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Session Theme: “Potentially game-changing technology and evaluation”

Paper Title: "Tandem Shockwave-Enabled Technologies For Capturing CO₂ and Converting GHG Into Valuable Chemical End-Products, Alcohols and Liquid Fuels"

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Direct Web Page Link: <http://www.cefcoglobal.com/>

Abstract: CEFCO Global Clean Energy, LLC (“CGCE” herein) is ready and able to provide the recently patented necessary technology (“Technology A” or “A”) and a related patent-pending technology to address the issues of capturing CO₂ (GHG) and converting the carbon content into viable, value-based products (“Technology B” or “B”) that will stimulate the creation of a “virtuous carbon-based economy”, thereby achieving the conversion of carbon from a liability into an asset. CGCE wishes it be known that the components comprising GHG, such as CH₄ and the captured and re-used CO₂ (which is captured by “A”) could be made useful, productive and very beneficial in a low-cost and high-efficiency capture, conversion and re-use, which could be consumed in an industrial process; and then its emissions further recaptured, re-converted, re-produced, and re-used in a virtuous, repetitive, recycling of said resources. If methanol-derived fuels or advanced diesel or combustion fuels resulting from such a cyclical re-production process using “B” are utilized in stationary power or stationary process heat generation, CGCE's process could re-convert them repetitively, cyclically, into renewable fuels in a “virtual near closed-loop recycling” of 99+% of the same re-captured emissions; and additionally to do the same for any new fossil fuel being added and combusted in wider usage, and its carbon emissions being recaptured and re-converted cyclically. That would bring endless, incalculable and repetitive benefits to society. The availability and applicability of the CEFCO’s technology will foster many new industrial and business enterprises surrounding and down-stream of such technology for the economy. Additionally, “Technology B” further provides for the follow-on re-combination of shorter-chained compounds into longer-chained compounds by subsequently sequenced, designed and induced shockwave-enabled reactions, and thereby to make other more valuable chemical compounds beyond making liquid fuels.

■ **Acknowledgement:** Co-Authors wish to thank and acknowledge the distinguished members of the Carbon Management Technology Conference (CMTC–2013) Papers Selection Committee comprising members of the AIChE and ASME and the Chairing Committee for introducing this Paper herein.

■ **Background of Technology Presented:** In the previous CMTC–2012 Conference Paper ID #149808 presented on February 9, 2012 under the Session titled “CCS Capture R&D”, the co-authors have shown that the patented and proven

CEFCO Process technology (“A”) will capture CO₂ into Alkaline-BiCarbonate precipitate in water (commonly known as baking powder in a slurry form) or, at the election of the users, de-watered and dried into solids. Both alternative forms of the captured-product offer the advantage of easy transportation by conventional slurry transmission line or by conventional trucking, railroading or barging of the solid powder form, without the necessity of installing new Stainless Steel Pipeline and the costly compression of CO₂ into liquid form, and without the conventional “slippage” of Ammonia or Amine contaminating the CO₂ gas in the eventual release of CO₂ (which disadvantage often occurring in the conventional methods of carbon capture by Chilled Ammonia or Amine). The CEFCO results have been reported by *The Carbon Capture Journal (London)* for four months in the January-February 2012 issues and the March-April 2012 issues, respectively under the titles: “Part 1. Lower Energy Penalty CO₂ Capture System – Capture and Conversion” and “Part 2. Lower Energy Penalty CO₂ Capture System – Capture and Conversion Pilot Plant”. Additionally, the *Modern Power System Magazine* in the October 2011 issue published an article on the CEFCO Process called “How Shockwaves Can Cut the Energy Penalty”. Copies of these publications are available from the publishers. The published steps are provided herein below:

Steps	Carbon Capture Module, for low-cost re-cycling and re-generation of BiCarbonate-Carbonate reagent: we can use both Na ₂ CO ₃ and NaOH for the Repetitive Capture of CO ₂	Enthalpy [ΔH _f ^o] kJ/mole	Equiv. BTU (IT)
1a	(Eq. 1) CO ₂ + Na ₂ CO ₃ + H ₂ O → 2NaHCO ₃ (precipitation)	[ΔH = -84]	-79.61
1b	(Eq. 2) CO ₂ (g) + NaOH (aq) → NaHCO ₃ (precipitation)	[ΔH = -80.1]	-75.92
Outside of Shockwave System	After CO ₂ Capture, the BiCarbonate (precipitation) can be re-liberated into CO ₂ (gas) for Subsequent Utilization by User employing a Low Range of Heating Energy-Input at a Time and Place of the User’s Choice. Add Heating Equipment or Heat Input if and when needed for productive uses.	<u>Example:</u> Deploy the Return Steam-Loop with “Un-insulated” Coil winding at the bottom of the Carbon Product Re-Liberation Tank to provide Heat ¹ at the cheapest energy-input cost.	
2	(Eq. 3) 2NaHCO ₃ → CO ₂ + Na ₂ CO ₃ + H ₂ O	[ΔH = + 84]	+79.61
	Reagent Na ₂ CO ₃ reagent is re-generated and can be re-used after Filtering. Cheap re-cycling of same Resource leading to very low reagent-input cost. Adding NaOH makes more Na ₂ CO ₃ reagent or can refresh stale reagent.	Return-Loop Steam Coil does not leak naked steam into the Tank Liquid. No commingling of valuable-reusable resources.	
User can employ KOH and K ₂ CO ₃ in lieu of Sodium-based reagents to achieve similar effect.			

Quick I.P. Summary:

■ “Technology A” — (issued Nov. 30, 2010) Cooper, Tang et al. U.S. Pat.

¹ Heating the BiCarbonate in water in the range of 210° F to 250° F will suffice. This method will contribute to the Condensation of the Return-Steam into water. Such condensed water will have to be pumped to the Filtering and Re-Boil Steps for further conservation and re-use of the resources.

#7,842,264B2ⁱ Patent for capturing all CO₂ gas from any hydrocarbon source, esp. from combustion of coal, pet coke, asphaltene, bitumen, crude oil, natural gas, sour gas, post-treatment gas, etc.

- “Technology B” — (2012) Tang Pat. Pending U.S. Application #61/720,919ⁱⁱ converts all CO and CO₂ and CH₄ plus any form of GHG from any hydrocarbon source into products by using the proprietary Shockwave Reaction Mechanism (“SRM”) as an alternative to conventional thermo-chemistry.

Description of “Technology B” to Science and Engineering Colleagues and Peers:

The major focus of this Paper is on “Technology B” converting GHG content much more cost-efficiently and time-efficiently into viable, value-based liquid products that will help to create a “carbon-based economy”, thereby converting Carbon “from a liability into an asset”, because “B” does not require the very heavy input of energy (heat, pressure), catalyst and time, which are needed by conventional thermo-chemistryⁱⁱⁱ.

CGCE has a supersonic free-jet collision capture and product-conversion technology “B” based on aerospace science and gas dynamics where reaction kinetics and molecular surface chemistry supersede traditional thermodynamics (which has been the popular and wide-spread basis of thermochemistry taught by J.W. Gibbs and many others in the current, conventional “closed” or “nearly-closed” systems).

To understand the dramatic difference, I would re-direct your attention to known aerospace science involving wholly or partially “open systems” in the following familiar examples. I will use two sets of realistic experience below: (A) one involving your own field engineering colleagues in the Natural (and Synthetic) Gas production and Gas Dynamics area, and (B) another involving CEFCO’s colleagues^[1] in the aerospace science (U.S. Ordnance Aerophysics Lab and NASA) and Applied Physical and Theoretical Chemistry area.

To begin this explanation and comparison:

- A. In Natural (and Synthetic) Gas production and Gas Dynamics: In the HPHT production field such as in Southern Texas or the Gulf of Mexico where the summer air temperature is at least 35° C, when an engineer (wearing protection from H₂S and other toxic gases) turns on a pressure relief valve, he sees a Natural Gas jet shoots out and icicles are formed extending beyond the exit and around the valve-nozzle, but at the end of the icicles he sees liquid dripping down and forming a puddle on the ground or floor, plus a whiff of gas, etc. in the air and a glimmering sheen on the slippery surface of that liquid

^[1] CEFCO’s co-founder, aerophysicist T.K. Ewan (deceased 2009), was the former Director-in-Chief of the U.S. Ordnance Aerophysics Lab and designed Air Frames and Re-Entry Vehicles for the Military and NASA. He was an early pioneer and proposed the design of Air Frame and Engine for Hypersonic Flight in 1966. Also, the Oxford University Physical and Theoretical Chemistry Laboratory provides lectures and written explanation of such molecular surface chemistry as described by the Applicant. The U.S. Department of Energy’s Brookhaven National Laboratory (BNL) Website provides as reference a very descriptive pictorial illustration of such molecular surface chemistry.

puddle. Prior to the valve opening, the temperature inside the feed pipe was somewhere between 500° C to over 1,000° C, but ice at $\leq 0^\circ$ C is formed at the open-end of the valve-nozzle, and liquid drippings appear at the end of the icicles where the temperature gets warmer (being further away from the coldness). Then if this engineer's instruments were to face the valve-opening at a distance of ≤ 1 meter away, his instrument would be blasted or damaged by freezing cold; but if the instruments were facing the valve-opening at a distance of 3 meters away, they would be just cooled-chilled; and if they were 6 meters away, they would show similar indications of a windy fan blowing at them but the temperature would recover closer and closer to ambient; and finally, at about 8 meters away, the temperature would recover to circa 33° to 35° C. That is the result of an "open system". All this development occurs within one or two seconds — on a consistent basis — for as long as the valve is open and the gaseous jet is shot out. This image I will ask you to keep in mind when I introduce another segment of knowledge and empirical experience.

- B. In Aerospace Science: Please see the photos of a Navy Jet at 150 meters above sea level outside of Florida Coast where the air temperature was over 35° C and humid. Notice the Prandtl-Glauert "Shock-Collar" or "Skirting" Effect surrounding the Jet in both photos.



- C. The left-side photo shows a common sight available to the public. However, in the right-side photo of interest to aerophysicists, with a slightest time-delay shot, please see the rapid collapse of moisture and formation of condensation under very cold temperature and the collapse of pressure into very tiny ice crystals which quickly melts into fine liquid droplets at the tail-end of the shock-effect on the right, near the airplane tail (see the reverse-shape at the underside of the shockwave-skirt, forming a "reverse-skirt", looking like a standing-up Track-and-Field discus). Then, of course, in an open-system environment, the ice quickly melts and the liquid forms very fine rain-mist. Everything seems to have occurred "in a second". If you were an observer near there within a few hundred meters, you would feel the very fine rain-mist on your face but you will not see any rain under a sunny sky. I now also ask you to keep that image in mind.

CGCE introduces "collision physics" for development of multiple applications in the chemical industry by means of using the supersonic Shockwave Reaction Mechanism ("SRM") to form the proper and necessary reaction mechanism for energy-and-mass transfer

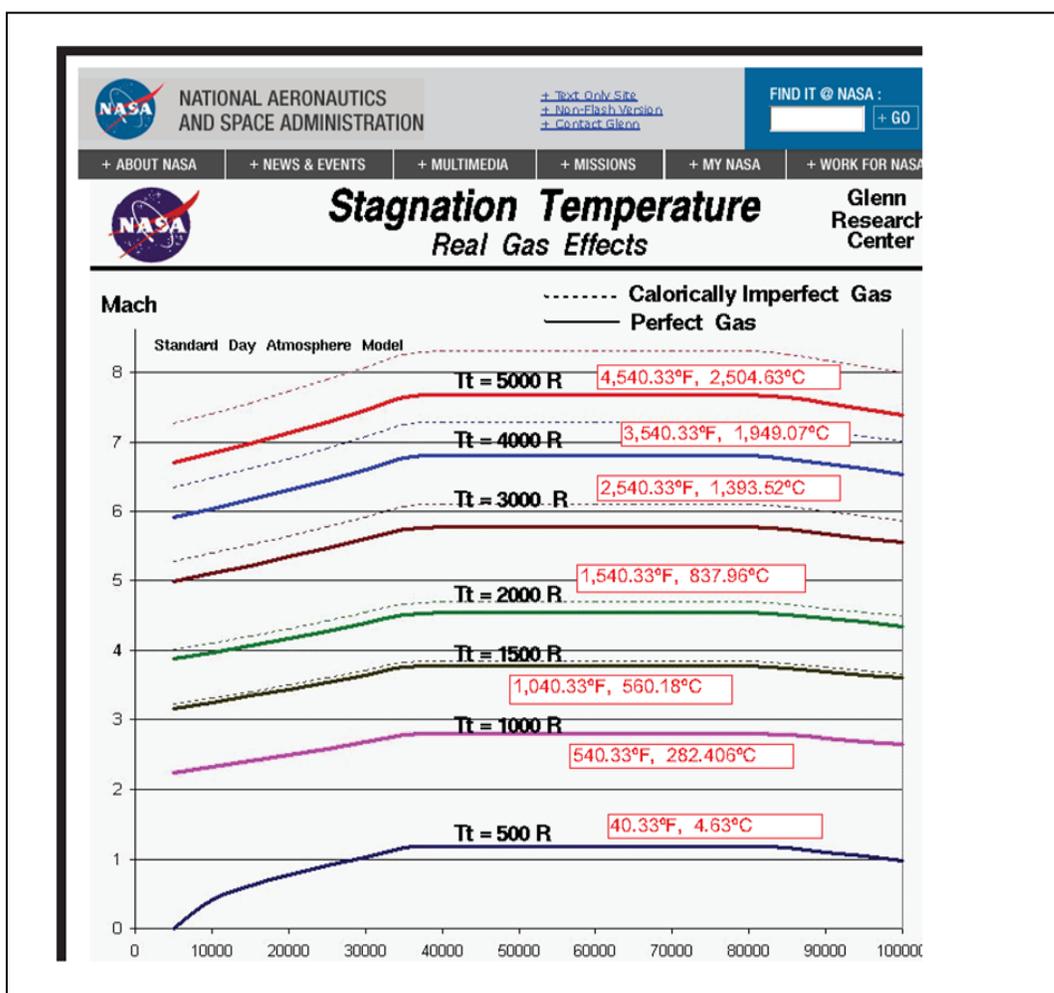
as the center-piece of molecular surface chemistry. It shows “collision physics” inducing “collision chemistry” at the molecular surfaces; therefore, the essence of molecular surface chemistry^{iv}. The chemical conversion or compound transformation reaction will occur in a split-second inside a localised reaction zone inside aerodynamically-shaped reactor chamber. The “YYY kJ/mole” energy required will be very endothermic delivered by the Mach-speed physical impact, i.e. the heat-and-pressure of the shockwave collision/interaction at the molecular point-of-impact (exactly where the energy-input is needed for activating and driving the reaction, with the shockwave itself becoming a part of the catalyst), and then followed by another phenomenon of rapid cooling and rapid pressure drop underneath the “stern” of the shockwave as the reformed and converted reactants pass beyond the shockwave, which will enable “locking-in” the state of the end-product of the collision chemistry in a very exothermic mode, with no possibility of reaction-reversal because there will be no equilibrium state for the reaction just concluded (known as the “non-Gibbs condition” or the adiabatic cooling “Joule-Thomson (Kelvin) Effect”). This comprehensive mechanism of endothermic-then-exothermic reaction condition is offered by CGCE as the “quantum-leap” breakthrough in scientific chemical production methodology. The act of chemical-capture is the same act of chemical product-conversion reacting in seconds via the use of a designed reactant under the supersonic SRM: a shockwave-enabled contemporaneous “capture-and-convert” technology. No targeted gas or reactant can escape the shockwave collision (energy-and-mass transfer effect) upon it. Thus, SRM becomes the more-efficient alternative to traditional re-iterative heating-up and pressurising the conventional reaction chamber vessel, its surrounding environment, and its chemical masses and all of the third-party (or non-reactive) accessory masses over many minutes, or even hours, of time (as currently required and practised under conventional gasification-refining-distilling methods, which require re-iterative steps, using the “Gibbs Free Energy” system requiring the equilibrium conditions) — thus the SRM results in a great break-through of savings in energy and operating time, and with using smaller equipment set, thus leading to lower CapEx also. This is a transformational quantum-leap. Not “business as usual”.

What is “Collision Physics” inducing “Collision Chemistry”:

“Collision physics” is the molecule-to-molecule contact or collision applied at the point-of-use, where the target and reactant are present interacting with the shockwaves which provide the input of kinetic energy, temperature and pressure, resulting in “near-instantaneous” reactions. The collision will cause the generation of heat and pressure at molecule-on-molecule contact. Energy and mass transfer is achieved in a “split-second” — breaking the original molecular bonds and causing new re-bonding and conversion into designer-products. The collision physics and surface chemistry reactions take place when the reactants are injected at supersonic speeds into a designed collision zone, i.e. the localized reaction zone. This invention uses high speed collisions, so the reactants are compressed and delivered at designed Mach speeds into collisions with each other. The physical shockwave causes collision-induced Molecular Surface Chemistry reactions, and such use is in sharp contrast to conventional thermo-chemistry. In essence, the energy-and-mass transfer occurs inside the SRM tunnel because of the effect of the shockwaves. The reaction-products are heavily influenced by Hess’s Law. When we have injected the proper balance of reactant

chemicals in stoichiometric molarity ratios matching the desired stable final products as predicted in balanced equations, the SRM should produce such results by applying Hess's Law. Additionally, with the aid of certain catalyst, we can further define the selectivity among resulting compounds of the same family in various structural configurations having the same chemical components. For such discrete product-selectivity, the application of catalyst expertise is desired. Otherwise, we allow Hess's Law to maximize the production-effect and product-selectivity, where the resulting product possessing the lowest state of enthalpy of formation and the most stability will predominate.

To illustrate the collision energy and heat occurring at the moment of impact, the following U.S. NASA (National Aeronautics and Space Administration) explanation is provided below, NASA Graphic Table Illustration (Stagnation Temperature).



In the first Graphic Table Illustration, NASA shows the Stagnation Temperature delivered at the collision-impact, which is described in the SRM of this invention as the "input of endothermic energy and pressure" into driving a collision-caused chemical reaction. NASA explains: For a moving flow of gas, there are several different values for the temperature of the gas. The "total temperature" is the sum of the static temperature and the dynamic

temperature, and the value of total temperature depends on the Mach Number of the flow. If the moving flow is isentropically brought to a sudden halt on the body *such as by a collision*, NASA measures the “**Stagnation Temperature**”. The stagnation temperature is defined as the temperature that occurs at a stagnation point (not-moving, a collision-caused stop) on the object. Because the total overall temperature does not change through a shockwave, the stagnation temperature and the total temperature have the same value at a stagnation point. There exists a correlation between the temperature derived and the Mach speed of the flow. In the process of slowing or stopping the flow by collision-impact, the gas is heated due to the kinetic energy of flow. The amount of the heating depends on the specific heat capacity of the gas. If the specific heat capacity is a constant value, the gas is said to be “**calorically perfect**” and if the specific heat capacity changes, the gas is said to be “**calorically imperfect**”. At subsonic and low supersonic Mach numbers, air is calorically perfect. But under low hypersonic conditions, air is calorically imperfect. Derived flow variables, like the speed of sound and the isentropic flow relations are slightly different for a calorically imperfect gas than the conditions predicted for a calorically perfect gas because some of the energy of the flow excites the vibrational modes of the diatomic molecules of nitrogen and oxygen in the air. NASA has plotted the value of stagnation temperature in Fahrenheit for a standard day atmosphere as a function of altitude and Mach number. There are two sets of lines on the figure because of the inclusion of real gas effects. The solid line is the computed stagnation temperature for a calorically perfect gas and the dashed line is the computed stagnation temperature for a calorically imperfect gas. At the lower Mach numbers, below Mach 3, the values of stagnation temperature are the same, because the temperature is not high enough to excite the vibrational modes. But beginning around Mach 3, real gas effects become increasingly important with increasing Mach number.

In a proprietary CGCE graph (not shown) related to the production of Methanol according to the formula:



The left Y-axis shows the upstream edge temperature for the shockwaves for Mach numbers between M1 and M7 while the X-axis shows the corresponding downstream edge temperature of the shockwave. The line entitled “Cumulative Energy of Shocks - with Steam” shows the total energy of the reactants CO₂, CH₄, H₂, and steam. If the upstream temperature (T1) is 250° F and the Mach speed is approximately 6, the temperature at the downstream edge of the shock is approximately 3,700° F. It follows that at circa 3,700° F, the enthalpy at the downstream edge of the shock will be about 510 kJ/Mol with using steam injection, and approximately 310 kJ/Mol without using steam injection. As noted, Methanol possesses an enthalpy of formation value of $\Delta H_{298K} = -238.4 \text{ kJ/mol}$. Thus, it is clear that Mach 6 shockwaves are generally more than sufficient for the SRM process and that Mach 4.3 (with Steam) or even Mach 5.8 (without Steam) shockwaves would be adequate.

It will be appreciated that for any desired product, the enthalpy of formation can be calculated based upon the enthalpy of formation of the reactants. The downstream shockwave temperature T2 of a specific gas with a specific heat capacity ratio, gamma (γ), and a Mach number M1 may be calculated as indicated below.

For Normal shocks:

$$\frac{T_2}{T_1} = \frac{2\gamma M_1^2 - \gamma + 1}{\frac{1}{2}(\gamma + 1)^2} \times \frac{1 + \frac{1}{2}(\gamma - 1)M_1^2}{M_1^2}$$

For Oblique shocks:

$$\frac{T_2}{T_1} = \frac{2\gamma M_1^2 \sin^2 \theta - \gamma + 1}{\frac{1}{2}(\gamma + 1)^2} \times \frac{1 + \frac{1}{2}(\gamma - 1)M_1^2 \sin^2 \theta}{M_1^2 \sin^2 \theta}$$

The enthalpy H of each reactant is calculated from the following formula:

$$H = C_p T$$

Where C_p is that specific heat capacity at T2. This is also a linear equation. Assuming that each gaseous reactant is at about the same temperature in the localized reaction zone, we can calculate the enthalpy of each reactant. C_p is specific to each gas and, for the reactants in [Fig. RRR](#), is as follows:

CO ₂	= 0.844 kJ/kg Deg. K	[equiv. to 19.192 kJ/mole]
CH ₄	= 2.220 kJ/kg Deg. K	[equiv. to 138.75 kJ/mole]
H ₂	= 14.32 kJ/kg Deg. K	[equiv. to 7,160 kJ/mole]
Steam	= 2.260 kJ/kg Deg. K at 350 Deg. F (134 psia saturated)	
	[equiv. to 125.556 kJ/mole]	

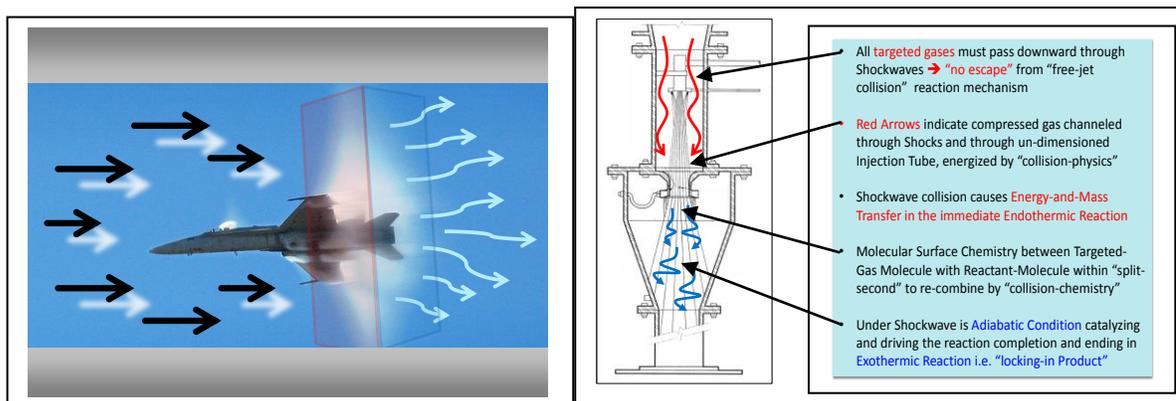
From the above table, it is apparent that Hydrogen is the principal source of energy due to its high heat capacity relative to the other reactants.

It is to be noted that the temperature at the collision surface of a Mach-4 class or higher-Mach nozzle forming shockwave is well over 1,500° F (815.55° C) and sometimes ranging into 3,000° F (1,648.9° C), but at the underside of the Mach 4 or a higher-Mach shockwave is colder than -159.9° C (and -255.95° F), which would reflect the almost outer-space condition, ≤ circa 30 to 100 km above the earth.

As an example of Temperature at the underside of a Mach 4-class shockwave, NASA provided a quick reference formula for shockwave caused by steam at 235 psig at nozzle entrance temperature of 855.57° Rankine and the temperature at the exit-underside of the shockwave is factored at 0.238496 x 855.57° Rankine = 204.045° Rankine (or -255.95° F). And as we explained earlier, when the molecules move a little away from the shockwave effect a moment later in a partially-open system with distance and time moderating and dissipating the shockwave effect, the associated temperature and pressure will begin to

recover to nearer ambient condition, but still slightly sub-atmospheric. Therefore, in such a gas dynamic environment, having been formed by the endothermic reactions and moving-passing through the underside of the shockwave, the cooled Methane and CO₂ cannot and will not survive as frozen solids, but will take the respective physical state at near ambieny. Methane will rain-down as liquid and CO₂ will regain gaseous state, just like the recalled images of Case (A) for your Natural Gas production engineer, and of Cases (B-C) for everybody else. Therefore, there should not be any concern of how to remove and retain the end-product in a rapid exothermic flow, because the products will not become frozen solids, but will resume more normal liquid or gaseous state (as appropriate) very quickly as illustrated in Cases A-B-C (supra), and the liquid-phase product will run down and be removed to a Captured Liquid Product Tank and the gas-phase product will flow as a gas through a phase-separation apparatus and onto the next treatment or removal stage.

So, in CGCE's design, let us imagine the flow of reactant gases in the SRM is in the direction from Left-to-Right, just like the photos of the Jet airplane (shown *infra*). But our SRM is a narrow tunnel-shaped vessel that all relevant air-gases must flow (like the Jet must fly through). Thus, by analogy in our chemical conversion situation, all gases in the SRM tunnel must pass through the continuous shockwave(s) as illustrated by the Prandtl-Glauert "skirt" (as seen by the public) and the "reverse-skirt" (as seen by aerophysicists). No molecule in the tunnel can escape the effect of the shockwave. Physics governs. It is absolute.



It is CGCE's position that the SRM does not represent a closed system with reversible reactions. The SRM is collision-physics that could occur regardless of what the chemical reaction environment may be at any temperature and/or pressure, any changing temperature and/or pressure, at any time, and even changing while in process. *It applies universally in collisions of galaxies, stars, planets in outer space, as well as in collisions of molecules and atoms in either outer or inner space. Thus the SRM works in open, mostly-open, and partially-closed systems.* And SRM's collision-physics causes collision-chemistry.

What Problem Does this Solve: According to MIT Paper dated May 11, 2009 called: "Thermodynamic Analysis of Coal to Synthetic Natural Gas Process" which general conclusion is instructive and is universally applicable to a wide range of processes and applications in the gasification industry as well as in many other industries: We see that the

conventional thermodynamic comparisons between and among the major competing gasification technology providers: Lurgi, Siemens, KBR, ConocoPhillips, Shell, GE Energy/Texaco, and others always circled around comparing relatively minor variations or changes of energy-inputs, temperatures, pressures, use of catalysts and stoichiometric ratios resulting in the slightest incremental yield-rate improvements, but all within the range of 55% to 62%, and a 65% yield-rate becomes an ideal goal. Very little novel thinking and breakthrough has been introduced. To reach anywhere over a 70% yield-rate, extraordinary high consumption of energy and pressure inputs are required thus making it a costly sacrifice and uncompetitive with the others.

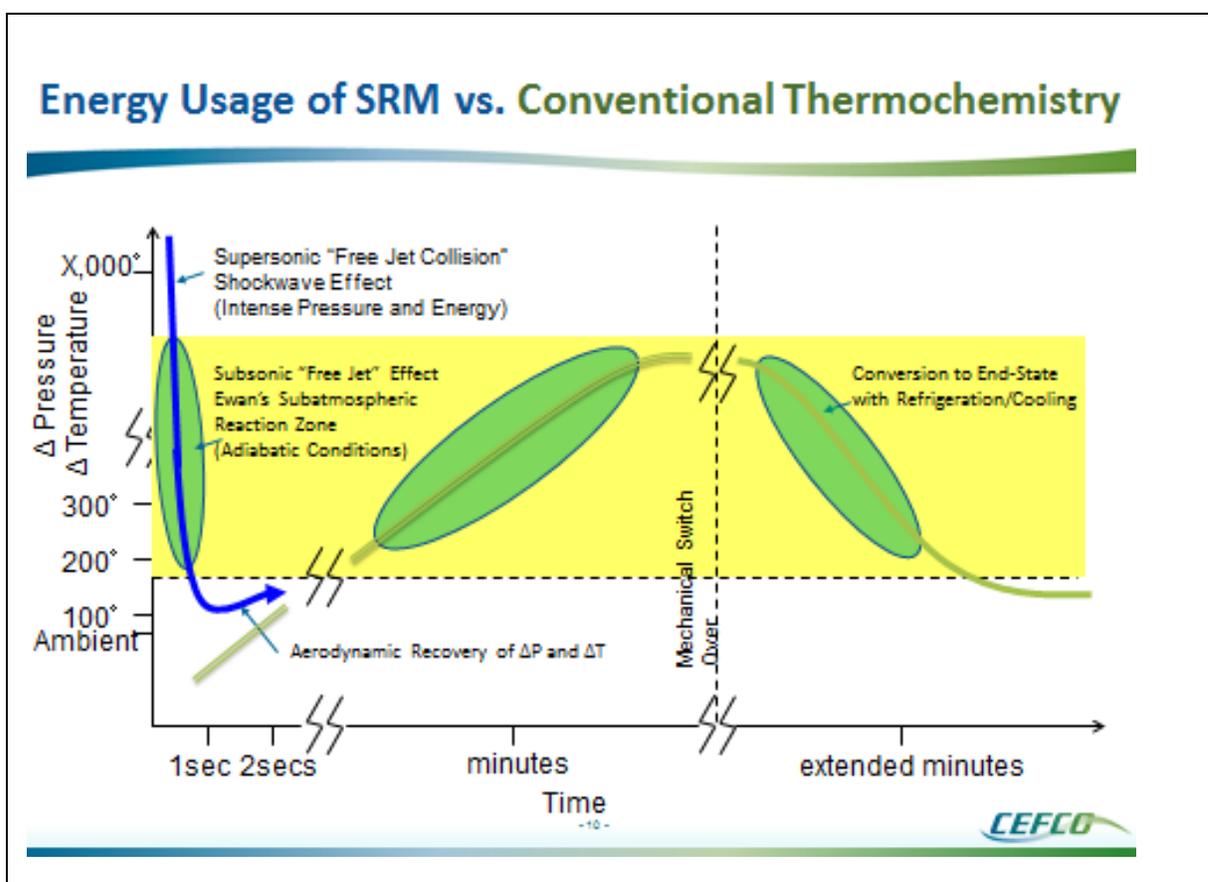
Novel SRM is described in great details in Pat. Pending USA#61/720,919. SRM enables the phenomenon of using any targeted gas to collide with another targeted gas acting as its intended reactant, or to collide with another intended liquid reagent (finely atomized in shockwave collision), so as to make a new compound from such collision, reaction and re-combination, known as “molecular surface chemistry” to the physical chemists. In the case of GHG gases, we can use either CH₄ or CO₂ (especially the captured and re-used CO₂) as the first targeted gas, and collide it with the other second reactant gas or reagent (which could be another stream of CO₂ or CH₄, and/or with any addition of intended reactants or reagents). One or both of the reactant gas(es) will be pressurised and directed to collide into each other by directional supersonic nozzles. To be clear: SRM does not need to segregate each unique gas into its own separate stream, the user can split the gross inlet gas stream of gases into two or more streams, and pressurise and channel one of said inlet gas stream (containing either of/or any combination of GHG: H₂, CO, CO₂, H₂O, O₂, CH₄) directly into our shockwave nozzle configurations to collide against the said first, the said second or the said third of the inlet gas streams of similar or different composition also re-vectored and entering from an opposing angle, or at a designed angle, into the shockwave nozzle configurations to create the products under the SRM. The innovative concept here is to use our highly-pressurised gaseous or steam components and collide them against one another at various designed Mach speeds — as long as we have balanced out the requisite stoichiometric molarity for each gaseous component in balanced equations to create usable products. Sufficient residence time is engineered into the apparatus to allow the reformation of the desired compound. For example: Methanol possesses the enthalpy of formation value of $\Delta H_{298K} = -238.4\text{kJ/mol}$. Hess’s Law is observed as follows where ΔH^θ is the standard energy of the reaction and ΔH_f^θ is the standard energy of formation.

$$\Delta H^\theta_{\text{reaction}} = \sum \Delta H^\theta_{f(\text{product})} - \sum \Delta H^\theta_{f(\text{reactants})}$$

Application of Hess’s Law to the current SRM invention explains the locking-in the state of the end-product: *At the collision-impact of the shockwave(s), all molecules in reactant gases are affected by the shockwave and discontinuities therein, and there can be no escape from its effect.* Hess’s Law explains that 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 are important as expressed in the final result. All reaction-intermediates are transitional and will rapidly reform or recombine into the end-product that possesses the lowest enthalpy governs when all intermediates and transitional reactions are “netted out” in the rapid exothermic condition that results in a stable end-

product at much lower range of temperatures — closer to operational standard. We know that if the net enthalpy change is negative ($\Delta H_{\text{net}}^{\theta} < 0$), the reaction will be exothermic and is more likely to be “spontaneous” (which means: in “a split-second”). Such exothermic reactions release heat to the gas phase while the end-product will be cooler and remains “locked-in” inside a lower state of energy. CGCE has engineered the assurance of cooling condition under the “Joule-Thomson (Kelvin) Effect” of free-jet expansion of gas. That lower state and stability effect helps with product-selectivity. We can further define the selectivity among resulting compounds of the same family of the same chemical components and with near-similar net enthalpy values. For such discrete product-selectivity, the application of catalyst expertise from our Teaming Partner is desired. Otherwise, we allow Hess’s Law to maximise the production-effect and product-selectivity, where the resulting product possessing the lowest state of enthalpy of formation and the most stability will predominate.

The following graphic illustration compares the Energy Consumption of the SRM (in blue line finishing within 2 seconds) versus Conventional Thermo-Chemistry (in yellow-greenish line requiring many minutes weaving through the graph) as used by many current processes. Thus, the SRM is much faster, uses substantially less energy-input, and using smaller equipment size and space:



Methanol-Ethanol Examples using SRM Technology: For an illustration, in a practical example specifically demonstrating the selected GHG: CO₂ may be injected at a designed Mach speed via supersonic nozzle into the SRM, and CH₄ gas may be injected at a designed Mach speed; and then H₂ gas may also be injected at a designed Mach speed. Within the reactor(s) the following collision-reactions occur for the Methanol-formation example, together with the materially-balanced resultant equation as shown in Eq. 5, because all transient-intermediate steps of Eq. 2 through Eq. 4 will be eliminated very rapidly according to Hess's Law (below):

1. CO₂ + CH₄ + **SRM** → 2CO + 2H₂
2. CO₂ + 3H₂ + **SRM** → CH₃OH + H₂O [Methanol + Water = Net Exothermic ΔH, etc.]
3. CH₄ + H₂O + **SRM** → CO + 3H₂
4. CO + 2H₂ + **SRM** → CH₃OH [Methanol]
5. CO₂ + CH₄ + 2H₂ + **SRM** → 2CH₃OH [Methanol = Net exothermic ΔH, explained in Pat. App.] Then to make Ethanol subsequently in another Reactor:
6. CH₄ + CH₃OH + **SRM** → C₂H₅OH + H₂ [Ethanol 'A']
7. CH₃OH + CH₃OH + **SRM** → C₂H₅OH + H₂O [Ethanol 'B']
8. CO₂ + 3 CH₄ + **SRM** → 2 C₂H₅OH [Ethanol 'C']
9. 2 CO₂ + 2 CH₄ + 4 H₂ + **SRM** → 2 C₂H₅OH + 2 H₂O [Ethanol 'D']

The Alcohol (Methanol or Ethanol) and water, if any, will drop as liquids to the bottom of the reactor(s) and enter the captured product tank. If the gaseous reactant supplies are properly balanced, only Alcohol should be produced and flows down into said product-tank. If there is a stoichiometric imbalance of gas reactant inputs, then there is a possibility of CO and H₂ appearing in the exiting gas stream and these may be used directly as a fuel, or re-directed into a secondary reactor to complete their consumption with chemical adjustment for balancing of the reactants.

This is “shockingly-different” from the results normally expected in a lower-yielding “Gibbs system” equilibrium environment typically requiring between 950° C to 1,950° C and between 30 to 300 atm, where 24 theoretical reaction varieties of transient-or-intermediate-reactions or side-reactions could occur in conventional “gasification”. Many of them are undesirable, i.e. making too much CO₂, water — requiring “reiterative” steps to increase yields. In contrast, for those who uses **SRM**, the practical application is the enabling power of the “energy-and-mass transfer” shockwave reaction mechanism to achieve superior yields faster and cheaper, and to design long-chain hydrocarbons and other chemical compounds following the **SRM** steps, which can be shown in the generalised equation, below:

$C_nH_x + C_nH_x + yH_2 + [CHONPS]^2 + SRM/Catalyst \rightarrow$ Designer's Long-Chain Hydrocarbons or Alkanes or Alcohols or Liquid Fuels or other Chemical Compounds.

END NOTES and BIBLIOGRAPHY (Begin Hereinbelow and in Attachment Files):

ⁱ US Patent #7,842,264B2 (Nov. 30, 2010) and WO 2008/127557A1 (Oct. 28, 2008); and numerous national patent numbers, including Canada and GCC countries, etc. **Title:** "PROCESS AND APPARATUS FOR CARBON CAPTURE AND ELIMINATION OF MULTI-POLLUTANTS IN FLUE GAS FROM HYDROCARBON FUEL SOURCES AND RECOVERY OF MULTIPLE BY-PRODUCTS".

ⁱⁱ US Patent Application #61/720,919 (2012) and PCT application titled: "PROCESS AND APPARATUS FOR SUPERSONIC COLLISION SHOCKWAVE REACTION MECHANISM FOR MAKING CHEMICAL COMPOUNDS".

ⁱⁱⁱ Thermo-chemistry outlined above requires a series of steps to provide very high energy input, including but not limited to, repeated heating and cooling as well as raising the pressure at several points in the process. Such prior art includes the synthesis gas processes commonly known as any of the following: BASF, ICI, Johnson-Matthey, Methanex, Exxon-Mobil, Shell, GE Energy/Texaco, ConocoPhillips, KBR, Siemens, Lurgi, and Fischer-Tröpsch, etc., etc. In order to increase the efficiency of the process to produce Methanol, any other hydrocarbon compounds or chemicals, it would be desirable to limit the required steps as well as to reduce the energy-input required in the overall process. Reduction in the number of steps would also reduce the CAPEX and the OPEX. The SRM invention described in this paper is directed to a method and apparatus for directly producing Methanol, other alcohols and hydrocarbons, and other organic and inorganic chemicals, through the use of a supersonic Shockwave Reaction Mechanism ("SRM").

^{iv} Molecular surface chemistry describes the phenomena that occur at the surfaces or interfaces between one molecule with another molecule. It deals with molecular surface energy transfer, electron charge transfer, adsorption, dissolution of original bonds, reformation of new bonds, intermediates and transitional dissociation and re-association of possible new bonding or pairing of components, desorption, mass and energy transfer, catalysis, and so forth. Since the formation of a new surface involving reactants requires breaking of attractions between the original constituent molecules, which is an endothermic process, the surfaces of the involved molecules are made relatively more unstable and involve the flow of positive free energy of formation. Surfaces contribute such free energy to the total system, which is also known as surface tension. Nevertheless, in an energy conservation mode, the system tries to minimise such unfavorable free energy at the involved surfaces. Such a surface quickly makes attraction with other molecules available to the system. New bonding and a new compound is formed. The result is to reduce surface tension and to re-instate surface integrity. The Oxford University Physical and Theoretical Chemistry Laboratory provides lectures and written explanation of such molecular surface chemistry as described by the Applicant. The U.S. Department of Energy's Brookhaven National Laboratory (BNL) Website provides as reference a very descriptive pictorial illustration of such molecular surface chemistry.

² CHONPS is a mnemonic for the main elements that occur naturally in living systems: any Carbon, Hydrogen, Oxygen, Nitrogen, Phosphorus, or Sulphur.

Presentation to CMTC – 2013

Shockwave-Enabled Technologies Capturing
CO₂ and Turning GHGs into Chemical
End-Products, Alcohols, and Liquid Fuels

**Proposed cheapest, most-efficient method to create chemicals
(alcohols, fuels, PVC) as alternative to Thermo-Chemistry**

CEFCO GLOBAL CLEAN ENERGY, LLC

Robert Tang – CEO, Inventor

Brian Tang – Co-Author



Previous CMTC–2012 Conference Paper ID #149808 presented February 9, 2012 under the Session titled “CCS Capture R&D”

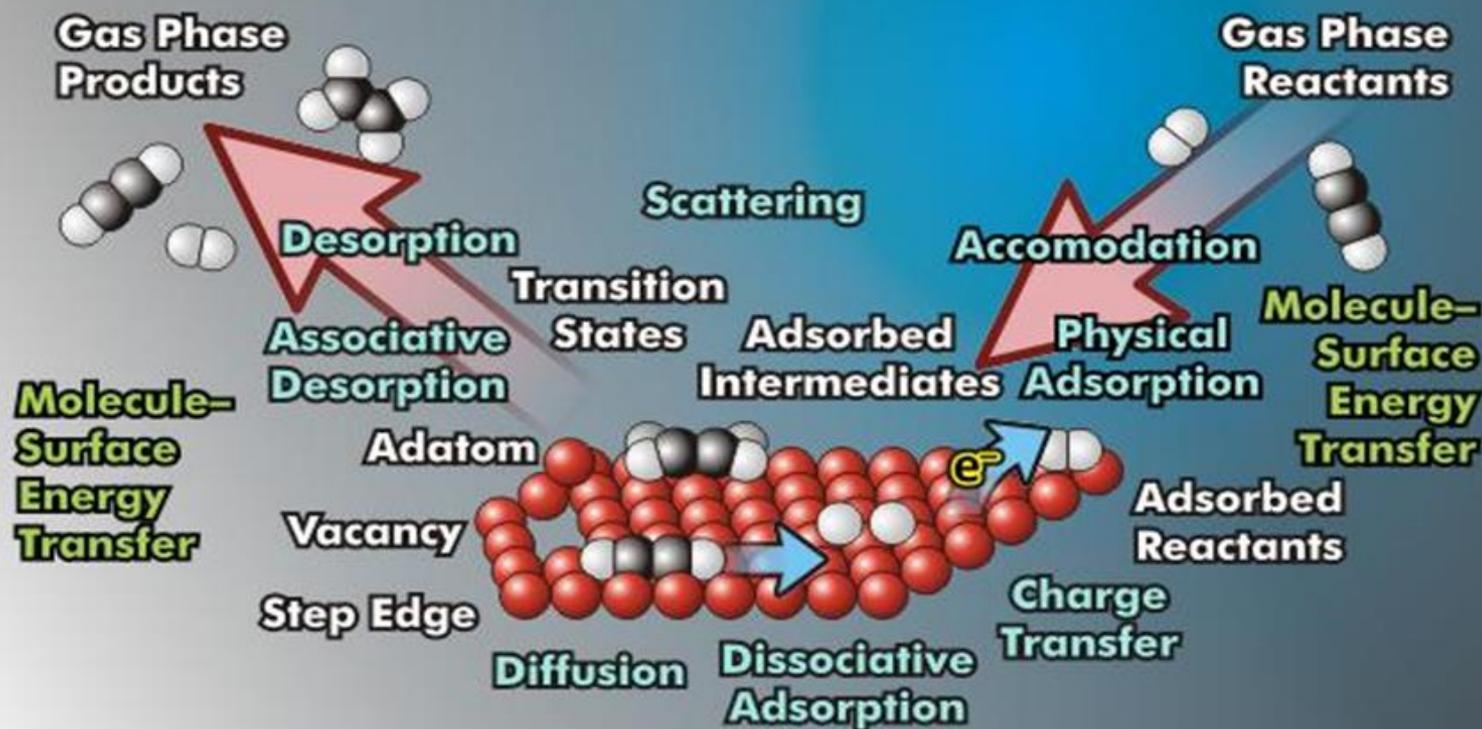
Steps	Carbon Capture Module, for low-cost re-cycling and re-generation of Bi-Carbonate-Carbonate reagent: we can use both Na ₂ CO ₃ and NaOH for the Repetitive Capture of CO ₂ . User can use KOH and K ₂ CO ₃ to achieve similar effect.	Enthalpy [ΔH _f ^o] kJ/mole	Equiv. BTU (IT)
1a	(Eq. 1) CO ₂ + Na ₂ CO ₃ + H ₂ O → 2NaHCO ₃ (precipitation)	[ΔH = -84]	-79.61
1b	(Eq. 2) CO ₂ (g) + NaOH (aq) → NaHCO ₃ (precipitation)	[ΔH = -80.1]	-75.92
Outside of Shockwave System	After CO ₂ Capture, the Bi-Carbonate (precipitation) can be re-liberated into CO ₂ (gas) for Subsequent Utilization by User employing a Low Range of Heating Energy-Input at a Time and Place of the User’s Choice. Add Heating Equipment or Heat Input if and when needed for productive uses.	<u>Example:</u> Deploy the Return Steam-Loop with “Un-insulated” Coil winding at the bottom of the Carbon Product Re-Liberation Tank to provide Heat at the cheapest energy-input cost.	
2	(Eq. 3) 2NaHCO ₃ → CO ₂ + Na ₂ CO ₃ + H ₂ O	[ΔH = + 84]	+79.61
	Reagent Na ₂ CO ₃ reagent is re-generated and can be re-used after Filtering. Cheap re-cycling of same Resource leading to very low reagent-input cost. Adding NaOH makes more Na ₂ CO ₃ reagent or can refresh stale reagent.	Return-Loop Steam Coil does not leak naked steam into the Tank Liquid. No commingling of valuable-reusable resources.	

ⓘ Heating the Bi-Carbonate in water in the range of 210° F to 250° F will suffice. This method will contribute to the Condensation of the Return-Steam into water. Such condensed water will have to be pumped to the Filtering and Re-Boil Steps for further conservation and re-use of the resources.

Shockwave Reaction Mechanism “SRM” Science

- “Shockwave” is a sharp change of pressure, temperature, and density in a narrow region for an object moving faster than the speed of sound while travelling through a gaseous medium. *Mach Number* measures the speed of sound. (Each Mach \approx 1,200 ft./second)
- “Collision physics” is the molecule-to-molecule contact or collision applied at the point-of use, where the target and reactant are interacting with shockwaves, which act as the driving force to provide the input of energy-and-mass transfer of requisite kinetic energy, temperature and pressure to break the original molecular bonds and to cause new re-bonding in rapid “molecular surface chemistry” reactions.
- The “YYY kJ/mole” energy required will be endothermic and delivered by Mach-speed physical collision-impact with the shockwave which also becomes a catalyst for chemical reactions.
- Subsequent phenomenon of rapid cooling and pressure drop underneath the “stern” of the shockwave will “lock -in” the end-product in an exothermic mode, with no possibility of reaction-reversal (a.k.a. the “non-Gibbs condition” or the adiabatic cooling “Joule -Thomson (Kelvin) Effect”).
- This comprehensive mechanism and application of endothermic-then-exothermic reaction is offered as a “quantum leap” breakthrough in chemical re-combination methodology.

Gas-on-Gas Molecular Collision: Physical Chemistry



Graphic image by Brookhaven National Laboratory (BNL)

“Shockwave Skirts” at Tail of Navy Jet – flying at Mach Speed off a Humid 35°C Florida Coast



Left: Collision of jet air-frame against H₂O vapor molecules. Shockwaves shown as Prandtl-Glauert “Shock collar” or “Skirting” effect.

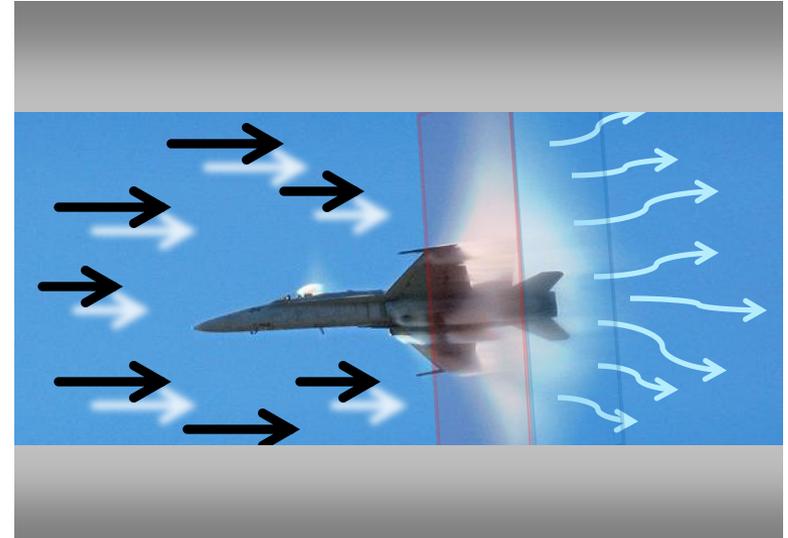


Right: “Reverse Skirt” – very rapid collapse of moisture, temperature, and pressure to form condensed ice crystals adiabatically under very cold temperature which further melt into ambient liquid mist

Inside the SRM

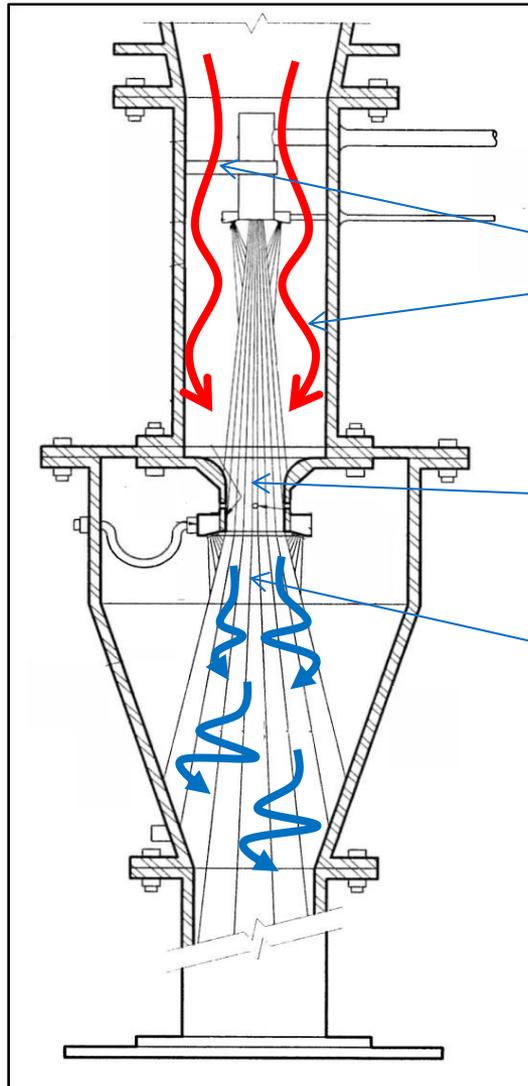


Left: Schlieren photography – multiple shockwaves generated by shuttle craft at high Mach speed showing intensive Energy and Mass Transfer Effect



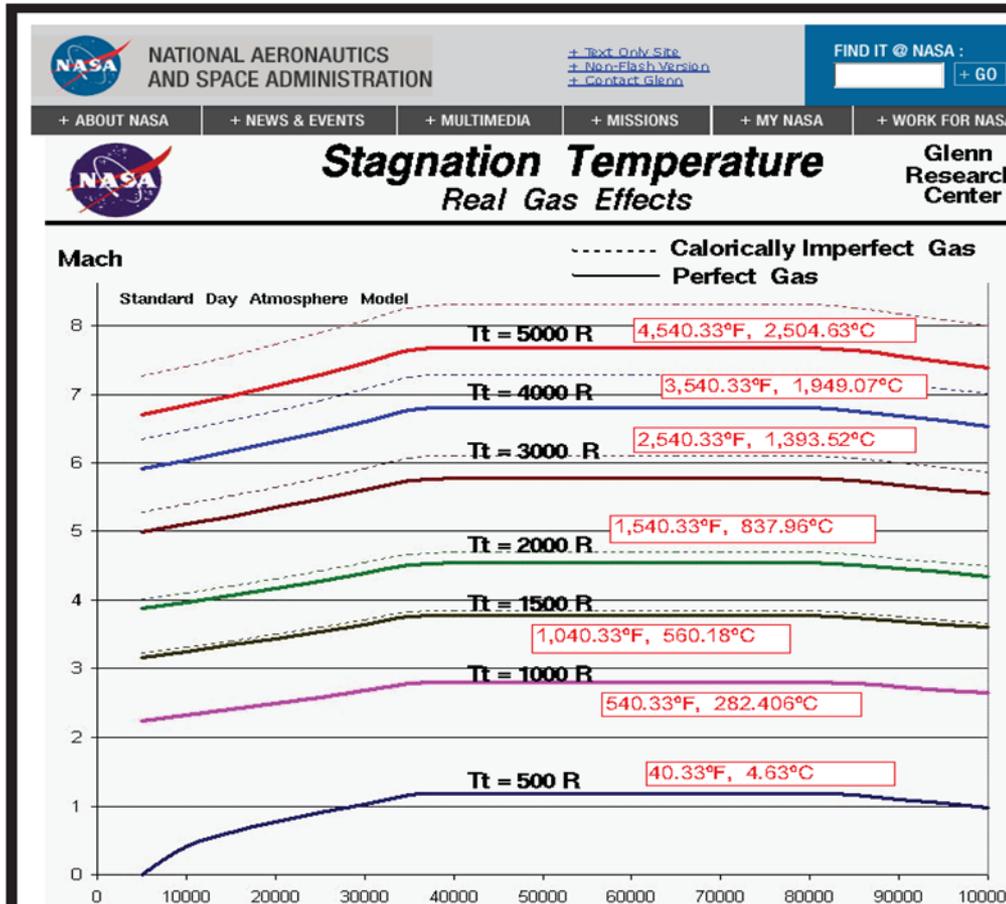
Right: Imagine inside a wind tunnel where the jet represents a SRM supersonic nozzle. Here, all black/white reactant gases must flow through the shockwave collision “Skirt” and “Reverse-Skirt” Effects

Visualizing CEFCO's SRM Dynamics – Un-Proportioned and Un-Dimensioned



- All **targeted gases** must pass downward through Shockwaves → “no escape” from “free-jet collision” reaction mechanism
- **Red Arrows** indicate compressed gas channeled through Shocks and through un-dimensioned Injection Tube, energized by “collision-physics”
- Shockwave collision causes **Energy-and-Mass Transfer in the immediate Endothermic Reaction**
- Molecular Surface Chemistry between Targeted-Gas Molecule with Reactant-Molecule within “split-second” to re-combine by “collision-chemistry”
- Under Shockwave is **Adiabatic Condition** catalyzing and driving the reaction completion and ending in **Exothermic Reaction** i.e. “locking-in Product”

“Shock” Energy-Input for Collision Physics



US NASA: The “Stagnation Temperature” is defined as the temperature that occurs at a stagnation point (a collision-caused stop) on the object.

When the flow abruptly stops by collision impact, the gas rapidly heats up due to the kinetic energy of flow.

A correlation exists between the collision-temperature resulted and the Mach speed of the flow.

The selected Mach speed for SRM will provide requisite energy, temperature and pressure transfer to cause collision physics and chemical reaction.

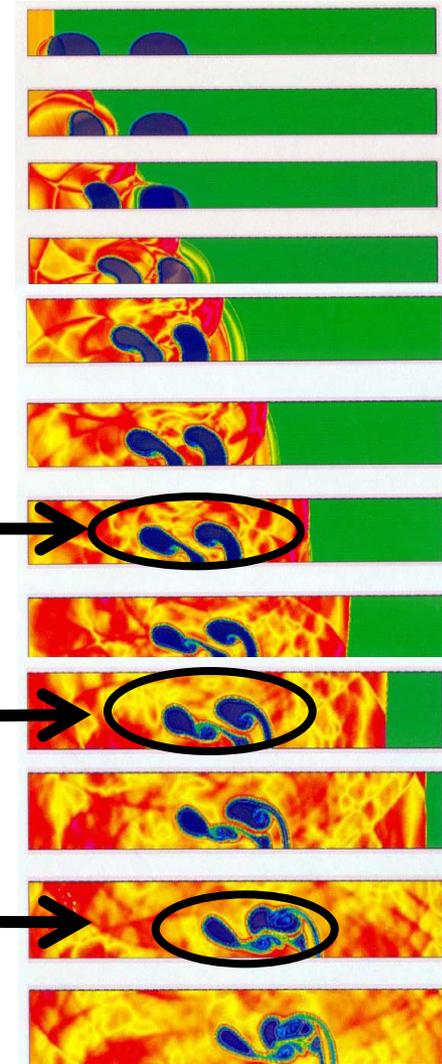
SRM-Induced Intimate Gas Mixing

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

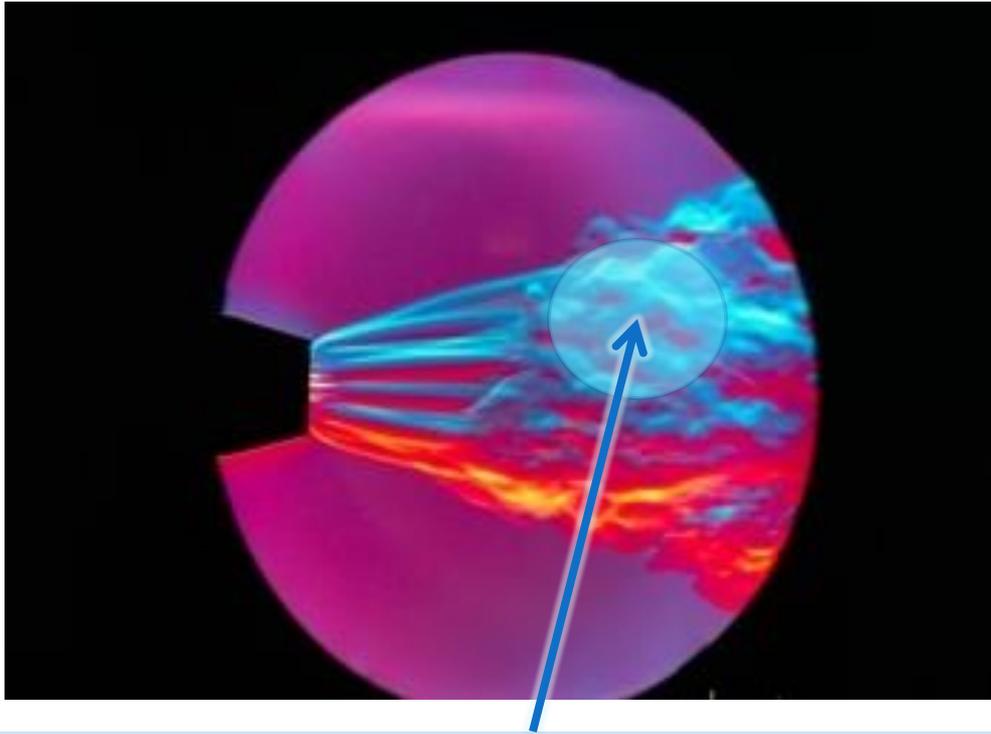
Shockwave envelopment

Inter-mixing

Re-combination



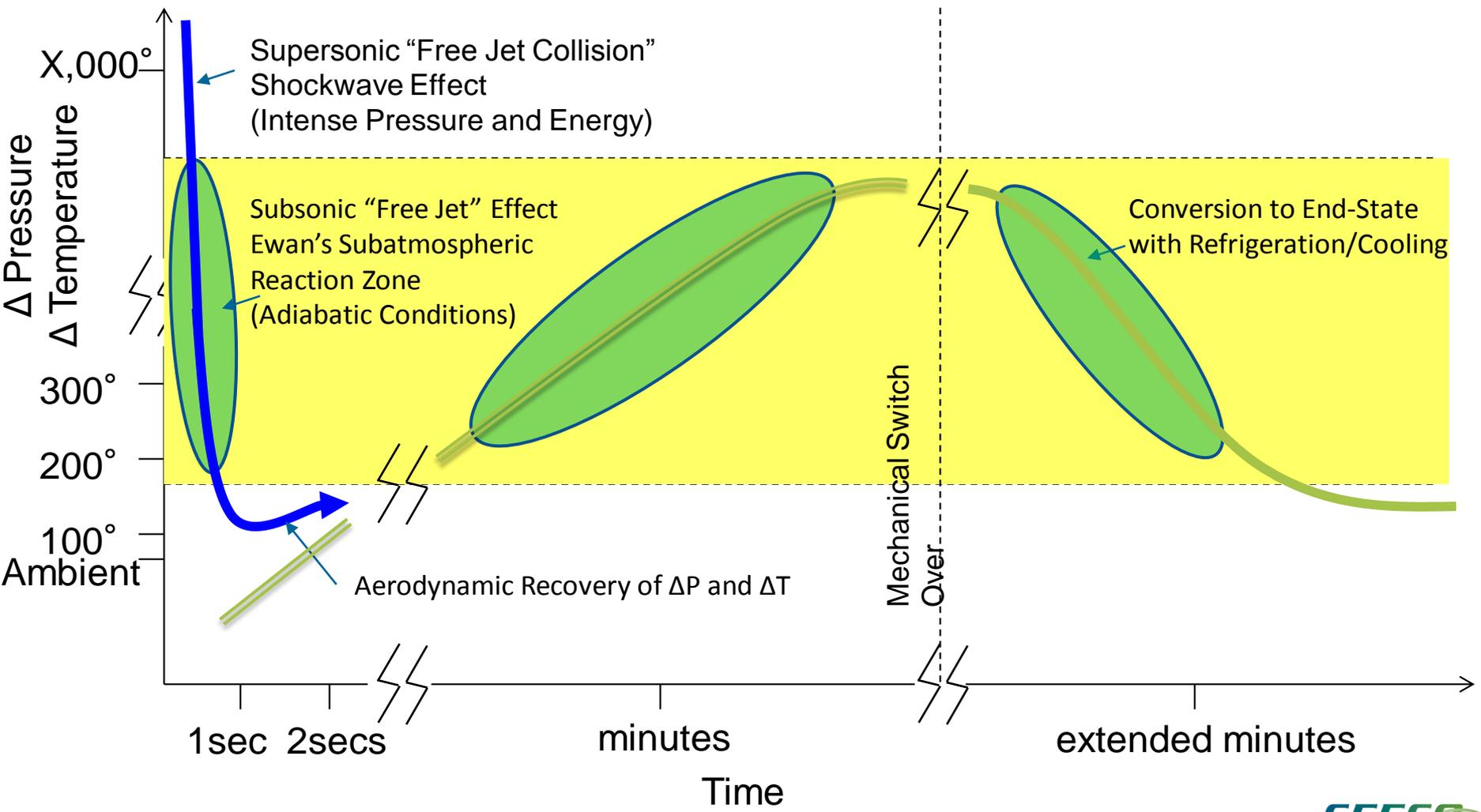
Free-Jet Expansion & Reaction Zone



NASA formula shows that a Mach-4 class shockwave at nozzle entrance using 235 psig steam is 855° Rankine Degree (395.33° F, or 201.85° C). At shock-collision surface, the Mach 4+ shockwave heat ranges from $1,500^{\circ}$ F (815.5° C) to $3,000^{\circ}$ F ($1,648.9^{\circ}$ C). But the shock's exit underside is $0.238496 \times 855.57^{\circ}$, thus $R = 204.045^{\circ}$ (or -255.95° F, or -159.97° C), very cold, for about one second.

- Image: Schlieren Photography of Free-Jet Expansion (“Joule-Thomson (Kelvin) Effect”) inside reaction chamber causing shockwave-induced exothermic “sub-atmospheric reaction zone”
- Enabling Exothermic Chemical Reactions, and “lock-in” the product with no reversibility (i.e., “Non-Gibbs” condition)
- Phenomenon of Extremely Rapid Cooling (with extreme drop in Δ Temperature and Δ Pressure) → No need for conventional cooling equipment and re-iterative process

Energy Usage of SRM vs. Conventional Thermochemistry



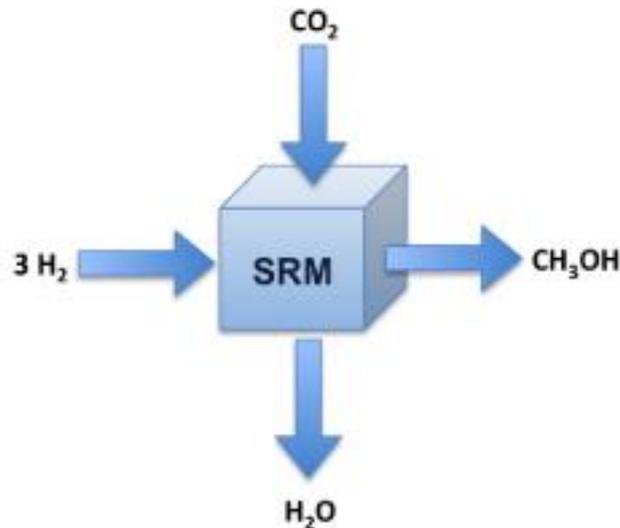
Application of Hess's Law

$$\Delta H_{\text{reaction}}^{\ominus} = \sum \Delta H_{\text{f}}^{\ominus}(\text{products}) - \sum \Delta H_{\text{f}}^{\ominus}(\text{reactants})$$

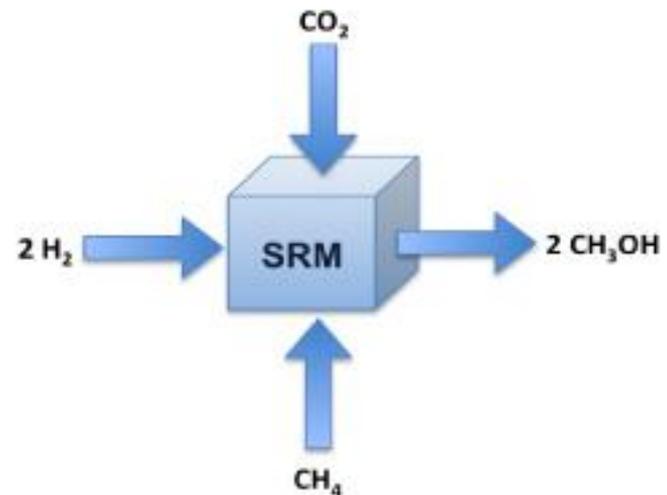
- All molecules in gases are affected by shockwave = no escape
- Hess's Law: energy or enthalpy change (ΔH values) for any chemical or physical process is independent of the pathway or number of steps required to complete the process; only the initial and final states being important
- Reaction-intermediates 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 ($\Delta H_{\text{net}} < 0$), 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 gas phase and assists in energy and pressure recovery = lower energy usage

Aero-Physics Science

Shockwave Reaction Mechanism

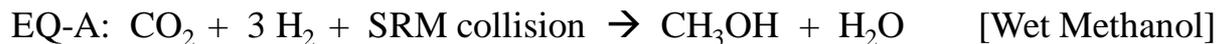


Methanol 'A' Production

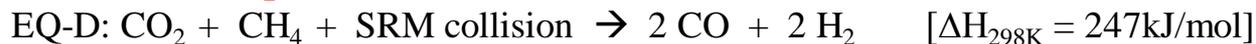


Methanol 'B' Production

Methanol Production via "SRM"



Pre-Fischer-Tropsch "G-T-L" Feedstock Production via "SRM"



SRM Production Examples - Ethanol

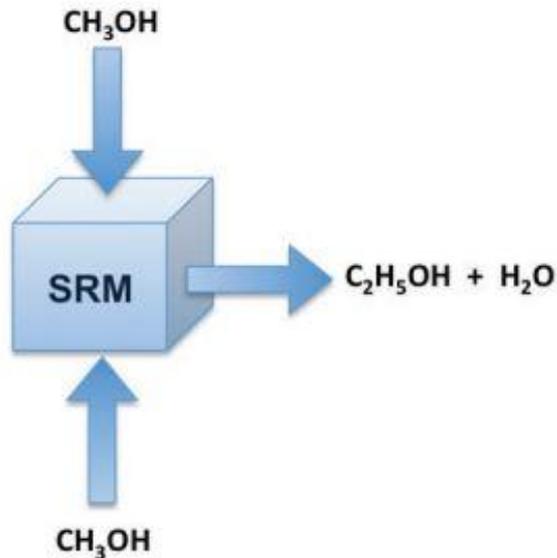


Fig. 5B: Ethanol 'B' Production

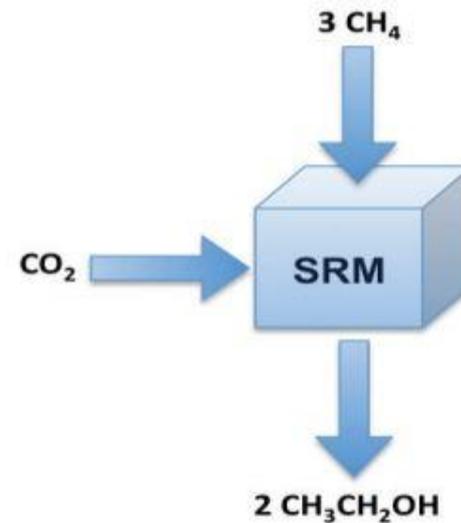
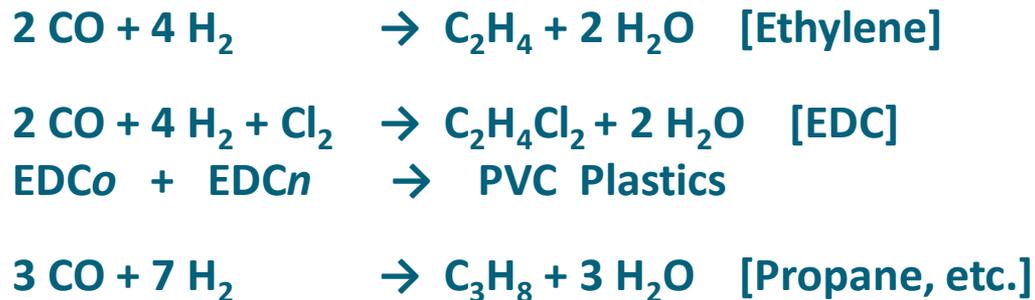


Fig. 5C: Ethanol 'C' Production



Innovation: SRM can be Developed for the Petro-Chemical & Refinery Industry

- Using the SRM to make Chemicals, such as Alcohols, Fuels and Plastics from any Hydrocarbon Feedstock could be a significant Energy-Reduction, Time-Reduction, Equipment and Steps Reduction, and overall Cost-Reduction application
- Colliding any gas with another gas/vapor or liquid reagent using SRM: including **CO + H₂** or **CH₄ + H₂** with any combination of **Carbon, CO or CO₂, O₂** with or without **H₂O re-combination** can form Polyethylene (PE) and Polypropylene (PP), and can add **HCl** or **Cl₂** to form Ethylene Dichloride (EDC) to make PVC Plastic.



SRM: Cheapest and Most-Efficient Production Technology

- Slipstream of compressed fluid or Targeted “**Gas x**” flow to collide with itself or another Compressed Gas as “**Reactant y**” (using proprietary SRM Nozzles at desired Mach speed) to create **Mach 1 < v velocity < Mach 6** — continuously delivering Molecule-to-Molecule Collisions inside SRM at “ultra low cost” energy input
- Liquid Reagent (if used) could be atomized by Shockwave inside the Reactor for super-enhanced (micro-droplet size) allowing intimate mixing with Targeted Gas(es)
- Supersonic Collision delivers Energy and Pressure for endothermic-then-exothermic reactions, ending in adiabatic condition (“Joule-Thomson (Kelvin) Effect”) to reform products to their lowest Enthalpy state (**Hess’s Law**)
- Smaller system equipment size, quicker production flow, using available process steam and compressible fluids, and I.D. Fan) → **Low CAPEX**

Questions & Answers

Thank you very much for your attention.

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