

**ZEROS**  
**The Zero-emission Energy Recycling Oxidation**  
**System**  
**A Description for Non-Engineers**

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# **ZEROS**

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### **Executive Summary**

ZEROS (Zero-emission Energy Recycling Oxidation System) is an innovative “oxy-fuel” technology that uses pure oxygen to completely oxidize a variety of organic/hydrocarbon fuels with no air or water emissions and with complete sequestration of CO<sub>2</sub>. ZEROS technology was developed, patented, and commercialized in the late 1980s and 1990s by Mr. Steve L. Clark to clean up oilfield waste without producing atmospheric emissions or water pollution.

ZEROS combines several well-known technologies into a unique system with many advantages. Fuels are oxidized with pure oxygen from a co-located air separation unit. Initial gasification—partial oxidation of the fuels—is accomplished in the primary reaction vessel, a rotary kiln. The synthesis gas that is produced in the rotary kiln (primarily CO, CO<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>, and H<sub>2</sub>O) moves either

1. to a secondary reaction vessel where it is completely oxidized with pure oxygen to CO<sub>2</sub> and H<sub>2</sub>O (which are captured as pure liquid (or solid) CO<sub>2</sub> and distilled water) and the heat released is used to drive a steam turbine and electrical generator or
2. to a steam reformer and a modified, carbon-recycling Fischer-Tropsch reaction vessel to produce diesel fuel.

By using pure oxygen as the oxidant, the system can use low quality fuels that normally would not be considered for traditional incineration technologies. A variety of organic materials—including coal, lignite, municipal solid waste, wood waste, scrap tires, agricultural and forestry biomass, animal manure, sewage sludge, and a number of hazardous organic wastes—can be used as feedstocks to power the system. Finally, a ZEROS facility has no smokestack and has no

air or water emissions; it captures and renders harmless all oxides of nitrogen and sulfur, heavy metals, organic compounds, and other potential contaminants, including asbestos.

The ZEROS process is currently being commercialized in projects designed to produce up to 100,000,000 million gallons of diesel fuel per year and up to 50 MW (gross) of base load electrical energy. All CO<sub>2</sub> produced by the facility will be captured for sale/sequestration, mostly for enhanced crude oil recovery in mature oil fields. In addition, commercial quantities of pure N<sub>2</sub>, Ar<sub>2</sub>, distilled H<sub>2</sub>O, and several minor products will be sold through existing markets. These facilities will produce no air or water emissions, including the greenhouse gas CO<sub>2</sub>.

## **ZEROS Processes**

This document gives an easily understood, nontechnical description of ZEROS (Zero-emission Energy Recycling Oxidation System).

The ZEROS process is designed to produce diesel fuel, electricity, and pure CO<sub>2</sub>, N<sub>2</sub>, Ar<sub>2</sub>, distilled water, and several minor products from a variety of fuel sources, including traditional fuels such as coal, lignite, natural gas, and petroleum products, as well as combustible materials in municipal and industrial solid, liquid, and hazardous wastes. The process sequesters all CO<sub>2</sub> produced, releases no greenhouse gases, and produces no air or water emissions.

Nontechnical process information about most individual component processes of ZEROS is widely available from sources such as Wikipedia and other websites. More detailed discussions of many of component processes are available in ZEROS-related patents summarized at the end of this document. More quantitative descriptions of the amounts of fuel used and products produced, as well as economic projections for the project, are available in *pro forma* documents for specific ZEROS projects. Figures 1A, 1B, 1C, and 2 (at the end of this document, from US Patent Application 20080275278), illustrate the principal components and processes of a typical ZEROS facility. Numbers in the text (in bold italics) correspond to those in these diagrams.

## **Brief History of ZEROS Development**

The ZEROS process was developed and patented by Mr. Steve L. Clark over almost 20 years. The initial impetus for the system began with a contract to Oilwell Control Services (OCS) from a major oil company to remediate a large oil spill on land northwest of Los Angeles, California in 1992. Because of the large amount of oil-contaminated soil involved, the project required that the soil be cleaned and the site remediated with no air or water emissions or landfill disposal. To accomplish the project, OCS used a modified rotary kiln as a primary combustion chamber and a secondary oxidation chamber. Both chambers were a fired process with liquefied petroleum gas and pure oxygen, and were used to completely oxidize the organic contaminants in the soil at high temperatures. The system was operated below atmospheric pressure to avoid fugitive air emissions. The combustion gases, consisting primarily of CO<sub>2</sub> and H<sub>2</sub>O, were recycled as a synthetic combustion chamber atmosphere without N<sub>2</sub> to eliminate formation of NO<sub>x</sub>. The

resulting oxidation products, CO<sub>2</sub> and H<sub>2</sub>O, were condensed cryogenically, and the CO<sub>2</sub> and H<sub>2</sub>O were injected into an oil reservoir near the site of the spill.

The project was successful and OCS moved the transportable zero-emission waste disposal unit to several other locations in the southwest United States and used it to test remediate a number of contaminated sites (with no air or water emissions). Through this testing process, a number of feed constituents were tested and the process was improved. The development and improvement of the intellectual property was started and a number of patents were applied for and ultimately issued.

Because of a serious medical condition, Mr. Clark ceased operation of the OCS zero-emission waste disposal business and dismantled the transportable unit. After recovering from the medical condition, in 2003 Mr. Clark began the process of converting the process from a waste remediation to the ZEROS electrical and liquid fuel production process.

Mr. Clark has been granted ten U.S. patents and patents pending related to the ZEROS process. Between 1996 and 2011, these patents were conveyed to M-Ltd., a technology holding company. Patent summaries are given at the end of this document.

## **Fuel Sources**

One of the most important characteristics of ZEROS is its ability to use multiple types of fuel. These include traditional fuels such as coal, lignite, and natural gas, as well as nontraditional fuels like municipal and industrial/construction wastes, animal manure and sewage sludge, and agricultural and forestry biomass. In addition, these fuel sources can be mixed or fed sequentially into the ZEROS primary gasifier (rotary kiln). This flexibility is discussed in greater detail under “gasification” below.

## **Fuel Preparation and Injection.**

The fuel for a typical ZEROS solid waste-to-fuel facility can include a mix of combustible materials like paper, cardboard, wood, plastics, tires, and shingles. Other materials often found in municipal and construction/demolition waste include stones, concrete, gypsum board, and metals. If necessary, lighter materials, which normally include more combustible materials, are separated from denser materials by blowing the lighter materials over a short wall, leaving denser material behind for further separation and recycling.

Less dense materials that blow over the wall are loaded, typically with a front-end loader, into a barrel shredder. Shredded materials then enter an auger into which hot recirculating gas—principally CO<sub>2</sub> and H<sub>2</sub>O—is continuously injected, preheating the fuel and excluding N<sub>2</sub> from the ambient air. The preheated fuel, without significant N<sub>2</sub> from the ambient air, is then injected into the primary gasification chamber, a rotary kiln.

## **Rotary Kiln, Oxy-Fuel, Primary Gasification.**

The fuel is converted to gas in **primary combustion (gasification) chamber (10)**, a rotary kiln (approximately 8'x50'), which operates under high temperature (approximately 985°F or 529°C) and subambient pressure (approximately 10 psi) in a continuous process. The kiln is a large cylindrical vessel inclined slightly to the horizontal), which is rotated slowly about its axis. The basic components of a rotary kiln are the shell, the refractory lining, support rollers, and drive gear. The kiln shell is made from a rolled mild steel plate, usually between 15 and 30 mm thick, welded to form a cylinder. The refractory lining protects the steel shell from the high temperatures inside the kiln and the corrosive properties of the process material. Steel rollers support the kiln and allow rotation that is as nearly frictionless as possible. The kiln is usually turned by a variable-speed electric motor. The fuel to be gasified is fed into the lower end of the cylinder by the auger described above (designed to exclude almost all ambient air from the compacted fuel). As the kiln rotates, the fuel is stirred, mixed, and gasified as it gradually moves up the inclined kiln. Recirculating gases from the primary gasification chamber and secondary oxidation chamber constitute a synthetic gas atmosphere that allows production of a synthesis gas (syngas) composed primarily of CO<sub>2</sub>, CH<sub>4</sub>, CO, H<sub>2</sub>O, and H<sub>2</sub>. The temperature and oxygen concentration of the recirculating gases are carefully controlled by injecting H<sub>2</sub>O and pure O<sub>2</sub>, maintaining the chamber approximately 5% oxygen-starved or deficient. The carbon, oxygen, and hydrogen in the fuel (as well as some contaminants) are gasified before reaching the upper end of the kiln. Syngas is withdrawn from the rotary kiln and pumped to the secondary oxidation chamber or the liquid fuel synthesis unit (discussed below).

The rotary kiln is sealed with water jackets that surround all openings (like those where fuel, waste or recirculating gases enter or exit the kiln). These water seals assure that ambient air, and the N<sub>2</sub> it contains, cannot enter the kiln. Because the pressure of the synthetic gas atmosphere of the kiln is below that of ambient air outside the kiln, some water from the water jackets may enter the kiln. This is not problematic because a great deal more water must be injected into the kiln to help maintain temperatures within the optimal range for gasification.

### **Ash Removal from the Rotary Kiln (60)**

Solids that do not gasify (like calcium, magnesium, and potassium carbonates and silicates, as well as small amounts of metals) move down the sloping kiln bottom and are removed from the lower end by the ash drag for separation, packaging and sale, usually to cement manufacturers.

### **Oxy-Fuel Combustion**

Oxy-fuel combustion is the process of burning a fuel using pure oxygen instead of ambient air (with 80% N<sub>2</sub>) as the primary oxidant. In a ZEROS facility pure O<sub>2</sub> is injected into the rotary kiln in amounts needed for combustion and heating but not enough to completely oxidize the carbon in the fuel to CO<sub>2</sub> (approximately 5% starved). This process produces approximately 75%–80% less flue gas than air fueled combustion. Since the N<sub>2</sub> component of air is not present and does not need to be heated, less fuel is needed to raise internal kiln temperatures (to approximately 985°F or 529°C) for gasification. Pumps are used to remove gas from the kiln to maintain

subambient internal pressures. A portion of the flue gas (consisting primarily of CO, CO<sub>2</sub>, H<sub>2</sub>O, CH<sub>4</sub>, and H<sub>2</sub>) is recirculated to the kiln to maintain optimal temperature and composition of the kiln atmosphere. The remainder of the flue gas flows either to the secondary oxidation chamber or the liquid fuel reactor. Both these systems are described below.

Oxy-fuel combustion has significant advantages over traditional air-fired combustion. Among these are

- The flue gas is primarily CO<sub>2</sub>, suitable for sequestration.
- The mass and volume of the flue gas are reduced by approximately 75%–80%.
- Because the flue gas volume is reduced, less energy must be used to heat the flue gas.
- The size of the flue gas treatment equipment can be reduced by 75%.
- The concentration of pollutants in the flue gas is higher, making separation easier.
- Most of the flue gases are condensable; this makes compression separation possible.
- Heat of condensation can be captured and reused rather than lost in the flue gas.
- Because nitrogen from air is not allowed into the oxidation chamber, production of NO<sub>x</sub> is greatly reduced.

## **Oxygen Production for Oxy-Fuel Combustion**

An **air separation** plant is used to separate atmospheric air into O<sub>2</sub>, N<sub>2</sub>, and Ar<sub>2</sub>. The project is expected to use the most common air separation process, cryogenic distillation. This process was pioneered by Dr. Carl von Linde in the early 20th century and is still used today to produce high purity gases. To achieve the low distillation temperatures requires a refrigeration cycle, and the cold equipment has to be kept within an insulated enclosure (commonly called a "cold box"). The cooling of the gases requires a large amount of energy (provided by the ZEROS electrical generation unit) to drive the air compressor in the refrigeration unit. The air also has to be "clean" enough for cryogenic distillation, since water and CO<sub>2</sub> as well as other minor constituents of air can freeze in the cryogenic equipment.

The air separation plant includes the following main processes:

- Prefiltering to remove dust
- Removal of water vapor and CO<sub>2</sub> with a molecular sieve
- Refrigeration to produce liquid air
- Distillation to produce pure O<sub>2</sub>, N<sub>2</sub>, and Ar<sub>2</sub>
- Refrigeration to produce liquid O<sub>2</sub>, N<sub>2</sub>, and Ar<sub>2</sub>
- Storage until use or sale

## **Vacuum Chamber for Emergency Plant Shut-Down (124)**

Though highly unlikely, it is possible that control systems might fail, and the rotary kiln or secondary oxidation chamber might overheat, damaging the equipment. An emergency vacuum chamber is included in the design to quickly reduce the pressure (and temperature) within the kiln and secondary oxidation chamber if operating limits are exceeded.

## **Cyclone for Removal of Particulates (62)**

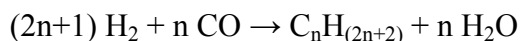
The producer gases exiting the kiln contain particulates (dust) and other undesirable constituents such as sulfur dioxide or hydrogen chloride. A cyclone is located near the exit of the rotary kiln to scrub particulates from exhaust gases before they pass to other ZEROS processes.

## **Liquid Fuel Synthesis (140, 142, 144, 148)**

ZEROS Fuel Technology (ZEROS FT) uses a combination of oxy-fuel syngas production and liquid fuel synthesis, a modified **Fischer-Tropsch (FT)** process that converts carbon monoxide and hydrogen into liquid hydrocarbons. The FT process, a key component of most gas-to-liquids technologies, has long been used to produce a number of synthetic fuels and lubricants, typically from coal, natural gas, or biomass.

A primary commercial product of a typical ZEROS project is up to 100,000,000 gallons of diesel fuel per year. ZEROS FT converts syngas from the primary gasification chamber (rotary kiln) to liquid fuel. In order to maximize liquid fuel production, up to 70% of the syngas exiting the primary gasification chamber, is diverted to the liquid fuel reactor (**144**). The remaining syngas is used to generate energy in the form of electricity, steam, and heat needed to power the entire ZEROS facility.

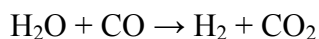
The Fischer-Tropsch-like ZEROS FT process involves a series of chemical reactions that lead to a variety of hydrocarbons, including straight-chain alkanes, some of which can be used to produce ultra-low sulfur synthetic diesel with high cetane ratings. Useful reactions give straight-chain alkanes by the following general reaction:



Usually, only relatively small quantities of nonalkane products are formed.

Syngas derived from coal or biomass tends to have relatively low H<sub>2</sub>:CO ratios (<1). However, for the reaction to maximize alkane production, the optimum ratio of H<sub>2</sub>:CO is above 2. ZEROS uses a **steam reformer** to increase the H<sub>2</sub>:CO ratio of reactant gases entering the liquid fuel reactor to at least 2.

The **water gas shift reaction** in the steam reformer (**140**) increases the content of H<sub>2</sub> in the ZEROS syngas.



The reaction is produced by injecting steam from any one of several ZEROS facility sources into the syngas stream between the primary gasification chamber and the liquid fuel synthesis reactor. In addition, H<sub>2</sub> derived from some of the CH<sub>4</sub> in the syngas may be converted to H<sub>2</sub> in the steam reformer.

After passing through the steam reformer, the H<sub>2</sub>-enriched syngas passes to the (Fischer-Tropsch-like) liquid fuel synthesis reactor, which in the ZEROS facility is operated in the low temperature range of 200°C–240°C (392°F–464°F), to maximize production of high quality fuels like diesel. Nevertheless, the liquid fuel synthesis reaction produces a variety of hydrocarbons of differing molecular weights. The liquid hydrocarbons produced can be sent to an isomerization unit (**148**) to upgrade the quality of the fuel. Additionally, a cracking tower may be used to convert the larger hydrocarbon chains, such as waxes and paraffins, to smaller molecules such as diesel, kerosene, and naphtha. A fractionation column (**142**) can be used to separate diesel from other products; if these other products do not have a ready market, they can be returned to the primary gasification chamber (**10**) as feedstock.

The percentage conversion (by weight) by the Fischer-Tropsch process of different feedstocks to diesel fuel varies:

- Wood (fresh cut) 45%
- Cellulose/lignin 45%
- Switch grass 43%
- Western coal 42%
- Bituminous coal 42%
- Petroleum coke 40%
- Dairy waste 29%

For example, 16.7 tons of switch grass containing 10% ash, 20% moisture, and 6,700 btu/lb will produce approximately 7.15 tons (2,000 gal) of diesel fuel (assuming 85% efficiency and 70% of the flue gas is sent to the Fischer-Tropsch reactor).

The largest scale implementation of Fischer-Tropsch technology is in a series of plants operated by Sasol in South Africa, a country with large coal reserves but lacking in oil. Sasol uses coal and natural gas as feedstocks and produces a variety of synthetic petroleum products, including most of the country's diesel fuel. On a smaller scale, Syntroleum has produced over 400,000 gallons of diesel and jet fuel from the Fischer-Tropsch process using natural gas and coal at its demonstration plant near Tulsa, Oklahoma.

## Secondary Oxidation

Syngas that is not diverted to liquid fuel synthesis moves to the **secondary combustion (oxidation) chamber (20)**. In this vertical combustion chamber, the syngas is combined with



pure O<sub>2</sub> (approximately 5% oxygen rich) from the air separation unit to completely oxidize the syngas to CO<sub>2</sub>. The temperature of this highly exothermic oxidation process is controlled (2,400°F or 1,316°C) by injecting water into the chamber. Additional CO from the high-temperature reaction of CO<sub>2</sub> and activated carbon (the Boudouard equilibrium reaction, see description below) can also be added to the secondary oxidation chamber, increasing heat yield.

Reaction products, consisting primarily of CO<sub>2</sub> and H<sub>2</sub>O, exit the top of the secondary oxidation chamber. Any solids, ash, or other particulates that are not oxidized to CO<sub>2</sub> are removed from the bottom cones section of the secondary oxidation chamber.

## Generation of Electricity

A **Rankine cycle** steam turbine and generator converts heat from the secondary oxidation chamber to electricity. This is process used in conventional power generation plants. The working fluid in a Rankine cycle follows a closed loop and is reused constantly. There are four processes in the Rankine cycle:

**Process 1-2:** The working fluid is pumped from low to high pressure, as the fluid is a liquid at this stage the pump requires little input energy.

**Process 2-3:** The high pressure liquid enters the **energy recovery boiler (14)** where it is heated at constant pressure by heat from the secondary oxidation chamber to become a dry saturated vapor.

**Process 3-4:** The dry saturated vapor expands through a **steam turbine (130)** that drives a **generator (132)**. This decreases the temperature and pressure of the vapor, and some condensation may occur.

**Process 4-1:** The wet vapor then enters a **condenser (136)** where it is condensed at a constant pressure to become a saturated liquid (the working fluid in Process 1-2).

The steam turbine driven by the Rankine cycle turns a generator to produce electricity. Typical ZEROS projects are designed to produce a maximum of 50 MW gross (39 MW net after powering the operations of the plant) when electricity generation is maximized. A minimum of 13 MW is needed to power ZEROS component systems when synthetic diesel fuel production is maximized. Electricity in excess of that used by the ZEROS facility will be sold to the electrical grid at rates defined by the Texas Public Utility Commission for small (less than) 50 MW generation facilities.

## Flue Gas Processing

After heating the working fluid of the Rankine cycle boiler, the dusty gases from the secondary oxidation chamber must be scrubbed of any remaining contaminants in order to purify and sequester the CO<sub>2</sub> and other constituents it contains.

After heating the working fluid of the Rankine cycle **heat exchanger/energy recovery boiler (14)**, the flue gas is transferred to the **baghouse (66)**, where fabric collectors filter dust particulates from dusty gases. They are one of the most efficient and cost effective types of dust

collectors available and can achieve a collection efficiency of more than 99% for very fine particulates. The bags can be of woven or felted cotton, synthetic, or glass-fiber material in either a tube or envelope shape. The high efficiency of these collectors is due to the dust cake formed on the surfaces of the bags. The fabric primarily provides a surface on which dust particulates collect, and activated carbon can be injected into the baghouse to assist in the removal of particulates.

Filtered gas at approximately 450°F (232°C) and consisting primarily of CO<sub>2</sub> (but also containing any excess O<sub>2</sub> from the secondary oxidation chamber, oxides of nitrogen from nitrogen in the fuel, acid gases, and small amounts of heavy metal contaminants) enters the **combustion gas manifold (70)**. From the manifold, the majority of the gas is routed for additional gas polishing, purification, and condensation for sale.

The remaining gas is split into two streams. Each of the streams is passed through an **activated carbon filter (78)** and **plasma torch (122)**. At this temperature (450°F) carbon from the activated carbon filter reacts with the CO<sub>2</sub> in the gas to form CO (the Boudouard equilibrium reaction, see section below). This endothermic reaction reduces the temperature of the gas to approximately 175°F (79°C), and it is then injected into the primary gasification chamber (rotary kiln) and secondary oxidation chamber. These two gas streams are carefully monitored for their O<sub>2</sub> concentrations, and their flow rates are adjusted to help control the O<sub>2</sub> concentrations of the primary gasification chamber and the secondary oxidation chamber.

The **Boudouard equilibrium**, which is endothermic, is used to produce additional CO and heat energy from CO<sub>2</sub> and C.



The ZEROS process combines activated carbon with CO<sub>2</sub> to increase the CO concentration of the gas stream by means of the Boudouard equilibrium reaction. The carbon used by the reaction to produce CO is derived from consumption of the activated carbon filters **(78)** located between the combustion gas manifold **(70)** and the primary **(10)** and secondary **(20)** gasification/oxidation chambers. In either case, the CO-enriched hot gas is used to supplement the syngas fuel produced by the primary gasification chamber and/or secondary oxidation chamber. The use of this additional source of carbon fuel substantially increases the heat energy production of the ZEROS process.

The flue gas that is destined for purification and condensation is passed through an **electron beam reactor/ozone oxidation chamber (80/82)**. The electron beam/ozone reactor breaks down (oxidizes) any residual organic compounds in the flue gas and electrostatically charges particulate matter in the gas stream. The gas then moves to an **electrostatic precipitator and catalytic reactor (84)** to remove particulates.

The acidic flue gas is cooled by allowing it to expand, water is added to remove acid gases (such as HCl that may be formed by oxidation of halogenated feedstocks), and the liquid is passed through an **acid scrubber (86)** that uses alkali to neutralize the acid. The resulting salt solution is

filtered and partially evaporated using low-pressure steam to generate a 42% brine solution that can be marketed for use by the oil and gas industry.

The gas exiting the acid scrubber is composed largely of CO<sub>2</sub> from oxidation of syngas and H<sub>2</sub>O from (1) syngas oxidation, (2) quench water used to moderate gas temperatures, and (3) the liquid fuel synthesis reaction. The gas is cooled to condense the water vapor, and the remaining dry CO<sub>2</sub> is refrigerated, pressurized, and prepared for sale as either dry ice or supercritical CO<sub>2</sub> by the **CO<sub>2</sub> recovery unit (18)**.

The condensed H<sub>2</sub>O moves to the electrolyzer **(150)**, where low voltage electrical current converts it into H<sub>2</sub> and O<sub>2</sub>. These gases, along with residual H<sub>2</sub>O, are passed through a series of gas reverse osmosis **membranes (154, 156, 158)** for separation and eventual sale.

## **CO<sub>2</sub> Sequestration**

Carbon sequestration refers to long-term storage of CO<sub>2</sub> or other forms of carbon to either mitigate or defer global warming. It has been proposed as a way to slow the atmospheric and marine accumulation of greenhouse gases, which are released by burning fossil fuels.

CO<sub>2</sub> has been used extensively in enhanced crude oil recovery operations in the United States, beginning in 1972. There are in excess of 10,000 wells that inject CO<sub>2</sub> in the state of Texas alone. The gas comes in part from anthropogenic sources, but is principally from large naturally occurring geologic formations of CO<sub>2</sub>. It is transported to the oil-producing fields through a large network of over 5,000 kilometers (3,100 mi) of CO<sub>2</sub> pipelines.

Typical ZEROS projects will sequester all CO<sub>2</sub> produced by the facility for sale, either as dry ice or supercritical CO<sub>2</sub>. Below  $-78.51^{\circ}\text{C}$  ( $-109.3^{\circ}\text{F}$ ), CO<sub>2</sub> exists as a solid, **dry ice**, which changes directly from a solid phase to a gaseous phase through sublimation. It can often be found in grocery stores and laboratories and is used in the shipping industry. The largest noncooling use for dry ice is blast cleaning.

**Supercritical CO<sub>2</sub>** refers to CO<sub>2</sub> that is in a fluid state while also being at or above both its critical temperature and pressure, yielding rather uncommon properties. CO<sub>2</sub> usually behaves as a gas in air at standard temperature and pressure or as dry ice when frozen. If the temperature and pressure are both above the critical point for CO<sub>2</sub>, it can adopt properties midway between a gas and a liquid. More specifically, it behaves as a supercritical fluid above its critical temperature (31.1 C, 88.0°F) and critical pressure (72.9 atm/7.39 MPa/1,071 psi), expanding to fill its container like a gas but with a density like that of a liquid. Supercritical CO<sub>2</sub> is becoming an important commercial and industrial solvent due to its role in chemical extraction in addition to its low toxicity and environmental impact. The relatively low temperature of the process and the stability of CO<sub>2</sub> also allows most compounds to be extracted with little damage or denaturing.

CO<sub>2</sub> is used in enhanced oil recovery where it is injected into or adjacent to producing oil wells, usually under supercritical conditions. It acts as both a pressurizing agent and, when dissolved into the underground crude oil, significantly reduces its viscosity, enabling the oil to flow more rapidly through the earth to the removal well. The unique properties of supercritical CO<sub>2</sub> ensure that it will remain out of the atmosphere. Supercritical CO<sub>2</sub> has been used for more than 30 years to enhance oil recovery in mature oil fields, where extensive pipe networks are used to carry the CO<sub>2</sub> to the injection points.

## Why is ZEROS Unique?

The ZEROS process is unique for several reasons.

- 1. Standard Components.** ZEROS uses well-known and well-tested technologies. Air separation units, barrel shredders, rotary kilns, heat recovery steam generators, gas turbines, electric generators, Fischer-Tropsch-like liquid fuel synthesis equipment, cracking towers, isomerization units, steam reformers, fractionation columns, vacuum chambers, cyclones, bag houses, refrigeration units, condensers, acid scrubbers, cryo-separation units, and other components are well known off-the-shelf components.
- 2. Rotary Kiln Gasification.** The 8'x50' **rotary kiln** primary oxidation (gasification) chamber (with a synthetic, O<sub>2</sub>-starved, N<sub>2</sub>-free, subambient-pressure, recirculating, synthetic atmosphere) provides an excellent environment for primary gasification. Its continuous rotary agitation of the fuel provides repeated exposure to the hot gases of the synthetic atmosphere. Finally, it is a robust technology that tolerates a wide variety of fuel types with wide variation in moisture contents and noncombustible materials like calcium, silicon, and other minerals.
- 3. Oxyfuel Combustion.** ZEROS uses an oxyfuel combustion process that eliminates almost all N<sub>2</sub> (and NO<sub>x</sub>) from the flue gas. The synthetic hot gas mixture generated in the primary (gasification) and secondary (oxidation) combustion chambers is used to heat boilers and other equipment throughout the facility, as well as providing the synthetic atmosphere in the primary gasification chamber (the rotary kiln). This recirculating hot gas atmosphere is composed primarily of CO<sub>2</sub>, H<sub>2</sub>O, and CO (and contains almost no N<sub>2</sub>). Since CO<sub>2</sub>, H<sub>2</sub>O, and CO are good emitters of thermal energy, but N<sub>2</sub> is not, the synthetic gas atmosphere in an oxyfuel ZEROS facility more efficiently heats boilers and other equipment than does the N<sub>2</sub>-rich flue gas of air blown systems. This substantially increases the fuel efficiency of the energy recovery boiler used to drive the steam turbine and generator.
- 4. No N<sub>2</sub>.** By eliminating the N<sub>2</sub> of ambient air from the combustion chambers, the ZEROS process also drastically reduces (by 75%–80%) the volume of flue gas that must be processed. Because there is no N<sub>2</sub> to heat, several energy-demanding processes are possible.
  - More heat energy is available to heat the CO<sub>2</sub>, H<sub>2</sub>O, and CO in the combustion gases.

- No heat is lost in gases emitted to the atmosphere (ZEROS has no smokestack).
- Heat energy is available to drive the endothermic Boudouard equilibrium and the water gas shift reaction, which enrich the syngas stream with CO and H<sub>2</sub>, respectively, increasing diesel fuel yields.
- Heat energy is available to produce steam and electricity needed to power the air separation unit and refrigeration units needed to separate and capture O<sub>2</sub>, N<sub>2</sub>, H<sub>2</sub>O, CO<sub>2</sub>, and Ar<sub>2</sub>.

**5. Input-Output Flexibility.** No summary of the ZEROS process would be complete without a brief discussion of input-output (fuel/product) flexibility. Because a rotary kiln is the primary gasification chamber, the ZEROS process can use a wide variety of carbon-based fuels, including traditional fuels like coal, lignite, and natural gas as well as many “low quality” fuels that are difficult or impossible to use with other systems. These include municipal and industrial solid wastes, agricultural and forestry wastes, sewage sludge and animal manures, scrap tires, petroleum coke, and soil-contaminated coal and lignite. Many of these nontraditional fuels generate both a substantial tipping fee and produce adequate syngas and heat to power ZEROS processes. The robust character of the primary gasification system allows these fuels to be mixed or introduced sequentially throughout the day or season, greatly facilitating use of seasonal fuels such as agricultural biomass.

Output flexibility includes both design and operational flexibility. Depending on local energy and water needs, a ZEROS facility can be designed and/or operated to maximize production of transportation fuel, electricity, or distilled water. In fact, allocation of system syngas and heat energy can be changed on short notice (hours) to produce more liquid fuel or electricity, as desired and in response to local markets.

- 6. Historic Operation.** With the exception of the ZEROS FT synthetic diesel production process, all ZEROS components were operated as integrated units for most of the 1990s by OCS. During this period, four complete zero-emission units were operated in California, Arizona, Texas, and Mississippi on several projects funded by oil companies and the U.S. Government, and to clean up oil field waste, hazardous military munitions and wastes on military bases, and a variety of agricultural wastes, all with no air or water emissions.
- 7. Hazardous Waste Disposal.** ZEROS plants can completely destroy (convert completely to CO<sub>2</sub> and H<sub>2</sub>O) a wide variety of toxic or dangerous wastes (dioxins, furans, PCBs, red bag medical wastes, dead animals, etc.) and denature asbestos to harmless sand-like granules. Such services typically demand substantial tipping fees. In addition, production of electricity and transportation fuels from renewable sources and sequestration of large amounts of atmospheric CO<sub>2</sub> may have substantial monetary or regulatory value to the owner/operators of ZEROS facilities.

- 8. Profitability.** Output (economic product) flexibility is another near-unique feature of ZEROS. The system can simultaneously produce for sale: low sulfur synthetic diesel (or other transportation) fuel, electricity, dry ice or supercritical CO<sub>2</sub>, N<sub>2</sub> and Ar<sub>2</sub> (from the air separation unit), O<sub>2</sub>, H<sub>2</sub>, distilled H<sub>2</sub>O, concentrated salt solutions, ash products, and steam. At any particular ZEROS facility, the value of these outputs (and the tipping fees for disposing of municipal and industrial wastes) will vary depending on the needs of surrounding industries and the capacities of local transportation systems. However, it is safe to assume that most or all of these products will have substantial markets long into the future.

## **ZEROS Patents**

The ZEROS process is protected by the following U.S. patents and patent applications:

### **U.S. 5,906,806 — Reduced Emission Combustion Process with Resource Conservation and Recovery Options “ZEROS” Zero-emission Energy Recycling Oxidation System.**

A system and a process for combusting hydrocarbons to recover energy and the CO<sub>2</sub> resulting from the combustion is provided. The process utilizes a two-stage combustion process, each stage utilizing water injection and a recirculation stream to increase the efficiency of combustion to generate larger proportions of CO<sub>2</sub>. An energy recovery boiler is used to recover heat energy from the combustion product. Combustion product is then cleaned and the CO<sub>2</sub> is separated and condensed into a useable liquid CO<sub>2</sub> product.

### **U.S. 6,024,029 — Reduced Emission Combustion System.**

The invention is a combustion process which maximizes the ratio of CO<sub>2</sub> level to the level of all other combustion gas constituents in the post combustion chamber gas stream and facilitates the efficient capture and liquefaction of the CO<sub>2</sub> produced by the hydrocarbon fuels combustion process for use as a commercial product. When optimally employed the process yields only CO<sub>2</sub>, water vapor and oxygen as constituents of the combustion gas stream. All of these constituents may be segregated, captured, contained and reused in the process, filtered and discharged as liquid or sold to other interests as a commercial product for beneficial use. In less than optimum applications the hydrocarbon fuels being combusted might contain chemical impurities such as sulphur, chlorine, nitrogen, and inorganic refractory constituents. To facilitate the employment of the process in these less than optimum circumstances various means of removal, neutralization and containment of the combustion byproducts from the fuel impurities are included in the invention. When practical these "undesirable" combustion byproducts may be converted into usable commercial products.

### **U.S. 6,119,606 — Reduced Emission Combustion Process.**

The invention is a combustion process which maximizes the ratio of CO<sub>2</sub> level to the level of all other combustion gas constituents in the post combustion chamber gas stream and facilitates the

efficient capture and liquefaction of the CO<sub>2</sub> produced by the hydrocarbon fuels combustion process for use as a commercial product. When optimally employed the process yields only CO<sub>2</sub>, water vapor and oxygen as constituents of the combustion gas stream. All of these constituents may be segregated, captured, contained and reused in the process, filtered and discharged as liquid or sold to other interests as a commercial product for beneficial use. In less than optimum applications the hydrocarbon fuels being combusted might contain chemical impurities such as sulphur, chlorine, nitrogen, and inorganic refractory constituents. To facilitate the employment of the process in these less than optimum circumstances various means of removal, neutralization and containment of the combustion byproducts from the fuel impurities are included in the invention. When practical these "undesirable" combustion byproducts may be converted into usable commercial products.

**U.S. 6,137,026 — ZEROS Bio-Dynamics, A Zero-Emission Non-Thermal Process for Cleaning Hydrocarbon from Soils.**

A combination of parallel processes is disclosed to provide optimal remediation operations for contaminated soil. Soils with high levels of heavy petroleum hydrocarbons are directed to a thermal process for destruction in a combustion process. CO<sub>2</sub> generated and recovered in the thermal process is employed as a solvent in a solvent process to clean other soils of petroleum hydrocarbons and certain chlorinated hydrocarbon compounds. In the solvent process, contaminated soils are run through a closed soil separator where the soils are washed with CO<sub>2</sub>. The CO<sub>2</sub> is then dried from the soil and the soil is sent for segregation. Soils with the lightest forms of hydrocarbon contamination (gasoline, etc.) are subjected to a vaporization process utilizing heat energy generated in the thermal process to heat the soil, under a partial vacuum, and the vapors generated are captured, condensed, and recovered as product.

**U.S. 6,688,318 B1— Process for Cleaning Hydrocarbons from Soils.**

The present invention is a combination of parallel processes that provide optimal remediation operations for contaminated soil. Soils with high levels of heavy petroleum hydrocarbons are directed to a thermal process for destruction in a combustion process. CO<sub>2</sub> generated and recovered in the thermal process is employed as a solvent in a solvent process to clean soils having moderate contamination with petroleum hydrocarbons and chlorinated hydrocarbon compounds. In this solvent process, contaminated soils are run through a closed soil separator where the soils are washed with CO<sub>2</sub>. The CO<sub>2</sub> is then dried from the soil and the soil is sent for segregation. Additionally, soils with the lightest forms of hydrocarbon contamination, such as gasoline, etc., are subjected to a vaporization process utilizing heat energy generated from the thermal process to heat the soil under a partial vacuum. The vapors generated are captured, condensed, and recovered as product.

**U.S. 7,338,563 B2 — Process for Cleaning Hydrocarbons from Soils.**

The present invention is a combination of parallel processes that provide optimal remediation operations for contaminated soil. Soils with high levels of heavy petroleum hydrocarbons are directed to a thermal process for destruction in a combustion process. CO<sub>2</sub> generated and recovered in the thermal process is employed as a solvent in a solvent process to clean soils

having moderate contamination with petroleum hydrocarbons and chlorinated hydrocarbon compounds. In this solvent process, contaminated soils are run through a closed soil separator where the soils are washed with CO<sub>2</sub>. The CO<sub>2</sub> is then dried from the soil and the soil is sent for segregation. Additionally, soils with the lightest forms of hydrocarbon contamination, such as gasoline, etc., are subjected to a vaporization process utilizing heat energy generated from the thermal process to heat the soil under a partial vacuum. The vapors generated are captured, condensed, and recovered as product.

**U.S. Patent 7,833,296 --- Reduced-Emission Gasification and Oxidation of Hydrocarbon Materials for Power Generation.**

A system and process for maximizing the generation of electrical power from a variety of hydrocarbon feedstocks. The hydrocarbon feedstocks are first gasified and then oxidized in a two-chamber system and process using oxygen gas rather than ambient air. Intermediate gases generated in the system and process are recirculated and recycled to the gasification and oxidation chambers in order to maximize energy production. The energy produced through the system and process is used to generate steam and produce power through conventional steam turbine technology. In addition to the release of heat energy, the hydrocarbon feedstocks are oxidized to the pure product compounds of water and CO<sub>2</sub>, which are subsequently purified and marketed. The system and process minimizes environmental emissions

**U.S. Patent Application 20080078122 A1 — Reduced-Emission Gasification And Oxidation Of Hydrocarbon Materials for Hydrogen And Oxygen Extraction.**

A system and process for maximizing the generation of marketable products from a variety of hydrocarbon feedstocks. The hydrocarbon feedstocks are first gasified and then oxidized in a two-chamber system and process using oxygen gas rather than ambient air. Intermediate gases generated in the system and process are recirculated and recycled to the gasification and oxidation chambers in order to maximize both energy generation and the resulting stoichiometric reaction products. The energy produced through the system and process is used to generate steam and produce power through conventional steam turbine technology. In addition to the release of heat energy, the hydrocarbon feedstocks are oxidized to the pure product compounds of water and CO<sub>2</sub>. The CO<sub>2</sub> is subsequently purified and marketed. The water recovered from the system and process is collected and electrolyzed to generate oxygen and hydrogen gases. These gases are separated using conventional gas separation technologies and also marketed. The system and process minimizes environmental emissions.

**US Patent Application 20080184621 – Reduced-Emission Gasification and Oxidation of Hydrocarbon Materials for Power Generation.**

A system and process for maximizing the generation of electrical power from a variety of hydrocarbon feedstocks. The hydrocarbon feedstocks are first gasified and then oxidized in a two-chamber system and process using oxygen gas rather than ambient air. Intermediate gases generated in the system and process are recirculated and recycled to the gasification and oxidation chambers in order to maximize energy production. The energy produced through the system and process is used to generate steam and produce power through conventional steam



turbine technology. In addition to the release of heat energy, the hydrocarbon feedstocks are oxidized to the pure product compounds of water and CO<sub>2</sub>, which are subsequently purified and marketed. The system and process minimizes environmental emissions.

**US Patent Application 20080275278 - Reduced-Emission Gasification and Oxidation of Hydrocarbon Materials for Liquid Fuel Production.**

A system and process are disclosed for the controlled combustion of a wide variety of hydrocarbon feedstocks to produce thermal energy, liquid fuels, and other valuable products with little or no emissions. The hydrocarbon feeds, such as coal and biomass, are first gasified and then oxidized in a two-chamber system/process using pure oxygen rather than ambient air. A portion of the intermediate gases generated in the system/process are sent to a Fischer-Tropsch synthesis process for conversion into diesel fuel and other desired liquid hydrocarbons. The remaining intermediate gases are circulated and recycled through each of the gasification/oxidation chambers in order to maximize energy production. The energy produced through the system/process is used to generate steam and produce power through conventional steam turbine technology. In addition to the release of heat energy, the hydrocarbon fuels are oxidized to the pure product compounds of water and CO<sub>2</sub>, which are subsequently purified and marketed. The system/process minimizes environmental emissions.

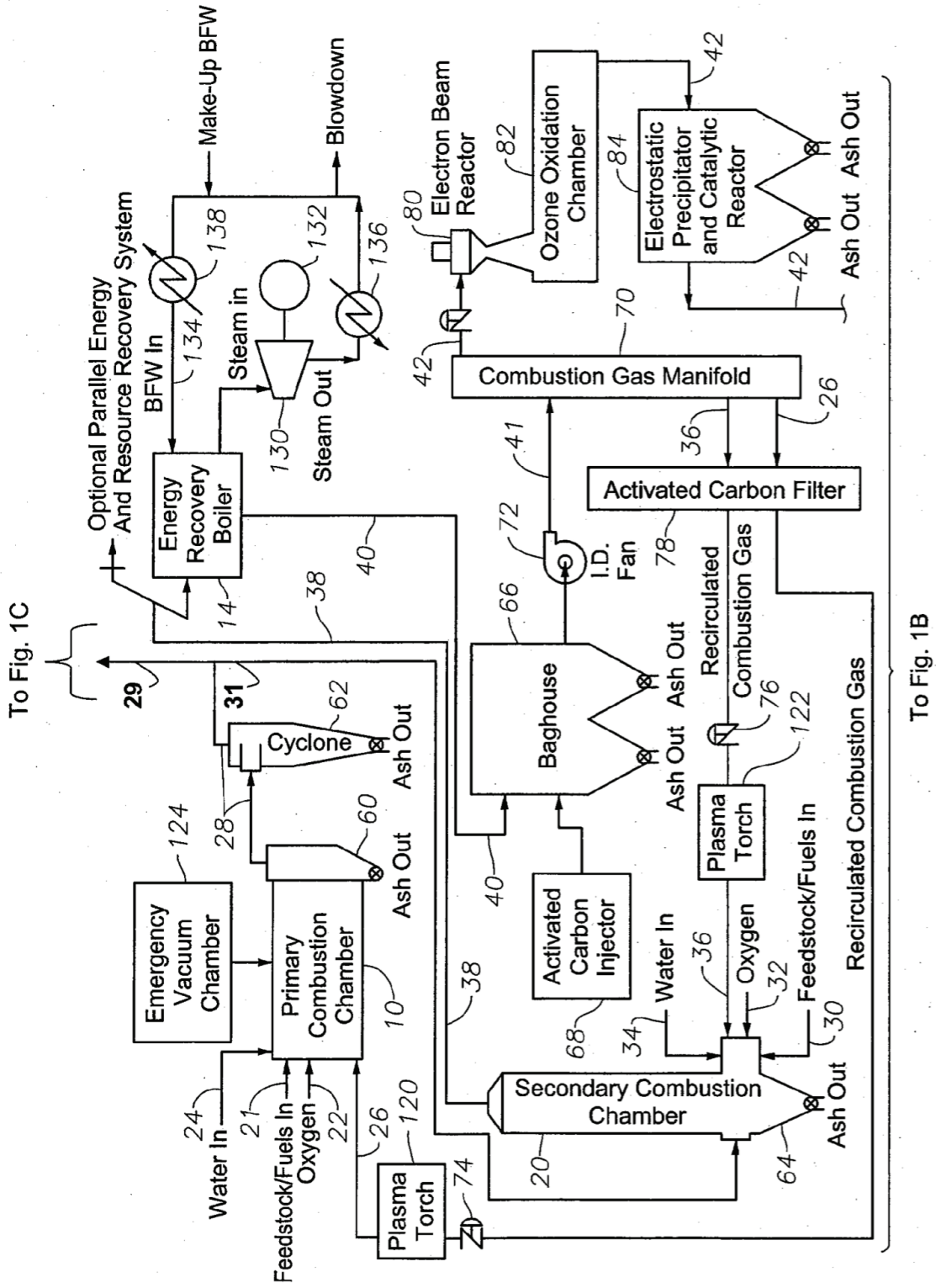


Figure 1A

To Fig. 1C

To Fig. 1B

From Fig. 1A

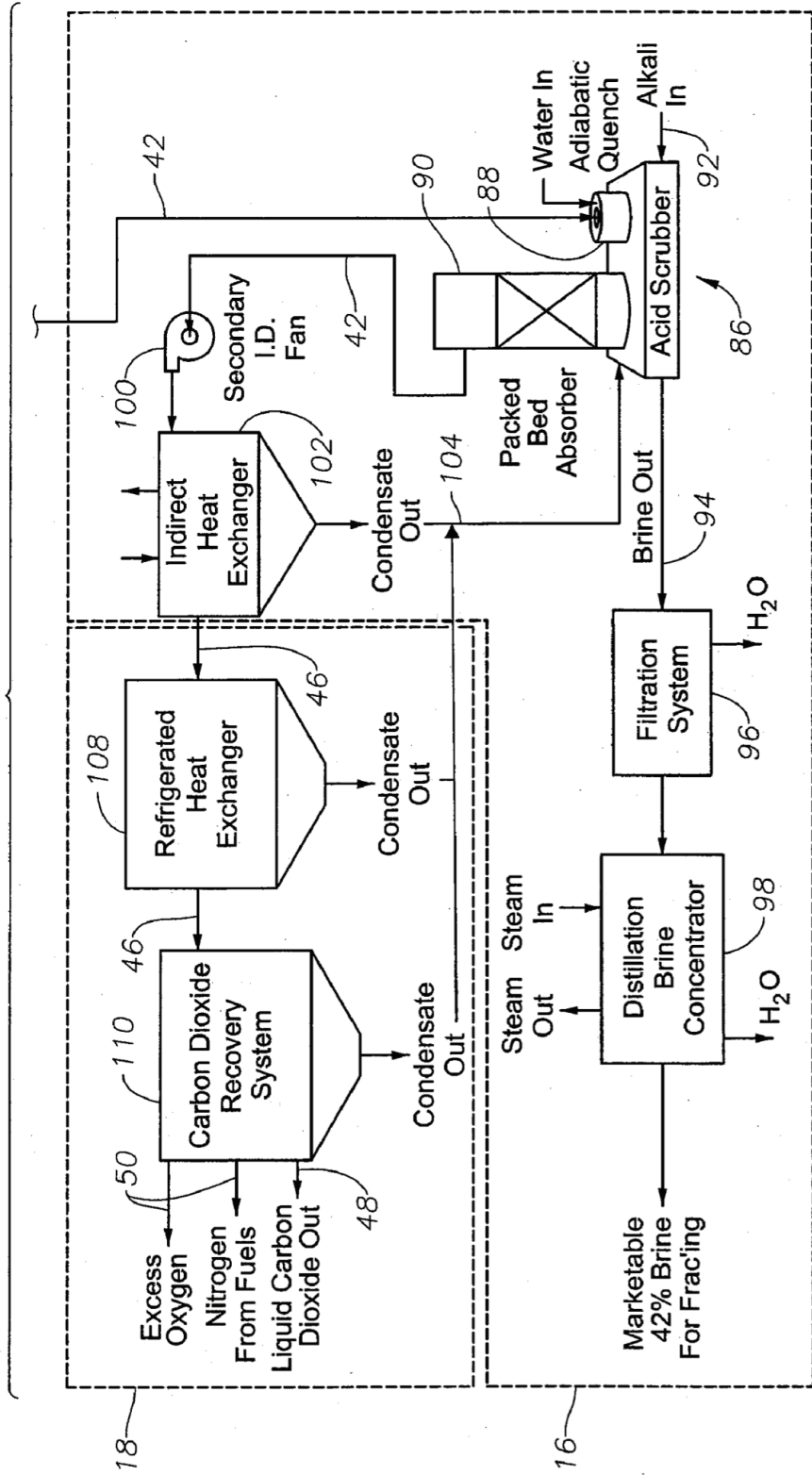


Figure 1B

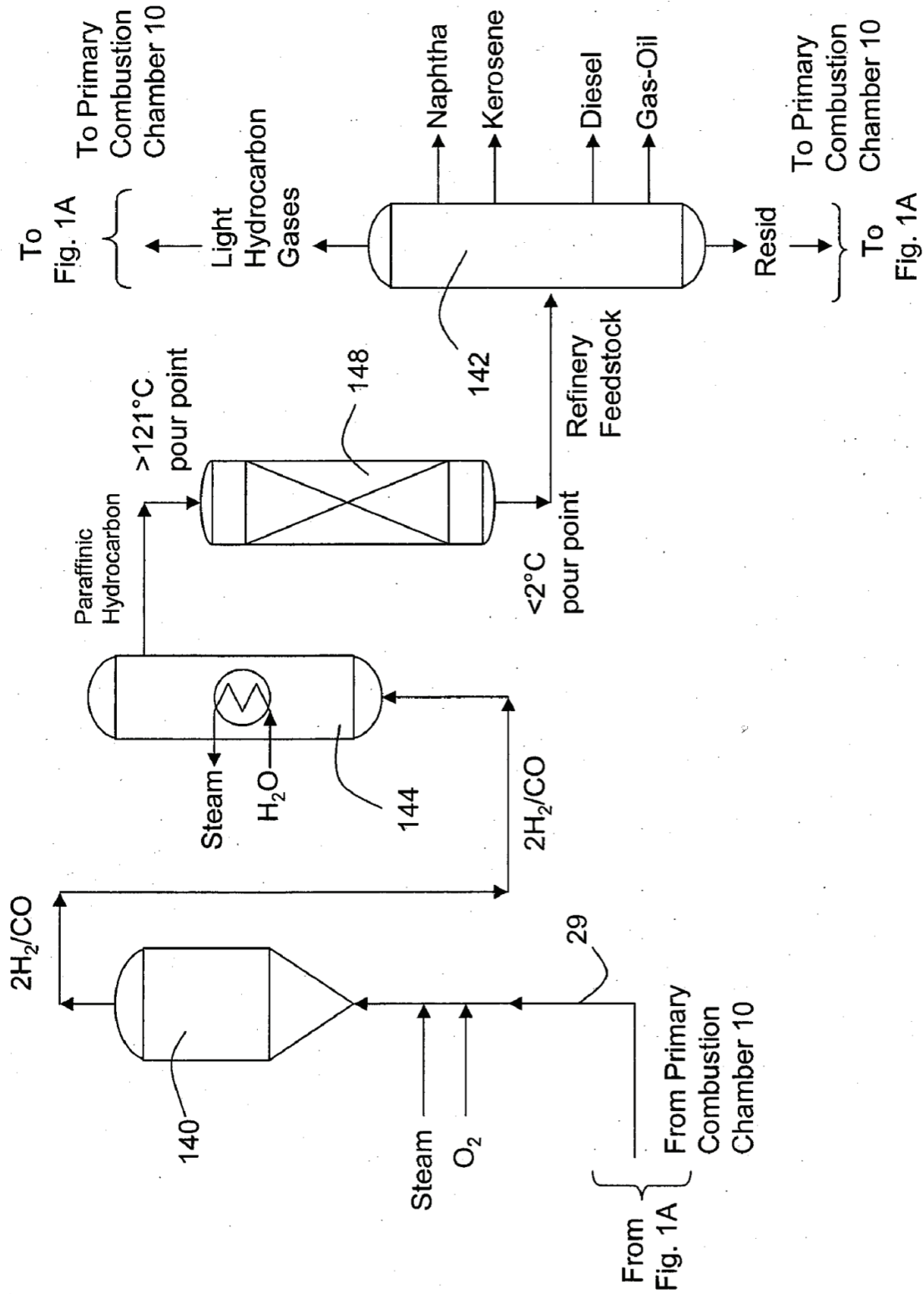


Figure 1C

