Heterogeneous Combustion: Recent Developments and New Opportunities for Chemical Engineers

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Introduction

Combustion is arguably the first chemical process used by humans. The reason for this is simple: Combustion is generally a self-sustained process and, once initiated, does not require external energy input; on the contrary, it releases heat that can be put to use in various ways. Since Prometheus times, the applications of combustion have become prevalent throughout our life: car engines, power generation, firearms, cigars and cigarettes, rocket propulsion, etc. While, in some cases, combustion occurs in premixed homogeneous gaseous mixtures, most of the earlier examples involve heterogeneous processes.

From a chemical engineer's viewpoint, the self-sustainability and relative simplicity are attractive features to use combustion in addressing important problems facing society. Novel experimental techniques are constantly bringing new insight about processes occurring during combustion of condensed media. Based on these, fundamental concepts related to heterogeneous combustion are being developed which open new possibilities for applications. The scope of this article is to describe recent findings in the field and to discuss how these can contribute to the solution of contemporary chemical engineering problems. In this context, we focus attention on four specific topics of significant current and emerging interest: *combustion synthesis of advanced materials, hydrogen production for fuel cells, carbon sequestration, and in-situ resource utilization in extraterrestrial environments*.

It is widely agreed that energy is a critical problem facing humanity today,[1] so the demand for industrial processes with low energy consumption will continue to increase. An example of such technology is combustion synthesis (CS), which has been applied successfully for production of advanced materials, such as nanoscale oxide powders, implants and functionally graded materials.[2,3] The development of CS processes depends on progress in understanding combustion mechanisms in heterogeneous media. Recent achievements in this field offer promise for new exciting applications.

Another energy-related problem is the lack of robust power sources, which inhibits further growth opportunities for portable electronic devices. Heterogeneous combustion is likely to play an important role in this field, leading particularly to new methods for hydrogen storage.

The rapid worldwide growth in energy consumption is increasing greenhouse gas emissions. To avoid further global warming, carbon sequestration technologies are required. In this direction, along with other CO_2 capture methods, novel processes, such as chemical looping combustion offer great potential.

Finally, in future space exploration, the need for propellants and materials will expand chemical engineering approaches beyond the bounds of Earth. In this context, heterogeneous combustion is expected to play an important role.

Combustion Synthesis of Advanced Materials

We discuss two wide classes of CS processes. These are the original *solid flame* CS or *self-propagating high-temperature synthesis* (SHS)[2,4] and the process of combusting a liquid (typically aqueous) solution of reactants.[3] The CS of initially solid samples can be used to obtain such compounds as borides, carbides, hydrides, intermetallics, nitrides, oxides and silicides in the form of powders, poreless, porous or functionally graded materials, while *solution combustion synthesis* (SCS) is an attractive method for producing nanomaterials, particularly oxides.

When using these methods, in each case some specific properties of the resulting material are targeted. For example, biocompatibility of CS products is of critical importance in fabricating biomaterials. In addition, by fine-tuning the operating pressure, it was possible to synthesize poreless orthopedic implants.[5] The CS technique also proved useful in producing porous functionally graded biomaterials.[6]

Mechanisms of combustion wave propagation in heterogeneous media

The general idea about movement of combustion waves, suggested more than 100 years ago,[7] is that layer-by-layer

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propagation occurs because of initiation of the reaction between premixed components by heat conducting from a neighbor layer in which the exothermic reaction is proceeding. Thus, the propagation is determined by two main factors: kinetics of the reaction heat evolution and rate of heat transfer from the reaction zone to the unreacted mixture. In heterogeneous systems, reaction kinetics is the controlling step for dense compact media containing fine particles (*quasi-homogeneous mechanism*), while particle-to-particle heat conduction is limiting for loosely packed coarse mixtures (*relay-race mechanism*).[8]

Developments in experimental techniques have led to observations of new features and to microheterogeneous modeling approaches. These are increasing fundamental understanding of the involved processes, and enhance progress toward the synthesis of advanced materials with tailored microstructures and properties.

A novel digital high-speed video recording technique was developed, which allows *in situ* observation of rapid processes occurring at the microscopic level.[9] Using this technique, significant information about the microstructure of gasless combustion waves was obtained and a basis was created for understanding the mechanisms of fast chemical reactions occurring in heterogeneous media. It was found that the combustion wave may exhibit unexpectedly complex dynamics. Although on macroscopic length and timescales the combustion reaction front may appear to move in a steady manner, on the microscopic level it has a complex character that is related to the reaction mechanism.

Over a wide range of experimental conditions, macroscopically steady reaction fronts in heterogeneous mixtures may exhibit random microscopic fluctuations in shape and instantaneous velocity, which are directly related to the microstructure of the reaction mixture (i.e. the initial heterogeneity of the reaction medium).[10] The reaction wave can propagate in two qualitatively different modes. The first mode, *quasi-homogeneous reaction wave* (QRW), involves a continuous front which moves uniformly and there is practically no variation of behavior along the surface of this front (Figure 1a). Another type of combustion wave propagation (Figure 1b) exhibits a lower average temperature, but relatively bright spots appear randomly, indicating local regions of high temperature along the front. Thus, the front moves forward only as a consequence of appearance of the hot spots, and the overall progress of the front occurs only locally in the vicinity of the spot. Based on these features, this mode of propagation is called *scintillating reaction wave* (SRW).

The classical consideration of combustion in condensed systems[11] is based on mass and energy balances at the macroscopic scale and using average values for reactant concentrations and temperature. It appears that in heterogeneous media, the characteristic length of heat conduction may often approach the scale of particle size,[12] leading to the SRW regime. The hot spots appear when the local region reaches the ignition temperature. Interestingly, in mixtures where the reaction is initiated by the melting of a component (note that the SRW mode was observed only in those systems where at least one reactant melts), the melting point plays the role of ignition temperature due to melt spreading and reaction rate acceleration induced by dramatic increase in the contact area and diffusion coefficients.

To capture the features of the SRW propagation mode, a *micro-heterogeneous cell model* was developed, involving regular lattice with random voids.[13,14] The model was applied to simulate combustion wave in heterogeneous media by considering a discrete matrix of reaction cells, of particle size dimension, with physical and transport properties varying due to random organization of the phases in the reaction mixture. The model captures well the observed peculiarities of heterogeneous combustion wave propagation. Specifically, model predictions agree with experimentally determined threshold between quasi-homogeneous and relay-race combustion modes (see Figure 2).

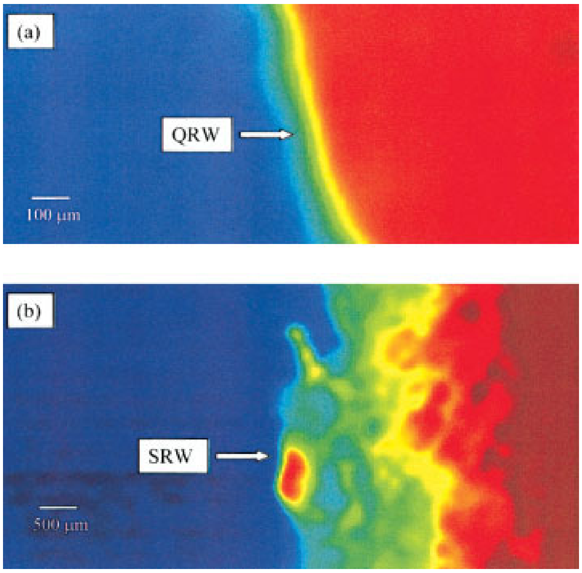

Figure 1. Two modes of combustion wave propagation: (a) quasihomogeneous; (b) scintillating (from Varma et al.[9]).

While the variety of dynamic behavior of homogeneous combustion processes can itself be overwhelming,[15] the features of the observed SRW[9] are certainly related to the heterogeneity of the reacting media. Even a quasi-homogeneous steady-state consideration for combustion of imperfectly mixed solid-solid systems demonstrates that significant deviations in reaction conversion and combustion temperature may arise.[16] Another approach, based on localized reaction sites in a regular lattice for one[17]- and two[18]- dimensional cases, allows one to compute the instantaneous combustion velocity distributions for both relay-race and quasi-homogeneous mechanisms.

It is evident from the above that significant progress has been made, both experimentally and theoretically, in understanding how combustion waves travel in heterogeneous media leading to the CS of advanced materials. The prediction and precise control of product properties based on reactant composition and microstructure, however, still remains a challenge for the future.

Synthesis of nanoscale oxides by solution combustion

Solution combustion synthesis (SCS) is a flexible technique where oxidizing and reducing precursors are mixed on the molecular level and, under unique conditions of rapid high-temperature reactions, nanoscale powders of desired compositions can be synthesized in one step. The oxidizer (typically nitrates or oxalates) and fuel (e.g., hydrazine, glycine, urea) are

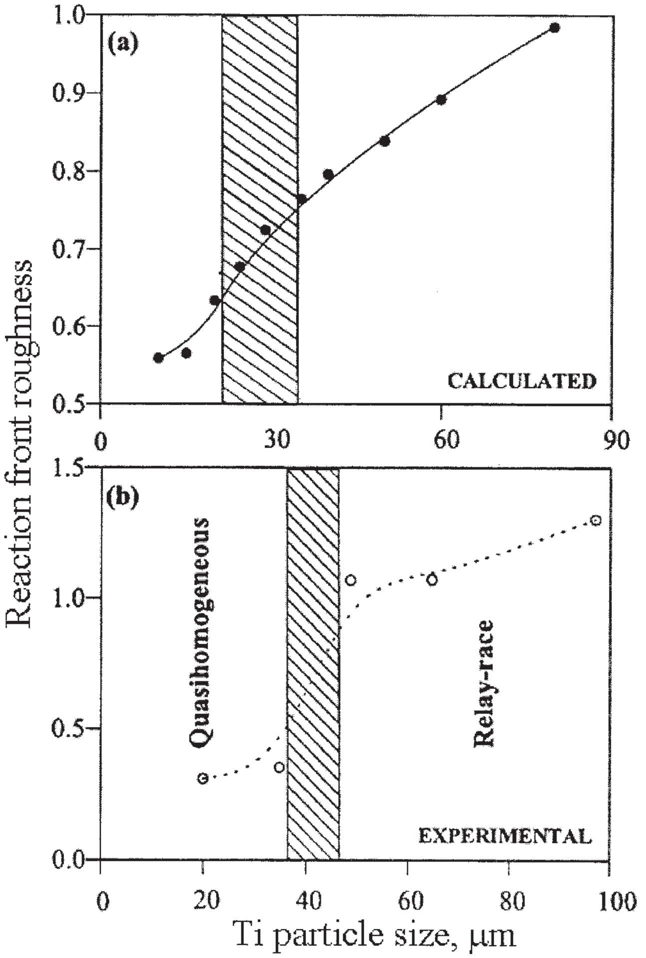

Figure 2. Combustion wave propagation with varying particle size at constant density; Ti-air system (from Varma et al.[14]).

mixed in an aqueous solution, and heated until self-ignition, yielding product gas and nanoscale oxide powders. Solution combustion is a relatively new topic in CS, and is being widely used by researchers to obtain materials for a vast variety of applications, such as oxygen storage capacitors, support and catalyst for catalytic converters, ceramic pigments, solid oxide fuel cell electrode and electrolyte materials, magnetic ferrites, dielectric and piezoelectric components.[3]

The exploration of SCS continues by searching for more suitable and *environmentally friendly fuels*. For example, Prakash et al.[19] developed an SCS technique leading to the formation of complex metal oxides using hexamethylenetetramine, which unlike other fuels (e.g., oxalyldihydrazide, carbohydrazide), can be synthesized by condensation of ammonia with formaldehyde, avoiding potentially harmful hydrazine.

A way to optimize the properties of SCS nanocomposites is by applying *fuel mixtures* and varying their ratio. Thus, depending on the fuel mixture consisting of ammonium acetate, urea and glycine, nanoscale zirconia toughened alumina composite was synthesized in various particle sizes.[20] The fuel-to-oxidizer ratio variation has also been shown to influence product chemical composition in the microwave initiated SCS of Ni and NiO powders.[21] It was demonstrated that Ni particles can be synthesized directly by SCS in air atmosphere, without reducing the product. Further, using the SCS of iron oxide nanopowders as an example, it was shown recently that varying the mixture compositions, both for fuels and oxidizers, is an attractive methodology to control the product composition and properties.[22]

Studies directed toward understanding the mechanisms of SCS are important to tailor desired product properties. In this context, experimental data concerning mixture reactivity are important and TGA/DTA measurements coupled with mass-spectrometry are useful.[19] The data become yet more informative when related to *in situ* SCS measurements.

Dynamic *in situ* temperature measurements during SCS of various iron oxides were related to TGA/DTA results.[22] In this manner, the mechanisms of solution ignition and combustion were addressed in detail. It was shown that specific characteristic phase transformations, which vary with the individual fuel-oxidizer system, are responsible for the observed rapid chemical reactions. Similar experimental studies of iron(III) nitrate interactions with model fuels identified the relative reactivities of different functional groups and led to the formulation of reaction mechanisms.[23]

Interestingly, the variation of fuel-to-oxidizer ratio also affects the combustion mode of the mixture, as shown for SCS of lanthanum-strontium chromite perovskites.[24] Depending on this ratio, the maximum reaction temperature varied, and either smoldering, volume combustion or SHS occurred, leading to different product properties. The rate-controlling step during SCS was also established.

Based on limited mechanistic studies of SCS conducted to-date, it is clear that reactant composition and reaction conditions significantly influence product properties. The relationship between these, however, is not straightforward, and its further development is a promising direction for the future. Detailed mechanistic studies are expected to play a key role in this development.

Hydrogen for Fuel Cells

Hydrogen storage for fuel cells is an important multidisciplinary area of contemporary research, especially attractive for chemical engineers.[25] There are several possible methods for hydrogen storage, such as compressed and liquefied hydrogen, hydrogen adsorption on carbon materials of large surface area, and metal hydrides,[26] but all have limitations which prevent their immediate use in practice. In this context, some promising heterogeneous combustion based techniques have recently been proposed and are described in this section.

Power sources for portable electronic devices

The number and performance characteristics of portable electronic devices in consumer, industrial, medical and military markets are increasing continuously. They include mobile phones, notebook computers, PDAs, digital cameras, DVD players, RFID and barcode scanners, autonomous robots, handheld diagnostics, infusion pumps, defibrillators, etc. The total number of such units in use is difficult to evaluate, but even conservative estimates suggest more than a billion. Simultaneously with increasing performance, the power demand of portable electronic devices is also increasing. Rechargeable batteries are approaching their limits of specific energy (~0.2 Wh/g for the most advanced lithium-ion batteries). This situation is well illustrated by the fact that batteries in notebook computers typically require recharging after 2 h of operation.

Fuel cells provide much higher specific energy and, for this reason, are expected to be widely used in the near future. In contrast to batteries, a fuel cell power system includes separate conversion device (fuel cell itself) and fuel storage/feeding system, analogous to internal combustion engine and gasoline tank/pump in an automobile. Thus, the future power source for portable electronics will include a permanent fuel cell unit inside the device and replaceable fuel cartridges which can be refilled, recycled or discarded.

Methanol and hydrogen are the most promising candidate fuels to feed portable fuel cells. They have specific energies 6.3 and 39.3 Wh/g, respectively. The assumption that direct methanol fuel cells (DMFC) can reach conversion efficiency about 25% leads to the conclusion that specific energy of methanol cartridge would be ~1.5 Wh/g, which is significantly higher than for the best batteries (~0.2 Wh/g). Unfortunately, DMFCs have many drawbacks, such as low power density, methanol crossover, electrode poisoning, methanol toxicity, and catalyst cost, which are serious obstacles to their use.

Hydrogen fuel cells provide much higher power density, do not have any methanol-related problems, and operate with conversion efficiency about 50%. The key problem in development and use of hydrogen fuel cell power sources is *hydrogen storage*. High pressure gas containers are too heavy (thus, leading to much lower specific energy than DMFC) and liquid hydrogen (temperature 20 K) is not possible for use in portable applications. It is generally agreed that chemical methods for hydrogen storage provide the maximum H_2 yield and are the most promising for portable fuel cell applications. A simple estimate shows that 8 wt. % H_2 yield results in specific energy of hydrogen fuel cartridge ~1.5 Wh/g, the same as for DMFCs. The hydrogen fuel cell with the same specific energy as DMFC would be advantageous because of much higher power density and elimination of the methanol-related problems. Thus, the natural question arises: What chemicals and technology should be used to reach the maximum H_2 yield?

Heterogeneous combustion methods for hydrogen generation

Borohydrides of light metals (Li, Be, Na, Mg, Al) are known to be excellent sources of hydrogen, which can be obtained by reactions of these compounds with water or oxidizing agents. Sodium borohydride ($NaBH_4$), discovered during World War II by Nobel laureate Herbert C. Brown of Purdue, is produced for various applications at the rate of about 10,000 tons per year. *Hydrolysis of sodium borohydride* is a well-known process,[27] extensively studied for hydrogen generation.[28,29] Aqueous alkaline $NaBH_4$ solutions are stable and their contact with selected catalysts (e.g., Ru) leads to the reaction

$$NaBH_4 + 2\,H_2O \rightarrow NaBO_2 + 4\,H_2. \tag{1}$$

High theoretical hydrogen yield (10.8 wt. % for stoichiometric mixture) makes this process attractive for applications. The other reaction product, sodium metaborate, is water-soluble, environmentally benign and can either be discarded or recycled to generate new sodium borohydride. Unfortunately, the practical strength of aqueous $NaBH_4$ solution is limited to 30 wt. % borohydride, thus decreasing maximum H_2 yield to 6.3 wt. %.[30] Furthermore, reaction initiation requires introducing the catalyst to the mixture, which is difficult particularly for portable applications. This problem is overcome in combustion-based approaches for hydrogen generation, which require only ignition and no catalyst.

It should be noted that combustion of solid mixtures is widely used for gas generation to create thrust in rocket engines, inflate air bags in case of car collisions, provide emergency oxygen to airplane passengers, etc. The amounts of gases stored in chemical compounds, for example, oxygen in sodium chlorate ($NaClO_3$) and hydrogen in sodium borohydride ($NaBH_4$), are comparable with storage abilities of liquid (cryogenic) O_2 and H_2, respectively, and much larger than those of pressurized gas tanks. The gas generating compositions can be easily and safely stored for years, and ignited when the product gas is required.

Recently, new *hydrogen-generating pyrotechnic compositions* were proposed to feed fuel cells for portable electronics by researchers from CEA (French Commission on Atomic Energy) and SNPE (French company for development of energetic materials).[31-33] In these mixtures, hydrogen is generated by combustion reactions of metal borohydride with oxidizer salt, such as NH_4ClO_4, $NaClO_4$ and $Sr(NO_3)_2$. These reactions are highly exothermic, easily initiated, and do not require any catalyst, which makes the method cost-effective and attractive for portable applications. Stoichiometric mixtures of the proposed reactants, however, exhibit low hydrogen yield, while those with high metal borohydride content do not burn. As a result, the maximum experimental H_2 yield obtained by this method was 5.9 wt. %.[31]

An alternative approach for hydrogen generation, proposed in Russia, uses *combustion of nanoscale aluminum with gelled water*.[34] Here, water acts as an oxidizer for Al and simultaneously as the sole source of hydrogen. The adiabatic combustion temperature of Al/H_2O stoichiometric mixture is close to 3,000 K (at 1 atm pressure). Despite this high temperature, for self-sustained combustion, the use of nanoscale Al powder and gelling of water (for example, by adding polyacrylamide) are necessary. The use of nanopowder decreases the ignition temperature of Al, while gelling inhibits water evaporation during combustion. Hence, the mixture ignites easily and burns in inert atmosphere, producing hydrogen

$$Al + 3/2\,H_2O \rightarrow 1/2\,Al_2O_3 + 3/2\,H_2. \tag{2}$$

Unfortunately, low hydrogen yield of the Al/H_2O system (theoretical limit 5.6 wt % for the stoichiometric mixture) is a drawback of this method.

A new combustion-based method for hydrogen generation was recently proposed by us.[35] To simultaneously reach high hydrogen yield and combustion efficiency, we use *triple sodium borohydride/aluminum/water mixtures*, in which water acts as an oxidizer for both sodium borohydride and aluminum and also as a source of hydrogen (parallel reactions (1) and (2) in one mixture). Sodium borohydride is an additional hydrogen source, while aluminum increases combustion temperature, eliminating the need for catalyst. Nanoscale aluminum pow-

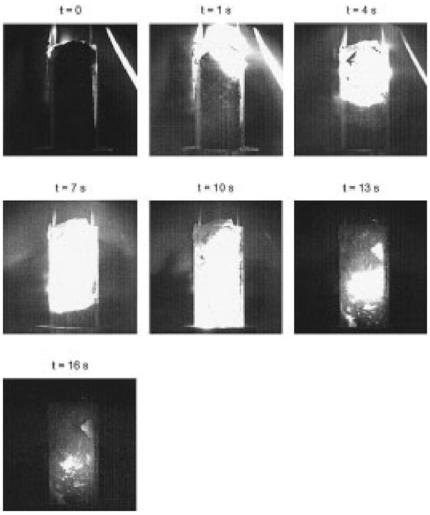

Figure 3. Combustion front propagation in borohydride/aluminum/water mixture; mass ratio $NaBH_4$:Al:H_2O = 1:2:3 (from Shafirovich et al.[35]).

ders are used to ensure high combustion efficiency. Along with the three reactants, the mixtures include small quantities of a gelling agent (e.g., polyacrylamide) and a stabilizer (e.g., NaOH) to prevent hydrolysis of borohydride at room temperature.

It should be noted that the reaction products include, besides hydrogen, sodium metaborate and alumina. Both compounds are environmentally benign materials. They can be either discarded or, if economically justified, recycled.

Experiments with $NaBH_4$/nanoAl/gelled H_2O mixtures show that[35]

- they exhibit stable self-sustained combustion (see Figure 3);
- hydrogen yield, measured by gas chromatography, approaches 7 wt %;
- hydrogen release efficiency is 74–77%.

The proposed novel technology of hydrogen storage, combustible borohydride/metal/water mixtures, makes it possible to develop hydrogen fuel cell power systems with high specific energy, high power density, no catalyst and safe reaction products.

Power systems based on this technology can be used as chargers for various electronic devices, and have the potential to dramatically increase their portability. Larger-scale hydrogen generators can be used for emergency power supplies and in some specific applications, such as power for spacecraft and undersea vehicles. Note that the Apollo 13 accident was caused by explosion of a liquid oxygen tank, which was used to feed a fuel cell power supply of the spacecraft. The use of chemical oxygen (also using heterogeneous combustion)[36] and hydrogen generators instead of cryogenic liquids in fuel cell power systems would eliminate such accidents, while providing comparable oxygen and hydrogen storage densities. In addition, the combustion heat release can be converted to electricity (for example, using turbine cycles or thermoelectric effect). This is of particular interest for apparatus with limited energy sources, such as spacecraft in deep space or autonomous weather stations and buoys in polar regions.[37]

Carbon Sequestration

Methods based on heterogeneous combustion could also help to solve another important global problem engaging attention of chemical engineers: carbon sequestration. According to the President's Global Climate Change Initiative, by the year 2012 the greenhouse gas intensity of the U.S. economy should be decreased by 18%. Carbon sequestration, along with making energy systems more efficient and increasing the use of low carbon fuels, is the key to accomplishing this goal. Carbon sequestration is the capture and storage of CO_2 and other greenhouse gases that would otherwise be emitted to the atmosphere. A clear priority for near-term deployments, among various sequestration possibilities, is to capture CO_2 from large-scale emission sources, such as power plants, and store it in underground formations.[38]

There are three main *CO_2 capture* technologies, classified as post-combustion, precombustion, and oxyfuels. Post-combustion refers to capturing CO_2 from a flue gas after a fuel has been burnt in air. The CO_2 in flue gas is dilute (3–15 vol %), at low-pressure (0.1–0.2 MPa), and often contaminated with traces of sulfur and particulate matter. Thus, a very large volume of flue gas has to be treated, so that equipment is large and capital costs are high.

Precombustion refers to a process where a hydrocarbon fuel is reacted with oxygen, air or steam to give mainly synthesis gas (CO and H_2). The carbon monoxide then reacts with steam in a water-gas shift (WGS) catalytic reactor to give CO_2 and more hydrogen. Finally, the CO_2 is removed and the hydrogen is used as a fuel in a turbine cycle. This technology significantly facilitates CO_2 removal because the product gas contains CO_2 in high concentration (30 – 50 vol %) and at high pressure (1.5 – 3 MPa). There are, however, few gasification-based power systems currently in operation.

Oxyfuel is an approach where a hydrocarbon fuel is burnt in pure or nearly pure oxygen rather than air. The combustion product is then a mixture of CO_2 and water, from which CO_2 can be easily separated. The basic infrastructure for oxygen is available in coal gasification plants, but the added oxygen capacity increases capital and operating expenses.

In this article, we focus on an alternative approach for oxygen supply, the so-called *chemical looping combustion* (CLC). The chemical-looping reaction technology is based on the cyclic use of solid medium which reacts with gaseous reactants. This technology has been used in many processes such as catalytic cracking and sulfur removal in coal gasification. The idea to use chemical looping in combustion-based power plants was originally proposed by Richter and Knoche[39] in 1983. In recent years, CLC has attracted much attention because of easy separation of CO_2 in this method. Ishida in Japan has conducted extensive research of CLC since 1994.[40-42] In Europe, CLC has been investigated vigorously for the last five years.[43-46] To our knowledge, few research efforts have been devoted to CLC in the U.S. so far.[47]

In CLC technology, a metal oxide (MeO) is used as an oxygen carrier, which transfers oxygen from air to the fuel. The oxygen carrier circulates between two interconnected fluidized bed reactors (see Figure 4), similar to the VPO-catalyzed butane to maleic anhydride process commercialized by DuPont.[48] In one reactor, the MeO is reduced by a gaseous fuel, such as natural gas

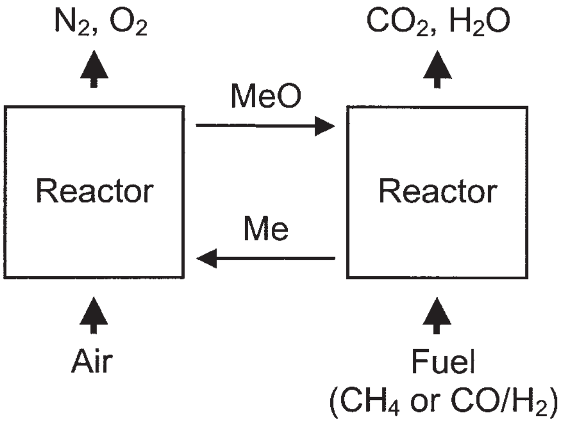

Figure 4. Chemical looping combustion.

$$MeO + CH_4 \rightarrow Me + CO_2 + H_2O. \tag{3}$$

An almost pure CO_2 stream can be obtained after cooling the exit gas and condensing H_2O. The particles of reduced carrier (Me) are transferred to the second reactor and oxidized with air, regenerating the metal oxide

$$Me + O_2 \rightarrow MeO. \tag{4}$$

This reactor gives a flue gas containing only N_2 and unreacted O_2. The oxidized carrier (MeO) is then returned to the first reactor for a new cycle.

CLC can also be used in power plants based on coal gasification.[42] In this case, synthesis gas produced from the gasifier reacts with metal oxide

$$MeO + CO + H_2 \rightarrow Me + CO_2 + H_2O, \tag{5}$$

while the other steps are the same as described earlier.

The total amount of heat evolved in CLC is the same as for conventional combustion, where the oxygen is in direct contact with the fuel (e.g., CH_4). The advantage of CLC is that CO_2 is not diluted with N_2 but obtained in a separate stream and can be easily recovered by simple steam condensation.

The necessity to use the same oxygen carrier in many cycles is a critical problem for CLC technologies. Iron, nickel, cobalt, copper, manganese and cadmium (and their corresponding oxides) have been considered as possible candidates for CLC process, and iron and nickel have been shown as most promising. The nickel-based oxygen carriers withstand a higher operating temperature, while iron has lower cost and its oxides are environmentally friendly materials. A suitable carrier for CLC exhibits high reaction rate and conversion, coking resistance, cycle durability and high mechanical strength. For this reason, the metal oxides are combined with an inert (such as Al_2O_3, TiO_2, ZrO_2, SiO_2, MgO), which acts as a porous support providing high surface area for reaction, and as a binder for increased mechanical strength and attrition resistance.

Methods for preparation of oxygen carriers have been developed and the obtained composite particles tested using TGA and experimental reactors, which identified suitable compositions and confirmed the potential of CLC. Much work remains to be done, however, to advance this concept from laboratory experiments and estimates to industrial technology. Experimental and modeling methods developed in studies on heterogeneous combustion of metals, coal, propellants and other energetic materials will be useful in this regard. It should be noted that combustion of light metals (such as Al and Mg) in gaseous oxidizers (including air and water vapor) was studied extensively for propulsion applications,[49] see also next section. Similarly, combustion of porous carbon particles in air and oxygen was investigated widely for power generation.[50] This experience could be effectively applied for oxidation and reduction reactions (3–5) involving oxygen carrier particles. Thus, heterogeneous combustion approaches can play an important role in solving carbon sequestration problems.

Extraterrestrial Production of Materials and Propellants

Space exploration opens new opportunities for chemical engineers. In the near future, missions to the Moon and Mars will require propellants and structural materials to support extraterrestrial activities there and to return crews and/or samples to Earth. *In situ resource utilization* (ISRU) would be economically attractive as compared to transportation of propellants and materials from earth. For example, a human mission to Mars, designed by NASA in response to the Space Exploration Initiative (1989), and relying completely on earth resources, required $450 billion, while NASA's mission design using ISRU (1994) decreased the price tag to $55 billion.[51] The new U.S. space policy, Vision for Space Exploration, includes ISRU as a core component:"*In situ* resource utilization will enable the affordable establishment of extraterrestrial exploration and operations by minimizing the materials carried from earth, and by developing advanced, autonomous devices to optimize the benefits of available *in situ* resources."[52]

Heterogeneous combustion can be used in space for both *production of material*s and *propulsion*. First, CS has the potential to produce materials and net-shape articles in space. Indeed, an important advantage of this method is low external energy consumption, which is required only to initiate the self-sustained combustion process. This makes CS especially attractive for use in space missions, where energy availability is limited. One potential application of CS in space is fabrication of replacement parts in long-duration exploration missions. It would be desirable to make spares of malfunctioned items aboard the spacecraft, when required, rather than carry a reserve of spares for all parts. The CS method makes it possible to fabricate replacement parts and custom tools on-site with either *in situ* materials or reactant powders carried from earth. They can be made to near-net shape, with tight tolerances, reliably, quickly, and safely. Furthermore, CS can be used to join different types of materials by compositional and functional grading.[53] Studies in drop towers, research aircraft and space stations have demonstrated that a majority of CS technologies developed in normal gravity can be successfully adopted under microgravity conditions. In fact, many materials produced in microgravity possess superior properties as compared to those synthesized on earth.[54]

Besides materials synthesis, another promising application of heterogeneous combustion in space is related to propulsion.

Specifically, metal fuel could be burnt in propulsion systems with CO_2 of Mars and Venus instead of propellants brought from Earth. To demonstrate the importance of this idea for Mars exploration, let us first briefly review the history of Mars ISRU concept, which involves much chemical engineering. Most Mars ISRU suggestions are based on use of martian atmosphere which contains 95% CO_2. One of the first ideas was to produce methane and oxygen (which constitute an excellent rocket bipropellant) from martian CO_2 and water in a small chemical processing plant.[55] To obtain water on Mars, however, is much more difficult than CO_2. For this reason, in a later modification of this approach, a small feedstock of liquid H_2 is transported along with the chemical plant from Earth to Mars for use instead of water (Sabatier reaction)[56]

$$CO_2 + 4\,H_2 \rightarrow CH_4 + 2\,H_2O. \tag{6}$$

The attractive features of this concept are the relatively simple technology and the high performance of the produced CH_4/O_2 bipropellant. The long-term storage and deep space transport of liquid H_2 is, however, a significant problem. This drawback is eliminated in another methodology, which postulates production of CO and O_2 directly by electrolysis of the Martian CO_2 in a zirconia cell.[57,58] The resulting CO and O_2 are then used as a liquid bipropellant. The zirconia electrolyzers, however, are fragile and require high operating temperature (>1,000 K). The common problem in all Mars ISRU scenarios mentioned previously is the significant power required to produce, liquefy, and store cryogenic propellants.

An alternative, combustion-based approach in the Mars ISRU suggests burning CO_2 directly as an oxidizer with metals or metal hydrides as fuel in a rocket or jet engine.[59,60] For rocket applications, CO_2 should be collected and liquefied, without any further chemical processing, while the fuel could be either delivered from earth or produced on mars. Carbon dioxide is not a typical oxidizing agent in industrial practice, but there exist fuels (e.g., magnesium and aluminum) which can burn with CO_2. Analysis of thermodynamic performance characteristics, combustion parameters, and other properties for various candidate fuels (Li, Be, B, Mg, Al, Si, Ca, Ti, Zr, their hydrides and mixtures with hydrogen compounds) has led to the conclusion that Mg is the most promising for rocket engines using CO_2 as an oxidizer.[60,61] Magnesium particles ignite in CO_2 environment at relatively low temperature (~1,000 K) and exhibit vigorous vapor-phase combustion[62-64] (see Figure 5). Because of use of *in situ* oxidizer, Mg-CO_2 rocket engines provide significant advantages in missions with ballistic flights on Mars, even with Earth-imported Mg fuel.[65] To improve metal-CO_2 engine performance, aluminum can be used instead of magnesium if a method is developed to decrease its ignition temperature in CO_2 (~2,300 K). One such possibility is to coat Al particles with a thin layer of nickel. Recent studies on combustion of Ni-clad Al particles have shown that they ignite at much lower temperature (~1,000 K), which is associated with the intermetallic reactions between Ni and Al on the particle surface.[66,67]

This brief review clearly demonstrates that novel combustion-based processes have great potential for applications under extraterrestrial conditions (microgravity, atmosphere of Mars, etc.). They will facilitate the production of materials and power in future space exploration missions.

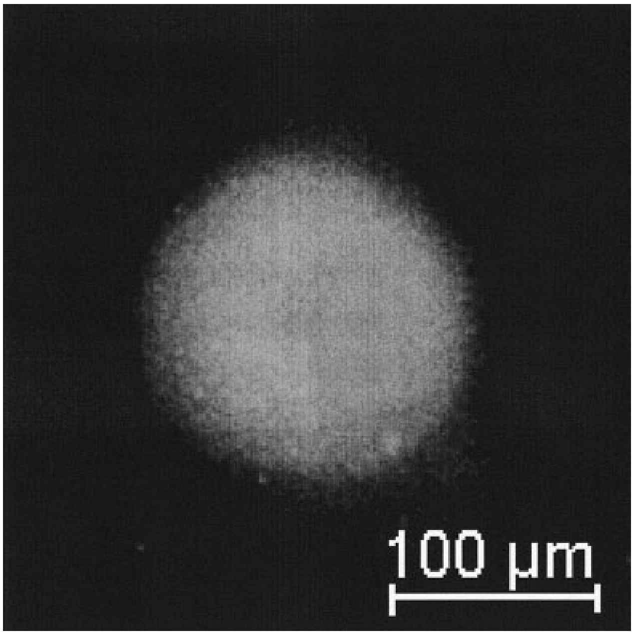

Figure 5. Spherical flame around Mg particle (50–63 μm) burning in CO_2 (from Legrand et al.[63]).

Concluding Remarks

In this article, we focused attention on four specific topics of significant contemporary interest to society: *combustion synthesis of advanced materials, hydrogen production for fuel cells, carbon sequestration, and in-situ resource utilization in extraterrestrial environments*. On the basis of our expertise and because of space limitations, we did not consider other important areas, such as catalytic combustion, soot formation, droplets and spray combustion, gaseous flame synthesis, coal and explosives.

All of the earlier are seemingly unrelated topics, yet each includes heterogeneous combustion as the central theme. We hope that this article will attract more chemical engineers to this fascinating area, which is rich both in fundamental concepts and important applications. Furthermore, progress in this field will arise from a deeper understanding of the combustion mechanisms, and will be aided by development of novel experimental techniques capable of detecting phenomena at shorter time and length scales, along with detailed theoretical and simulation approaches that quantitatively describe the experimental observations. The prospects of new opportunities for chemical engineers in heterogeneous combustion are indeed glowingly bright.

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