

COMBUSTION SYNTHESIS AND MATERIALS PROCESSING

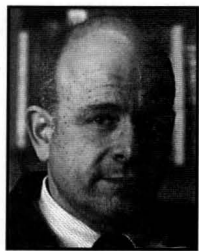
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The focus of the Yale University graduate course described in this paper is on aspects of *combustion* not usually part of the education of applied scientists or engineers (especially mechanical and aerospace engineers). Indeed, most available books in the field describe combustion almost exclusively in terms of *power production and/or propulsion*. These are, undeniably, areas in which combustion is usually an attractive option. But as emphasized here, combustion is also an extremely effective (and frequently the most economical) way to *synthesize and/or upgrade needed materials*.

Consider, for example, titania (white) pigment, briefly discussed later in this article. Each year, megatons are sold throughout the world at prices that exceed \$1/kg. Most titania pigment is made by a chemical synthesis process involving combustion to generate high temperature oxygen and water vapor that react with injected titanium tetrachloride vapor to produce the desired pigment particles. More generally, it will be seen that not only are there many proven, highly developed combustion processes for synthesizing commodity chemicals world wide, there are also new processes, (some discovered only in the last ten years) that exploit combustion. Examples are the production of diamond films (Section 2.3) or fullerene molecules (C_{60} , polymer of carbon) (Section 2.4).

Buckminsterfullerene, C_{60} , is a completely novel (discovered in 1985) and rather expensive (\$10,000/kg in 1996) "polymorph" of carbon that can be produced using benzene/oxygen flames. It happens to be a form of carbon presently "in search of applications." Not surprisingly, alternate syn-



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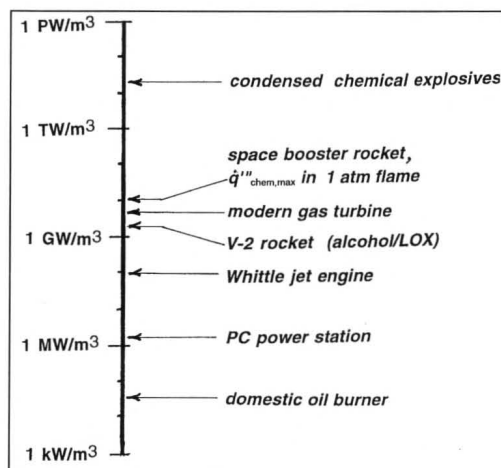


Figure 1. Orders of magnitude of volumetric chemical energy release rates, \dot{q}_{chem}'' , in mixing-limited engineering applications.^[2]

thesis and separation methods are very active areas of research.

These relatively recent discoveries are now being exploited and commercialized. Thus, an important point to make at the outset is that there are not only mature technologies (constantly in need of improvement to retain their competitive edge) that exploit combustion to synthesize commodity chemicals, but combustion is also an option for synthesizing valuable new materials (films, fibers, particles, or molecules) that will motivate synthesis-oriented combustion research and development in the future.

In the graduate course described here, we have selected and discussed several instructive examples of both mature and recent materials synthesis technologies that exploit combustion. In each case, valuable glimpses were provided of these relevant issues: What are the current technological and competitive challenges? What kinds of fuels, oxidizers, and additives are involved? What are the reagent contacting patterns? How can such equipment be sized? What operating conditions (pressure, temperature, composition, etc.) will be optimal?

Additionally, materials can be upgraded using combustion techniques, *i.e.*, there are many methods for cutting, resurfacing, or otherwise changing the nature of materials using combustion technology (Section 4). These examples, again, lead to the conclusion that if you and your students or colleagues find yourselves thinking of combustion only in terms of power generation and/or propulsion, you will inevitably

miss important opportunities. Indeed, much good research and development will be needed on these nontraditional (chemical engineering-) facets of combustion.

Another important purpose of this graduate course is to give engineering students from different disciplines an idea of how rather simple (preliminary) calculations can be made to estimate approximately how large these reactors must be in order to produce, say, a metric ton of product every hour using, in some cases, conventional types of combustion. For this purpose, frequent reference was made to the summary of attainable volumetric chemical energy release rates shown in Figure 1. Instructive student exercises were developed for each of these topics. Students were asked to put in real numbers and make the associated preliminary design calculations as a necessary first step to the more detailed follow-on calculations (often using proprietary codes). Each student also researched and prepared a written term paper on a particular combustion synthesis and materials processing (CS/MP) topic of interest to him or her (see Table 1).

Several introductory lectures were devoted to combustion fundamentals, including the chemical engineering core subjects of chemical thermodynamics and homogeneous/heterogeneous chemical kinetics. But CS/MP examples were used to teach the principles of chemical thermodynamics and chemical kinetics, flame stability (parametric sensitivity), etc. Thus, we considered the thermodynamics of diamond production (Section 2.3), and similarly, for chemical kinetics, we deliber-

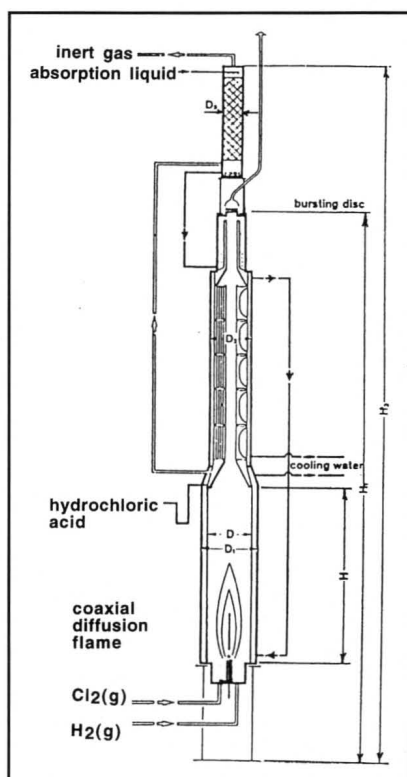


Figure 2.
"Off-the-shelf"
HCl
synthesis
reactor
via
 $H_2(g) + Cl_2(g)$
"diffusion
flame." [3]

ately selected inorganic systems (e.g., the kinetics of $Na(g) + TiCl_4(g)$) (Section 2.1), and not the usual hydrocarbon chemistry.

In its original form, this course was comprised of a two-part lecture each week for one semester (see Table 1). As done in this summary, the examples were divided into the production of valuable vapors (e.g., HCl, SO_2 , $(P_2O_5)_2$, O_2 , N_2 , etc.), fine particles (carbon black, fumed silica, titania pigment, doped glass microdroplets for optical waveguides, etc.), and monolithic solids, all discussed later in this article. We went on to some interesting combustion applications in the area of materials processing (coating, cladding, smoothing, cutting, slurry drying, etc.) and concluded with remarks about the future importance of this less visible but commercially important branch of combustion engineering.

SECTION 1

Combustion Synthesis of Vapors

1.1 HCl Synthesis via $H_2(g) + Cl_2(g)$

An early "combustion-like" example I encountered for synthesizing vapors is really a class of co-flowing non-premixed gas burners. The reactor shown in Figure 2 can be purchased off-the-shelf for combining hydrogen and chlorine to produce (and then to condense) pure hydrochloric acid. In this way, one could specify

TABLE 1
Organization of Graduate Course on Combustion for (Chemical-) Synthesis and Materials Processing

Lecture #	Topic(s)
1	Introduction to CS/MP: Course Scope, Fundamental/Technical Importance
2	Review of Relevant Thermochemistry and Chemical Kinetics
3	Review of Essential Features of Combustion of Vapors, Liquids, and Solids: Transport Phenomena in Pre-Mixed and Non-Premixed Systems
4	Combustion-Synthesis of Valuable Vapors: Acetylene, HCl, SO_2 , P_2O_5 . . .
5	Combustion-Synthesis of Ultrafine Particles: carbon black, fumed SiO_2 , TiO_2
6	Combustion-Synthesis of Ultrafine Particles (continued): doped SiO_2 , V_2O_5 - TiO_2 catalyst
7	Chemical Stability of Powders: "Pyrophoricity" and Ceramic Monolith Synthesis via Powder Chemical Reactions ("SHS")
8	Combustion Synthesis of Coatings; e.g., diamond films
9	Combustion-Driven "Guns" for Applying Coatings: Deton. Gun, HVOF Thermal Spray, . . .
10	Combustion Surface Treatment: Flame 'Polishing,' Spheroidization, Sintering, and Cladding
11	Oxy-Fuel Combustion for Cutting, 'Gas' Welding, and Brazing
12	"Submerged" Combustion for "Direct Contact" Heat/Mass Exchange: Spray-drying of ceramic slurries, . . . Combustion as a Separation Technique: U Recovery in Fluidized Beds, . . .
13	Summary/Overview/Trends—Opportunities; Topics for Further Study/Investigation

the indicated dimensions for the required burner-condenser combination for synthesizing HCl from its elements. These are indeed examples of combustion synthesis—one just has to broaden one's notion of what is the “fuel” and what is the “oxidizer,” both gaseous in this instance.

1.2 Spray Combustion of S(l) and P(l)

A commercially important two-phase (liquid fuel) example, familiar to many chemical engineers (and going back to early in this century), is the use of a molten sulfur spray combustor as one step in the ultimate production (via the contact process) of the commodity chemical sulfuric acid. The process,^[4] which even to this day is an eye-opener to other engineers, involves melting sulfur, spraying the molten sulfur at 420K into a burner with dried air, and burning the resulting sulfur droplets to form the intermediate product SO₂(g) (see Figure 3). The resulting SO₂(g)/nitrogen stream is first cooled and then oxidized to SO₃(g) in a downstream catalytic converter, and the SO₃(g) is finally combined with water in an absorber to produce sulfuric acid. This is, and has been for most of this past century, the bread-and-butter technique for making sulfuric acid. As a result, many chemical engineers are quite familiar with the burning of molten sulfur, which may be regarded as an unusual fuel.

A similar example is the combustion of liquid phosphorus for the ultimate production of phosphoric acid in support of agricultural chemicals production. Thus, the burning of such liquid fuels, ‘weird’ from the viewpoint of traditional combustion engineers, has been part of the tradition of chemical synthesis using combustion techniques for a long time.

1.3 Acetylene Synthesis via the Combustion-Driven Pyrolysis of CH₄(g)

An important technique for making acetylene (about one Mt/y, worldwide) is really a rich preheated, premixed vapor combustion process. The 1.4 atm vapor mixer-reactor is shown schematically in Figure 4.^[5] Some of the hydrocarbon vapor (here, methane) is sacrificed (burned) to produce high temperature methane-rich gas. The surviving methane is then pyrolyzed to form acetylene, ethylene, soot, etc., in a small plug-flow reaction space downstream of the block of

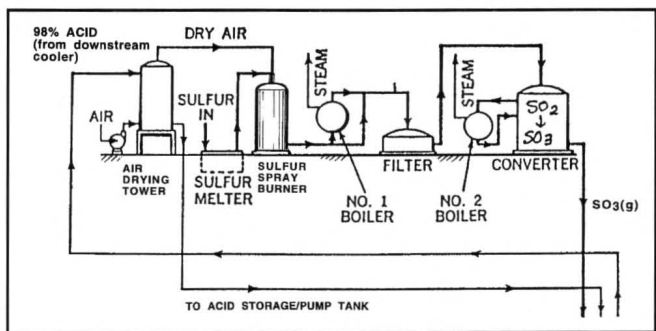


Figure 3. Synthesis of SO₂(g) via molten sulfur spray combustion as first step in the synthesizing the commodity chemical: H₂SO₄(l).^[4]

flame stabilizers, prior to a water (or oil) quench. With about 1-ms mean residence time at about 1800K, an acceptable yield (about 24 wt pct. of the hydrocarbon feed) of acetylene is achieved. Unfortunately, soot is an inevitable by-product (about 5% yield), but acetylene is the principal goal. This particular example is also useful to illustrate the principles governing flame stabilization (*i.e.*, what does it take to design a device that avoids extinction by blow-off, or potentially dangerous flashback of these rich preheated/mixed gaseous flames on such multi-hole, water cooled burners?).

1.4 Acetylene Synthesis via a “Submerged Flame” in Crude Oil

There is another interesting partial combustion method for making acetylene at about 10% yield using pressurized oxygen gas bubbling through hot liquid petroleum (crude oil), *i.e.*, the so-called “Submerged Flame” (also BASF) reactor.^[5] In contrast to ordinary liquid fuel spray combustors, in this class of reactors the (difficult to atomize) liquid fuel/feedstock is the continuous (not dispersed) phase!

1.5 O₂(g) or N₂(g) Generation from Decomposing Inorganic Solids

There is yet another important class of combustion-synthesis gas generators that should be mentioned here: those using the exothermic decomposition of an unstable solid compound to generate the desired gas. One such example is a type of oxygen generator used in many current aircraft.* To design such a system, an appropriate oxygen-containing compound (here, NaClO₃(s)) must be selected, formulated, packaged, and ignited on demand. Of course, the resulting dust-free oxygen must also be produced-released-delivered

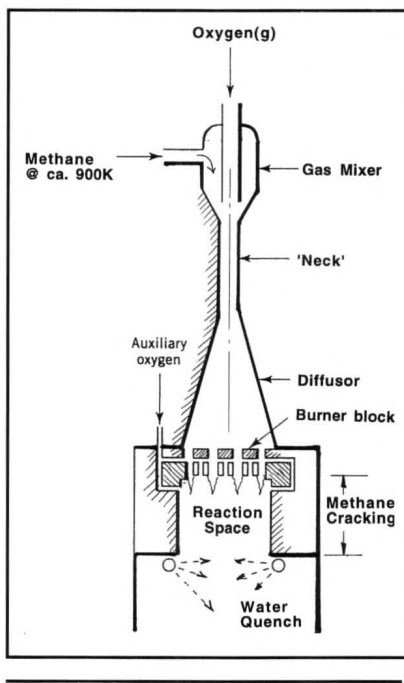


Figure 4. Acetylene synthesis via combustion-driven CH₄(g) pyrolysis.^[5]

* Unfortunately, this generator was involved in the recent fiery crash of a ValueJet DC-9 aircraft (which was improperly transporting more than fifty presumably expired versions of such canisters).

in a reasonable length of time. In this case the ignition process involves the sudden mixing of a fine iron powder with the sodium chlorate. When the second main O₂ generator (based on the electrolysis of waste water) on the Russian Mir space station failed (August 5, 1997), the crew was forced to rely on “chemical” O₂ from canisters filled with lithium perchlorate, some 70 of which were kept on board for just such an occasion. Earlier, the failure of one such canister (in February, ‘97) had caused a smoke-fume emergency for the astronauts on board.

A generically similar and commercially important example is the so-called automotive airbag system, which also served as the basis for several instructive student calculations related to boundary conditions^[1,6-7] and ignition. This is a compact device in which sodium azide, NaN₃(s), an unstable solid compound rich in the element nitrogen, is ignited in response to the vehicle deceleration. The decomposing solid propellant, which also contains an oxidizer (*e.g.*, about 30 wt. pct. KClO₃(s) or NaNO₃(s)) generates the hot nitrogen gas that inflates-deploys the bag in the automobile cabin, thereby protecting the onrushing passenger. Providing automotive air bags (front and side) that are safe and environmentally friendly is a large and growing industry around the world. Indeed, companies prominent in the automotive airbag inflator business are or were chemical-propulsion oriented (solid propellant) companies.

SECTION 2

Combustion Synthesis of Fine Particles and Coatings

2.1 Carbon Black, Fumed Silica, Titania Pigment, TiB₂(s) Nano-Spherules

Combustion is now routinely used to generate ultra-fine particles (*e.g.*, pigments, adsorbents, or viscosity modifiers^[8,9]). These are frequently particles with remarkably high surface area per unit volume or mass, *i.e.*, their constituent spherules are very small. Carbon black and ordinary soot are comprised of aggregates with spherules only tens of nanometers in diameter, so that the corresponding area per gram is hundreds of square meters! Carbon black is used as a pigment or as an additive to improve wear characteristics (*e.g.*, synthetic rubber tires). Of course, optimizing the nature of the carbon black (surface chemistry and morphology) depends on the specific application, and involves controlling the surfaces of the carbon particles themselves.

The titania industry mentioned above is also a mature one, with the original chloride-process patents going back to DuPont in the 1940s. In the case of titania pigment processes, the feed is usually impure TiO₂(s) (rutile ore). This is chlorinated in the presence of coke to generate titanium tetrachloride vapor on site using chlorine vapor in a fluidized bed reactor. This titanium tetrachloride is ultimately fed to an oxidation or hydrolysis reactor that is frequently the hot-oxygen effluent of a high-pressure, turbulent, liquid hydrocarbon fuel-lean spray combustor in co-flowing oxygen

(with, perhaps, water vapor added). In the tandem turbulent mixer-reactor, one oxidizes the titanium chloride, and nucleates/grows the titanium oxide particles. For pigment particles there must be enough residence time in this reactor (and in downstream tubing) to grow the coagulating particles into the pigment size range (spherule diameters roughly equal to the wave length of visible light).

Much of the titania marketed around the world is made by this chloride process—incrementally improved on a continuing basis but apparently hard to replace with a more economical alternative. What differs from company to company are such details as what the quality of the input rutile must be, what additives are used to control the coagulation process, and how to control the bond strength between the primary particles, etc. It remains to be seen whether the presently accepted concepts of turbulent mixing and particle production in turbulent non-premixed flows can be used to provide useful predictions of the resulting size distribution and evolution of particles in these complex environments. Incidentally, this is another illustration of where, because of the demands of industrial productivity, suspended particle mass fractions are *not* negligibly small (in many environmental applications of aerosol science, particle mass fractions are less than 0.1 pct.). As in the case of the optical wave guide application^[10] described briefly below (Section 2.2), the mass fraction of the particles being produced and collected is appreciable (about 25 wt. pct.).

The most recent International Combustion Symposia contain several interesting papers on gas phase combustion methods to synthesize valuable condensed products.^[11-13] For example, DeFaux and Axelbaum^[12] describe a method for producing coated nano spherules of titanium diboride using a co-flowing vapor axisymmetric burner for reacting sodium vapor with a mixture of titanium tetrachloride and boron trichloride, with argon serving as the carrier gas. The sodium chloride subsequently condenses on the TiB₂(s) particles, in effect preventing the spherules from binding tightly together. These sodium chloride coatings can then be dissolved away in a post-processing step.

2.2 Doped Glass Microdroplets for Optical Waveguide Fiber Synthesis

Currently used processes for making continuous optical wave guide glass fiber (see Figures 5a,b, next page) also make use of combustion-generated particles. In such cases, the burner frequently uses methane or hydrogen fuel. The oxy-fuel flame is ‘doped’ not only with a precursor of silica, but also phosphorous-, germanium-, and boron-containing vapors. Such seeded flames produce a high temperature mist of doped silica submicron droplets. By controlling the (phosphorus, germanium, boron, etc.) dopant flow rates, one can control the refractive index of the resulting particles and, by gradually changing the ratios of those dopant compounds in the burner, one can produce microdroplets with different refractive indices. These deposit at different depths in a

cooler preform to produce a porous glass deposit with a built-in refractive index gradient. This soot preform is then pulled through a furnace to produce kilometers of OWG fiber, about 125 μm diameter. Not surprisingly, there are several variants of this process around the world. The particular one sketched in Figure 5a is essentially the Corning method. Nippon Telegraph uses a version (Figure 5b) in which the preform is spinning and pulled vertically through a furnace. One (or more) burner(s) produces and deposits the particles on the end of the withdrawn target (as opposed to the Corning process, where the burner basically moves back and forth relative to the spinning but otherwise fixed preform). An interesting feature of this class of applications is the simultaneous role of high particle mass loading and submicron particle transport dominated by the “non-Brownian” mechanism of thermophoresis.^[10,15]

2.3 Combustion Synthesis of Diamond Films

Since the startling report of Hirose,^[16] combustion has also been used to grow high-quality diamond films on hot (about 1200K) substrates, even at one atmosphere pressure! Whereas thermodynamically, this result was certainly not anticipated, it turns out that within a narrow range of flame stoichiometry and substrate temperatures one can grow about 20 micrometer crystallite-sized polycrystalline diamond films at rates up to about 200 $\mu\text{m}/\text{h}$ from, say, low-pressure rich acetylene/oxygen flames. This is apparently because such flames contain large concentrations of methyl radicals and atomic hydrogen—but diamond films can be grown even if one just generates (via electrical discharge or laser-heated graphite) C atoms or C_2 molecules. Not surprisingly, the interfacial chemical kinetics are not fully understood. But the combustion method is simple and has been used to obtain rapid diamond film growth rates with areas up to about 100 cm^2 on the substrates Si, Mo, Al_2O_3 , and TiN.^[17]

2.4 Combustion Synthesis of Fullerenes and “Nano-Tubes”

Combustion (*e.g.*, premixed $\text{O}_2/\text{benzene}$ at 100 torr) has also been used for synthesizing the so-called Buckminsterfullerene molecule: C_{60} —a polyatomic carbon ‘soccerball.’^[18-20] With a diameter of only 0.71 nm, each of these objects can be regarded either as a high molecular weight “vapor” molecule (see Section 1), or as a “nanoparticle” (this Section). In 1996, research quantities of C_{60} were selling for about 0.1 M\$/kg. While the mechanisms of flame-generated C_{60} , C_{70} , and soot-formation may have some features in common, optimum C_{60} yields (reported to be of the order of 0.5 wt. pct. of the fuel carbon) appear to require both high temperatures (more than 2100K) and low pressures, and the chemical route to C_{60} appears to require the formation of vibrationally excited polycyclic aromatic hydrocarbon (PAH) molecules containing 5-member rings.^[18] Recently, close-packed bundles of carbon nanotubes have been synthesized using the laser ablation of graphite. Each

such nanotube is a sheet of hexagonally bonded carbon rolled up into a seamless cylinder, capped at both ends with semi-fullerene molecules! It remains to be seen whether controlled combustion techniques can be developed to economically synthesize such interesting structures.

SECTION 3

Synthesis of Monolithic Solids via Combustion of Powders

3.1 Self-Propagating High Temperature Synthesis (SHS)

Unconsolidated powder blends (*e.g.*, $\text{Ti(s)} + 2\text{B(s)}$, or $\text{Ti(s)} + \text{C(s)}$) can be ignited at one end to form blocks of useful but somewhat porous ceramic materials (*e.g.*, $\text{TiB}_2(\text{s})$ or TiC(s)) by a method sometimes called a “solid flame,” “gasless combustion,” or “self-propagating high temperature synthesis” (SHS).^[21,22] Indeed, SHS (investigated extensively in Russia since 1967^[23]) is sometimes (erroneously) thought to be the principal application of combustion to materials synthesis. This thermite-type process has also been used for welding materials together, often in the field, and (with the help of centrifugation) for putting refractory coatings on the inside of large cylindrical pipes. Not surprisingly, wave propagation speeds, often of the order of centimeters per second, are system-specific and powder-grain-size dependent. Only now are mechanistically realistic flame theories being developed and applied to these pseudo-premixed flame propagation problems.

3.2 Other Examples of Solid Combustion Synthesis

Garnet luminescent phosphors with submicron particle size for, say, field-emission displays (television screens, etc.) can be synthesized by combusting powders, although the mode of combustion is not self-propagating and the product may itself be a powder (*e.g.*, Eu^{2+} -doped Y_2O_3 phosphors via the reaction of metal nitrates (oxidizer) with organic fuel (urea, carbonylhydrazide, glycine) at 773K^[24]).

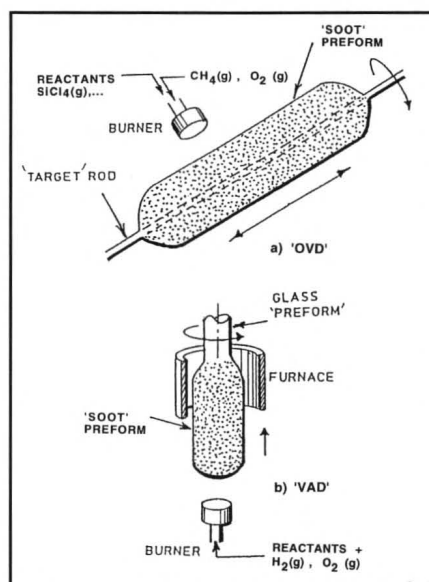


Figure 5a,b. Optical waveguide ‘preform’ synthesis techniques using Si-seeded, B, P-doped CH_4/O_2 and H_2/O_2 flames.^[14]

SECTION 4

Combustion for Materials Processing (MP)

Materials synthesized by many other techniques are often modified (upgraded) using some form of combustion device. Several interesting examples are outlined below, with emphasis on more recent or, perhaps, less familiar cases.

4.1 Combustion-Driven "Guns" for Depositing Coatings

Figure 6 (schematically) shows a steady flow particle accelerator based on liquid-fueled rocket combustor technology.^[25] This so-called jet (J-) gun is really a miniature liquid-propellant rocket motor except that for a real rocket motor (whose purpose is a compact thruster), one might select liquid oxygen (LOX) as the oxidizer and operate at chamber pressures far in excess of 9.2 atm. But in a ground-based laboratory for coating, say, turbine parts, one can use gaseous oxygen from cylinders. This oxygen and some convenient liquid fuel (here kerosene) are fed into a small water-cooled moderate-pressure combustion chamber-nozzle com-

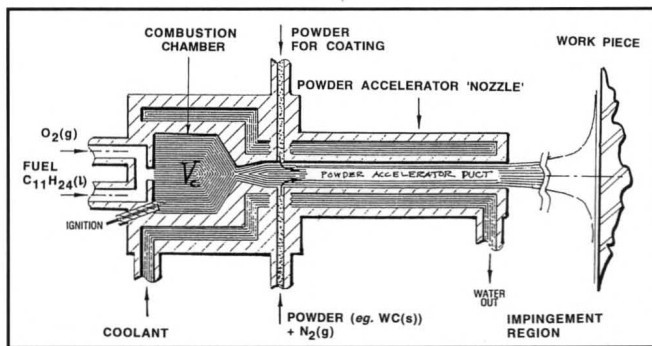


Figure 6. Rocket-type jet (J-) gun for depositing refractory coatings on downstream workpieces.^[25]

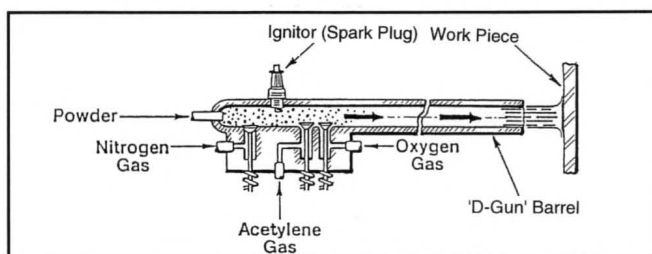


Figure 7. Detonation (D-) gun for accelerating powders to deposit coatings on downstream workpieces.^[26]

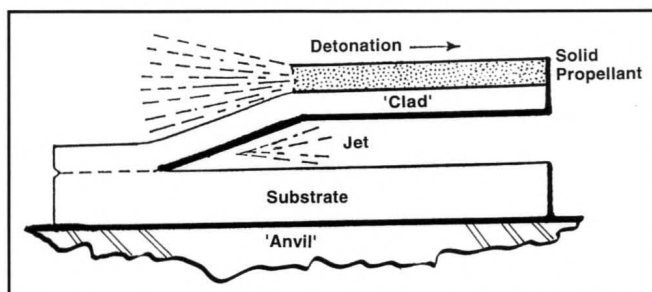


Figure 8. Solid-propellant-driven cladding technique (schematic of typical arrangement).

ination, for the purpose of creating a supersonic exhaust jet of hot gaseous combustion products. This jet is used to accelerate (to about 1 km/s) and heat the powders put into suspension, *e.g.*, 20- μm diameter tungsten carbide. Particle impaction on the target placed downstream results in the desired coating (*e.g.*, thermal- or erosion-barrier, perhaps 250 μm thick). These high-velocity oxy-fuel (HVOF) coating devices are not terribly energy efficient—they heat up a great deal of water, but they accomplish their purpose (adding value to the target) at an acceptable total cost. Several student exercises were developed to address the optimum conditions for accelerating and heating such particles. With a typical system, including the jet gun itself, a powder feeder, a tank of liquid fuel, and oxygen gas cylinders, it is possible to coat a wide variety of materials placed immediately downstream in the rocket+particle accelerator exhaust.

A rather different type of combustion gun, which is intermittent, is the detonation (D-) gun (see Figure 7^[26]). Here, repetitive $\text{H}_2(\text{g})/\text{O}_2(\text{g})$ detonations are propagated through a suspended powder and each detonation wave acts like a piston to propel the hot particles onto the workpiece. This process is repeated about every 1/6 of a second. Praxair (formerly Union Carbide) Surface Technologies has a proprietary coating business based on the D-gun. This device is an excellent vehicle to teach the theory of detonations—*viz.*, supersonic combustion waves that produce high pressures and temperatures behind them. Accordingly, they are capable of heating and accelerating particles suspended in the combustible gas mixture. Note that the pressure vessel is, indeed, like a gun barrel—with repetitive spark-ignited oxy-hydrogen detonations that shoot each fresh charge of suspended particles out onto the target. Using the principles of detonation theory, and the heat/momentum/mass transfer properties of the suspended particles, each engineering student can go through the steps of designing such a gun. This includes sizing, determining how rapidly it can be fired and reloaded, what kind of coating rates are achievable, etc. These are instructive, yet conceptually simple, calculations for engineering students.

The reader probably already suspects that it is possible to carry out many types of explosive processing for the cladding or (re-)shaping of materials. For example, to clad one material onto the surface of another (substrate) without the need for a huge mechanical press, it is possible to assemble a sandwich of the ingredients on an anvil, with a sheet of solid propellant above the cladding material (see Figure 8). Upon igniting the solid propellant, a propagating detonation slams these two materials together. Many controlled explosive procedures of this type are being used for cladding, shaping, or sintering materials, including powdered metals.

4.2 Combustion-Driven Cutting or "Gas" Welding Operations

Most engineers are already familiar with the fact that gaseous acetylene/oxygen flames are hot enough (about

3500K at 1 atm) and compact enough to provide local work-piece heat fluxes (more than 3 MW/m²) adequate for cutting or welding operations on metal sheet materials. Indeed, by combining the principles of turbulent jet mixing and convective heat transfer with a steady-flow energy balance, engineering students can make useful estimates of torch requirements and attainable cutting or welding rates (crucial topics often not even present in handbook accounts of these operations). Perhaps less familiar is the fact that after localized work-piece heat-up, for several important metals (including iron and titanium alloys) the fuel supply can actually be cut off completely and metal combustion (with molten metal oxide runoff) alone will continue the cutting operation! This cutting technology, in which an acceptably small fraction of the workpiece becomes the fuel, is not new (Air Products Corporation was supplying such O₂(g) lances in 1941 and such an example is shown in the introduction of Spalding's convective mass-transfer textbook,^[27] but this type of microjet "oxygen lance cutting" certainly deserves attention in this short CMP-review.

4.3 Surface Treatments: Flame Polishing, Spheroidizing, etc.

Another noteworthy MP example in which combustion is conveniently used is surface (fire-) polishing. For example, could you predict how long it would take to smooth an initially rough metal or ceramic surface by the mechanism of surface-energy (curvature) driven surface diffusion using a high temperature torch? Can you design an economical process using hot combustion products to spheroidize a powder that presently has poor flow characteristics because of irregular grain shape?

Changing near-surface compositions (hence properties) by metal workpiece exposure to tailored combustion-product environments (*e.g.*, containing ammonia, devoid of SO₂, CO₂, and H₂O, etc.) is also a widely used technique for the nitriding, carburizing, carbo-nitriding, etc., of ferrous and nonferrous metals.^[28] Many of these practical examples can be used to teach the principles of transient one-dimensional Fickian solute diffusion. This includes calculations of the required process time at temperature, again without recourse to proprietary (black-box) computer codes.

CONCLUDING REMARKS

Other important CS/MP examples were used in the course, including (for the MP segment) combustion-driven spray drying of ceramic slurries and submerged burners for heating aggressive molten baths. But the particular examples selected above will be sufficient for our present introductory purposes. In principle, the instructor will have little difficulty finding yet others, perhaps better suited to the background of an individual class. Unfortunately, however, there is not yet any coherent account of this overall subject that can be used as a textbook for a CS/MP course—a situation that motivates the writer to embark on this project.^[2] Useful

information on many of the individual chemical processes included here can be found in the chemical engineering encyclopedias: Kirk-Othmer^[5] and/or Ullmans^[5]. But, of course, proprietary details are, at best, found only in the patent literature. For the underlying transport and combustion principles, the situation is much better—for this course I simply used my review papers,^[6,29] Rosner and Papadopoulos,^[1] and the 3rd printing of my 1986 textbook *Transport Processes in Chemically Reacting Flow Systems*,^[7] which most Yale students already had. (A second edition should be available, with additional CS/MP content, by 1998-9.) Other recent, readable accounts of the fundamentals of combustion^[30] were put on reserve in the Engineering Library.

Pedagogically, for teaching the principles of thermodynamics, chemical kinetics, gas-dynamics, mixing, chemical reactor design, detonations, materials science, etc., engineering students from many disciplines can relate to the practical yet extraordinary examples above. They transcend the traditional power generation/propulsion combustion topics and are, accordingly, appealing to broaden our perspective. Indeed, for graduate students, many of these examples will also suggest interesting, perhaps hitherto intractable, research projects that probably could be tackled now. I hope these representative examples convince the reader once and for all that combustion is not limited to power generation/propulsion or process heat, and that there are many both mature and/or evolving technologies in which combustion can be used to produce very valuable materials (in some cases worth thousands of dollars per kilogram). This class of combustion applications also forces the engineer to broaden his or her conception of what is a useful fuel and what is a useful oxidizer, and to consider contacting and mixing configurations that are, more often than not, rather different from the canonical ones displayed in most combustion textbooks.

It is also evident from these CS/MP topics that if you are trying to optimize a combustion reactor process for, say, diamond film growth, you would be well advised to team up with materials scientists who can characterize such deposits and the prepared substrate, flame chemists, and experts in flame aerodynamics and transport phenomena. Thus, while chemical engineers are in an extraordinarily strong position to contribute, an interdisciplinary attack will probably be essential for success in the CS/MP arena.

As summarized above, in this graduate course we considered interesting practical examples where further combustion research may, in fact, make combustion the most attractive route to synthesizing and/or processing valuable new materials, rather than (as is sometimes the case) a cheap but still poorly understood or controlled alternative.

We also demonstrated that with simple rate-controlling postulates, it is usually possible to estimate the size and performance of the required equipment. Needless to say, in any particular case, this would be the logical first step before

going to more elaborate, often proprietary or black-box, computer models. In the writer's opinion, from a pedagogical point of view, this is a healthy and confidence-building orientation for engineering students, too often neglected. Moreover, to design processes that are intrinsically novel, chances are that the packaged programs commercially available do not anticipate the circumstances of present interest!

To conclude, many readers will appreciate that there are also many attractive research topics lurking among these examples.^[31,32] Especially if you have not been thinking along these lines, I commend them to your attention as viable and healthy directions for combustion research to take in the future.

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EDITOR'S NOTE: Due to space restrictions, we were not able to include several instructive student exercises. They will be published in the next (Winter '98) issue of CEE.

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