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(54) Title: METHODS FOR OPTIMIZING THE SYNTHESIS OF HYDROCARBONS FROM SYNTHESIS GAS

(57) Abstract: Methods for discovering optimum catalyst systems for the conversion of syngas to higher molecular weight products via a methanol or other low molecular weight oxygenate intermediate are disclosed. A combinatorial approach is used to identify combinations of catalyst systems useful for performing the reactions. 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 are combined in a logical manner, for example, in the form of arrays. The combinations of catalysts can be evaluated using varied reaction conditions, which can provide a) a combinational 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.



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## **Methods for Optimizing the Synthesis of Hydrocarbons from Synthesis Gas**

### **Field of the Invention**

5           This invention is generally in the area of combinatorial chemistry, in particular the use of combinatorial chemistry to optimize the synthesis of hydrocarbons from synthesis gas.

### **Background of the Invention**

10           The majority of fuel today is derived from crude oil. Crude oil is in limited supply, and fuel derived from crude oil tends to include nitrogen-containing compounds and sulfur-containing compounds, which are believed to cause environmental problems such as acid rain.

          Although natural gas includes some nitrogen- and sulfur-containing compounds,  
15           methane can be readily isolated in relatively pure form from natural gas using known techniques. Many processes have been developed which can produce fuel compositions from methane. Most of these processes involve the initial conversion of methane to synthesis gas ("syngas").

          Fischer-Tropics synthesis converts syngas to a hydrocarbon product stream that  
20           tends to include either low molecular weight olefins or methane or high molecular weight paraffins (mostly wax), depending on the catalyst. The olefins can be oligomerized and the waxes hydrocracked, to form hydrocarbons in the distillate fuel range.

          Another strategy for converting syngas to fuel is to first convert syngas to methanol, and then convert methanol to higher molecular weight products. These products tend to  
25           include low molecular weight olefins such as ethylene when the catalyst is an ELAPO, in particular a small-pore SAPO, and aromatics or isoparaffins when the catalyst is a relatively acidic zeolite.

          There have been several processes for forming methanol (or other low molecular weight oxygenates) from syngas and converting the methanol to these and other higher  
30           molecular weight products, which are referred to herein as "isosynthesis" The use of the term "isosynthesis" herein is meant to be distinguished from the direct synthesis of isobutane over thoria catalysts, which has also been referred to as isosynthesis.

Isosynthesis processes are well known to those of skill in the art. For example, EP 120 510 to Shell discloses forming iso-paraffins from syngas using ZSM-5 plus zinc and copper, chromium or aluminum. JP 59175443 to Toyo Engineering Company discloses using platinum and ruthenium with a Y-type zeolite to produce an iso-paraffin product in the C<sub>4-10</sub> range with a majority of the product being pentanes. However, there remains a need to optimize these processes, and also to be able to tailor these processes such that they can provide a desired product stream.

It would be advantageous to provide methods for discovering optimum catalyst systems for converting syngas to higher molecular weight products, for example iso-paraffins in the distillate fuel and/or lube base stock base oil ranges. The present invention provides such methods.

### Summary of the Invention

The present invention is directed to methods for optimizing the conversion of syngas to higher molecular weight products via a methanol (or other low molecular weight oxygenate) intermediate (referred to herein as “isosynthesis” or “isosynthesis reactions.” The methods use a combinatorial approach to identify combinations of catalyst systems useful for performing isosynthesis reactions. The methods can advantageously be used to generate a database of combinations of catalyst systems 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.

Libraries of catalysts suitable for use in a first catalyst system (which converts syngas to methanol) and a second catalyst system (to convert methanol to higher molecular weight products) are prepared. The libraries can optionally include catalysts that possess both types of activity, namely, which can convert syngas to methanol and methanol to higher molecular weight products. Optionally, a third catalyst system can be used to convert carbon dioxide, methane and water to a “virtual syngas” for use in the isosynthesis reaction.

The libraries of catalysts can include catalysts with the same composition, but which have been subjected to varying pre-treatment steps. Such variation increases the size of the catalyst libraries and also the amount of information that can be obtained.

The catalysts are preferably combined in a logical manner, for example, in an A x B array (or A x B x C array if virtual syngas is prepared), where each position in the A column includes one or more catalysts from the first catalyst system, and each position in the B row includes one or more catalysts from the second catalyst system. 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.

The methods referred to herein are directed to a one-step process, where methanol is synthesized and converted in a single step. However, in an alternate embodiment, the synthesis can be a two-step process in which methanol synthesis and methanol conversion are separate. The combinatorial methods described herein can also evaluate libraries of various methanol formation and methanol conversion catalyst compositions, where the library can also include catalysts with similar compositions but which are prepared with varying catalyst pre-treatments (such as steaming, acid-leaching, calcination, pH adjustment, ion-exchange, etc.)

The products can include olefins such as ethylene, aromatics, cycloparaffins, iso-paraffins, 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. If the desired product stream includes low molecular weight olefins such as ethylene, the second catalyst system preferably includes one or more small-pore zeolites or ELAPOs and, more preferably, SAPOs. If the desired product stream includes isoparaffins or aromatics, the second catalyst system preferably includes one or more medium-pore, acidic zeolites.

### **Detailed Description of the Invention**

The present invention is directed to methods for discovering optimum catalyst systems for performing isosynthesis. The methods use a combinatorial approach to identify combinations of catalyst systems useful for performing isosynthesis reactions.

The catalyst combinations include a first catalyst system which converts syngas to methanol and a second catalyst system which converts methanol to higher molecular weight products ("methanol conversion catalysts"). As used herein, "methanol" is intended to also

include other low molecular weight oxygenates such as ethanol, propanol, acetic acid, dimethyl ether and the like, although methanol is preferred.

The catalyst combinations can be laid out in a logical fashion, for example in arrays.

Where different classes of methanol conversion catalysts are used, they can advantageously be placed in sub-arrays. For example, sub-arrays can include catalyst groups, for example zeolites, ELAPOs and borosilicates, where the entire array includes all of the above catalysts. The arrays can be ordered in such a fashion as to expedite synthesis and/or evaluation, to maximize the informational content obtained from the testing and to facilitate the rapid evaluation of that data.

The reactions are preferably carried out in a reaction vessel capable of performing a plurality of simultaneous or substantially simultaneous reactions that involve gas reagents, solid phase catalysts and relatively high temperatures and pressures.

The optimum overall catalyst combination for producing a desired product may not be the one that includes the optimum catalyst for methanol synthesis and the optimum catalyst for methanol conversion, since both steps may require totally different reaction conditions to be optimized. The overall optimum combination may be one that is the optimum for methanol conversion which defines a set of conditions, and then a methanol synthesis component that is optimized to work at the conditions needed for use with the conversion catalyst. For example, the optimum conditions for methanol conversion may involve temperatures above 700°F, but the optimum methanol catalysts may operate best at temperatures below 300°F. When these "optimum" methanol synthesis catalysts are operated at temperatures in excess of 700°F, they may produce too much methane. Accordingly, it is preferred that the catalyst combinations include a combination that is optimum for both steps, methanol synthesis and methanol conversion, under the operating conditions imposed by the methanol conversion catalyst (satisfactory activity and relatively low methane yields). Alternatively, the method can determine an optimum methanol conversion catalyst that operates satisfactorily under the optimum methanol synthesis conditions. Either way, it is important to test both catalyst components together, at least where both are to be combined in a single reactor using a single set of reaction conditions. However, leads for this screening of optimum catalyst combinations can come from searching the individual catalysts.

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 combinations of catalysts. By screening numerous combinations of catalysts, the selection of the optimal combinations is more a function of the data collection method than the "rational" basis for selecting a useful catalyst combination. Optimum combinations can be rapidly determined by directly correlating the product streams obtained with the catalyst combinations within a particular array or sub-array. Due to the relatively large number of catalysts in the first and second catalyst libraries, particularly considering the variety in possible pre-treatment steps, it may be advantageous to identify optimum pre-treatment steps for each of the catalysts before including them in the catalyst libraries.

### Syngas

The syngas is a gaseous mixture of hydrogen and carbon monoxide. The  $H_2/CO$  ratio is from about 1:10 to about 10:1, preferably from about 1:3 to about 3:1. It is normally derived by heating coke in the presence of air and then steam. Alternatively, it can also be produced by partial combustion of coal, natural gas or petroleum hydrocarbons. Synthesis gas normally contains a very low amount of sulfur compounds. It may also contain small amounts of carbon dioxide, nitrogen and other inerts. The concentration of sulfur compounds in the syngas should be as low as possible since sulfur is a known poison for many types of catalysts.

### Products

The products can include olefins such as ethylene, aromatics, cycloparaffins, iso-paraffins 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. If the desired product stream includes low molecular weight olefins such as ethylene, the second catalyst system preferably includes one or more ELAPOs, more preferably, SAPOs. If the desired product stream includes isoparaffins or aromatics, the second catalyst system preferably includes one or more relatively acidic zeolites.

Preferred products are iso-paraffins in the jet, diesel or lube base stock ranges. The degree of isomerization is preferably greater than 1, and more preferably greater than 3, moles of isoparaffin per mole of n-paraffin. When used in a diesel fuel composition, the

products preferably have a cetane number of at least 60. When used in a lube oil composition, the products preferably have a viscosity index of at least 80, more preferably at least 100, and most preferably at least 110. The lube base stock is suitable for use in lube oil compositions. Cycloparaffins are also preferred products in the jet range.

5

### Catalysts

#### A. Types of Catalysts in the First Catalyst System

Synthesis gas is typically converted to various reduction products of carbon monoxide, including methanol, at a temperature between about 300 to about 850°F, at pressures between about 1 and 1000 atmospheres pressure, over a fairly wide variety of catalysts. Any type of catalyst useful for converting syngas to methanol can be incorporated into the catalyst library. As used herein, the catalysts can also produce other products, such as higher molecular weight alcohols, aldehydes and acids, in addition to or in place of methanol, provided that a second catalyst converts the initial product to a higher molecular weight product. The catalyst libraries can be used in both lead generation and lead optimization.

Typical catalysts for converting syngas to methanol include one or more transition metals. Common methanol synthesis catalysts include the metals or oxides of copper, zinc, iron, cobalt, nickel, ruthenium, thorium, rhodium and/or osmium, and can also include chromia, alumina and known modifications thereof. Zinc or zinc oxide containing catalyst compositions, copper-containing catalyst compositions, and their use as synthesis gas conversion catalysts, are well known.

Examples of high pressure ( $\text{ZnO-Cr}_2\text{O}_3$ ) catalysts and low pressure ( $\text{Cu/ZnO/Al}_2\text{O}_3$ ) versions are described, for example, in G.W. Bridger and M.S. Spenser, The Catalyst Handbook, M.V. Twigg, Editor, Wolfe Publishing Co. Frome, England 1989, the contents of which are hereby incorporated by reference. Those authors also describe Pd/silica and Rh/silica catalysts as having high activity for methanol synthesis, but with poorer selectivity than copper catalysts. Additional examples of suitable catalysts are described, for example, in Pichler, H and Ziesecke, K. H., "The Isosynthesis", *U.S. Bureau of Mines Bulletin*, 488 (1950) and French Patent No. 2037567. U.S. Pat. No. 2,061,470 discloses using the reduction product of a fused mixture of copper oxide and manganese oxide, or copper oxide and zinc oxide, and an oxide of an element selected from the group consisting of chromium,

vanadium, zirconium, aluminum, magnesium, titanium, thorium, silicon and cerium as a methanol synthesis catalyst. U.S. Pat. No. 4,298,354 discloses using an oxide-complex catalyst containing copper, thorium, an alkali metal and at least one other metal selected from the group consisting of Ca, Mo, Rh, Mn, Pt, Ce, Cr, Zn, Al, Ti, La, V, U, Ru, Re and Pd. U.S. Pat. No. 4,377,643 discloses using a catalytic complex containing ruthenium, copper, an alkali metal and a promoter selected from the group consisting of Rh, Ir, Pd and Pt).

All of these catalysts can be included in the catalyst library. The contents of each of these patents and publications is hereby incorporated by reference.

The conversion of syngas to methanol is most often an equilibrium process. For that reason, it can be advantageous to form methanol as an intermediate which is immediately converted to higher molecular weight products using the methanol conversion catalysts described below, to drive the equilibrium to the right.

#### B. Methanol Conversion Catalysts

Any catalyst which converts methanol (or other products produced using the methanol synthesis catalysts described above) to higher molecular weight products, and which is compatible with the catalyst used to convert syngas to methanol, can be used. Typically, ELAPOs, preferably small-pore SAPOs, are used to convert methanol to low molecular weight olefins such as ethylene and relatively acidic, medium-pore zeolites such as ZSM-5 are used to convert methanol to isoparaffins and aromatics.

In one embodiment, a first catalyst is used to convert syngas to methanol, a second catalyst is used to convert methanol to olefins, and a third catalyst is used to dimerize, trimerize or oligomerize the resulting olefins. In this embodiment, operation at relatively higher pressures is favored as the overall stoichiometry of the reaction involves several moles of syngas reacting to form one mole of isoparaffin (with some moles of water). In this embodiment, the goal would be to find catalysts with both sufficient activity and selectivity for heavy isoparaffins (in the diesel fuel or lube base stock ranges).

Catalysts and reaction conditions for oligomerizing olefins are well known to those of skill in the art. Such catalysts and conditions are described, for example, in U.S. Patent Nos. 6,013,851; 6,002,060; 5,942,642; 5,929,297; 4,608,450; 4,551,438; 4,542,251;



4,538,012; 4,511,746; 4,465,788; 4,423,269; 4,423,268; 4,417,088; 4,414,423; 4,417,086; and 4,417,087, the contents of which are hereby incorporated by reference.

ELAPOs (Including SAPOs)

5 Various molecular sieves, particularly small-pore silicoaluminophosphates (SAPOs), are known to promote the conversion of oxygenates such as methanol to olefins such as ethylene and propylene. The methanol to olefin conversion process is preferably carried out at pressures between about 0.001 atmospheres (0.1 kPa) and about 1000 atmospheres (101.3 MPa), preferably between about 0.01 atmospheres (0.1 kPa) and about 100 atmospheres  
10 (10.13 MPa), more preferably, between about 1 and about 20 atmospheres (101.3 kPa to 1.013 MPa). The operating pressures are mainly dictated by the operating temperatures, because of the equilibrium constraint on methanol synthesis. The temperatures may vary over a wide range depending, at least in part, on the selected molecular sieve catalyst. In general, the temperatures are between about 200°C and about 500°C. Temperatures and  
15 pressures outside the stated ranges are not excluded and, of course, must be consistent with the temperatures used in the conversion of syngas to methanol.

Preferred catalysts have relatively small pores, for example less than about 5 Angstroms, as determined by measurements described in D. W. Breck, Zeolite Molecular Sieves by John Wiley & Sons, New York (1974), hereby incorporated by reference in its  
20 entirety. The process may be conducted in the presence of one or more diluents which may be present in the feed in an amount between about 1 and about 99 molar percent.

The reactions tend to provide mixtures of olefins that are predominantly ethylene and propylene, where the ratio of ethylene/propylene on a carbon basis typically ranges from between about 0.1 and about 10, and more typically ranges from between about 0.8 and  
25 about 2.5.

Catalysts useful for this conversion, and which can be incorporated into the catalyst libraries and evaluated using the methods described herein, are described, for example, in U.S. Pat. Nos. 3,928,483, 4,025,575, 4,252,479 (Chang et al.); U.S. Pat. No. 4,496,786 (Santilli et al.); U.S. Pat. No. 4,547,616 (Avidan et al.); U.S. Pat. No. 4,677,243 (Kaiser);  
30 U.S. Pat. No. 4,843,183 (Inui); U.S. Pat. No. 4,499,314 (Seddon et al.); U.S. Pat. No. 4,447,669 (Harmon et al.); U.S. Pat. No. 5,095,163 (Barger); U.S. Pat. No. 5,191,141 (Barger); U.S. Pat. No. 5,126,308 (Barger); U.S. Pat. No. 4,973,792 (Lewis); and U.S. Pat.

No. 4,861,938 (Lewis), the contents of each of which are hereby incorporated by reference. Additional catalysts and conditions are also described in PCT WO 98/57743, the contents of which are hereby incorporated by reference.

Non-zeolitic molecular sieves include molecular sieves that have the proper effective pore size and are embraced by an empirical chemical composition, on an anhydrous basis, expressed by the empirical formula:



where EL is an element selected from the group consisting of silicon, magnesium, zinc, iron, cobalt, nickel, manganese, chromium and mixtures thereof, x is the mole fraction of EL and is at least 0.005, y is the mole fraction of Al and is at least 0.01, z is the mole fraction of P and is at least 0.01 and  $x+y+z=1$ . When EL is a mixture of elements, x represents the total amount of the metal mixture present. Preferred elements (EL) are silicon, magnesium and cobalt with silicon being especially preferred. Numerous ELAPOs are known in the art and are described, for example, in U.S. Pat. No. 5,191,141 (ELAPO); U.S. Pat. No. 4,554,143 (FeAPO); U.S. Pat. No. 4,440,871 (SAPO); U.S. Pat. No. 4,853,197 (MAPO, MnAPO, ZnAPO, CoAPO); U.S. Pat. No. 4,793,984 (CrAPO), U.S. Pat. Nos. 4,752,651 and 4,310,440, the contents of each of which are hereby incorporated by reference.

Generally, the ELAPO molecular sieves are synthesized by hydrothermal crystallization from a reaction mixture containing reactive sources of EL, aluminum, phosphorus and a templating agent. Reactive sources of EL are the metal salts such as the chloride and nitrate salts. When EL is silicon, a preferred source is fumed, colloidal or precipitated silica. Preferred reactive sources of aluminum and phosphorus are pseudo-boehmite alumina and phosphoric acid. Preferred templating agents are amines and quaternary ammonium compounds.

Especially preferred ELAPOs are those in which EL is silicon (usually referred to as SAPOs). Examples of SAPOs that can be included in the catalyst libraries include those described in U.S. Pat. Nos. 4,440,871, 5,126,308, and 5,191,141. Preferred SAPOs include SAPO-11, SAPO-17, SAPO-31, SAPO-34, SAPO-39, and SAPO-41, and the catalyst libraries preferably include these catalysts when conversion of methanol to olefins is desired.

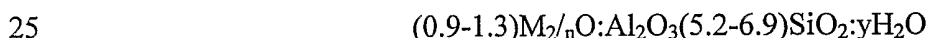
### Zeolites

Catalysts useful for converting methanol to aromatics and iso-paraffins typically include one or more zeolites and/or non-zeolitic molecular sieves.

5       The zeolites and/or molecular sieves are preferably intermediate pore size zeolites, although zeolites with large and/or small pore sizes can be included in the catalyst libraries. Small pore zeolites tend to be selective for olefins, like the small-pore SAPO's. However, increased space velocities or reductions in crystallite size may favor removing olefins from the zeolite environment before they can react further, which tends to alter the product  
10       distribution to favor olefins over iso-paraffins or aromatics. Large pore zeolites tend to produce pentamethylbenzene and hexamethylbenzene, which are undesirable because they are solids at ambient temperatures.

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;  
15       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  
20       is described in U.S. Patent No. 5,624,657 (Vaughan) are also preferably included in the libraries. Preferred zeolites are intermediate pore (10-ring) zeolites, as these limit the formation of polynuclear aromatics. Most preferred are ZSM-5 and ZSM-11.

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



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.

Examples of useful large pore zeolites include ZSM-3, ZSM-4, ZSM-10, ZSM-12, ZSM-20, zeolite beta, zeolite omega, zeolite L, zeolite X, zeolite Y, REY, USY, RE-USY, mordenite, LZ-210, LZ-210-M, LZ-210-T, LZ-210-A, SSZ-24, SSZ-26, SSZ-31, SSZ-33, SSZ-35, SSZ-37, SSZ-41, SSZ-42, SSZ-44 and MCM-58, any and all of which are preferably incorporated into the libraries. ZSM-3 is described in U.S. Patent No. 3,415,736. ZSM-4 is described in UK Application No. 1,117,568. ZSM-10 is described in U.S. Patent No. 3,692,470. ZSM-12 is described in U.S. Patent No. 3,832,449. ZSM-20 is described in U.S. Patent No. 3,972,983. Zeolite beta is described in U.S. Patent No. Re. 28,341 (of original U.S. Patent No. 3,308,069). Zeolite omega is described in U.S. Patent No. 4,241,036. Zeolite L is described in U.S. Patent No. 3,216,789. Zeolite X is described in U.S. Patent No. 2,882,244. Zeolite Y is described in U.S. Patent No. 3,130,007. LZ-210, LZ-210M, LZ-210-T, LZ-210-A and mixtures thereof are described in U.S. Patent No. 4,534,853. SSZ-24 is described in U.S. Patent No. 4,834,977. SSZ-26 is 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.

Examples of useful intermediate pore size zeolites include ZSM-5, ZSM-11, ZSM-22, ZSM-23, ZSM-35; ZSM-48, ZSM-57, SUZ-4, SSZ-23; SSZ-25; SSZ-28, SSZ-32, and SSZ-36. ZSM-5 is described in U.S. Patent No. Re. 29,948 (of original U.S. Patent No. 3,702,886). ZSM-11 is described in U.S. Patent No. 3,709,979. ZSM-22 is described in U.S. Patent No. 4,556,477. ZSM-23 is described in U.S. Patent No. 4,076,842. ZSM-35 is described in U.S. Patent No. 4,016,245. ZSM-48 is described in U.S. Patent No. 4,585,747. SUZ-4 is described in EP Application No. 353,915. SSZ-23 is described in U.S. Patent No. 4,859,422. SSZ-25 is described in U.S. Patent Nos. 4,827,667 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.

The catalysts typically also include a binder such as a refractory oxide, e.g., silica, alumina, chlorided alumina or silica-alumina.

Combinations of relatively non-acidic and relatively acidic zeolites can be prepared to tailor the acidity and used to effect a desired conversion without forming undesired aromatics. "Virtual" arrays of zeolite types versus treatment methods/levels can be prepared. For example, one can synthesize some zeolites with only a narrow range of Si/Al ratios. These can then be adjusted up or down by various dealumination or aluminum insertion processes. Zeolites with relatively low Si/Al ratios can be prepared from the corresponding borosilicate versions by Al insertion.

The entire contents of all the above-cited patents are incorporated herein by reference, and any and all of the zeolites described therein can be included in the catalyst libraries.

#### Borosilicates and Metallosilicates

The term "silicate" refers to a zeolite having a high mole ratio of silicon oxide relative to aluminum oxide, preferably a mole ratio greater than 100. As used herein, the term "aluminosilicate" refers to a zeolite containing both alumina and silica, and the term "borosilicate" refers to a zeolite containing oxides of both boron and silicon. Zeolites may also contain other elements in place of silicon that can contribute a weaker form of acidity than aluminum, for example gallium (gallosilicates), iron (ferrosilicates), indium, titanium and vanadium.

Crystalline aluminosilicates are usually prepared from aqueous reaction mixtures containing alkali or alkaline earth metal oxides, silica, and alumina. Crystalline borosilicates are usually prepared under similar reaction conditions except that boron is used in place of aluminum. For example, borosilicates can be prepared by (1) preparing a mixture containing an oxide of silicon, an oxide of boron, a hydroxide of an alkali metal or an alkaline earth metal, an alkyl ammonium cation or a precursor of an alkyl ammonium cation, and water; and (2) maintaining said mixture at suitable reaction conditions to effect formation of said borosilicate, said reaction conditions comprising a reaction temperature within the range of about 25°C to about 300°C, a pressure of at least the vapor pressure of water at the reaction temperature, and a reaction time that is sufficient to effect

crystallization. By varying the synthesis conditions and the composition of the reaction mixture, different zeolites can often be formed.

Crystalline borosilicates useful in the combinatorial libraries preferably have the following compositions in terms of mole ratios of oxides:

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where M is at least one cation having a valence of n, Y is between 4 and about 600, and Z is between 0 and about 160.

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Examples of borosilicates that can be included in the second catalyst library include those described in U.S. Pat. No. 4,268,420, U.S. Pat. No. 4,269,813, U.S. Pat. No. 4,292,457, and U.S. Pat. No. 4,292,458, the contents of which are incorporated herein by reference. Specific examples include AMS borosilicate molecular sieves, Amoco Borosilicate (AMS-1B) ZSM-5 as described in U.S. Pat. No. 4,269,813;

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Niobium-borosilicate ZSM-5 as described in EP 0 089 574; Borosilicate (ZBH) Pentasil as described in EP 0 077 946; borosilicate ZSM-5 as described in EP 0 046 504; Titanoborosilicate (ZMQ-TB) ZSM-5 as described in EP 0 104 107; Ironborosilicate ZSM-5 as described in EP 0 148 038, Hoechst Boro-aluminosilicate as described in EP 0 073 482, Idemitsu Borosilicate as described in Japan O7 817, National Distillers Borosilicates (USI-10B) as described in U.S. Pat. No. 4,423,020, Snamprogetti Borosilicate (Boralite A) as described in Nu-1 Italy 22 638, and Boralites B, C, D and E ZSM-5 as described in Italian Patent No. 22 638 and German Patent No. 3 316 488.

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Borosilicates are typically prepared by (1) preparing a mixture containing an oxide of silicon, an oxide of boron, a hydroxide of an alkali metal or an alkaline earth metal, an alkyl ammonium cation or a precursor of an alkyl ammonium cation, and water; and (2) maintaining said mixture at suitable reaction conditions to effect formation of said borosilicate, said reaction conditions comprising a reaction temperature within the range of about 25°C to about 300°C, a pressure of at least the vapor pressure of water at the reaction temperature, and a reaction time that is sufficient to effect crystallization.

30

If the borosilicates are not acidic enough for use in a desired conversion, they can be combined, in varying amounts, with relatively more acidic zeolites. The combinatorial

approach can advantageously be used to find an appropriate balance in the acidity of the catalysts - enough to effect the desired conversion, but not enough to result in the formation of undesired aromatics.

5        Carriers

Any of the catalysts described above, and combinations thereof, may be formed in any conventional manner, such as tableting, pelleting, or supporting the active catalyst material on a carrier. The carrier is preferably inert and may include silica, alumina, Alundum, clay, alumina-silica, silicon carbide, zeolite, and the like. The catalysts can be  
10 incorporated into solid particles in which the catalyst is present in an amount effective to promote the desired conversion.

In one aspect, the solid particles comprise a catalytically effective amount of the catalyst and at least one matrix material, preferably selected from the group consisting of binder materials, filler materials, and mixtures thereof to provide a desired property or  
15 properties, e.g., desired catalyst dilution, mechanical strength, and the like to the solid particles. Filler and binder materials include, for example, synthetic and naturally occurring substances such as metal oxides, clays, silicas, aluminas, silica-aluminas, silica-magnesias, silica-zirconias, silica-thorias, silica-beryllias, silica-titanias, silica-alumina-thorias, silica-alumina-zirconias, aluminophosphates, mixtures of these and the like. If matrix  
20 materials, e.g., binder and/or filler materials, are included in the catalyst composition, the catalysts preferably comprise about 1 to 99%, more preferably about 5 to about 90% and still more preferably about 10 to about 80%, by weight of the total composition.

The preparation of solid particles comprising catalyst and matrix materials is conventional and well known in the art and, therefore, need not be discussed in detail  
25 herein.

Pre-treatments

In addition to catalyst composition and reaction conditions, a third set of variables with great influence on the catalytic activity/selectivity is the manner in which various "pre-  
30 treatment" steps are carried out. Such pre-treatment variations include the time and temperature of catalyst washing; heating rate, hold time, hold temperature, and relative

humidity during drying. The same pre-treatments can be varied during catalyst calcining, reduction and activation. In catalyst reduction, the hydrogen content and total pressure can also be varied, as can the pressure and CO partial pressure during activation in CO. Other reduction methods can also be used, including as treatment with citrate, alcohols and metal hydrides. Additional pre-treatments can also be performed, including modifying the acidity using acid leaching, base titration, ion exchange, vapor deposition of Si or Al species and steaming. These pre-treatments can be done individually or in combination on the individual catalyst components or on the composite. These different pre-treatments can be used with the different catalyst compositions to increase the size of the catalyst libraries. Alternatively, a single catalyst can be subjected to a plurality of different pre-treatments, or a library of catalysts can be subjected to a single pre-treatment, with the process repeated as desired.

#### Arrays

Libraries of catalysts can be prepared and evaluated using the devices and methods described herein. The first and second catalyst systems are preferably arranged in the reaction vessels in the form of arrays. The catalysts can be, but need not be, synthesized directly in the reaction vessels, but rather can be formed ahead of time and evaluated using the devices and processes described herein. In a less preferred embodiment, a single catalyst of a first type (a methanol synthesis or methanol converting catalyst) is used with a plurality of a second type of catalyst, and then subsequent catalysts of the first type can be evaluated with a plurality of the second type of catalyst, with the process repeated as desired.

Preferably, the process involves generating a matrix including a first catalyst system and a second catalyst system, where the first catalyst system converts syngas to methanol and the second catalyst system converts the methanol to higher molecular weight products. The synthesis is performed in a device which can handle the temperature and pressure requirements, as well as being able to handle a plurality of catalyst combinations (preferably more than 5 catalyst combinations at a time, more preferably greater than 20 catalyst combinations at a time, and, more preferably, more than about 50 catalyst combinations at a time) and the product stream from the various reactions is then evaluated. Reaction vessels



useful for conducting reactions under relatively high temperatures and pressures are well known to those of skill in the art.

The process preferably involves a combination of lead generation and lead optimization. Given the relatively large number of combinations of catalysts, pre-treatment  
5 conditions, reaction conditions and the like, it may be desirable to keep one set of conditions constant while varying another set of conditions, to arrive at reasonable leads. Once the leads are generated, they can be optimized by varying the other conditions. In one embodiment, an  $A \times B \times C \times D \times E$  array can be evaluated over the course of successive lead generation and lead optimization, where A and B are the catalysts to be used (including  
10 zeolite pre-treatments), C is their relative proportion, D is variation in activation, and E is variation in test conditions. In this manner, what might otherwise be millions of possible combinations can be narrowed to a more manageable number.

The identity of the catalyst system in each reaction vessel or in each position in a reaction vessel can be stored in a computerized device. The products of the reaction can be  
15 readily identified, for example by gas chromatography (GC), a combination of gas chromatography and mass spectrometry (GC/MS), infrared heat emissions or 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  
20 solid phase extraction (SPE) column.

In one embodiment, a mixture of methane, water and carbon dioxide is reacted in the presence of a third catalyst system to form "virtual" syngas, which is converted to methanol, which is then converted to higher molecular weight products. Optimization of combination of three catalyst systems provides an  $A \times B \times C$  array.

#### Reactors suitable for conducting chemistry

As used herein, a reaction vessel is any suitable container which can hold a plurality of combinations of catalyst systems, which can contain from about 200 mg to about 100 g,  
30 preferably, from about 1 mg to about 10 g of each catalyst combination, and which can handle the reaction conditions necessary for converting syngas to methanol and methanol to

product streams including higher molecular weight hydrocarbons, for example, conditions of increased pressure and temperature.

Any reaction vessel that is capable of being used to conduct a plurality of simultaneous reactions using gas phase reactants and solid catalysts under conditions of elevated temperature and pressure can be used. Such reaction vessels are well known to those of skill in the art. Examples of suitable devices include those described, for example, in U.S. Patent No. 5,980,839 to Bier et al., U.S. Patent No. 6,036,923 to Laugharn, Jr. et al., U.S. Patent No. 6,030,917 to Weinberg et al., U.S. Patent No. 6,001,311 to Brennan, the contents of each of which are hereby incorporated by reference.

The reaction vessel can contain multiple sample vessels, in parallel or in series, to perform combinatorial or sequential operations, respectively. The reactor can include a reaction region that includes a plurality of individual reaction cavities, each of which can have a port adapted to supply or remove reagents, solvents, gases and/or vacuum suction to the cavity. There can be a mixing region disposed adjacent to the reaction region, such that the reaction cavities open into the mixing region. The vessel can be constructed from a variety of materials, depending on the pressure and temperature requirements of the isosynthesis, examples of which can include certain plastics, glass and certain metals such as stainless steel.

The scale of the synthetic reactions is preferably in the range of greater than about 200 mg, more preferably between one mg and 100 g, although the scale can be modified depending on the amount of compound necessary for the particular application. The reactions are typically performed under conditions of relatively high temperature and/or pressure. Following the reactions, the products can be characterized using a variety of means, for example GC, GC/MS, HPLC and the like.

In one embodiment, syngas is converted to methanol in a first reaction vessel using the first catalyst system, and methanol is then converted to higher molecular weight products in a second reaction vessel using the second catalyst system. In a preferred embodiment, syngas is converted to methanol and then directly to higher molecular weight products in a single reactor using a mixed catalyst bed that includes both the first and second catalyst systems.

Robotic arms and multi-pipet devices can be used to add appropriate catalysts to the appropriate locations in the reaction vessel. When appropriate, the chemistry can be performed under varying conditions of temperature, pressure, flow rate and the like. When elevated temperatures and pressures are required, devices capable of handling elevated temperatures and pressures, particularly for use in combinatorial chemistry, are used.

In one embodiment, the reactions are carried out via computer control. The identity of each of the catalysts can be stored in a computer in a "memory map" or other means for correlating the data regarding the chemical reactions to the catalyst combinations in the reaction vessels. Alternatively, the chemistry can be performed manually, and the information stored, for example on a computer.

Those of skill in the art can readily determine appropriate sets of reactions and reaction conditions to generate and/or evaluate the libraries of interest.

#### Method Steps

The method steps in the preferred embodiment of the present invention involve:

a) preparing a logical array of catalysts in one or more reaction vessels, where the array includes one or more catalysts from a first catalyst system which converts syngas to methanol, and one or more catalysts from a second catalyst system which converts methanol to higher molecular weight products,

b) storing the identity of the catalyst systems in each position in the logical array in a relational database,

c) introducing syngas to the reaction vessel(s) under conditions which convert syngas to methanol and methanol to product streams including higher molecular weight products,

d) analyzing the contents of the product streams, and

e) optionally storing information regarding the contents of the product streams in a relational database.

While it is preferred that step c) be performed in a single reactor, the syngas can be converted to methanol in a first reactor and transferred to a second reactor where the methanol is converted to higher molecular weight products. It is preferred that the catalyst

combinations (or composites) be evaluated in a single reactor, although it is possible that the catalysts can be evaluated in separate reactors.

In one embodiment, to effectively compare catalyst combinations, the reaction conditions (syngas composition, temperature and pressure) should be kept reasonably constant while evaluating the entire library. However, the reaction conditions can be varied in subsequent runs to provide additional data. Accordingly, steps a-e can be repeated one or more times, with varying reaction conditions (for example, changes in syngas composition, temperatures and/or pressures, to obtain additional information). In another embodiment, many variables are modified simultaneously, and the experiments are performed in sequences chosen to cancel out changes in the experimental apparatus with time. In either embodiment, some variables will likely be held constant for a given set of parallel tests.

Preferably, the absolute pressure is not more than 50%, more preferably 35%, most preferably, 20% higher or lower than would be used in a commercial plant. The temperature is preferably not more than 200°F, more preferably not more than 100°F, and most preferably, not more than 50°F higher or lower than would be used commercially. Preferably, the flow of reagents follows the same path (i.e., downflow, upflow, mixed reactor) as they would in a commercial plant. Preferably, the reagents are in the same phases as would be used commercially. The devices and processes described herein can be used for the rapid determination and optimization of desired catalyst activity for producing a given desired product stream. An array of catalysts systems can be screened and the optimum candidates for providing a desired product stream identified. This process can be repeated as desired to provide information regarding the catalyst systems of interest and the selection can be accelerated by the rapid modular synthesis of arrays for use in testing.

Combinations of catalysts which appear to provide desired product streams can optionally be scaled up (for example, in a lead optimization step) to obtain additional data and to fine-tune the process. For example, once ideal catalyst combinations are identified in a lead generation step, the reaction conditions (syngas composition, temperature and pressure) can be optimized in a lead optimization step.

The devices and processes described herein can be used for the logical and rapid analysis of synthetic results for various properties, including cetane and/or octane values,

degree of isomerization, olefin concentration, aromatic concentration, and the like. One can determine the efficacy of a synthetic strategy by testing a series of loci within any given array. Accordingly, the general usefulness of various catalyst combinations for providing a desired product stream can be determined.

5           The devices and methods described herein provide for the complete control of the analysis of entire libraries of catalyst combinations.

#### Analytical Chemistry

10           The products of the reactions can be analyzed in a high throughput manner, for example using HPLC, GC and/or other analytical methods. The products can be assayed for various properties, including octane and/or cetane values, degree of isomerization, olefin concentration, aromatics concentration, and the like.

15           Any device that can take samples from the individual positions in the reaction vessels and analyze the resulting compounds can be used. Preferably, the device is a chromatographic device, such as an analytical or preparative scale HPLC, GC or column chromatography, although other devices can be envisioned, depending on the chemistry performed.

20           After the chemical reactions take place, the contents of the reaction vessels (or a representative sample thereof) can be individually transferred to an analytical device. 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.

25           Preferably, in those embodiments in which a chromatographic column (HPLC, GC or column chromatography) is used, the device has the ability to identify when the compound(s) of interest is eluting from the column. Various means have commonly been used to identify when compounds of interest are eluting from a column, including ultraviolet (UV), infrared (IR), thin layer chromatography (TLC), GC-MS, flame ionization detector (FID), nuclear magnetic resonance (NMR), electron light scattering detector (ELSD), nitrogen detection and the like. Any of these means, and others known to those of skill in the art, can be used, alone or in combination. However, in those embodiments where the  
30           product stream does not include UV-active compounds, the analytical equipment preferably includes an ELSD detector.

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.

5           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. A suitable model for product distributions can easily be prepared that assigns a value for each product, and together with  
10   the activity and selectivity data, can calculate both CAPEX and OPEX for a commercial operation. This can be used to estimate a net present value. The number can be optimized, within certain constraints, for example limits on how much aromatics, methane or other products would be acceptable.

#### 15           Database

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

The device preferably includes 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  
25   on the computer. Relational database software can be used to correlate the identities of the catalysts, the reaction conditions (for example, reagent composition, temperature and pressure) and the analytical data from each product stream. Numerous commercially available relational database software programs are available, for example from Oracle, Tripos, MDL, Oxford Molecular ("Chemical Design"), IDBS ("Activity Base"), and other  
30   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 that 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.

We claim:

1. A method for discovering optimum catalyst systems for the conversion of syngas to higher molecular weight products via a methanol intermediate comprising:

- a) preparing a first library of catalysts for converting syngas to methanol,
- 5 b) preparing a second library of catalysts for converting methanol to higher molecular weight products,
- c) preparing a plurality of combinations of catalysts from the first and second libraries in a logical manner, and
- d) reacting syngas with the catalysts under appropriate reaction conditions to form  
10 a plurality of reaction products.

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

3. The method of claim 1, further comprising storing information regarding the identity of the catalysts in the plurality of combinations of catalysts in a database.

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

5. The method of claim 1, wherein the combinations of catalysts are arranged in a logical array.

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

20 7. The process of claim 6, wherein the reaction conditions which are varied are selected from the group consisting of temperature, pressure, syngas composition, and flow rate.

8. The method of claim 1, wherein the first and/or second catalyst library include catalysts with similar composition but which are prepared using different pre-treatments  
25 and/or catalyst activations.

9. The method of claim 1, wherein at least one of the catalysts is a SAPO.

10. The method of claim 1, wherein at least one of the catalysts is an intermediate pore size zeolite.

30 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 oil range

5        14. The method of claim 1, wherein the syngas is prepared *in situ* via conversion of carbon dioxide, methane and water in the presence of an appropriate catalyst.

15. The method of claim 1, wherein the products include C<sub>2-4</sub> olefins.

16. The method of claim 1, wherein the products include aromatics.

17. The method of claim 1, wherein the products include iso-paraffins.

10       18. A method for rapidly determining an appropriate set of reaction conditions and catalyst combinations to form a desired product via conversion of syngas to methanol and conversion of methanol to higher molecular weight products comprising:

a) preparing a first library of catalysts for converting syngas to methanol,

b) preparing a second library of catalysts for converting methanol to higher  
15 molecular weight products,

c) preparing a plurality of combinations of catalysts from the first and second libraries in a logical manner, optionally pre-treating them in a plurality of ways and

d) reacting syngas with the catalysts under a plurality of reaction conditions to form a plurality of reaction products, wherein each set of reaction conditions is applied to all  
20 or substantially all of the catalyst combinations,

e) storing information regarding the products of the reactions in a database, and

f) identifying an appropriate set of reaction conditions and catalyst combinations to produce the desired product.

19. A method for rapidly determining an appropriate set of reaction conditions and  
25 catalysts to form a desired product via conversion of syngas to methanol and conversion of methanol to higher molecular weight products comprising:

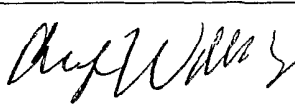
a) preparing a library of catalysts that are active at both converting syngas to methanol and converting methanol to higher molecular weight products,

b) reacting syngas with the catalysts under a plurality of reaction conditions to  
30 form a plurality of reaction products, wherein each set of reaction conditions is applied to all or substantially all of the catalysts,

- c) storing information regarding the products of the reactions in a database, and
- d) identifying an appropriate set of reaction conditions and catalysts to produce the desired product.

## INTERNATIONAL SEARCH REPORT

national application No.  
PCT/US01/22129

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> IPC(7) : B01J 21/16, 29/04, 29/06, 29/87, 31/00; G01N 31/00, 33/00 US CL : 502/60, 64, 67, 84, 104; 436/37, 139, 140, 141, 142, 143 According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) U.S. : 502/60, 64, 67, 84, 104; 436/37, 139, 140, 141, 142, 143 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) Please See Extra Sheet.		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	SENKAN, S.M. High-Throughput Screening of Solid-State Catalyst Libraries. Nature, 23 July 1998, Vol. 394, pp. 350-353, see entire document.	1-19
Y, P	US 6,214,195 B1 (YADAV et al) 10 April 2001, see Abstract; column 16, lines 14-18; Table 1; Tables 5A - 5F; Tables 6A and 6B; Tables 7D - 7G.	1-19
Y	PITTMAN et al. Sequential Multistep Reactions Catalyzed by Polymer-Anchored Homogeneous Catalysts. J. Am. Chem. Soc., April 1975, Vol. 97, No. 7, pp. 1749-1754, see entire document, especially Abstract, Scheme I and Tables I and II.	1-19
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
*	Special categories of cited documents:	
"A"	document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E"	earlier document published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means	"G" document member of the same patent family
"P"	document published prior to the international filing date but later than the priority date claimed	
Date of the actual completion of the international search	Date of mailing of the international search report	
09 SEPTEMBER 2001	<b>19 NOV 2001</b>	
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	Authorized officer  MAURIE E. GARCIA 	
Facsimile No. (703) 305-3230	Telephone No. (703) 308-0196	

## INTERNATIONAL SEARCH REPORT

national application No.  
PCT/US01/22129

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	KLEIN et al. Combinatorial Material Libraries on the Microgram Scale with an Example of Hydrothermal Synthesis. Angew. Chem. Int. Ed. December 1998, Vol. 37, No. 24, pp. 3369-3372, see entire document.	1-19
Y	AKPORIAYE et al. Combinatorial Approach to the Hydrothermal Synthesis of Zeolites. Angew. Chem. Int. Ed. March 1998, Vol. 37, No. 5, pp. 609-611, see entire document.	1-19
Y	WO 00/32308 A2 (SYMYX TECHNOLOGIES, INC.) 08 June 2000 (08.06.00), see Abstract; page 2, lines 1-23; page 28, line 31 through page 29, line 13; claims 32, 75, 81 & 82.	1-19
Y	US 4,099,923 A (MILBERGER) 11 July 1978, see entire document.	1-19
Y	WO 96/11878 A1 (THE REGENTS OF THE UNIVERSITY OF CALIFORNIA) 25 April 1996 (25.04.96), see page 1, lines 17-34; page 13, line 26; page 14, lines 22-24; page 53, line 6; page 70, line 25 through page 72, line 21.	1-19
Y	US 6,030,917 A (WEINBERG et al) 29 February 2000, see Abstract; column 1, lines 15-25; column 3, lines 29-54; column 26, line 56 through column 30, line 59; Figures 16 & 21.	1-19

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/US01/22129

## Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
  
2. ☐ Claims Nos.:  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
  
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Please See Extra Sheet.

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☒ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
  
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐

The additional search fees were accompanied by the applicant's protest.

☐

No protest accompanied the payment of additional search fees.

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US01/22129

### B. FIELDS SEARCHED

Electronic data bases consulted (Name of data base and where practicable terms used):

WEST, STN (CAPLUS, SCISEARCH)

Terms: catalyst, catalysis, zeolite, Fischer-Tropsch, hydrogenation, dehydrogenation, combinatorial, library, array, reactor

### BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING

This ISA found multiple inventions as follows:

This application contains the following inventions or groups of inventions which are not so linked as to form a single inventive concept under PCT Rule 13.1. In order for all inventions to be searched, the appropriate additional search fees must be paid.

Group I, claim(s) 1-18, drawn to a method for discovering optimum catalyst systems and/or reaction conditions using two libraries of catalysts.

Group II, claim(s) 19, drawn to a method for rapidly determining an appropriate set of reaction conditions and catalysts using a single library of catalysts.

The inventions listed as Groups I-II do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons:

The groups lack a same or corresponding special technical feature that links them. The technical feature that links the claims in each group are the specific steps, materials needed and end results of each of the methods. The method of each of the groups is different from the others. The methods are distinct, each from the other because they use different steps, require different reagents and will produce different products. They therefore have different issues and represent distinct subject matter. This is elaborated upon below.

The methods of Groups I and II differ from each other because each represents a different method. The method of Group I requires two separate libraries, while the method of Group II requires only a single library.

See 37 CFR § 1.475 Unity of invention before the International Searching Authority, the International Preliminary Examining Authority and during the national stage, cited in part below.

*(a) An international and a national stage application shall relate to one invention only or to a group of inventions so linked as to form a single general inventive concept ("requirement of unity of invention"). Where a group of inventions is claimed in an application, the requirement of unity of invention shall be fulfilled only when there is a technical relationship among those inventions involving one or more of the same or corresponding special technical features. The expression "special technical features" shall mean those technical features that define a contribution which each of the claimed inventions, considered as a whole, makes over the prior art.*

*(b) An international or a national stage application containing claims to different categories of invention will be considered to have unity of invention if the claims are drawn only to one of the following combinations of categories:*

*A product and a process specially adapted for the manufacture of said product; or*

*A product and process of use of said product; or*

*A product, a process specially adapted for the manufacture of the said product, and a use of the said product; or*

*A process and an apparatus or means specifically designed for carrying out the said process; or*

*A product, a process specially adapted for the manufacture of the said product, and an apparatus or means specifically designed for carrying out the said process.*

*(c) If an application contains claims to more or less than one of the combinations of categories of invention set forth in paragraph*

*(b) of this section, unity of invention might not be present.*

*(d) If multiple products, processes of manufacture or uses are claimed, the first invention of the category first mentioned in the claims of the application and the first recited invention of each of the other categories related thereto will be considered as the main invention in the claims, see PCT Article 17(3)(a) and § 1.476(c).*

The instant international application does **not** contain combinations of categories of invention set forth in paragraph (b) above. The application instead contains multiple methods, as discussed in (c) and (d) above. Thus, the instant claims lack unity of invention for this reason and the reasons set forth above.