

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
23 July 2009 (23.07.2009)

PCT

(10) International Publication Number
WO 2009/091978 A2

(51) International Patent Classification:
H05H 1/24 (2006.01)

(21) International Application Number:
PCT/US2009/031249

(22) International Filing Date: 16 January 2009 (16.01.2009)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/011,363 16 January 2008 (16.01.2008) US
61/070,809 26 March 2008 (26.03.2008) US

(71) Applicant (for all designated States except US): **NORTH CAROLINA STATE UNIVERSITY** [US/US]; 920 Main Campus Drive, Venture Building II, Suite 400, Raleigh, NC 27695 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **CUOMO, Jerome, J.** [US/US]; 108 Kinnard Lane, Cary, NC 27511 (US).

KING, Matthew, R. [US/US]; 3411 Melrose Ridge Ct., Apt 116, Raleigh, NC 27603 (US). **OLDHAM, Christopher, J.** [US/US]; 700 Mial Street, Raleigh, NC 27608 (US).

(74) Agent: **GLOEKLER, David, P.**; The Eclipse Group LLP, 10605 Balboa Blvd., Suite 300, Granada Hills, CA 91344 (US).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM,

[Continued on next page]

(54) Title: NON-CATALYTIC SYNTHESIS AND PROCESSING UTILIZING ATMOSPHERIC-PRESSURE PLASMA

(57) Abstract: An atmospheric-pressure plasma flame discharge is utilized to synthesize various chemistries without the use of a catalyst. An atmospheric-pressure plasma flame discharge is also utilized to treat cellulosic material.

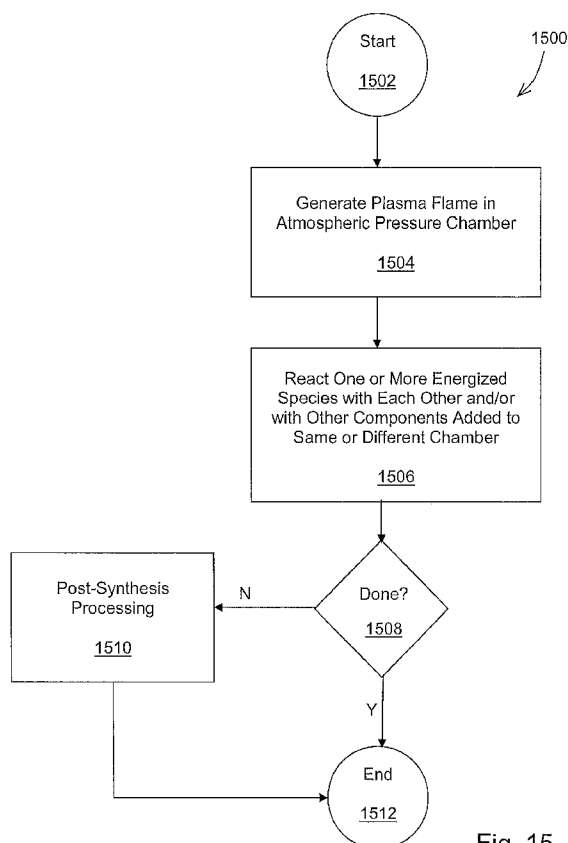


Fig. 15



ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI,
FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK,
MT, NL, NO, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ,
CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN,
TD, TG).

Published:

— *without international search report and to be republished
upon receipt of that report*

PATENT
Docket No. NS08001WO

**NON-CATALYTIC SYNTHESIS AND PROCESSING UTILIZING
ATMOSPHERIC-PRESSURE PLASMA**

RELATED APPLICATIONS

[001] This application claims the benefit of U.S. Provisional Patent Application Serial No. 61/011,363, filed January 16, 2008, titled "NON-CATALYTIC SYNTHESIS UTILIZING ATMOSPHERIC-PRESSURE PLASMA", the content of which is incorporated by reference herein in its entirety. This application also claims the benefit of U.S. Provisional Patent Application Serial No. 61/070,809, filed March 26, 2008, titled "NO₂ SYNTHESIS USING A NON-EQUILIBRIUM ARC", the content of which is incorporated by reference herein in its entirety.

BACKGROUND

[002] **1. Field of the Invention**

[003] This invention relates to the synthesis of chemistries utilizing atmospheric-pressure plasma. The invention also relates to the use of atmospheric-pressure plasma in the processing of biomass such as cellulosic material to produce sugars and the fermentation of such sugars to produce alcohols and other chemicals.

[004] **2. Related Art**

[005] Plasma may generally be described as a volume of highly-energetic ionized gas composed of electrons, ions and neutral molecules. Plasma is typically generated by application of an electrical field to a background gas, although some types of plasmas may be generated by chemical means or very high temperatures. The electrical field may be constant (direct current or DC) or alternating (alternating current or AC, and particularly radio frequency or RF). Atmospheric-pressure (AP) plasma is generated without the requirement of a sealed vacuum environment and thus may be utilized in a broad range of process environments.

[006] The generation and use of atmospheric-pressure (AP) plasmas in various configurations is well known, both in research and in the industrial sector. In general, the addition of electrical energy up to and beyond the breakdown requirements of a gas gap between two electrodes produces a discharge that is strongly responsive to electromagnetic fields. By

modifying the apparatus and input gas mixtures of AP plasma configurations, researchers have found many applications that have impacted diverse industrial sectors. Among many other things, atmospheric plasmas are used for surface functionalization of various substrates; alteration of substrate phobicity; mineralization of organic compounds; reduction of pathogens and surface contaminants to trivial levels; and deposition and synthesis of various materials.

[007] AP plasmas can be generated in many different configurations (e.g. dielectric barrier discharges, corona discharges, plasma arcs, microplasmas, inductively coupled plasmas, laser-assisted plasmas, thermal plasmas, plasma torches) and with many different gases (e.g. He, Ne, Ar, O₂, N₂, air, H₂, H₂O, CO₂, CH₄). These configurations and various input gas mixtures produce a large array of very different environments such as high and low temperatures, oxidizing or reducing atmospheres, chemically reactive or inert environments, and combinations of the foregoing. The parameters of the plasma discharge (and hence the type of discharge) are chosen based on the application of interest. Choosing an application governs the boundaries in which the plasma operates, such as the appropriate temperature, pressure, and energy ranges, current-voltage regime, frequency range, gap size, and gas compositions, as well as the type of chemical species produced by the discharge.

[008] Many chemistries (chemicals and chemical compounds) commonly synthesized on a large industrial scale require large amounts of raw feedstock materials and attendant transportation costs, energy inputs and catalysts, multiple processing steps, and elaborate processing equipment. The synthesis of such chemistries is therefore costly and complex.

[009] As an example, syngas (synthesis gas) is a gas mixture containing carbon monoxide (CO) and diatomic hydrogen (H₂). Syngas may be utilized as a fuel or as an intermediate product in the synthesis of other chemical products such as hydrogen gas, ammonia and methanol. Syngas is typically produced from natural gas (methane, CH₄) via the well-known steam reforming reaction:

[010] $\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$.

[011] The steam reforming reaction is endothermic, occurring at high temperatures (700-1100 °C) and thus requiring a large input of heat energy. The heat energy is typically provided by an external source of hot gas that heats tubes in which the reaction takes place. Moreover, a nickel catalyst is utilized.

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[012] As another example, the Haber (or Haber-Bosch) process is widely utilized to produce ammonia (NH₃), which in turn is widely utilized for various purposes as well as a precursor chemical species for other products. For instance, ammonia is often supplied as a source of nitrogen for use in the production of electronic and electro-mechanical devices and sensors, micro-scale analytical instruments, coatings for tools and other articles, etc. In addition, ammonia is often oxidized to produce nitrates and nitrites to produce various products such as munitions, fertilizer (ammonium nitrate, NH₄NO₃) and acids (most notably nitric acid, HNO₃). Many ammonia-derived chemicals are produced by the megaton each year. It has been estimated that the carrying out of the Haber process accounts for as much as 1% of the world's annual energy usage. In the Haber process, ammonia is produced by reacting diatomic nitrogen (N₂) and hydrogen (H₂) gases over an iron catalyst (Fe³⁺) from iron oxide or magnetite (Fe₃O₄), which further requires aluminum oxide (Al₂O₃) and potassium oxide (K₂O) as promoters. To obtain a high reaction rate at the expense of relatively low production yield (10-20%), the reaction is carried out in a high-pressure environment (250 atmospheres) at a temperature of 450-500 °C. The production yield can be increased by increasing the pressure even higher, but it is not practical to do so. The cost, catalysts, and energy requirements of producing and supplying hydrogen gas as a feedstock for the Haber process is, in and of itself, significant. The hydrogen gas must be obtained from methane or natural gas utilizing heterogeneous catalysis. Multiple process steps are required, including steam reforming, secondary reforming, water gas shift reaction, methanation, and carbon dioxide removal. Various process steps may require sulfur scrubbing to prevent sulfur from poisoning the required catalysts, and reactions with zinc oxide (ZnO), steam and potassium carbonate. Catalysts employed at different stages include nickel oxide; a mixture of iron, chromium and copper; and a mixture of copper, zinc and aluminum.

[013] In a typical application of the Haber process, methane is cleaned to remove sulfur and other impurities and is then reacted with steam to form syngas as follows, using nickel oxide as a catalyst:



[015] Methane not converted by steam reforming may be subjected to secondary reforming reactions for further conversion as follows:

[016] $2\text{CH}_4 + \text{O}_2 \rightarrow 2\text{CO} + 4\text{H}_2$, and

[017] $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$.

[018] Additional oxygen may then be obtained via the following water gas shift reaction:

[019] $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$.

[020] Intermediate products may then be processed in a methanator to recover methane from as-produced carbon dioxide, as follows:

[021] $\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$.

[022] In the final stage of the Haber process, nitrogen (N_2) and hydrogen (H_2) gases are processed over beds of magnetite under the conditions noted above to produce ammonia, according to the reaction:

[023] $\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$.

[024] As another example, ammonia produced according to the Haber process is in turn utilized as a feedstock in the Ostwald process to produce nitric acid (HNO_3). In the Ostwald process, ammonia is oxidized by heating with diatomic oxygen gas (O_2) in the presence of a platinum/rhodium catalyst to produce nitric oxide and water. Pressure ranges from 4-10 atmospheres, and temperature is about 900 °C. The nitric oxide is then oxidized using diatomic oxygen, which produces nitrogen dioxide (NO_2). The oxidation reactions are as follows:

[025] $4\text{NH}_3 + 5\text{O}_2 \rightarrow 4\text{NO} + 6\text{H}_2\text{O}$ and

[026] $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$.

[027] The nitrogen dioxide is then adsorbed by water, optionally in the presence of air, to produce nitric acid, which may thereafter be distilled to a desired concentration. The reactions are as follows:

[028] $3\text{NO}_2 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3 + \text{NO}$ or

[029] $4\text{NO}_2 + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{HNO}_3$.

[030] Ammonia produced according to the Haber process may also be utilized to produce ammonium nitrate according to the following acid base reaction with nitric acid:

[031] $\text{HNO}_3(\text{aq}) + \text{NH}_3(\text{g}) \rightarrow \text{NH}_4\text{NO}_3(\text{aq})$.

[032] Syngas may also be utilized to produce methanol (CH_3OH). The carbon monoxide and hydrogen react on a catalyst at a pressure of 50-100 atmospheres and a temperature of 250 °C. The catalyst is a mixture of copper, zinc oxide and alumina. The reaction is as follows:

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[033] $\text{CO} + 2\text{H}_2 \rightarrow \text{CH}_3\text{OH}$.

[034] In another example, various processes have been employed to synthesize chlorine dioxide (ClO_2). Chlorine dioxide has important applications such as disinfecting municipal water supplies and bleaching wood pulp. Chlorine dioxide, however, has a tendency to explosively decompose into chlorine and oxygen. Consequently, the costs associated with the safe handling of chlorine dioxide are high, and it is preferable that chlorine dioxide be synthesized on site where it is to be utilized.

[035] The production costs attending the synthesis of widely-used chemistries such as the foregoing would be lower if processes could be developed that utilize less energy input, lower pressure, alternative catalysts of lesser cost or no catalysts at all, a lesser amount of raw materials, less processing steps, etc. According to the present disclosure, AP plasmas may be utilized to synthesize widely-used chemistries such as the foregoing. In contrast to conventional methods for synthesizing well-known chemistries, implementations taught in the present disclosure are much less energy-intensive, require no catalysis, and consequently are relatively inexpensive.

[036] Other chemistries pertinent to the present disclosure include acids utilized in the processing of cellulosic materials. Cellulosic materials, including lignocellulosic materials, biomass, etc., occur abundantly in nature and constitute a significant source of sugars from which alcohols and other industrial chemicals may be derived. Cellulose, hemicellulose, and lignin are three primary components of cellulosic materials. Cellulose forms the primary structural component of plant cell walls. The secondary cell wall of green plants contains lignin as well as cellulose. Lignocellulose (cellulose and lignin) such as wood is the most common terrestrial biopolymer, by some accounts comprising approximately 50% of the biomass in the world. Cellulose holds particular interest because it can be processed to yield glucose monomers. Glucose can be converted to fuel-grade alcohols such as ethanol ($\text{CH}_3\text{CH}_2\text{OH}$, or $\text{C}_2\text{H}_6\text{O}$) by fermentation (i.e., bioethanol). Rendering bioethanol commercially available is considered to be a viable way for reducing the environmental effects of and dependence on fossil fuels. Accordingly, cellulosic materials are considered to be an important potential renewable source—particularly a domestic source of alternative fuels—and thus the efficient

conversion of cellulosic components to alcohols, particularly ethanol, is the subject of ongoing research.

[037] Cellulose and hemicellulose are carbohydrate polymers. Cellulose is a long-chain polysaccharide carbohydrate of β -glucose monomers, which may be chemically represented as $(C_6H_{10}O_5)_n$. More specifically, cellulose is a polymer of D-glucose ($C_6H_{12}O_6$) with β [1 $\rightarrow$ 4] linkages (glycosidic bonds) between each of the about 500 to 10,000 glucose units. Cellulose is a straight-chain polymer that exhibits a rod-like conformation, unlike starch which exhibits coiling. Cellulose constitutes about 35-60% by weight of typical cellulosic materials. Hemicellulose is a non-cellulosic, heteropolymer polysaccharide of primarily D-xylose ($C_5H_{10}O_5$) and other pentoses and some hexoses with β [1 $\rightarrow$ 4] linkages. Hemicellulose may be found as a branched polymer of glucose or xylose, substituted with arabinose, xylose, galactose, fucose, mannose, glucose, or glucuronic acid. The molecular weights of hemicellulose polymers are usually lower than that of cellulose, and hemicellulose polymers have a weak undifferentiated structure compared to crystalline cellulose. Hemicellulose, however, binds with pectin (a heterosaccharide) to cellulose to form a network of cross-linked fibers that serves as the structural backbone of plant cell walls. Hemicellulose constitutes about 20-35% by weight of typical cellulosic materials. Lignin may be characterized as a complex, cross-linked, random, amorphous, three-dimensional polyphenolic polymer that typically is based on variously substituted p-hydroxyphenylpropane units. Lignin generally permeates the matrix of cellulose fibers and largely fills in the interstices between the cellular structures (cellulose, hemicellulose and pectin components) of the cellulosic material. However, lignin appears to be more intimately cross-linked or otherwise associated with hemicellulose than with the distinct crystalline phase of cellulose. Lignin constitutes about 10-30% by weight of typical cellulosic materials.

[038] Cellulosic materials are converted to alcohols by releasing the component sugars of the cellulosic materials, and fermenting the sugars to alcohols. The carbohydrate polymers of cellulosic materials are typically depolymerized (degraded or broken down) into fermentable monomeric sugars by hydrolysis. Component sugars may include six-carbon sugars (hexoses) such as glucose, galactose, and mannose, and five-carbon sugars (pentoses) such as xylose and arabinose. Both chemical and enzymatic hydrolytic processes have been utilized.

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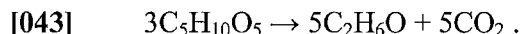
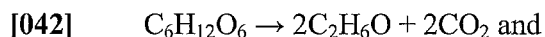
[039] Chemical hydrolysis typically entails the use of an acid such as sulfuric acid as a catalyst. Generally, microcrystalline cellulose is relatively resistant to typical acid hydrolysis, amorphous cellulose is less resistant, hemicellulose (which is also amorphous) is even less resistant, and lignin is highly resistant but may be dissolved by certain organic solvents. Acid hydrolysis utilizes either concentrated acids or diluted acids. Acid hydrolysis generally is around 10-40% efficient in terms of sugar recovery, depending on process conditions. Concentrated acid hydrolysis involves short reaction times, but requires a large amount of expensive acid(s), corrosion-resistant equipment, and energy-demanding means for recycling the acid. Moreover, concentrated acid hydrolysis requires significant control over the reaction to avoid degrading the desired sugars and forming toxic byproducts. Dilute acid hydrolysis is a lower cost process involving a relatively low consumption of acid(s), but requires longer reaction times and results in a decreased glucose yield as compared to concentrated acid hydrolysis. Moreover, dilute acid hydrolysis requires high temperatures to attain acceptable rates of conversion of cellulose to sugar monomers. High temperatures require a high input of energy, promote equipment corrosion, and increase the rates of hemicellulose-derived sugar decomposition. For example, the products of decomposing hemicellulose may include furfural and hydroxymethylfurfural. It is known that sugar decomposition products can inhibit the subsequent fermentation process.

[040] To reduce sugar decomposition, a two-stage acid hydrolysis process has been employed. The first stage is carried out under relatively mild conditions to release sugars as a result of hydrolysis of the hemicellulose, and the second stage is carried out under relatively harsher conditions to hydrolyze the cellulose fraction. The first stage enables the second stage to proceed under the harsher conditions without decomposing the hemicellulose into undesired by-products, but the glucose yield is still unacceptably low (e.g., 50%).

[041] Fermentation of hydrolyzate sugars involves the use of digesting or metabolizing agents such as yeast. Yeast readily metabolizes glucose, which is the predominant hydrolyzate of many types of cellulosic materials. Yeast, however, cannot metabolize other hydrolyzates such as xylose, and thus other organisms such as certain species of bacteria (e.g., *Zymomonas* sp. and *E. coli*) have been employed for this purpose, including organisms genetically

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engineered to consume a specific type of hydrolyzate such as xylose. The stoichiometric expressions for the conversion of glucose and xylose into ethanol are, respectively:



[044] Once fermentation is completed, the resulting alcohols may be separated (e.g., distilled) and purified according to any suitable processes. Residual components of the fermentation process may include lignin, unreacted cellulose and hemicellulose, ash, enzymes, microorganisms, etc.

[045] Due to its crystalline structure, cellulose is generally water-insoluble and resistant to depolymerization. The highly packed and crystalline structure of cellulose also means that the surface area available for hydrolytic and fermentative activity is low. Moreover, as noted above, the presence of hemicellulose and lignin impedes hydrolysis of the cellulose. As a result, the efficiency and costs associated with the conversion of cellulosic material into alcohols are less than desirable. In view of this, various pre-treatment methods have been proposed that endeavor to disrupt the cellulose-hemicellulose-lignin complex, expose the cellulose, and/or modify the pores of the matrix, and thereby make the cellulose more available for hydrolysis such as by allowing enzymes to penetrate into the fibers of the matrix. As in the case of hydrolytic process steps, some of these pre-treatment methods entail the use of acids such as H_2SO_4 or HCl . Many of these pre-treatment methods require high pressures, temperatures and energy inputs, and are costly.

[046] Therefore, in view of the foregoing, despite some advances in pre-treatment and hydrolytic methods, it is well-recognized by persons skilled in the art that an ongoing need exists for providing improved methods, apparatus and systems for the conversion of cellulosic materials to sugars and further conversion of sugars into alcohols and other chemicals. Higher efficiency is desired in terms of yield, energy consumption, and cost. U.S. Patent App. Pub. No. 2008/0006536, assigned to the assignee of the present disclosure and incorporated herein by reference in its entirety, teaches techniques for processing cellulosic materials with AP plasma in the production of alcohols for use as biofuels or industrial applications. Various configurations of AP plasma apparatus were operated to generate plasmas effective to degrade cellulosic materials, either in combination with acids or pretreatments or as a complete substitution for

acid hydrolysis and pretreatments. In the present disclosure, it is now taught that the AP plasma may be utilized to conduct an *in situ* acid treatment, in which AP plasma is utilized to synthesize acid directly within the structure of cellulosic materials.

SUMMARY

[047] According to one implementation, a method is provided for synthesizing a chemistry. A plasma flame is ignited in a chamber at atmospheric pressure in the presence of a gas including a plurality of gas-phase components, by applying a periodic signal to at least one of a pair of electrodes in the chamber. The plasma flame includes a thermal core in a gap between the electrodes and a non-equilibrium region adjacent to the thermal core. A synthesis reaction is conducted by reacting at least one component of the gas with either another component of the gas or with a precursor component introduced in the chamber separately from the gas.

[048] According to another implementation, the synthesis reaction is conducted for a first period of time. After the first period of time, a post-discharge reaction region including energetic species of the gas is created in the chamber, by ceasing application of the periodic signal such that the plasma flame is extinguished. For a second period of time after the plasma flame has been extinguished, the synthesis reaction is conducted in the post-discharge reaction region. The steps taken during the first and second periods of time may be repeated one or more times.

[049] According to another implementation, the plurality of gas-phase components includes oxygen and nitrogen; igniting the plasma flame produces energetic oxygen species from the oxygen, energetic nitrogen species from the nitrogen, and energetic nitrogen oxides from both; and conducting the synthesis reaction includes combining nitrogen and oxygen from the energetic species to form nitrogen dioxide.

[050] According to another implementation, the reaction products are combined with water to produce nitric acid. This step may take place in the reaction chamber, in a secondary chamber or holding device, or at any location not inherently connected to the chamber.

[051] According to another implementation, a method is provided for synthesizing syngas including carbon monoxide and diatomic hydrogen. A plasma flame is ignited in a chamber at atmospheric pressure, by applying a periodic signal to at least one of a pair of electrodes in the

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chamber. The plasma flame includes a thermal core in a gap between the electrodes and a non-equilibrium region adjacent to the thermal core. A mixture of a hydrocarbon and water is flowed toward the plasma flame. Species of the hydrocarbon and water energized by the plasma flame are reacted to form syngas.

[052] According to another implementation, a method is provided for synthesizing ammonia. A plasma flame is ignited in a chamber at atmospheric pressure, by applying a periodic signal to at least one of a pair of electrodes in the chamber. The plasma flame includes a thermal core in a gap between the electrodes and a non-equilibrium region adjacent to the thermal core. Nitrogen species and hydrogen species, obtained from a hydrogen source not limited to diatomic hydrogen gas, energized by the plasma flame are reacted to form ammonia.

[053] According to another implementation, a method is provided for synthesizing chlorine dioxide. A plasma flame is ignited in a chamber at atmospheric pressure, by applying a periodic signal to at least one of a pair of electrodes in the chamber. The plasma flame includes a thermal core in a gap between the electrodes and a non-equilibrium region adjacent to the thermal core. Chlorine species and oxygen species, energized by the plasma flame are reacted to form ammonia.

[054] According to another implementation, a method is provided for synthesizing methanol. A plasma flame is ignited in a chamber at atmospheric pressure, by applying a periodic signal to at least one of a pair of electrodes in the chamber. The plasma flame includes a thermal core in a gap between the electrodes and a non-equilibrium region adjacent to the thermal core. A hydrogen source, carbon source, and/or oxygen source is flowed toward the plasma flame. Carbon-, hydrogen-, and/or oxygen-containing species are reacted with the species energized by the plasma flame to form methanol.

[055] According to another implementation, a method is provided for synthesizing ammonium nitrate by reacting ammonia and nitric acid. The ammonia, nitric acid, or both, are produced by operating a plasma flame.

[056] According to another implementation, a method is provided for treating a cellulosic material. The method includes operating a plasma flame to synthesize nitrogen dioxide and exposing the cellulosic material to the nitrogen dioxide.

[057] According to another implementation, the method further includes subjecting the cellulosic material to an atmospheric-pressure plasma. The atmospheric-pressure plasma to which the cellulosic material is subjected may be the plasma flame utilized to synthesize the nitrogen dioxide. Alternatively, the atmospheric-pressure plasma to which the cellulosic material is subjected may be a separate plasma distinct from the plasma flame utilized to synthesize the nitrogen dioxide. This separate plasma may be of the same type as the plasma flame or may be a different type of plasma. The separate plasma may be operated (i.e., ignited and maintained) in the same chamber as the plasma flame utilized to synthesize the nitrogen dioxide, or the separate plasma may be operated in a separate chamber.

[058] According to another implementation, nitric acid is formed within the cellulosic material by reacting the nitrogen dioxide with hydrogen species supplied by a gas or by the cellulosic material. The cellulosic material is degraded by exposing the cellulosic material to the nitric acid.

[059] According to another implementation, one or more components of the plasma-treated cellulosic material are fermented. Fermenting may produce, for example, an organic compound such as, for example, an alcohol.

[060] According to another implementation, a method is provided for treating a cellulosic material. The cellulosic material is subjected to an atmospheric-pressure plasma to produce a plasma-treated cellulosic material. One or more components of the plasma-treated cellulosic material is subjected to an acid hydrolysis process to produce a hydrolyzed cellulosic material, by operating a plasma flame to synthesize nitrogen dioxide and exposing the cellulosic material to the nitrogen dioxide, forming nitric acid within the cellulosic material by reacting the nitrogen dioxide with hydrogen species supplied by a gas or by the cellulosic material (i.e. part of the cellulosic material itself or the water inherently contained within its structure), and degrading the cellulosic material by exposing the cellulosic material to the nitric acid.

[061] According to another implementation, a method is provided for treating a cellulosic material. The cellulosic material is subjected to a first degradation process to produce a first degradation-processed cellulosic material. One or more components of the first degradation-processed cellulosic material are subjected to an atmospheric-pressure plasma to produce a plasma-treated cellulosic material. One or more components of the plasma-treated cellulosic

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material are subjected to a second degradation process to produce a second degradation-processed cellulosic material. Subjecting the cellulosic material to at least one of the first and second degradation processes includes operating a plasma flame to synthesize nitrogen dioxide and exposing the cellulosic material to the nitrogen dioxide, forming nitric acid within the cellulosic material by reacting the nitrogen dioxide with hydrogen species supplied by a gas or by the cellulosic material, and degrading the cellulosic material by exposing the cellulosic material to the nitric acid.

[062] According to another implementation, a method is provided for treating a cellulosic material. The cellulosic material is subjected to a pretreatment process. The cellulosic material is subjected to an atmospheric-pressure plasma. The cellulosic material is subjected to a degradation process. Subjecting the cellulosic material to at least one of the pretreatment process and the degradation process includes operating a plasma flame to synthesize nitrogen dioxide and exposing the cellulosic material to the nitrogen dioxide, forming nitric acid within the cellulosic material by reacting the nitrogen dioxide with hydrogen species supplied by a gas or by the cellulosic material (i.e. part of the cellulosic material itself or the water inherently contained within its structure), and degrading the cellulosic material by exposing the cellulosic material to the nitric acid.

[063] According to another implementation, a method is provided for treating a cellulosic material. A plasma flame is operated to produce nitrogen dioxide, the nitrogen dioxide is liquefied or solidified, and the cellulosic material is exposed to the liquefied or solidified nitrogen dioxide.

[064] According to another implementation, a method is provided for treating a cellulosic material. A plasma flame is operated to produce nitrogen dioxide. Water is reacted with the nitrogen dioxide to produce nitric acid. The nitric acid is liquefied. The cellulosic material is exposed to the liquefied nitric acid.

[065] Other devices, apparatus, systems, methods, features and advantages of the invention will be or will become apparent to one with skill in the art upon examination of the following figures and detailed description. It is intended that all such additional systems, methods, features and advantages be included within this description, be within the scope of the invention, and be protected by the accompanying claims.

BRIEF DESCRIPTION OF THE FIGURES

[066] The invention can be better understood by referring to the following figures. The components in the figures are not necessarily to scale, emphasis instead being placed upon illustrating the principles of the invention. In the figures, like reference numerals designate corresponding parts throughout the different views.

[067] Figure 1 is a schematic diagram illustrating an example of an atmospheric-pressure (AP) plasma apparatus provided in accordance with one or more implementations taught in the present disclosure.

[068] Figure 2 is a plot of ignition and stabilized I-V characteristics for a plasma flame discharge according to one or more implementations taught in the present disclosure.

[069] Figure 3 is a plot of curves indicating absorbance of NO₂ as a function of wavelength, as the reaction time of air in a plasma flame discharge increases, according to one or more implementations taught in the present disclosure.

[070] Figure 4 is a plot of absorbance of NO₂ at 435.4 nm as a function of time for various electrode materials, according to one or more implementations taught in the present disclosure.

[071] Figure 5 is a plot indicating nitrogen dioxide concentration as a function of time for a gas mixing ratio of 1N:1O subjected to a plasma flame discharge and for different times at which the plasma flame discharge was turned off, according to one or more implementations taught in the present disclosure.

[072] Figure 6 is a plot indicating nitrogen dioxide concentration as a function of time for a gas mixing ratio of 1N:4O subjected to a plasma flame discharge and for different times at which the plasma flame discharge was turned off, according to one or more implementations taught in the present disclosure.

[073] Figure 7 is a plot indicating nitrogen dioxide concentration as a function of time for a gas mixing ratio of 4N:1O subjected to a plasma flame discharge and for different times at which the plasma flame discharge was turned off, according to one or more implementations taught in the present disclosure.

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[074] Figure 8 is a plot of absorbance as a function of time for plasma flame discharge-synthesized nitrogen dioxide, according to one or more implementations taught in the present disclosure.

[075] Figure 9 is a plot of curves indicating the temperature of a background gas in an AP plasma reactor as a function of time for different plasma “on” times, according to one or more implementations taught in the present disclosure.

[076] Figure 10 is a plot of curves indicating nitrogen dioxide concentration as a function of time for a plasma “on” time of 10 minutes, and background gas temperature as a function of time, according to one or more implementations taught in the present disclosure.

[077] Figure 11 is a plot of curves indicating intensity as a function of wavelength for an O₂ emission band, according to one or more implementations taught in the present disclosure.

[078] Figure 12 is a plot of curves indicating intensity as a function of wavelength for an atomic O emission band, according to one or more implementations taught in the present disclosure.

[079] Figure 13 is a plot of curves indicating reaction rates as a function of reactant temperature for various reactions that may be initiated by the plasma flame discharge according to one or more implementations taught in the present disclosure.

[080] Figure 14 is a plot of partial pressures of various species as a function of time, including syngas synthesized by plasma flame discharge, according to one or more implementations taught in the present disclosure.

[081] Figure 15 is a flow diagram illustrating an example of a method for synthesizing a chemistry by plasma flame discharge according to one or more implementations taught in the present disclosure.

[082] Figure 16 is a flow diagram illustrating an example of another method for synthesizing a chemistry by plasma flame discharge according to one or more implementations taught in the present disclosure.

[083] Figure 17 is a flow diagram illustrating an example of a method for treating cellulosic material according to one or more implementations taught in the present disclosure.

[084] Figure 18 is a flow diagram illustrating an example of another method for treating cellulosic material according to one or more other implementations taught in the present disclosure.

[085] Figure 19 is a flow diagram illustrating an example of another method for treating cellulosic material according to one or more other implementations taught in the present disclosure.

[086] Figure 20 is a flow diagram illustrating an example of another method for treating cellulosic material according to one or more other implementations taught in the present disclosure.

[087] Figure 21 is a schematic diagram illustrating another example of an AP plasma apparatus provided in accordance with one or more implementations taught in the present disclosure.

[088] Figure 22 is a schematic diagram illustrating another example of an AP plasma apparatus provided in accordance with one or more implementations taught in the present disclosure.

DETAILED DESCRIPTION

[089] For convenience, the term “air” is intended to encompass not only ambient air but also a mixture including O₂ and N₂ in any ratio suitable or desired for a particular implementation of the presently disclosed subject matter. Additional gases may also be included in the air or mixture for such purposes as cooling, material transport or flow, conducting a particular type of synthesis, dilution, modification of pH, modification of polarity or volatility, etc. Additional gases may include, for example, noble or inert gases, reactive gases, water vapor, etc.

[090] As used herein, the “atmospheric” or “ambient” is intended to take into account the fact that atmospheric pressure varies according to geographic location and ambient temperature, and thus is not restricted to conditions occurring precisely at sea level. Moreover, the term “atmospheric pressure” is not limited to the exact value of 760 Torr but may range from, for example, about 10 to about 1000 Torr. Accordingly, as used herein, the term “atmospheric” encompasses the term “near atmospheric.”

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[091] For convenience, the term “AC signal” (or “AC current,” “AC voltage,” “AC power,” etc.) is intended to also encompass a pulsed DC signal. Moreover, the term “AC” encompasses any suitable periodic waveform, including not only sinusoidal but also square, sawtooth, pulsed, and the like. Devices, circuitry, hardware and/or software utilized to generate AC and pulsed DC power, with various waveform configurations, are readily known to persons skilled in the art.

[092] As used herein, the term “chemistry” refers to one or more chemical compounds, or one or more types of chemical compounds, depending on the particular synthesis contemplated. As an example, “chemistry” may refer to nitrogen dioxide, i.e., one or more molecules of NO₂. As another example, “chemistry” may refer to syngas, i.e., a mixture of one or more molecules of H₂ and one or more molecules of CO.

[093] According to implementations of the invention, described by way of example in the present disclosure, AP plasma is employed in direct, non-catalytic processes for the production of various chemistries that may be utilized in a wide variety of applications and/or as basic chemical building blocks in the synthesis of other high-value chemistries. As noted above, the synthesis of such chemistries conventionally require complex process steps that utilize high energy inputs, high temperatures, high pressures and expensive catalysts. By contrast, according to implementations taught herein, such chemistries may now be synthesized by techniques entailing the application of AP plasma in a manner that simplifies and reduces the cost of synthesis. AP plasma-driven synthesis as taught herein occurs at low (atmospheric) pressure, without the use of catalysts, through the use of a unique type of plasma flame discharge. Most discharges are characterized as being either completely thermal or completely non-thermal. Discharges which do contain both thermal and non-thermal components have temporal and spatial variations such that the thermal and non-thermal regions do not exist simultaneously. The plasma flame discharge disclosed herein is unique in that, during stable operation, this plasma flame discharge simultaneously and continuously exhibits two distinct regions or zones: a core sustained at thermal equilibrium and a non-thermal, non-equilibrium region. Atomic species and other active species form within the thermal region and react to form new compounds as they diffuse outward into cooler regions. By utilizing this AP plasma to directly

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synthesize various important chemistries, a significant impact will be made on industries in which well-established cost- and energy-intensive processes are ubiquitous.

[094] According to some implementations, ambient (or atmospheric) air (or, as noted above, a mixture of oxygen and nitrogen in controlled concentrations) is utilized as the reaction gas in an AP plasma reactor apparatus. The ambient air is subjected to the novel “plasma flame” discharge generated in the reactor. In comparison to plasmas known in the art, the plasma flame discharge taught herein is unique in the atmospheric plasma domain due to its mode of operation and the resultant products when using air as the reaction gas.

[095] Industrial plasmas typically fall into two categories, thermal and non-thermal (alternatively, equilibrium and non-equilibrium). Two hallmarks of thermal plasmas are the massive amounts of current (tens or hundreds of amps) and power (kilowatts to tens of kilowatts) utilized to sustain the discharge. Thermal plasmas, as the name implies, are extremely hot and are utilized, for example, in welding applications. Since most of the energy in these discharges is converted to heat, little in the way of chemical activity can be seen. Non-thermal plasmas on the other hand, have some chemical reactivity. This results from the use of low current (milliamps) and power levels (tens to hundreds of watts) such that very little energy is converted to heat; rather, the electrons become energized and contribute to activation of heavy species within the discharge (i.e. ionic and neutral gas species). Despite their reactivity, these active species in conventional plasmas do not have the energy to support high-energy reactions important in many industrial applications (e.g. formation of ammonia, syngas and nitrogen dioxide).

[096] On the other hand, the plasma flame discharge disclosed herein is novel in that, unlike thermal discharges, it is driven using low power and current; and, in contrast to non-thermal discharges which use low power and low current, the plasma flame discharge is highly energetic and highly reactive. The temperature of the plasma flame discharge is high enough to produce high energy active species in large quantities (to an extent which is not feasible in purely non-thermal discharges), but low enough to avoid complete thermalization of the discharge. This is accomplished by simultaneously sustaining a thermal core and a non-equilibrium region. The plasma flame discharge is ignited by applying AC (or, as noted above, pulsed DC) power to two bare metallic electrodes provided in the reactor chamber that are

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separated by a gas gap. The electrical current associated with this plasma flame discharge is on the order of hundreds of milliamps (as one example, 0.1 A or thereabouts) as opposed to tens or hundreds of amps. Also, the voltage is significantly higher than many thermal plasmas (as one example, 1000 V or thereabouts). The plasma flame discharge is very energetic, with a core gas temperature of approximately 3000K as determined from OH rotational band emission. These are surprising characteristics as most types of artificially produced plasmas at this energy level require an input power on the order of kilowatts. The plasma flame discharge taught herein, however, only requires an input power of, as one example, 100 W or thereabouts. The plasma flame is quiescent and uniform with no electrical instabilities.

[097] Given the intense nature of the plasma at a meager 100W and the fact that the phase angle between the current and voltage waveforms is 5.5° or less according to some experiments, it is believed that the power supply couples strongly to this discharge configuration. This coupling or impedance matching facilitates near-complete power transfer from the power supply to the discharge. The frequency of the AC signal applied to ignite the plasma flame may range, for example, from about 120 to about 160 kHz. A frequency of about 158 kHz has been found particularly effective for generating the quiescent plasma flame from which chemistries such as nitrogen dioxide may be synthesized. It will be noted, however, that the operating parameters needed for coupling or impedance matching may depend on the particular electronics utilized for operating the plasma reactor, and thus no limitation is placed on such operating parameters as regards the broad aspects of the invention.

[098] In some implementations, a pulsed DC signal may be substituted for a true AC signal, and thus the signal applied to the electrode(s) may be characterized generally as a periodic signal. In various implementations, the periodic signal is applied at a power ranging from about 20 to 500 W, at a current ranging from about 0.025 to 0.5 A, and at a voltage ranging from about 600 to 6000 V. In another example, the periodic signal is applied at a power ranging from about 50 to 150 W. An AC signal may also be cycled on or off to likewise alternate the plasma flame discharge between operating and extinguished stages.

[099] The thermal core of the plasma flame discharge produces highly energetic species which then migrate to the non-equilibrium region of the discharge. The types of energetic species specifically produced in thermal core depend on the gas or gases present in the reaction

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chamber. Additional energetic species may be produced in the non-equilibrium region, which may depend also on the composition of any background gas present outside the discharge as well as the composition of any precursor gas that may be added to the reaction chamber to synthesize a desired compound. Compounds may be synthesized directly in the highly reactive non-equilibrium region, but also may be synthesized outside of the discharge, or both. The region of the reaction chamber outside of the discharge in many implementations is much cooler than the discharge itself. Controlling the ratio between the plasma temperature and the ambient gas temperature directs pertinent reactions toward formation of a desired intermediate or final product.

[0100] As noted elsewhere in the present disclosure, the synthesis of a desired chemistry may depend strongly on the temperature conditions within the reaction chamber. Hence, in various implementations of the presently disclosed subject matter, the temperature of the plasma flame discharge and the region of the reaction chamber outside of the discharge may be controlled as desired. The temperature of the plasma flame discharge may be controlled, for example, by controlling the temperature of the gas provided to the electrodes for striking the plasma flame, by controlling the operating parameters of the periodic signal applied to the electrodes (e.g., current, voltage, frequency, etc.) and/or by controlling the plasma density (i.e. controlling the number of electrons and ions in a given volume). The temperature of the plasma flame discharge may be controlled through selection of the material comprising the electrodes, and/or by externally heating the electrodes. The temperature of the region of the reaction chamber outside of the discharge may be controlled by, for example, heating the reaction chamber by any suitable means (e.g., resistive or inductive heater, circulation of a fluidic heat transfer medium, etc.), heating a gas that is flowed into the chamber separately from the gas utilized to ignite the discharge (for example, a precursor gas introduced to provide one or more desired reactants).

[0101] Control of the plasma flame discharge may include control of the temperature gradient between the thermal core and the non-equilibrium region. Control of the plasma flame discharge may also include control of the volumetric ratio of the plasma flame, which is defined in the present disclosure as the ratio of the volume of the thermal core to the volume of the non-equilibrium region. In various implementations, the volumetric ratio of the plasma flame may

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range from 1:3 to 1:100. The volumetric ratio of the plasma flame may be controlled by, for example, controlling the operating parameters of the periodic signal applied to the electrodes, and may also depend on the properties (e.g., composition, temperature, etc.) of the gas utilized to ignite the discharge. The volumetric ratio can also be controlled by changing the plasma density by any means known to those familiar in the art. This may include, for example, adding electrons or ions to the plasma (e.g. promoting thermionic emission from the electrodes) and/or changing the lifetime of electrons and ions in the plasma (e.g. supplying an external magnetic field which sustains the electrons and ions). The ratio of the volume of the plasma flame discharge to the volume of the interior of the reaction chamber may also be controlled by controlling the size (volume) of the discharge. In various implementations, the ratio of the volume of the plasma flame discharge to the volume of the interior of the reaction chamber may range from 1:10 to 1:10,000. The ratio of the volume of the plasma flame discharge to the volume of the interior of the reaction chamber may also be controlled by, for example, controlling the operating parameters of the periodic signal and may also depend on the properties of the gas utilized to ignite the discharge. Depending on the product being synthesized, one or more of the foregoing conditions may play a significant role in directing the desired reactions appropriately.

[0102] All or part of a desired synthesis reaction may occur in a second reaction chamber (or enclosure, compartment, etc.) or in more than one additional reaction chamber, separate from the first reaction chamber in which the plasma flame discharge is operated. The second reaction chamber may selectively communicate with the first reaction chamber by any suitable means such as, for example, baffles, valves, etc. As an example, the first reaction chamber may initially be fluidly isolated from the second reaction chamber while the discharge in the first reaction chamber is being maintained. After a period of time during which energetic species are produced by the discharge, an isolation or sealing device (e.g., baffle, valve, etc.) may then be opened to enable energetic species, and possibly products already synthesized in the first reaction chamber, to flow into the second reaction chamber. The second reaction chamber may provide a contained area that is held at a different temperature than the first reaction chamber to enable a desired synthesis reaction to proceed. Depending on the desired synthesis, one or more precursor materials may be provided in the second reaction chamber for reaction with

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intermediate components produced in the first reaction chamber. In some implementations, the second reaction chamber (or one or more additional reaction chambers) may also include electrodes for producing a plasma flame discharge of the type disclosed herein, or may be configured to produce different types of plasmas such as, for example, plasma arcs, corona discharges, microplasmas, dielectric barrier discharges, glow discharges, and gliding arcs. As a further alternative, the same reaction chamber may include more than one set of electrodes for igniting more than one plasma flame discharge. A flow of energetic species, gases, partially or wholly synthesized products, and the like, may be established from one discharge to another in this same chamber.

[0103] Figure 1 is a schematic illustration of an example of an AP plasma system or apparatus **100** according to one implementation. The AP plasma system **100** includes a reactor enclosure **102** that may include a lid or other means (not shown) for alternately opening and closing off the interior space of the enclosure **102**. In one specific example, the reactor enclosure **102** is a nearly cylindrical acrylic structure having a height of 45 cm, a diameter of 14 cm, and a wall thickness of 3 mm. Two bare metallic electrodes **104** and **106** extend into the interior space of the enclosure **102** in any parallel or non-parallel orientation that results in a gap **108** being defined between the respective distal tips of the electrodes **104** and **106**. In the specific example, each electrode **104** and **106** is cylindrical with a flat cross-section and the dimension of the gap **108** between the electrode tips is one inch. For simplicity, the components utilized to conduct gases into and out from the enclosure **102** are not shown. An AC high-voltage power supply **110** is coupled to one of the electrodes **104** and the other electrode **106** is coupled to a suitable ground **112**. In the specific example, the power supply **110** is manufactured by AP Solutions, Inc., Cary, NC, as model designation DBD-5000. This particular power supply **110** was operated at 1-1.2 kV, 50-80 mA, 158 kHz, and a phase angle of 8° or less in many of the experiments conducted in accordance with the present disclosure. In operation, the AP plasma system **100** generates the above-noted unique plasma flame discharge **114** that extends into a discharge zone **118** within the interior space of the enclosure **102**. As noted above, the plasma flame discharge **114** includes two distinct regions or zones: a thermal core **122** and a non-thermal, non-equilibrium region **124**.

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[0104] An implementation similar to that illustrated in Figure 1 was configured for experimental data acquisition. In such configuration, analytical instrumentation provided with the AP plasma system 100 included a high-voltage probe 132 communicating with the output side of the power supply 110 and the corresponding electrode 104, a current probe 134 communicating with the grounded electrode 106, and an oscilloscope 136 for monitoring the various electrical characteristics of the power input (e.g., voltage, current, frequency, etc.). In addition, the analytical instrumentation included an optical detection system utilized for measuring absorbance values of, and thereby identifying, gas-phase components synthesized in the plasma flame discharge 114 and the discharge zone 118 of the enclosure 102. Also in the specific example, the optical detection system included a 150-W fluorescent (halogen) light source 142 operated at its lowest power level to transmit incident light signals into the discharge zone 118 via a fiber-optic line 144 and 25-cm collimating lens 146, and a monochromator 152 receiving attenuated light signals from the discharge zone 118 via a fiber-optic line 154 and 0.55-cm collimating lens 156. The optical data were processed in a CPU 158 communicating with the monochromator 152. In a typical experiment, absorbance values as a function of wavelength (e.g., 400-700 nm) were taken at 30-second intervals and employing a 4-msec integration time, 100 averages, and a boxcar of 5.

[0105] According to some implementations, the AP plasma flame generated between the two electrodes is reacted with ambient air. The energy of the applied AP plasma flame enables the reformation of air into nitrogen dioxide. The presence of nitrogen dioxide is visually observable as a significant brown-colored gas emanating from the AP plasma flame.

[0106] In a unique aspect of the teachings, the plasma-driven synthesis of nitrogen dioxide from air is enhanced by first subjecting the air to the AP plasma flame and then turning off the AP plasma flame after a designated period of time. After the AP plasma flame is turned off, the reaction kinetics proceed predominantly in the direction of the desired synthesis for another designated period of time. In one example, the AP plasma flame is left "on" for about five minutes. After this 5-min period, the AP plasma flame is turned off and the reaction continues for another five minutes or so. In Figure 1, after the AP plasma flame is turned off, a region roughly corresponding to the region 114 depicting the active plasma flame discharge, and a portion of the discharge zone 118 in the vicinity of the region 114, becomes a post-discharge

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reaction zone. Air is reacted in this post-discharge reaction zone whereby the synthesis of nitrogen dioxide continues forward. The synthesis may also continue in regions outside of the post-discharge reaction zone into which activated and/or neutral gaseous species are dispersed, such as above or below the post-discharge reaction zone

[0107] More generally, the durations of time during which synthesis of a given chemistry occurs via the activated plasma flame discharge and the post-discharge reaction zone, respectively, may be greater or less than 5 minutes. The optimal time durations may vary for different chemistries. During the course of synthesizing any given chemistry, synthesis may occur over several cycles alternating between the active discharge and the post-discharge reaction zone.

[0108] In one example, the AP plasma flame is activated for 5 min utilizing a power input of 60-70 Watts in an enclosure volume of about 5.9 liters. The process produces 0.055 moles of nitrogen dioxide. This typically requires a high activation energy because of the large bond energies associated with N_2 and O_2 .

[0109] Significant NO_2 production can be obtained when reacting a static volume of air in the plasma, i.e., a batch process involving a single volume of air for a given period of time, as opposed to maintaining a continuous flow of air into the reaction chamber during operation of the plasma flame discharge and ensuing synthesis. In particular, it has been found that the formation of NO_2 may have a negative dependency on the flow rate of air. That is, in various experiments it has been found that introducing any flow rate through the vessel causes the residence time of the active species to be reduced to the point where no appreciable NO_2 is formed.

[0110] Figure 2 illustrates the current-voltage (I-V) characteristics of the AP plasma flame discharge during ignition and stabilization according to one experiment. The current curve is designated **202** and the voltage curve is designated **204**. The data were obtained by setting a 50-mA trigger on the digital oscilloscope in a 2-ns window. That is, a 50-mA current spike within a 2 ns window causes the oscilloscope to collect a single set of data over a given time frame. Based on the graph, the breakdown voltage of this discharge configuration is approximately 9 kV. In practice this value can be as low as 6 kV, and it is very dependent on the gap height. Concurrent with a 5A current spike, the voltage drops precipitously. The plasma then begins to

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stabilize and the voltage remains nearly constant as a function of input power at approximately 1.0-1.8 kV. The current varies as a function of input power and may range from 30-180 mA.

[0111] Figure 3 illustrates the optical absorption of the gas within the enclosure as a function of wavelength according to one experiment. Each set of data points was taken at 30-second intervals over the course of 10 minutes. It can be seen that as the reaction time is increased, a compound is produced that absorbs in the visible range. This compound is assumed to be NO₂, a corrosive brown gas, given that other potential reaction products (e.g. N₂, O₂, NO, N₂O₄, N₂O₅, N₂O, O, O₃, and other stable/metastable compounds) have no appreciable absorption in the visible range. It will be noted that the data in Figure 3 were obtained by operating the plasma reactor with steel electrodes. Experiments in which electrodes having other material compositions were found to yield spectrums equivalent to those shown in Figure 3.

[0112] Figure 4 illustrates the time dependence of NO₂ absorbance at λ_{max} (435.4 nm) for various electrode materials. All electrode materials follow the same general curve and are within experimental error ranges of one another. They are therefore governed by similar, if not equivalent, reaction rates.

[0113] Considering that the absorbance values are indicative of the concentration of nitrogen dioxide in the enclosure, Figure 4 is also illustrative of the rate of synthesis of nitrogen dioxide while the plasma discharge is turned on and while the plasma discharge is turned off. From 0 to about 3 min the absorption increases at a rate of about 0.2 AU/min, at which point the rate decreases by about 40% from about 3 to 4.5 min. At 4.5 min, the plasma discharge is turned off and the absorbance is measured for another 5 minutes. Following the point at which the plasma is turned off, the absorbance increases at a rate of 0.55 AU/min until a saturation point is reached around 5.5-6 min. It can be seen that after the plasma flame is turned off, the reaction proceeds rapidly and preferentially in the desired direction.

[0114] Figures 5-7 show that the reaction kinetics entailing the synthesis of nitrogen dioxide, as discussed above in conjunction with Figure 4, follow similar curves at different plasma off times and different nitrogen/oxygen ratios. In particular, in each case the rate of synthesis jumps immediately following the turning off of the plasma.

[0115] Figure 5 illustrates the concentration of as-synthesized nitrogen dioxide as a function of time. In the experiments shown in Figure 5, the input gas had a nitrogen/oxygen ratio of 1:1

and the plasma was turned off at different times: 30 sec (curve 502), 1 min (curve 504), 2 min (curve 506), 5 min (curve 508), and 10 min (curve 510).

[0116] Figure 6 illustrates the concentration of as-synthesized nitrogen dioxide as a function of time. In the experiments shown in Figure 6, the input gas had a nitrogen/oxygen ratio of 1:4 and the plasma was turned off at different times: 30 sec (curve 602), 1 min (curve 604), 2 min (curve 606), 5 min (curve 608), and 10 min (curve 610).

[0117] Figure 7 illustrates the concentration of as-synthesized nitrogen dioxide as a function of time. In the experiments shown in Figure 7, the input gas had a nitrogen/oxygen ratio of 4:1 and the plasma was turned off at different times: 30 sec (curve 702), 1 min (curve 704), 2 min (curve 706), 5 min (curve 708), and 10 min (curve 710).

[0118] Figure 8 illustrates absorbance of NO₂ at 435 nm as a function of time similar to Figures 5-7. A plasma flame as described above was utilized to synthesize nitrogen dioxide in a quartz enclosure. The plasma flame was turned off at 120 seconds. The absorbance curve, obtained from 5-second data acquisition intervals, is similar to those illustrated in Figures 5-7.

[0119] Figure 9 includes plots of the temperature of the background (or "ambient") gas (i.e., not the gas in the plasma) as a function of time for different plasma "on" times. The information provided in Figure 9 may be correlated with nitrogen dioxide concentration vs. time plots such as Figures 5-7 to demonstrate the relationship between temperature and nitrogen dioxide synthesis.

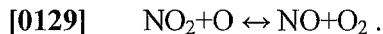
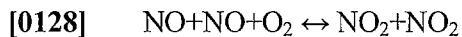
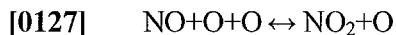
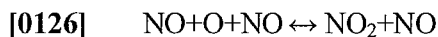
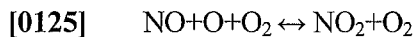
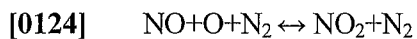
[0120] Figure 10 includes a plot of nitrogen dioxide concentration as a function of time for a plasma turn-off time of 10 minutes, along with a plot of background gas temperature as a function of time for the same experiment. Figure 10 further demonstrates the relationship between temperature and nitrogen dioxide synthesis.

[0121] Figures 11 and 12 show examples of species activated in the plasma flame discharge and available for synthesis of a desired product such as nitrogen dioxide. Specifically, Figure 11 plots the intensity (in arbitrary units) as a function of wavelength (in nm) for an O₂ emission band at different N:O ratios. Likewise, Figure 12 plots the intensity (in arbitrary units) as a function of wavelength (in nm) for an atomic O emission band at different N:O ratios. A spectrometer was utilized to take these measurements, which are representative of active O₂ and O in the plasma region, respectively.

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[0122] Figure 13 includes plots of reaction rates as a function of reactant temperature for various reactions that may be initiated by the plasma flame discharge. This is based on theoretical kinetic calculations for these reactions. Figure 13 demonstrates how active species are formed in the thermal core of the plasma flame discharge. Once the active species cool off outside the plasma flame discharge, they form nitrogen dioxide.

[0123] An explanation for the increase in NO₂ once the plasma flame is extinguished may be found by analyzing theoretical kinetic parameters provided by Lu, X., *J. Applied Physics*, Vol. 102, 033302 (2007). Formation and destruction of NO₂ in an air plasma follows from various reactions involving NO, O, O₂, and N₂ as follows:



[0130] Most of these reactions kinetically favor the formation of NO₂, with the exception of the last-listed reaction. As a result, the reactions generating NO₂ are rate limited for approximately 2-5 min, until the fraction of available O₂ is exhausted. A stable equilibrium is found at this point, in which atomic oxygen bonds to and dissociates from NO. This may explain why different plasma reaction times (i.e., time during with plasma is on until subsequently turned off) reach an equivalent concurrent discharge concentration of NO₂. Once the plasma is turned off the source for O formation is removed. As a result, the fraction of O remaining in the post-discharge reaction zone is consumed by reactions that continue form NO₂ until no O remains.

[0131] In addition to reaction kinetics, the increase in production of NO₂ may also be explained by the significant role of temperature as demonstrated by experiments described above. Within the plasma flame discharge itself, a temperature gradient exists such that the highest temperatures are found in the core and the lowest temperatures are found at the interface between the discharge and the ambient gas. This discharge, then, simultaneously stabilizes both thermal and non-thermal regimes. As a result, extremely energetic, and often atomic, species are created within the thermal plasma region (i.e., the "core"). As these species migrate toward the

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outer portion of the discharge, they first interact with cooler active species residing in the non-thermal region and finally with cold species located outside the plasma region. It has been found that in the different regions of the discharge, temperature is a significant factor in determining the dominant reaction pathways for a particular reaction. For example, in the air plasmas described above, atomic N, atomic O, and NO are generated in the thermal core of the plasma flame discharge. Once the N, O, and NO interact with the cooler gas surrounding the thermal core, they quickly form NO₂. Once the discharge is turned off, the gas in the post-discharge reaction zone cools rapidly and the remaining active species are either quenched or react to form NO₂.

[0132] As further disclosed herein, nitrogen dioxide produced according to the present disclosure may be utilized to produce various other chemistries, as well as to treat biomass. As yet another example, the nitrogen dioxide may be utilized for etching materials such as metals as is needed in the fabrication of microelectronics and other fields of microfabrication. The above-described processes may also be utilized to produce excited states useful for catalytic reactions, a few non-limiting examples being CH₃^{*} and NO_x.

[0133] According to another implementation, the nitrogen dioxide produced as described by way of example above may then be utilized to produce, for example, nitric acid (HNO₃). For instance, 0.055 mol nitrogen dioxide may be employed to produce 0.055 mol nitric acid. As an example, the AP plasma process may be carried out to replace the first two oxidation stages of the Ostwald process described earlier in this disclosure. In lieu of the foregoing two stages, the AP plasma process produces the nitrogen dioxide directly and non-catalytically from ambient air. The nitrogen dioxide output from the AP plasma process is then easily synthesized to nitric acid by carrying out reaction with water, or water and air, also described earlier.

[0134] According to another implementation, the AP plasma flame as described above is utilized to produce syngas. The system described above and illustrated in Figure 1 was modified to enable methane to be bubbled through water. The resulting gases are flowed through the reactor enclosure and encounter the plasma flame generated between the two electrodes.

[0135] Figure 14 illustrates the acquisition of partial pressure data as a function of time (minutes) resulting from production of syngas as just described above. In Figure 14, the process proceeds from right to left. The data were acquired by flowing the product gases from the

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enclosure to a residual gas analyzer (RGA), which in this case was a mass spectrometer. The legend in the upper right area of Figure 14 identifies the various species for which partial pressure was measured by atomic number, including carbon monoxide ($z = 28$) and diatomic hydrogen gas ($z = 2$). The production of syngas resulting from the applied AP plasma flame can be observed by the increase in partial pressures of carbon monoxide and diatomic hydrogen gas after the plasma was turned on, at a frequency of 158 kHz.

[0136] According to additional implementations, it is anticipated that the processes utilizing the above-described AP plasma flame may be extended to the production of ammonia (NH_3) by the direct reaction of $\text{N}_2 + \text{H}_2$, or N_2 with some other hydrogen source, without requiring catalysts; the production of methanol (CH_3OH) by the reaction of $\text{CH}_4 + \text{CO}_2$ without requiring catalysts; the production of chlorine dioxide (ClO_2) by reacting chlorine and oxygen species excited by the plasma flame, the production of biofuels by atmospheric plasma processing of fats and glycerin; and the synthesis of carbon nanotubes using methane (CH_4). Ammonia may be produced, for example, by flowing a hydrogen source toward the plasma flame discharge to produce hydrogen, and by flowing a nitrogen source into the reaction chamber. Nitrogen species and hydrogen species energized by the discharge may then be combined to synthesize ammonia. Methanol may be synthesized by energized carbon, oxygen and hydrogen species. Ammonia and nitric acid produced according to the present disclosure may be combined to form ammonium nitrate (NH_4NO_3). Either or both of the ammonia and nitric acid may be provided through synthesis driven by the plasma flame.

[0137] Figure 15 is a flow diagram 1500 illustrating an example of a method for synthesizing a chemistry. The flow diagram 1500 may also represent an apparatus or system capable of performing the illustrated method. The method begins at the starting point 1502. At block 1504, a plasma flame as described above is generated in an AP environment. At block 1506, one or more components of a gas or gases of appropriate composition are reacted with each other in the reaction chamber, as for example air in the case of nitrogen dioxide as described above, or are reacted with other components added to or entrained in the gas or gases as for example in the case of syngas, methanol, etc. as described above. If desired (block 1508), post-synthesis processing may be performed at block 1510. For example, the chemistry synthesized at block 1506 may serve as an intermediate product that is then utilized to

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synthesize another chemistry. Examples are described above, such as utilizing nitrogen dioxide to produce nitric acid, utilizing syngas to produce ammonia or methanol, etc. The method ends at the ending point **1512**.

[0138] Figure 16 is a flow diagram **1600** illustrating another example of a method for synthesizing a chemistry. The flow diagram **1600** may also represent an apparatus or system capable of performing the illustrated method. The method begins at the starting point **1602**. At block **1604**, a plasma flame as described above is generated in an AP environment. At block **1606**, the plasma flame is utilized to synthesize a desired chemistry. At block **1608**, the plasma flame is turned off after a desired period of time to generate a post-discharge reaction zone as described above. At block **1610**, synthesis of the chemistry continues in the post-discharge reaction zone. As indicated at decision block **1612**, the plasma flame may be cycled on and off in desired time intervals to perform the synthesis in alternating environments of plasma flame discharge and post-discharge reaction zone. This cycling may facilitate the scaling up of the production yield of the chemistry being synthesized. For instance, after each iteration and prior to re-igniting the plasma flame, the chemistry synthesized in the last iteration may be routed from the reactor to a suitable collection designation. The method ends at the ending point **1614**.

[0139] U.S. Patent App. Pub. No. 2008/0006536, assigned to the assignee of the present disclosure and incorporated herein by reference in its entirety, teaches techniques for processing cellulosic materials with AP plasma in the production of alcohols for use as biofuels or industrial applications. As noted previously, conventional acid treatments facilitate the hydrolysis of biomass for production of bioethanol, and most often involve the use of dilute sulfuric acid (H_2SO_4). These processes consume tons of acid, which then must be either disposed of or recycled for further use. While acid treatments are well established techniques, the acid itself must be produced off-site, which therefore incurs additional transportation and integration costs. According to another implementation of the present disclosure, the production of NO_2 via the plasma flame as described above may be utilized as a cost- and energy-efficient alternative to the delivery of acid for treatment of biomass. We find that exposing a biomass feedstock to an NO_2 -containing atmosphere generated by the plasma flame facilitates the degradation of the material into fermentable sugars. As such, according to the present teachings, this process may be carried out as a replacement to conventional acid treatments. Preliminary results indicate that

the corrosive gases are sorbed by the substrate, which then facilitate degradation of the biomass structure.

[0140] Additionally, while not wishing to be bound by any particular theory, it is postulated herein that the nitrogen dioxide along with activated plasma species penetrate the structure of the cellulosic feedstock. Hydrogen species, supplied from air in the reactor enclosure (e.g., water vapor) and/or from the cellulosic material itself (e.g., from the structure itself or the water inherent in the material), react with the nitrogen dioxide to form nitric acid that is immediately available for reaction with the structure of the cellulosic material. Accordingly, an aspect of implementations for treating cellulosic material is directed to a novel *in situ* acid hydrolysis technique, or “acid-on-demand” technique, that is initiated by the plasma flame as described above. These findings are significant, given the ease with which such a process can be implemented into current processes for bioethanol production, as well as the significant benefits of doing so. Specifically, continuous treatment is easily established and the need for off-site production of acid is eliminated.

[0141] According to implementations of the invention, described by way of example in the present disclosure, cellulosic material or other biomass is treated by atmospheric-pressure (AP) plasma. In some implementations, the treatment by AP plasma is employed as a substitute for conventionally known degradation or depolymerization processes such as acid hydrolysis and enzymatic hydrolysis. That is, the treatment by AP plasma is in some implementations sufficient to activate, expose, and/or even release or produce fermentable sugars from the cellulosic material. In other implementations, the treatment by atmospheric plasma is utilized to improve or enhance other processes for converting the cellulosic material to sugars (e.g., hydrolysis), including processes for converting the cellulosic material to fermentable sugars followed by converting the sugars to alcohols as well as other industrial chemicals. As compared to conventional hydrolytic techniques, AP plasma treatment is less harsh or rigorous in terms of its effects on cellulosic material and the process conditions required. Accordingly, the AP plasma treatment of cellulosic materials may be characterized as a “soft” degradation technique (e.g., soft depolymerization, soft hydrolysis, etc.). The treatment by AP plasma renders the cellulosic material more susceptible or accessible to methods for breaking down the cellulosic material into constituent sugars—such as glucose in the case of cellulose, and xylose

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and/or other pentoses in the case of most hemicelluloses—such methods including chemical hydrolysis and enzymatic hydrolysis. Moreover, the treatment by AP plasma renders fermentation techniques for producing chemicals of interest (e.g., ethanol) more effective, including techniques entailing co-fermentation of more than one type of sugar and techniques entailing simultaneous depolymerization and fermentation. Accordingly, the treatment by AP plasma facilitates not only the extraction of sugars but also the conversion of the hydrolyzate sugars into ethanol and/or other alcohols and chemicals of interest. As such, the treatment by AP plasma is a low-cost, low-energy (e.g., low-temperature, low electrical demand) alternative to conventional treatments. Moreover, in at least some implementations, AP plasma treatment enables the conversion of cellulosic material to sugars or further to alcohols or other chemicals to be performed as a continuous process.

[0142] In still other implementations, as described above, the AP plasma treatment may be configured to initiate a new technique of acid hydrolysis via *in situ* synthesis of nitric acid. The technique is also characterized herein as acid-on-demand.

[0143] The structure and composition of typical cellulosic materials was briefly summarized earlier in this disclosure and is described in more detail in readily available literature. Without wishing to be bound by any particular theory, it is believed that the application of AP plasma in accordance with the invention degrades the coating (e.g., lignin) protecting the cellulose and opens up the cellulose-hemicellulose-lignin complex by enlarging spatial features existing in the complex and/or creating new spatial features, thereby creating greater access to internal structures of value, i.e., saccharide components. It is also believed that the AP plasma treatment prevents further interference from secondary protective coatings such as lignin and other binders in biomass material. Additionally, or alternatively, it is believed that the AP plasma disrupts at least some of the bonds or linkages existing within the complex, including bonds between the cellulose, hemicellulose and lignin (e.g., delignification) and/or at least some of the bonds or linkages existing within one or more individual components of the cellulose, hemicellulose and lignin. As a result, the treatment by AP plasma renders the cellulose component of the cellulosic material more amenable to hydrolytic cleavage or other types of depolymerization and, more generally, increases both the chemical and biochemical reactivity of the cellulose. The AP plasma-treated cellulosic material provides greater surface area available for hydrolyzing,

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solubilizing and fermenting activity, and greater access and contact with hydrolyzing, solubilizing and fermenting agents, thereby improving the efficiency of yield as well as the effectiveness and rates of reaction.

[0144] In addition, as described above, an AP plasma flame may be configured to synthesize nitrogen dioxide, which subsequently is combined with hydrogen species to synthesize nitric acid directly at reaction sites within the structural matrix of the cellulosic material. The nitric acid may contribute to a form of acid hydrolysis that breaks down bonds or linkages within the cellulosic structure. In some implementations, nitrogen dioxide or nitric acid synthesized with the use of the AP plasma flame as described above, may then be liquefied by cooling and/or compression. Cellulosic material or other biomass may be treated by exposing the cellulosic material to the liquefied nitrogen dioxide or nitric acid such as by, for example, dipping the cellulosic material in a container of liquefied nitrogen dioxide or nitric acid, placing the cellulosic material in a container with liquefied nitrogen dioxide or nitric acid and allowing the nitrogen dioxide or nitric acid to migrate into the cellulosic material via liquefaction, evaporation, diffusion, capillary action, etc.

[0145] Figures 17 – 20 illustrate examples of methods for treating cellulosic material. In some implementations, such methods may be practiced for at least partially converting the cellulosic materials into sugars. In other implementations, such methods may be practiced for at least partially converting the sugars into alcohols, such as ethanol, or other desired chemicals.

[0146] Figure 17 is a flow diagram 1700 illustrating an example of a method for treating cellulosic material. Depending on the cellulosic material being processed and the process conditions, the treatment of the cellulosic material by AP plasma according to the method may, in and of itself, result in degradation of at least some of the biopolymeric components of the cellulosic material such that monomeric sugars are released (or oligomeric compounds readily convertible to monomeric sugars). In such implementations, the AP plasma treatment may be performed in conjunction with enzymatic treatment for producing alcohols or other desired chemicals, or may be directly followed by such enzymatic treatment. In other implementations, the AP plasma treatment at least may result in conditioning the cellulosic material in a manner that optimizes or facilitates a subsequent degradation process such as, for example, hydrolysis. In some implementations, the hydrolysis may be acid hydrolysis utilizing locally synthesized

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nitric acid via operation of a plasma flame in air as described above. The flow diagram **1700** may also represent an apparatus or system capable of performing the illustrated method.

[0147] The method begins at starting point **1702**. In implementations where the cellulosic material is initially provided as a raw feedstock, the starting point **1702** may be representative of any suitable preliminary steps that may be taken to prepare the cellulosic material for treatment by AP plasma. For instance, if the cellulosic material is initially provided in the form of large pieces of wood, the wood may be further comminuted into wood chips or sawdust. As another example, the cellulosic material may be washed to remove dirt or other undesired substances. As another example, the cellulosic material may be dried by any suitable means to remove moisture if desired. The cellulosic material **1704** (raw feedstock, or feedstock prepared such as by the afore-mentioned preliminary steps) is introduced to an apparatus for generating an AP plasma (AP plasma apparatus). The AP plasma apparatus may be adapted for either batch processing or continuous processing, and therefore the term “introduced” is used to indicate any manner by which the cellulosic material **1704** is exposed to the AP plasma such as, for example, loading or feeding the cellulosic material **1704** into the AP plasma, apparatus directing an AP plasma plume or jet toward the cellulosic material, etc. At block **1706**, the AP plasma apparatus is operated to generate and maintain a suitable AP plasma, thereby subjecting the cellulosic material **1704** to the AP plasma.

[0148] Examples of AP plasma apparatus or systems are described above with reference to Figure 1, and in above-cited U.S. Patent App. Pub. No. 2008/0006536. In implementations entailing the synthesis of nitrogen dioxide, the plasma flame discharge generated by the apparatus illustrated in Figure 1 of the present disclosure may be utilized in accordance with the operating parameters described in conjunction with Figure 1. The same apparatus may also be utilized to generate plasma discharges for use in AP plasma treatment steps that do not entail the synthesis of nitrogen dioxide. The same plasma flame may be utilized for these non-synthesis steps, or alternatively the apparatus may be configured to generate the above-described plasma discharge as well as other types of plasmas such as those described in U.S. Pat. App. Pub. No. 2008/0006536. Alternatively, the apparatus utilized for generating acid locally in the cellulosic material may be separate from the apparatus utilized for treating the cellulosic material in accordance with the subject matter disclosed in U.S. Pat. App. Pub. No. 2008/0006536.

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[0149] In implementations entailing the use of an apparatus as described in U.S. Pat. App. Pub. No. 2008/0006536, generally the plasma may be an ionized gas stream or cloud generated in, for example, a radio frequency (RF), direct current (DC), pulsed DC, asymmetrical pulsed, or alternating current (AC) electromagnetic field, or by microwave energy. U.S. Pat. App. Pub. No. 2008/0006536 additionally describes examples of a parallel plate dielectric barrier discharge (DBD) apparatus, a drop-tube DBD apparatus, a fluidized-bed apparatus, a liquid-bath apparatus, and a plasma-jet apparatus. Generally, the input current for the generation of a suitable plasma may typically range from about 30 to about 300 mA, although the invention is not limited to this range. The voltage applied to the plasma may typically range from about 500 to about 50,000 V, although the invention is not limited to this range. The working frequency of the plasma may typically range from about 0.050 to about 150 kHz, although the invention is not limited to this range. The power density of the plasma may typically range from about 0.1 to about 500 W/cm³, although the invention is not limited to this range. Any suitable working gases for the AP plasma may be utilized. Examples of working gases include, but are not limited to, air, oxygen, hydrogen, helium, water-saturated helium, neon, argon, hydrogen, nitrogen, xenon, carbon dioxide, SF₆, CF₄, NH₃, and combinations of two or more of the foregoing. Flow rates may typically range from about 100 to about 50,000 standard cubic centimeters per minute (sccm), although the invention is not limited to this range. The particular species of the AP plasma that serve an active role in altering the structure or chemistry of the cellulosic material to attain the beneficial effects described herein will generally depend on the type of working gases employed. Examples of active species of the plasma may include, but are not limited to, oxygen radicals, hydroxide radicals, monatomic nitrogen, NO_x, and ozone. Other liquid or vapor precursors may also be added to the AP plasma environment. This may be for the generation of specific chemical species to be used as a reactant in the production of other desired chemistries, for the purpose of synthesizing such chemical species as the desired product, or both. Examples of such compounds are glycerol, industrial wastes, and hazardous materials, although the invention is not limited to these compounds. The temperature in the chamber of the apparatus containing the AP plasma may range from about 25 to about 700 °C, although the invention is not limited to this range. The duration of the AP plasma treatment may range from about 1 to about 30 minutes, although the invention is not limited to this range.

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[0150] Continuing with Figure 17, the treatment of the cellulosic material **1704** by AP plasma at block **1706** results in an AP plasma-treated cellulosic material **1708**. The plasma-treated cellulosic material **1708** may include oligosaccharide and/or monosaccharide species released from components of the cellulosic material (cellulose and/or hemicellulose) as a result of the AP plasma treatment **1706**, as well as residual polysaccharide species, lignin and other components of the cellulosic material not appreciably affected by the AP plasma treatment **1706**. As described previously, however, the AP plasma treatment may have the effect of removing lignin or at least disrupting the structure of lignin and its bonds so as to reduce interference of the lignin with the treatment of the cellulose. The released monosaccharide species may include hexose sugars such as, for example, glucose, galactose and/or mannose, and/or pentose sugars such as, for example, xylose and/or arabinose, and/or other monosaccharides.

[0151] At this stage, if desired, the sugars (particularly the monosaccharides) may be recovered and separated from the plasma-treated cellulosic material **1708** by any suitable means such as, for example, cyclone separation, centrifugation, decanting, filtration, washing, etc. If desired, the sugars may then be subjected to any suitable purification and/or refinement processes as necessary to provide commercial-grade sugars. In the case where sugars are the intended end product, the method ends at **1714**.

[0152] Generally, the sugars (particularly the monosaccharides) produced or released as a result of the AP plasma treatment **1706** are microbially fermentable and hence may be utilized as a fermentation medium to produce desired alcohols and/or any other desired chemicals or organic compounds such as various ketones and organic acids. Accordingly, in other implementations, as illustrated in Figure 17, the process may continue by subjecting AP plasma treatment-derived sugars to any suitable fermentation processing **1710** to produce a fermentation product **1712** that includes alcohols such as ethanol or other chemicals.

[0153] Generally, the fermentation process **1710** may entail the use of any microorganisms capable of converting the sugars (e.g., oligosaccharides, monosaccharides, and the like) into the desired alcohols or other chemicals. Generally, in the case of producing ethanol, any suitable ethanologenic strains of microorganisms may be employed. As appreciated by persons skilled in the art, more than one fermentation step may be required, depending on the desired chemical(s) to be produced (e.g., ethanol, xylitol, etc.), the type(s) of sugars to be fermented

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(e.g., glucose, xylose, etc.), and other factors. Moreover, different fermentation processes may be carried out in the same reaction vessel or in different reaction vessels. Furthermore, fermentation may be carried out as a batch process or as a continuous process. Still further, the fermentation of different types of components of the plasma-treated cellulosic material **1708** may be carried out sequentially or simultaneously.

[0154] It will be understood that the fermentation process **1710** may be preceded by any suitable pre-conditioning steps deemed necessary in preparation for fermentation, such as neutralization or other pH adjustment, removal of any components deemed to act as fermentation inhibitors, and the like. In addition, the fermentation product **1712** may be subjected to any suitable post-fermentation processes as needed, such as distillation and/or adsorption to separate the desired alcohols or other chemicals from the fermentation medium and concentrate and purify the alcohols or other chemicals for commercially-acceptable uses. In addition, residual materials such as lignin may be recovered for utilization as an energy source, as appreciated by persons skilled in the art. The method ends at **1714**.

[0155] As noted above, Figure 17 may also represent an example of an apparatus or system **1700** for treating cellulosic material. Accordingly, block **1706** may be considered as depicting a means for subjecting cellulosic material to AP plasma. An example of such means is a plasma-generating apparatus or system and associated components and materials required for its operation. Specific examples of plasma-generating apparatus or systems are described elsewhere in this disclosure and are illustrated in Figure 17 as well as in above-cited U.S. Patent App. Pub. No. 2008/0006536. Block **1710** may be considered as depicting a means for fermenting plasma-treated cellulosic material. An example of such means is one or more vessels, tanks or the like suitable for carrying out fermentation, as well as associated components and materials required for its operation, as appreciated by persons skilled in the art. The apparatus or system **1700** may be configured for continuous processing or batch processing, or partially for continuous processing and partially for batch processing. Accordingly, in the context of an apparatus or system **1700** for treating cellulosic material, one or more of the arrows shown in Figure 1 may represent physical components (e.g., pipes, conduits, containers, or the like) employed for holding the cellulosic material being processed or transporting the

cellulosic material from one location or device to another, or may otherwise represent the direction of process flow between locations or devices of the apparatus or system **1700**.

[0156] According to another implementation, the AP plasma treatment **1706** does not necessarily entail subjecting the cellulosic material the plasma itself. Instead, a plasma flame as described above may be utilized to synthesize nitrogen dioxide, and the cellulosic material is exposed to the nitrogen dioxide for treatment.

[0157] In yet another implementation, the AP plasma treatment **1706** includes both subjecting the cellulosic material to an atmospheric-pressure plasma and exposing the cellulosic material to nitrogen dioxide synthesized via a plasma flame. In this case, the atmospheric-pressure plasma to which the cellulosic material is subjected may be the plasma flame utilized to synthesize the nitrogen dioxide. Alternatively, the atmospheric-pressure plasma to which the cellulosic material is subjected may be a separate plasma distinct from the plasma flame utilized to synthesize the nitrogen dioxide. This separate plasma may be of the same type as the plasma flame or may be a different type of plasma. The separate plasma may be operated (i.e., ignited and maintained) in the same chamber as the plasma flame utilized to synthesize the nitrogen dioxide, or the separate plasma may be operated in a separate chamber.

[0158] Figure 18 is a flow diagram **1800** illustrating another example of a method for treating cellulosic material. The flow diagram **1800** may also represent an apparatus or system capable of performing the illustrated method.

[0159] The method begins at the starting point **1802**. As in the case of the method illustrated in Figure 17, the starting point **1802** may be representative of any suitable preliminary steps taken to prepare the cellulosic material for treatment by AP plasma. The raw or prepared cellulosic material **1804** is introduced to an AP plasma apparatus. At block **1806**, the AP plasma apparatus is operated to generate and maintain a suitable AP plasma that interacts with the cellulosic material **1804**. The process conditions (pressure, temperature, duration, etc.) of the AP plasma treatment **1806** may be the same as or similar to those described above for the method illustrated in Figure 17.

[0160] The treatment of the cellulosic material **1804** by AP plasma at block **1806** results in an AP plasma-treated cellulosic material **1808**. As described above, the plasma-treated cellulosic material **1808** may include oligosaccharide and/or monosaccharide species released

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from components of the cellulosic material (cellulose and/or hemicellulose) as a result of the AP plasma treatment **1806**, as well as residual polysaccharide species and lignin not affected by the AP plasma treatment **1806**. At this stage, if desired, the released sugars may be recovered and separated from the plasma-treated cellulosic material **1808** by any suitable means and then subjected to further processing as necessary to provide commercial-grade sugars. Alternatively, as indicated by the schematic process line **1810** in Figure 18, the released sugars may be recovered for subsequent fermentation.

[0161] The portion of the plasma-treated cellulosic material **1808** that has not been degraded by the AP plasma treatment step **1806** is nevertheless, as a result of the AP plasma treatment step **1806**, optimally conditioned for subsequent degradation processing. Accordingly, at block **1812**, the plasma-treated cellulosic material **1808** may then be subjected to any suitable cellulosic material degradation or depolymerization process. The degradation process **1812** may be any process suitable for yielding desired sugars such that the sugars may then be subsequently processed for commercial consumption or fermented for producing alcohols or other chemicals. Examples of suitable degradation processes **1812** include, but are not limited to, acid hydrolysis processes and enzymatic hydrolysis processes. Acid hydrolysis generally entails reacting the plasma-treated cellulosic material **1808** with water and employing a suitable acid or acidic compound as a catalyst. Examples of suitable acids and acidic or acid-like compounds include, but are not limited to, mineral acids such as sulfuric acid, sulfurous acid, hydrochloric acid, hydrofluoric acid, phosphoric acid, formic acid and nitric acid, and acidic salts such as aluminum sulfate, ferric sulfate, ferrous sulfate, magnesium sulfate, ferric chloride, aluminum chloride, aluminum nitrate, and ferric nitrate. More generally, a variety of organic and inorganic acids may be employed as appreciated by persons skilled in the art, but particularly toxic or corrosive acids should be avoided. Enzymatic hydrolysis generally entails reacting the plasma-treated cellulosic material **1808** with one or more appropriate carbohydrase enzymes such as various known cellulases and hemicellulases. For instance, a cellulase enzyme complex may be employed for the saccharification of the cellulose of the plasma-treated cellulosic material **1808** to yield glucose.

[0162] In some implementations, the degradation process **1812** entails reacting air in a plasma flame discharge to synthesize nitrogen dioxide. The nitrogen dioxide reacts with

hydrogen to synthesize nitric acid. Synthesis of the nitric acid occurs before and/or after the nitrogen dioxide penetrates the cellulosic material. As noted above, processes represented by **1806** and **1812** may be carried out in separate AP plasma reactors or in the same reactor. Moreover, as an alternative to the order shown in Figure 18, the process **1812** may be carried out prior to the process **1806**.

[0163] The degradation process **1812** results in (at least partially) degraded cellulosic material **1814**. The degraded (or degradation-processed) cellulosic material **1814** may include oligosaccharide and/or monosaccharide species released from components of the cellulosic material (cellulose and/or hemicellulose) as well as residual polysaccharide species and lignin not affected by the degradation process **1812**. Due to the preceding AP plasma treatment **1806**, the degradation process **1812** may result in a much higher yield of monosaccharides than had the degradation process **1812** been carried out alone without the AP plasma treatment **1806** or had the degradation process **1812** been preceded by a conventional pre-treatment process. At this stage, if desired, the released sugars may be recovered and separated from the degraded cellulosic material **1814** by any suitable means and then subjected to further processing as necessary to provide commercial-grade sugars. In the case where sugars are the intended end product, the method ends at **1820**.

[0164] In other implementations, as illustrated in Figure 18, the process may continue by subjecting the sugars obtained from the degraded cellulosic material **1814** to any suitable fermentation processing **1816** to produce a fermentation product **1818**. The fermentation product **1818** may include alcohols such as ethanol and/or other desired chemicals. The method ends at **1820**.

[0165] As noted above, Figure 18 may also represent an example of an apparatus or system **1800** for treating cellulosic material. Accordingly, block **1806** may be considered as depicting a means for subjecting cellulosic material to AP plasma. Examples of such means are referred to above in connection with the apparatus or system **1700** illustrated in Figure 17. Block **1812** may be considered as depicting a means for degrading cellulosic material to produce sugars. An example of such means is a plasma flame reactor as described and illustrated in Figure 1, or alternatively may be an apparatus configured for carrying out a conventional hydrolysis or other type of degradation technique. The apparatus utilized to carry out the functions of blocks **1806**

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and **1812** may be the same apparatus or two different reactors. Block **1816** may be considered as depicting a means for fermenting plasma-treated cellulosic material as previously noted.

[0166] Prior to fermentation, more than one iteration of AP treatment and/or degradation may be performed. For example, Figure 19 is a flow diagram **1900** illustrating another method for treating a cellulosic material. The flow diagram **1900** may also represent an apparatus or system capable of performing the illustrated method. This example entails a two-stage degradation process that is enhanced by one or more AP plasma treatment steps.

[0167] The method begins at the starting point **1902**. Raw or prepared cellulosic material **1904** is subjected to a first-stage degradation process at block **1906**, in which at least some of the components of the cellulosic material **1904** are degraded or depolymerized without the aid of AP plasma treatment. For example, the first-stage degradation process **1906** may entail dilute acid hydrolysis effected by localized synthesis of nitric acid as described above. The first-stage degradation process **1906** may serve as a relatively mild process that acts on certain polysaccharide components of the cellulosic material **1904** that, due to their initial structure (e.g., degree of crystallinity or amorphousness) or accessibility (e.g., exposure, freedom from lignin binding, etc.), are readily degradable without the aid of a pre-treatment step. Alternatively, or additionally, the first-stage degradation process **1906** may serve as a pre-treatment process in and of itself, for example to break down the hemicellulose for removal, and/or more generally to at least partially disrupt the cellulose-hemicellulose-lignin complex, in preparation for hydrolyzing or otherwise degrading the cellulose (and particularly the crystalline phase) in a subsequent degradation step.

[0168] The first-stage degradation process **1906** produces (at least partially) degraded cellulosic material **1908**, which may be a mixture of sugar solution and residual cellulosic material such as unreacted cellulose and lignin. At this stage, if desired, any suitable separation process may be performed to separate the sugar solution from the residual cellulosic material. The sugars obtained at this stage may be processed for commercial use or, as indicated by line **1910** in Figure 19, recovered for subsequent fermentation. At block **1912**, the cellulosic material is subjected to AP plasma treatment as described elsewhere in this disclosure. The process conditions (pressure, temperature, duration, etc.) of the AP plasma treatment **1912** may be the same as or similar to conditions described above.

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[0169] The plasma-treated cellulosic material **1914** may include oligosaccharide and/or monosaccharide species released from components of the cellulosic material (cellulose and/or hemicellulose) as a result of the AP plasma treatment **1912**, as well as residual polysaccharide species and lignin not affected by the AP plasma treatment **1912**. At this stage, if desired, the released sugars may be recovered and separated from the plasma-treated cellulosic material **1914** by any suitable means and then subjected to further processing as necessary to provide commercial-grade sugars. Alternatively, as indicated by the schematic process line **1916** in Figure 15, the released sugars may be recovered for subsequent fermentation.

[0170] The portion of the plasma-treated cellulosic material **1914** that has not yet been degraded at this stage is, as a result of the previous steps **1906** and **1912**, optimally conditioned for subsequent degradation processing. Accordingly, at block **1918**, the plasma-treated cellulosic material **1914** may then be subjected to a second-stage cellulose degradation or depolymerization process. To the extent that the cellulosic material undergoing the second-stage degradation **1918** was not degraded into sugars in the first-stage degradation process **1906** or AP plasma treatment process **1912** and hence is more difficult to degrade, the second-stage degradation process **1918** may be a more rigorous process in comparison to the first-stage degradation process **1906**. For example, the second-stage degradation process **1918** may entail a plasma flame-initiated localized synthesis of nitric acid under more rigorous conditions, or alternatively may entail a conventional acid hydrolysis process in which a high concentration of acid is employed such as in a 1.0M (9.8% w/w) H₂SO₄ solution. Alternatively, depending on the nature of the cellulosic material being processed, the effectiveness of the AP treatment process **1912** may be such that the second-stage degradation process **1918** need not be more rigorous, or may even be less rigorous, than the first-stage degradation process **1906**. As another example, the second-stage degradation process **1918** may be an enzymatic process that employs enzymes (e.g., cellulases) specifically selected to hydrolyze the more difficultly hydrolyzable components of the cellulosic material such as crystalline cellulose.

[0171] The processing of the plasma-treated cellulosic material **1914** by the second-stage degradation process **1918** yields further degradation-processed cellulosic material **1920** that includes sugars. At this stage, the sugars may be subjected to any post-degradation processes such as purification and refinement as necessary to provide commercial-grade sugar.

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Alternatively, at block **1922**, the process may continue by subjecting the sugars to any suitable fermentation process to produce alcohols or other desired chemicals. As noted previously, any sugars produced from the first-stage degradation process **1906** and the AP plasma treatment process **1912** may likewise be fermented. In some implementations, the sugars produced from the first-stage degradation process **1906** and/or the AP plasma treatment process **1912** may be combined with the sugars produced from the second-stage degradation process **1918**, and all sugars co-fermented simultaneously. The process illustrated in Figure 19 ends at **1924**.

[0172] Depending on the composition of the cellulosic material to be processed, one or more AP plasma treatment steps may be combined with one or more degradation processes, as well as with “pre-treatment” processes traditionally associated with conventional degradation processes such as acid hydrolysis and enzymatic hydrolysis. The pre-treatment process may be any chemical, biological, biochemical, physical, or physio-chemical process or processes now known or later developed that is effective in enhancing conventional degradation processes. Examples of pre-treatment processes include, but are not limited to, comminution, uncatalyzed steam explosion, hydrothermolysis, the addition of acids, bases, solvents, or ammonia, ammonia fiber/freeze explosion (AFEX), ammonia recycled percolation (ARP), etc. In some implementations, the pre-treatment process entails the use of a plasma flame discharge to directly supply nitric acid to the cellulosic material as described above.

[0173] An example of a process that combines pre-treatment with AP plasma treatment is illustrated in Figure 20, which is a flow diagram **2000** illustrating another method for treating a cellulosic material. The flow diagram **2000** may also represent an apparatus or system capable of performing the illustrated method. The method begins at the starting point **2002**. Raw or prepared cellulosic material **2004** is introduced to a suitable AP plasma apparatus and subjected to a first-stage AP plasma treatment at block **2006**, which yields plasma-treated cellulosic material **2008** as previously described. As also previously described, the plasma-treated cellulosic material **2008** may include sugars as a result of the AP plasma treatment **2006**, as well as residual polysaccharide species and lignin not affected by the AP plasma treatment **2006**. At this stage, if desired, the released sugars may be recovered and separated from the plasma-treated cellulosic material **2008** by any suitable means and then subjected to further processing as necessary to provide commercial-grade sugars. Alternatively, as indicated by the process

schematic line **2010** in Figure 20, the sugars resulting from the first-stage AP plasma treatment **2006** may be recovered for subsequent fermentation. At block **2012**, the plasma-treated cellulosic material **2008** is subjected to any suitable pre-treatment process to enhance a subsequent degradation technique or techniques. The pre-treatment process **2012** yields pre-treated cellulosic material **2014**.

[0174] In other implementations, as indicated by the process schematic line **2016**, raw or prepared cellulosic material **2004** is subjected directly to the pre-treatment process **2012** without an intervening AP plasma treatment **2006**.

[0175] The pre-treated cellulosic material **2014** is then subjected to a second-stage AP plasma treatment at block **2018**, which yields further plasma-treated cellulosic material **2020**. The second-stage AP plasma treatment **2018** may serve to enhance the role of the pre-treatment step **2012** (and the first-stage AP plasma treatment **2006**, if employed) in optimizing the cellulosic material for a subsequent degradation process or processes. On the other hand, the pre-treatment step **2012** may be considered as enhancing the role of the first-stage AP plasma treatment **2006** and/or the second-stage AP plasma treatment **2018** in optimizing the cellulosic material for subsequent degradation. Moreover, as in the case of the first-stage AP plasma treatment **2006**, the second-stage AP plasma treatment **2018** may yield sugars as a result of second-stage AP plasma treatment **2018**. At this stage, if desired, these sugars may be recovered and separated from the plasma-treated cellulosic material **2020** by any suitable means and then subjected to further processing as necessary to provide commercial-grade sugars. Alternatively, as indicated by the process schematic line **2022** in Figure 20, the sugars resulting from the second-stage AP plasma treatment **2018** may be recovered for subsequent fermentation.

[0176] After the second-stage AP plasma treatment **2018**, at block **2024**, the plasma-treated cellulosic material **2020** is subjected to any suitable degradation process such as, for example, acid hydrolysis or enzymatic hydrolysis to break down remaining polysaccharide components of the plasma-treated cellulosic material **2020** into sugars. Acid hydrolysis at this stage may be carried out by way of the *in situ* technique initiated by a plasma flame discharge as taught in the present disclosure. The degradation process **2024** yields a mixture **2026** of sugar solution and residual cellulosic material such as lignin.

[0177] In other implementations, as indicated by the process schematic line **2028**, the pre-treated cellulosic material **2014** is subjected directly to the degradation process **2024** without an intervening AP plasma treatment **2018**.

[0178] At this stage, any suitable separation process may be performed to separate the sugar solution from the residual cellulosic material. The sugars obtained at this stage may be processed for commercial use. Alternatively, as indicated at block **2030**, the resulting sugars may be subjected any suitable fermentation process to produce a fermentation product **2032** that includes alcohols or other desired chemicals. As noted previously, any sugars produced from the first-stage AP plasma treatment **2006** and/or the second-stage AP plasma treatment **2018** may likewise be fermented, together with or separately from the sugars derived from the degradation process **2024**. The process illustrated in Figure 20 ends at **2034**.

[0179] Any of the methods, apparatus and systems described by example above and illustrated by example in Figures 17 – 20, in implementations involving fermentation, may be adapted for separate hydrolysis and fermentation (SHF), simultaneous saccharification and fermentation (SSF), and/or simultaneous saccharification co-fermentation (SSCF).

[0180] The foregoing examples of methods for treating cellulosic materials are significant as they relate to the long felt need related to economic and ecological aspects of this invention. Fewer steps are required, and expensive acids, high temperatures, high pressures, and costly enzymes are bypassed by providing a direct pathway to the sugars through plasma-enhanced soft degradation as taught in the present disclosure.

[0181] Figure 21 is a schematic diagram illustrating an example of an atmospheric-pressure (AP) plasma apparatus **2100** adapted for continuous processing. The apparatus **2100** includes two or more distinct reaction zones **2102**, **2104**, **2106**, **2108**. At least one of these reaction zones **2102**, **2104**, **2106**, **2108** includes a set of electrodes **2114** and **2116** for generating a plasma flame discharge **2124** as described herein, and one or more inlets **2126** for supplying background gases for igniting the plasma flame discharge **2124** and/or precursor gases for driving a desired synthesis reaction. One or more of the additional reaction zones **2102**, **2104**, **2106**, **2108** may also include electrodes **2114** and **2124** for generating additional plasma flame discharges **2124**. One or more of the additional reaction zones **2102**, **2104**, **2106**, **2108** may also include inlets **2126** for supplying background gases and/or precursor gases. One or more of the reaction zones

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2102, 2104, 2106, 2108 may serve as post-discharge reaction zones into which active, metastable and/or neutral species from an active or recently active plasma area are conducted. The reaction zones **2102, 2104, 2106, 2108** may be stacked vertically to produce a resultant upward process flow of gases that are subjected to multiple plasma flame discharges **2124**, or alternatively may be arranged in series in another orientation such as horizontal. An exhaust line **2128** may be provided at or near the top of the apparatus **2100** for collection of synthesized gas-phase products. Another outlet line **2130** may be provided at a lower elevation to collect condensate products at a suitable receptacle **2132**. One or more of the reaction zones **2102, 2104, 2106, 2108** may be defined, at least in part, by tapered inside surfaces **2134** that facilitate the collection and separation of condensate **2136** from the gas-phase components. The apparatus **2100** illustrated in Figure 21 may be utilized to synthesize a wide variety of chemistries, such as those described earlier in this disclosure, on a continuous basis.

[0182] Figure 22 is a schematic diagram illustrating another example of an atmospheric-pressure (AP) plasma apparatus **2200** adapted for continuous processing. This apparatus **2200** is particularly suitable for treating solid materials with gas-phase products synthesized by a plasma flame discharge as described earlier in the present disclosure. Taking the treatment of cellulosic materials as an example, biomass feedstock **2201** may be fed from a hopper **2202** onto a suitable conveying device **2204** such as may include an endless belt or chain. While the biomass **2201** is transported by the conveying device **2204** through a reaction chamber **2206**, a separate reaction chamber **2208** containing one or more plasma flame discharge sources **2210** is utilized to produce nitrogen dioxide as described earlier in the present disclosure. The as-produced nitrogen dioxide is flowed into the first reaction chamber **2206** as indicated by an arrow **2212** and into contact with the biomass **2201**. The nitrogen dioxide may be conducted in counterflow relation to the direction of transport of the biomass **2201** as in the illustrated example, but alternatively may be introduced by other pathways. As examples, the nitrogen dioxide may be conducted in parallel or concurrent flow with the flow of biomass **2201**, or in a mixed counterflow/ concurrent flow relative to the biomass **2201**. In another example, the nitrogen dioxide may be introduced into the first reaction chamber **2206** at several locations simultaneously by employing suitable means such as a gas distributor (not shown). The nitrogen dioxide penetrates the cellular structure of the biomass **2201** as described earlier, combining

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with hydrogen species to form nitric acid that degrades the biomass **2201** in a direct, *in situ* fashion. The treated biomass **2201** is then collected at a suitable reception site **2214**. Apparatus of the type illustrated in Figure 22 according to the present teachings, in which a plasma reaction zone operatively communicates with a distinct non-plasma or post-plasma reaction zone, may be referred to as a tandem reactor.

[0183] As used herein, the term “cellulosic material” generally encompasses any cellulose-containing material, including lignocellulosic material and biomass, either living or existing as a waste product of industry or nature. Examples of cellulosic material include, but are not limited to, the following: forestry products, including forestry wastes, such as woods of various species of trees, including softwoods (e.g., gymnosperms such as conifers, pine, spruce, etc.), hardwoods (e.g., angiosperms such as maple, poplar, etc.), etc., including in the form of log slash, bark, trunks, stumps, branches, twigs, and the like, as well as grasses (e.g., angiosperms); agricultural products, including agricultural wastes, such as corn stover, corn cobs, rice straw, orchard and vineyard trimmings, manure, etc.; biomass crops such as grasses (e.g., switch grass), woods (e.g., poplar trees), crop residue, etc.; municipal/industrial wastes such as paper, gardening and yard refuse, etc.; and the outer coverings of various fruits, vegetables, seeds, and other plant matter such as maize (e.g., corn), straw, cereals, rye, rape-seed, cotton-seed, sunflower seed, alfalfa, oats, barleys, wheat, millet, sorghum, buckwheat, bagasse, etc.; sawdust, wood chips, wooden plant material, non-wooden plant material, etc. Generally, wooden and non-wooden plant material may be in any form, including, but not limited to, stems, stalks, shrubs, foliage, leaves, bark, roots, shells, rinds, pods, nuts, husks, hulls, fibers, vines, straws, hay, grasses, bamboo, reeds, etc. Wooden material may include heartwood (e.g., duramen) as well as outer wood (e.g., xylem). Moreover, the cellulosic material may be a mixture or combination of one or more of the foregoing items.

[0184] As used herein, the term “degradation” generally encompasses any process that results in a molecule being broken down into simpler molecules, radicals, and/or charged species. For example, the term “degradation” may encompass the breaking down of a polymer into smaller polymers (e.g., oligomers, trimers, dimers, etc.) and/or monomers such as, for example, the breaking down of a cellulose into glucose units. The term “degradation” may also encompass the breaking up or removal of physical and/or chemical bonds among different types

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of components of a complex material, and/or bonds internal to such components. For example, degradation may encompass the breaking up of bonds between cellulose, hemicellulose, and/or lignin, and/or the breaking down of polymeric cellulose or hemicellulose into component sugars. The term “degradation” may also encompass the removal, in whole or in part, of a component from a complex material. For example, in a complex of cellulose, hemicellulose and lignin, degradation may encompass the removal of at least some of the lignin from the complex, thereby providing greater access to the cellulose and hemicellulose components. The term “degradation” may also encompass the alteration or modification of the structure of a biomaterial. For example, degradation may encompass the opening up of interstices, voids, recesses or pores (more generally, spatial features) existing within the structure of a complex of cellulose, hemicellulose and lignin, and/or the creation of new interstices, voids, recesses or pores in such material. Degradation may entail physical, chemical, and/or biological work. Degradation may entail processes that are aided or unaided by catalytic activity. In view of the foregoing, the term “degradation” encompasses such terms as depolymerization, hydrolysis, dissociation, dissolution, disruption, delignification, removal of material, conversion of a complex material into simpler components, and release or extraction of components from a complex material.

[0185] While the foregoing implementations entailing the processing of biomass have focused primarily on the treatment of cellulose, the invention may also be applicable to the treatment of starch. As readily appreciated by persons skilled in the art, starch is a water-insoluble, complex carbohydrate containing around 2500 glucose monomer units. In general, starches have the formula $(C_6H_{10}O_5)_n$, where “n” denotes the total number of glucose monomer units. More specifically, starch is a combination of the two polysaccharides amylose and amylopectin. Amylose constitutes a straight chain of glucose units joined to one another by α -1,4 linkages. Amylopectin, on the other hand, includes branches, with an α -1,6 linkage every 24-30 glucose units. That is, starch forms clusters of linked linear polymers, where the α -1,4 linked chains form columns of glucose units which branch regularly at the α -1,6 links. As previously noted, a starch molecule as a result has a coiled conformation unlike a straight-chain cellulose molecule. Starches can be digested by hydrolysis into simpler saccharide units. The

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hydrolysis may be catalyzed by enzymes known as amylases, which break the glycosidic bonds between the α -glucose components of the starch polysaccharide molecule.

[0186] In general, the term “communicate” (for example, a first component “communicates with” or “is in communication with” a second component) is utilized in the present disclosure to indicate a structural, functional, mechanical, electrical, optical, magnetic, ionic or fluidic relationship between two or more components (or elements, features, or the like). As such, the fact that one component is said to communicate with a second component is not intended to exclude the possibility that additional components may be present between, and/or operatively associated or engaged with, the first and second components.

[0187] The foregoing description of implementations has been presented for purposes of illustration and description. It is not exhaustive and does not limit the claimed inventions to the precise form disclosed. Modifications and variations are possible in light of the above description or may be acquired from practicing the invention. The claims and their equivalents define the scope of the invention.

CLAIMS**What is claimed is:**

1. A method for synthesizing a chemistry, the method comprising:
igniting a plasma flame in a chamber at atmospheric pressure in the presence of a gas including a plurality of gas-phase components, by applying a periodic signal to at least one of a pair of electrodes in the chamber, wherein the plasma flame includes a thermal core in a gap between the electrodes and a non-equilibrium region adjacent to the thermal core; and
conducting a synthesis reaction to produce the chemistry, by reacting at least one component of the gas with either another component of the gas or with a precursor component introduced into the chamber separately from the gas.
2. The method of claim 1, wherein the periodic signal is an AC signal or a pulsed DC signal.
3. The method of claim 1, wherein the periodic signal is applied at a power ranging from about 20 to 500 W.
4. The method of claim 1, wherein the periodic signal is applied at a current ranging from about 0.025 to 0.5 A.
5. The method of claim 1, wherein the periodic signal is applied at a voltage ranging from about 600 to 6000 V.
6. The method of claim 1, wherein the synthesis occurs in a region selected from the group consisting of the thermal core, the non-equilibrium region, a region of the chamber outside the plasma flame, and a combination of one or more of the foregoing.
7. The method of claim 1, wherein the temperature of the thermal core ranges from 1000 to 10,000 K, and the temperature of the non-equilibrium region ranges from 270 to 1000 K.

8. The method of claim 1, wherein the volumetric ratio of the plasma flame, defined as the ratio of the volume of the thermal core to the volume of the non-equilibrium region, ranges from 1:3 to 1:100,
9. The method of claim 1, further comprising controlling the volumetric ratio of the plasma flame, defined as the ratio of the volume of the thermal core to the volume of the non-equilibrium region, by controlling a current or a voltage of the periodic signal.
10. The method of claim 1, wherein the ratio of the volume of the plasma flame to the volume of the chamber ranges from 1:10 to 1:10,000.
11. The method of claim 1, further comprising flowing the gas into the chamber while the plasma flame is active.
12. The method of claim 1, further comprising flowing a reactant into the chamber including a gas-phase precursor component, wherein the synthesis reaction is conducted by reacting at least one component of the gas energized by the plasma flame with the precursor component.
13. The method of claim 1, further comprising, while conducting the synthesis reaction, pulsing the plasma flame on and off one or more times by applying the periodic signal in a pulsed manner.
14. The method of claim 1, further comprising flowing energized species produced by the plasma flame into an enclosure separate from the chamber, wherein at least a portion of the synthesis is conducted in the enclosure.
15. The method of claim 14, further comprising controlling a temperature of gas-phase components in the enclosure to control the synthesis.

16. The method of claim 14, further comprising, after flowing the energized species into the enclosure, reacting the energized species with a reactant present in the enclosure.

17. The method of claim 1, wherein the chamber includes more than one pair of electrodes, and more than one periodic signal is applied to the respective electrodes to ignite more than one plasma flame, wherein conducting the synthesis reaction includes flowing energized species produced by at least one of the plasma flames to another one of the plasma flames.

18. The method of claim 1, wherein the chamber includes a plurality of compartments, at least two of the compartments each include a respective pair of electrodes, and respective periodic signals are applied to the respective electrodes to ignite respective plasma flames, wherein conducting the synthesis reaction includes flowing energized species produced by at least one of the plasma flames in one compartment to another one of the plasma flames in another compartment.

19. The method of claim 18, wherein the compartments that include electrodes are fluidly isolated from each other by an isolating device, and the isolating device is switchable between a closed position at which fluid cannot flow between the compartments to an open position at which fluid can flow between the compartments.

20. The method of claim 1, wherein the synthesis reaction is conducted for a first period of time, and further comprising:

after the first period of time, creating in the chamber a post-discharge reaction zone including energetic species of the gas, by ceasing application of the periodic signal wherein the plasma flame is extinguished; and

for a second period of time after the plasma flame is extinguished, conducting the synthesis reaction in the post-discharge reaction zone.

21. The method of claim 20, further including repeating the steps recited in claim 20 one or more times.
22. The method of claim 1, wherein the plurality of gas-phase components includes diatomic oxygen and diatomic nitrogen, igniting the plasma flame produces energetic oxygen species, energetic nitrogen species, and energetic nitrogen oxide species, and conducting the synthesis reaction comprises reacting nitrogen and oxygen to form nitrogen dioxide, the nitrogen being provided by the nitrogen species, the nitrogen oxide species, or both the nitrogen species and the nitrogen oxide species, and the oxygen being provided by the oxygen species, the nitrogen oxide species, or both the oxygen species and the nitrogen oxide species.
23. The method of claim 22, further comprising flowing a precursor component into the chamber and reacting the precursor component with the nitrogen dioxide to synthesize another chemistry.
24. The method of claim 22, wherein reacting the nitrogen and oxygen occurs for a first period of time, and further comprising:
after the first period of time, creating in the chamber a post-discharge reaction zone including the nitrogen species, the oxygen species and the nitrogen oxide species by ceasing application of the periodic signal wherein the plasma flame is extinguished; and
for a second period of time after the plasma flame has been extinguished, synthesizing additional nitrogen dioxide by reacting the nitrogen and the oxygen in the post-discharge reaction zone.
25. The method of claim 22, further comprising reacting water with the nitrogen dioxide to produce nitric acid.
26. A method for synthesizing syngas including carbon monoxide and diatomic hydrogen, the method comprising:

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igniting a plasma flame in a chamber at atmospheric pressure, by applying a periodic signal to at least one of a pair of electrodes in the chamber, wherein the plasma flame includes a thermal core in a gap between the electrodes and a non-equilibrium region adjacent to the thermal core;

flowing a mixture of a hydrogen source, an oxygen source and a carbon source toward the plasma flame; and

reacting species of the carbon source, the oxygen source and the hydrogen source energized by the plasma flame to form syngas.

27. A method for synthesizing ammonia, the method comprising:

igniting a plasma flame in a chamber at atmospheric pressure, by applying a periodic signal to at least one of a pair of electrodes in the chamber, wherein the plasma flame includes a thermal core in a gap between the electrodes and a non-equilibrium region adjacent to the thermal core; and

reacting nitrogen species and hydrogen species energized by the plasma flame to form ammonia.

28. The method of claim 27, further comprising flowing a hydrogen containing compound toward the plasma flame to produce hydrogen from which the energized hydrogen species is derived, and flowing nitrogen into the chamber from which the energized nitrogen species is derived.

29. A method for synthesizing chlorine dioxide, the method comprising:

igniting a plasma flame in a chamber at atmospheric pressure, by applying a periodic signal to at least one of a pair of electrodes in the chamber, wherein the plasma flame includes a thermal core in a gap between the electrodes and a non-equilibrium region adjacent to the thermal core; and

reacting chlorine species and oxygen species energized by the plasma flame to form chlorine dioxide.

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30. A method for synthesizing methanol, the method comprising:
igniting a plasma flame in a chamber at atmospheric pressure, by applying a periodic signal to at least one of a pair of electrodes in the chamber, wherein the plasma flame includes a thermal core in a gap between the electrodes and a non-equilibrium region adjacent to the thermal core;
flowing a source of carbon, hydrogen or oxygen toward the plasma flame to form energetic species of carbon, hydrogen or oxygen; and
reacting the carbon, hydrogen or oxygen with species energized by the plasma flame to form methanol, the energized species including carbon, hydrogen or oxygen.
31. A method for synthesizing ammonium nitrate, the method comprising reacting ammonia and nitric acid, including operating a plasma flame to synthesize at least one of the ammonia and the nitric acid.
32. The method of claim 31, wherein:
operating the plasma flame comprises:
igniting a plasma flame in a chamber at atmospheric pressure, by applying a periodic signal to at least one of a pair of electrodes in the chamber, wherein the plasma flame includes a thermal core in a gap between the electrodes and a non-equilibrium region adjacent to the thermal core; and
reacting nitrogen species and hydrogen species energized by the plasma flame to synthesize ammonia; and
the synthesized ammonia is reacted with the nitric acid to form the ammonium nitrate.
33. The method of claim 31, wherein:
operating the plasma flame comprises:
igniting a plasma flame in a chamber at atmospheric pressure in the presence of a gas including oxygen and nitrogen, by applying a periodic signal to at least one of a pair of electrodes in the chamber, wherein the plasma flame

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includes a thermal core in a gap between the electrodes and a non-equilibrium region adjacent to the thermal core;

reacting nitrogen species and oxygen species energized by the plasma flame to synthesize nitrogen dioxide; and

reacting the nitrogen dioxide with water to synthesize nitric acid; and
the synthesized nitric acid is reacted with the ammonia to form the ammonium nitrate.

34. A method for treating a cellulosic material, comprising operating a plasma flame to synthesize nitrogen dioxide, and exposing the cellulosic material to the nitrogen dioxide.

35. The method of claim 34, wherein the nitrogen dioxide is synthesized by:

igniting the plasma flame in a chamber in the presence of oxygen and nitrogen to produce energetic oxygen species, energetic nitrogen species, and energetic nitrogen oxide species, by applying a periodic signal to at least one of a pair of electrodes in the chamber, wherein the plasma flame includes a thermal core in a gap between the electrodes and a non-equilibrium region adjacent to the thermal core; and

combining the nitrogen species, the oxygen species, and energetic nitrogen oxide species.

36. The method of claim 34, further including forming nitric acid within the cellulosic material by reacting the nitrogen dioxide with hydrogen species supplied by a gas or by the cellulosic material, and degrading the cellulosic material by exposing the cellulosic material to the nitric acid.

37. The method of claim 34, further comprising fermenting one or more components of the plasma-treated cellulosic material.

38. The method of claim 37, wherein fermenting produces a fermentation product including an organic compound.

39. The method of claim 38, wherein the organic compound includes an alcohol.
40. The method of claim 38, wherein the alcohol includes ethanol.
41. The method of claim 34, further comprising subjecting the cellulosic material to the plasma flame or to an atmospheric-pressure plasma separate from the plasma flame, to produce a plasma-treated cellulosic material.
42. A method for treating a cellulosic material, comprising:
subjecting the cellulosic material to an atmospheric-pressure plasma to produce a plasma-treated cellulosic material; and
subjecting one or more components of the plasma-treated cellulosic material to an acid hydrolysis process to produce a hydrolyzed cellulosic material, by operating a plasma flame to synthesize nitrogen dioxide and exposing the cellulosic material to the nitrogen dioxide, forming nitric acid within the cellulosic material by reacting the nitrogen dioxide with hydrogen species supplied by a gas or by the cellulosic material, and degrading the cellulosic material by exposing the cellulosic material to the nitric acid.
43. The method of claim 42, wherein the atmospheric-pressure plasma to which the cellulosic material is subjected to produce a plasma-treated cellulosic material, and the plasma flame from which the nitrogen dioxide is synthesized, are the same plasma source.
44. The method of claim 42, wherein the atmospheric-pressure plasma to which the cellulosic material is subjected to produce a plasma-treated cellulosic material, and the plasma flame from which the nitrogen dioxide is synthesized, are separate plasma sources.
45. A method for treating a cellulosic material, comprising:
subjecting the cellulosic material to a first degradation process to produce a first degradation-processed cellulosic material;

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subjecting one or more components of the first degradation-processed cellulosic material to an atmospheric-pressure plasma to produce a plasma-treated cellulosic material; and

subjecting one or more components of the plasma-treated cellulosic material to a second degradation process to produce a second degradation-processed cellulosic material,

wherein subjecting the cellulosic material to at least one of the first and second degradation processes includes operating a plasma flame to synthesize nitrogen dioxide and exposing the cellulosic material to the nitrogen dioxide, forming nitric acid within the cellulosic material by reacting the nitrogen dioxide with hydrogen species supplied by a gas or by the cellulosic material, and degrading the cellulosic material by exposing the cellulosic material to the nitric acid.

46. A method for treating a cellulosic material, comprising:

subjecting the cellulosic material to a pretreatment process;

subjecting the cellulosic material to an atmospheric-pressure plasma; and

subjecting the cellulosic material to a degradation process,

wherein subjecting the cellulosic material to at least one of the pretreatment process and the degradation process includes operating a plasma flame to synthesize nitrogen dioxide and exposing the cellulosic material to the nitrogen dioxide, forming nitric acid within the cellulosic material by reacting the nitrogen dioxide with hydrogen species supplied by a gas or by the cellulosic material, and degrading the cellulosic material by exposing the cellulosic material to the nitric acid.

47. A method for treating a cellulosic material, comprising operating a plasma flame to produce nitrogen dioxide, liquefying the nitrogen dioxide, and exposing the cellulosic material to the liquefied nitrogen dioxide.

48. A method for treating a cellulosic material, comprising operating a plasma flame to produce nitrogen dioxide, reacting water with the nitrogen dioxide to produce nitric acid, liquefying the nitric acid, and exposing the cellulosic material to the liquefied nitric acid.

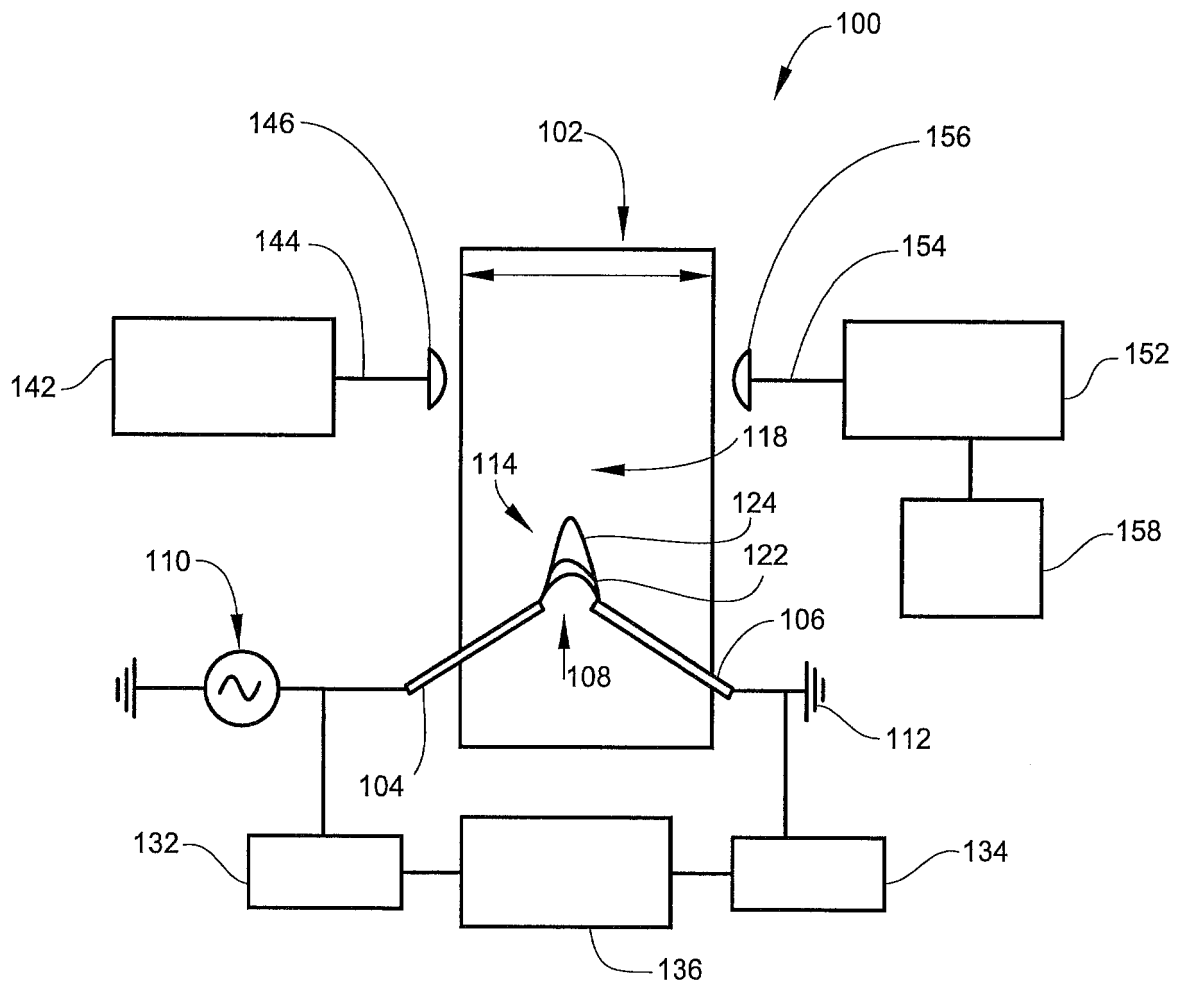


Fig. 1

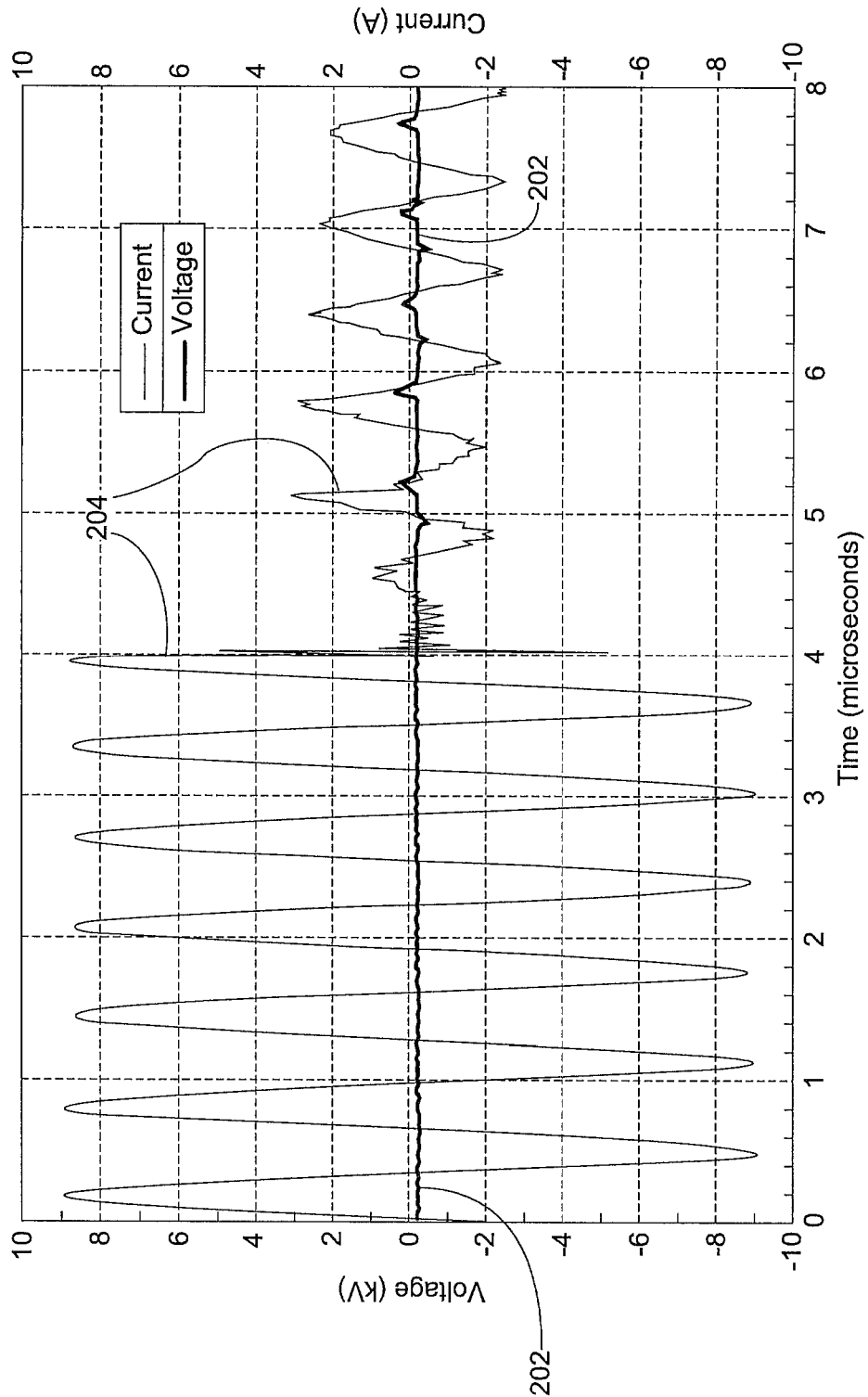


Fig. 2

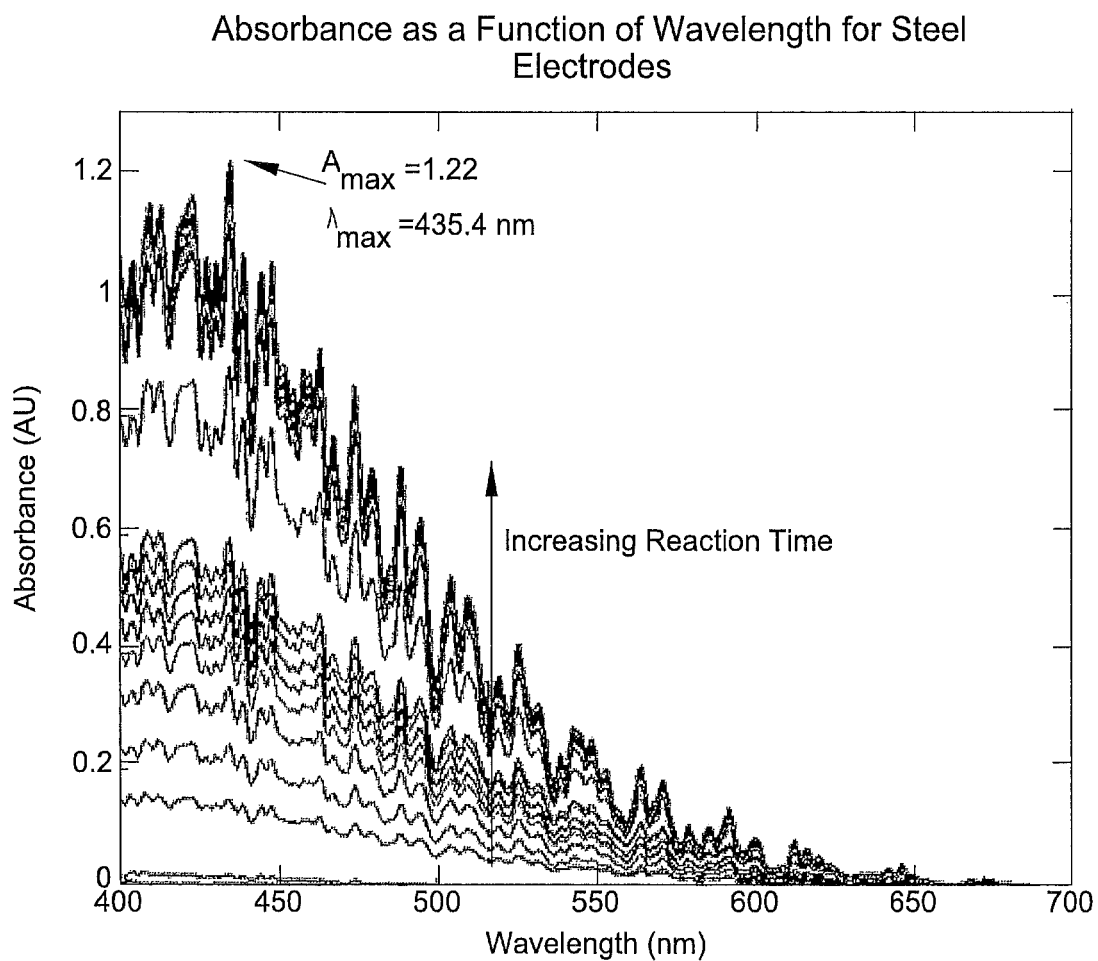


Fig. 3

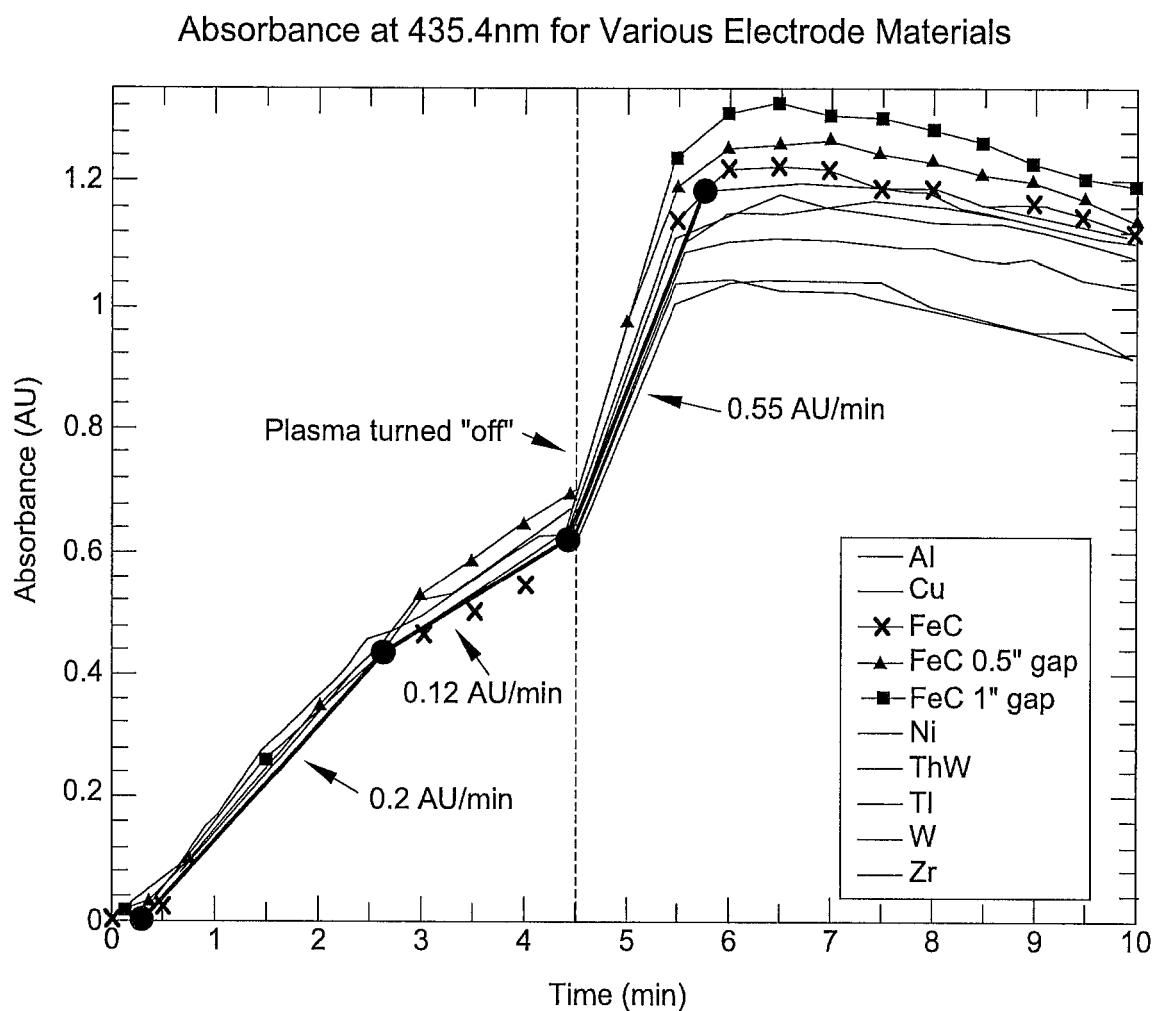


Fig. 4

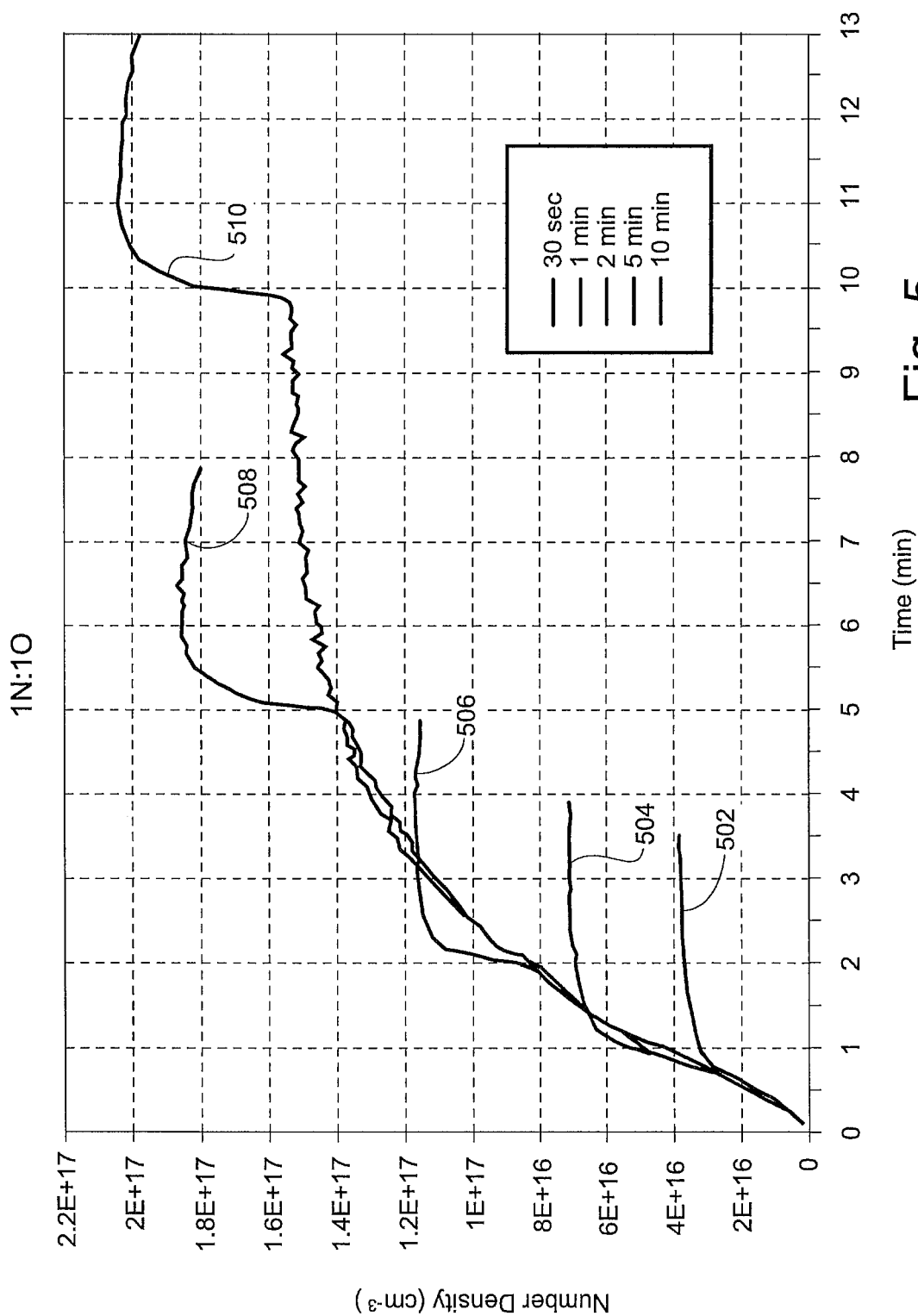


Fig. 5

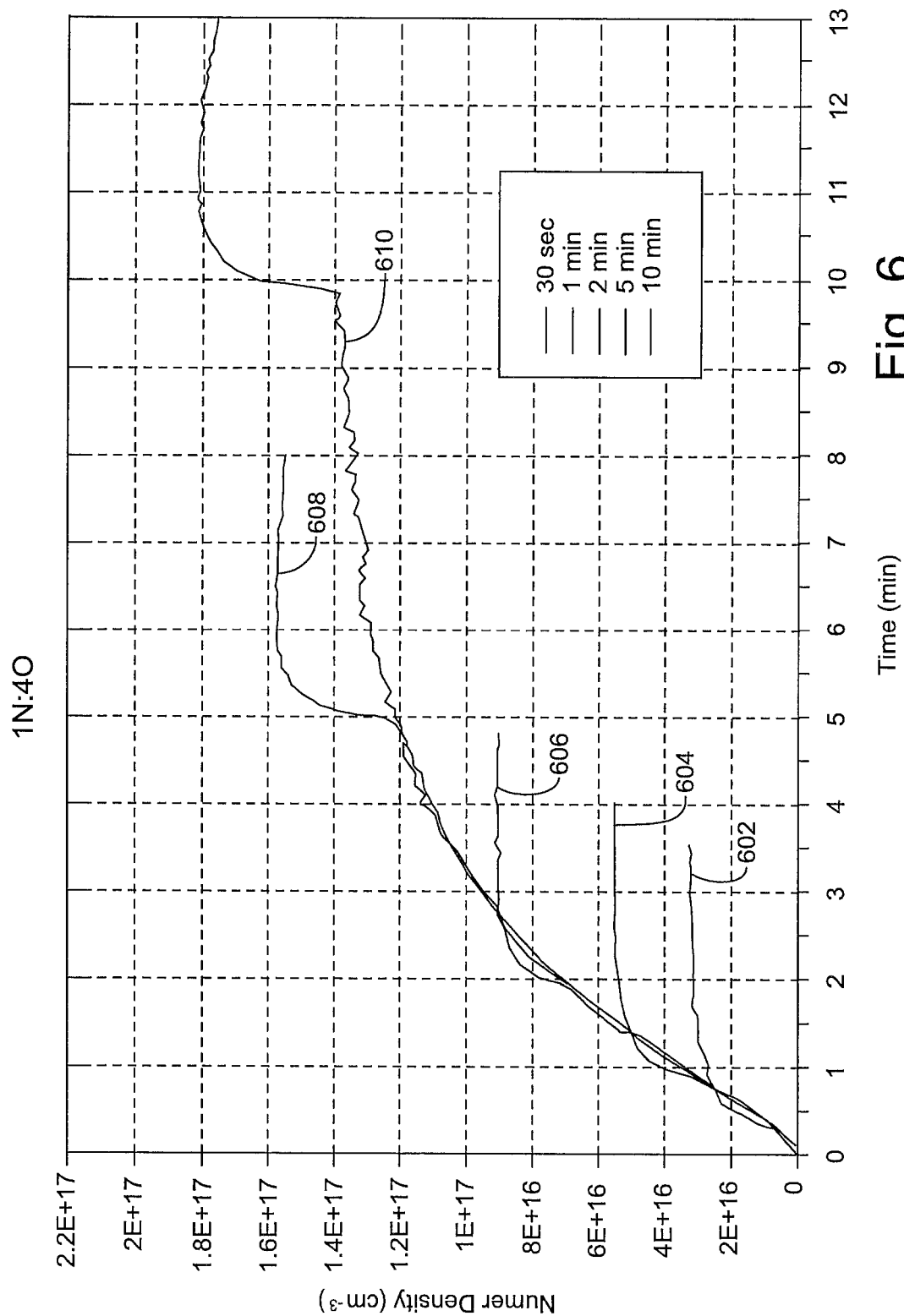


Fig. 6

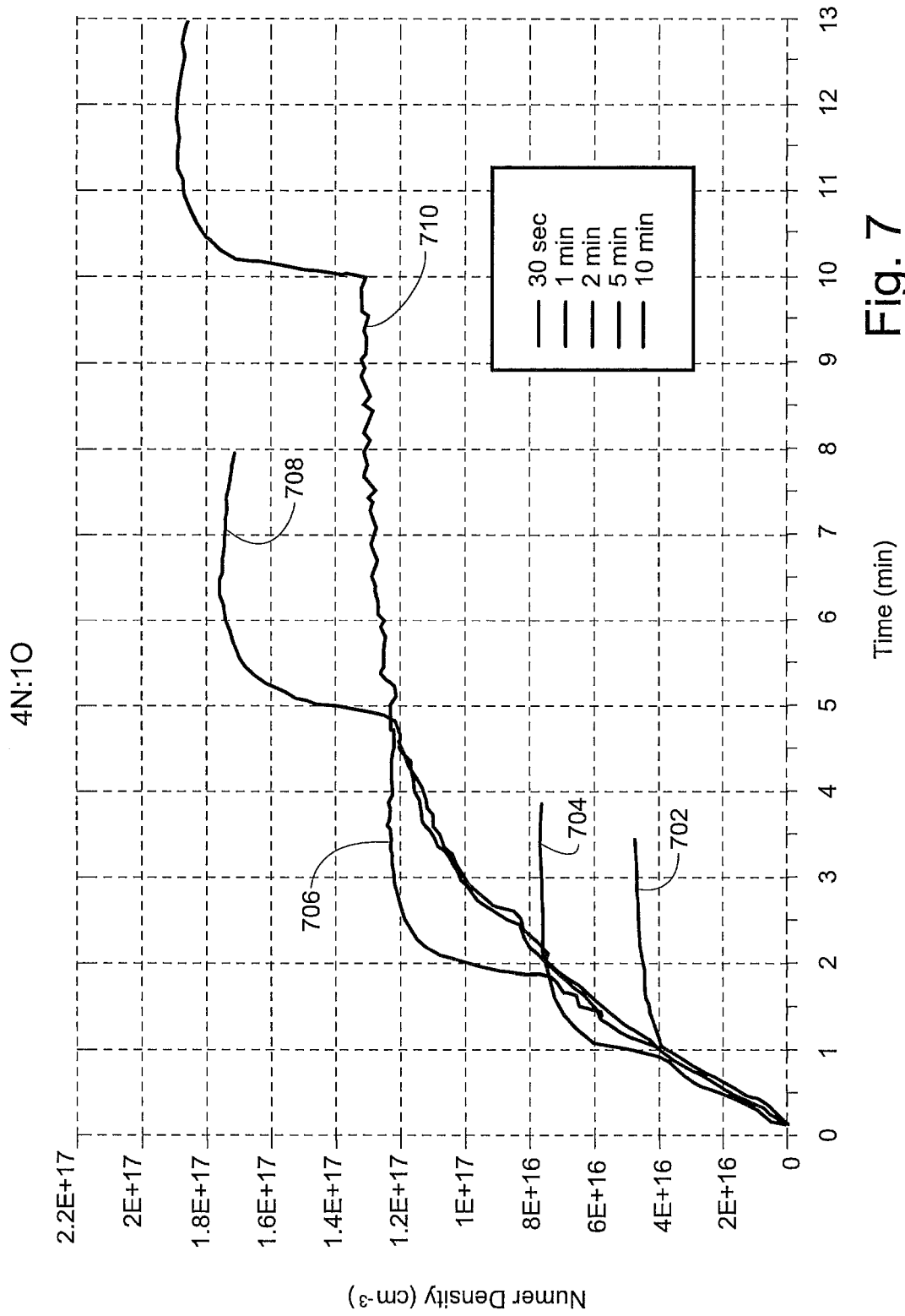


Fig. 7

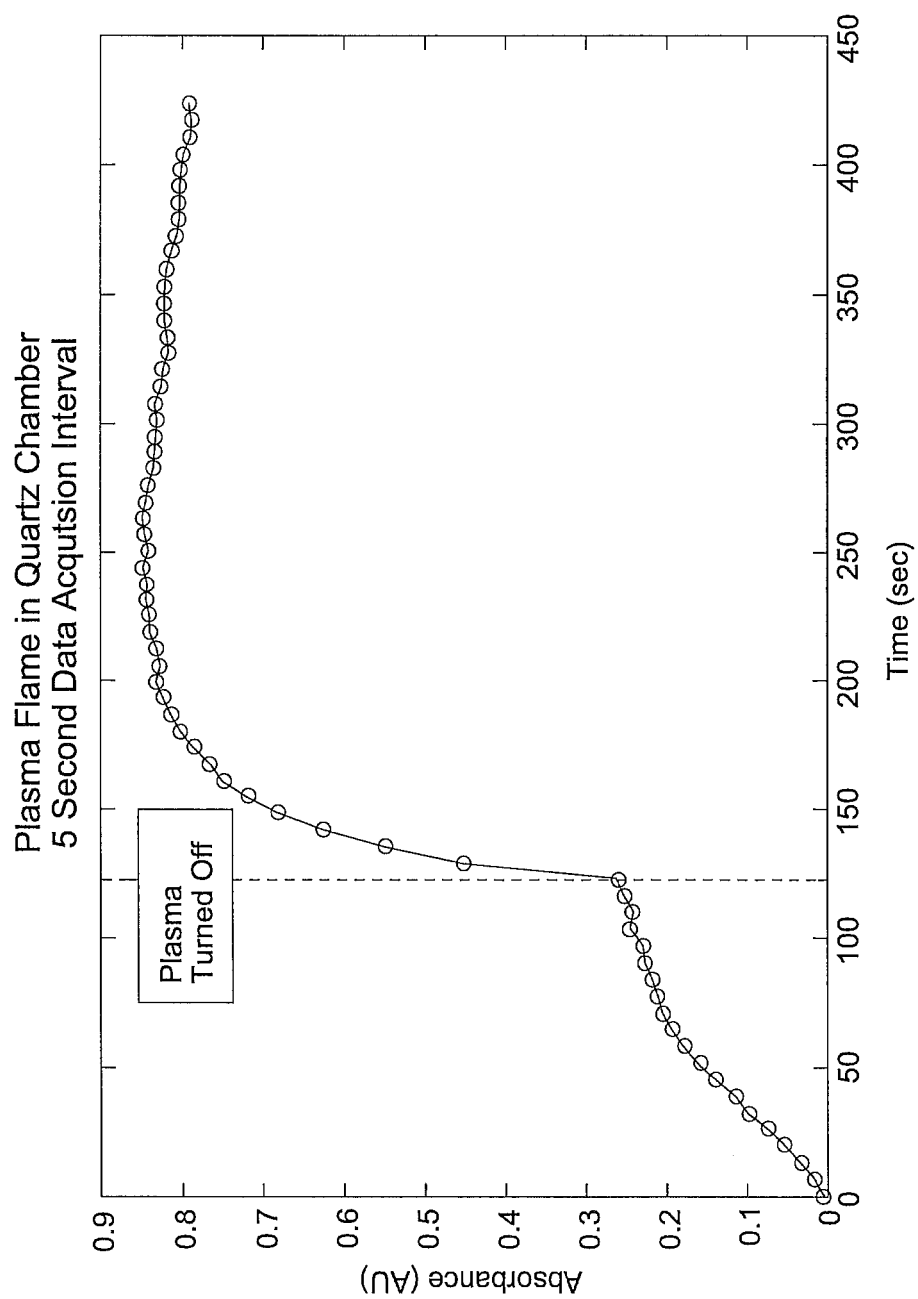


Fig. 8

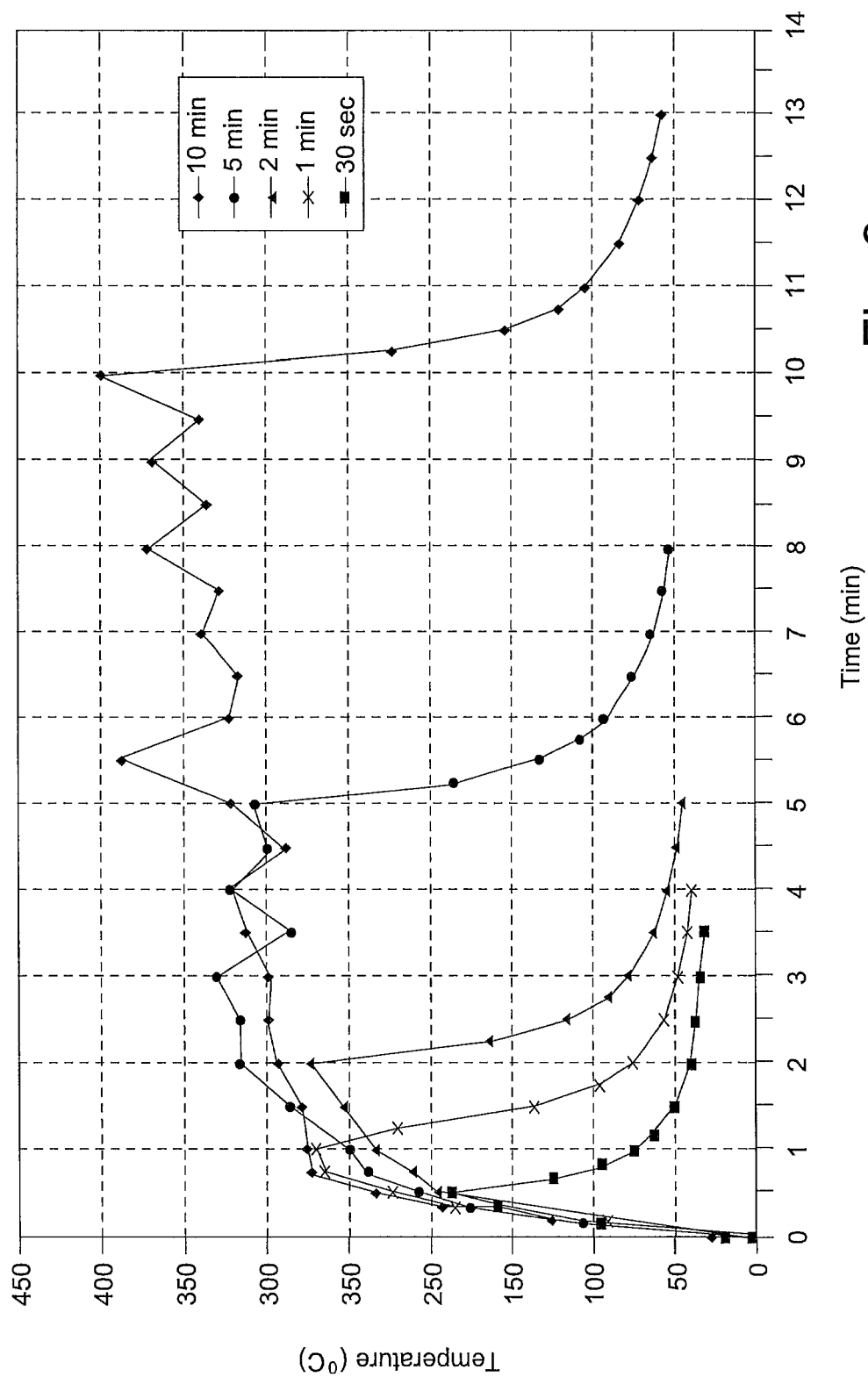


Fig. 9

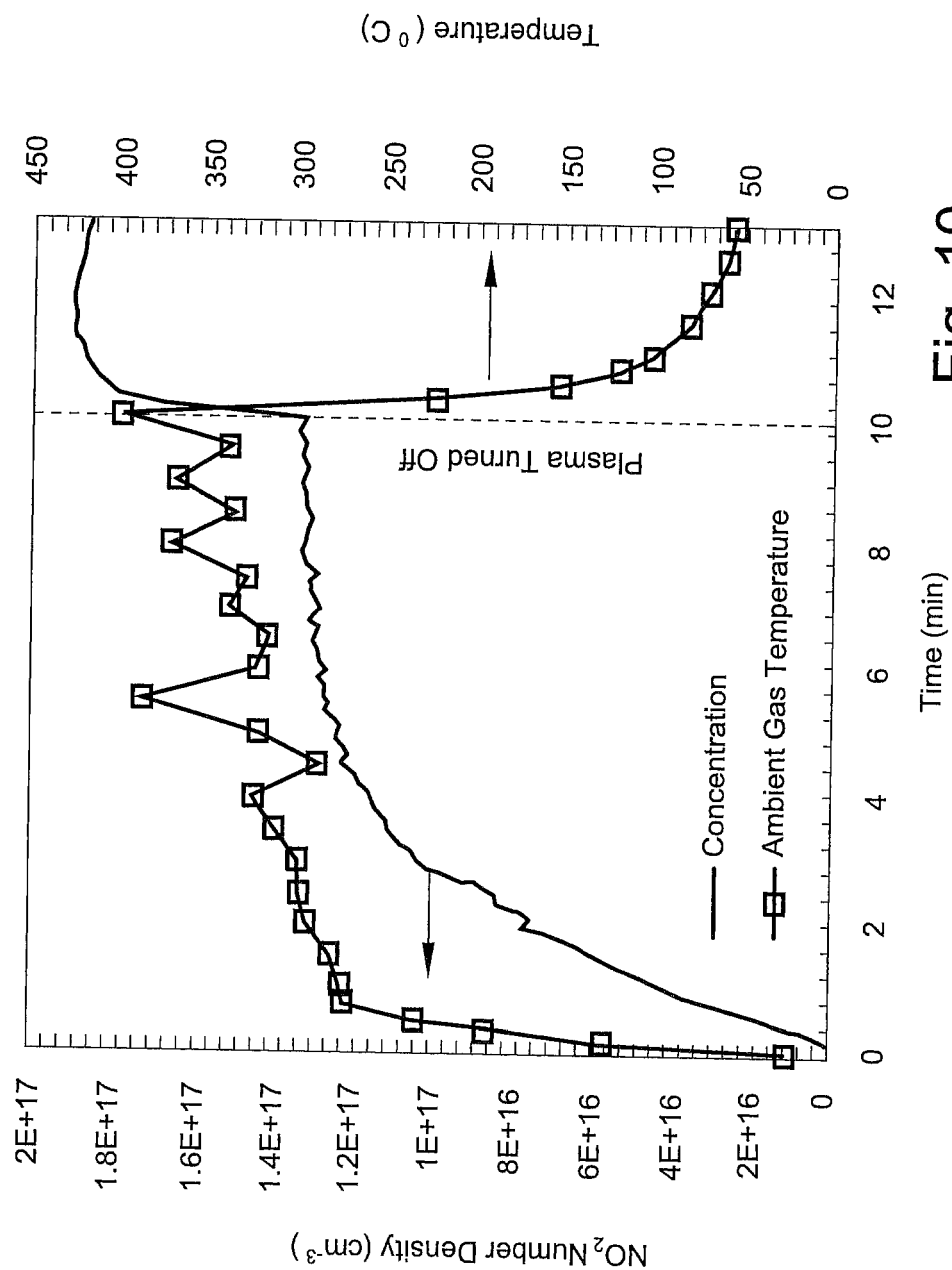


Fig. 10

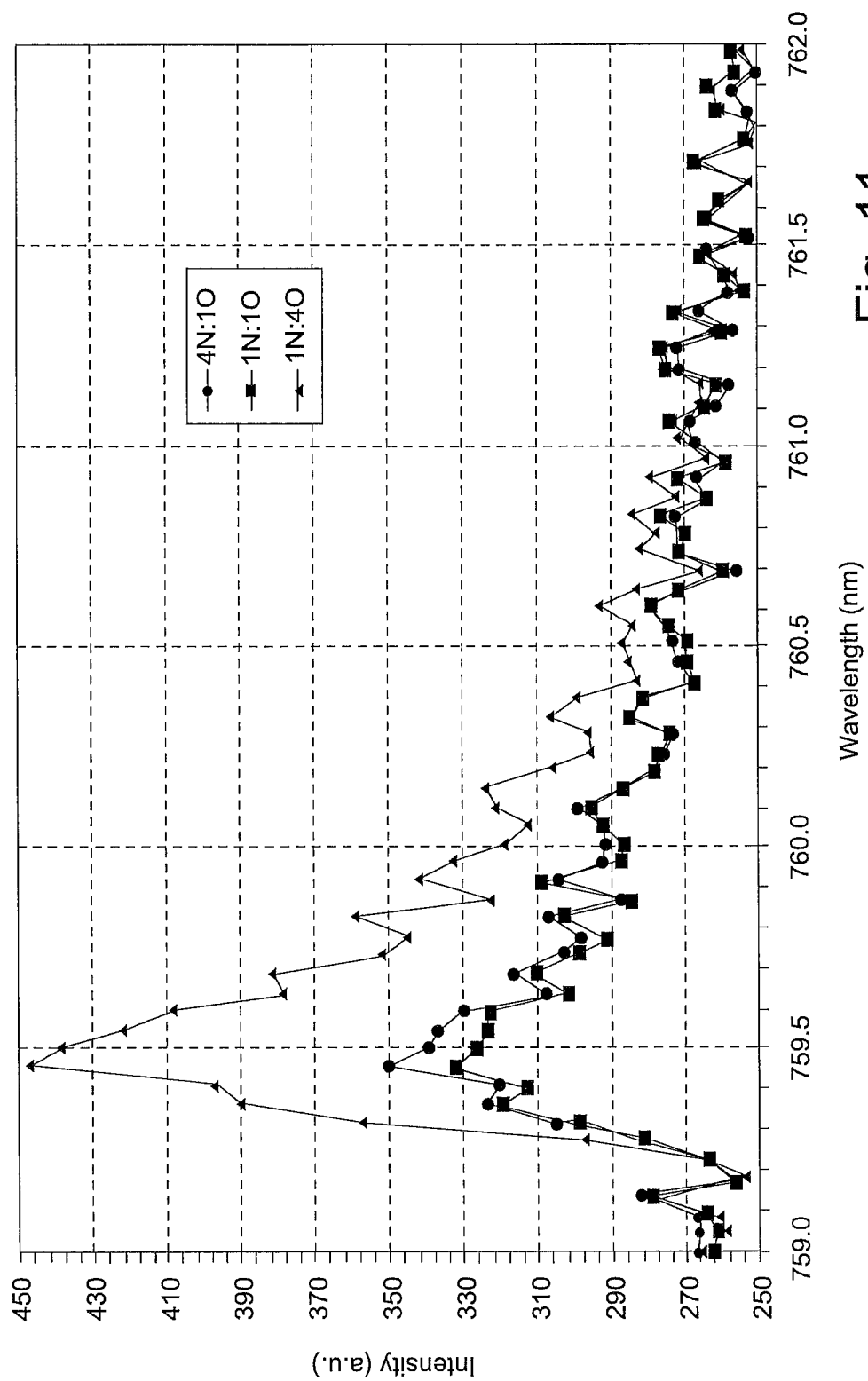


Fig. 11

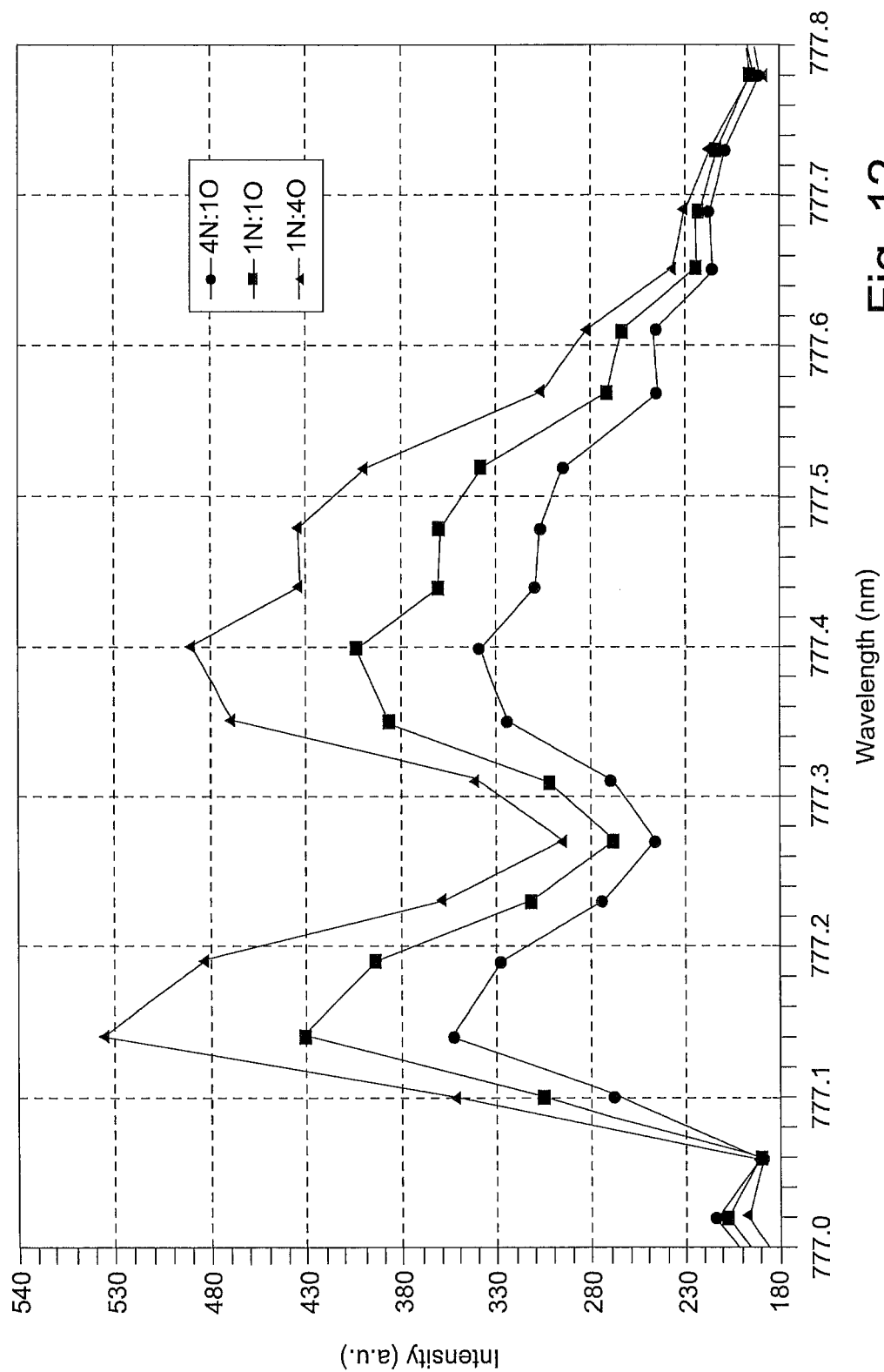


Fig. 12

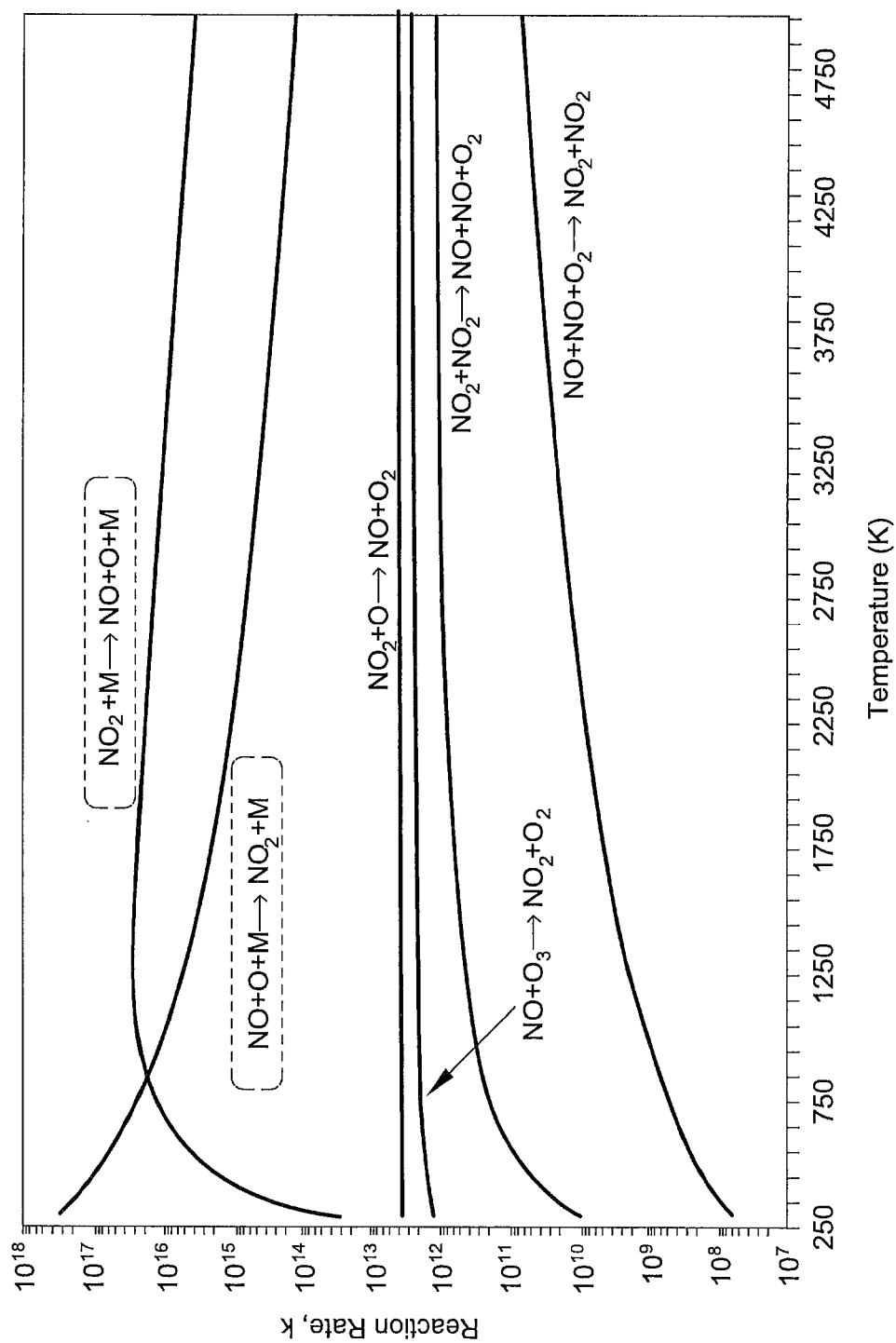


Fig. 13

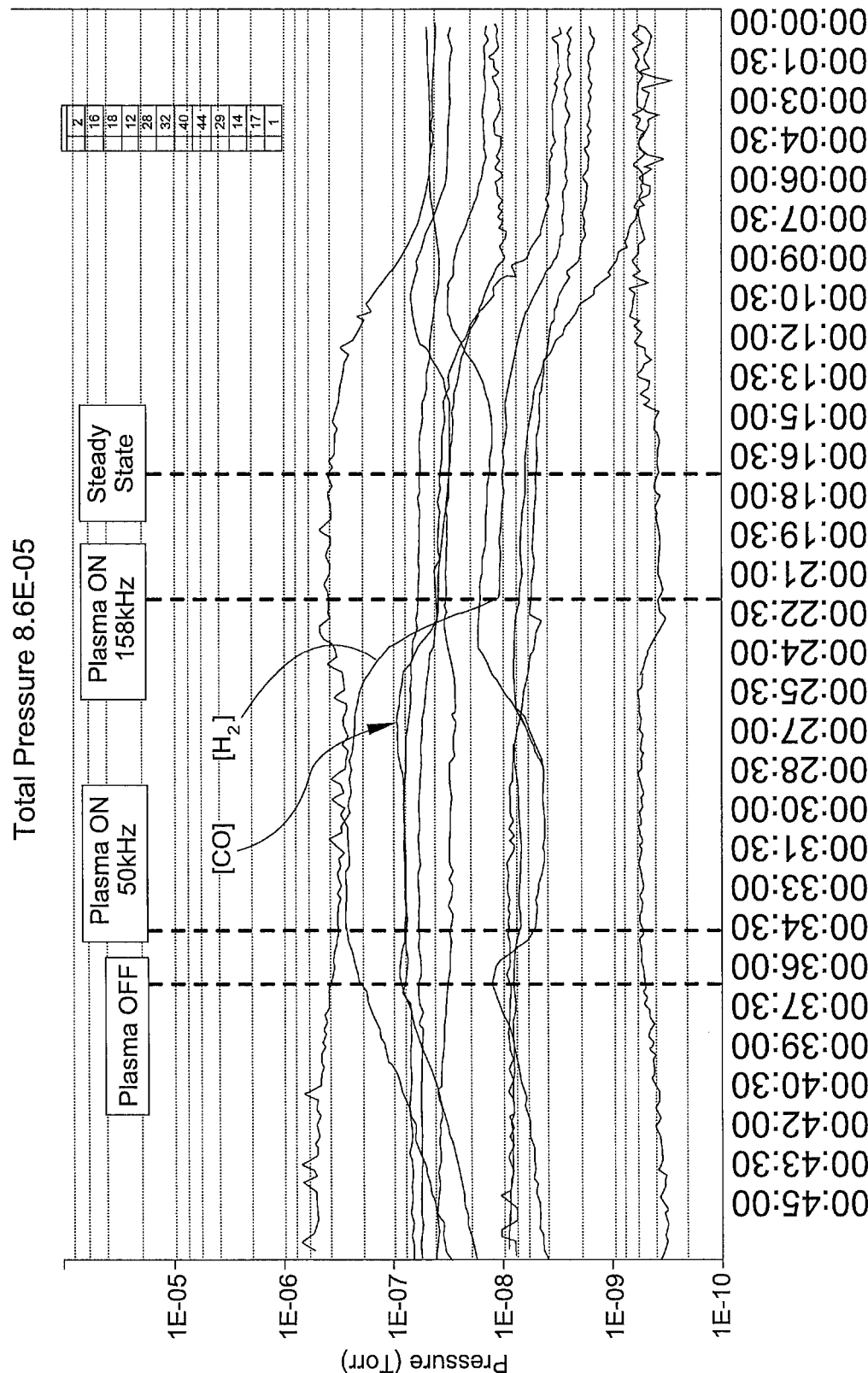
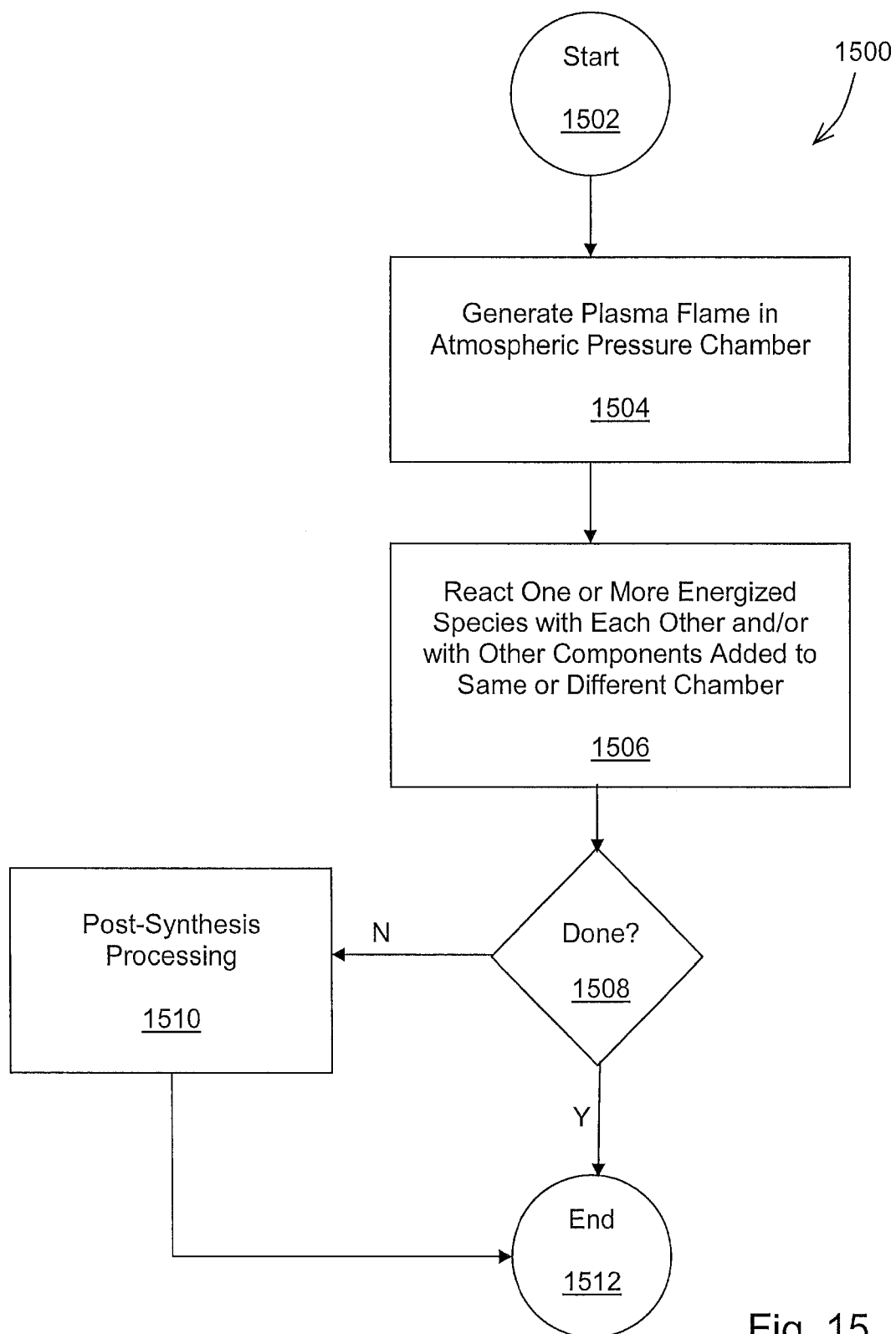
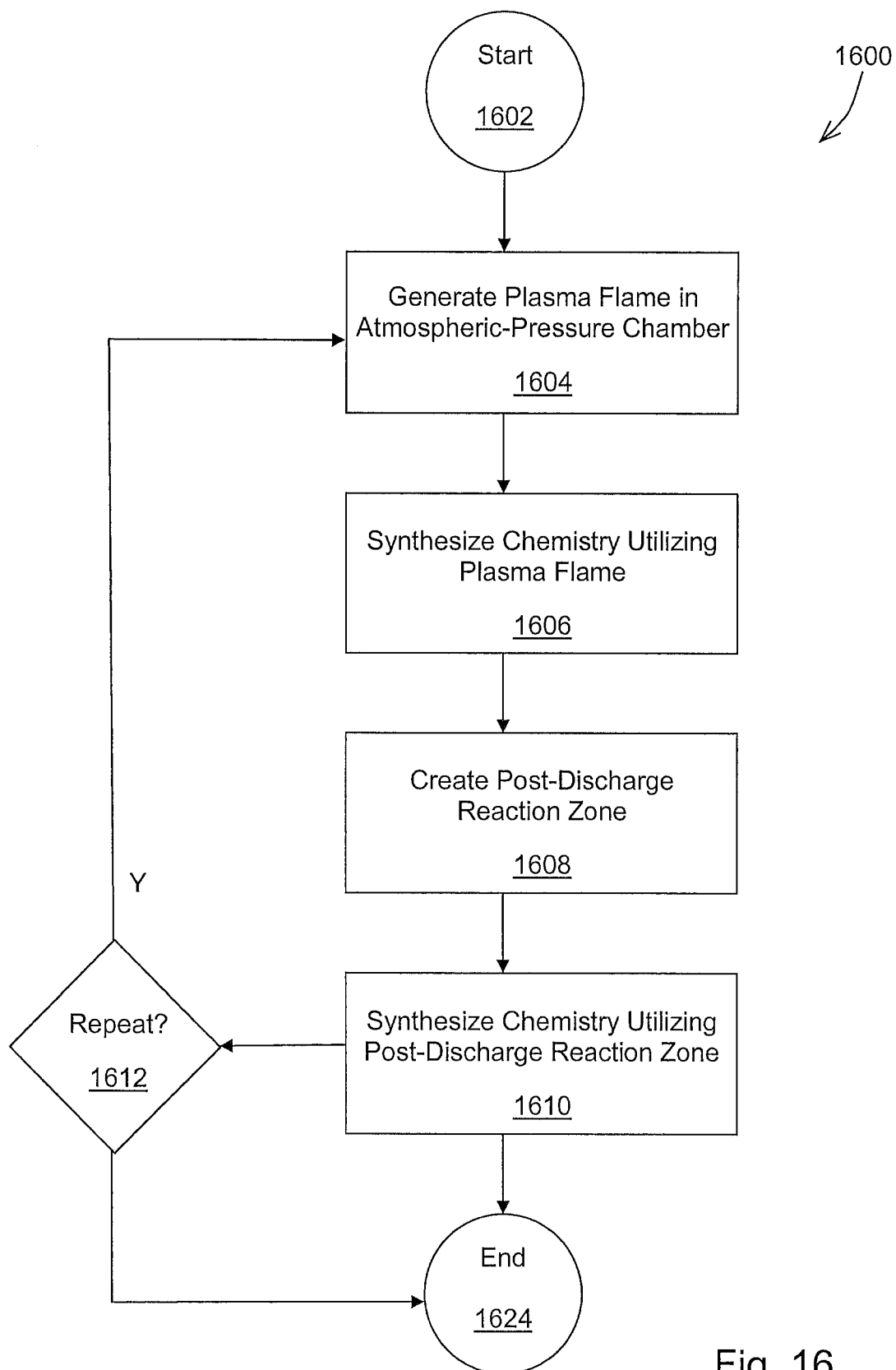


Fig. 14





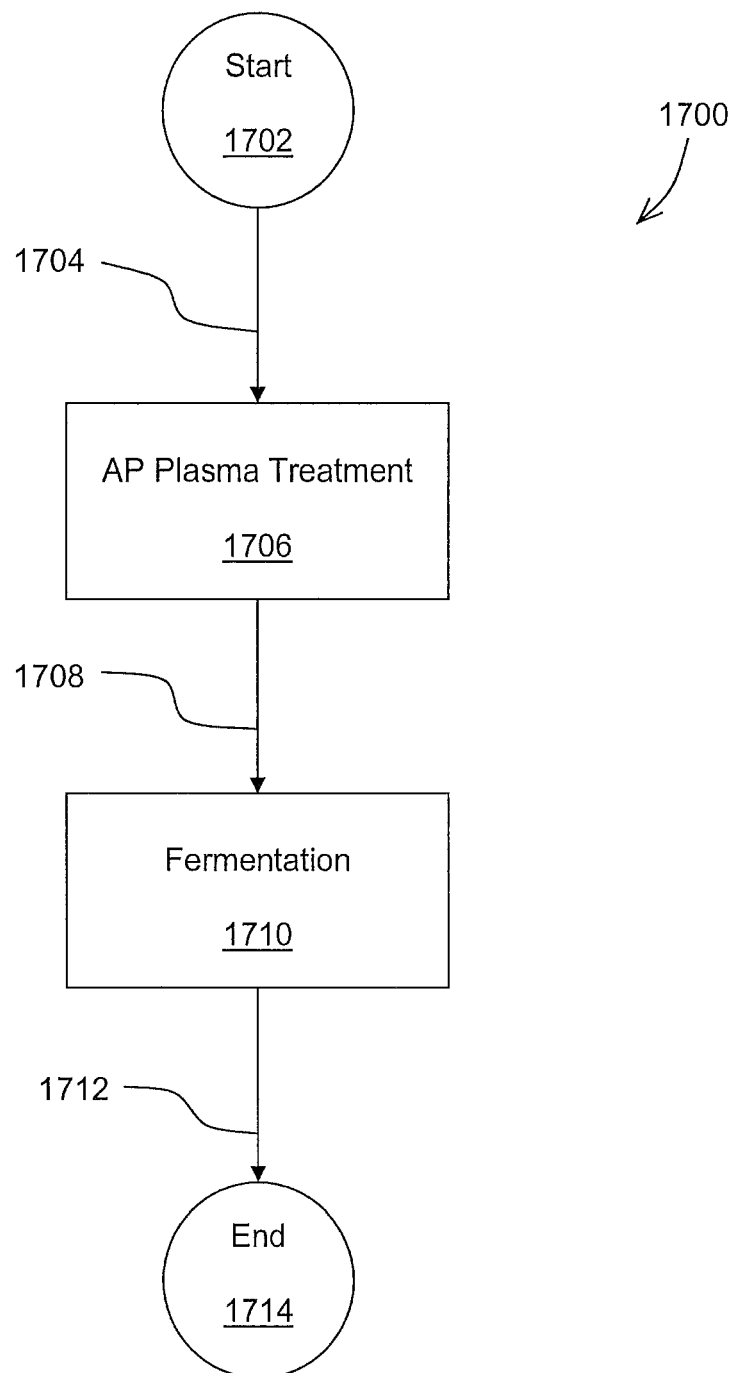


Fig. 17

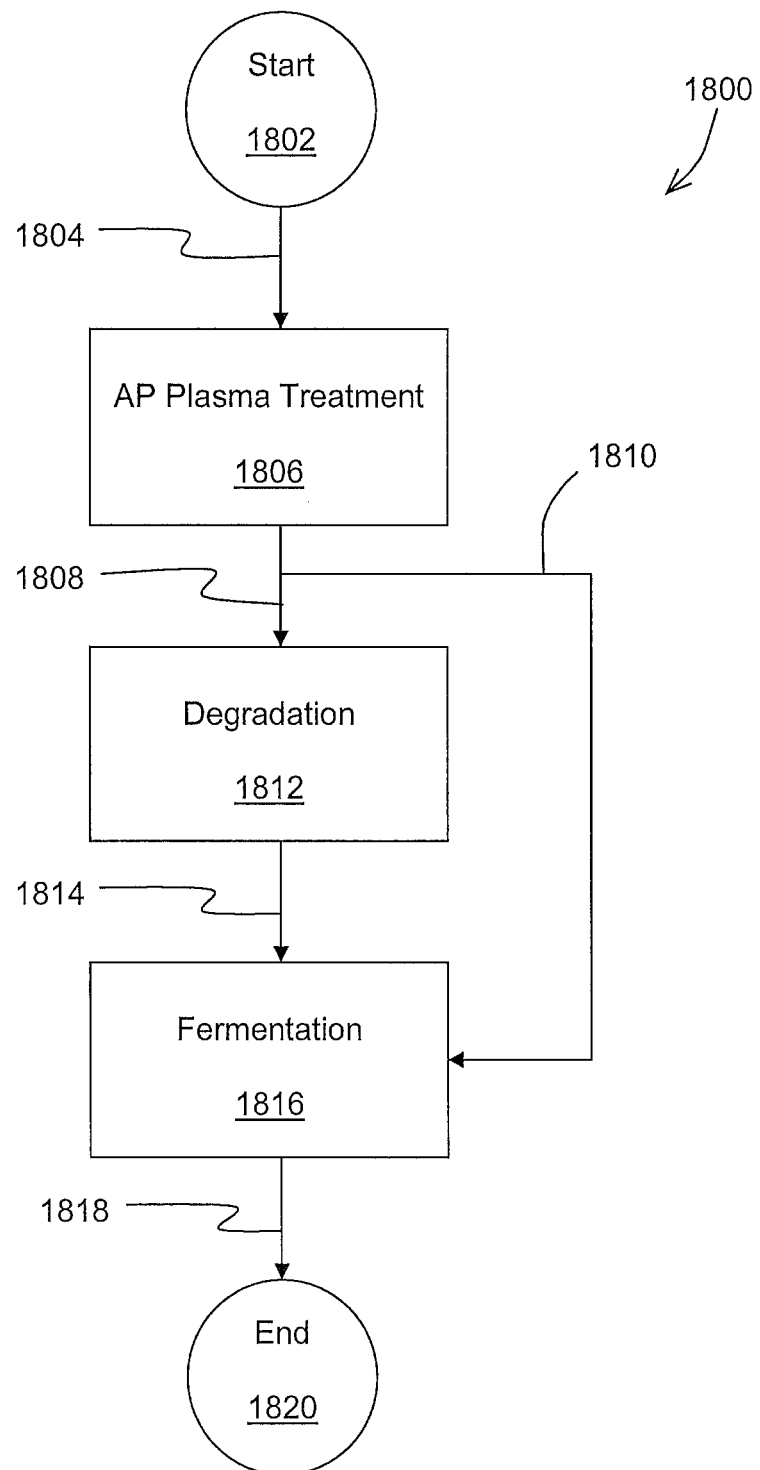


Fig. 18

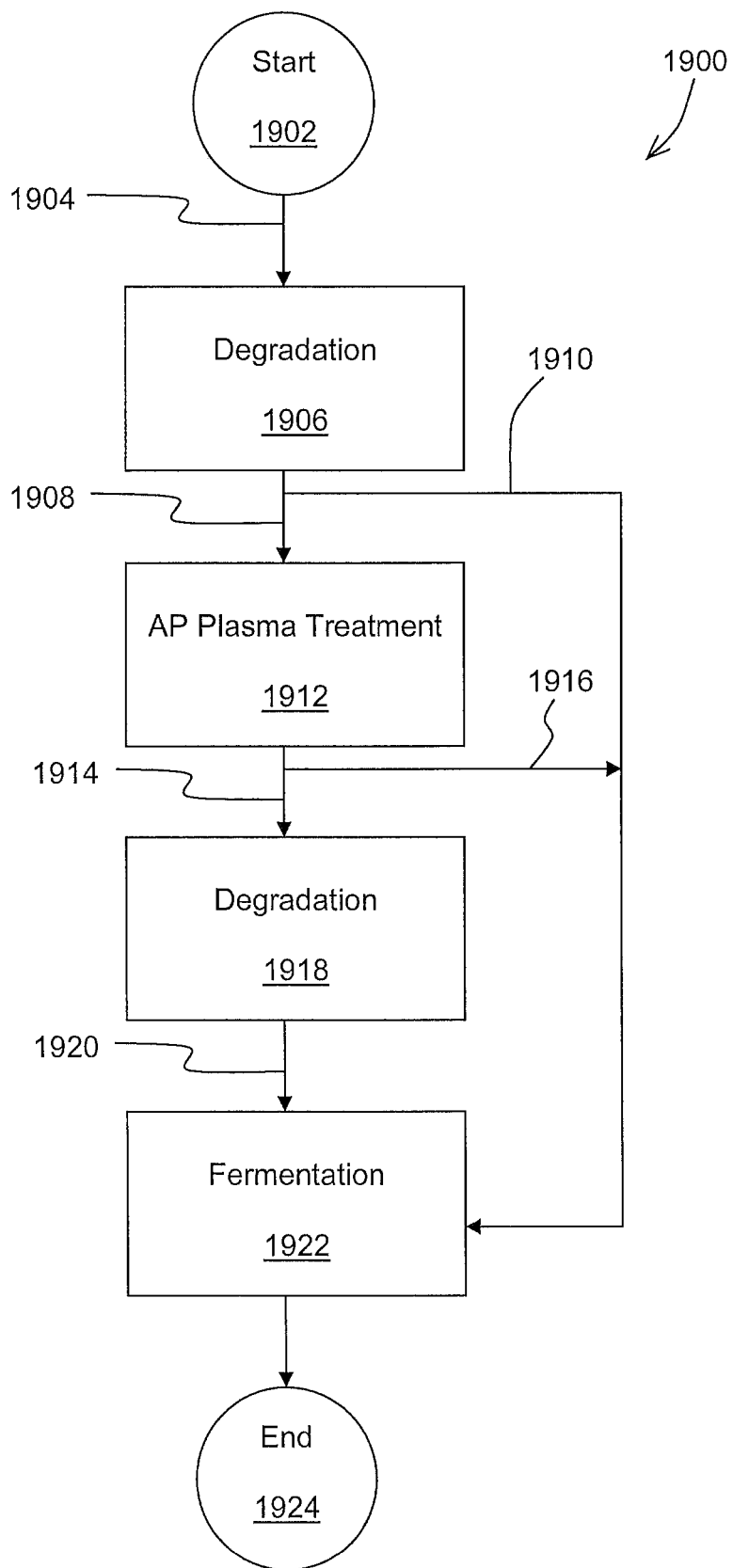


Fig. 19

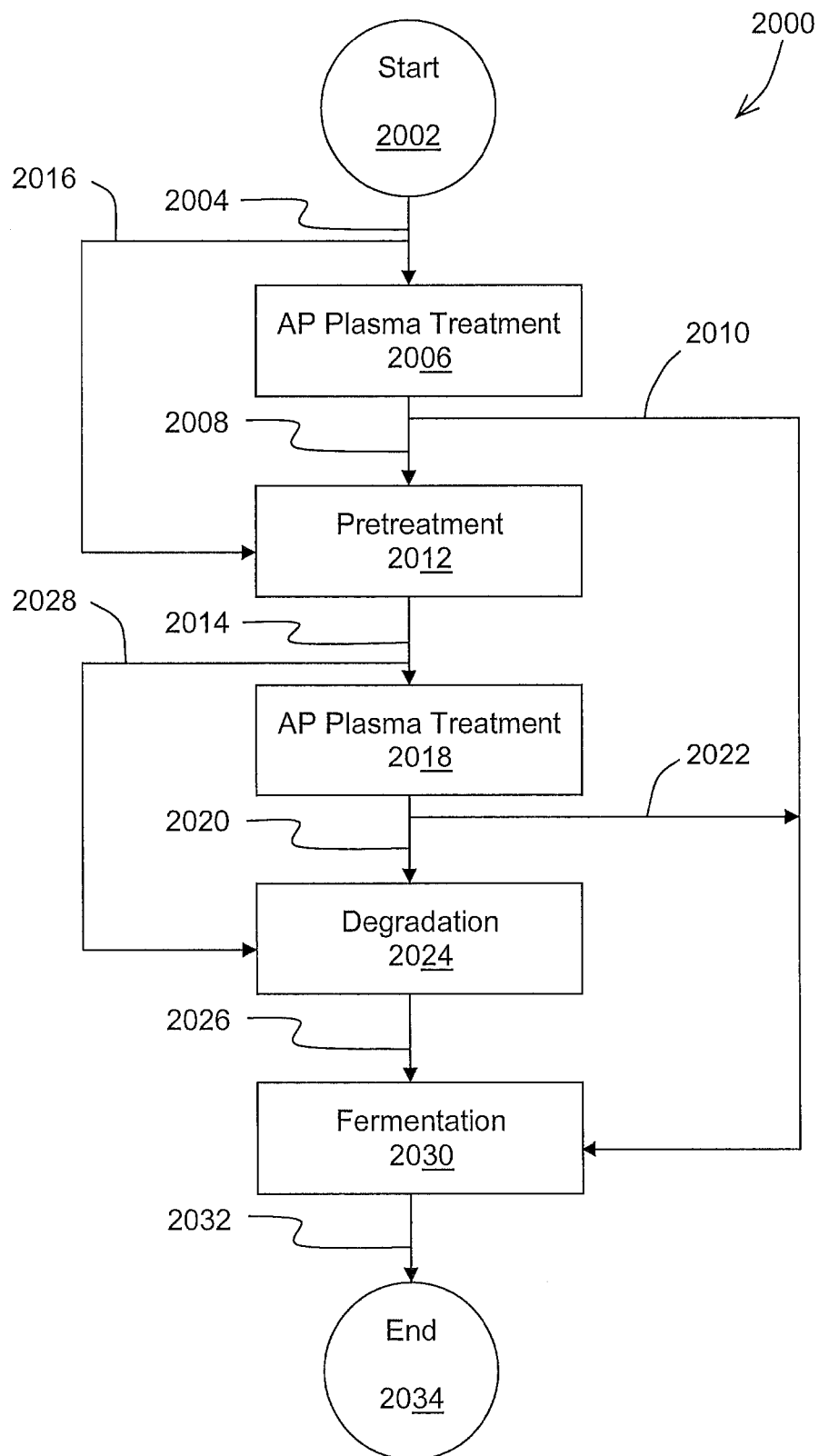


Fig. 20

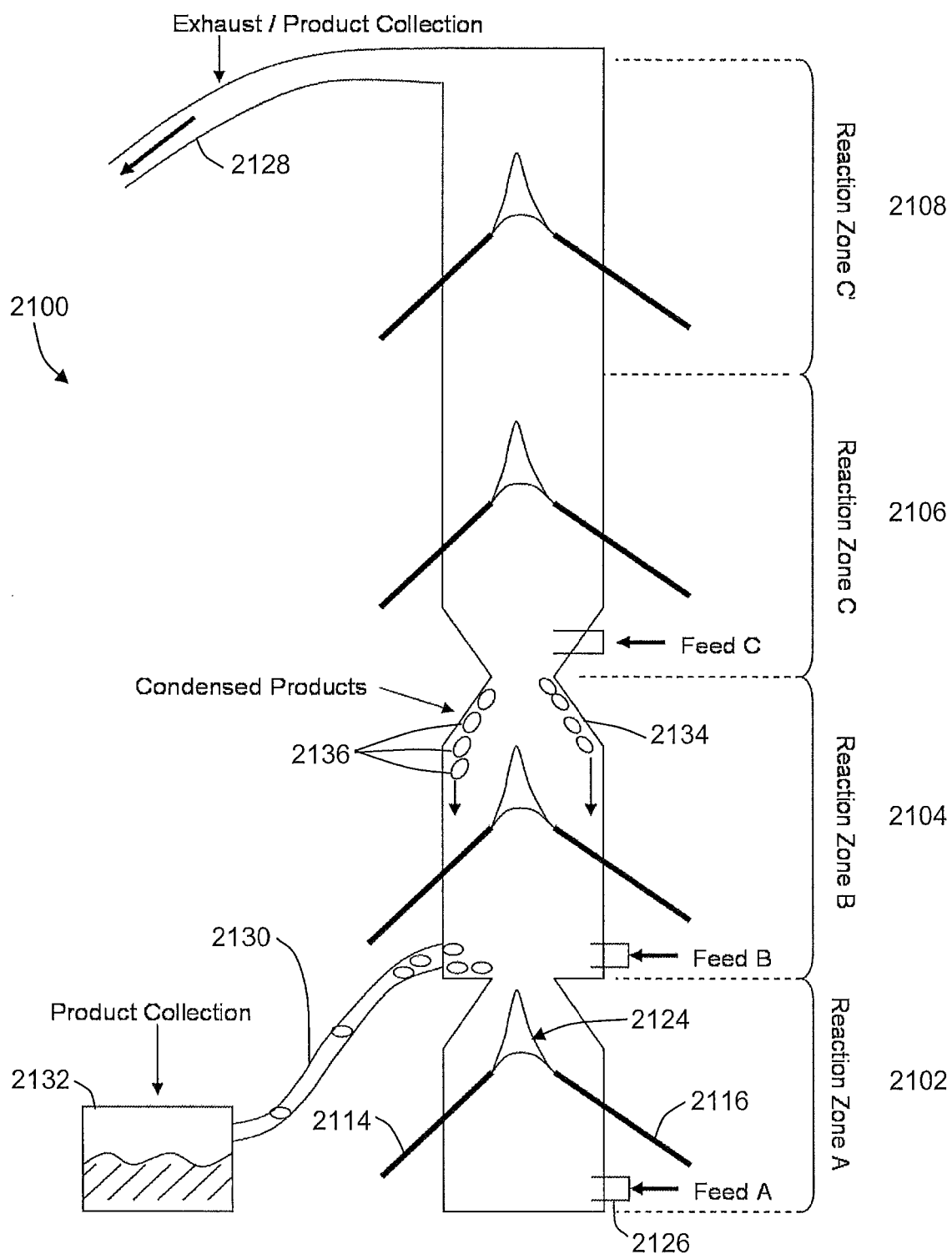


Fig. 21

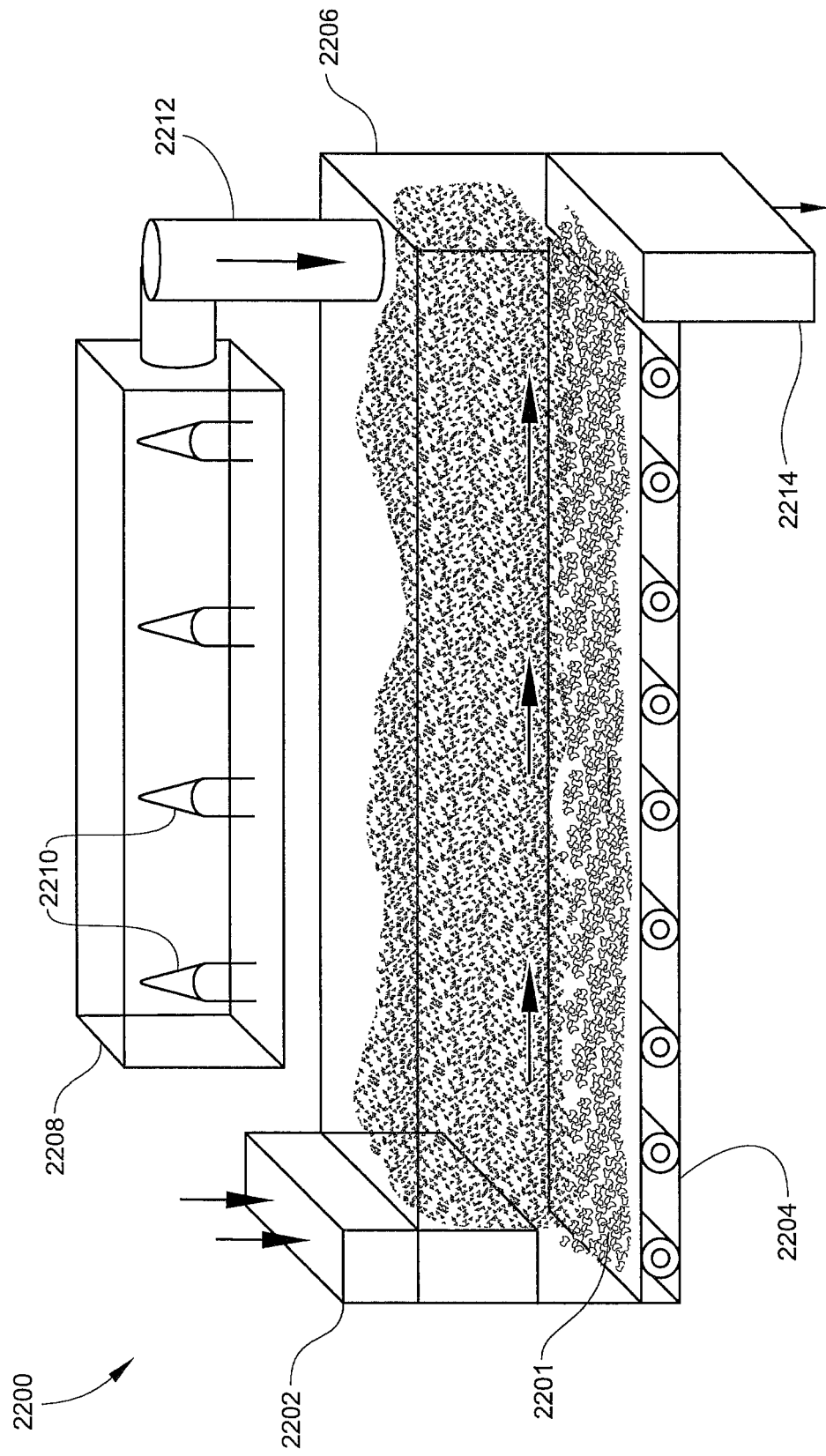


Fig. 22