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(71) **Applicants** (for all designated States except US): **UNIVERSITY OF DELAWARE** [US/US]; 1 Innovation Way, Delaware Technology Park, Building 1, Suite 500, Newark, DE 19711 (US). **ETH ZURICH** [CH/CH]; Institute of Energy Technology, Sonneggstr. 3, CH -8092 Zurich (CH).

(72) Inventors; and

(75) **Inventors/Applicants** (for US only): **KOEPP, Ernest Erik** [US/US]; 42 Woodhill Drive, Newark, DE 19711 (US). **PRASAD, Ajay K.** [US/US]; 510 Briar Lane, Newark, DE 19711 (US). **ADVANI, Suresh G.** [US/US]; 274 Dallam Road, Newark, DE 19711 (US). **STEINFELD, Aldo** [CH/CH]; Reinerstrasse 30, CH-5200 Brugg (CH). **BRUNNER, Douglas A.** [US/US]; 2332 Red Lion Road, Bear, DE 19701 (US).

(74) **Agents:** **DONNELLY, Rex A.** et al.; RatnerPrestia, P.O. Box 980, Valley Forge, PA 19482 (US).

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(54) **Title:** BEAM-DOWN SOLAR-THERMOCHEMICAL REACTOR FOR THE ULTRA-HIGH TEMPERATURE DISSOCIATION OF SOLID-OXIDES AND CREATION OF SOLAR FUELS AND MATERIALS AND METHODS OF USE THEREOF

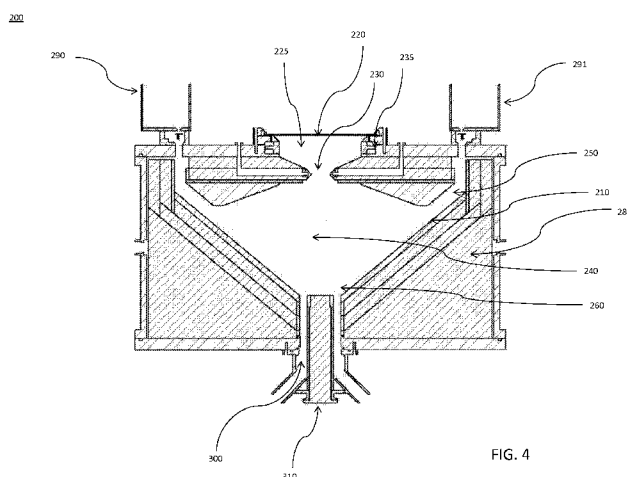


FIG. 4

(57) **Abstract:** A cavity reaction chamber including a reaction surface in the shape of an inverted cone and having a top and a bottom. Powder supply containers supply a layer of powdered reactant to the reaction surface. A beam of incident radiation diverges onto the reaction surface. A gas outlet receives gas exiting the reaction chamber. In semi-continuous operation, the reactor further includes an annular solids outlet, surrounding the gas outlet and positioned to collect solids exiting the reaction chamber. The reactor may be used in a process for producing solar fuels and solar materials, for example, by concentrating sunlight as incident radiation, feeding ZnO as the powdered reactant, collecting dissociated Zn and O₂ as gaseous products, cooling gaseous products to precipitate solid Zn particles, reacting collected Zn particles with H₂O to create ZnO and H₂, recycling resulting ZnO into the feed stream, and capturing the H₂ and/or the O₂.

BEAM-DOWN SOLAR-THERMOCHEMICAL REACTOR FOR THE ULTRA-HIGH
TEMPERATURE DISSOCIATION OF SOLID-OXIDES AND CREATION OF SOLAR FUELS
AND MATERIALS AND METHODS OF USE THEREOF

CROSS REFERENCE TO RELATED APPLICATIONS

5 This application claims priority to U.S. Provisional Patent Application
No. 61/424,139, entitled "BEAM-DOWN SOLAR-THERMOCHEMICAL REACTOR FOR THE
ULTRA-HIGH TEMPERATURE DISSOCIATION OF SOLID-OXIDES AND CREATION OF
SOLAR FUELS," filed on December 17, 2010. The contents of this provisional
application are incorporated herein by reference in their entirety.

10 STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH

The subject matter of the present invention was funded at least in part
under National Science Foundation Grant No. NSF 05-517 and Federal Transit Authority
Grant No. MEEG372132. The U.S. Government may have certain rights in this
invention.

15 FIELD OF THE INVENTION

The present invention relates to thermochemical reactors, and the use of
these reactors to generate solar fuels and solar materials.

BACKGROUND OF THE INVENTION

20 Solar fuels are emerging as a viable pathway towards closing the gap
between fuel production and consumption. Production of these fuels on large scale,
while concurrently achieving carbon-neutrality, would result in a truly sustainable
energy solution. Whether used in a PEM fuel cell or combustion engine, hydrogen as a
fuel produced from sunlight and water represents an elegant energy harvesting cycle,
with zero-emissions, high efficiency, and exceptional power-density.

25 Solar fuels offer several unique advantages, including high efficiency,
large scale application, and diversity in both feed-stock and final fuel form. Production
of solar fuels via the direct solar thermolysis of H₂O and CO₂ requires ultra-high
temperatures (>2,500K) and a concomitant separation of the gaseous products to
avoid recombination and/or the formation of a potentially explosive mixture. In an
30 effort to avoid these complications, a two-step thermochemical cycle based on metal
oxide redox reactions may be employed in which only the first step requires solar
process heat, and the production of H₂ and/or CO occurs in a subsequent step,
separately and independent of solar energy availability. The H₂ and CO so produced,
and the Zn produced in the first step, are characterized as "solar fuels" because they
35 store solar energy that may be used to later fuel, *inter alia*, combustion (H₂ and CO) or
dissociation (Zn) reactions.

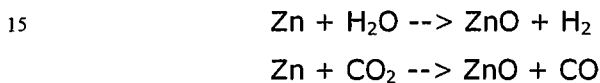
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The Zn/ZnO thermochemical cycle has been identified as a promising candidate by researchers in the United States and around the world. In the first step, ZnO is reduced to metallic Zn inside a cavity-type reactor by exposure to temperatures approaching 2000K and solar flux concentrations of over 10,000C. Zn can serve
5 directly as a solar fuel in a Zn-air fuel cell or battery; however, a more elegant solution can be attained by completing step two of the thermochemical cycle, wherein Zn is reacted with water exothermically to produce hydrogen and ZnO.

The Zn/ZnO thermochemical cycle includes, as a first step, the endothermic dissociation of ZnO using solar process heat:



This thermal dissociation can occur in a cavity-type reactor by exposure to temperatures approaching 2000K and solar flux concentrations of over 10,000C. In the second step, the Zn gas evolved from the first step reacts exothermically with H₂O and/or CO₂ to generate H₂ and/or CO respectively:



The ZnO produced in the second step may then be recycled to the first step, and the net reaction is hydrogen and/or carbon monoxide produced by sunlight and water and/or carbon dioxide. A thermodynamic and kinetic investigation of this
20 thermochemical cycle, as well as unit process considerations in view of the then-prevailing solar reactor technology, is set forth in *Review of the Two-Step H₂O/CO₂-Splitting Solar Thermochemical Cycle based on Zn/ZnO Redox Reactions* by Loutzenhiser et al. (1996).

As an alternative reaction, the Zn harvested from the first step may be
25 combined with copper to form brass. In this regards, the resulting brass is a sustainable "solar material," to wit, a product formed, in part, through the addition of solar energy.

Despite the evident benefits of solar fuels and solar materials, substantial technological hurdles must be overcome. For large scale, power-tower applications,
30 the heliostat field still remains a major cost-driver. Haultiwanger et. al. have recently made a strong case for the value of demonstration projects and initial commercial ventures on the rate of maturity of an energy-technology and its cost-competitiveness. These two points call into priority the design and demonstration of novel solar-fuel receiver/reactors that simultaneously address efficiency, which leads to unit cost
35 reduction, and concept viability, which leads to technology demonstration.

Accordingly, there exists a need for high-efficiency and commercially viable batch and semi-continuous thermochemical reactors that chemically store radiation, including solar energy, in the form of solar fuels and solar materials.

SUMMARY OF THE INVENTION

5 Aspects of the present invention relate to thermochemical reactors, and processes employing the use of the inventive thermochemical reactors to generate solar fuels and materials.

In accordance with one aspect of the present invention, a cavity reactor for inducing a chemical reaction in a powdered reactant is disclosed. In an exemplary
10 embodiment in which the reactor is configured for batch operation, the reactor includes a cavity reaction chamber, powder supply containers, a radiation window, a focal plane aperture, and a gas outlet. The cavity reaction chamber includes a reaction surface in the shape of an inverted cone and having a top and a bottom. The powder supply containers are located above the top of the reaction, and are chamber configured to
15 supply a layer of powdered reactant. The powdered reactant is distributed about the reaction surface into the reaction chamber. A radiation window is positioned in an upper chamber above the reaction chamber for receiving a conical beam of incident radiation. A focal plane aperture, smaller than the radiation window, is aligned with a focal point of the conical beam of incident radiation and separates the upper chamber
20 from the reaction chamber such that the beam diverges onto the reaction surface of the reaction chamber below the focal plane aperture. A gas outlet receives gas exiting the reaction chamber.

In another embodiment, the reactor is configured for semi-continuous operation, and further includes an annular solids outlet. The annular solids outlet is
25 positioned below the bottom of the reaction chamber for collecting solids exiting the reaction chamber. The gas outlet is located within the annular solids outlet. The one or more powder supply containers are configured to supply a continuous layer of falling powdered reactant distributed about the reaction surface.

In accordance with another aspect of the present invention, a process for
30 reacting a powdered reactant in the presence of incident radiation is disclosed. The process includes feeding the powdered reactant into the disclosed cavity reactor, and providing the incident radiation through the radiation window.

In accordance with yet another aspect of the present invention, a process for using solar energy to convert H_2O into H_2 and O_2 is disclosed. The process includes
35 concentrating sunlight as the incident radiation fed to the cavity reactor, feeding ZnO as the powdered reactant to the cavity reactor, collecting dissociated Zn and O_2 as gaseous products from the cavity reactor, cooling the gaseous products to precipitate

solid Zn particles, collecting the solid Zn particles, reacting the collected Zn particles with H₂O to create ZnO and H₂, recycling the resulting ZnO into a feed stream, and capturing the H₂ and/or the O₂.

BRIEF DESCRIPTION OF THE DRAWINGS

5 The invention is best understood from the following detailed description when read in connection with the accompanying drawings, with like elements having the same reference numerals. When a plurality of similar elements are present, a single reference numeral may be assigned to the plurality of similar elements with a small letter designation referring to specific elements. When referring to the elements collectively or to a non-specific one or more of the elements, the small letter designation may be dropped. This emphasizes that according to common practice, the various features of the drawings are not drawn to scale unless otherwise indicated. On the contrary, the dimensions of the various features may be expanded or reduced for clarity. Included in the drawings are the following figures:

15 FIG. 1 is a schematic illustrating a prior art thermochemical cavity reactor;

 FIG. 2 is a three dimensional cross-sectional view of an exemplary thermochemical cavity reactor in accordance with aspects of the present invention;

 FIG. 3 is a partial cross-sectional view of the exemplary thermochemical cavity reactor of FIG. 2 in accordance with aspects of the present invention;

20 FIG. 4 is two dimensional cross-sectional view of an exemplary thermochemical reactor in accordance with aspects of the present invention;

 FIG. 5 is a profile view of exemplary reactor surfaces in accordance with aspects of the present invention;

25 FIG. 6 is three dimensional view of a reactor surface in accordance with aspects of the present invention;

 FIG. 7 is a cross-sectional view of an exemplary ring of inlet jets in accordance with aspects of the present invention; and

 FIG. 8 is a graph plotting feed rate vs. RPM for splines of various tooth count in an exemplary reactor in accordance with aspects of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

35 The various aspects of the present invention relate generally to a novel solar-thermochemical reactor designed and constructed for ultra-high temperature thermochemical reactions including, but not limited to, the first step in a closed two-step thermochemical cycle to produce hydrogen from water as a solar fuel.

Abbreviated as GRAFSTRTM (Gravity-Fed Solar-Thermochemical Receiver/Reactor), the reactor is closed to the atmosphere, and features an inverted conical-shaped reaction

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surface. In semi-continuous operation, a powdered metal oxide reactant, such as ZnO powder, descends continuously upon the inverted conical-shaped reaction surface as a falling sheet and undergoes a thermochemical reaction upon exposure to incident radiation. The reactant feed may be introduced through a vibration-induced, metered, and gravity-driven mechanism. Incident radiation, e.g., beam-down, highly concentrated sunlight, enters the reaction cavity through an aperture, and product gas, e.g., Zn gas, is siphoned into a centrally-located exit stream via a stabilized vortex flow of inert gas originating from above the aperture plane. Unreacted or partially reacted solids exit annularly around the product stream.

The thermochemical reactors and methods described herein exhibit high efficiency in both batch and semi-continuous operation. Moreover, the reactors and methods of the present invention provide design concepts that are commercially viable by practically resolving challenges presented by concepts of materials, fluid flow, heat transfer, and reaction kinetics.

While the invention is described herein primarily with respect to a Zn/ZnO thermochemical cycle, it will be understood that the invention is not so limited. The disclosed embodiments may employ a thermochemical cycle based on any suitable metal oxide redox reaction, or any solid particle in powder-form in general. Additionally, while the invention is described herein primarily with respect to beam-down, highly concentrated sunlight, it will be understood that the invention is again not so limited. The disclosed thermochemical reactors and methods may be fueled by any source of suitably concentrated incident radiation, including radiation of any wavelength or frequency, visible or invisible, natural or manmade, broad spectrum or narrow spectrum. The incident radiation having desired characteristics may be directed into the reactor from outside of the reactor by any means known in the art for directing, amplifying, dispersing, passing, and/or focusing radiation, such as but not limited to the use of heliostats, mirrors, lenses, apertures, filters, windows, and the like.

BASIC REACTOR CONCEPTS

Referring now to the drawings, FIG. 1 schematically illustrates the basic characteristics of a prior art cavity reactor 100. Cavity reactor 100 is comprised of a cooled top-face plate 105 and a radiation window 110. Cooled top-face plate 105 may be comprised of copper and cooled by a fluid such as water. Radiation window 110 is located at the apex of the reaction chamber 120. Reaction chamber 120 consists of a reaction surface 130 formed of, for example, alumina tiles lined on one or more layers of insulating ceramic 140. In the first step of the thermochemical cycle, the solid reactants 160 are fed into reaction chamber 120, disposed about reaction surface 130,

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and exposed to incident solar radiation through radiation window 110. Radiation window 110 causes incident radiation to diverge upon and about reaction surface 130, thereby providing an ultra-high temperature source. Dissociation of the solid reactant progresses in the ultra-high temperature environment, and evolved product gases and unreacted solids are extracted through a product outlet 150. In semi-continuous mode, unreacted solids may be returned to reaction chamber 120, as described in subsequent embodiments.

As shown, in addition to fueling the endothermic reaction within reaction chamber 120, heat energy dissipates to the atmosphere by radiative, conductive and convective transfer to and through the solid reactants, product gases, and the walls of the reactor. Conductive heat transfer, of course, is minimized by ceramic insulation 140.

THE GRAFSTRR REACTOR

Turning next to FIGS. 2-4, an exemplary thermochemical cavity reactor 200 includes a reaction chamber 240 having a reaction surface 210 defined by an inverted conical geometry. Like cavity reactor 100 of FIG. 1, cavity reactor 200 utilizes concentrated incident radiation in a beam-down orientation. A converging beam of radiation energy, such as concentrated solar energy enters the reactor through a radiation window 220 and passes through an upper chamber 225 and a focal plane aperture 230. Radiation window 220 may be comprised of quartz, or any material suitable for causing the divergence of incident radiation. Focal plane aperture 230, preferably smaller than radiation window 220, separates upper chamber 225 from reaction chamber 240. Sized in this manner, focal plane aperture 230 minimizes or prevents re-radiation of solar energy back through radiation window 220. As shown in FIG. 3, aperture 230 is aligned with the optical focal-plane 410 of the beam 400. The divergence of beam 400 upon reaction surface 210 creates a high temperature environment in cavity reaction chamber 240 due to the high effective absorption efficiency of cavity reactor 200.

Reaction surface 210 is characterized by an inverted conical geometry in which reaction surface 210 has a top 250 and a bottom 260. In one exemplary embodiment, the inverted conical geometry results from a plurality of trapezoidal components 270 arranged in a side-by-side configuration. Each individual trapezoidal component 270 is characterized by a length that tapers from a relatively wide top width to a relatively narrow bottom width. FIG. 3 illustrates reactant-coated reaction surface 210 consisting of a single trapezoidal component 270, 15 of which are used in forming the inverted conical geometry shown in FIG. 2. The invention is not limited, however, to any particular number and/or size of such components. Reaction surface 210 may

be comprised of alumina tile, or any other surface suitable to generate and maintain an ultra-high temperature environment. Other reaction surface geometries and materials of construction will become apparent to those of ordinary skill as falling within the teachings set forth herein. For example, although ideally characterized by an inverted conical shape, any geometry, such as but not limited to segments of an inverted cone or a single trapezoidal (or other geometric shaped) component 270 surrounded by walls, having an inclined plane suitable for receiving applied incident radiation, coupled with suitable optics and/or radiation sourcing to provide the desired quantity and quality of radiation, may provide an effective design in certain applications. The symmetrical, full inverted conical shape is ideal, however, for the efficient use of concentrated sunlight as the radiation source in a cavity reactor designed for high-temperature processes. Non-symmetric configurations may require large amounts of active-cooling, and therefore may waste incoming energy and/or may be less desirable for achieving extremely high temperatures over large areas of reaction surface. For lower temperature processes, non-symmetric configurations present fewer such drawbacks. Although the exemplary embodiment described herein may be ideally utilized as a high-temperature, high-efficiency cavity receiver/reactor designed specifically to attack the high-temperature processes, the invention is not limited to reactors designed for use in any particular type of process or for operation at any particular temperatures.

In order to maximize the absorptive efficiency and sustain the ultra-high temperature environment, insulation, such as but not limited to a layer of porous ceramic insulation 280, surrounds and supports reaction surface 210. For example, KVS184™, a ceramic matrix composite comprising 80% Al₂O₃- 20% SiO₂ manufactured by ALTRA® Composite Systems of Newark, Delaware, has been shown to provide the requisite mechanical, chemical, and thermal stability.

Cavity reactor 200 includes one or more, and typically a plurality of, powder supply containers 290, 291 that are configured to supply a powder to reaction surface 210. Powder supply containers 290, 291 may be vats, bins, tubs, baskets or any containment device that can store solid reactant powder until necessary to feed the solid reactant powder to reaction surface 210. In one exemplary embodiment, configured for semi-continuous operation, plurality of powder supply containers 290, 291 are hoppers arranged in a circular pattern above the top of reaction chamber 240. Each trapezoidal component 270 has a corresponding hopper 290, 291 positioned to feed the powdered reactant to top 250 of reaction surface 210 such that the powdered reactant falls by gravity down the inclined reaction surface 210 towards bottom 260. An annular solids outlet 300 positioned at bottom 260 of reaction surface 210 collects,

inter alia, unreacted solids. The recovered unreacted solids may be recycled into the feed stream provided by hoppers 290, 291. Gaseous products are collected by a gas outlet 310, which is housed within annular solids outlet 300.

In one embodiment, in which cavity reactor 200 is configured for batch mode, powder supply containers 290, 291 coat reaction surface 210 with ZnO powder. The coating occurs at temperatures below 1900K but preferably above sintering temperatures around 1100K. After sufficient coating, the temperature is increased and the reactant layer is decomposed completely before recoating.

In batch mode, various forms of surface texturing can be advantageous in ensuring a fully reactant-coated surface. Surface texturing creates crevices for solid reactants to gather, thereby impeding movement of the solid reactants along the decline of reaction surface 210 towards bottom 260. FIG. 5 depicts a saw-tooth surface 400, a staggered pattern 500, and a smooth surface 600. In a particularly preferred embodiment, depicted in FIG. 6, trapezoidal component 270 is characterized by textured surface 500. Texturizing an alumina tile requires an increased tile thickness to prevent cracking while machining.

In semi-continuous mode, smooth surface 600 is preferred as a substrate for the falling solid reactant powder fed by powder supply containers 290, 291. As used herein, "falling" means "rolling, slipping, tumbling, and/or entrained solid reactant powder." When solid particles are released into the reactor from powder supply containers 290 above, smaller particles may first become suspended, and then entrained into the slow-moving boundary-layer inert gas flow that travels just above the reaction surface (described below). The largest agglomerations of smaller particles may tumble until broken into smaller agglomerations, which then roll along the surface or slip while further breaking up, burning off, sintering to the reaction surface, and/or eventually exiting the reaction cavity. In the ideal case, reactants dissociate as they travel by force of gravity along the decline of reaction surface 210, and are fully dissociated before reaching bottom 260 of reaction surface 210.

In a hybrid between batch mode and semi-continuous mode, a moving layer of solid reactants passes over the top of a partially sintered surface, coating the partially sintered surface, reacting itself, and replenishing surface coatings that have evolved. More specifically, the feed-rate may be adjusted to allow some particles to react directly, and others to coat the surface and react after longer residence times.

FEEDING MECHANISM

For feeding powder from the powder supply containers, various mechanisms may be used, including but not limited to a spinning disk, vibrating annular sieve-ring, and an electromagnetic-induced element vibration. While a

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preferred mechanism is the spline-metering technique, the present invention is not so limited. Spline-metering is particularly advantageous in that it allows extremely accurate feed rates, consistent feed over time and varying hopper fill level, highly uniform falling powder profile, and mechanical strength and durability. With respect to spline design, number of teeth, tooth depth, bottom land angle and radius, pitch and swept area determine the desired feed rate, and its effectiveness and accuracy, based on a set motor speed. For example, a spline characterized by an acute bottom land angle or tight radius will tend to accumulate and hold powder through multiple rotations, which may be undesirable. Motor speed is typically matched to the solid material bulk density, after an assessment of effective motor speed range.

If the spline turns too slowly, a pulsing feed profile may be created. If the rotational speed is too high, powder can be "blown back" into the hopper by the tooth tips. An accurate, controllable, and reliable powder feeding mechanism may be designed by plotting feed rate vs. RPM for splines of various tooth count, such as is shown in the exemplary graph of FIG. 8. The overlapping zones indicate desired operating ranges. A spline composed of 15 teeth falls directly across the intended operating range for the design shown and described in detail herein. It is understood to one of skill in the art that each specific reactor design and reactant feed requirement may dictate a different range than that shown in FIG. 8.

In one exemplary embodiment, in addition to ZnO powder, each hopper may contain an additive mixed in to improve free-flow, prevent particle conglomeration, and aid in spline clearing. Depending on the application and desired temperature, various additives are commercially available. For the ultra-high temperature environment in which 1-5 μ m ZnO powder is the solid reactant, pure alumina milling balls of 0.1mm diameter can be used.

EFFECTIVE PARTICLE SIZE

Powders are generally very difficult to handle, especially with decreasing particle size. Small particle sizes provide increased reactive surface area per unit volume, but the powder quickly becomes unmanageable unless it is fully aerosolized. While many different particle sizes are compatible with and contemplated by the present invention, by way of example, two different rated sizes of 99.9% pure ZnO were analyzed: 1-5 μ m and 40 μ m. In addition to rated particle size, the effective particle size (agglomeration of smaller particles) is an important parameter for continuous-feed application. The analysis of effective particle size distribution under typical hopper feeding conditions for the 1-5 μ m rated batch was performed using SEM images. The average effective particle size after thorough desiccation, sufficient vibration, and collision with the reaction surface from a drop height of 2cm, was

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determined to be 165 μ m. Interestingly, the effective particle size was similar (175 μ m) for the larger rated batch that contained particles that were almost an order of magnitude larger in rated size (40 μ m). This is an important finding because metallic Zn will likely be melted and then evaporated in a flow or steam to create reactive nano-
5 particles. Once these particles oxidize to split water in step 2 of the thermochemical cycle, the resulting ZnO particles to be recycled will potentially be much smaller than the originating particle size. The observation that true particle size has little influence on the bulk and effective-particle properties suggests that the smaller particles originating from the recycle stream may have an inconsequential impact on operations.
10 Thus, although referred to herein as a "powdered" reactant, it should be understood that the reactant is not limited to any specific definition of the term "powder" and that any type of solid particulate feed may be acceptable, depending upon the characteristics and reactivity of the particle, the residence time in the reactor, and other factors that will be well understood by those of skill in the art. Furthermore, it
15 should be understood that the general reactor design as described herein is not limited to any specific type or state of reactant feed, and that with appropriate attention to relevant design details well understood to one of skill in the art, may be optimized for use with a liquid feed.

Bulk density is highly dependent on the packing mechanism of the
20 powder, how it was handled previously, and how it is moved through the feeding mechanism. Assessment of this parameter can assist with calibrating the feeding mechanism. Once bulk density is determined for the exact operating conditions, it can be used to assess feed rates. For the 1-5 μ m powder, bulk density was found to vary between 0.6 and 1 g/cm³, corresponding to a loose-fill condition and a container-
25 compaction condition respectively.

When operating in batch mode, powder can be deliberately over-fed until reaction surface 210 is coated. When operating in continuous mode it is desirable to strike a balance, feeding as little reactant onto reaction surface 210 as is necessary to maintain sufficient coating. In one exemplary embodiment, the minimal feed rate
30 required to coat reaction surface 210 is approximately 1g/s. Surface powder-coverage can be correlated to feed rate by imaging the reaction surface during feeding. The feed rate is directly related to the residence time of the particle in the reaction zone as it descends along the inclined walls of the reactor. The desired residence time, in turn, depends on the rate at which a ZnO particle of a given size can be fully decomposed
35 into Zn and O₂.

PARTICLE RESIDENCE TIME

The extent of solid particle dissociation is a function of exposure time in the high-flux/high-temperature environment. Using a general shrinking particle model for spherical particles undergoing a decomposition reaction under a uniform surface temperature condition, the minimum required residence times for complete decomposition can be obtained for design purposes. A key parameter in assessing particle decomposition time is surface area. Where the effective particle is composed of smaller particles, such as has been shown with ZnO, the effective surface area can be as much as 50% greater than that of simply assuming that the particle is perfectly spherical.

The required residence time for complete decomposition as a function of initial particle diameter can be evaluated as a function of surface temperatures. As expected, the decomposition time increases with increasing particle diameter, and decreases for higher particle temperatures. These results suggest that it is not practical to expect particles of the average effective size to fully dissociate in a single pass through the reactor. For example, residence times greater than a certain threshold may require the reactor to become impractically and inefficiently large. It is, however, reasonable to expect the outer shell of large particles to decompose in addition to the full decomposition of smaller particles. The inverted conical shape of the exemplary reactor chamber, namely the symmetrical and declined reaction surface provided by this configuration, can provide suitable reaction extents for a variety of solid particle reactant materials and particle sizes.

Because a single pass of the solid reactants through the reactor achieves a lower particle conversion, higher efficiency may be realized through the utilization of one or more recycle streams in which unreacted ZnO is returned to the feed stock. Suitable recycling mechanisms will be apparent to those of ordinary skill in the art.

POWDER FALL VELOCITY

The interaction between the falling ZnO powder and the alumina tile surface has not been found to strongly correlate to the temperature of reaction surface 210. Particle speed does vary, however, with drop-height, due to a higher initial velocity relative to average falling speed. Speeds approach that of free-fall as the declination angle approaches 90°.

FLOW GENERATION AND VORTEX STABILIZATION

In one exemplary embodiment, product gas removal and prevention of fouling radiation widow 220 may be facilitated by a vortex flow coupled with a downward jet impingement is generated proximate to the plane of aperture 230 and transitioned into the reaction-cavity. Returning to FIG. 2, the flow pattern ideally

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should simultaneously keep product gases away from radiation window 220, upper chamber 225, and the region proximate to aperture 230, and be able to sweep Zn vapor from reaction surface 210 into gas outlet 310. An exemplary mechanism for generating such a flow pattern is shown in FIG. 7. To achieve and manipulate the flow pattern, a tangential series of jets 246 created by an impeller-like arrangement are positioned below a radial set of jets 245. Together, a stable vortex flow pattern can be achieved and the updraft created by low pressure in the vortex core can be successfully mitigated. Velocities of tangential jets 246 and radial jets 245 may be balanced against one another for optimization.

The vortex flow may be fed by any gas inert to the thermochemical cycle to occur in the inventive reactor.

To fully understand the flow patterns developed inside the reactor for optimizing the jet balance, a "cold" visualization reactor mock-up was built to full scale out of transparent materials. Smoke was uniformly diffused through reaction surface 210 to simulate the evolution of Zn vapor from the reaction surfaces. A vortex flow was then generated using a combination of tangential jets 246 and radial jets 245 positioned above aperture 230, and the transport of smoke within the upper and lower cavities was visualized. Air was used for the vortex flow pattern instead of inert gas. A He-Ne laser split into a sheet was used to illuminate the entire cross-section of cavity reaction chamber 240.

In general tangential jets 246 create sufficient rotation to draw Zn vapor/smoke from cavity reaction chamber 240. To counter the upward draw of the vortex flow, radial jets 245 positioned above tangential jets 246 collide on the reactor's centerline and just below radiation window 220, turning downwards and plunging into the vortex core to minimize fouling of radiation window 220.

Under ideal tangential and radial jet velocities, radiation window 220 is effectively cleaned and vapor-state Zn takes a direct path to gas outlet 310 to avoid condensation. In the smoke-modeled example, operation in a regime at an approximate ratio of 3:2 tangential to radial jets gas flow established a stable vortex flow. Although not necessarily directly applicable to the ultra-high temperature domain, these results may still be extremely useful after calibration for the on-sun environment. In view of the disclosures herein, configurations other than the disclosed tangential/radial jet arrangement are contemplated by the present invention and will become obvious to one of ordinary skill. Likewise, other suitable tangential and radial jet velocities and will be known to one of ordinary skill in the art from the description herein. Computer modeling, such as using FLUENT or other commercially available software, may be used to model surface reaction kinetics, fluid flow, and heat transfer.

Such modeling in one embodiment predicted vortex formation consistent with the experimental methods described herein.

METHODS OF PRODUCING SOLAR FUELS

Another aspect of the invention is a process for reacting a powdered
5 reactant in the presence of incident radiation. The processes disclosed relate the use of the inventive cavity reactor to react powdered reactant in the presence of incident radiation. First the powdered reactant is fed into cavity reactor 200 as described above. Incident radiation is introduced through radiation window 220. The process may, for example, comprise providing powdered ZnO as the reactant, providing
10 concentrated sunlight as the incident radiation to dissociate the ZnO to Zn and O₂, and collecting unreacted ZnO at the annular solids outlet. The process may further comprise reacting the outlet Zn to create a solar fuel, such as by reacting the Zn with H₂O to form ZnO and H₂. In particular, the process described above may use solar energy to convert H₂O into H₂ and O₂, by concentrating sunlight as the incident
15 radiation fed to cavity reactor 200 described above, feeding ZnO as the powdered reactant to the cavity reactor, and collecting dissociated Zn and O₂ as gaseous products from the cavity reactor. Subsequent process steps, that will be well understood to those of skill in the art, include cooling the gaseous products to precipitate solid Zn particles, collecting the solid Zn particles, reacting the collected Zn particles with H₂O
20 to create ZnO and H₂, recycling the ZnO thus created back into the process, and capturing the H₂ and/or the O₂ created by the process.

OVERALL ADVANTAGES AND DESIGN CONSIDERATIONS OF THE EXEMPLARY EMBODIMENT

The novel, ultra-high temperature, solar-thermochemical reactor
25 embodiment as described herein, is designed to, continuously or in batch-mode, solar-thermally dissociate solid particles, collect the un-reacted particle stream for recycling, and siphon off the products to an exit flow for collection. One non-limiting example of an applicable process is the thermochemical dissociation of a metal-oxide powder into the pure metal or reduced metal-oxide, for instance ZnO to Zn. The solar-thermal
30 dissociation occurs in the reaction chamber through prolonged exposure to ultra-high reactor-cavity temperatures and direct incidence of concentrated solar radiation.

The exemplary reactor is designed to efficiently effect high temperature (approaching 2000K) thermochemical reactions by utilizing the "cavity-effect", which is defined as the containment of highly concentrated electromagnetic radiation by use of
35 a small entrance aperture into a larger reaction cavity. The "cavity-effect" coupled with highly concentrated solar energy has been found to be highly effective at efficiently achieving and sustaining ultra-high reaction temperatures over large surface areas.

In addition, at such high temperatures and solar-fluxes, it is preferable in semi-continuous operation to continuously supply reactants to the solar-incident surfaces to prevent local melting of reactor material and to make the most efficient use of the incoming concentrated sunlight. Concentrated radiation exposure to non-
5 reactive surfaces may lead to, in addition to concerns regarding materials of construction, potentially fatal process efficiency and throughput reductions.

3-dimensional non-imaging optics, such as a 2D active tracking parabolic dish system or heliostat-fields coupled to secondary parabolic or hyperbolic reflectors, may be used to achieve solar concentration levels of over 10,000C. Such optical
10 systems produce converging cones of concentrated solar radiation and can be directed to any receiver orientation.

Solid-particle dissociation reactions are described by various models, all of which include reference to temperature, reaction kinetics, and residence time. While these parameters may vary for a given reactant and reactor design, time of exposure
15 to the reaction environment typically determines the extent to which a solid-particle dissociates.

To effect the process described herein, and in light of the considerations discussed above, an ideal cylindrically-symmetric solar receiver/reactor has been described herein in a beam-down configuration, with reactants fed annularly on the
20 perimeter and driven by gravity into the reaction chamber to be exposed directly to a diverging beam of concentrated solar energy (with the solar beam focal-plane located at cavity aperture) and ultra-high cavity temperatures, with products exiting centrally from the bottom, and non-reduced reactants exiting annularly around the product-exit. While this orientation and general design is ideally suited for a continuous, ultra-high
25 temperature, solar-thermochemical process driven by gravity, the reactor can also be modified, as described herein, for batch operation, or a hybrid operation incorporating characteristics of both batch and continuous modes.

The extent of particle dissociation is generally a function of exposure time in the high-flux and high-temperature environment. An inverted-cone shape
30 reaction surface supported by high temperature ceramics therefore allows the particle residence time to be controlled by design of the decline geometry, resulting in suitable reaction extents for a variety of reactant materials and particle sizes. Two methods primarily drive this residence time: frictional interaction with the reaction surface as gravity drives the particles along the decline to the exit, and an aerosolized boundary
35 layer above the reaction surface that travels at a similar velocity to the bulk particle flow. In one experimental embodiment, for a given flux concentration of the testing

facility and a required residence time of 1-5 μ m ZnO particles, a cone geometry of 40 degrees from horizontal was used.

To achieve uniform, consistent, and precisely controllable bulk-powder feeding into the reaction chamber, a rotating spline in the base of a hopper and driven
5 by a motor has been found to be ideal for accurately metering reactants into the cavity below. With 15 reaction-surfaces comprising the inverted cone geometry of the reaction chamber as described in the exemplary embodiment, 15 hopper-spline combinations therefore provide uniform reactant flow to the entire reaction-surface.

Vortex-flow generation in the frustum area of the reactor (above the
10 aperture) may be used to cool the quartz window, suppress products from nearing and/or condensing on the quartz window, and to sweep products off of the reaction surface and into the reactor outlet. The flow may be generated by an impeller-like arrangement of radially and tangentially oriented jets. Relative spacing between these jet inlets in the frustum area, as well as the magnitude of their jet velocity, may be
15 influential in controlling the degree to which the window is cooled and protected and the degree to which the products are removed effectively from the reaction surface. A symmetric reactor geometry leads naturally to the use of a swirling flow for these purposes. Minimizing and optimizing the amount of inert gas to suitably cool and protect the quartz window, as well as help remove product vapor, is desirable, because
20 the introduction of inert gas drives down system efficiency through parasitic heating in the reaction chamber and subsequent gas-separation costs in the exit stream.

Although the invention is illustrated and described herein with reference to specific embodiments, the invention is not intended to be limited to the details shown. Rather, various modifications may be made in the details within the scope and
25 range of equivalents of the claims and without departing from the invention.

What is Claimed:

1. A cavity reactor for inducing a chemical reaction in a powdered reactant, the reactor comprising:

5 a cavity reaction chamber having a reaction surface characterized by an inverted conical shape having a top and a bottom;

one or more powder supply containers located above the top of the reaction chamber configured to supply a layer of powdered reactant distributed about the reaction surface into the reaction chamber;

10 means for providing a beam of incident radiation onto the reaction surface; and

a gas outlet for receiving gas exiting the reaction chamber.

2. The cavity reactor of claim 1, wherein the means for providing a beam of incident radiation onto the reaction surface comprise:

15 a radiation window positioned in an upper chamber above the reaction chamber for receiving a conical beam of incident radiation; and

a focal plane aperture, smaller than the radiation window, aligned with a focal point of the conical beam of incident radiation and separating the upper chamber from the reaction chamber such that the beam diverges onto the reaction surface of the reaction chamber below the focal plane aperture.

20 3. The cavity reactor of claim 1 and 2, further comprising:

an annular solids outlet positioned below the bottom of the reaction chamber for collecting solids exiting the reaction chamber, wherein the annular solids outlet contains the gas outlet, and wherein the one or more powder supply containers are configured to supply a continuous layer of falling powdered reactant distributed about the reaction surface into the reaction chamber.

4. The cavity reactor of claim 1-3, wherein the reaction is a dissociation reaction that dissociates ZnO into Zn and O₂.

30 5. The cavity reactor of claims 1-4, wherein the incident radiation is concentrated sunlight.

6. The cavity reactor of claims 1-5, wherein the one or more powder supply containers comprises a plurality of hoppers arranged in a circular pattern above the top of the reaction chamber.

35 7. The cavity reactor of claims 2-6, further comprising a ring of inlet jets positioned below the radiation window in a configuration that creates a gas vortex, and an inert gas source attached to the inlet jets.

8. The cavity reactor of claim 7, wherein the configuration of inlet jets comprises a tangential set of jets positioned below a radial set of jets.

9. A process for reacting a powdered reactant in the presence of incident radiation, the process comprising feeding the powdered reactant into the cavity reactor of claims 2-8, and providing the incident radiation through the radiation window.

10. The process of claim 9, comprising providing powdered ZnO as the reactant, and providing concentrated sunlight as the incident radiation to dissociate the ZnO to Zn and O₂.

11. The process of claim 10, further comprising collecting unreacted ZnO at the annular solids outlet, and recycling the unreacted ZnO to the reactor

12. The process of claim 10, further comprising later reacting the outlet Zn to create a solar fuel or solar material.

13. A process for using solar energy to dissociate ZnO into Zn and O₂, the process comprising the steps of:

(a) concentrating sunlight as the incident radiation fed to the cavity reactor of claims 1-8;

(b) feeding ZnO as the powdered reactant to the cavity reactor;

(c) collecting dissociated Zn and O₂ as gaseous products from the cavity reactor;

(d) cooling the gaseous products to precipitate solid Zn particles; and

(e) collecting the solid Zn particles.

14. The process of claim 14, wherein the process comprises a portion of an overall process for converting H₂O to H₂ and O₂, wherein the overall process further comprises the steps of:

(f) reacting the collected Zn particles with H₂O to create ZnO and H₂;

(g) recycling ZnO created in step (f) to step (b); and

(h) capturing the H₂ created in step (f), the O₂ created in step (c), or a combination thereof.

15. The cavity reactor of claims 1-8, wherein the inverted cone comprises a plurality of trapezoidal components defining a planar inclined surface having a length that tapers from a relatively wide top width to a relatively narrow bottom width, each trapezoidal component having a corresponding powder supply hopper positioned to feed the powdered reactant to the top of the trapezoidal surface such that the powdered reactant falls by gravity down the inclined surface toward the bottom.

16. The cavity reactor of claim 15 wherein the planar inclined surface of the trapezoidal components is a textured surface.

17. The cavity reactor of claim 15, wherein the planar inclined surface of the trapezoidal components is a smooth surface.

18. The cavity reactor of claims 14-17, further comprising one or more splines which feed the powdered reactant from the powder supply hoppers to the top of
5 the trapezoidal surface.

19. A cavity reactor for inducing a reaction in a reactant, the reactor comprising:

a cavity reaction chamber having a reaction surface sloped from a top elevated relative to a bottom;

10 one or more reactant containers located above the top of the reaction chamber configured to supply a layer of reactant to the reaction surface in the reaction chamber;

means for providing incident radiation onto the reaction surface sufficient to cause a reaction in the reactant; and

15 one or more outlets for receiving the reaction products exiting the reaction chamber.

20. The cavity reactor of claim 19, wherein the reaction surface is in the shape of an inverted cone or a segment thereof.

21. The cavity reactor of claims 18 and 19, wherein the reactant as provided
20 to the reaction surface is in the form of a particulate solid.

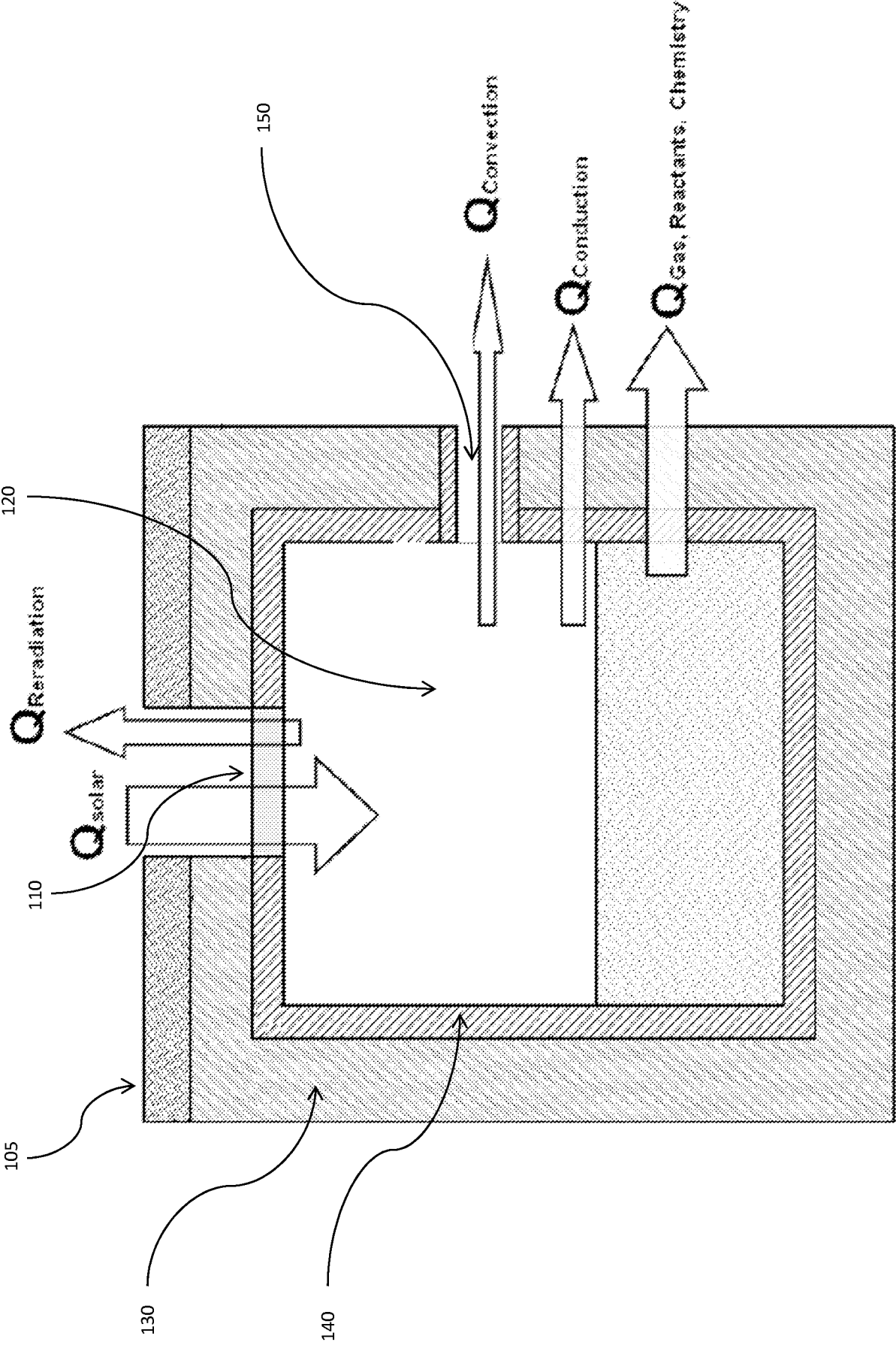
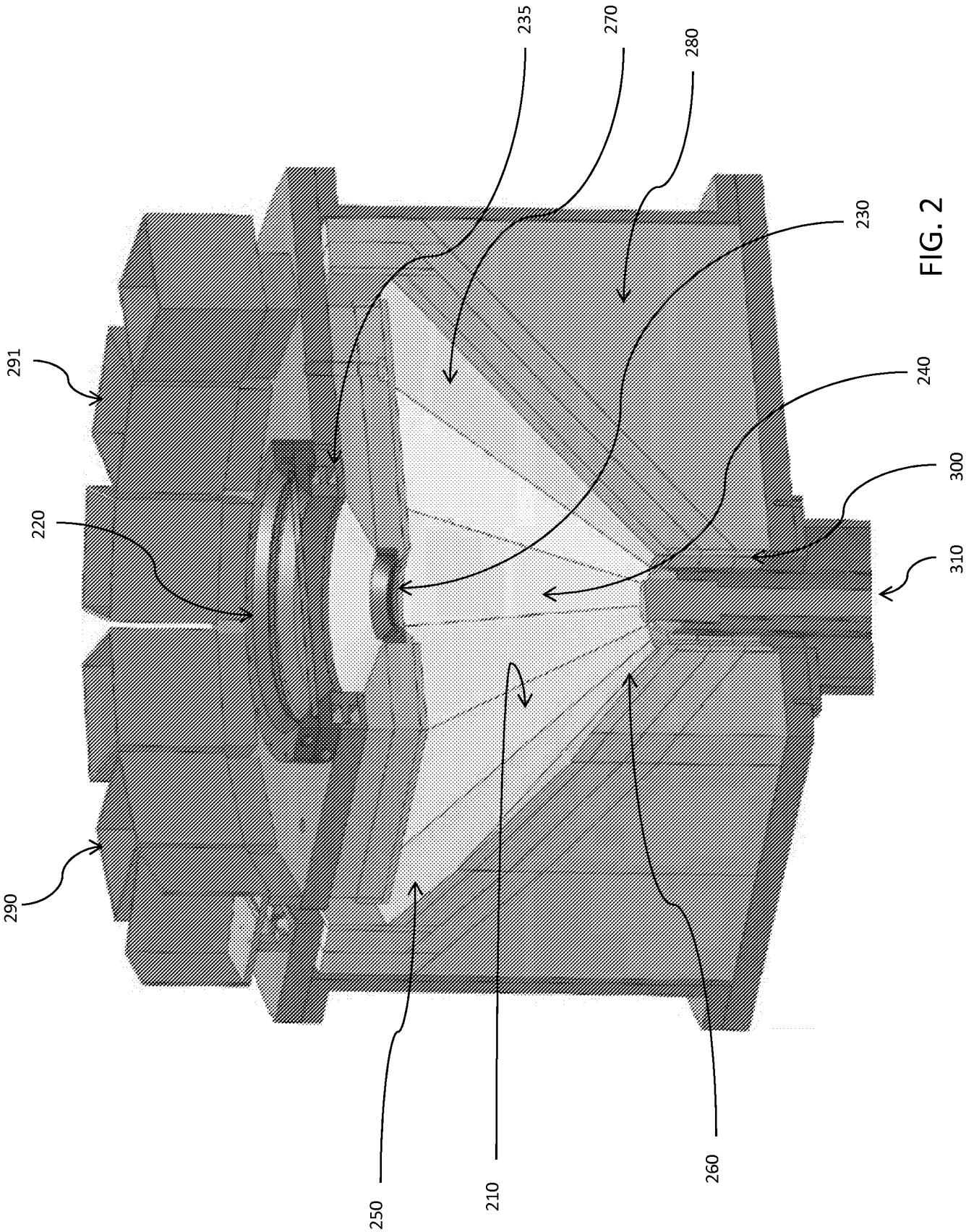


FIG. 1 – PRIOR ART



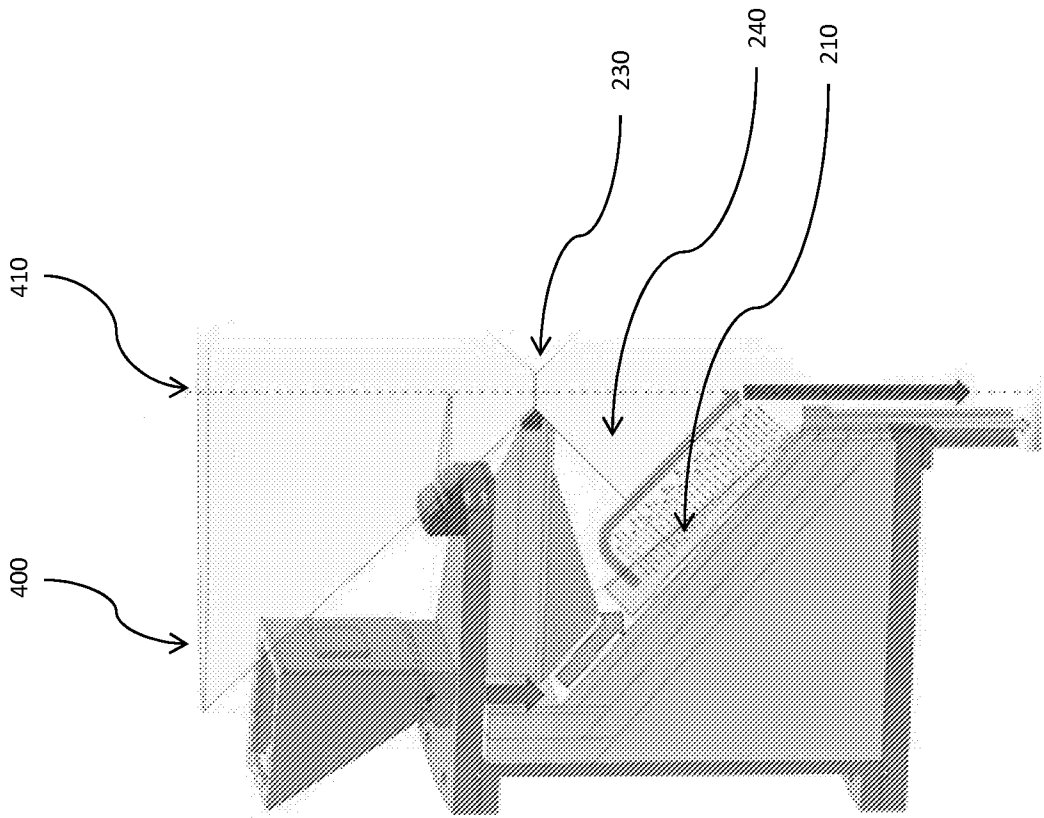


FIG. 3

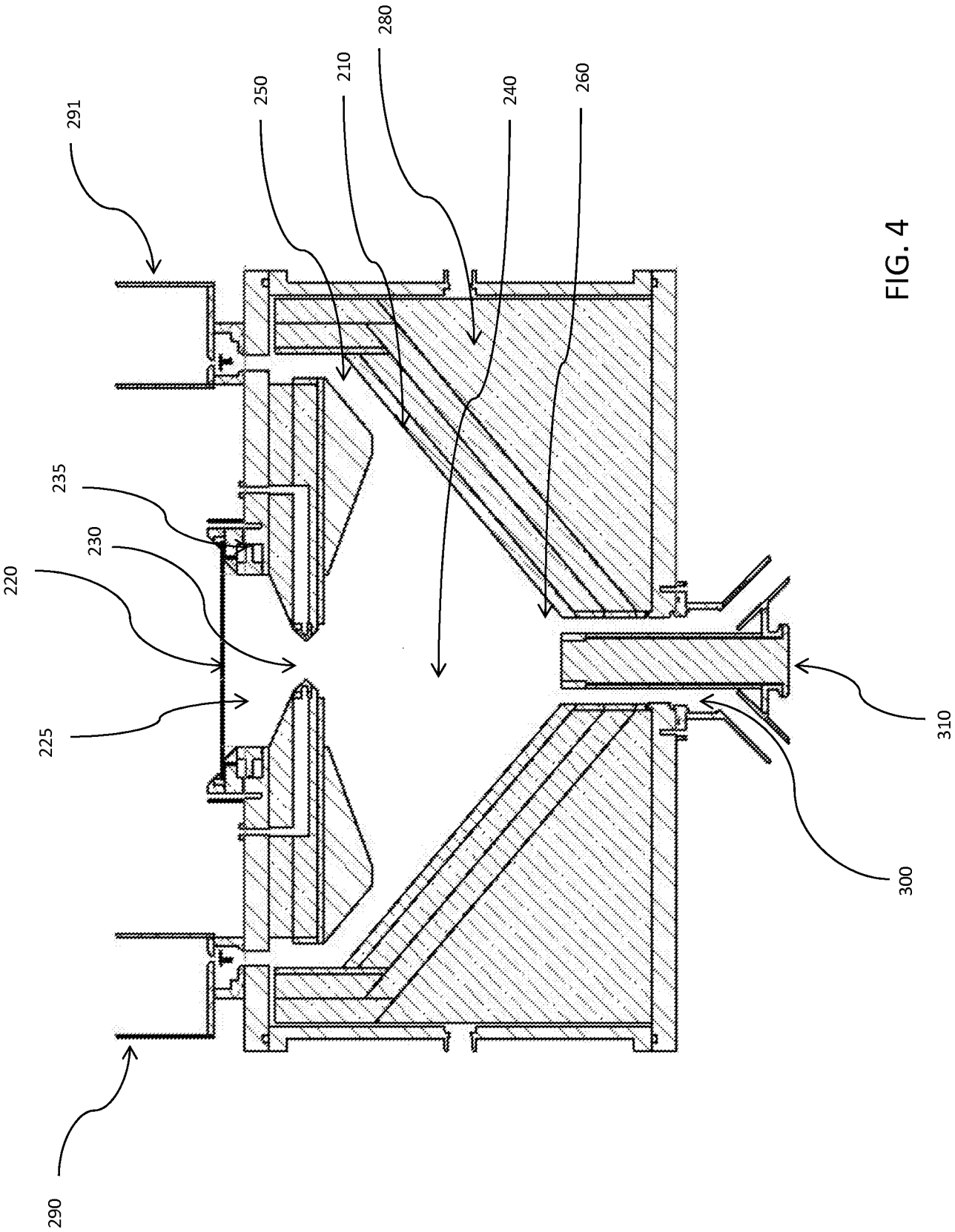


FIG. 4

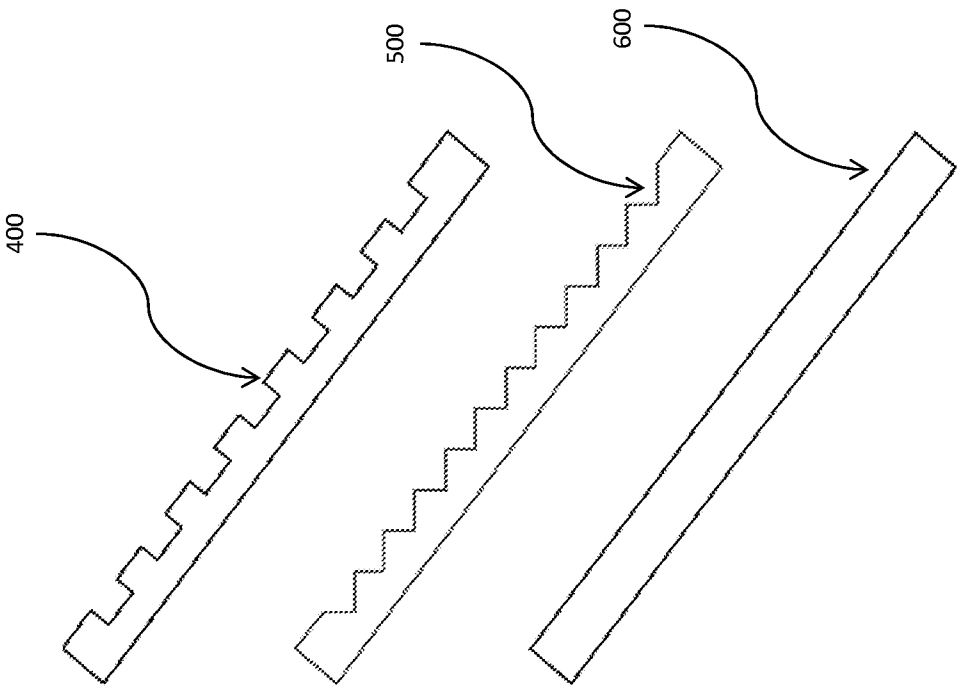


FIG. 5

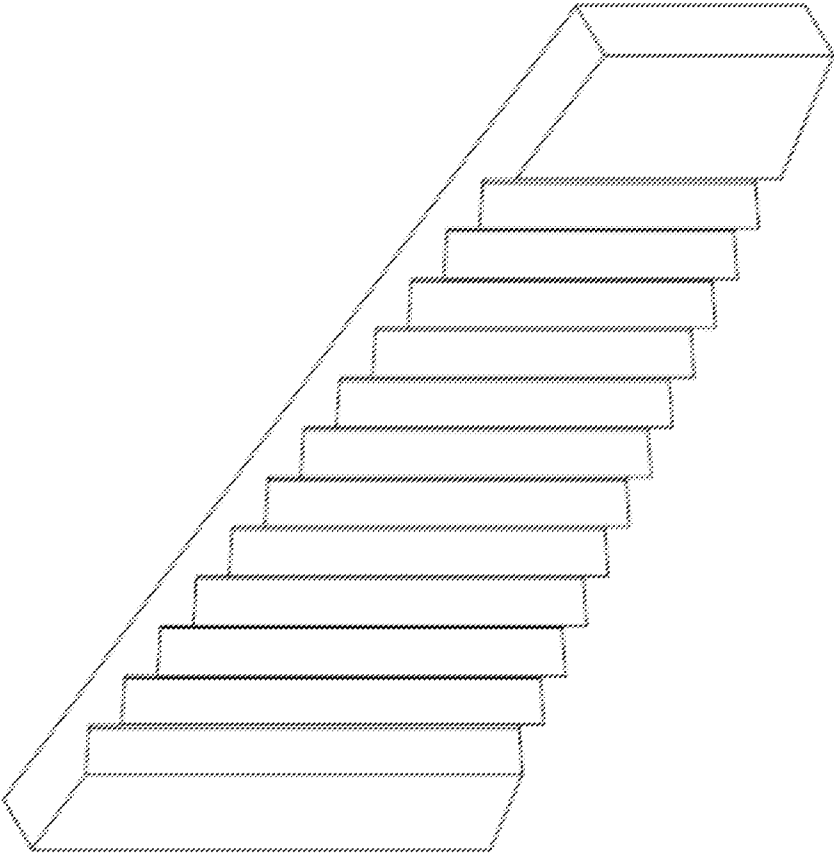


FIG. 6

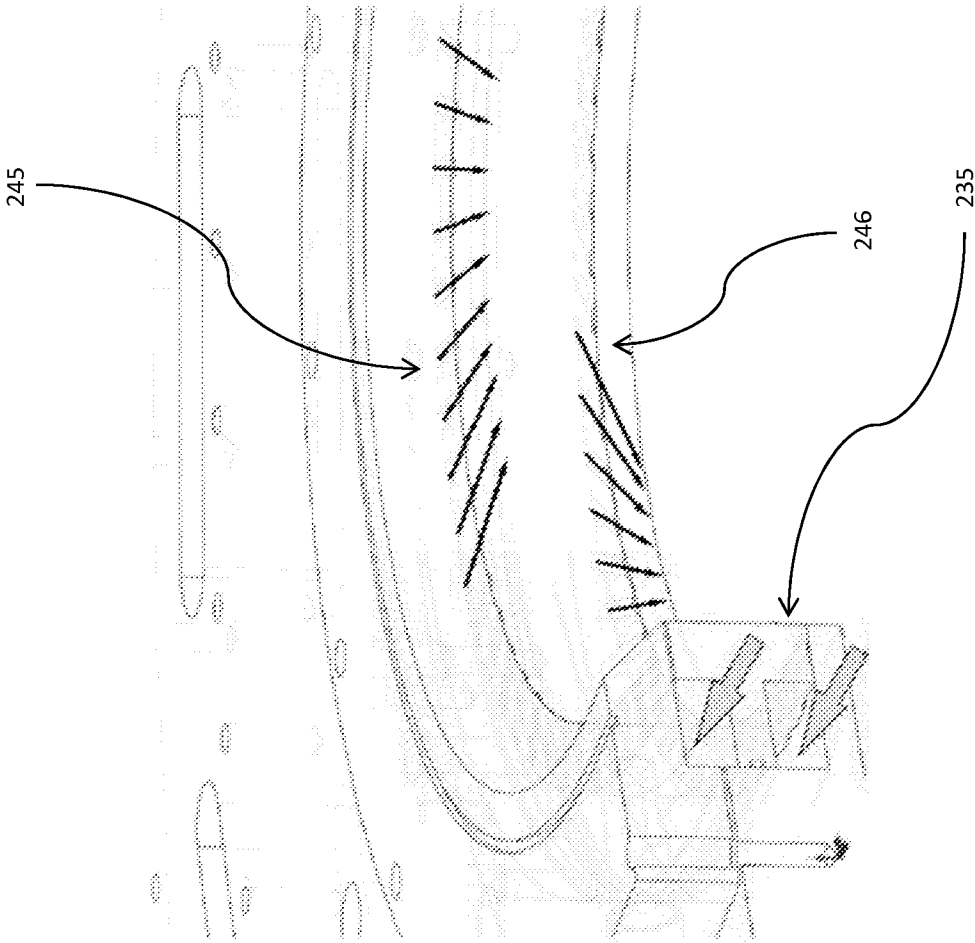


FIG. 7

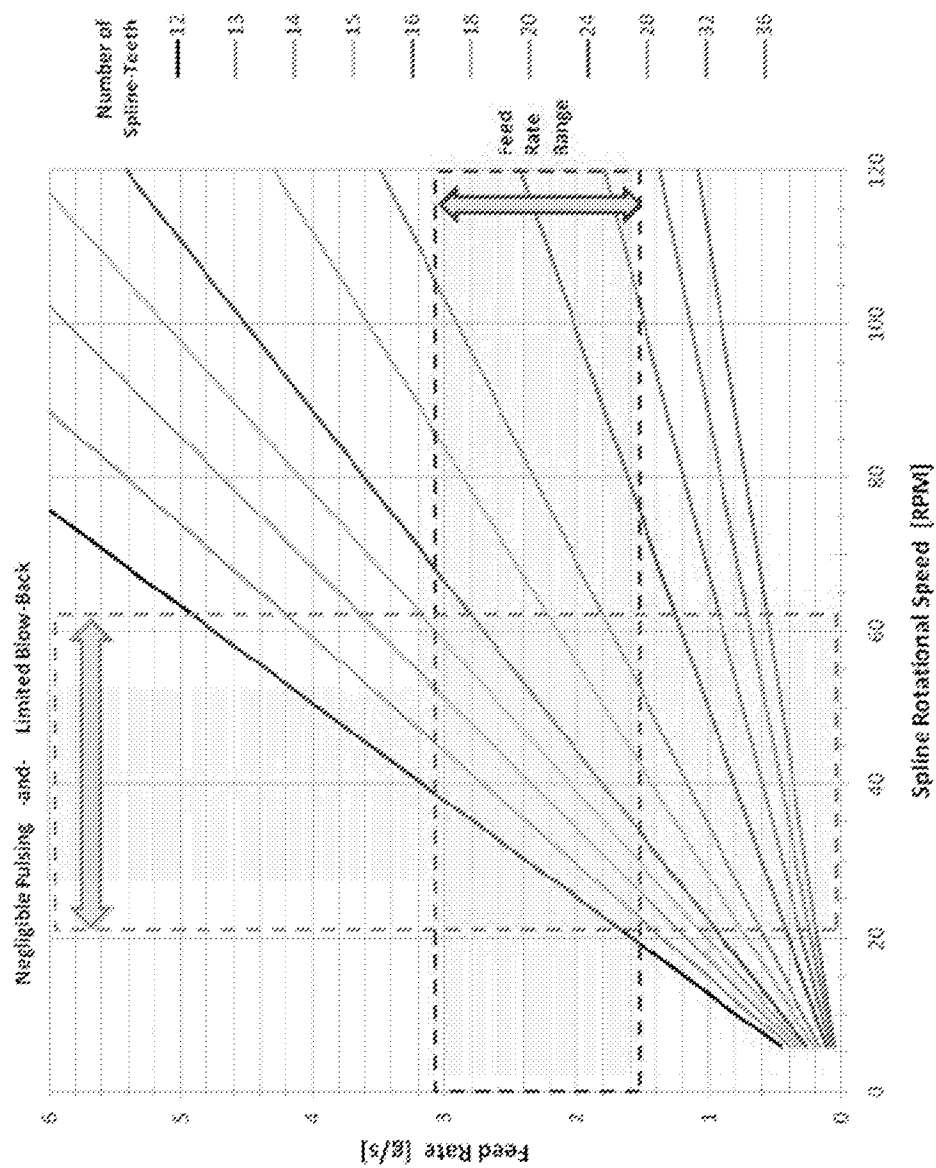


FIG. 8