(57) Abstract: Reagents and methods with low thermodynamic barriers can convert lower alkanes such as methane into methanol or other derivatives. One system uses a small quantity of a non-salt radical initiator such as Marshall’s acid, a di-acid peroxide that can be split into two radicals. These radicals will remove hydrogens from methane, to generate methyl radicals. Sulfur trioxide is added, and methyl radicals combine with it to form methylsulfonate radicals. Methane is added, and the methylsulfonate radicals will remove hydrogens from it, to form stable methane-sulfonic acid (MSA) while creating new methyl radicals to sustain the chain reaction. MSA that is removed can be sold or used, or it can be split into methanol (which can be used on site, or shipped as a liquid) and sulfur dioxide (which can be oxidized to sulfur trioxide and returned to the reactor). This anhydrous system creates no salts and minimal waste. An alternate system uses a bifunctional reagent with electrophilic and nucleophilic domains (such as a bromate-sulfate compound) to create coordinated proton and electron shifts in methane, using symphoric and anhimeric effects to create transitional intermediates with low energy barriers, allowing selective formation of intermediates that can be cracked to release methanol. Either system can improve the selectivity and yield of methanol from methane.
Published: without international search report and to be republished upon receipt of that report

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ANHYDROUS CONVERSION OF METHANE AND OTHER LIGHT ALKANES INTO METHANOL AND OTHER DERIVATIVES, USING RADICAL PATHWAYS AND CHAIN REACTIONS WITH MINIMAL WASTE PRODUCTS

RELATED APPLICATIONS
This application claims the benefit under 35 USC 119(e) of provisional application 60/424,091, filed on November 5, 2002, and of provisional application 60/480,183, filed on June 21, 2002.

FIELD OF THE INVENTION
This invention relates to organic chemistry, and to chemical processing of methane (or other light alkanes) to convert it into methanol or other useful derivatives.

BACKGROUND OF THE INVENTION
Despite intensive efforts by numerous research teams over at least 60 years, no one has previously succeeded in discovering and clearly identifying an efficient and economical chemical reaction scheme for converting methane into methanol or other derivatives.

Methane (\(\text{CH}_4\)) is a highly volatile and explosive gas, and its presence in crude oil renders the crude oil more difficult, dangerous, and expensive to handle and transport. As an illustration, if crude oil is going to be pumped into a pipeline, a high methane content would lead to the formation of large gas bubbles, inside the pipeline. If these gas bubbles were allowed to form, they would begin acting in a manner comparable to springs, and each stroke of a pump would
simply compress the bubbles, rather than driving the liquid forward. Therefore, methane must be
removed, before crude oil can be pumped into a pipeline.

Similarly, methane must also be removed before crude oil can be loaded into a tanker or
holding tank. Otherwise, the high pressures generated by the methane gas, as it tries to escape
from the oil, would require stronger and more expensive tanks, as well as complex and expensive
vapor-handling systems, and the constant emergence of volatile methane from the oil would
greatly increase the risk of explosion or fire.

Therefore, crude oil that emerges from a wellhead usually must be run through a
separator, to remove the methane from the liquid components, before the crude oil can be safely
pumped into pipelines, tankers, or tanks.

In many small and moderate-sized oil fields throughout America, and in many very large
oil fields in Africa, Indonesia, the North Slope of Alaska, and elsewhere (including many
offshore oil fields and platforms), there are no gas pipelines nearby that can transport methane
gas to commercial markets. As a result, the methane produced at those oil facilities is usually
referred to by terms such as "stranded" gas, or "waste gas". Relatively small portions of it are
burned as fuel, to keep the oil-producing equipment running, but normally a huge volume of gas
remains left over, and cannot be efficiently utilized. It also cannot be released into the
atmosphere, partly because it can create an explosion risk near the release site, and partly because
it is roughly 20 times more potent as carbon dioxide, on a per weight basis, in contributing to the
greenhouse effect and global warming.

Therefore, every month, literally billions of dollars worth of methane gas must be
disposed of, as waste gas. Much of it is burned in wasteful, unproductive flares (which emit large
quantities of carbon dioxide, a greenhouse gas that aggravates the problem of global warming).
Another large portion is injected back into the ground.

Another major source of "stranded" natural gas is located in natural gas fields that do not
produce large quantities of crude oil. Numerous such gas fields are known to exist in various
locations around the world, but the gas cannot be extracted from them and then transported to
distant commercial markets, in a economically feasible manner.

Still other sources of unused methane are located at coal mines, since methane is
commonly associated with coal. In addition, smaller quantities of methane are produced at
various types of waste-handling facilities, including landfills that handle organic wastes, and livestock facilities that handle large quantities of animal manure. Although such sources are frequently excluded when "stranded" gas is being discussed by those who are focusing on the huge reserves of stranded gas at remote oil and gas fields, the numerous smaller sources nevertheless add up to very large quantities, when considered in the aggregate, on a global level.

Many people and companies have attempted to create various methods for using "stranded" methane gas; however, all such efforts have been severely limited, by very high expenses and operating costs. As one example, specially-designed tanker ships have been built which can transport "liquefied natural gas" (LNG) across oceans. Liquified natural gas requires extremely cold ("cryogenic") temperatures, far below the freezing point of water (LNG is typically transported at temperatures of roughly -260° Fahrenheit). Therefore, LNG tanker ships typically contain three or four huge spherical insulated tanks (often referred to as "thermos bottles"), which typically are partially visible as a row of three or four giant semi-circles above the decks of these types of ocean-going ships.

Specialized LNG tankers, the manufacturing facilities required to refrigerate natural gas down to hundreds of degrees below zero, and the specialized types of pumps and pipelines that are required to store, handle, and pump LNG in a safe manner, are extremely expensive, costing multiple billions of dollars for a large facility and a fleet of tankers. Just as importantly, they burn up a large fraction of the feedstock methane, to drive the cooling and heating equipment. To drive the refrigeration systems that will chill methane to a temperature where it will liquify, such facilities usually burn about 40% of their total methane feedstock; then, once the liquified methane has been loaded onto a tanker, shipped to a destination port, and unloaded from the tanker, another substantial portion of the methane must be burned, in order to re-vaporize the remainder and bring it up to reasonable operating temperatures that can be handled by conventional pipelines. Therefore, LNG systems typically must burn up almost half of their entire starting feedstock, in order to deliver the other half to a commercial market.

Similar operating economics also apply to a product that is usually called synthesis gas, synthetic gas, or simply "Syngas". This gas is predominantly a mixture of carbon monoxide, and hydrogen. It can be created by using methane as the major feedstock, usually by "steam reforming" using a nickel catalyst, but this process requires large amounts of energy to drive it.
Therefore, roughly 20 to 30% of a natural gas supply must be burned, to convert the remainder into Syngas. The wastage problem is then aggravated even more, because the resulting Syngas typically requires another highly endothermic (energy-consuming) reaction to convert the Syngas into liquid hydrocarbons and/or alkane hydroxides (e.g., methanol, etc.). Syngas processing is described in numerous articles, patents, and chapters of books (see, e.g., Olah, *Hydrocarbon Chemistry*, 1995, at p. 15).

Other efforts to create economically viable uses for "stranded" methane involve on-site conversion of the methane into useful chemical feedstocks. As one example, the hydrogen atoms from methane molecules can be chemically processed to convert nitrogen (present as N\textsubscript{2} in the atmosphere) into ammonia (NH\textsubscript{4}). The ammonia can then be converted into fertilizer. However, this is not an efficient use, and it has not become widespread, even in developing countries that badly need fertilizers.

Since none of the above reactions are efficient, many researchers have tried to find ways to convert methane into methanol (i.e., methyl alcohol). Methanol has a formula that can be written as CH\textsubscript{3}OH, as H\textsubscript{2}COH, or H\textsubscript{3}C-OH; as indicated by all three formulas, it has three hydrogen atoms, and a hydroxy group (-OH), all bonded to a central carbon atom. The preferred formula herein is H\textsubscript{2}C-OH, since that version helps focus attention on a certain bond.

For similar reasons, various formulas herein are written in ways that focus attention on certain component structures and bonds. For example, the preferred formula herein for methanesulfonic acid is H\textsubscript{2}C-SO\textsubscript{3}H, and the preferred formula herein for Marshall's acid is HO\textsubscript{3}SO-OSO\textsubscript{3}H, rather than the simpler version H\textsubscript{2}S\textsubscript{2}O\textsubscript{8}.

In principle, converting methane into methanol is a highly appealing reaction, for two reasons. First, it merely requires adding a single oxygen atom to methane, and oxygen atoms are abundantly available from the atmosphere. Second, methanol is a liquid that can be easily and safely handled, at normal temperatures and pressures that do not require special and expensive equipment to reach cryogenic temperatures or sustain very high pressures.

The methanol pathway is even more appealing, since methanol has numerous important and valuable uses. As one example, it is a good, clean-burning fuel in its own right, and can be used directly in internal combustion engines that have been "tuned" for methanol; indeed, it is the fuel of choice for certain types of race cars, including high-powered dragsters that need a clean-
burning fuel. Since the engines in those cars usually are run for only very short periods of time, they need a clean-burning fuel that will not generate particulates or residues that will gradually accumulate and foul an engine. Therefore, if a sufficient supply of methanol were available, it could be burned as the primary or sole fuel, in clean-running cars.

Methanol can also be used as an additive for conventional gasoline, in a manner directly comparable to ethanol. When used in that manner, methanol will increase the volume of the gasoline (thereby requiring less gasoline to fill a tank), and it can also help reduce the air pollution from such cars.

Methanol is also a very useful chemical feedstock, for a wide variety of chemical manufacturing operations. In effect, the hydroxy group on methanol serves as a form of "handle", allowing methanol to be easily grabbed and manipulated by any number of other reagents, in ways that cannot be done with methane, a completely symmetric molecule that has no convenient handle.

For all of these reasons, enormous commercial markets for methanol would quickly arise and take shape, if the huge quantities of "stranded" methane gas could be economically converted into methanol. Large-scale methanol creation, at remote oil or gas fields and other sources of that generated wasted or unwanted methane gas, would provide enormous commercial and job-creating benefits, by making efficient use of a valuable energy supply and chemical feedstock. It would also provide major environmental benefits, by eliminating the emissions of huge quantities of carbon dioxide into the atmosphere.

It also should be recognized that even if the supply of gas at a very large oil field can justify the construction and operation of a gas pipeline, the construction and operating expenses, environmental disruptions, and other costs and burdens created by that pipeline (which may include guarding it against a potential terrorist attacks) could be avoided, if methanol conversion could be accomplished efficiently. As one example, the U.S. and Canadian governments, as well as various private companies, must soon decide whether to build a gas pipeline, currently estimated to cost at least 15 billion dollars, from the North Slope of Alaska, through highly sensitive and fragile arctic regions in both Alaska and Canada, to locations that can feed the gas into existing pipeline systems in southern Canada and the northern United States. However, the existing Alaskan oil pipeline (which travels almost directly south, to the port of Valdez on the
southern coast of Alaska) is no longer running at capacity. It has been helping drain the giant Prudhoe Bay reservoir for nearly 30 years, and after that many years, that reservoir is approaching a state of depletion.

Therefore, the Alaska pipeline could handle both crude oil, and methanol, by using a well-known process in which alternating batches of crude oil and methanol would be pumped through a single shared pipeline. To prevent the crude oil from mixing with the methanol, these alternating batches of different liquids can be separated from each other, by mechanical plugs that can be sent through a pipeline. These types of plugs that travel inside pipelines are usually called "pigs", and they are widely used to clean and inspect the insides of oil pipelines.

Accordingly, if methanol could be efficiently converted into methanol at the already-existing Prudhoe Bay oil production facilities, it could eliminate the need to build a huge new gas pipeline through the arctic regions of Alaska and Canada. That would saving billions of dollars in costs, it would avoid major environmental disruptions in highly sensitive and fragile arctic areas, and it would cleanly sidestep-and avoid a long series-of severely divisive, negative, and unhelpful political struggles and distractions.

Similarly, if methane could be efficiently and economically converted into methanol, it could be used as an energy-releasing fuel in various types of fuel cells. In general, the term "fuel cell" is used to refer to any type of reaction vessel that uses controlled chemical reactions to release energy, while stopping short of burning the fuel in ways that create explosive bursts of energy (as occur in internal combustion engines).

Fuel cells that use methanol have never previously been commercialized, since the existing supplies of methanol could not justify large investments in research, development, or commercialization. However, if huge supplies of methanol could be made available by an efficient process that converts stranded methane (at remote oil or gas fields and elsewhere) into methanol, the research efforts that are currently being spent on attempts to create hydrogen-burning fuel cells, for automobiles, likely would be diverted to creating fuel cells that use methanol instead, since methanol offers a number of important advantages over hydrogen fuel. Those advantages include (i) a much higher energy content and density, in a tankful of methanol compared to a tankful of hydrogen; and (ii) greatly reduced requirements for generating extremely high pressures, which are required for hydrogen-burning fuel cells.
Despite all of these known potentials, incentives, and opportunities, no one has previously been able to discover and create an efficient and economical chemical method for converting methane into methanol, or into other useful and functional chemical derivatives. Despite at least 60 years of focused efforts by literally thousands of researchers at major universities and oil companies of all sizes, huge quantities of methane are still being wasted, by being burned in unproductive flares, or pumped back into the ground.

Since numerous skilled chemists have been attempting to find ways to convert methane into methanol for at least 60 years, a brief overview of several such efforts is provided below. This is not intended as an exhaustive or comprehensive history, and anyone interested in this subject should consult additional articles (e.g., Srivastava et al 1992, Fierro 1993, Crabtree 1995, and Labinger 1995) and books (e.g., Olah et al 1995) that provide more information on such efforts.

In addition, at least one networking organization, the Gas Utilization Research Forum, has been formed by academic researchers and industrial managers working on the issues of stranded gas, and a series of annual conferences, called "Monetizing Stranded Gas Reserves" (MSGR), is organized each year by a company called Zeus Development Corporation. Information about these organizations can be located on the Internet at www.remotegasstrategies.com, which is run by Zeus Development Corporation. The agendas and speaker lists for those yearly conferences can be used to identify numerous companies, experts, and areas of focused research that are active in this field.

**PRIOR ART ON CONVERTING METHANE TO METHANOL**

One of the earliest relevant attempts to convert methane to methanol was disclosed in US patents 2,492,983; 2,493,038; and, 2,553,576. All three of those patents were invented by John Snyder and Aristid Grosse, were filed in May 1946, and were assigned to the Houdry Process Corporation.

The information in those three US patents were consolidated into British patent specification GB 632,820, which accordingly is somewhat broader and more useful, in some respects, than any one of the US patents taken alone. However, numerous typographical errors were injected into GB 632,820 by the process that converted it into a computerized "Adobe PDF"
file that can be located and downloaded via the Internet; in addition, the British specification that is available in the PDF version does not contain any page or column numbers. Therefore, the discussion below refers to US patent 2,493,038.

The US 2,493,038 and GB 632,820 patents describe a method for reacting methane with sulfur trioxide, in the presence of a catalyst chosen from the Group II-2 metals (such as mercury). This process resulted in the creation of various sulfonated and/or oxygenated derivatives, including methanesulfonic acid (MSA, with a formula of H3C-SO2H), which could then be broken apart to release methanol. Other oxygenated derivatives included methionic acid, and various esters (such as various methyl sulfate esters, and methyl methane sulfonate).

Regrettably, the teachings of those patents that were filed in the 1940's, and the data provided in the examples, were not expressed with the level of detail or precision that has become expected and standard in patents on chemical inventions today. As one example, the examples do not indicate what type of solvent was used in any particular reaction; instead, US 2,493,038 merely states that water and/or sulfuric acid might or might not be present (e.g., column 3, lines 66-75). Similarly, most examples merely referred to "liquid organic reaction products" as the products formed by the reactions. Although some examples stated that methanol was recovered, even that statement needs to be viewed with caution, since the '038 patent stated in column 4, lines 10-12 that, "when methanol is referred to herein, this term will be understood to include either free methanol, or methanol in the form of a sulfuric acid ester."

Another major problem identified in that early work also should be noted and considered, because it raises a crucially important issue that will have major impacts on any proposed commercial operation. This problem centers on the fact that mixtures of different reaction products were created by the reaction schemes disclosed by Snyder and Grosse. As a general rule, such mixtures are not desirable in systems being evaluated for potential commercialization. Instead, the goal of most efficient reactor systems of this nature is to produce a single desired product, in the highest possible quantities. Therefore, any other byproducts must be regarded as highly unwelcome competitors, parasites, and problems, since they will decrease the yield of the desired product.

The issue of multiple mixed products, created by a candidate reaction scheme, becomes crucial when evaluating the selectivity and yield of individual reactions, as well as multi-step
reaction systems. Selectivity generally refers to the extent to which a certain step (or complete system) creates a single desired and intended product, with minimal quantities of competing and unwanted byproducts. Yield is a related concept, and can be expressed in various terms, such as (i) percentages of reactants converted into intended products, or (ii) weight of products, divided by time (such as kilograms per minute, or tons per hour).

Despite the limitations of that work done in the 1940's by Snyder and Grosse, it formed a major pioneering effort, and it focused attention on sulfur compounds as potentially useful reagents that could be reacted with methane. Numerous efforts by others followed that work, and also focused on ways to react sulfur compounds with methane.

In the 1980's, various US patents, including 4,543,434 (Chang 1985) and 4,864,073 (Han et al, 1989), both assigned to Mobil Oil Corporation, disclosed the use of reaction schemes that passed through intermediates having sulfide (-SH) groups, such as methyl mercaptan (H₃C-SH), to create heavier combined hydrocarbons. Although methyl mercaptan is used in various ways (such as in the manufacture of methanesulfonic acid), it is not used for any purposes that involve the manufacture of methanol.

In the early 1990's, Roy Periana and his coworkers at Catalytica Inc. developed methods for creating methanol, by using concentrated sulfuric acid and mercury catalysts to convert methane into methyl bisulfate, which could then be hydrolyzed to release methanol. These methods are disclosed in US patent 5,233,113 (Periana et al 1993), which used a Group VIII noble metal catalyst (such as platinum or palladium), and a strong inorganic acid such as sulfuric acid (H₂SO₄) or "triflic acid" (trifluoro-sulfonate, F₃CSO₂H), and in US patent 5,306,855 (Periana et al 1994), which used a soft or borderline metal catalyst (such as platinum, palladium, mercury, etc.) and sulfur trioxide (SO₃), in concentrated ("fuming") sulfuric acid (H₂SO₄). This line of research is also described in various articles, including Periana et al 1993.

An analysis of those patents, and of Periana et al 1993 in particular, discloses a strong preference by Periana for avoiding the creation of methyl radicals, and working instead with electrophilic reagents and pathways. As described by Periana, methyl radicals are more reactive than methane, and any methyl radicals that are formed, as intermediates, will tend to react, rapidly and in uncontrollable ways, with other reagents in the system, before those reagents can react in a desired way with methane. In Periana's words, "Methane can be made to react by using
very reactive species. Radicals are among the most reactive species, and radical chemistry has been traditionally used for reaction with methane. These species can be generated under very forcing conditions or with very reactive reagents. However, under these conditions, the initial (and most useful) products of reaction are more reactive than methane, and selective reaction of methane in high yield is very difficult. Thus, reactions with oxygen can be accomplished but require temperatures above 700° C. Under these conditions, only low selectivities (<30%) to methanol have been reported at methane conversions above 10%, giving 3% overall yields [footnote 6]. Reactions with more reactive species such as chlorine can be carried out at 350° C, but the reaction selectivity to methyl chloride is still low and significant amounts of polychlorinated methanes are generated [footnote 7]. Given the low proton affinity and acidity of methane, it would not be expected that reaction of typical acids or bases with methane would occur at temperatures lower than those of radical processes. This unreactivity has been reported. Only with extremely reactive species, such as protons in "superacid" media (SbF5/HF) [antimony fluoride in hydrofluoric acid] are reactions with methane observed at lower temperatures [footnote 8]. However, these reactions are stoichiometric or use expensive reagents and thus are not practical for the large-scale oxidation of methane.

The 3% conversion figure that was cited by Periana can be placed in perspective by two additional comments. In his text, he stated, "The scientific and engineering community accepts as a general, conservative guideline that a high-selectivity (at least 85%), high-conversion (at least 30%) process for the oxidation of methane to methanol, with molecular oxygen as the final oxidant, could provide the basis for an economical process for the conversion of methane to a transportable material." Also, in his footnote 3, he stated, "Achieving high selectivity at 30% conversion is much more challenging than at low (<5%) methane conversion because as product builds up with increasing conversion, it can become the preferred substrate for over-oxidation."

More recent work by Periana has involved iodine catalysts, in concentrated sulfuric acid, as described in Periana et al 2002. That same approach is also claimed in US patent 6,380,444 (Bjerrum et al 2002, assigned to Statoil Research Centre of Norway; also see Patent Cooperation Treaty published application WO 99/24383).

Other items that relate to catalysts or reagents that can be used to convert methane to other compounds include:
1. US patent 6,384,271 (Jacobson et al, 2002, assigned to DuPont), which discloses methods of causing sulfur trioxide to form complexes with solid inorganic supports, such as zeolite or silicates, in order to make the sulfur trioxide easier to work with, and to make the resulting products easier to extract and purify, when making sulfonated organic products such as detergents, dyes, and oils.

2. US patent application 09/772,775, published in August 2002 as publication number 2002/103,402, by Chang et al, assigned to ExxonMobil, which discloses an ionic system that uses a variety of steps and reagents. The main example of that system uses chlorine gas to convert methane into methyl chloride (H₃CCl), then it reacts the methyl chloride with an electrophilic ion, such as "nitrosonium" ions (O=N-O-SO₃⁻), to form methyl bisulfate, with O=N-Cl as a byproduct. The methyl bisulfate is then hydrolyzed, by adding water (in the form of steam), to break off methanol and release sulfuric acid.

Reaction systems which either use or create large quantities of sulfuric acid tend to generate large quantities of corrosive and hazardous byproducts and other potentially toxic wastes (such as O=N-Cl, in the system disclosed in Chang 2002. Even if they can be recycled somehow, those unwanted byproducts poses serious obstacles to the economics and efficiency of any such system, especially when compared against the improved reaction systems disclosed herein.

There are also other efforts to create sulfur-containing methane derivatives that can be subgrouped based on the particular products created by those reaction schemes. Two such recent efforts have focused on two particular reactions products, which differ from each other by a single oxygen atom. One of those compounds, methanesulfonylic acid (abbreviated as MSA) contains a methyl group (H₃C-) bonded directly to a sulfonic acid group (-SO₃H), to form H₃C-SO₃H. The other compound is identical, except that it has an oxygen atom positioned between the carbon atom and the sulfur atom, to form H₃C-O-SO₂H, which is called methyl bisulfate.

CONVERSION OF METHANE INTO METHANESULFONIC ACID

A number of recent efforts to convert methane into methanesulfonic acid (MSA) merit attention, although they are different from the current invention in a number of important respects.
The first report that apparently triggered interest in this line of research was Basickes et al 1996, which described the testing of several "initiator" compounds to convert methane into MSA. Those initiator compounds included several metal salts, such as HgSO₄ (mercury sulfate), Ce(SO₄)₂ (cesium sulfate), and PdSO₄ (palladium sulfate), as well as the potassium salt of a peroxide compound called Marshall’s acid. The formula for Marshall’s acid can be written most simply as H₂S₂O₅; however, the formula HO₅SO-OSO₃H gives a better idea of its structure, as a symmetric di-acid compound with a peroxide (double-oxygen) linkage in the middle. The formula for the potassium salt can be written as KO₅SO-OSO₃K.

That initial work, reported in Basickes et al 1996, was done by a research group headed by Prof. Ayusman Sen, at Penn State University. Subsequently, that line of inquiry was picked up by a different research group, headed by Prof. Alexis Bell, at the University of California, Berkeley, and it apparently is being commercialized by an Italian company, Atotina Chemicals Inc. The research reports on MSA production that have been published to date by Bell’s group include Lobree and Bell 2001 and Mukhopadhyay and Bell 2002 (both of which used the potassium salt of Marshall’s acid, K₂S₂O₈), as well as Mukhopadhyay and Bell 2003a and 2003b (which shifted to a system that evaluated a number of radical initiators, including K₂S₂O₈, K₄P₂O₈, H₂O₂, CaO₂, Br₂, Cl₂, and I₂, in the presence of metal chlorides such as calcium chloride, iron chloride, and especially rhodium chloride, RhCl₃).

Three important points should be noted about that work, to distinguish it from the subject invention.

First, all of the above cited articles, from Basickes et al 1996 through Mukhopadhyay and Bell 2003b, describe methods for making MSA, which is a valuable chemical commodity, used in processes such as electroplating, circuit board manufacturing, and manufacturing detergents. None of those items propose any method for making methanol, which is a much less valuable, as evidenced by comparing their prices. As of late October 2003, the price of methanol was about 22 cents per kilogram, from suppliers such as Methanex. By contrast, the price of MSA was roughly ten times higher, for the same weight. Accordingly, if a reaction scheme is designed to manufacture MSA as a product, it would be foolish to take that product and degrade it by breaking it apart to form methanol, which has only a fraction of the value of MSA.

However, it must also be recognized that while there is only a small and limited market
for MSA, there is an effectively limitless market for methanol, as both a chemical reagent, and as a clean-burning fuel (either by itself, or as a gasoline additive). Therefore, a reaction scheme that proceeds through MSA as merely one step in a series of intermediates, and which can then pass beyond the MSA to form methanol in huge quantities as a final product (while also allowing the sulfonic acid group to be endlessly recycled, as more methane is continuously passed through the system and converted into methanol) is a very different reaction system, with an entirely different purpose.

A second major difference between the MSA production methods as previously disclosed (by Ayusman Sen's research group, and then by Alexis Bell's research group), compared to the current invention, involves their use of salt compounds as radical initiators, in acidic media. It is believed and suspected by the Applicant herein that salt compounds (such as the potassium salt of Marshall's acid), if used in acidic media, cannot perform effectively in the reaction systems disclosed herein.

The reasons for this are believed to involve at least three factors, which are complex but which can be summarized briefly as follows. First, when Marshall's acid anions (S₂O₅²⁻) are released by a potassium salt (or other salt) of Marshall's acid, in an acidic medium that contains a large quantity of H⁺ protons, those anions and protons will reach equilibrium concentrations of various ionic species, including certain ionic compounds that are likely to quench and terminate the radical-initiated chain-reaction mechanisms that are involved in this current invention.

The second factor relates to the tendency of metal ions (such as potassium ions) to interfere with certain reactions that are involved in the current invention.

The third factor, which is also addressed below in a broader discussion of unwanted byproducts and wastes, is that salt compounds tend to generate larger quantities of unwanted byproducts, including (in many cases) layers of crystalline metallic deposits that tend to accumulate on the insides of pipes and vessels, and that impede flow rates, heat transfer, etc.

Because of those and other factor, it should be recognized that most research using reagents such as potassium salts of Marshall's acid is done solely in small-scale tests that are done in small-scale benchtop academic research, rather than in commercially-oriented industrial research. An insightful and compelling commentary on the industrial potential of reactions that use K₂S₂O₅ as a radical initiator was offered by a researcher who works for Shell International...
Exploration and Production, a subsidiary of one of the world's largest and most successful oil companies. In an article entitled, "A Chemical Alternative to Natural Gas Flaring," that researcher and a coauthor bluntly stated, "At any rate, the reaction would only be of industrial interest with an aerobic oxidant. For that reason we never examined what happened to K$_2$S$_2$O$_8$, which one would never use in an industrial process." (Golombok et al 2003).

For all of the foregoing reasons, the Applicant chose to pursue the use of "free acid" peroxo-acids, such as Caro's acid or Marshall's acid, rather than using salts of those acids. Subsequently, this hunch by the Applicant was strongly supported by direct experimental evidence, which used parallel tests under identical conditions to show that the potassium salt of Marshall's acid was ineffective in triggering the reactions disclosed herein, while the free acid form of Marshall's acid was highly effective and selective. Those laboratory tests were carried out by a skilled expert in this field of research, at his own initiative, since he believed that a K$_2$S$_2$O$_8$ system would work, until he saw the actual experimental evidence to the contrary.

A third major difference between the MSA production methods of the prior art, and the different reagents and methods of the current invention, further reveals why the reaction systems discovered by Sen's research group, and refined by Bell's research group, were recognized as being well-suited for making limited quantities of MSA, but were not suited for making huge quantities of methanol. This factor involves the undesired waste products that are generated, as a byproduct of the potassium salts and other radical initiators and reagents that were tested by the Sen and Bell research groups. Those reaction schemes produce substantial quantities of acids and salts, as unavoidable and generally corrosive and/or fouling waste products, for each pound or kilogram of MSA that is created from methane.

By contrast, the reaction scheme disclosed herein is highly efficient and economical, in large part because it uses a combination of chain reactions and recycling steps that generate a remarkably small and easily manageable quantity of undesired chemical byproducts and waste.

On a theoretical basis, if the chain reactions can continue indefinitely, this system can produce absolutely no waste products at all. However, since no chain reaction system is perfect or can continue forever, it is presumed that: (i) a small "makeup" quantity of a radical initiator should be added continuously to the system, presumably by means such as spraying a fine mist of liquid droplets into a fast-moving gas stream, in order to keep the selectivities and yields of the
desired reactions as high as possible; and (ii) a waste product (which most likely will comprise a mixture of various chemicals) will gradually accumulate, in proportion to the small quantities of radical initiators that will need to be continually added to the system to keep it running under optimal conditions.

This type of waste generation, at very low levels as a result solely of chain reaction limitations, is expected to be orders of magnitude less than the generation of acidic and salt wastes that are generated as unavoidable byproducts of the reaction systems that use potassium salts and other radical initiators, as disclosed in the above-cited papers that include Basickes et al 1996 through Mukhopadhyay and Bell 2003b.

CONVERSION OF METHANE INTO HALOGENATED PRODUCTS

Finally, for completeness, it should also be noted that still other efforts to convert methane into functional derivatives have used entirely different systems, which do not involve sulfur. As examples, US patents 3,979,470 (Firnhaber et al 1976), 4,523,040 (Olah 1985), 4,804,797 (Minet et al 1989), and 6,452,058 (Schweitzer et al 2002, assigned to Dow Global Technologies) describe various halogenation processes that can create methyl chloride, methyl fluoride, methyl bromide, or other methane derivatives that contain halogen atoms. These systems each have their own types of valuable but limited industrial utility, in forming halogenated chemicals; however, they are not suited for creating a commodity chemical such as methanol, which has effectively unlimited markets both as a reagent, and as a fuel source and gasoline additive.

The articles and patents cited above represent just a small fraction of the efforts, over at least 60 years, by numerous skilled researchers, including researchers at chemistry and chemical engineering departments at major universities around the world, and researchers working for large and well-funded multinational oil companies. Many of those researchers have had access to powerful computers for at least the past 10 years, and those researchers were strongly motivated, since they knew about the enormous benefits and rewards that could be gained if an effective and economical reaction scheme could be developed for converting methane into methanol.

However, despite all those efforts over a span of more than half a century, no one has ever previously disclosed a reaction scheme that was efficient enough to justify widespread
commercial adoption and use, for creating methanol from stranded methane. Instead, at thousands of oil and coal fields around the world that are not served by gas pipelines, companies that produce oil or coal continue to burn huge quantities of methane in unproductive flares (thereby aggravating the greenhouse effect, by pumping huge quantities of carbon dioxide into the air), and they continue to pump huge quantities of methane back into the ground. Multinational oil companies are planning to spend many billions of dollars to create liquified natural gas facilities and fleets, even though LNG technology requires that roughly half of the methane must be burned up, to drive the refrigeration and heating processes. In addition, companies and politicians in the U.S. and Canada are wrestling with very difficult and divisive decisions about whether to build a huge and extremely expensive gas pipeline through fragile arctic regions in Canada, because they know of no way to convert that gas into methanol, which could be shipped easily through the existing oil pipeline that already crosses Alaska.

These and other huge and pressing problems could be avoided entirely, and solved easily, if an efficient and economical method became available for converting methane gas into methanol.

Accordingly, one object of this invention is to disclose a reaction system that can converting methane into methanol, in a more efficient, more selective, and less expensive manner than any previously known reaction system.

Another object of this invention is to disclose a reaction system that converts methane into methanol, using a reaction pathway with calculated thermodynamic barriers that are lower than have ever been disclosed for any previous system.

Another object of this invention is to disclose a reaction system that efficiently converts methane into methanol, in a manner that generates only very small quantities of waste or unwanted byproducts, by using a combination of (i) chain reactions that lead from methane to methanol, and (ii) recycling methods that continually recover, recycle, and reuse any inorganic reagents, catalysts, or intermediates.

Another object of this invention is to disclose a reaction system that efficiently converts methane into methanol, by using radical initiators to launch a system that creates methyl radicals, and which then uses those methyl radicals in a reaction cascade that generates additional methyl radicals that will keep the system running, thereby minimizing the quantities of radical initiators.
that must be added to the system to sustain rapid kinetics and high yields.

Another object of this invention is to disclose a reaction system that efficiently converts methane into methanol, in a manner that generates only very small quantities of waste or unwanted byproducts, by using a combination of (i) chain reactions that lead from methane to methanol, and (ii) recycling methods that continually recover, recycle, and reuse any inorganic reagents, catalysts, or intermediates.

Another object of this invention is to disclose a reaction system that efficiently converts methane into methanol in a completely anhydrous system, in a manner that fully exploits and utilizes the advantages that can be achieved by carrying out this reaction scheme in a system that does not require or generate either water or sulfuric acid.

Another object of this invention is to disclose a reaction system that can convert small hydrocarbons (such as methane) into oxygenated or other functionalized intermediates (such as methanol), by using "symphoric" or "anchimeric" reactions that involve bi-functional reagents having both electrophilic and nucleophilic domains, in a manner that will enable a hydrocarbon molecule to undergo coordinated electron and proton shifts simultaneously or nearly simultaneously, to generate transitional intermediates that will lead to high yields of desired intermediates or products, through energy pathways that minimize any thermodynamic barriers.

Another object of this invention is to propose and disclose a chemical processing system that can convert small hydrocarbons, including but not limited to methane, into oxygenated or otherwise functionalized products, in an efficient manner that will generate high yields and minimal wastes, using anhydrous reactions that do not use or generate water.

These and other objects of the invention will become more apparent through the following summary, description, and figures.

**SUMMARY OF THE INVENTION**

Reagents and methods with low thermodynamic barriers are disclosed, for converting small hydrocarbons such as methane into oxygenated or other intermediates or products, such as methanol. This reaction system uses a small quantity of a radical initiator, such as Marshall's acid, which can be generated on-site and then split into radicals by mild heating. These radicals
will remove a hydrogen atom (i.e., both a proton and a nucleus) from methane, to generate methyl radicals (H$_3$C*) and a small quantity of sulfuric acid. Sulfur trioxide (SO$_3$) is added, and the methyl radicals will combine with it to form methyl sulfonate radicals. Additional methane is added, and the methyl sulfonate radicals will attack it, to form methanesulfonic acid (MSA, H$_3$C-SO$_3$H), in a reaction that will regenerate a renewed supply of methyl radicals (H$_3$C*). This allows the process to be continued, in a chain reaction, by continuously adding more sulfur trioxide and methane. The MSA can be removed and sold as a product, or it can be heated, to split it into methanol and sulfur dioxide. The sulfur dioxide can be regenerated into sulfur trioxide, which can be fed back into the system. The methanol can be condensed, and transported to market in liquid form via pipelines, tankers, etc. Since the process generates only very small quantities of byproducts (mainly sulfuric acid from the Marshall's acid), this system can be used to convert huge quantities of stranded and wasted methane gas, from oil or coal production facilities and other sources, into useful products that can serve unlimited markets.

Methods and reagents are also disclosed for using bi-functional reagents (such as a bromate sulfate compound, HO$_2$S-O-BrO$_2$) with electrophilic and nucleophilic domains positioned adjacent to each other in the same molecule. Such reagents can create coordinated proton and electron shifts in methane or other hydrocarbons, using symphoric, anchimeric, or other "neighboring group" effects, to create transitional intermediates with reduced thermodynamic barriers. This can improve the selectivity and yield of reaction systems for converting methane or other lower alkanes into methanol or other valuable intermediates or products.

Finally, it is hoped and believed that methods and reagents can be developed for reacting methanol with carbon dioxide, to form acetic acid, a valuable chemical commodity. If that can be accomplished in an efficient and economical manner, it might justify the efforts and investments that would be necessary to install equipment to remove carbon dioxide directly from exhaust gases, at electrical generating facilities and various other large factories and other sources of carbon dioxide emissions. This could do a great deal of good, in reducing worldwide carbon dioxide emissions and the threat of global warming and climate change. However, certain crucially important and unavoidable thermodynamic barriers have been identified that must be addressed, and resolved, before that area of inquiry can be regarded as an invention or discovery.
Accordingly, the Applicant hereby discloses that (i) he is working on that aspect of this project, using various aspects of the technical disclosures herein, but (ii) his work has not reached a state of completion that justifies full disclosure at this time, and it is not regarded as part of the invention being disclosed herein.

**BRIEF DESCRIPTION OF THE DRAWINGS**

FIGURE 1 depicts a chemical reaction scheme that uses hydrogen peroxide and sulfur trioxide to create Marshall's acid, \( \text{H}_2\text{S}_2\text{O}_8 \), which is mildly heated to break the peroxide bond. This releases radicals, \( \text{HO}_3\text{SO}^* \), which will "activate" methane by taking away a hydrogen atom, converting the methane (\( \text{CH}_4 \)) into a methyl radical (\( \text{H}_3\text{C}^* \)).

FIGURE 2 depicts a chemical reaction that uses methyl radicals (\( \text{H}_3\text{C}^* \)) and sulfur trioxide, to form methanesulfonic acid (MSA), by means of a multi-step process that will also create a new methyl radical. This establishes a chain reaction, and the newly created methyl radicals will react with newly-added \( \text{SO}_3 \). The stable MSA can be removed from the vessel by condensation. It can be sold as a product, used as a reagent, or "cracked" to release methanol, and sulfur dioxide which can be regenerated back into sulfur trioxide.

FIGURE 3 depicts a set of reactor vessels that can be used to convert methane into methanol, using the Marshall's acid pathway.

FIGURE 4 depicts two potential unwanted side reactions, involving free radicals, that might pose concerns for a radical initiator system as shown in FIG. 1. However, computer modelling indicates that either of these two possible reactions will simply return to the desired state, by re-forming the desired reactants, rather than degenerating into unwanted byproducts.

FIGURE 5 depicts a reaction system using a bi-functional bromate-sulfate reagent that can activate lower alkanes such as methane, by using coordinated proton and electron shifts to create intermediates with low thermodynamic barriers.

FIGURE 6 depicts the energy profile of a pathway for converting methane to methanol using the bromate-sulfate reagent, compared to an iodine system of the prior art.

**DETAILED DESCRIPTION**

As briefly summarized above, reagents and methods are disclosed for converting small
hydrocarbons (such as methane) into oxygenated or other intermediates or products (such as methanol or methanesulfonic acid).

The pathways that are provided by these reagents and methods offer several important advantages. These will be briefly listed, then they will be discussed and illustrated in more detail by using an exemplary system that uses Marshall's acid as a radical initiator, to trigger a chain reaction that uses methyl radicals to convert methane into methanol, in large quantities, without generating any substantial quantities of waste.

The advantages offered by this system include:

1. These pathways have low thermodynamic barriers. This includes low "heat of activation" levels, and low entropic (or "free energy") losses.

2. As a direct result of their low thermodynamic barriers, these reactions can be carried out at relatively low and mild temperature and pressure combinations, and will result in relatively high efficiency, selectivity, and yield, all of which are highly valuable.

3. These pathways can generate large quantities of product without also generating large quantities of waste, by using a small quantity of a "radical initiator" compound to set a chain reaction in motion, and then allowing the chain reaction to sustain the process, while adding only small "makeup" quantities of the radical initiator.

4. These pathways allow the endless regeneration and recycling of all sulfur compounds that are used or produced by the system. In specific, sulfur trioxide (SO$_3$) is pumped into the reactor vessel. It reacts with methyl radicals to form methanesulfonic acid (MSA) radicals, which then react with more methane to form stabilized MSA. The MSA is removed from the reactor, and can be "cracked" to release methanol (the main product) and sulfur dioxide. This sulfur dioxide can be regenerated back into sulfur trioxide, and the regenerated sulfur trioxide can be pumped directly back into the reactor vessel. This cycle (SO$_3$ to MSA to SO$_2$, then back to SO$_3$ again) can be repeated an endless number of times, without generating any sulfuric acid or other acidic or toxic wastes.

5. These pathways are run in an entirely anhydrous manner, which does not use or produce water, and these pathways also avoid any use of any salts. This anhydrous, non-salt approach offers numerous advantages; among other things, it makes the system more efficient, less corrosive, and less subject to fouling by mineral deposits inside the vessels or pipes, and it
greatly reduces the formation of unwanted byproducts and waste materials.

These factors and advantages can be better understood by considering an exemplary reaction system, described below.

**CONVERSION OF METHANE INTO METHANESULFONIC ACID (MSA)**

A preferred embodiment of this invention, referred to herein as "the Marshall's acid system" uses a small quantity of a compound called Marshall's acid to initiate a chain reaction, involving the conversion of methane into "activated" methyl radicals. This part of the process is illustrated in FIG. 1.

As shown near the top of FIG. 1, the manufacture of Marshall's acid is carried out by reacting hydrogen peroxide (HOOH) with sulfur trioxide (SO₃), to form a compound called peroxy-monosulfuric acid, which has the common name Caro's acid. Reactor vessels and preferred conditions for carrying out this reaction are disclosed in US patents 2,789,954 (Fell, 1957), 3,900,555 and 3,939,072 (Jourdan-Laforte, 1975 and 1976), and 5,304,360 (Lane et al).

Additional SO₃ is then reacted with the Caro's acid, to convert it into peroxy-disulfuric acid, which has the common name Marshall's acid. This reaction can be carried out as disclosed in US patent 3,927,189 (Jayawant 1975, assigned to DuPont). The '189 patent, which disclosed methods for creating Marshall's acid in a relatively stable form that could be stored for some period of time, indicated that the reaction should be done under mild conditions, with temperatures not to exceed 45°C, since higher temperatures would lead to more rapid decomposition of the resulting product.

However, the goal of manufacturing Marshall's acid for the purposes herein is not to create a stable and storable product, but instead to create a compound that will immediately be split in half, to release free radicals that will then react with methane, to strip hydrogen atoms away from the methane. Accordingly, certain precautions described in the '189 patent will not come into play here, and various modifications of those procedures (such as the use of higher reaction temperatures, which may include simply omitting any efforts to remove heat from the reaction vessel, since heat will be released by the exothermic creation of Marshall's acid) should be tested and evaluated, since they may be able to speed up and/or increase the efficiencies and yields of reactions used to create Marshall's acid.
If Marshall's acid is used in large-scale industrial facilities for converting huge quantities of methane into methanol or other products, various methods and devices are likely to be developed for improving its methods of on-site manufacture followed by immediate use. In particular, higher-than-normal temperature and pressure combinations should be evaluated, which are designed to lead, not to the formation of cool and stable Caro's acid, but to the rapid conversion of Caro's acid into Marshall's acid, preferably at temperatures that will help promote the breakage Marshall's acid, to release HSO₄⁻ radicals.

Regardless of whether any such improved methods are developed, Marshall's acid is a well-known compound, and methods have already been disclosed for making it in commercial quantities (in particular, US patent 3,927,189, Jayawant 1975, is entirely devoted to a process for manufacturing Marshall's acid). Therefore, the manufacture of Marshall's acid can be carried out using known equipment and methods.

After Marshall's acid has been created, it is then split into two equal and identical halves, by breaking the peroxide bond. This can be done by mild heating; alternately, it may be possible to accomplish it even more rapidly and controllably by other means, such as ultraviolet radiation, or by using radiation having a specific wavelength, from a "tuned" laser (see, e.g., US patent 4,469,574, Keehn et al 1984).

The resulting Marshall's acid radicals (HO₃SO*) are highly unstable, and highly reactive, due to the presence of an unpaired electron on one of their oxygen atoms. This makes them well-suited for use as "radical initiators" in the reactions disclosed herein. When mixed with methane, a Marshall's acid radical will extract a complete hydrogen atom (both a proton, and an electron) from the methane. This transfer of a hydrogen atom converts a Marshall's acid radical into stable sulfuric acid (HSO₄), and it generates a methyl radical, H₃C*. As shown in FIG. 1, each mole of Marshall's acid will release two identical radicals, and each radical can then attack a methane molecule, to create a methyl radical.

After a set of methyl radicals has been created by a radical initiator, the methyl radicals will then launch a chain reaction, as illustrated in FIG. 2, which leads to the formation of methanesulfonic acid (MSA). This process requires a multi-step sequence. A selected oxidant compound, such as sulfur trioxide (SO₃), is pumped into the reactor, and the methyl radicals will combine with it, to form methyl sulfonate radicals. As more methane gas is added, the methyl
sulfonate radicals will attack the added methane, and remove a single hydrogen atom from each methane molecule, thereby creating a new methyl radical.

This process allows MSA radicals to create complete and stabilized molecules of MSA, which can then be removed from the system, for further processing.

At the same time, that hydrogen transfer also generates a renewed supply of methyl radicals (H₃C*). Accordingly, this series of reactions allows the process to be continued and sustained, as a chain reaction. As long as more sulfur trioxide and methane continue to be added to the system, they can continue to form MSA.

It should be noted that because of certain types of electron shifts, a methyl radical (H₃C*) that has already lost one hydrogen atom will not readily or easily give up a second hydrogen atom. This is an important feature of this invention, and it directly contrasts with certain other chemical reactions involving methane. For example, when methane is treated with a halogen such as chlorine, the loss and displacement of a first hydrogen atom tends to enable or even accelerate the loss of additional hydrogen atoms, thereby leading to mixtures of carbon dichloride, trichloride, and tetrachloride. However, the opposite happens when methane loses a hydrogen atom and becomes a radical. That realization was another crucially important insight, which helped the Applicant develop the reaction scheme disclosed herein, in a way that can lead to a single product with good selectivity, rather than being pulled in four different directions, once the reaction commenced.

As mentioned above, MSA can be removed from the reactor vessel, by using conventional condensation devices. After removal from the reactor, any of several things can be done with it, as indicated in FIG. 2.

One option is to sell the MSA, as a valuable product in its own right. Another option is to use the MSA as a feedstock in any of various other chemical processes.

However, the market for MSA, and the known uses for MSA, are both limited. They are believed to amount to only a few tens of millions of dollars per year, worldwide, while literally billions of dollars worth of methane are being burned and wasted in flares, or reinjected back into the ground, every month.

Therefore, the larger value of this system comes from the fact that MSA can be "cracked" to release methanol and sulfur dioxide. This cracking can be done by thermolysis (also called
pyrolysis) at elevated temperatures, as described in US 2,553,576 by Grosse and Snyder, who used silver carbonate as a catalyst, and refluxing temperatures between 300 and 350°C.

Other catalysts, temperature ranges, and operating parameters can be evaluated if desired, and if the worldwide supplies of MSA suddenly increase by orders of magnitude, due to its synthesis from stranded methane, it is extremely likely that improved methods and refinements for cracking MSA into smaller compounds can and will be developed, including various methods that will be patentable in their own right.

The sulfur dioxide which is released by cracking MSA can be regenerated back into SO₃, by contacting it with oxygen (O₂, which can be obtained in purified form, from air), in the presence of a catalyst such as vanadium pentoxide, V₂O₅. The regenerated SO₃ can be pumped directly back into the reactor vessel, without creating any waste, to keep the process running.

Methanol which is released from MSA by thermal cracking has a virtually unlimited market; among other things, it can be used as a chemical feedstock, as a clean-burning fuel, and as a gasoline additive that can reduce air pollution from automobiles, and that also can reduce their consumption of gasoline. As a compound that remains in liquid form even at room temperatures and low pressures, it can be pumped through pipelines, and loaded into tanks, tanker trucks, and ocean-going tanker ships, for delivery to commercial markets.

Since the process generates only very small quantities of byproducts (mainly a small quantity of sulfuric acid, from the small quantity of Marshall's acid that is added to the system in limited "makeup" volumes) this system can be used to convert huge quantities of stranded and wasted methane gas, from oil or coal production facilities and other sources, into useful products that can serve unlimited markets.

On the subject of "makeup" volumes of Marshall's acid, no chain reaction can ever reach an ideal and theoretical 100% yields, and there are always minor losses, inside any reactor vessel in the real world. As just one example, if two methyl radical happen to collide and react, they will simply form ethane, C₂H₆, which is a stable lower alkane. This will terminate both of the radicals, and they will no longer be reactive.

Because of these and other losses and chain terminations, it will be necessary to introduce, during the reaction (and preferably in a continuous manner) a relatively small quantity of free radicals, from Marshall's acid or another radical initiator, into the system. This typically
can be done by injecting a fine mist of a liquid, into a reactor vessel.

Accordingly, when this reaction is described in terms appropriate for a patent claim, the process comprises a method for converting methane into an oxygenated derivative, comprising the following steps:

a. removing hydrogen atoms from methane, thereby generating methyl radical intermediates, each having an unpaired electron, within a reactor device;

b. contacting the methyl radical intermediates with a selected oxide compound (such as sulfur trioxide, in the system shown), under conditions that cause the methyl radicals to react with the selected oxide compound in a manner that forms a methylated oxide radical, wherein the methylated oxide radical has sufficient reactivity to remove hydrogen atoms from newly-added methane; and,

c. reacting the methylated oxide radical with methane, under conditions that cause removal of hydrogen atoms from the methane, thereby forming stabilized methylated oxide molecules while also generating newly-formed methyl radicals.

Stated in alternate terms, this system comprises a method for converting a lower alkane into an oxygenated derivative, comprising the following steps:

a. removing hydrogen atoms from at least one lower alkane compound, thereby generating alkane radicals;

b. contacting the alkane radicals with a selected oxide compound under conditions that will cause the alkane radicals to bond to the selected oxide compound, thereby forming alkylated oxide radicals;

c. reacting the alkylated oxide radicals with at least one lower alkane, under conditions that cause removal of hydrogen atoms from the lower alkane, thereby forming stabilized alkylated oxide molecules while also generating newly-formed alkane radicals.

**Manufacturing System (Plant Layout)**

FIG. 3 provides a schematic layout of a manufacturing system 100 (often called a "plant" in the petrochemical industry) that can be used to carry out the reactions of this invention. Starting near the upper left, reagent supply container 110 contains hydrogen peroxide, H₂O₂. Reagent supply container 120 contains stabilized anhydrous liquid SO₃, or an alternate
sulfonating agent that can be converted into Caro's acid and/or Marshall's acid. Both of these reagents are pumped into a suitable acid formation vessel 150, where they will combine and react to initially form Caro's acid, and preferably to then form Marshall's acid, H₂S₂O₈, in a second stage of the sulfonation reaction. Acid formation vessel 150 is modelled after a similar vessel having annular reaction zones, shown in US patent 5,304,360, and used to create Caro's acid; it has been modified by the addition of a separate and additional inlet, to allow additional SO₃ to be added to the vessel, to convert the Caro's acid to Marshall's acid.

The Marshall's acid will emerge from the bottom of acid formation vessel 150, and it will be heated, subjected to UV or laser radiation, or otherwise treated, to split it into HSO₄⁻ free radicals, as shown in FIG. 1. These free radicals will be pumped, presumably in the form of a fine mist, entrained liquid, etc., into a main reactor vessel 200, which preferably should contain internal baffles, agitators, and/or other structures that will promote high levels of liquid/gas contact and interaction.

Main reactor vessel 200 will be receiving a steady supply of both methane and SO₃, from supply tanks 210 and 220 (via pump 225), and also from one or more recycling conduits 250 that will collect any unreacted methane or SO₃ that emerge from reactor 200. In most facilities that will deal with large volumes of methane that has been separated from crude oil at an oil field, the methane supply pump 210 presumably will receive its supply of methane gas from a storage or surge tank that receives and holds semi-pressurized methane gas, after the gas has been removed from crude oil in a separation vessel.

In cases in which sulfonated products are not removed and sold, the SO₃ supply will be continuously recycled; therefore, the "makeup" volumes that will be required to replace small and gradual losses will not be nearly as large as the volumes of methane that will be processed.

However, it also should be recognized that methanesulfonic acid (MSA, CH₃SO₃H) is a valuable and useful chemical product in its own right; indeed, it is worth roughly 10 times more than methanol, on an equal-weight basis. Therefore, it can be sold as a valuable product, or used as a valuable chemical feedstock.

It should be noted that the much higher value for MSA, compared to methanol, can help explain why the results seen by Sen's group and Bell's group, involving methods for manufacturing MSA by using K₂S₂O₈, apparently were not recognized as suggesting potential
pathways that might offer an economical method for manufacturing methanol. As mentioned above, methanol has only about 1/10th the value of MSA.

Nevertheless, now that this new approach to manufacturing methanol has been disclosed, it should be recognized that it also discloses a valuable new method for creating MSA, as a product, rather than just as an intermediate. Therefore, if desired, MSA (or various other sulfonated products or intermediates, if additional processing is carried out) can be removed directly from the new system disclosed herein, simply by sending some or all of the MSA that leaves the main reactor vessel 200 to a storage tank, rather than to a heating and cracking vessel 300 that will break the MSA into methanol and SO₂. It should also be recognized that if MSA or any other sulfonated products are removed from the system as products, the supplies of SO₃ that must be fed into the system also will need to be increased in a corresponding manner.

Any known method or machine for increasing the contact and interactions between the reagents inside the main reactor vessel 200 can be evaluated, using routine experiments, to determine their suitability for use as disclosed herein. For example, methane and SO₃ from supply pumps 210 and 220 might be pre-mixed, before they enter reactor vessel 200; alternately, they might be introduced in a counterflow manner, by introducing gaseous methane into the bottom of vessel 200, so that it will bubble and rise upward, while liquid SO₃ is pumped into the top of vessel 200 so that it will flow downward due to gravity. Similarly, any known or hereafter-discovered system, type, or combination of baffles, trays, meshes, fluidized particulate bed reactors, rotating bed reactors, SO₃-coated particulates, and other devices, methods, or formulations can be evaluated for use as disclosed herein, to determine whether they can improve the yields of the reactions disclosed herein.

In particular, one class of candidate reactor vessels that may be well-suited for such use includes spinning-bed reactors, as described in US patent 4,283,255 (Ramshaw et al 1981, assigned to Imperial Chemicals), and US patent 6,048,513 (Quarderer et al 2000, assigned to Dow Chemical Company). These devices normally use a fairly wide and thick disk that spins at a high speed, thereby acting as a centrifuge that drives gases and liquids from a center input point, toward the outside of the bed. They often use porous metallic mesh as the media. The wires that form the mesh can be made of stainless steel or other relatively strong and inexpensive material, which are coated with a thin layer of a more expensive catalyst, such as a vanadium oxide, by
means of electroplating, sputter-coating, or other means.

Another class of candidate reactor vessels that may be well-suited for such use includes "loop" reactors, as described in US patent 5,159,092 (Leuteritz 1992, assigned to Buss AG of Switzerland). These are often referred to as Buss (pronounced "boose") reactors. A subcategory of loop reactors that also deserves attention comprises "monolithic" loop reactors, as described in Broekhuis et al 2001. Loop reactors typically use a combination of (i) a main reactor vessel, which contains an ejector mixing nozzle, a solid catalyst bed, or some other device that cannot be removed from the main vessel; and, (ii) a separate and typically smaller "secondary" vessel, which receives a liquid or gas that has been removed from the main vessel, and which treats that liquid or gas by some chosen means (such as by a heat exchange process) before returning it to the main reactor vessel. In this manner, the secondary device (along with its piping and pumps, which form a loop that is connected at both ends to the main vessel) can be used to help control and regulate what is occurring inside the main vessel, without disrupting a catalyst bed or other system or device that is operating inside the main vessel.

It also should be recognized that various types of solvents can and should be evaluated for running the system disclosed herein. Stabilized liquid sulfur trioxide, methanesulfonic acid, or an MSA-sulfur trioxide mixture offer promising candidates for evaluation as liquid media that can allow everything to keep running smoothly and efficiently inside the main reactor vessel 200, since each of those compounds will already be present in the reactor vessel, as either reagents or products. Alternately, any other type of candidate solvent or liquid media that may be of interest can be computer-modeled at very low cost, and those that appear to be interesting based on such computer modeling can be tested, in scaleup or pilot plants.

The MSA (CH$_3$SO$_3$H) that is generated within the main reactor vessel 200 will be collected (such as by using condensate traps), and pumped to a separate heating or "cracking" vessel 300, where it will be heated to cause it to break apart into methanol (CH$_3$OH) and sulfur dioxide (SO$_2$). If desired, the breakdown reaction inside cracking vessel 300 can be catalyzed or promoted in any suitable manner, such as by using a platinum or other metal catalyst. This type of reaction, in which a larger molecule is broken into smaller fragments (without the addition of water components into either of the smaller molecules) can be referred to as pyrolysis, thermolysis, "cracking", or similar terms.
Methanol, the desired product, generally will be pumped into a collection or holding tank, shown as tank 500 in FIG. 3, if substantial volumes are involved, for subsequent pumping into a pipeline, tanker truck or ship, nearby factory, etc. Depending on various factors (including the purity of the methane stream that is being processed, as well as reaction parameters inside vessels 200 and 300), other organic compounds may be entrained in the methanol stream that emerges from heating vessel 300. Such impurities may include lower alkanes or alkane derivatives, olefins, alkenes, or other unsaturated compounds or derivatives, and benzene or other aromatic compounds. If desired, these can be separated out from the methanol stream, and collected for sale or use as valuable products in their own right. This type of separation can be carried out by, for example, a reactor bed 510 that contains a "Zeolite" (aluminosilicate) compound such as "ZSM-5", sold by the ExxonMobil Corporation. This material functions in a manner comparable to a molecular sieve, by separating different components from a mixed organic liquid stream. This can allow various separated products to be divided among different collection tanks 512 (which can receive and hold, for example, batches that have been separated into major categories, such as alkanes, olefins, and aromatics as shown in FIG. 3, or which can hold different batches that have been separated based on any other criteria).

Gaseous SO₂ also will emerge from the heating vessel 300. It can be passed through a suitable reactor 400, which will also receive oxygen (O₂) from a separate oxygen supply vessel 410, to oxidize the SO₂ to its higher oxidation state, SO₃. Reactor 400 preferably should contain a catalyst, such as vanadium pentoxide (V₂O₅), to facilitate reaction of the SO₂ and the O₂ to form SO₃. The SO₃ will be returned to the main reactor vessel 200.

During benchtop analysis and testing or other small-scale use of these reactions, the oxygen supply vessel 410 can use bottled oxygen, or any other available source. In large-scale manufacturing operations, the oxygen supply vessel 410 preferably should use a device that can extract O₂ directly from the atmosphere, such as a so-called "pressure swing absorber" (PSA) system, sold by companies such as IGS, Holtec, and other manufacturers known to those skilled in the art.

The handling and utilization of SO₃ can involve any known or hereafter-discovered method that will enhance the efficiency of the operations disclosed herein, or that will otherwise improve these operations in any other significant manner (such as by reducing waste products,
Numerous methods and reagents which facilitate various aspects of generating or handling SO\(_3\) are known, including (for example):

(i) the use of various derivatives of boron, phosphorous, or sulfur to stabilize SO\(_3\) in liquid form, as described in articles such as Gilbert 1965; and,

(ii) the use of solid supports (which can be in the form of small particles, to allow pumping and handling inside a fluidized or constrained "bed", column, or other device), to create relatively thin layers of liquid SO\(_3\) that will coat the surfaces of the particles.

Any such method or reagent, and any combination of such methods or reagents, can be evaluated to determine their suitability for use as disclosed herein.

PROGRESSION THAT LED TO THIS INVENTION

Under the patent law, inventors and applicants are not required or encouraged to disclose the history and the step-by-step progression that culminated in an invention. However, in view of several factors, the Applicant hereby discloses a narrative summary of the step-by-step progression that culminated in this invention.

The factors that led to this decision, by the Applicant, to offer a candid account of his progression through these steps include the following:

1. In view of the huge quantities of stranded methane that are being burned in flares and injected back into the ground every month, in view of the need for cleaner-burning fuels, and in view of the possibility that this invention may help lead to ways to efficiently remove carbon dioxide from exhaust gases and convert it into acetic acid or other valuable chemicals, this invention has potentially large and important commercial, energy, environmental, political and social implications, and may be able to help solve or at least alleviate a number of globally important problems. Accordingly, if additional skilled researchers are informed of this technology in ways that can help them study and understand not just the reactions shown in the drawings, but also a historical progression of how those reactions were arrived at, and how to follow and grasp various lines of relevant prior art that were developed by others and then woven, as strands or pieces, into a new and different creation, it may help accelerate not just the adoption, but also the expansion, of this line of useful and beneficial technology.

2. Even though patents do not contain "Acknowledgements" sections comparable to
articles in journals, researchers who made important and helpful advances in the prior art deserve fair and proper recognition and acknowledgement, even if those contributions do not entitle those earlier pioneers to be designated as coinventors of a new invention (such as, for example, because their contributions had already entered the public domain by means of published articles, patent expirations, etc.).

3. Although the reactions disclosed below have been fully simulated and modeled, using powerful computers and sophisticated chemical modeling software, and have also been confirmed in laboratory tests, they have not yet been confirmed as being efficient and economical, in pilot plants or scale-up reactors. Therefore, with due regard for both the capabilities and limitations of computer modeling and lab testing, the Applicant has decided that the best approach to take, both (i) with other experts who will receive this information, in confidence, during the pre-publication pendency of this application, and (ii) during the design, testing, and scale-up of this process, will be best served by full disclosure, including a history of how these reactions were arrived at. If the Applicant has misinterpreted or misapplied anything, or has overlooked a potentially even better process, catalyst, or reagent, an step-by-step description of the progression that led him to this invention may help other researchers figure out how to overcome or at least minimize any bottlenecks or obstacles, and how to adapt and expand various disclosures herein (and in various other items of art cited herein) to additional areas of hydrocarbon chemistry.

4. As described herein, two distinct reaction systems were developed by the Applicant. The radical initiator system, exemplified by the Marshall's acid system, is believed to offer the best system developed to date, for converting methane into MSA or methanol. However, that system would not and likely could not have been developed, if the Applicant had not been carefully studying and analyzing a symphoric and anchimeric bromate-sulfate system that is also disclosed herein. Even though the bromate-sulfate system might not be regarded as properly being a part of the radical initiator system, it is likely to offer helpful insights and useful tools for adapting and expanding the radical initiator system beyond just methane, and into other areas of hydrocarbon chemistry. Accordingly, the symphoric-anchimeric system is regarded by the Applicant as providing highly useful tools for expanding this invention beyond the conversion of methane into MSA or methanol, and into additional methods and reagents for manipulating and
controlling C¹ chemistry and other branches of hydrocarbon chemistry. Therefore, the legal obligation to fully disclose "the best mode of carrying out the invention", as required by the patent laws of nearly all nations, is interpreted by the Applicant as requiring disclosure of a set of additional and complementary options and tools that can be provided by symphoric-anchimeric reagents and methods.

Accordingly, the following account is offered, not as a description of the invention, but as an accompanying guide that can help shed additional light on how and why it works in the way it does, and on how it was created.

During the 1980's, the Applicant worked in the water treatment industry. During the course of that work, he helped design, install, and maintain water treatment equipment at a number of petrochemical plants and refineries.

While working at a food processing plant, he saw how efficiently hydrogen peroxide could oxidize and clean up a major fouling problem, that had been caused by bacteria. Years later, he happened to read an article by Colin Ramshaw (one of the inventors of spinning disk packed beds, as disclosed in US patent 4,283,255), in the Financial Times (London). In that article, Ramshaw discussed various ways in which chemical technology could be made smaller, better, and cheaper.

Those comments made good sense to the Applicant, and he began pondering them seriously. From his work at various petrochemical plants and refineries, he was aware that the single greatest unsolved problem in all of organic chemistry involved how to convert methane, which is difficult to handle and manipulate in controlled ways, into other products that could be handled more easily.

Since the most promising routes for methane manipulation (including conversion to methanol) involved various types of oxidation reactions, he began experimenting with hydrogen peroxide. When that did not work, he tried ozone, and that did not work either. Therefore, he began reading large numbers of chemistry papers, patents, and books, looking for better ways.

After years of effort, and after noticing various sporadic comments on symphoric and anchimeric reactions, he began studying bifunctional reagents that might be able to exert simultaneous effects on both protons and electrons, which he saw as the key to manipulating individual hydrogen atoms on methane. That work culminated in the bromate-sulfate system
described in above-cited U.S. provisional application 60/424,091, filed in November 2002, and further described and illustrated herein.

After reaching that plateau, the Applicant began searching for alternate catalysts or reagents that might be able to perform even better than the bromate-sulfate approach.

During that effort, the Applicant began reviewing the literature on sulfonating agents, including a book by E.E. Gilbert entitled *Sulfonation and Related Reactions* (Interscience Publishers, New York, 1965). Various comments by Gilbert, especially in chapter 1, suggested that perhaps an improved type of sulfonation reaction could be carried out under anhydrous conditions, containing neither water nor sulfuric acid (H₂SO₄), and instead using stabilized anhydrous liquid SO₃.

The Applicant soon recognized than an anhydrous pathway, if it could be achieved, might be able to avoid or minimize various problems. For example, if a sulfuric acid system were used, serious problems of corrosion, air pollution, and worker safety would arise, and spent acid would need to be discarded, leading to serious problems of toxic and hazardous waste disposal. Those problems would likely become extremely severe, if scaled up to the volumes and tonnages that would be involved if methane can be converted into methanol on an efficient and potentially worldwide basis.

By contrast, if an anhydrous and cyclical system could be developed, in which a sulfur reactant is simply cycled back and forth between SO₂ and SO₃, then all of the problems that would accompany a sulfuric acid system would be avoided, and the system would become much safer, and more workable and practical.

In addition, certain chemical factors also continued to drive the Applicant toward an anhydrous solution, as the best, potentially most efficient, and most elegant solution. If liquid anhydrous SO₃ can be used in a direct way, as an oxygen donor that will drop to SO₂ when it gives up its oxygen (thereby enabling the SO₂ to be regenerated directly back into SO₃), then that system will be more straightforward, and therefore is likely to be simpler and more efficient, than a more complex and indirect route, such as offered by the bromate-sulfate system. In the bromate-sulfate system, each oxygen atom that makes the multi-step journey to methanol must first be transferred to from SO₃ to a bromate compound, then to a bromate-sulfate compound, then to a bromate-sulfate-methyl intermediate, then to a methyl-bromate intermediate, and then to
a methyl bisulfate intermediate, which then must be broken apart to release methanol.

For all of these reasons, the Applicant had already realized, by the time provisional application 60/424,091 was filed in November 2002, that the system might be improved substantially, if an alternate and completely anhydrous system could be developed that would not require, involve, or generate water or sulfuric acid.

A few months later, in February 2003, the Applicant discovered a citation to German patent application DE 101 32 526 A1 (Jess et al, assigned to Rurhgas AG of Germany), which relates to forming alkane derivatives. This patent application, published in late January 2003, was discovered by the Applicant during a computerized search of items that cite work by Roy Periana. Since Roy Periana (formerly at the Catalytica company, and now a professor at the University of Southern California), Ayusman Sen (a professor at Penn State University), and Alexis Bell (a professor at the University of California, Berkeley) are all eminent and highly respected researchers in the field of alkane chemistry and derivatization, the Applicant periodically does a literature search for anything they have recently published or patented, and he obtains and reviews anything they have written that appears to be relevant to methane chemistry.

Just as importantly, the Applicant also periodically searches for any other patents or articles, by anyone else, that cites any articles or patents by Periana, Sen, or Bell. These types of articles that cite other previous works can be located by using a computerized system called "SciFinder", which is available to members of the American Chemical Society.

During one of those computerized searches, German patent application DE 10132526 A1 was noticed, since it cites work by Periana. Since the German application was available only in German, the Applicant obtained a translation, and he also noted that it cited an old British patent from the 1940's, GB 632,820.

The reference to the British patent stimulated the Applicant's interest, and he obtained a copy and studied it. That British patent only named the assignee company (Houdry Process Corporation), and it did not disclose the names of the inventors. Therefore, the Applicant began searching databases and footnotes for patents assigned to Houdry and issued in the late 1940's, and he located three corresponding US patents, numbers 2,493,038; 2,492,983; and 2,553,576, all coinvented by John Snyder and Aristid Grosse.

When the Applicant studied all three Snyder and Grosse patents, he noticed that they
discussed, in several locations, an apparently anhydrous system that created direct bonds between carbon and sulfur atoms (as occur in MSA, which is $\text{H}_3\text{C-SO}_2\text{H}$). These are very different from the types of indirect bonds that occur in methyl bisulfate, $\text{H}_3\text{C-O-SO}_3\text{H}$, in which the carbon and sulfur atoms are separated by oxygen atoms.

The discussion of direct carbon-sulfur bonds, in the Snyder and Grosse patents, stimulated the Applicant's interest, partly because he was already looking for an anhydrous system, and partly because the formation of MSA and other agents having direct C-S bonds indicated that one or more electron and proton rearrangement mechanisms were involved, which were likely to be entirely different from the various mechanisms he had been studying in the bromate-sulfate system.

During and shortly after that library research, he was also organizing and obtaining computer simulations of alternate reaction pathways. These simulations were carried out by a doctoral candidate who was working as a paid consultant, and who had proper access to powerful computers at a university. This modeling used the Amsterdam Density Functional program, release 2.3.3, by Scientific Computation and Modelling (www.scm.com). This software is complex and sophisticated, and is described in an extensive review article published in the *Journal of Computational Chemistry* (te Velde et al 2001).

The reaction schemes that were being modeled at about that time period included:

1. a mercury sulfate system, initially described in the Snyder and Grosse patents, and subsequently in Periana et al 1993 and US patent 5,306,855 (Periana et al 1994); and,

2. an iodine system, described in Periana et al 2002 and in US patent 6,380,444 (Bjerrum et al 2002).

The reaction pathways that the Applicant was analyzing, at that time, involved the use of mercury or iodine compounds, but not in the same manners proposed by Snyder, Periana, or Bjerrum. Instead, those reagents were modeled using the approach developed by the Applicant, using the bifunctional symphoric/anchimeric system he had developed with the bromate-sulfate catalyst. Furthermore, those systems were being modeled in both anhydrous systems, using liquid $\text{SO}_3$ as the sulfonating reagent, and in hydrous systems that contained sulfuric acid as well as water. It should also be noted that systems that contain both acid and water are often referred to as "protic" systems, since an acid, when dissolved in water, will release hydrogen protons ($\text{H}^+$)
into the aqueous solvent.

The results of those simulations indicated that mercury and iodine compounds might be useful, under some conditions, for generating stable methyl intermediates from methane, using various reaction schemes. However, those reaction schemes suffered from several apparent shortcomings and problems, including: (i) the fact that at least some of them involved transition states that would be difficult to reach, since they would require very high "free energy" (DG) states; and, (ii) concerns that any system using mercury or iodine would not be commercially practical, due to problems of potentially toxic waste, hazards to workers, etc.

Therefore, the Applicant's work did not dwell for long on the mercury or iodine systems. Using the "SciFinder" search system mentioned above, he did additional literature searches, and located Basickes et al 1996, since it cited Snyder's US patent 2,493,038, mentioned above. This 1996 article described work done in the labs of Prof. Ayusman Sen, at Penn State University.

-Basickes et al 1996 contains a graphic labeled "Scheme 1: Radical Mechanism for the Formation of Methanesulfonic Acid", which lists four reactions under two headings. This "scheme" was not asserted by those authors to be a proven fact; instead, the article stated, "A plausible mechanism for the K$_2$S$_2$O$_8$-initiated conversion of methane to CH$_3$SO$_3$H by fuming sulfuric acid is sketched in Scheme 1. ... In light of our observations, the possibility of a radical pathway operating in the Catalytica system [footnote to Periana et al 1993] must be considered seriously ..."

Under "Scheme 1", as set forth in Basickes et al 1996, the two "Initiation" reactions are as follows:

$$K_2S_2O_8 \longrightarrow 2 \text{KSO}_4^*$$

$$\text{KSO}_4^* + \text{CH}_4 \longrightarrow \text{KSO}_4\text{H} + \text{CH}_3^*$$

The two "Propagation" reactions are as follows:

$$\text{CH}_3^* + \text{SO}_3 \longrightarrow \text{CH}_3\text{SO}_3^*$$
CH₃SO₃* + CH₄ → CH₃SO₂H + *CH₃

Upon seeing that scheme, the Applicant was intrigued, and he soon learned from additional literature searches that the Basicikes/Sen pathway for making MSA (CH₃SO₂H) from K₂S₂O₈ had also been followed up by other researchers, as described in Lobree and Bell 2001, and in Mukhopadhyay and Bell 2002 and 2003a.

However, if possible, the Applicant wanted to avoid the use of K₂S₂O₈, which is the potassium salt of Marshall's acid. Although K₂S₂O₈ may be well-suited for making MSA in quantities that are not huge, any reaction scheme that uses a nonregenerated metallic salt, for a process such as large-scale conversion of methane to methanol at oil fields, would be plagued by serious metal accumulation and fouling problems, inside any reactors and pipes. In addition, the use of K₂S₂O₈ probably would also create substantial quantities of O₂ molecules, which would gradually accumulate; as oxygen atoms occasionally break free of their sulfur bonds. This could lead to substantial problems in a reaction scheme that depends on free radicals, since O₂ molecules act as a "radical trap", and will absorb and neutralize any free radicals, thereby seriously interfering with any reactions that utilize and depend upon free radicals.

Therefore, the Applicant began pondering acid (rather than salt) compounds that might be able to trigger and drive a free radical pathway, analogous to but different from the pathway described in Basicikes et al 1996. Initially, he pondered a compound called Caro's acid, or peroxy-monosulfuric acid. This compound is comparable to sulfuric acid, but it has an extra oxygen atom positioned between the sulfur atom and one of the hydroxy groups, so its formula can be written as HO₂SOOH, with the two oxygens in a row forming a peroxy linkage.

Accordingly, the Applicant began looking for ways that might might allow Caro's acid to be generated in an economically reasonable manner. He located US patent 5,304,360 (Lane et al), which described a device and reaction scheme for manufacturing Caro's acid, and that patent also cited several earlier patents that also disclose other processes for making Caro's acid, including US 2,789,954 (Fell, 1957), and 3,900,555 and 3,939,072 (Jourdan-Laforet, 1975 and 1976).

These inquiries led him to Marshall's acid, which is peroxy-di-sulfuric acid. The short formula is H₂S₂O₈. The more revealing formula is HO₂SO-OSO₂H, which makes it clear that Marshall's acid is a symmetric di-acid with a peroxy linkage in the middle.
If Marshall's acid breaks apart, it can generate two "strong" free radicals that are identical to each other, rather than just one, as created by Caro's acid and most other radical initiators. The reference to "strong" free radicals includes free radicals with a highly electronegative inorganic atom, such as HS\(_2\)SO\(_4\)*; it does not include simple hydroxy (HO*) free radicals, as released by hydrogen peroxide (and Caro's acid), since simple hydroxy free radicals are not strong enough to quickly and effectively remove a hydrogen atom from methane.

Therefore, the Applicant realized that Marshall's acid might be a good reagent, if it could be generated on-site, in an economically reasonable manner, and then used promptly. Accordingly, he began looking for ways that can be used to synthesize Marshall's acid, and he located US patent 3,927,189 (Jayawant 1975, assigned to DuPont). That method involves reacting hydrogen peroxide with sulfur trioxide, to first create Caro's acid, and then adding more sulfur trioxide, to drive at least a portion of the Caro's acid to Marshall's acid. The '189 patent indicated that this should be done under mild conditions, with temperatures not to exceed 45°C, while taking care to control certain molar ratios and to ensure that the liquids (and gases, if any) remain properly dispersed. This patent confirmed that any such reactions should be carried out quickly, before the Caro's acid intermediate (which is unstable) has time to decompose.

Accordingly, it appeared that a practical way to manufacture Marshall's acid had been disclosed. That provided the final piece of the puzzle, and the Applicant asked the doctoral candidate who was doing computer modeling for him to do some modeling of a Marshall's acid system.

The results of that computer modeling convinced both men that this system is indeed feasible and practical. The Applicant then disclosed the results, in confidence, to various people, including several officials at the U.S. Department of Energy, and Prof. Ayusman Sen at Penn State University, whose research group soon began doing laboratory tests, as described in the Examples below. The results of those tests confirmed that this system does indeed work, in the manner intended.

**CALCULATED DH AND DG VALUES**

As is known to anyone who works with computer modeling of chemical reactions, there are certain numerical values that can be calculated during computer modeling, to provide
indicators of how well and how efficiently a proposed pathway will be followed. One of those two values is usually expressed as DH. In chemical terms, the variable "H" refers to something that can be regarded as heat; however, it must be understood that this type of heat refers to heat potential that is stored in the form of chemical bonds, rather than to the current temperature of some particular compound or material. To distinguish this quantity from temperature, it is usually called enthalpy by chemists. The Greek symbol DDD (called "delta", in English) indicates that a numerical value for DH indicates the difference between two energy states, rather than an absolute value.

For many classes of chemical reactions, two different DH (enthalpy) values must be calculated, and both are crucially important. One value, called the "heat of activation" (abbreviated herein as DH\textsubscript{ACT}) indicates how much energy must be put into a material or mixture, in order to get a reaction started along a certain pathway. In a simple analogy, the "heat of activation" is comparable to saying that before a piece of paper or wood will begin to burn, the burning reaction must be started, somehow, by first putting energy into the system. This can be done by lighting a piece of paper or wood with a match, or some other source of flame or heat.

The heat of activation (DH\textsubscript{ACT}) for a chemical reaction can be shown on a graph, by plotting various calculated numbers in an energy profile, comparable to the profile shown in FIG. 3. When drawn on this type of graph, the energy state of a starting material (or combination of reagents) begins at a baseline value or starting point that is arbitrarily set at zero. This initial baseline value of zero simplifies the calculations, and makes it easier to quickly interpret any numbers that follow.

Starting at a zero point for unreacted reagents, the energy of the starting material or mixture must first climb over some sort of hump, or peak, which requires activation energy to be introduced into the system, to get the reaction started. This initial hump, or peak, represents an increase in energy, and the height of this hump or peak depicts the heat of activation (DH\textsubscript{ACT}). To use the analogy from above, this initial increase in enthalpy is what happens when a burning match is held to a piece of paper or wood; the flame from the match provides the activation energy that will cause the paper or wood to start burning.

When a material or mixture that is being heated reaches a "transition state" (abbreviated as TS in the graphs), it will begin burning (or otherwise chemically reacting) on its own, in a
manner that will release more heat than was required to start the burning process or other reaction. This is what enables a piece of paper or wood to keep burning, and begin releasing heat, once it has started to burn. This reaction is depicted by the large downward slope on the right side of the energy profile that can be drawn by calculating the energy states at each major point along a reaction pathway.

If the reaction is allowed to proceed all the way to completion, the amount of heat that was released by the overall reaction can be measured (or calculated, by computer software). This amount of "total heat release" is usually expressed as the "heat of reaction", abbreviated herein as $\Delta H_{\text{RXN}}$. By convention, it is measured and expressed, not compared to the peak that represents the highest-energy transition state with the heat of activation, but compared to the baseline zero value that applied to the initial, unheated and unreacted material or mixture. Therefore, it represents a "net" energy output.

The overall (net) heat of reaction ($\Delta H_{\text{RXN}}$) for a chemical reaction, is crucially important in analyzing the reaction, because it indicates how much more "stable" the reaction products are, compared to the unreacted starting material. It provides a numerical indication of how readily and easily a certain material or mixture can be converted to a certain set of desired reaction products. In addition, in a sophisticated computer model that also is able to recognize competing pathways (as well as competing intermediates and products that may be more stable than the desired intermediates and products), this type of modeling also can provide useful indicators of how efficient the yield(s) will be, and the quantities of unwanted byproducts or unreacted reagents that are likely to be generated by the process.

Both of those two values (the heat of activation, $\Delta H_{\text{ACT}}$, and the heat of reaction, $\Delta H_{\text{RXN}}$) are crucial in any complex chemical reaction, and both values must be calculated by a computer program used to model complex chemical reactions.

However, as is known to chemists, those two DH values tell only half of the story, when a chemical reaction is being modeled on a computer. The other crucial calculation involves DG, which refers to the change in entropy that is created by a certain chemical reaction. In layman's terms, entropy is a value that indicates unusable or wasted energy, which gets lost to the surrounding environment when a certain chemical reaction occurs, in terms that can be thought of as waste heat, "randomness", or "free energy" (free, not in a good sense, but in the way that
would be used by a livestock owner whose cattle or horses, which had been carefully gathered
and penned in a corral, have broken down a fence and are now running free). This type of "free"
or unusable energy is often referred to by chemists as "overhead", because it is analogous in some
respects to taxes, pension costs, time that must be diverted from other work to fill out
government forms, and inventory shrinkage due to thefts. These are some of the "overhead" costs
of running a business, and if they keep creeping higher and higher, until they collectively
accumulate to unacceptable or intolerable levels, they can render a business unprofitable and
eventually drive it into bankruptcy.

Since calculated DG values represent "overhead" or "unproductive costs," small or
negative DG values for a certain reaction indicate that the reaction is promising, and is likely to
proceed readily and with good yields. By contrast, high DG values are bad, and indicate that a
reaction will be troubled by sluggishness, low yields, and other problems.

As an example of how DG values can indicate whether a reaction pathway will proceed
efficiently, graphs of several successive DG values, for certain intermediate states that will occur
in a bromate-sulfate system as developed by the Applicant, and in an iodine system disclosed in
the prior art, is provided in FIG. 6 of this application. The elevated "humps" that represent the
transition states (TS) for both pathways indicate that energy must be put into the system to get the
reaction started, as discussed above. The negative final values indicate that the reactions can
proceed, if they can get past the transition-state "humps". By comparing the free energy states of
the bromate-sulfate system against the free energy states of the iodine system, as shown in FIG.
6, it becomes clear that the calculations indicate that the bromate-sulfate system offers a more
promising system that can probably generate better yields than the iodine system, since the
transition state of the bromate-sulfate system is not as high (and therefore not as difficult to reach
and cross, and not as likely to drive any reagents or intermediates toward alternate pathways that
can be taken with less energy) as the transition state that occurs in the iodine system.

The calculated DH\text{ACT}, DH\text{Rxn}, and DG values for a number of reaction pathways that are
disclosed herein turn out to be exceptionally or even extraordinarily promising, based on the
computer modeling done to date. Those calculated numbers are not enclosed with this patent
application, partly since the specific and detailed numbers are not necessary for actually carrying
out this invention once the conclusions, pathways, and mechanisms have disclosed, and partly
because the Applicant does not yet have a strong and reliable sense of how heavily and strongly those calculated numbers (which were generated by a graduate student) can be relied upon. Nevertheless, those numbers have been submitted to the U.S. Patent and Trademark Office, in an appendix that was included along with provisional application xxx. After this current utility patent application has been published, the file containing the provisional application, including the appendix containing the theoretical paper with the DH and DG energy calculations, will be opened for inspection and copying, by the public. Anyone is welcome to inspect those numbers, and to contact the Applicant directly if they wish to obtain them prior to publication of this application. However, it must be emphasized and understood that: (i) these computer simulations are not perfect, and instead are based entirely on computer simulations using highly complex software; (ii) any such computer modeling must rely upon various simplifying and other assumptions, which must be selected and chosen, as part of the programming, before any particular computer model of a complex system can be run; (iii) the only real proof of a modeled pathway must come from actual performance of the reaction system, both at small-scale benchtop levels, and in larger scaled-up facilities; and, (iv) this invention does not rest or rely upon any of those computer-modeled numbers, and instead rests on the disclosure of new and valuable chemical pathways that can be understood, followed, and used by those skilled in the art, based solely on the disclosures in this application, supplemented by the level of skill in the art among those who specialize in hydrocarbon chemistry.

POTENTIAL COMPETING REACTIONS

Several potentially competing reactions have been identified by the Applicant, which, if they were to occur in large quantities, might interfere with the desired pathway from methane to MSA or methanol.

The computer simulations that have been performed to date indicate that these potentially competing reactions generally should not create major problems that would seriously hinder the reaction schemes disclosed herein, for the reasons described below. Nevertheless, anyone who tests any of the reaction schemes disclosed herein, either on a small-scale benchtop level or in scale-up testing, should be aware of these potentially competing pathways, so that appropriate steps can be taken to monitor them, and to avoid or minimize them if necessary, by any
appropriate means (such as by adding one or more additives or inhibitors, by adjusting one or more reaction parameters to shift a thermodynamic drive or balance away from the unwanted compound(s), by passing a fluidized stream through an immobilized bed that will trap unwanted compounds, etc.).

Two potentially competing pathways are shown in FIG. 4, which comprises FIG. 4A and FIG. 4B.

In the top pathway, the methylsulfonic acid radical (H₃CSO₂⁻) may react with a completed molecule of MSA, H₃C-SO₂⁻, in a manner that would effectively (as the net result of a two-step process) transfer one of the hydrogen atoms from a methyl group, on completed methylsulfonic acid, to an oxygen atom, on a methylsulfonic radical. This would effectively transfer the highly reactive unpaired electron from an oxygen atom, to a methyl group, as shown in FIG. 4A. However, the computer simulations done to date indicate that if this happens, the resulting in a HO-SO₂-CH₂⁻ radical will either: (i) spontaneously rearrange by itself, or (ii) react with another molecule of MSA, in a way that will transfer the unpaired electron back to the oxygen atom, rather than leaving it on a methyl group. Either rearrangement will regenerate the same type of MSA radical that started the process, where the unpaired electron is on an oxygen atom, rather than on a methyl group.

In the other potentially competing pathway, shown in FIG. 4B, a molecule of completed MSA, H₃C-SO₂⁻, rather than being removed from the system quickly so that it can be broken into methanol and SO₂, might react instead with a methyl radical (CH₃), in a way that regenerates an MSA radical (CH₃SO₂⁻) while also regenerating methane (CH₄) from the methyl radical. However, the computer simulations done to date indicate that if this unwanted reaction occurs, the newly-created MSA radical will quickly attack a complete molecule of methane (since fresh quantities of methane presumably are being supplied in bulk to the system at all times), and the MSA radical will remove a hydrogen atom from the methane, to create completed MSA along with a new methyl radical (CH₃). In a properly-optimized and properly-run system, which constantly supplies fresh (i.e., regenerated and recycled) SO₂ to the system while also constantly removing MSA condensate from the system, the new methyl radical will be much more likely to attack an SO₂ molecule that has just entered the system, than a recently completed MSA molecule that is on its way out of the system.
SYMPhORIC AND ANCHIMERIC SYSTEMS; THE BROMATE-SULFATE SYSTEM

FIGURE 5 depicts the symphoric and anchimeric reaction system that was developed by the Applicant, a bi-functional reagent that has both an electrophilic (i.e., positively charged and electron-seeking) domain, and a nucleophilic (i.e., negatively charged and proton-seeking) domain. In order to qualify as symphoric and/or anchimeric, those two domains must be (i) contained in the same molecule, and (ii) spaced apart from each other, by a distance that will allow the reagent to provoke coordinated proton and electron shifts, in a particular type of targeted hydrocarbon molecule, in a manner that will create transitional intermediates having reduced thermodynamic barriers. These types of coordinated proton and electron shifts can improve the selectivity and yield of a reaction system for converting an otherwise stable and/or symmetric hydrocarbon (such as methane, or other lower alkanes) into other intermediates or products that are more reactive and easier to handle and work with.

A particular bromate-sulfate reagent, having the formula HO$_2$S-O-BrO$_2$, was settled upon by the Applicant as being exceptionally well-suited for exerting symphoric and anchimeric effects on methane. It can drive methane through a reaction pathway that can generate methyl bisulfate (H$_3$COSO$_3$H), as shown in FIG. 5. The methyl bisulfate can be hydrolyzed to release methanol, which can be used or sold, and this hydrolysis will also release sulfuric acid, which in this system can be recycled, without forming waste, to regenerate the bromate-sulfate reagent.

Accordingly, the bromate-sulfate reagent and system shown in FIG. 5 are disclosed as an exemplary system for converting methane into other products, such as methanol. Although the radical-initiator system (using Marshall's acid) that was subsequently developed by the Applicant is believed to offer a better pathway for converting methane into methanol, the bromate-sulfate system is believed to offer a better pathway than any other system that was ever known, prior to its discovery by the Applicant. Accordingly, as mentioned above, it should be studied carefully by any organic chemists who are interested in methane or other lower hydrocarbons, since it may offer a powerful set of tools and options that may be able to achieve various useful results, in a manner that will be complementary to the radical initiator system, and that may be applicable to various situations where a radical initiator system will not work (such as, in particular, when dealing with mixtures of reagents, in which highly reactive free radicals would react with too
many different compounds, thereby providing low and unsatisfactory selectivities and yields).

The bromate-sulfate reagent (or any other similar symphoric and/or anchimeric reagent having both electrohilic and nucleophilic domains, spaced apart from each other a controlled distance) can also be computer-modeled and laboratory-tested, to evaluate its ability to manipulate ethane, propane, or any other lower alkane molecule (as used herein, terms such as "lower alkane" or "lower hydrocarbon" include compounds that have up to four carbon atoms). Such symphoric and/or anchimeric reagents can also be modeled and/or tested with any other type of compound that contains carbon and hydrogen atoms (the term "hydrocarbon is used broadly herein, to include any compound that contains both hydrogen and carbon atoms, regardless of whether such compound also contains oxygen, sulfur, nitrogen, or any other element). Candidate compounds include (i) substituted alkanes; (ii) cycloalkanes, include hetero and/or substituted cycloalkanes that have non-carbon, non-hydrogen atoms, either as part of the ring, or attached to the ring; (iii) aromatic hydrocarbons; and (iv) unsaturated hydrocarbons.

VARIATIONS ON MARSHALL'S ACID, BROMATE-SULFATE, AND METHANE

It will be recognized by those skilled in organic chemistry that the reaction schemes disclosed above (the radical initiator system, as exemplified by the Marshall's acid system, and the symphoric and anchimeric system, as exemplified by the bromate-sulfate system) are merely exemplary, and the factors and principles that enable both of these systems to perform with low thermodynamic barriers and high selectivity, while minimizing and avoiding the generation of waste or unwanted byproducts, can be adapted to other types of hydrocarbon reactions, in various ways. As examples, these systems (alone, or in combination) can be adapted and used in various ways to convert other small hydrocarbons, including lower alkanes such as ethane and propane, and possibly cycloalkanes, aromatics, or other classes of hydrocarbons, into various "functionalized" intermediates and products that are chemically valuable and useful. It may also be possible to adapt these systems for use with unsaturated reagents, such as ethene, propene, etc.

EXAMPLES
EXAMPLE 1: EQUIPMENT AND REAGENTS

All tests described below were done in the laboratories of Prof. Ayusman Sen, in the Chemistry Department at Pennsylvania State University. All experiments were carried out under inert gas (nitrogen, N₂) in either a glovebox or a glovebag.

Except as noted below, the reactions were carried out in a sealed vessel designed to withstand high pressures (these devices are commonly referred to in chemistry labs as "bombs"), containing a glass liner (this liner, which can be easily removed for thorough cleaning and sterilization, will not break when high pressures are reached inside the bomb, because the pressures will be equal on both sides of the glass walls of the liner). The bomb used has a 3/8 inch stainless steel walls, and an internal chamber 1.5 inches in diameter and 4.5 inches high. The glass liner had an internal diameter of 1.24 inches, a height of 4 inches, and a wall thickness of 1/16 inch. A stirring bar was used in some experiments, 1 inch long and having a roughly circular cross section of 3/16 inch diameter.

In a number of experiments, a vial was placed inside the liner, to ensure that there was no direct mixing of a first liquid that was loaded into the bottom of the glass liner, and a second liquid that was loaded into the vial. The vial that was used had a 1 inch outside diameter, a wall thickness of 1/16 inch, and a height of 2.25 inches. The diameter of the opening on top (with external threads, to accommodate a screw cap) was 5/8 inch. A small stirring bar was sometimes placed inside the vial, with a length of 1/2 inch and a diameter of 1/8 inch.

EXAMPLE 2: PREPARATION OF MARSHALL'S ACID

To prepare Marshall's acid (peroxy-disulfuric acid), a gaseous mixture of SO₃, in inert nitrogen (N₂) was loaded into a vessel containing a solution of 70% hydrogen peroxide in water, at 13 to 15°C. The reaction was continued, with stirring, until essentially all liquid reagents had been consumed, which was confirmed by the presence of a consistent viscous solution with some solid crystals present, but with no inhomogeneous liquids.

In Run #1, 6.9 g (86.3 mmol) of SO₃ was absorbed in 1.1 g of 70% H₂O₂ (22.7 mmol) in water (17.7 mmol), for 5.5 hours. After accounting for the diversion of some SO₃ into H₂SO₄, the molar ratio of SO₃ to H₂O₂ was 3:1. It was presumed that all H₂O₂ was converted to Marshall's acid (H₂S₂O₈), and all water was converted to H₂SO₄. These calculations and assumptions
indicated that the solution contained Marshall's acid at 22.7 mmol (56.2% of the total solution, by weight), and sulfuric acid at 17.7 mmol (21.3%), with unreacted SO₃ present at 23.2 mmol (22.5%).

In Run #2, 5.2 g (65 mmol) of SO₃ was absorbed in 1.2 g of 70% H₂O₂ (25 mmol) in water (19.4 mmol), for 5.5 hours. Since the molar ratio of SO₃ (after subtracting a number of mmol of SO₃ for formation of H₂SO₄) to H₂O₂ is 1.8:1, it was presumed that the first equivalent of SO₃ reacted with H₂O₂ to form Caro's acid (H₂SO₃), and the rest of the 0.8 equivalent of SO₃ reacted with the Caro's acid to form Marshall's acid. These assumptions indicated a solution of Marshall's acid at 20.6 mmol (62.5%), sulfuric acid at 19.4 mmol (29.7%), and Caro's acid at 4.4 mmol (7.8%).

In Run #3, 8.3 g (103.8 mmol) of SO₃ was absorbed in 1.8 g of 70% H₂O₂ (37.0 mmol) in water (30.0 mmol), for 7 hours. After subtracting a number of mmol of SO₃ for formation of H₂SO₄, the molar ratio of SO₃ to H₂O₂ was 2:1. This indicated a solution of Marshall's acid at 37.0 mmol (71.3%), and sulfuric acid at 30 mmol (28.7%).

In Run #4, 8.3 g (103.8 mmol) of SO₃ was absorbed in 2.1 g of 70% H₂O₂ (43.2 mmol) in water (35.0 mmol), for 7 hours. The molar ratio of SO₃ (after accounting for H₂SO₄ formation) to H₂O₂ was 1.6:1. This indicated a solution of Marshall's acid at 25.6 mmol (47.7%), sulfuric acid at 35 mmol (33%), and Caro's acid at 17.6 mmol (19.2%).

EXAMPLE 3: PROCEDURES FOR TESTING MSA FORMATION

The tests described below use MSA/SO₃ mixtures as the liquid media. Gaseous SO₃ can be efficiently absorbed in methanesulfonic acid (MSA), at ratios up to about 10:1, so a solution of SO₃ absorbed in liquid MSA was placed in a glass vial, as described above, 1 to 2 grams of a Marshall's acid solution (prepared as described in Example 2) was placed in the same vial.

The vial was placed inside the somewhat larger glass liner (also described above) in the bomb, and 3 to 5 g of stabilized liquid SO₃ was loaded into the liner.

This approach (dividing the SO₃ into two separate zones) was taken to prevent the Marshall's acid from being overloaded with SO₃, since high concentrations of SO₃ can trigger degradation of Marshall's acid, causing it to release oxygen, and destroying its peroxyde bond.

The bomb was sealed and pressurized with 800-1400 psi of methane. It was heated to
48-52°C, and the pressure was monitored as it dropped. Heating was continued until the pressure no longer continued to fall, and reached an asymptotic level.

The bomb was then allowed to cool gradually to room temperature, over a couple of hours. The pressure was released slowly, the bomb was opened, and the solution in the vial was diluted with 5-10 mL of water. The liquid was then analyzed, via \(^1\)H nuclear magnetic resonance (NMR).

In most cases, MSA was the only product that was found in the liquid phase. It was quantified, using integration of peak intensity compared to a standard peak of dimethyl sulfoxide, in a capillary tube, to confirm that additional MSA had indeed been formed, in addition to the MSA that was already present in the liquid that was initially loaded into the vial.

The gas mixture that was present in the cooled bomb was also analyzed, by gas chromatography. No carbon dioxide was detected in the gas phase, in any of the test runs.

**EXAMPLE 4: FIRST RUN: METHANE YIELD 40.4%, SO_3 YIELD 96.0%**

In the first reaction test that was run as described above, 1.0 gram of the Marshall's acid preparation described in Run #1 (above) was used (with Marshall's acid at 56.2%, sulfuric acid at 21.3%, and SO_3 at 22.5%). This was added to a vial containing 50 mmol of MSA and 63 mmol of SO_3. 2.8 g (35 mmol) of stabilized liquid SO3 was added to the liner, outside the vial. The bomb was pressurized to 800 psi with purified methane, and heated at 48-52°C.

70 psi of pressure drop was observed within 2 hours, and the vessel was recharged with 50 additional psi of methane. The total pressure drop rose to 120 psi over the next 2 hours (i.e., after 4 hours total), and the vessel was recharged with an additional 50 psi of methane. The total pressure drop was 250 psi over 14 hours.

The total methane that was injected into the bomb was measured and calculated at 240 mmol, and the total amount of SO_3 in the liquid media (i.e., dissolved in MSA and placed inside the vial) was 101 mmol.

The yield of newly-formed MSA was measured and calculated to be 97 mmol (147 mmol total, minus 50 mmol already present in the MSA/SO_3 liquid media).

This indicated a methane conversion yield of 40.4%, and an SO_3 conversion yield of 96.0%.
EXAMPLE 5: SECOND RUN: METHANE YIELD 40.6%, SO₃ YIELD 99.1%

In the second reaction test that was run as described above, 1.0 g of Marshall's acid solution from Run #2 (above) was loaded into a vial containing 48 mmol of MSA and 71 mmol of SO₃. 3.0 g (38 mmol) of stabilized liquid SO₃ was loaded into the liner, outside the vial. The bomb was pressurized with 1000 psi of methane, and heated at 48-52°C.

100 psi of pressure drop was observed after 2 hours; 150 psi of pressure drop was observed after 4 hours; and 280 psi of pressure drop was observed after 12 hours.

The total methane in the bomb was measured and calculated to be 266 mmol. The total SO₃ in the liquid media was calculated at 109 mmol. The yield of MSA was measured and calculated to be 108 mmol (156 mmol minus 48 mmol).

This indicated a methane conversion yield of 40.6%, and an SO₃ conversion yield of 99.1%.

EXAMPLE 6: THIRD RUN: METHANE YIELD 43.3%, SO₃ YIELD 92.6%

In the third reaction test that was run as described above, 1.5 g of Marshall's acid solution from Run #3 (above) was loaded into a vial containing 43 mmol of MSA and 99 mmol of SO₃. 4.0 g (50 mmol) of stabilized liquid SO₃ was loaded into the liner, outside the vial. The bomb was pressurized with 1200 psi of methane, and heated at 48-52°C.

150 psi of pressure drop was observed after 2 hours; 250 psi of pressure drop was observed after 4 hours; and 300 psi of pressure drop was observed after 10 hours.

The total methane in the bomb was measured and calculated to be 319 mmol. The total SO₃ in the liquid media was calculated at 149 mmol. The yield of MSA was measured and calculated to be 138 mmol (181 mmol minus 43 mmol).

This indicated a methane conversion yield of 43.3%, and an SO₃ conversion yield of 92.6%.

EXAMPLE 7: FOURTH RUN: METHANE YIELD 33.6%, SO₃ YIELD 92.6%

In the fourth reaction test that was run as described above, 2.4 g of Marshall's acid solution from Run #4 (above) was loaded into a vial containing 43 mmol of MSA and 77 mmol
of SO$_3$. 4.6 g (58 mmol) of stabilized liquid SO$_3$ was loaded into the liner, outside the vial. The bomb was pressurized with 1400 psi of methane, and heated at 48-52°C.

100 psi of pressure drop was observed after 1 hours; 180 psi of pressure drop was observed after 2 hours; 240 psi of pressure drop was observed after 3 hours; and 300 psi of pressure drop was observed after 6 hours.

The total methane in the bomb was measured and calculated to be 372 mmol. The total SO$_3$ in the liquid media was calculated at 135 mmol. The yield of MSA was measured and calculated to be 125 mmol (168 mmol minus 43 mmol).

This indicated a methane conversion yield of 33.6%, and an SO$_3$ conversion yield of 92.6%.

Upon examination and comparison of these data, it appeared that the concentration of methane in the bomb was the rate determining factor, since increasing methane pressure increased the rate of the reaction. According to our previous calculation, the molar concentration of CH$_4$ (1200 psi) in H$_2$O at 50°C is 0.078M, solubility of CH$_4$ could be higher in MSA/SO$_3$ mixture, but it is still quite low comparison with the amount of SO$_3$ in the liquid phase. Therefore the key step for increasing rate of the reaction is increasing the solubility of CH$_4$ in liquid phase.

In addition, various calculations (including a calculated rate constant of 3.0 x $10^{-5}$ per second, for homolysis of Marshall's acid in SO$_3$ at 50°C) indicated that the rate of conversion of methane to MSA is around 20 times faster than the rate of homolysis of Marshall's acid. This helps explain why the pressure continued to drop over spans of 10 hours (in the laboratory test conditions that were used) and why conversion of SO$_3$ was in very high ranges, up to 99%. When scaled up to industrial levels, where continuous-flow devices that are designed for high throughput levels (such as loop reactors and/or spinning bed reactors) are used instead of small-volume batch reactors, it is anticipated that efficient and economical reaction levels can be achieved in minutes, or even seconds, rather than over a span of hours.

EXAMPLE 8: NO CONVERSION BY POTASSIUM SALT OF MARSHALL'S ACID

As a comparative experiment, 270 mg of the potassium salt of Marshall's acid (K$_2$S$_2$O$_8$; 1.0 mmol) was loaded into the vial, and 13.5 g of stabilized SO$_3$ was loaded into the liner, using
procedures identical to the testing of the free acid form of Marshall's acid, as disclosed above. The bomb was pressurized with 800 psi of methane, and heated at 48-52°C for 20 hours. However, no pressure drop was observed. Then temperature was then increased to 75-80°C, for an additional 16 hours, but still no pressure drop was observed.

The absence of any pressure drop indicates that the potassium salt of Marshall's acid failed to initiate any reaction between the methane, and the SO₃.

Thus, there has been shown and described a new and useful means for creating methanol from methane, and for creating other useful and valuable lower alkane derivatives, intermediates, and products, from methane and other lower alkane molecules. Although this invention has been exemplified for purposes of illustration and description by reference to certain specific embodiments, it will be apparent to those skilled in the art that various modifications, alterations, and equivalents of the illustrated examples are possible. Any such changes which derive directly from the teachings herein, and which do not depart from the spirit and scope of the invention, are deemed to be covered by this invention.

REFERENCES


CLAIMS

1. A method for converting methane into an oxygenated derivative, comprising the following steps:
   a. removing hydrogen atoms from methane, thereby generating methyl radical intermediates, each having an unpaired electron, within a reactor device;
   b. contacting the methyl radical intermediates with a selected oxide compound, under conditions that cause the methyl radicals to react with the selected oxide compound in a manner that forms a methylated oxide radical, wherein the methylated oxide radical has sufficient reactivity to remove hydrogen atoms from newly-added methane; and,
   c. reacting the methylated oxide radical with methane, under conditions that cause removal of hydrogen atoms from the methane, thereby forming stabilized methylated oxide molecules while also generating newly-formed methyl radicals.

2. The method of Claim 1 wherein a series of reaction steps is initiated by a radical initiator compound, and then sustained on a steady-state basis by adding appropriate quantities of the selected oxide compound, and additional methane, to a reactor device.

3. The method of Claim 2 wherein the series of reaction steps, taken together, generate non-recyclable byproducts in a total quantity of less than 10 percent, by weight, of stabilized methylated oxide molecules formed by the method.

4. The method of Claim 2 wherein the series of reaction steps, taken together, generate non-recyclable byproducts in a total quantity of less than 2 percent, by weight, of stabilized methylated oxide molecules formed by the method.

5. The method of Claim 1 wherein all reaction steps, taken together, generate non-recyclable byproducts in a total quantity of less than 2 percent, by weight, of stabilized methylated oxide molecules formed by the method.
6. The method of Claim 1 wherein the reaction steps are carried out using anhydrous reagents.

7. The method of Claim 1, wherein hydrogen atoms are initially removed from methane by means that comprise contacting methane with a radical-initiator compound that has been treated to cause it to form at least one unstable intermediate species having a substituent with an oxygen radical.

8. The method of Claim 7, wherein the unstable intermediate species are formed by treating an acidic inorganic radical-initiator compound, shortly before contacting the unstable intermediate species with methane.

9. The method of Claim 8, wherein the acidic inorganic radical-initiator compound is characterized by absence of any substantial quantity of metal ions or salt-forming substituents.

10. The method of Claim 7, wherein the radical-initiator compound comprises an inorganic acid having a peroxide linkage.

11. The method of Claim 10, wherein the radical-initiator compound comprises a symmetric inorganic di-acid having a peroxide linkage, wherein said compound will generate two identical oxygen radicals if the peroxide linkage is broken.

12. The method of Claim 11, wherein the symmetric inorganic di-acid is selected from the group consisting of peroxy-disulfuric acid and peroxy-diphosphoric acid.

13. The method of Claim 7, wherein the unstable intermediate species having a substituent with an oxygen radical is created by contacting an inorganic oxide compound with an oxidant.
14. The method of Claim 13, wherein the oxidant comprises ozone.

15. The method of Claim 13, wherein the inorganic oxide compound comprises sulfur trioxide.

16. The method of claim 1, wherein the stabilized methylated oxide molecules comprise methanesulfonic acid.

17. The method of Claim 16, wherein at least a portion of the methanesulfonic acid is treated in a manner that causes it to release methanol and sulfur dioxide.

18. The method of Claim 16, wherein:
   a. at least a portion of the sulfur dioxide is oxidized to convert it into sulfur trioxide; and,
   b. at least a portion of the sulfur trioxide is contacted with methyl radical intermediates.

19. A method for converting a lower alkane into an oxygenated derivative, comprising the following steps:
   a. removing hydrogen atoms from at least one lower alkane compound, thereby generating alkane radicals;
   b. contacting the alkane radicals with a selected oxide compound under conditions that will cause the alkane radicals to bond to the selected oxide compound, thereby forming alkylated oxide radicals;
   c. reacting the alkylated oxide radicals with at least one lower alkane, under conditions that cause removal of hydrogen atoms from the lower alkane, thereby forming stabilized alkylated oxide molecules while also generating newly-formed alkane radicals.

20. The method of Claim 19, wherein:
   a. the reaction is initiated by removing hydrogen atoms from at least one lower alkane by contacting the lower alkane with a radical-initiator compound; and,
   b. the reaction is sustained, as a steady-state reaction, by adding appropriate quantities of
the selected oxide compound, and lower alkanes, to a reactor device.

21. The method of Claim 20 wherein the steady-state reaction generates unwanted byproducts in a total quantity of less than 10 percent, by weight, of stabilized methylated oxide molecules formed by the method.

22. The method of Claim 21 wherein all reaction steps, taken together, generate unwanted byproducts in a total quantity of less than 2 percent, by weight, of stabilized methylated oxide molecules formed by the method.

23. The method of Claim 19 wherein the reaction steps are carried out using anhydrous reagents.
Fig. 1
METHYL RADICAL

H₃C* → SULFUR TRIOXIDE
→ SO₃

METHANE-SULFONIC ACID (MSA) RADICAL

O

H₃C ← S ← O*

METHANE
CH₄

HYDROGEN TRANSFER

METHYL RADICAL

STABLE MSA, H₃C-SO₃H

SHIP AS PRODUCT

FEEDSTOCK FOR OTHER REACTIONS

METHANOL, H₃COH

THERMAL CRACKING

SO₂

Fig. 2

O₂

V₂O₅
Fig. 4A

Fig. 4B

Potential Isomerizations That Will Self-Resolve

Fig. 4
\[
\text{H}_2\text{SO}_4 \; + \; \text{HBrO}_3 \quad \rightarrow \quad \text{Bromate–sulfate catalyst} = \text{HO}_3\text{S-O-BrO}_2
\]

Methane (CH\textsubscript{4})

Intermediate A

Intermediate B

\[
\text{H}_2\text{SO}_4 \; + \; \text{H}_3\text{C-BrO}_2 \quad \rightarrow \quad \text{H}_3\text{C-O-SO}_3\text{H} \; + \; \text{HBrO}_2
\]

Add H\textsubscript{2}O

Add SO\textsubscript{3}

\[
\text{H}_3\text{COH} \; + \; \text{H}_2\text{SO}_4 \quad \rightarrow \quad \text{Ship}
\]

\[
\text{HBrO}_3 \; + \; \text{SO}_2 \quad \rightarrow \quad \text{Recycle}
\]

**Fig. 5**
Comparison of Free Energy States of Bromate versus Iodine Systems, in Sulfuric Acid