CEFCO GLOBAL CLEAN ENERGY, LLC

Newly Patented CEFCO Technology Offers Cost-Efficient Alternative for Capturing "Pure CO2" and Not Necessarily for CCS or EOR, but for Algae-to-Biofuel and C-T-L (Advanced Fuel)

Robert E. Tang, CEO and Co-Inventor
Anupam Sanyal, President — International Energy and Environment Consultants

December 2012

CEFCO's Solution

- Use Ewan's shockwave "free-jet collision scrubbing" (recognized by EPA/DOE) to capture CO_2 and all pollutants

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- Cooper Process to convert CO_2 and all "captured pollutants" into recovered, segregated, valuable, and sellable End-Products

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- USPTO Patent issued on November 30, 2010 under: **US 7,842,264B2**

- CEFCO Users:
  - 1) Comply with all EPA's MACT and NESHAPs Requirements
  - 2) Benefit of selling End-Products: no longer "cost-center"
  - 3) Providing pure CO_2 gas to Users (via Capture in Bicarbonate Solid)

CEFCO

Providing "Pure CO_2" Gas to Makers of Advanced Fuels or Bio-Fuels

- Overcome High Cost and Energy Penalty associated with conventional Capture of CO_2
- Current Sources of Captured CO_2 contaminated by Traces of Amine or Ammonia
- Obstacles to Compression and Transmission of Liquid CO_2
- <u>Solution:</u> CO_2 can be Captured as Solid and Transported by Rail or Truck, and Released as "Pure" Gas

Newly-Patented Pathway —
Captured "Pure CO_2" to Liquid Alcohol(s) and Fuel

The Director of the United States Patent and Trademark Office

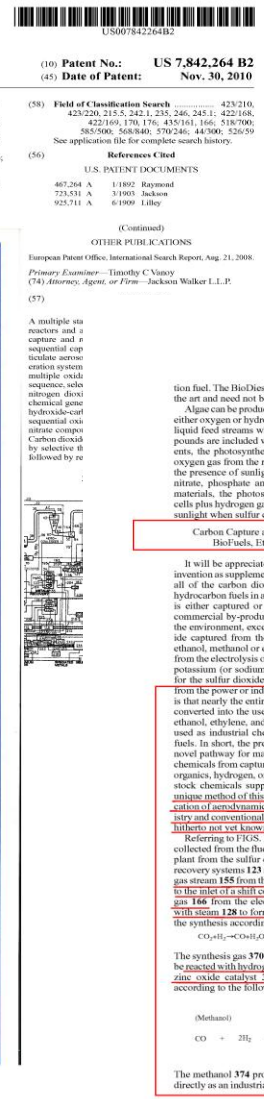
Has received an application for a patent for a new and useful invention. The title and description of the invention are enclosed. The requirements of law have been complied with, and it has been determined that a patent on the invention shall be granted under the law.

Therefore, this

United States Patent

Grants to the person(s) having title to this patent the right to exclude others from making, using, offering for sale, or selling the invention throughout the United States of America or importing the invention into the United States of America, and if the invention is a process, of the right to exclude others from using, offering for sale or selling throughout the United States of America, or importing into the United States of America, products made by that process, for the term set forth in 35 U.S.C. 154(a)(2) or (c)(1), subject to the payment of maintenance fees as provided by 35 U.S.C. 41(b). See the Maintenance Fee Notice on the inside of the cover.

Director of the United States Patent and Trademark Office



US007842264B2

(12) **United States Patent**
Cooper et al.

(10) **Patent No.: US 7,842,264 B2**
(45) **Date of Patent: Nov. 30, 2010**

(54) **PROCESS AND APPARATUS FOR CARBON CAPTURE AND ELIMINATION OF MULTI-POLLUTANTS IN FLUE GAS FROM HYDROCARBON FUEL SOURCES AND RECOVERY OF MULTIPLE BY-PRODUCTS**

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(73) Assignee: **Cefco, LLC**, Dallas, TX (US)

(58) **Field of Classification Search** 423/210, 423/220, 215.5, 242.1, 235, 246, 245.1; 422/168, 422/169, 170, 176; 435/161, 166; 518/700; 585/500; 568/840; 570/246; 44/300; 526/59
See application file for complete search history.

(56) **References Cited**
U.S. PATENT DOCUMENTS

467,264	A	1/1892	Raymond
723,531	A	3/1903	Jackson
925,711	A	6/1909	Lilley

(Continued)
OTHER PUBLICATIONS
European Patent Office, International Search Report, Aug. 21, 2008.

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tion fuel. The BioDiesel oil refining process is well-known to the art and need not be described here in detail.

Algae can be produced by photosynthetic reactions to form either oxygen or hydrogen gases along with algae solids. For liquid feed streams where sulfur in the form of sulfate compounds are included with nitrate, phosphate and other nutrients, the photosynthetic reactions produce algae cells plus oxygen gas from the reaction of carbon dioxide and water in the presence of sunlight. For liquid feed streams containing nitrate, phosphate and other nutrients plus organic waste materials, the photosynthetic reactions can produce algae cells plus hydrogen gas in place of oxygen in the presence of sunlight when sulfur compounds are absent.

Carbon Capture and Producing Methanol, Ethanol, BioFuels, Ethylene and Their Derivatives

It will be appreciated that, in accordance with the present invention as supplemented by the production of algae, almost all of the carbon dioxide generated by the combustion of hydrocarbon fuels in a power plant or other industrial process is either captured or consumed so as to become valuable commercial by-products, and is not available to escape into the environment, except as fugitive traces. The carbon dioxide captured from the flue gas also can be converted into ethanol, methanol or ethylene by the reaction with hydrogen from the electrolysis of the potassium (or sodium) chloride to potassium (or sodium) hydroxide as the absorbing solution for the sulfur dioxide, nitrogen dioxide and carbon dioxide from the power or industrial plant flue gas stream. The result is that nearly the entire balance of the carbon dioxide can be converted into the useable by-product chemicals (methanol, ethanol, ethylene, and all of their derivatives), which can be used as industrial chemical feedstocks or as transportation fuels. In short, the present invention describes, as follows, a novel pathway for making hydrocarbon fuels and derivative chemicals from captured flue gas comprising carbon dioxide, organics, hydrogen, or chlorine as direct substitutes for feedstock chemicals supplied by the petroleum industry. Such unique method of this invention is only enabled by the application of aerodynamic science with molecular surface chemistry and conventional chemistry, the combination of which is hitherto not yet known or practiced.

Referring to FIGS. **1a**, **1b** and **11**, the carbon dioxide gas is collected from the flue gas streams of the power or industrial plant from the sulfur dioxide and nitrogen dioxide chemical recovery systems **123** and **141**. This combined carbon dioxide gas stream **155** from the water vapor condenser **154** is brought to the inlet of a shift conversion reactor **368**, where hydrogen gas **166** from the electrolysis cell **120** are reacted together with steam **128** to form carbon monoxide and water vapor in the synthesis according to the following chemical reaction:

$$CO_2+H_2 \rightarrow CO+H_2O$$

The synthesis gas **370** comprising carbon monoxide can then be reacted with hydrogen gas **166** across a chromium oxide—zinc oxide catalyst **372** to produce liquid methanol **374** according to the following chemical reaction:

(Methanol)

$$CO + 2H_2 \xrightarrow[\text{Catalyst}]{CrO,\ ZnO} CH_3OH$$

The methanol **374** produced thereby can then either be used directly as an industrial chemical or passed through a heating

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unit or cracking furnace **376** to produce ethylene gas **378** by heating with steam or gas **128** and hydrogen gas **166** (to retain a reducing atmosphere) according to the following reaction:

(Ethylene)

$$2CH_3OH \xrightarrow{Heat} C_2H_4 + 2H_2O$$

The ethylene gas **378** (which can be produced from methanol) can then be reacted with chlorine gas **168** from the electrolysis cell **120** to produce ethylene dichloride **177** in reactor unit **176** according to the following chemical reaction:

$$C_2H_4+Cl_2 \rightarrow C_2H_4Cl_2 \quad \text{(Ethylene Dichloride)}$$

The ethylene dichloride (EDC) **177** can then be reacted with additional ethylene gas **121** to produce vinyl chloride monomer **179** and then further reacted with additional ethylene gas **121** to produce polyvinyl chloride plastic (PVC) **180**, while the unused or surplus ethylene gas can be transmitted elsewhere and also can be used to manufacture other petrochemicals. Ethylene **121**, **378** can also be reacted with water **111** and hydrogen gas **166** (to maintain a reducing atmosphere) in ethanol synthesis reactor **380** to produce ethanol liquid **382**, which can then be used to manufacture chemicals or used as a transportation fuel source according to the following chemical reaction:

$$C_2H_4+H_2O \rightarrow C_2H_5OH \quad \text{(Ethanol)}$$

In addition, methanol or ethanol can be directly converted to BioFuel (and Fuel Feedstock, such as components to making gasoline **384**), and can be assisted by passage over a catalyst **386**, such as zeolite.

Production of Air from Hot Combustion Gases (Flue Gas)

As demonstrated in the description of the invention up to the present point, the process of the invention first separates such metals (other than selenium) and particulates as may be present in the hot combustion gas in an aerodynamic reactor and isolates them for recovery or disposal as may be most economical. Then, the process removes selenium (if present) for recovery or disposal and the sulfur oxides in the form of a solid alkali metal sulfate together with a portion of the carbon dioxide to be released as a pure gas (and to be reclaimed and reused) from the decomposition of an alkali metal bicarbonate. Finally, the process removes the nitrogen oxides in the form of a solid alkali metal nitrate together with a portion of the carbon dioxide to be released as a pure gas (and to be reclaimed and reused) from the decomposition of an alkali metal bicarbonate.

Having removed the metals, particulates, sulfur oxides, nitrogen oxides and carbon dioxide from the combustion gas, the exit gas comprises oxygen, nitrogen, water vapor, and, possibly, trace amounts of other fugitive constituents. As this composition is essentially air (as is commonly and universally understood), the process of the invention may appropriately be defined as a process for producing air from combustion gases. In short, this process of the invention produces clean air from dirty flue gas.

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(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, SY, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

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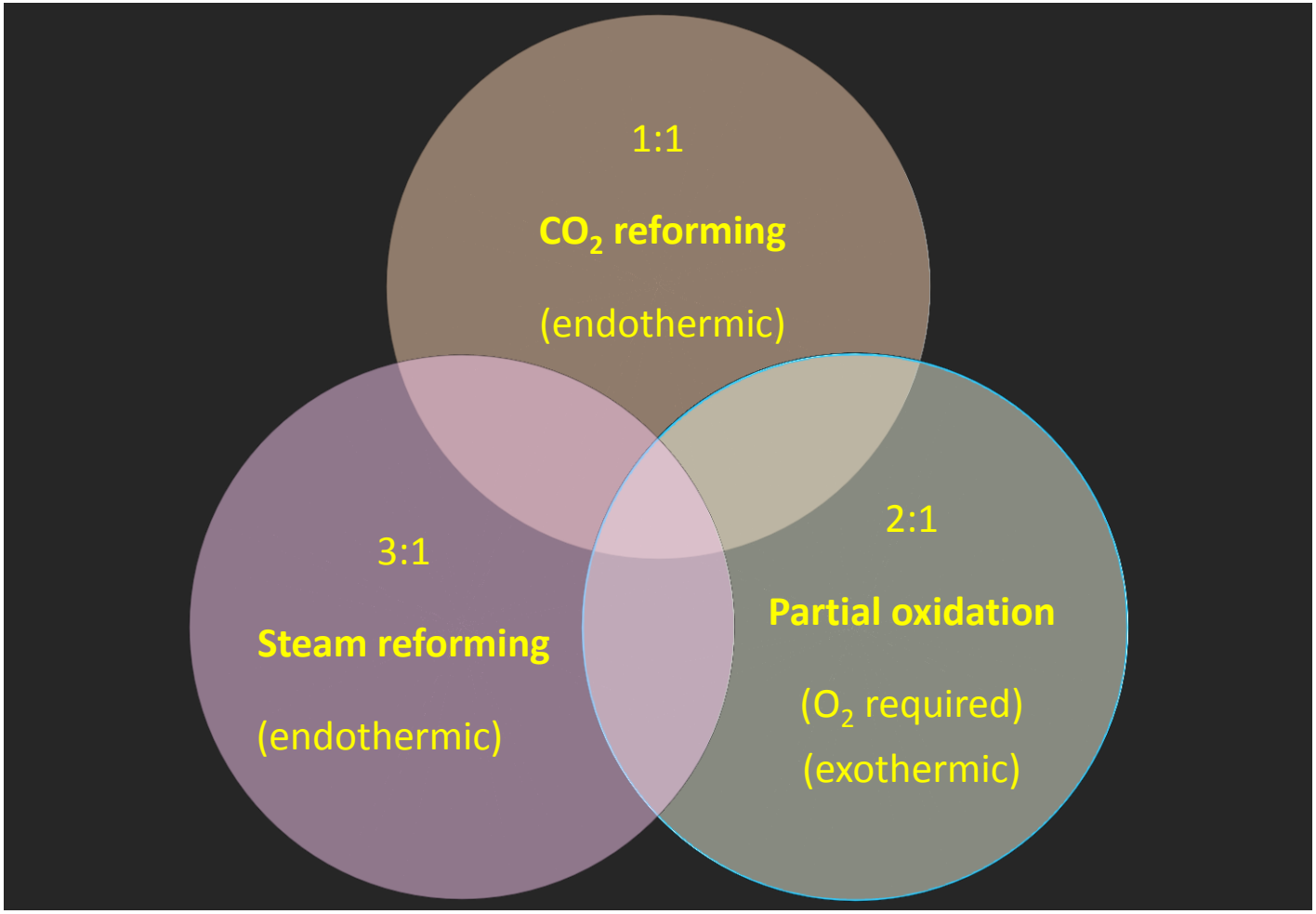
CAPTURE AND ELIMINATION OF MULTI-POLLUTANTS IN
D RECOVERY OF MULTIPLE BY-PRODUCTS

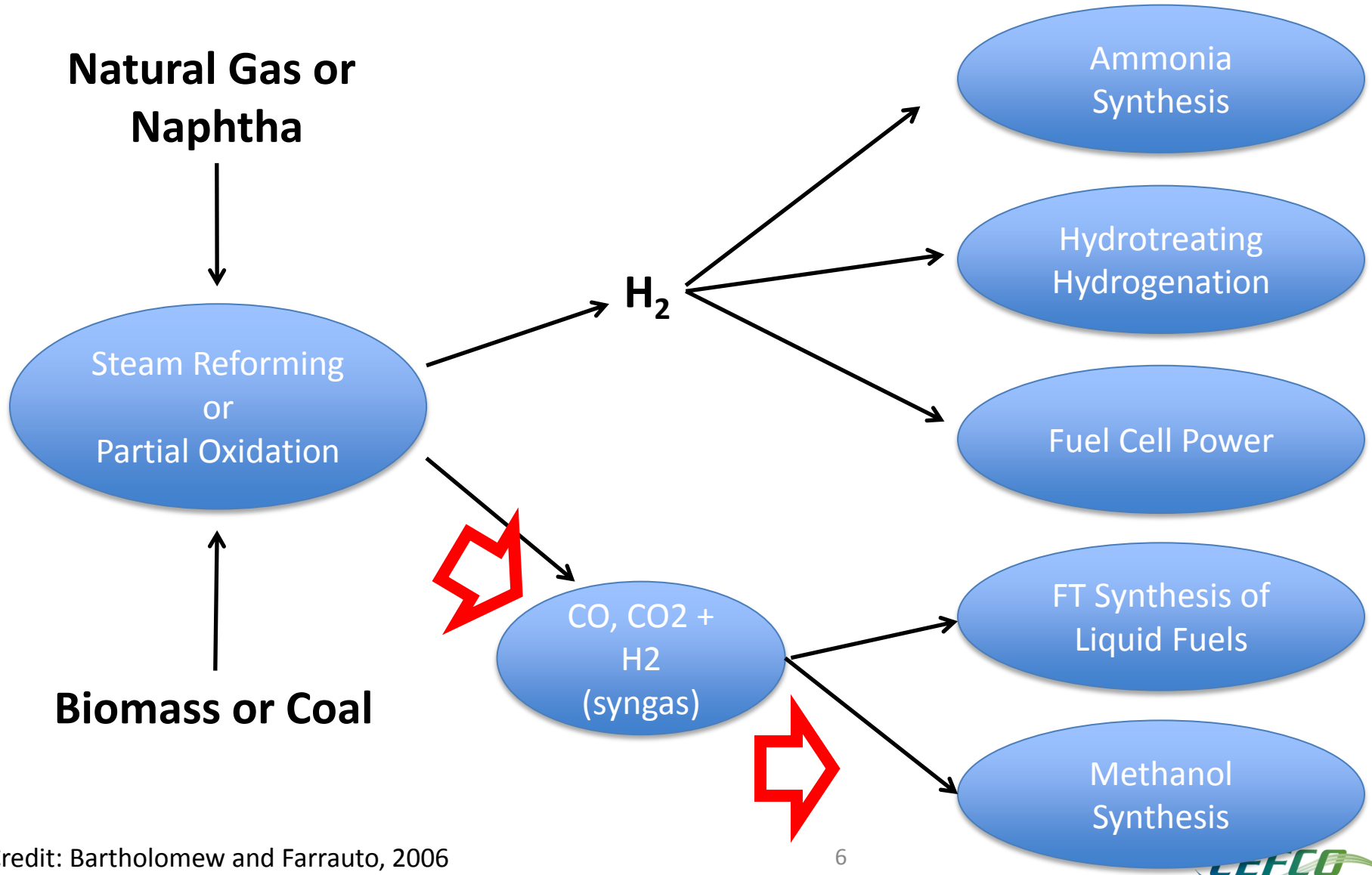
(57) **Abstract:** A multiple stage apparatus and process using aerodynamic reactors and aero- coalescers in sequence for the selective capture and removal of purified carbon dioxide gas, the sequential capture and removal of mercury, metal and particulate aerosols by a recycling chemical generation-regeneration system using alkali metal chloride solution following multiple oxidations of mercury vapor, and nitric oxide in sequence, selective capture and removal of sulfur dioxide and nitrogen dioxide by two stage absorption by a recycling chemical generation-regeneration system using alkali metal hydroxide-carbonate-bicarbonate solution together with sequential oxidation to alkali metal sulfate and alkali metal nitrate compounds through evaporation and crystallization. Carbon dioxide capture and recovery is achieved in sequence by selective thermal decarbonation from an alkaline liquid followed by recovery as a purified gas stream.

Energy Survey of Reforming Processes



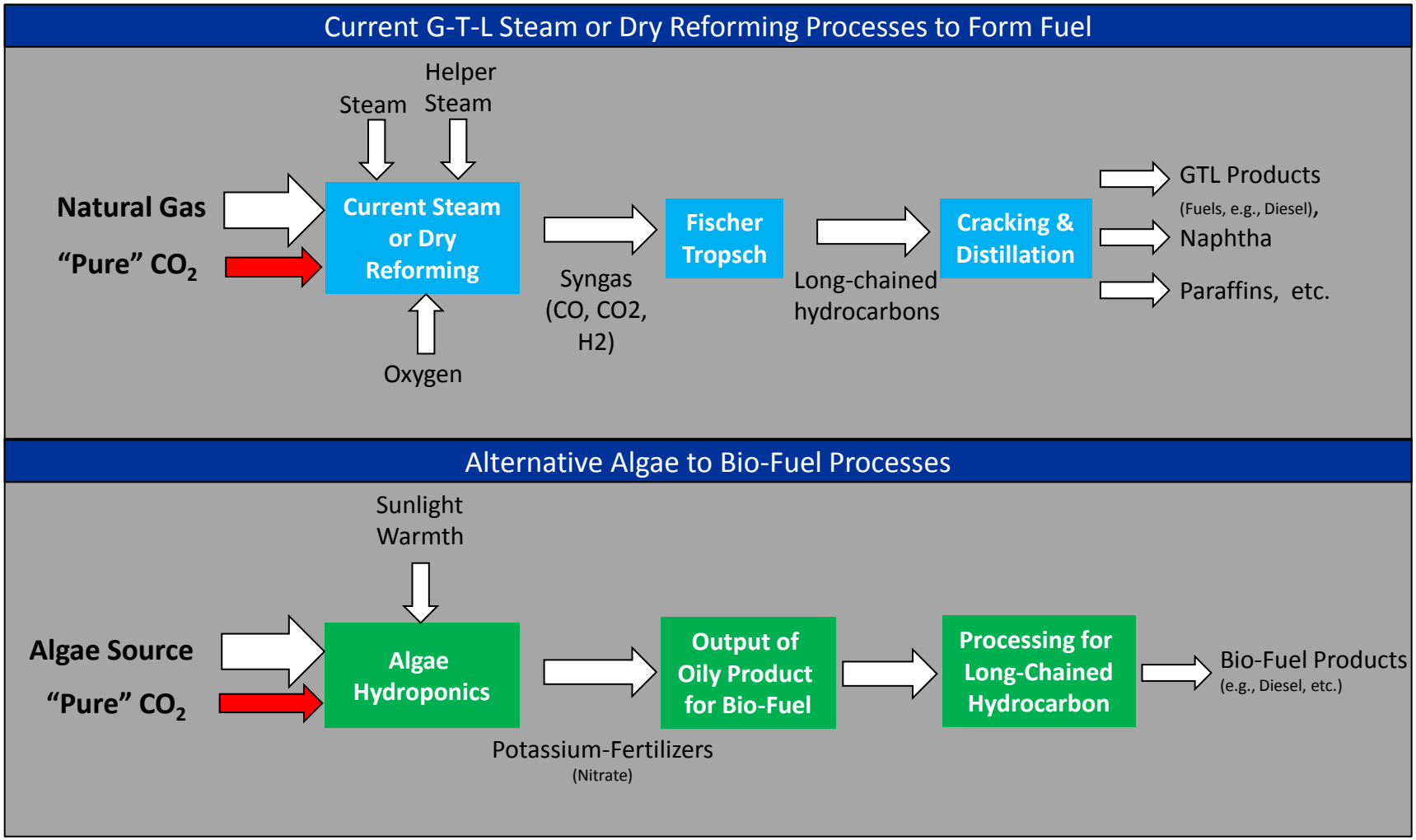
Many processes need to optimize Enthalpy of each reaction, and to minimize input of Energy, Pressure and Catalyst.

Background: Reforming Processes



Credit: Bartholomew and Farrauto, 2006

G-T-L Processes: Requiring Pure CO_2
Algae + CO_2 : Alternative Bio-Diesel



Aero-Physics Science
Shockwave Reaction Mechanism

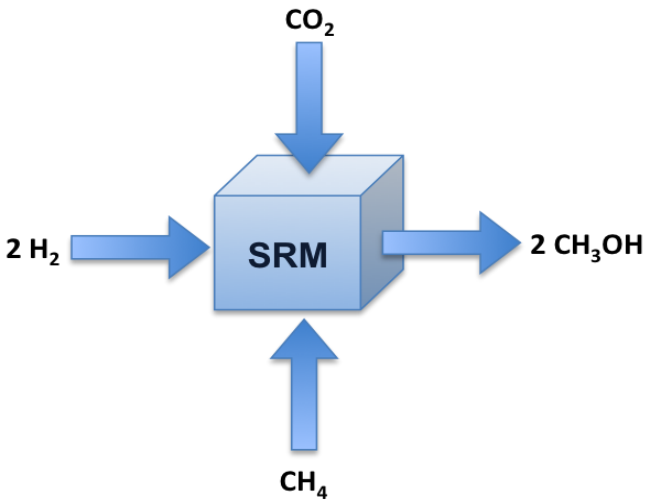


Fig. 4A: Methanol 'A' Production

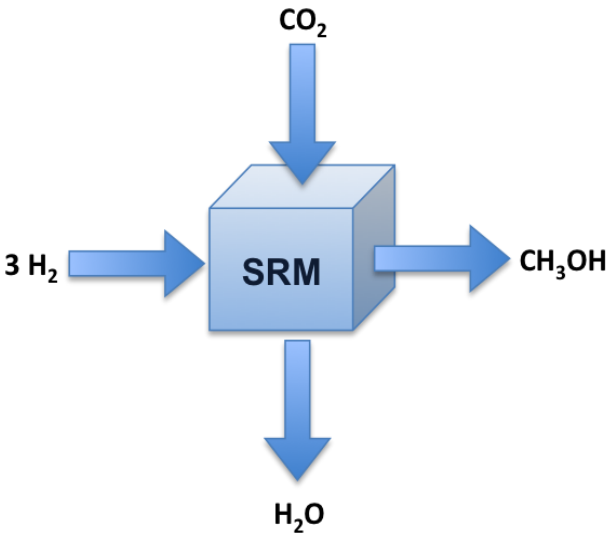
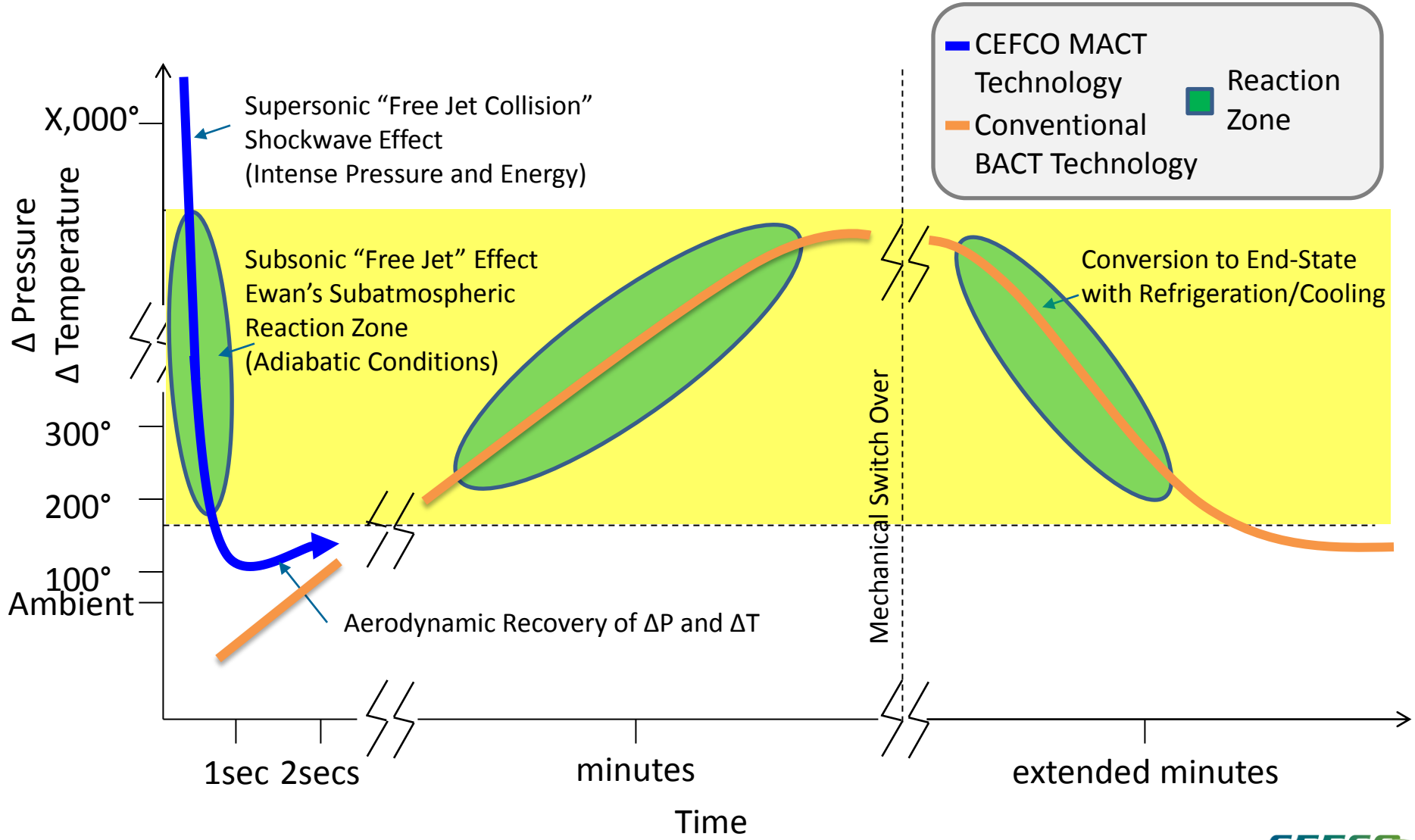


Fig. 4B: Methanol 'B' Production

Comparison of Parasitic Load or Energy Penalty



Seeing Shockwaves Being Formed

Image: Airplane beginning to cross sound barrier at Mach 1.0, showing first shockwave

Image: Schlieren Photography – multiple shockwaves generated by shuttle craft at much higher Mach speeds

Free-Jet Reaction Zone

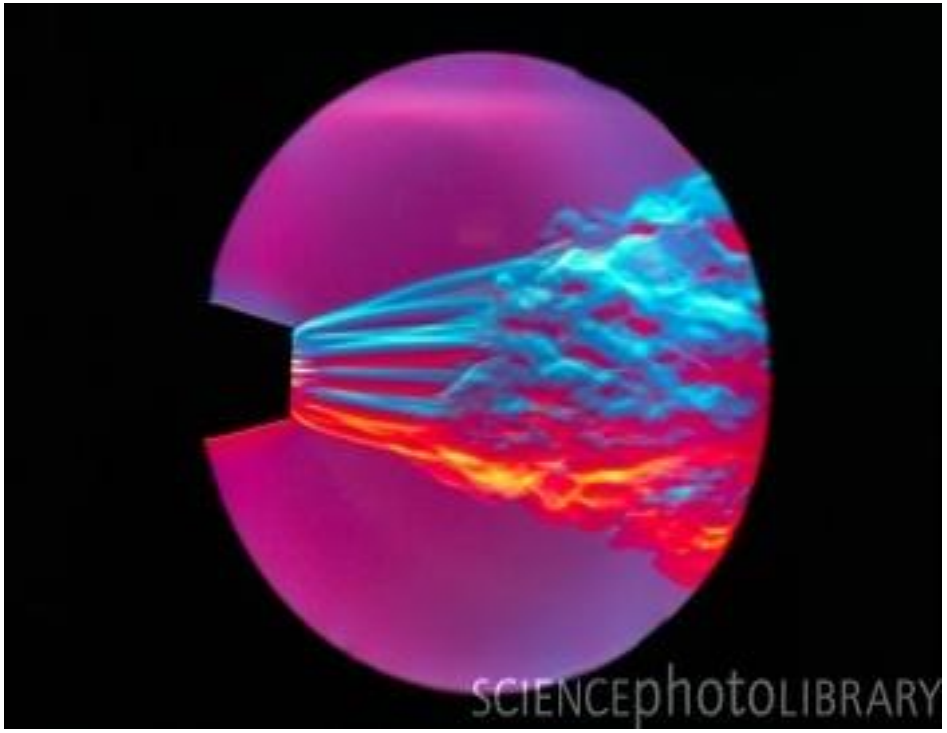
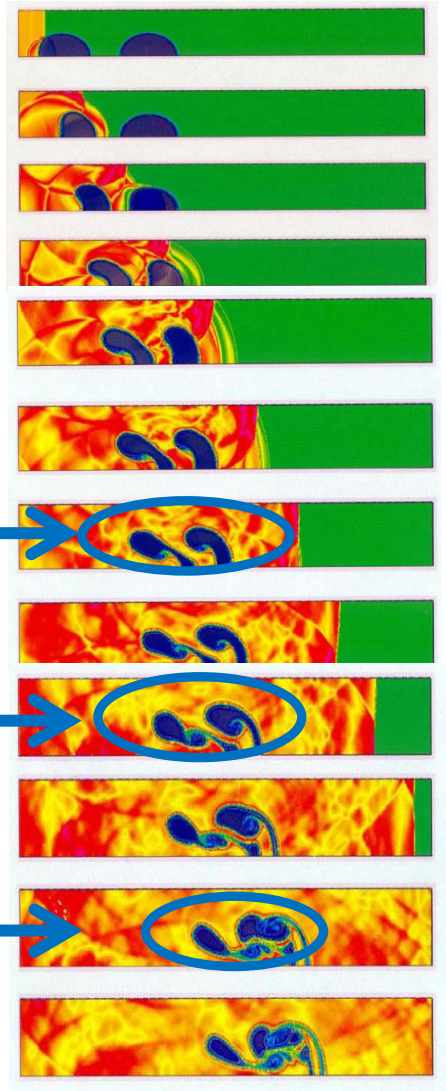


Image: Schlieren Photography of Free-Jet Collision inside CEFCO's reaction chamber causing an induced "subatmosheric reaction zone" with extreme adiabatic conditions

Shockwave-Induced Intimate Mixing

Image: Schlieren Photography showing shockwave-induced intimate inter-mixing and re-combination of two gas-phase molecules

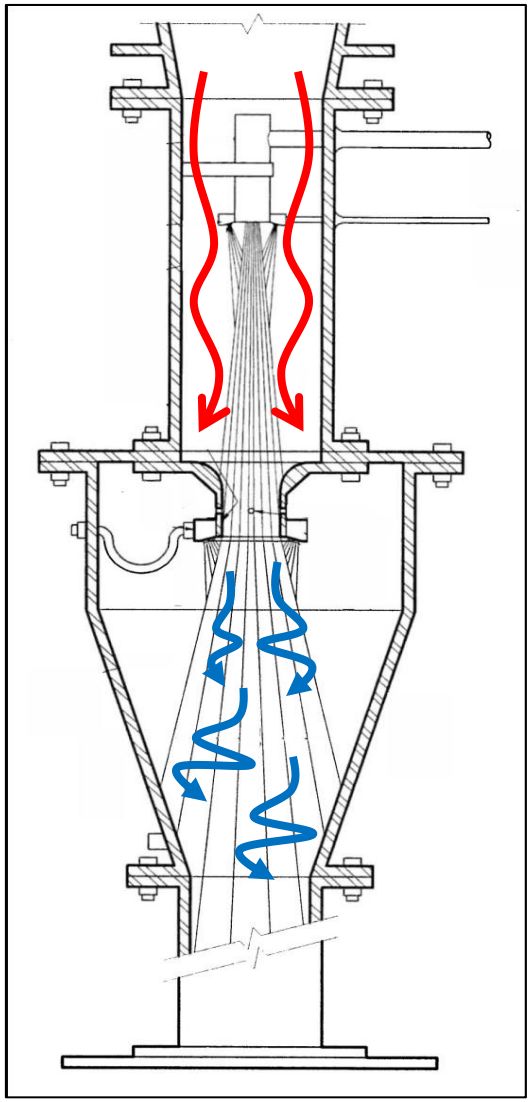


Shockwave envelopment

Inter-mixing

Re-combination

CEFCO's Unique Reaction Mechanism



- All flue gas must pass downward through Shockwaves ➔ "no escape" from "free-jet collision" and capture effect

- Pollutants are first captured using Physics then converted into valuable end-products by using Chemistry

Application of Hess's Law $\Delta H^{\Theta}_{reaction} = \sum \Delta H^{\Theta}_{f(products)} - \sum \Delta H^{\Theta}_{f(reactants)}$

- All molecules in flue gas are affected by shockwave = no escape
- Hess's Law: energy or enthalpy change (ΔH values) for any chemical or physical process is independent of the pathway or number of steps required to complete the process; only the initial and final states being important
- Reaction-intermediates are transitional and will rapidly reform or recombine into the end-product
- Final reaction equation "gets netted out" at end-product state in exothermic reaction and results in stable end-product at much lower range of temperatures
- If net enthalpy change is negative ($\Delta H_{net} < 0$), reaction will be exothermic and is more likely to be "spontaneous" (which means in "a split-second")
- Exothermic reaction provides fresh addition of heat being released into flue gas phase and assists in energy and pressure recovery = lower "parasitic loss"

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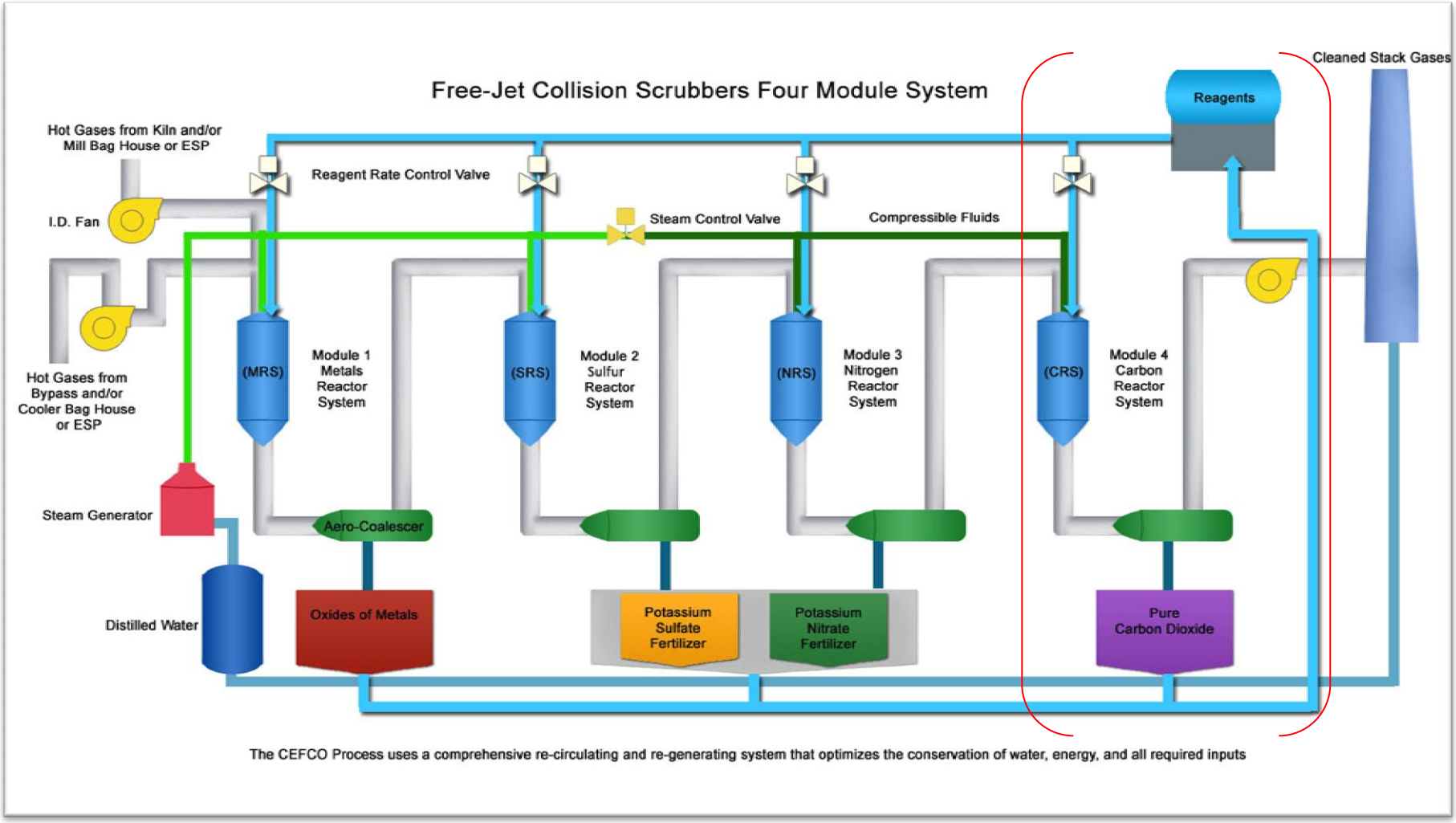
CEFCO System Flow Diagram



CRS (CO_2) Module

- Reactions inside the Aerodynamic System (verification of Hess's Law):
- $CO_2 + KOH_{(reagent)} \rightarrow KHCO_3$ (Carbon Capture)
- $CO_2 + \mathbf{K_2CO_3}_{(reagent)} + H_2O \rightarrow 2\ KHCO_3$ (Carbon Capture)

- Transient Reactions (Hess's Law):
- $CO_2 + H_2O \rightarrow H_2CO_3$
- $KOH_{(reagent)} + H_2CO_3 \rightarrow KHCO_3 + H_2O$ (Carbon Capture)

- Conventional Reactions after leaving the Aerodynamic Coalescer:
- Decarbonation = Liberation of Carbon Dioxide
- Heat + $2\ KHCO_3 \rightarrow \mathbf{K_2CO_3}_{(regenerated)} + CO_{2\ (liberated\ gas)} + H_2O$

- Note: $\mathbf{K_2CO_3}$ re-generation process liberates CO_2 as gas and produces supply of recovered water for many subsequent uses

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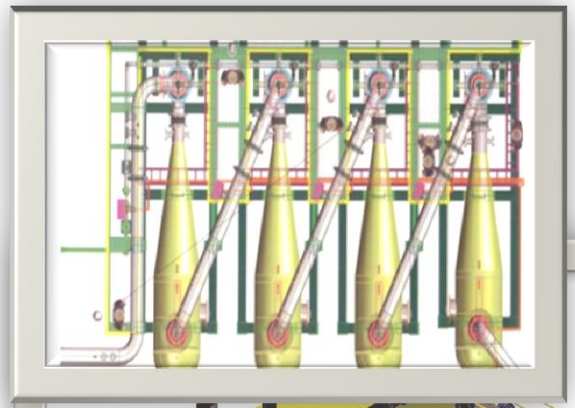
CEFCO's Reaction Mechanism

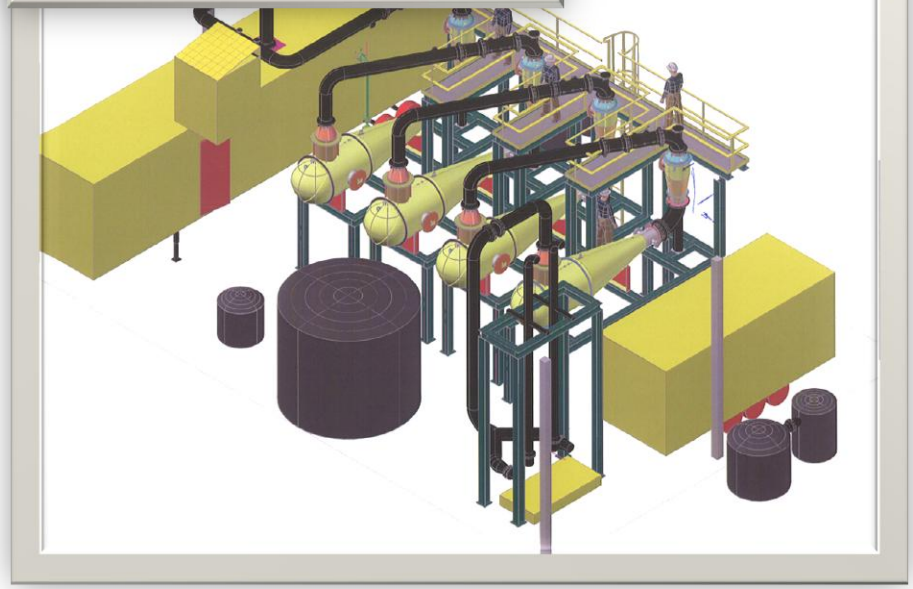
- Supersonic Shockwave itself = Input of Energy & Pressure + acts as needed Catalyst
- Shockwave "Free-Jet Collision" (DOE's and EPA's description in numerous reports) = Molecular Surface Chemistry
- Shockwave energizes Targets to react in shortest time + causes Adiabatic Condition that enables Endothermic-then-Exothermic Reactions
- Shockwave shatters Reagent Solution injected into finest micro-droplets = enhancing molecular surface contact areas
- Intimate and Rapid Intermixing & Reaction
- Reaction Kinetics predominates over other conventional thermodynamic issues
- Hess's Law explains the rapid conversion into End-Products

CEFCO

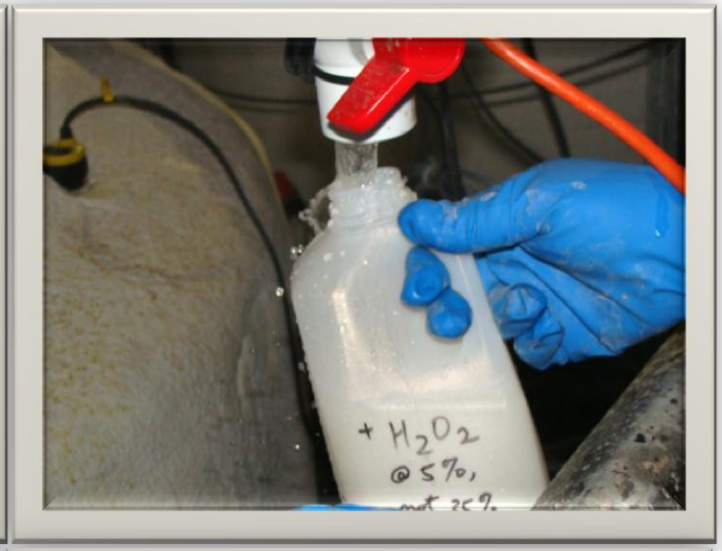
Pilot Plant at Peerless

- in Wichita Falls, TX
- 3 tons/hr of Flue Gas





Successful Capture of Potassium Fertilizer and CO_2



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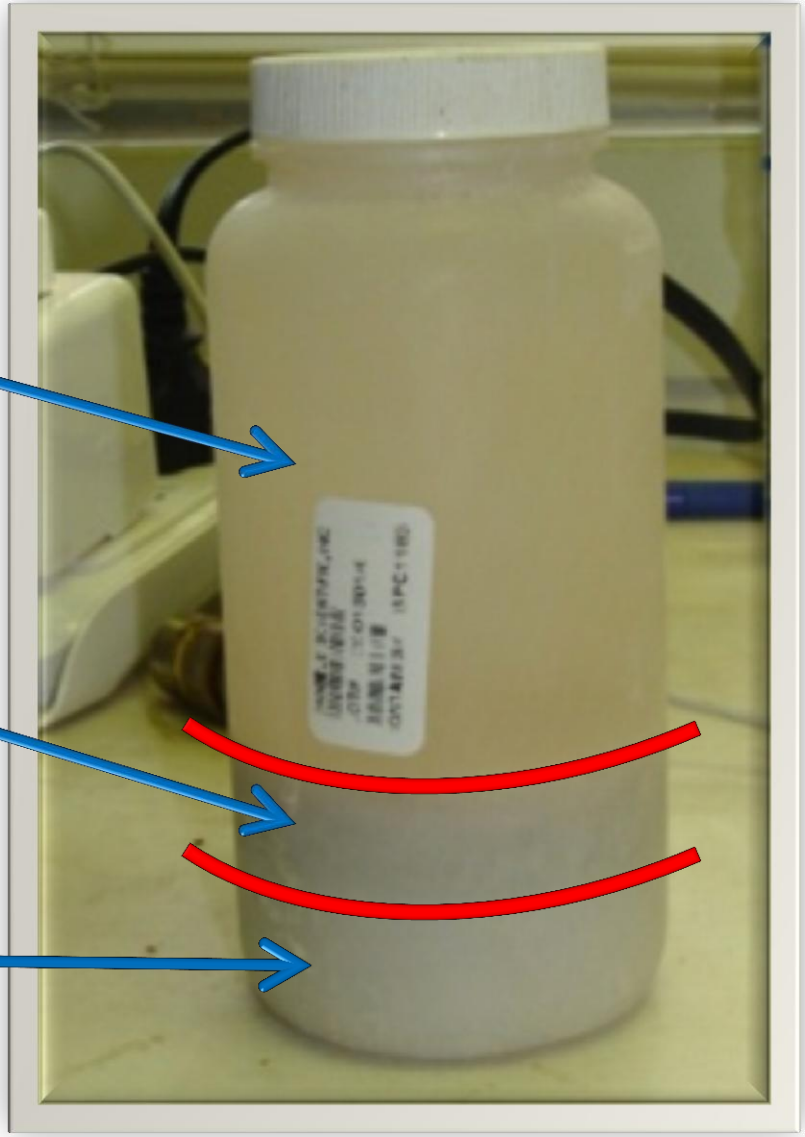
Three Layers of End-Products

Liquid Potassium Sulfite Fertilizer

Potassium Sulfate Fertilizer Crystals

Potassium Bicarbonate Crystals (CO_2 Capture)



CO_2 Captured and Converted into Easily Transportable Solids

Potassium Bicarbonate = $KHCO_3$ (Solid)

Sodium Bicarbonate = $NaHCO_3$ (Solid)

Heat + 2 $KHCO_3$ [or 2 $NaHCO_3$] → **K_2CO_3** (regenerated) [or Na_2**CO_3**] + CO_2 (liberated gas) + H_2O

<u>Note:</u> **K_2CO_3** [or Na_2**CO_3**] re-generation process liberates CO_2 as a pure food-grade gas and produces supply of recovered water for many subsequent uses. The **K_2CO_3** [or Na_2**CO_3**] can be returned to the CEFCO Process to be re-used as the Reagent in the CRS

Summary

- Game-changing "transformative reaction mechanism technology" = perfect marriage between Aerospace Physics and Chemistry

- Environmental responsibility = "Pure" CO_2 can be captured in Bicarbonate Solid
  - Much Cheaper and Safer to ship by Rail or Truck
  - Avoid high cost of Compression and Pipeline Transmission of amine-contaminated CO_2

- Reliable and affordable energy:
  - Aerospace science reaction mechanism as low-cost substitute for traditional thermodynamics and catalysts
  - Pollution Control = "profit-generation" business; ≠ "cost-center"

- Proposing Air-Gas Separation to Harvest the Remaining N_2, O_2 and Noble Gases in the exiting Flue Gas Stream

CEFCO

Questions & Answers

Thank you very much for your attention.

Please Contact Us At:

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