199,040. SSZ-44 is described in U.S. Patent No. 5,580,540. MCM-58 is described in U.S. Patent No. 5,437,855.


SSZ-23 is described in U.S. Patent No. 4,859,442. SSZ-25 is described in U.S. Patent Nos. 4,826,667 and 5,202,014. SSZ-28 is described in U.S. Patent No. 5,200,377. SSZ-32 is described in U.S. Patent No. 5,053,373.

The entire contents of all these patents and patent applications are incorporated herein by reference, and any and all of the catalysts described therein can be incorporated into the catalyst libraries. Mesoporous molecular sieves can also be included, for example the M41S family of materials, (J. Am. Chem. Soc., 114:10834-10843 (1992)), MCM-41 (U.S. Patent Nos. 5,246,689; 5,198,203; 5,334,368) and MCM-48 (Kresge et al., Nature, 359:710 (1992)), the contents of which are hereby incorporated by reference.

Catalyst Supports

Catalysts used in these reactions may be present on a support.

Suitable metal oxide supports or matrices which can be used include alumina, titania, silica, magnesium oxide, alkaline earth titanates, alkali titanates, rare earth titanates and mixtures thereof. The catalysts can include any or all of these supports, in varying ratios of weight of support to weight of catalyst.

Typically, the catalysts have a particle size of between 10 and 110 microns, preferably between 20 and 80 microns, more preferably between 25
and 65 microns, and have a density of between 0.25 and 0.9 g/cc, preferably between 0.3 and 0.75 g/cc. The catalysts typically include one or more of the above-mentioned catalytic materials.

**Logical Arrays**

Libraries of catalysts can be prepared and evaluated using the devices and methods described herein. The identity of the catalyst or combination thereof in each position in the microchannel reactors can be stored in a computerized device, or identified via other identifying means. The products of the reaction can be readily identified, for example by gas chromatography (GC), a combination of gas chromatography and mass spectrometry (GC/MS), infrared heat emissions, infrared species analysis, or UV spectral analysis. To avoid contaminating the columns in chromatographic devices, it may be desirable to filter a representative sample of the product stream before it is placed on the column, for example using an in-line filter or an in-line solid phase extraction (SPE) column.

The properties of the reaction products generated during the evaluation of the libraries for a particular chemical reaction can be measured and correlated to specific catalysts, combinations of catalysts, and/or reaction conditions. By screening numerous combinations of catalysts and/or reaction conditions, the selection of the optimal combinations is more a function of the data collection method than the "rational" basis for selecting a useful catalyst and/or set of reaction conditions.

There are several types of reactions in which two or more types of catalysts are used. These catalyst combinations may be used simultaneously or in series, for example in multi-step syntheses. Combinations of catalysts may be used, for example, in multi-step reactions, where one catalyst performs one step and a second catalyst performs a second step. Examples of such reactions include isosynthesis and Fischer-Tropsch synthesis where an acidic catalyst is used to isomerize or isomerize the olefins as they are formed. In such reactions, the optimum overall catalyst combination for producing a desired product may not be the one that includes the optimum catalysts for both steps, since the individual steps may require totally different
reaction conditions to be optimized. The overall optimum combination may
be one that is the optimum for the first step or for the second step.

For example, the optimum conditions for Fischer-Tropsch synthesis
may involve temperatures at a first temperature range, but the optimum olefin
isomerization catalysts may operate best at temperatures at a different
temperature range. When these Aoptimum@ olefin isomerization catalysts
are operated at temperatures in the first temperature range, they may be
inefficient. Accordingly, it is preferred that the catalyst combinations include a
combination that is optimum for all steps in the multi-step reaction. It is
therefore important to test both catalyst components together. However,
leads for this screening of optimum catalyst combinations can come from
searching the individual catalysts.

When catalyst combinations are used, the catalysts are preferably
combined in a logical manner, for example in an A x B array, where each
position in the A column includes one or more catalysts for performing the
first step of the reaction, and each position in the B row includes one or more
catalysts for performing the second step of the reaction. In this manner,
virtually every possible combination of catalysts in the libraries can be
evaluated. The combinations of catalysts can be evaluated using varied
reaction conditions, which can provide a) a combinatorial library of product
streams and a database including the combination of catalysts and reaction
conditions to provide each product stream and/or b) the optimum combination
of catalysts and reaction conditions for obtaining a desired product stream.

Reaction Conditions

The reaction conditions typically involve increased temperature and
pressure. Typical pressure ranges are from 10 to 100 bar. Typical
temperature ranges are from 100°C to 1000°C. These conditions may be but
need not be the same as those used in large scale commercial reactors. The
conditions are expected to be the same as when a plurality of microchannel
reactors are used to provide large scale conversions.

A preferred reaction which can be performed in the devices is Fischer-
Tropsch synthesis. Examples of catalysts and conditions for performing
Fischer-Tropsch type synthesis in fixed and fluidized bed reactors are well
known to those of skill in the art, and can be adapted for use in microchannel
reactors. Suitable conditions are described, for example, in U.S. Patent
Nos. 4,704,487; 4,507,517; 4,599,474; 4,704,493; 4,709,108; 4,734,537;
4,814,533; 4,814,534 and 4,814,538, the contents of each of which are
hereby incorporated by reference in their entirety.

Microchannel Reactors

Any suitable microchannel reactor can be used which can perform a
plurality of simultaneous or substantially simultaneous reactions. Such
reactors are well known to those of skill in the art and are described, for
example, in U.S. Patent No. 5,811,062 to Wegeng et al., the contents of
which are hereby incorporated by reference. The microchannel reactors are
capable of performing a plurality of simultaneous or substantially
simultaneous reactions which involve gaseous reagents, solid phase catalysts
and relatively high temperatures and pressures, although they are also
suitable for carrying out other types of reactions as well.

Preferably, the reactors include ten or more channels, more preferably
greater than 25 channels, most preferably greater than 50 channels. The
width \( W \) of the grooves or microchannels may range from about 1 micron to
about 1 millimeter and preferably range from about 10 microns to about 250
microns.

The voids are an appropriate size for receiving the catalysts used for
the endo- or exothermic reactions and for permitting the entry and exit of
reactants and products. The microchannel reactors can be prepared from
any suitable material, including metals and alloys, polymers, plastics, glass,
ceramics, semi-conductors, and the like. They can be formed from a solid
material or can be in the form of laminates. The materials must be able to
withstand the reaction conditions and also be inert to the catalysts and
reactants employed.

Some or all of the channels are used to carry out the desired endo- or
exothermic reactions. The individual channels include individual catalysts or
combinations thereof, such that all or part of a combinatorial library of
catalysts can be evaluated. The devices can also include channels which are used to provide heating and cooling, or heating and cooling can be provided using other means. For example, the reactor can be heated and/or cooled externally and thus heat and/or cool the reactions occurring in the various channels.

Preferably, the reactants are fed to the channels from a single source, for example using a splitter or other suitable means to pass the reactants at approximately the same flow rate to the channels in which the reactions are to occur.

The reactors can be formed from a plurality of laminates. Laminates may comprise material sheets which include a plurality of microcomponents embedded onto one or both sides of the material sheets, material sheets with no microcomponents, or material sheets with conduits through the material sheet thickness serving as a spacer or insulator. The microcomponents can be, for example, condensers, evaporators or non-phase change heat exchangers, compressors, expansion valves, or motors. These examples are not intended to be limiting, and there is practically no limit to the types and numbers of microcomponents and combinations thereof that may be included on a laminate or material sheet. In one embodiment, microcomponents are embedded on both sides of material sheets for use as dual fluid heat exchangers, for example feedwater preheating with condensed turbine exhaust.

The density of microcomponents on a material sheet typically ranges from about 1 microcomponent per square centimeter to about $10^{10}$ microcomponents per square centimeter. Within those density ranges, a range of unit lengths or unit diameters of microcomponents is from about 1 micron to about 1 centimeter.

The microcomponents or groove sets may be embedded into the material sheets by any conventional microchannel forming process, but is preferably done with micromachining or photolithography, with photolithography being particularly preferred. Microchannel forming processes generally etch a surface so that resulting channels are unconfined on the etched side. Channels are closed by bonding a second laminate to the
etched surface. A plurality of solid material lands defining a plurality of
lateral can be formed to function as heat transfer fins supporting a high heat
flux. Each land may be laterally closed or laterally open to permit cross flow
communication. The lands may be of any cross section including but not
limited to rectangular, rhomboid, and ellipsoid cross sections. Laterally open
lands increase flow area thereby reducing the possibility of clogging and
reducing the effect of a clog should it occur, and are particularly preferred
when solid catalysts are used. In microcomponents with laterally open lands,
the definition of a lateral is less distinct, especially if the lands are offset or
randomly spaced. Nevertheless, the spaces between the open lands are flow
paths.

A single microcomponent or a set of like microcomponents is capable
of performing at least one unit operation. A unit operation is defined as an
operation that changes the state (thermodynamic state including chemical
and/or physical state) of a working fluid, including condensation, evaporation,
compression, pumping, heat exchanging, expansion, or chemical process, for
example chemical conversion or separation. Chemical reactions may be and
preferably are endothermic or exothermic. Conversion reactions include
virtually any endo- or exothermic reaction, for example reduction, oxidation,
partial oxidation and combustion. Separation involves receiving at least one
chemical mixture having a chemical product and a product carrier and
separating the chemical product from the product carrier. Examples of
separations include distillation, ion exchange and solvent extraction. A
collection of unit operations is a system. An example of a single
microcomponent performing more than one unit operation is a
microcompressor in a thermally conductive material performing both
compression and heat transfer simultaneously. Of course,
macrocompressors conduct heat as a result of compressing a gas, but that
heat is small compared to the process heat, for example heat removed from a
refrigerated space. The distinct advantage of a microcomponent is that the
heat transferred simultaneous with the compression is indeed process heat,
and provides a substantially constant temperature compression (approaching
an ideal isothermal compression), which results in efficient energy
transfer/conversion. A system may include and preferably does include a microchannel chemical reactor placed upon an microchannel heat exchanger, preferably an evaporator, for temperature control of the chemical reaction thereby permitting control of endo- and exothermic chemical reactions.

In general, a system has a first laminate having a first plurality of microcomponents for performing at least one unit operation, attached to a second laminate having a second plurality of microcomponents for performing at least one additional unit operation. The first unit operation is combined with the additional unit operation and produces a system operation.

Alternatively, instead of having separate unit operations on separate laminates, separate unit operations may be placed on a single laminate having a first portion and at least a second portion. The first portion has first microcomponents for performing a unit operation and the second and subsequent portion(s) have second and subsequent microcomponents for performing another and subsequent unit operation(s). The unit operation is combined with the additional and/or subsequent unit operation(s) and produces a system operation.

Microcomponents performing one unit operation can be combined in several ways with microcomponents performing another unit operation. For example, several microscale pumps in parallel may feed a single heat exchanger, or one microscale pump may feed several heat exchangers in parallel. Similar variations with like microcomponents in series or a combination of series and parallel arrangements may be used advantageously in particular applications.

Laminates or laminate portions are combinable into a wide variety of systems including but not limited to heat pumps, heat engines, heat pipes, thermal sources, and chemical plants, for example chemical converters and chemical separators.

A heat pump of microscale components has the same basic unit operations as a macroscale heat pump. For a vapor compression heat pump, the basic unit operations are evaporation, compression, condensation, and expansion. The microscale components performing each unit operation can provide the same level of macroscale heating or cooling in terms of thermal
kilowatts or megawatts as the macroscale counterpart. By adjusting the
number of these microscale components, a microchannel reactor can provide
roughly the same heat transfer as a large scale reactor.

A heat pump formed of microscale components can include, for
example, a microscale evaporator laminate, an insulation laminate, a
microscale compressor laminate, and a microscale condenser laminate. The
microscale evaporator laminate and condenser laminate are ideally laminates
with groove sets, wherein each groove set is a microcomponent. The
microscale compressor microcomponent can be a solid piston linear
alternator, a piezoelectric diaphragm as described by Smits JG, 1990, "A
Piezoelectric Micropump with Three Valves Working Peristaltically", Sensors
and Actuators 15, 153-67, or other micro-mechanical actuator capable of
compressing a gas. Expansion valves or orifices may be etched in the
compressor laminate, or a separate laminate containing expansion valves
may be inserted between the compressor laminate and the insulation
laminate.

The previous description and example of microscale components for a
heat pump were centered around a vapor compression cycle. Those skilled
in the art of heat pumps would know that other thermodynamic cycles, in
addition to vapor compression, are used for heat pumps. For example,
Reverse Brayton, Stirling Cycle, and Absorption Cycle have been used.

Thermodynamically, a heat engine is the reverse of a heat pump.
However, practically they are quite different. For example, a heat engine
does not use an expansion valve, and extracts work from the working fluid.
The working fluid may be gas or liquid, but the macroscale heat engine is very
different from a macroscale heat pump.

There are numerous thermodynamic cycles upon which even more
numerous heat engine designs are based, including but not limited to
Rankine Cycle, Brayton Cycle, Stirling Cycle, Otto Cycle, Diesel Cycle, Kalina
Cycle, and the Ericcson Cycle. In addition, there are combinations or
combined cycles and various energy conservation measures. In the Rankine
Cycle, for example, reheat, superheat and feedwater preheating have been
used alone or in combination in various heat engine applications. All of these
cycles are distinct because of the type of working fluid, internal versus external combustion of fuel, and other characteristics well known to skilled practitioners. Nevertheless, all of these thermodynamic cycles and improvements thereto are the result of attempts to approach the performance of the ideal Carnot Cycle.

Use of microscale laminates, especially condensers and evaporators, have the potential of improving the efficiency of these cycles because of their high specific heat transfer rates.

Distributed production of certain feedstock chemicals, including toxic gases, at their point of use is enabled by the microcomponent sheet architecture in the microchannel reactors. By producing feedstock at the point of use, hazards and expenses of transportation and storage are reduced. Specifically, environmental restoration, particularly groundwater cleanup may involve deployment of a microcomponent sheet architecture chemical process at depth. These steps may also be optimized using combinatorial chemistry.

A microchannel chemical process system is one in which a chemical process unit operation is combined with at least one other unit operation. The use of microchannels for chemical processes permits greater control in the process that cannot be obtained in a conventional "macrochannel" large scale reactor. For example, a broad range of control of temperature is made possible by use of microchannel laminates. Specifically, microchannel chemical reactors used in a sheet architecture permit controlled temperature gradients or controlled temperature variation across a sheet of microchannels thereby permitting quenching and attainment of non-equilibrium states. In addition to temperature, other parameters may be closely controlled. Specifically, microchannel geometry is useful for control of residence time, or velocity profile or both. Energy other than thermal energy may be used to activate a reaction or to otherwise create an environment conducive to specific desired reactions, including electrical field induced reactions (e.g., plasmas or aqueous phase electrochemical reactors) magnetically induced or controlled chemical reactions and sonically induced reactions. An example of providing a temperature gradient is having a sheet of parallel microchannels
for a condenser or evaporator wherein adjacent microchannels are held at
different pressures, thereby experiencing phase change at different
temperatures. With a reactor sheet having microchannels positioned in
crossflow with respect to the condenser or evaporator microchannels, the
reactions conditions are controllable along the length of the microchannel
reactor.

Because microchannel reactors are typically used for reactions that do
not require materials or solids that would clog the microchannels and that do
not produce materials or solids that would clog the microchannel (see, for
example, U.S. Patent No. 5,8111,062), the size of the voids must be
adjusted to account for the use of solid catalysts. One approach is to coat
the voids with a coating of a catalyst, rather than to fill the voids with solid
catalyst. Because the microchannel sheet architecture is capable of precise
and accurate control of localized reaction conditions, for example reaction
temperature and temperature gradient control at predetermined reactor
location(s), it is preferred that the microchannel sheet architecture be used for
reactions wherein precise control is beneficial.

Control of reaction temperature is critical for all endo- and exothermic
reactions and control of residence time may be critical depending upon the
reaction and reaction conditions. For example, partial oxidation of methane
to hydrogen requires both control of temperature and residence time to avoid
combustion of methane to carbon dioxide and water. By placing a sheet of
microchannels for reaction on a sheet of microchannels for cooling, the
reaction temperature is controllable to maximize yield of hydrogen.

Temperature control may be achieved in any of several ways. For
example, when a first sheet or laminate is in a cross flow relationship to a
second sheet or laminate, a temperature gradient along a flow direction of the
first laminate is maintained by controlling temperature of coolant within
particular microchannels or microcomponents. When two-phase flow is used
in the heat transfer sheet or laminate, pressure would be used to control
phase change temperature. Alternatively, geometry of the microchannels,
e.g., variable flow path width, cross sectional area and/or shape may be used
to optimize heat transfer to or from a chemical process sheet or laminate.
In one embodiment, at least a portion of the channels are used to separate products from reactants. Chemical separations, as used herein, include any exchange of a compound or element from one solvent to another where the solvents may be liquid or gas or both. An example is an absorption cycle refrigeration system. In chemical separations, a porous membrane is used that is selected so that a first solvent containing the element or compound does not wet the porous membrane but a second solvent wets the porous membrane and the element or compound in the first solvent transfers to the second solvent through the porous membrane.

By making the depths of the solvents small, i.e., less than about 100 microns, higher absorption rates are achieved than with larger depths. A microporous contactor unit is a microporous contactor sheet placed between cover sheets. Each cover sheet has a microplenum or at least one microcomponent together with an inlet and an outlet permitting fluid flow across the microporous contactor sheet.

In most practical systems, to achieve high absorption/desorption rates, heat will need to be transferred either to or from the absorption/desorption fluids. Accordingly, a heat transfer sheet as previously described may be combined with the microporous contactor unit.

The pores are preferably as small as practical, on the order of a few microns, i.e., less than about 10 microns, and most preferably less than about 3 microns. The small pore size provides a strong resistance to a through-sheet velocity or pressure gradient. A cover is placed over the sheet having a fluid plenum that is less than about 10 microns in height from the sheet to the cover. Mass diffusion then occurs within a stagnant film and through the microporous contactor sheet. Micro-components may be manufactured on one or both sides of the microporous contactor sheet. Additionally, the microporous contactor sheet may have no microcomponents itself, but the cover sheet(s) may have microcomponents for directing fluid flow across the microporous contactor sheet. A further embodiment is simply a fluid microplenum on either side of the microporous contactor sheet.

The microporous contactor sheet may be made by micromachining a metal, ceramic or plastic by, for example, lithography, preferably
photolithography, electrodeposition, injection molding, or sintering.
Advantages of micromachined contactor sheets include precise control of the
pore size throughout the sheet.

In operation, fluids may flow in parallel, counterflow or crossflow. The
parallel flow results in lesser mass flux or extraction, but permits lesser
pressure differential or gradient across the microporous sheet. When gas is
one of the fluids and the gas is to be absorbed into a liquid, it is preferred that
the gas pass through the microporous sheet but not the liquid. Accordingly, it
is preferred that the microporous sheet either be coated so that the liquid
does not wet the microporous sheet or have pores sufficiently small so that
the liquid is supported by its surface tension and does not flow through the
pores.

In the case wherein a microporous sheet is not sufficiently self
supporting between the covers, the covers may be made with projections or
lands for support of the microporous sheet. Alternatively, as previously
discussed, the microporous sheet may have grooves or microcomponents. In
either case, projections or lands would support the microporous sheet.

Analytical Equipment

The products from the reactions are preferably analyzed after they
pass through the individual channels. Suitable analytical equipment for
analyzing the products of chemical reactions, particularly reactions common
to petroleum chemistry, are well known to those of skill in the art.

After the chemical reactions takes place, the reaction products can be
individually transferred from the individual channels to an analytical device.
Any device that can take samples from the individual channels in the reactors
and analyze the resulting compounds can be used.

The analytical device is a preferably chromatographic device such as
an analytical or preparative scale HPLC, GC or GC/MS, although other
devices can be envisioned, depending on the chemistry performed. Since the
product streams may not include UV-active compounds, the analytical
equipment preferably includes an ELSD detector or other detector which is
not dependent on UV absorption to detect a compound eluting from the
column.

Particularly when iso-paraffin concentration is evaluated using the
library, a combination of GC and MS is used. Isomers tend to have the same
MS peaks, but elute at different times from the columns, and this technique
allows rapid determination of the product stream.

The products can be assayed for various properties including octane
and/or cetane values, degree of isomerization, olefin concentration, and the
like. Preferably the products are analyzed in a high-throughput manner.
Conditions are known in the art for determining the octane or cetane values
based on known GC data, when a GC is performed on a representative
sample of the product stream. These techniques may be particularly useful in
evaluating the libraries for useful catalyst combinations for preparing products
with desirable properties.

Using information obtained in the analyses, those of skill in the art can
readily optimize the reactions by varying various process conditions, for
example reagent composition, temperature, pressure, flow rate and the like.

Database

Data regarding the catalysts or combinations thereof, reaction
conditions and product streams can be stored in a relational database. The
database can be used to find optimum catalyst combinations for producing a
desired product stream, and can be particularly useful when the desired
product stream varies depending on market factors. When the product
requirements change, appropriate catalysts and/or reaction conditions can be
selected to prepare the desired product.

The data is preferably stored in a computer system capable of storing
information regarding the identity of the catalysts and the product streams
obtained, particularly when a plurality of different reaction conditions are
used. Software for managing the data is stored on the computer. Relational
database software can be used to correlate the identity of the ionic liquids,
the reaction conditions (for example reagent composition, temperature and
pressure) and the analytical data from each product stream. Numerous

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commercially available relational database software programs are available, for example from Oracle, Tripos, MDL, Oxford Molecular ("Chemical Design"), IDBS ("Activity Base") and other software vendors.

Relational database software is a preferred type of software for managing the data obtained during the processes described herein. However, any software that is able to create a "memory map" of the catalysts in the reaction vessels and correlate that information with the information obtained from the chemical reactions can be used. This type of software is well known to those of skill in the art.

**Library Design**

Software for the design of test libraries can be used to design the original catalyst test libraries based on input from literature and previous experimental programs. This software can be used to efficiently design test libraries which cover the desired experimental space and utilize statistical experimental design methods.

Other software can be used to analyze the data from experiments and correlate that data with the structure of the catalysts and/or catalyst treatment conditions and/or reaction conditions. Such correlations are often referred to as SAR software (Structure Activity Relations). Such SAR can then be used by the software to design subsequent catalyst test libraries for further screening. The use of such SAR programs can add to the efficiency of screening. As more data is collected, these SAR programs can become more efficient at developing catalyst libraries with increased probability for finding desirable catalysts.

**Methods**

The methods use a combinatorial approach to identify optimum reaction conditions and catalysts or catalyst combinations for performing the desired reactions and/or for providing a desired product. The methods involve obtaining a microchannel device that includes a plurality of channels, placing an effective amount of a catalyst (or a catalyst combination) from one or more catalyst libraries in a channel, repeating this step as necessary with
different channels and different catalysts so that a plurality of catalysts can be
simultaneously evaluated, and performing the desired reactions. The product
streams are then preferably analyzed, more preferably by GC, HPLC or
GC/MS. The reaction conditions, catalysts, and analytical information
regarding the product streams are preferably stored in a database.

In one embodiment, the results are used to determine optimum
conditions for performing larger scale reactions using a plurality of
microchannel devices. In this embodiment, the results from the combinatorial
chemistry are directly applicable to the large scale synthesis.

In another embodiment, the results obtained using the microchannel
devices can be correlated with what would occur in a large scale commercial
reactor. The microchannel reactors can generate information regarding a
large number of catalysts and reaction conditions, which is then used to
design optimum conditions for running large scale reactions in commercial
reactors. In this embodiment, the heat transfer effects in the microchannel
reactors must be correlated with that observed in the large scale reactors.

The heating and/or cooling provided by the microchannel reactors can
be adjusted to approximate or at least can be correlated to that of a large
scale (commercial) reactor. One way to provide such a correlation is to place
a commercially known catalyst in one or more of the channels, and adjusting
the reaction conditions and heating/cooling such that the results can be
correlated with the results obtained commercially.

In either embodiment, it is preferred that the same catalyst is placed in
a plurality of channels to verify that the results obtained are reasonably
consistent throughout the reactor.

The methods can advantageously be used to generate a database of
catalysts and, optionally, reaction conditions, which provide various product
streams. As market conditions vary and/or product requirements change,
conditions suitable for forming desired products can be identified with little or
no downtime using the methods described herein.

While preferred embodiments of the present invention have been
shown and described, it will be apparent to those skilled in the art that many
changes and modifications may be made without departing from the invention
in its broader aspects. The skilled person would be able to apply pre-heating, intercooling, re-heating, combined cycles, chemical process unit operation(s) and other variations as has been done in macro systems. The appended claims are therefore intended to cover all such changes and modifications as fall within the true spirit and scope of the invention.
We claim:

1. A method for discovering optimum catalyst systems and/or reaction conditions for carrying out endo- or exothermic reactions, comprising:
   a) preparing a library of catalysts for carrying out the desired reaction,
   b) placing a catalyst from the library in a channel in a microchannel reactor,
   c) repeating step b until a desired number of catalysts have been placed in a desired number of channels, and
   d) feeding reactants to the channels containing catalysts under conditions which cause the reactants to be converted to products,

2. The method of claim 1, further comprising analyzing the reaction products.

3. The method of claim 1, wherein the catalysts comprise Fischer-Tropsch catalysts.

4. The method of claim 1, wherein the catalysts comprise zeolite catalysts.

5. The method of claim 1, wherein the catalysts comprise dehydrogenation catalysts.

6. The method of claim 1, further comprising storing information regarding the identity of the catalysts and their position in the microchannel reactor.

7. The method of claim 2, further comprising storing information regarding the analysis of the reaction products in a database.

8. The method of claim 1, wherein the catalysts are arranged in the microchannel reactor in the form of a logical array.

9. The method of claim 1, wherein step d is repeated at least one time using different reaction conditions.

10. The process of claim 9, wherein the reaction conditions which are varied are selected from the group consisting of temperature, pressure, reactant composition, and flow rate.
11. The method of claim 1, wherein the product stream includes iso-
paraffins in the jet fuel range.

12. The method of claim 1, wherein the product stream includes iso-
paraffins in the diesel fuel range.

13. The method of claim 1, wherein the product stream includes iso-
paraffins in the lube base oil range.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
   IPC(7) : G01N 21/10, 22/80, 21/76, 21/75
   US CL. : 436/37, 68, 98, 104, 147, 159, 161, 164, 178, 173

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 436/37, 68, 98, 104, 147, 159, 161, 164, 178, 173

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>WO 97/32208 A (WILLSON) 04 September 1997, see entire document.</td>
<td>1-13</td>
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<tr>
<td>X</td>
<td>US 6,063,633 A (WILLSON, III) 16 May 2000, see entire document.</td>
<td>1-13</td>
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<tr>
<td>X</td>
<td>WO 00/29844 A (SENKAN) 25 May 2000, see entire document.</td>
<td>1-13</td>
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<tr>
<td>X</td>
<td>WO 99/19724 A (ATKINS et al) 22 April 1999, see entire document.</td>
<td>1-13</td>
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</table>

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
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Date of the actual completion of the international search 05 NOVEMBER 2001

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