High Energy Systems for Transforming CO_2 to Valuable Products

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High Energy Systems for Transforming CO_2 to Valuable Products

- **Sponsor** U.S. DEPARTMENT OF ENERGY NETL NATIONAL ENERGY TECHNOLOGY LABORATORY **DE-FE0029787**

- **Funding**: Federal: $799,997, Cost-share: $206,000, Total: $1,005,997

- **Objective**: Develop a direct electron beam (E-Beam) synthesis (DEBS) process to produce valuable chemicals such as acetic acid, methanol, and carbon monoxide using carbon dioxide (CO_2) captured from a coal-fired power plant and methane (natural gas).

- **Team:**

Member	Roles
gti	• Overall project integration and management • Design, construct the E-Beam reactor and the testing unit • Conceptual design for coal-fired power plants with DEBS
Tba	• Provide guidance in E-Beam reactor design and E-Beam accelerator for testing
ESF State University of New York College of Environmental Science and Forestry	• Develop a kinetic model for the E-Beam reactor

Project Description – Performance Dates

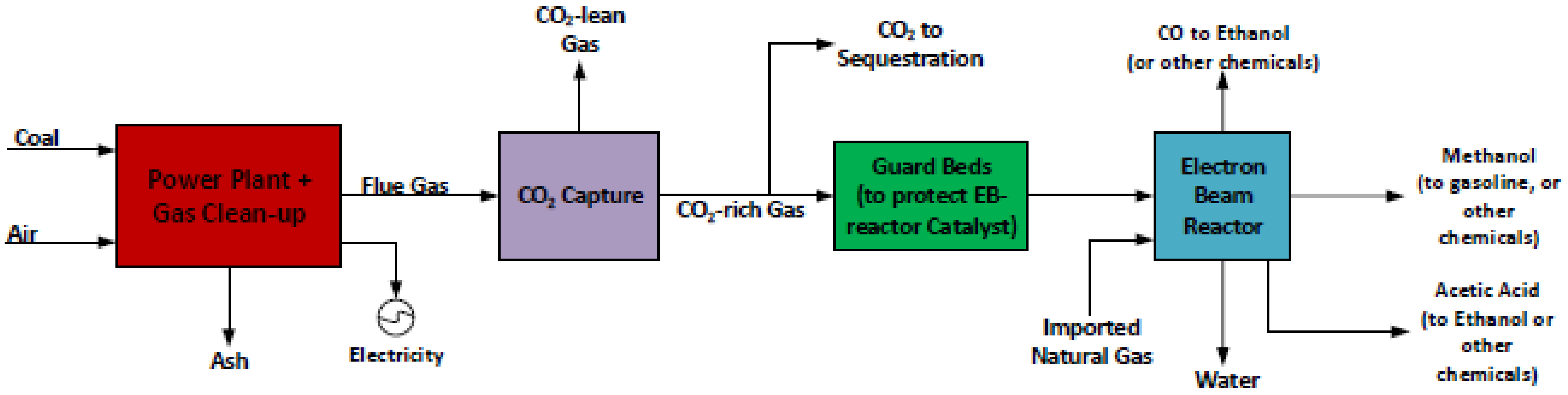
- Develop the DEBS process that uses high-energy e-beam to break chemical bonds.

- Produce valuable chemicals, such as acetic acid, methanol, and carbon monoxide, at relatively low severity (pressure near one atmosphere and temperatures <150°C) from near-pure CO_2 captured from a pulverized coal-fired power plant and methane, imported as natural gas.

- Creating such valuable products will offset the cost of carbon capture and storage.

Period of Performance	Budget Period 1	Budget Period 2
05/17-04/19	05/17-01/18	02/18-04/19

DEBS Process Flow Diagram



Coal

Air

Power Plant + Gas Clean-up

Ash

Electricity

Flue Gas

CO_2 Capture

CO_2-lean Gas

CO_2-rich Gas

CO_2 to Sequestration

Guard Beds (to protect EB-reactor Catalyst)

Electron Beam Reactor

Imported Natural Gas

CO to Ethanol (or other chemicals)

Water

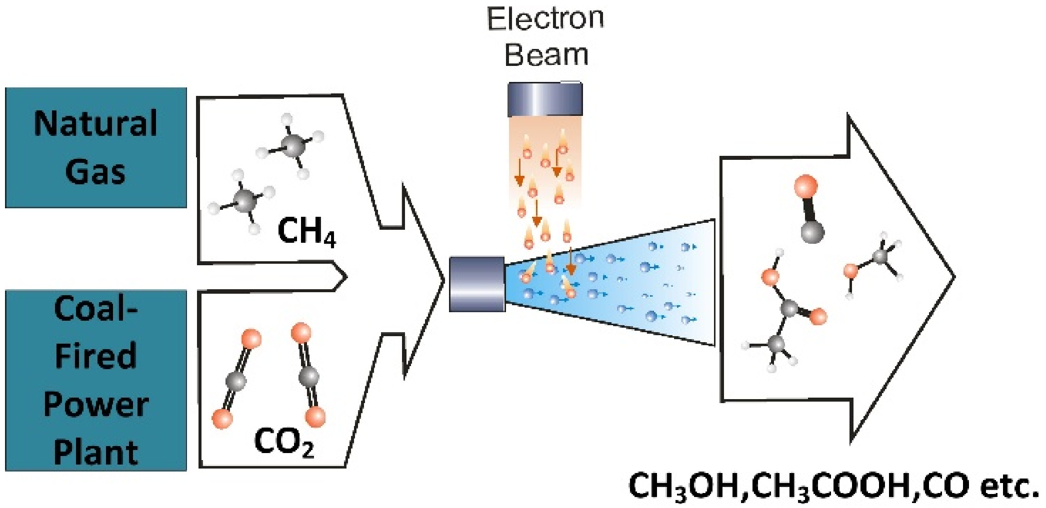
Methanol (to gasoline, or other chemicals)

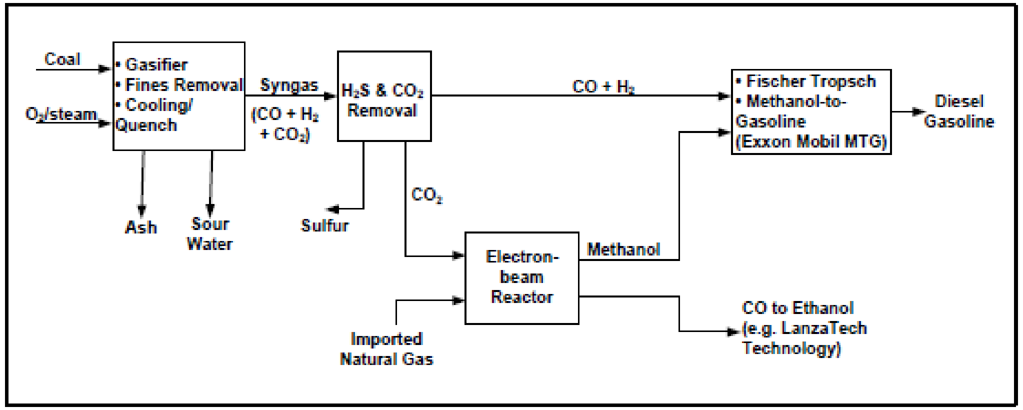
Acetic Acid (to Ethanol or other chemicals)

DEBS: non-equilibrium process that breaks bonds directly unlike conventional chemistry that requires heating the entire molecule

This project will expand on the concept of DEBS to:

- Develop a commercially viable process
- Minimize E-Beam energy requirements
- Maximize CO_2 conversion
- Selectively control the yield of more valuable products using catalysts





DEBS Integration in an IGCC Plant

- A kinetic model will be developed by SUNY based on the collected data and will be used to predict the chemical performance of the DEBS process.
- A conceptual design for coupling the DEBS process to a coal-fired power plant will be developed.

Valuable Chemical Products

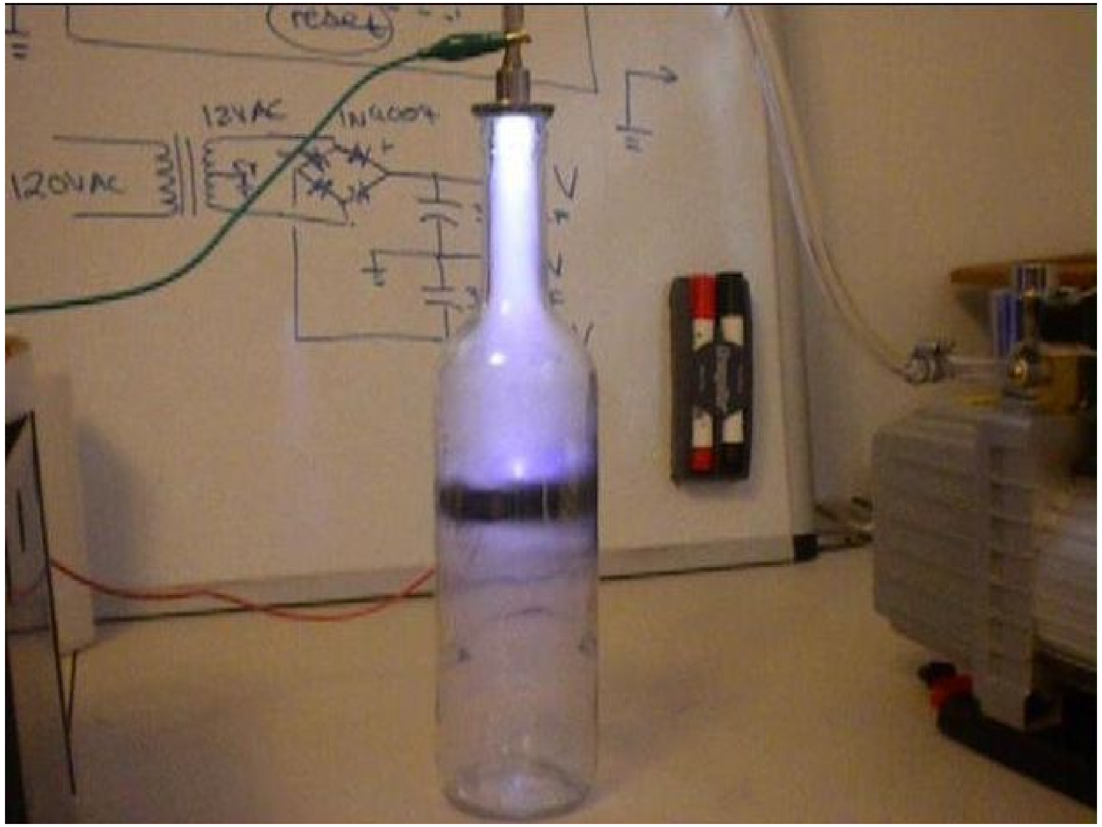
Advantages Over Traditional Processes

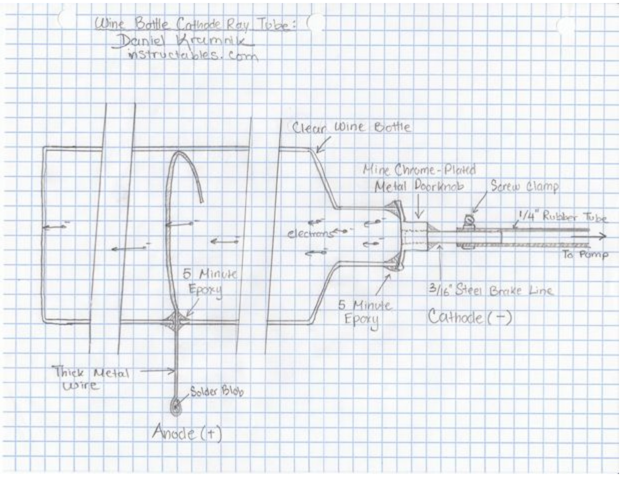
- Current technology for the commercial production of acetic acid, methanol, and carbon monoxide requires:
    - High temperatures and pressures
    - Expensive catalysts in multiple process steps
    - High capital and operating costs

- The DEBS process uses **high-energy electron beams** to break chemical bonds, allowing production of the desired chemicals at **near-ambient pressure and temperatures**.

- Successfully combining DEBS technology with CO_2 captured from coal-fired power plant flue gas provides a low-cost, energy-efficient process to produce valuable chemicals and reduce emissions.

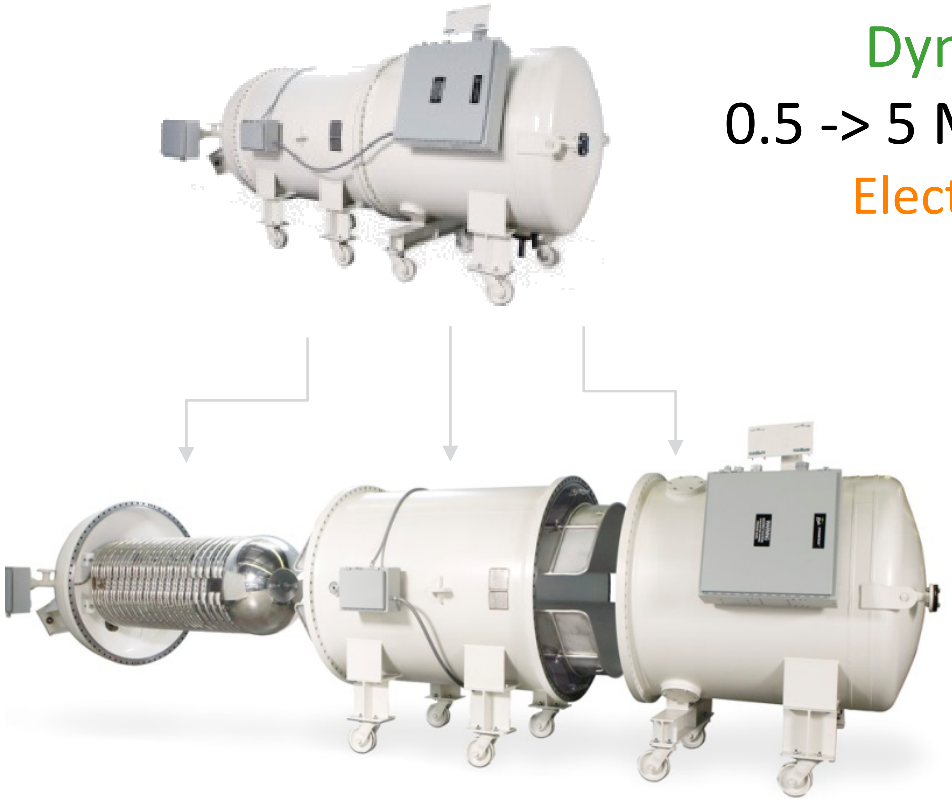
Electron Beam Deposition into Gas





Instructables.com
DIY Electron Accelerator:
a Cathode Ray Tube in a
Wine Bottle

Industrial E-Beam Accelerator



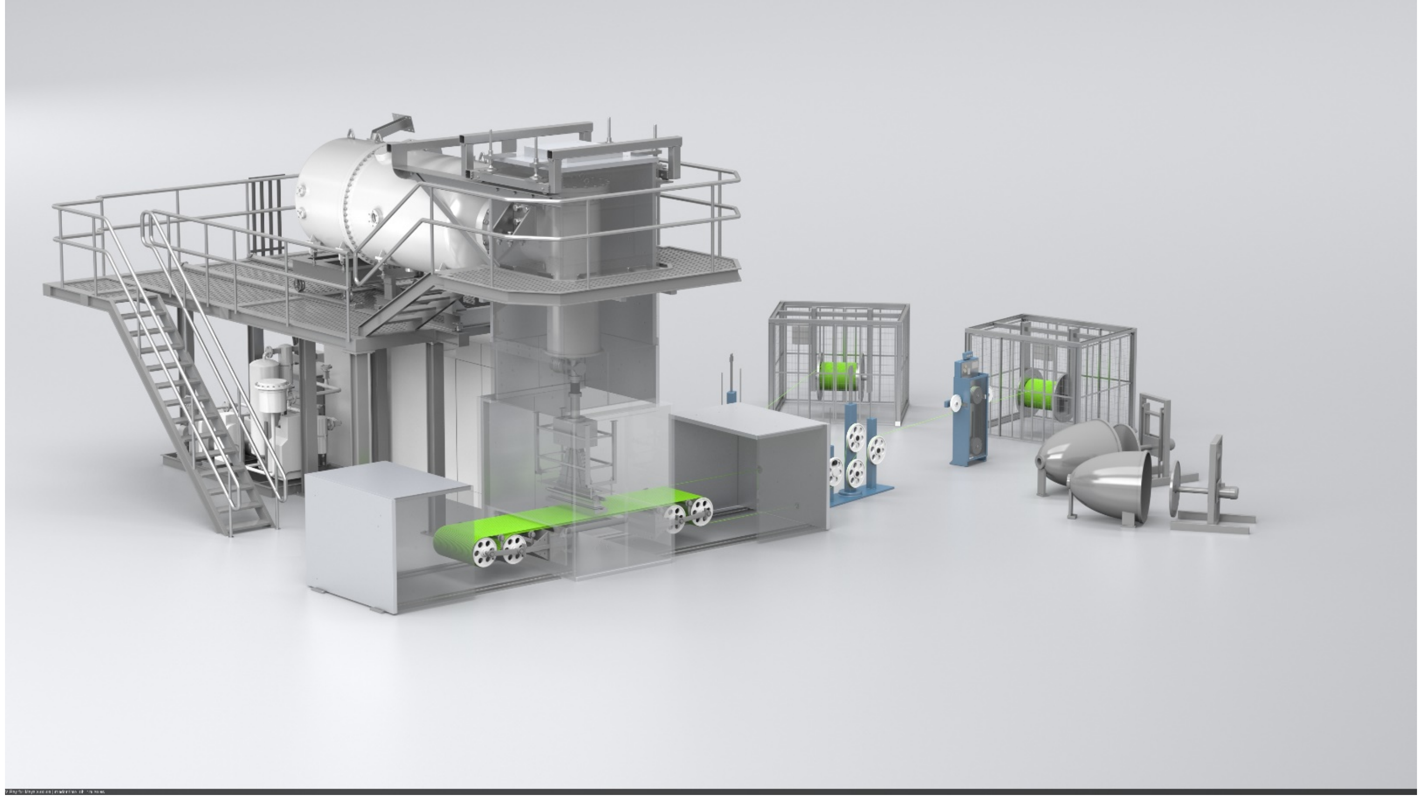
Dynamitron

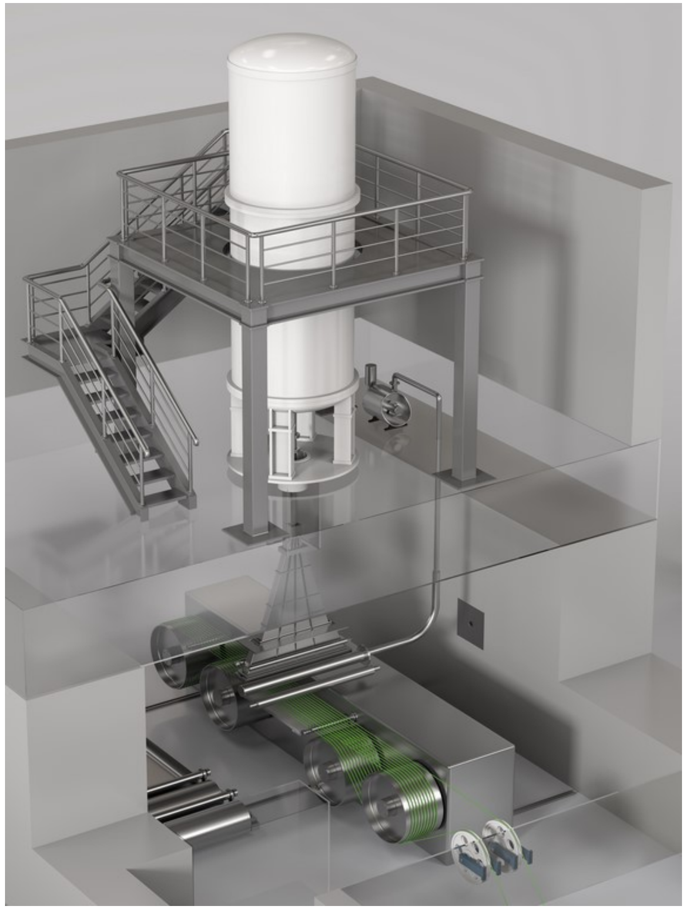
0.5 -> 5 MeV | 160 mA

Electron beam

Main application : **E-beam Crosslinking**

Industrial E-Beam Processes





Electron Beam Primer

V = Voltage (eV)
I = Current (amp)
V x I = Power (watt)

Current = Charge/Time
1 amp = 1 coulomb / 1 sec

Charge of an electron = 1.602×10^{-19} coulombs
1 coulomb = 6.25×10^{18} electrons

1eV = Kinetic energy of an electron accelerated to 1 volt

1 amp = 6.25×10^{18} electrons / sec

1 eV x 1 amp= 1 watt = 1 J/sec
1 eV = 1.602×10^{-19} J

Electron Beam Primer

V = Voltage (eV)
I = Current (amp)
V x I = Power (watt)

500keV & 15mA E-Beam:

Each electron will have:

8 x 10^{-14} J of energy

E-Beam will have:

9.3633 x 10^{16} electrons per second

E-Beam power = 7500 watt or 7500 J/sec

Each electron has the potential to achieve ~100,000 interactions

Electron Beam Primer

Bond Dissociation Energies

Bond	ΔHf_{298} (kJ/mol)
C-C	607
C-H	337.2
C-O	1076.5
C=O	749
C≡O	1075

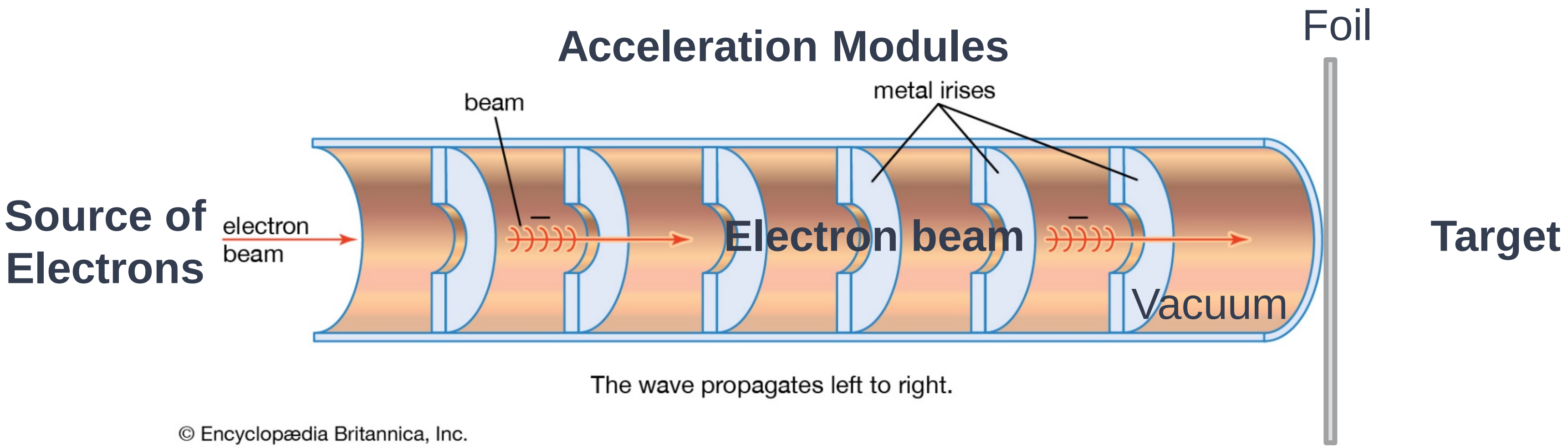
C-H bond energy ~5eV

One 500keV electron can break approximately 100,000 x (5 eV) bonds

Dehydrogenation of CH_x

	ΔH (kJ/mol)
$CH_4 \rightarrow CH_3\cdot + H\cdot$	405
$CH_3\cdot \rightarrow CH_2\cdot + H\cdot$	439
$CH_2\cdot \rightarrow CH\cdot + H\cdot$	488
$CH\cdot \rightarrow C + H\cdot$	685
$CH_4 \rightarrow CH_2\cdot + 2H\cdot$	808
$CH_4 \rightarrow C + 4H\cdot$	1266
$CH_2\cdot \rightarrow C + 2H\cdot$	857

Industrial Accelerator Design (linear)



The wave propagates left to right.

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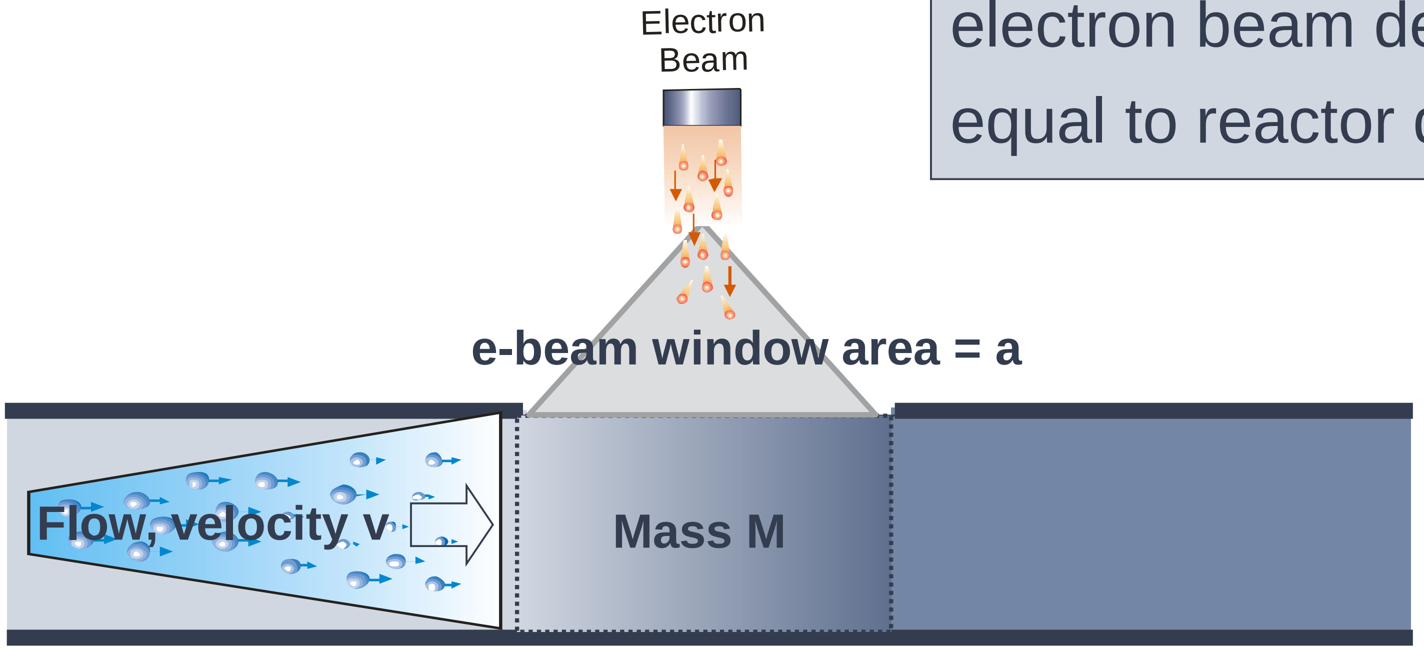
Typical Numbers in range of interest;
450 to 1000 keV
25 to 250 mA
11 - 100 kW
Efficiency: 45 – 60%

Voltage – Controls how FAR the electrons will go

Current - Controls how MANY electrons will be

Electron Beam Deposition

Maximum efficiency occurs when electron beam deposition depth is equal to reactor depth.

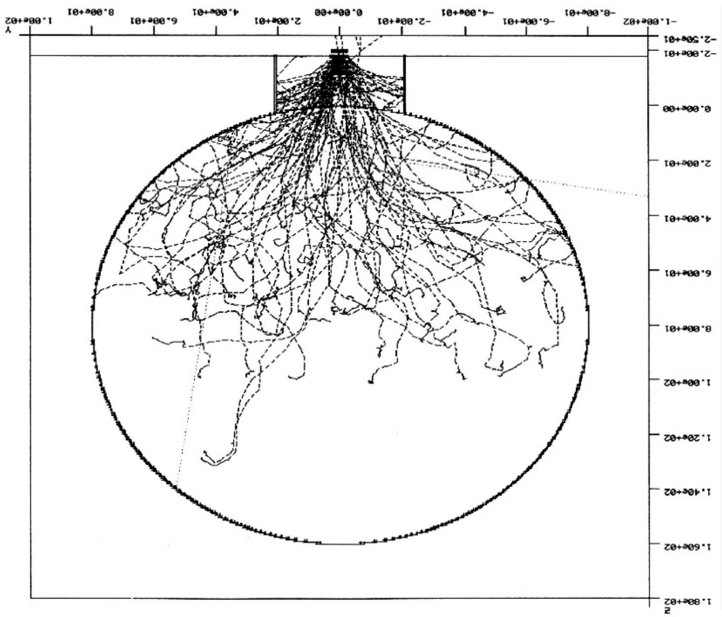


Monte Carlo Simulation

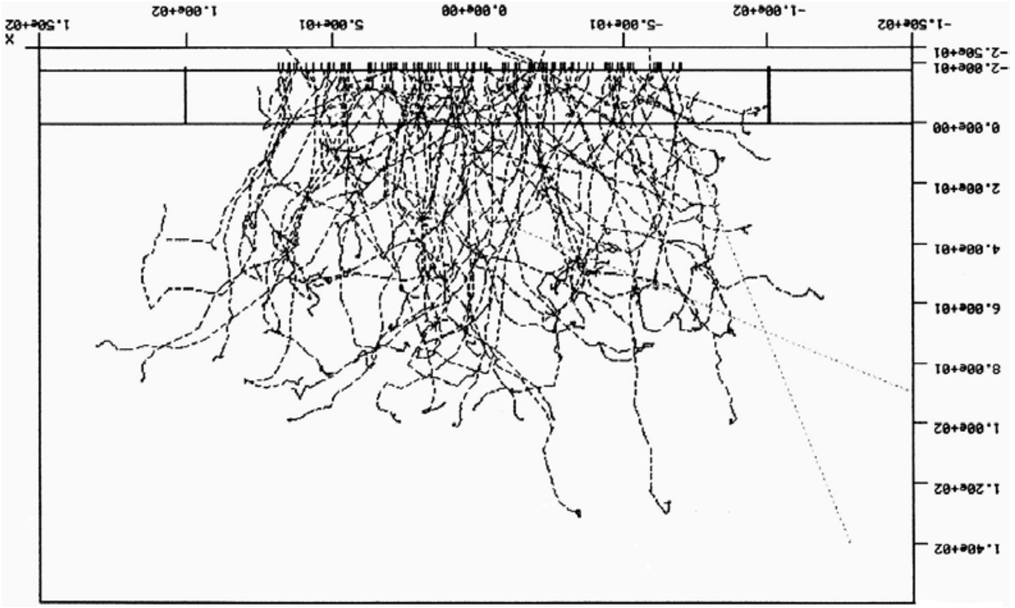
Monte Carlo simulations are used to model the probability of different outcomes in a process that cannot easily be predicted due to the intervention of random variables.

- The electron trajectories are simulated by using a Monte Carlo method.
- Each electron enters the reactor with a given energy, and its trajectory is followed until it comes to rest or exits the reactor.
- To simulate a beam, the process is repeated for a large number of electrons.
- Secondary electrons are generated and tracked within the "fast secondary" model.

Estimation of Electron Paths in Flue Gas Treatment



Y crossection of reactor vessel

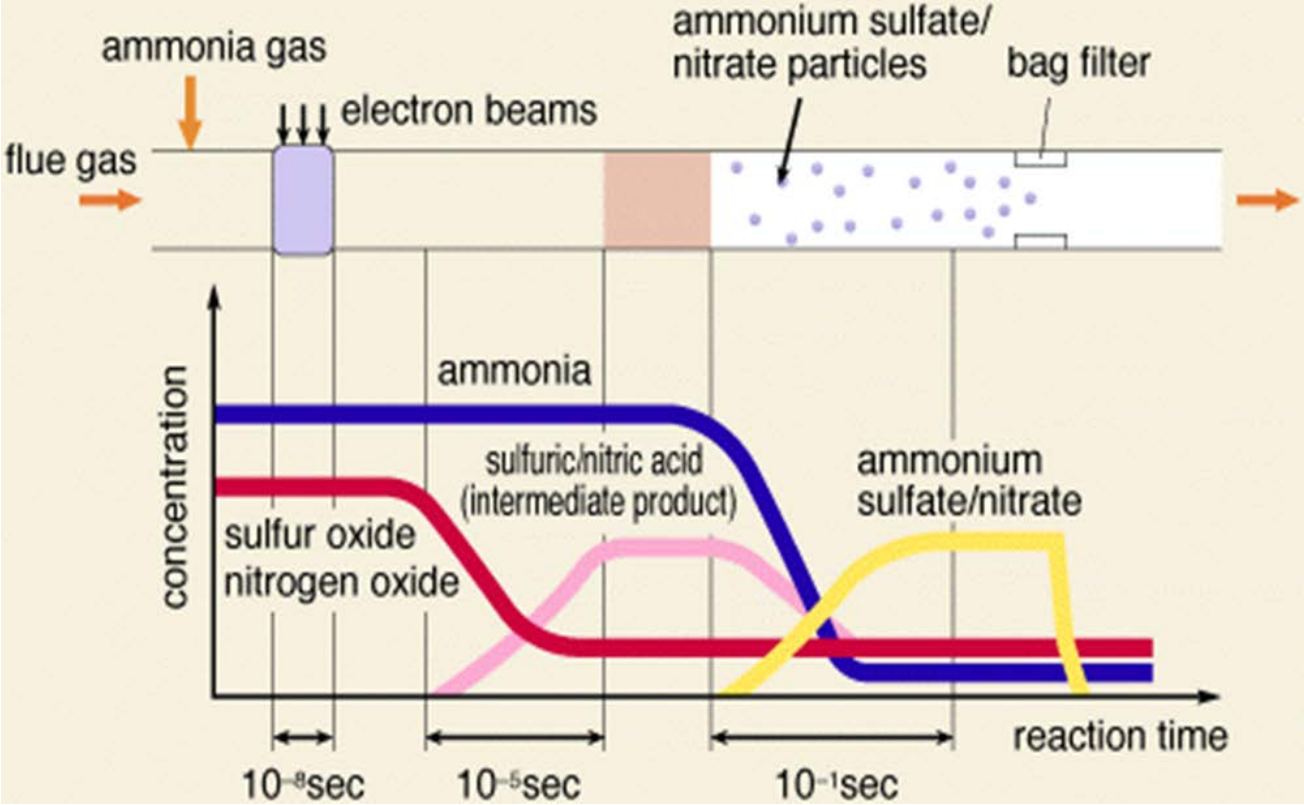


X crossection of reactor vessel

Initial electrons energy: 800 keV
Energy cut-off: 1 keV

Ref. : Presentation by Sylwester Bułka et al. International Atomic Energy Agency Meeting on Electron Beam Flue Gas Treatment, Warsaw, Poland 14 – 18 May 2007

Electron Beam Flue Gas Treatment



10^{-8} sec 10^{-5} sec 10^{-1} sec

Schematic diagram of the EBFGT technology

Ref. : Kim et al., "Electron-beam Flue-gas Treatment Plant for Thermal Power Station "Sviloza" AD in Bulgaria", J. of the Korean Physical Society, Vol. 59, No. 6, December 2011

"Due to very high concentrations of ions, radicals, ion-radicals and other reactive particles in E-Beam plasma, chemical reactions take place at extremely high rates of ~0.01-10 milliseconds"

Ref. : Vinokurov et al., "Plasma-Chemical Processing of Natural Gas", Chem & Tech. of Fuels and Oils, Vol. 41, No. 2, 2005

Target Range of E-Beam Dose and Residence Time

For E-Beam based H_2 production from methane, literature data indicates average gas residence time of about 2 milliseconds.

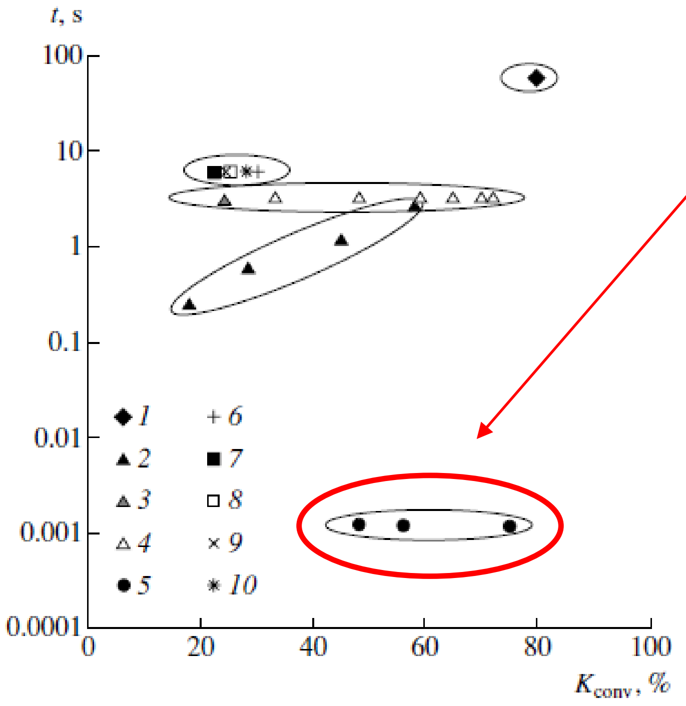


Fig. 2. A plot of the time *t* of gas occurrence in the reactor versus conversion coefficient K_{conv} for various methods of conversion: (*1*) steam conversion; (*2*) streamer discharge [12]; (*3*) barrier discharge [13]; (*4*) barrier discharge [14]; (*5*) this study; (*6*–*10*) SHS catalysts [15], including MgO (*6*), $LaCaB_6$–MgO (*7*), $SmCaB_6$–MgO (*8*), $LaBaB_6$–MgO (*9*), and $LaCaB_6$–MgO/Mn_3O_4–NaCl (*10*).

Ref. : "H_2 Production from Methane in E-Beam Plasma" ; Sharafutdinov et al., Technical Physics Letter, Vol. 31, 2005

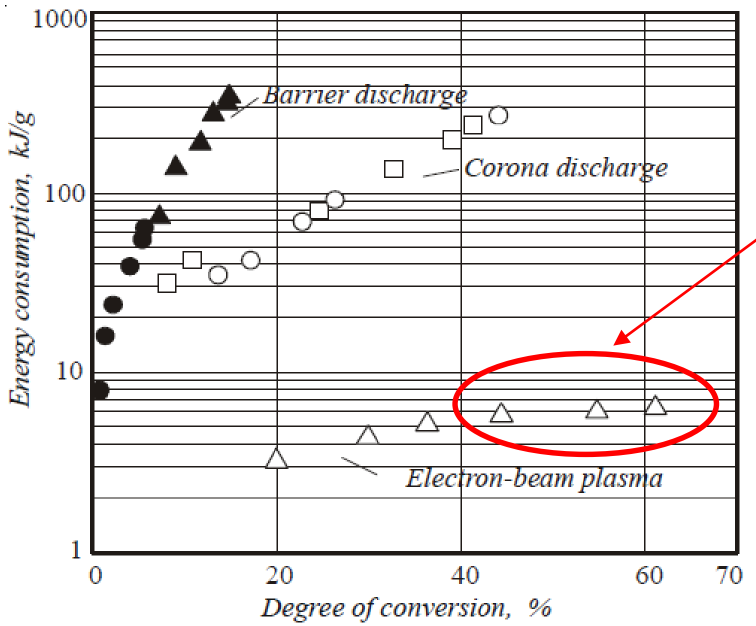
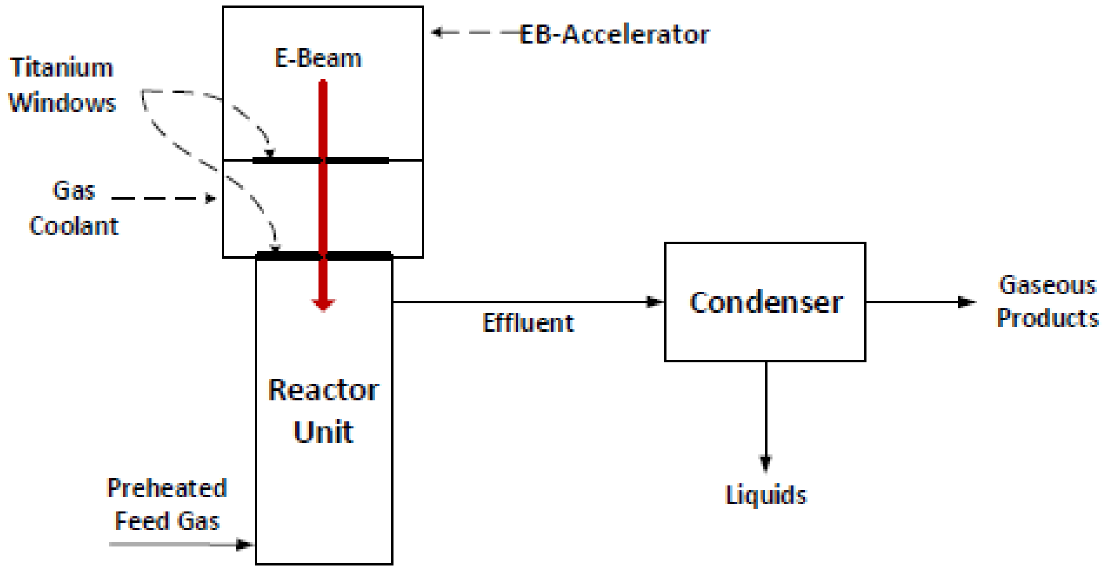


Fig. 1. Energy consumption vs. degree of conversion of methane using different methods of activation: ●, □, △ : 100% CH_4; ○,▲: mixture (1:1) of CH_4 and CO_2.

Experimental data in literature indicate ~ 4-7 kJ/gm methane (as electrical energy) for E-Beam based pure methane conversion to H_2, C_2-C_4 gases & C_5+ liquid fuels

Ref. : Vinokurov et al., Chemistry & Technology of Fuels and Oils, V-41, #2, 2005

Experimental Design & Key Experimental Parameters



Schematic drawing of the DEBS reactor

- E-Beam dose, (kJ/gm)
- Gas residence time in beam and off beam (ms)
- E-Beam energy : 300-500 keV
- Use of a promoter, such as, carbon monoxide
- Use of catalyst(s)

Project Task Plan

BP 1:

- **Design and construct a DEBS reactor and a testing unit**
- **Shakedown DEBS testing unit and calibrate analytical diagnostic equipment**
- **Transport the testing unit to IBA**

BP2:

- **Run parametric testing**
- **Develop a kinetic model based on the collected data**
- **Perform life cycle analysis, technology gap analysis, and economic analysis**

Project Scope and Timeline

Task	Description	Duration
1	Project Management and Planning	5/17-4/19
2	Design and Construction of Experimental System	5/17-9/17
3	Start-Up and System Checks at GTI	10/17-11/17
4	System Commissioning at IBA	12/17-1/18
7.1	Develop Preliminary Kinetic Model	6/17-1/18
BP2		
5	Conduct Parametric Testing	2/18-4/18
6	Conduct Parametric Testing with Catalyst	7/18-10/18
7.2	Develop Kinetic Model	9/18-4/19
8	Data Analysis, Life Cycle Analysis and Economics	10/18-4/19

Risk Management and Mitigation

Description of Risk	Prob.	Impact	Risk Management Mitigation and Response Strategies
Technical Risks:			
Reactor size too small for practical use in testing unit	Low	Mod.	• Reduce E-Beam power and increase reactor size
Recombination reactions occur too quickly	Low	Mod.	• Decrease residence time in reactor • Include a “recombination chamber” to allow reactions to take place. • Change location of catalyst to accommodate recombination reactions
Reactions produce unidentified products	Mod.	Low	• Increase analytical diagnostic capability to identify reaction products • Change catalyst to work with newly identified reaction products
Not high enough conversion	Low	Mod.	• Increase E-Beam accelerator power • Introduce recycle to the process

Milestones and Success Criteria

Budget Period	Task Number	Milestone Description	Planned Completion
1	1	Update Project Management Plan	6/27/17
1	1	Kickoff Meeting	7/13/17
1	2	Complete Final Design	9/1/17
1	1	Submit Continuation Application	11/1/17
1	7	Develop Preliminary Kinetic Model	12/31/17

Decision Point	Date	Success Criteria
Go/no-Go decision points	01/31/2018	• Successful commissioning of a viable reactor system and testing unit: o Verify gas flow meter control by measuring the vent using a dry test meter o Operate chiller for condenser to achieve less than -20°C in the condenser o Verify detection limit of acetic acid and methane using RGA at 100ppmv • Identify at least two catalysts to control the recombination and increase the yields for more valuable products

Progress and Current Status

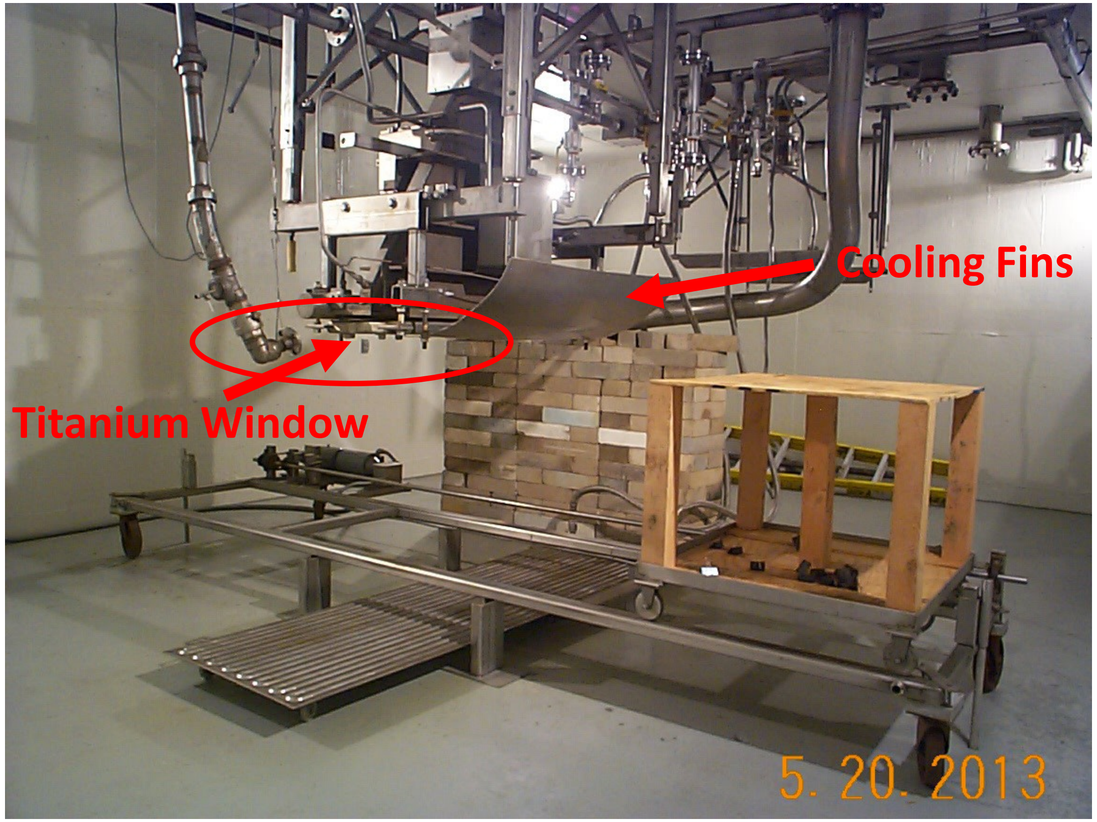
Technology Challenge: Delivering maximum e-beam dose while maintaining very short residence time

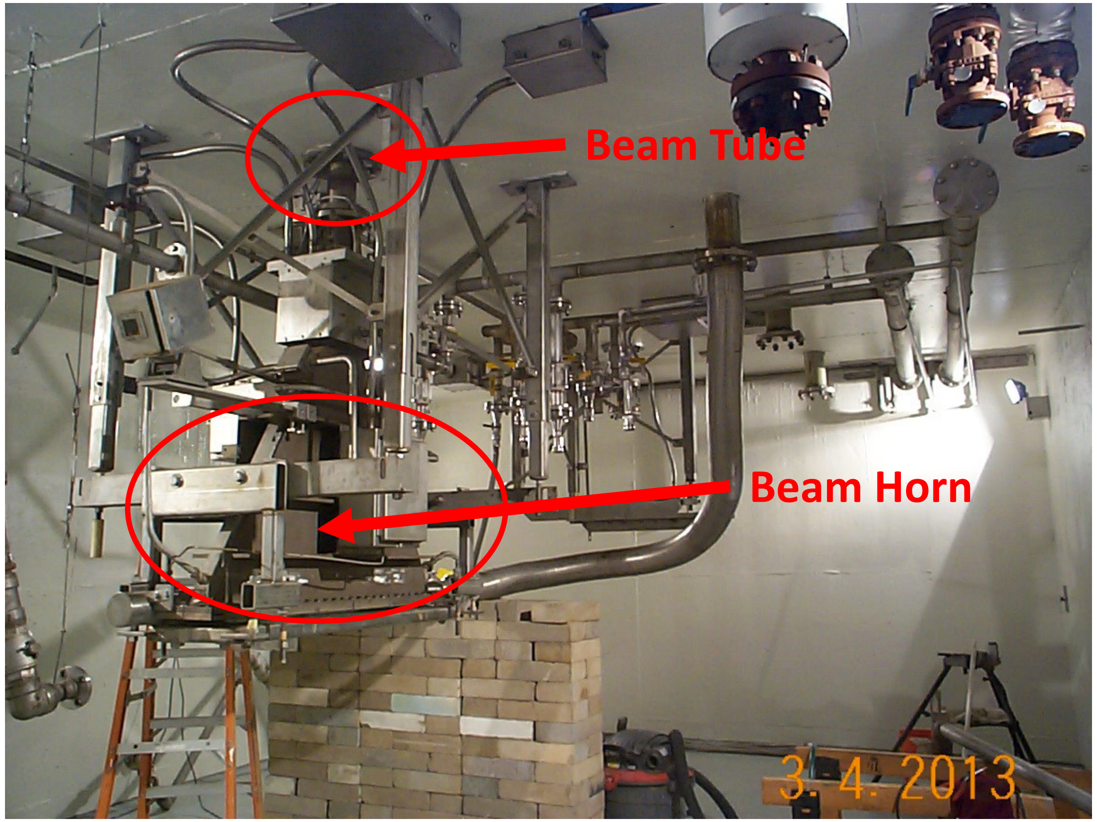
- Prepared 3 different reactor geometries
- IBA currently running Monte Carlo calculations
- Preparing reactor design to maximize e-beam utilization inside the reactor

Technology Challenge: Determining which of the many compounds formed are more probable

- SUNY is setting up the model reactions
- Thermodynamic properties for over 300 compounds (ions and radicals) are listed
- Preparing database containing reactions of these compounds

Experimental Equipment





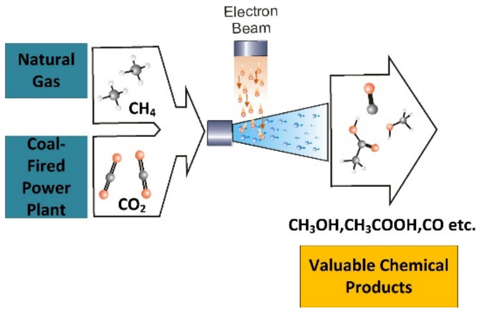
Plans for future testing/development

- Reactor and testing skid fabrication
- Analytical equipment setup

- BP2 Scope
  - Testing at IBA
  - Kinetic model verification
  - Techno-economic analysis

Summary

- Develop a commercially viable non-equilibrium process that breaks bonds directly unlike conventional chemistry that requires heating the entire molecule
- Each electron has the potential to achieve ~100,000 interactions
- Extremely high reaction rates (~10 milliseconds)
- Monte Carlo calculations to maximize e-beam utilization inside the reactor
- Thermodynamic properties database of reactions for over 300 compounds (ions and radicals)



BP1: Reactor fabrication and preliminary model setup

BP2: Testing and techno-economic analysis

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