the Energy to Lead

High Energy Systems for Transforming CO_2 to Valuable Products

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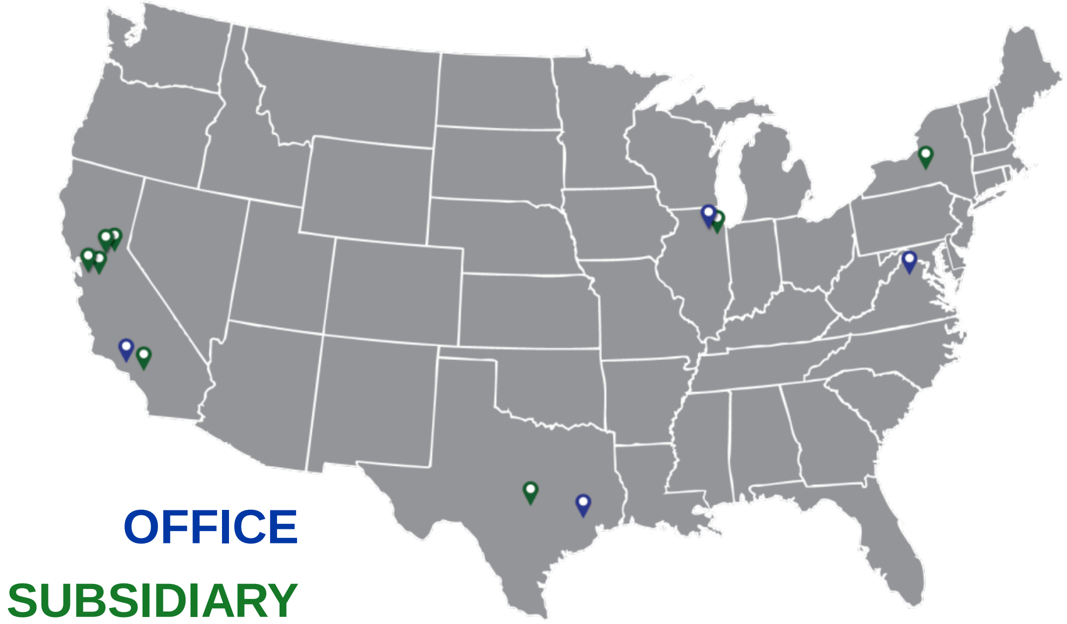
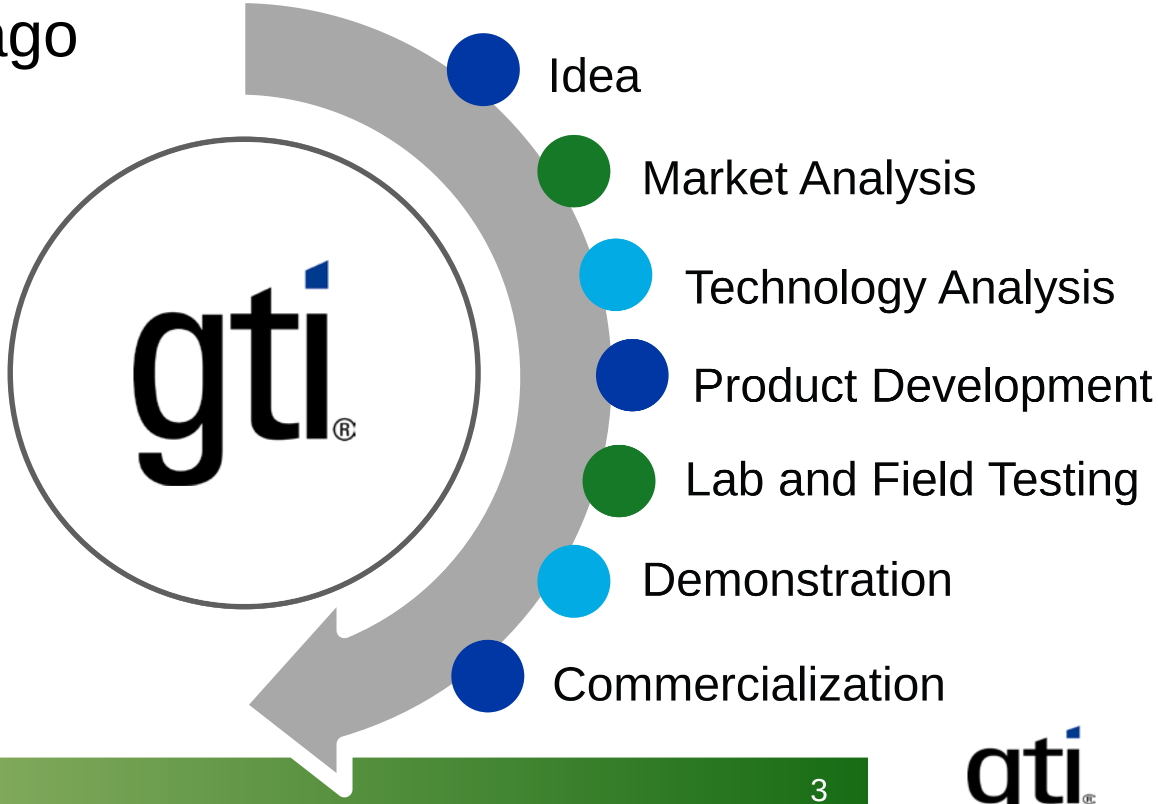
Outline

- **Background Information**
- **Technical Approach Discussion**
- **Progress and Current Status**
- **Modelling Results**
- **Plans for Future**

Introduction to GTI

- Research organization, providing energy and environmental solutions to the government and industry since 1941
- Facilities:18 acre campus near Chicago





High Energy Systems for Transforming CO_2 to Valuable Products

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

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

- **Objective**: Develop a direct electron beam synthesis process to produce valuable chemicals such as acetic acid, methanol, and carbon monoxide, using carbon dioxide captured from a coal-fired power plant and 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
Iba	• 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

Advantages Over Traditional Processes

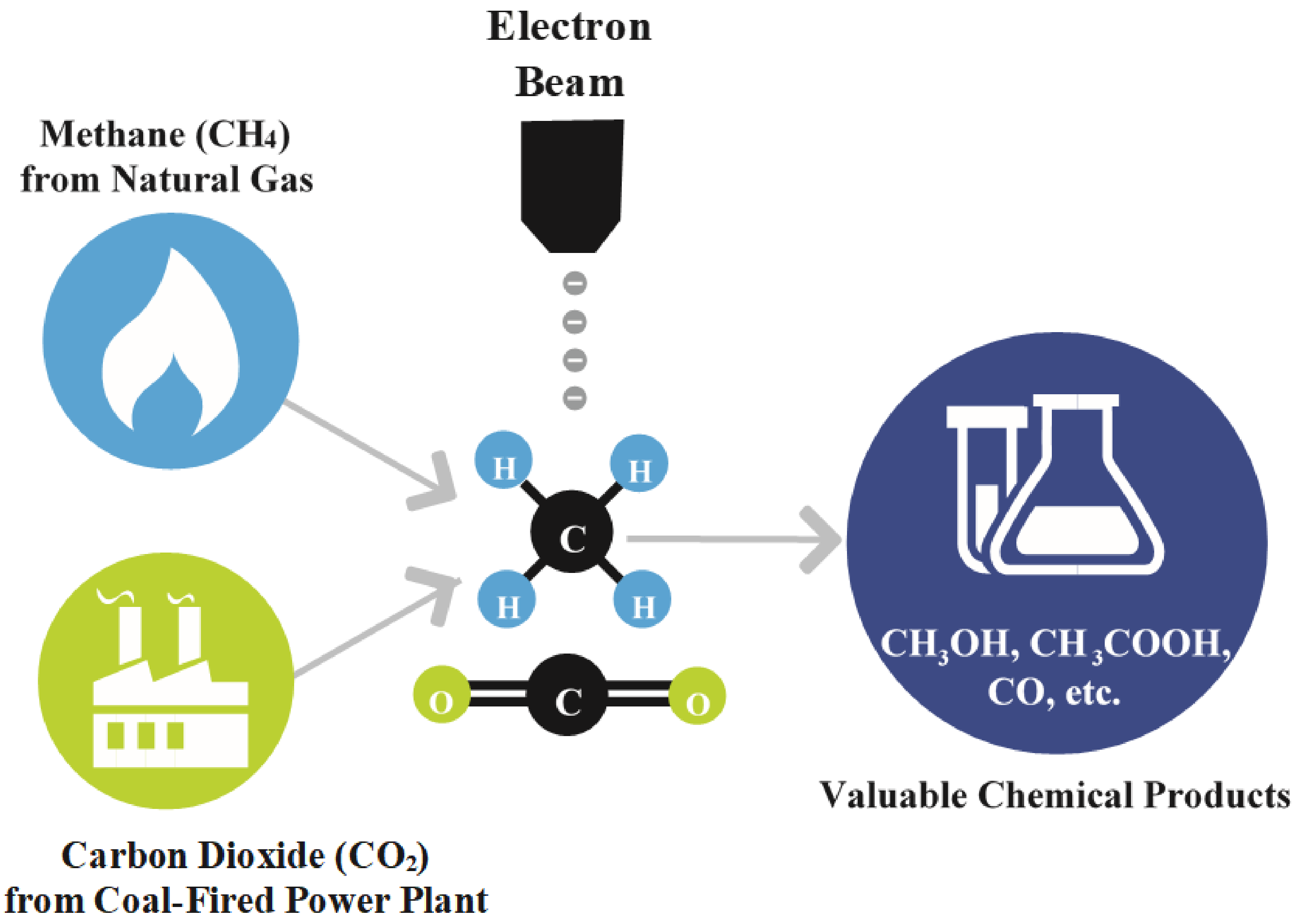
- **Current technology for the commercial production of acetic acid, methanol, and carbon monoxide requires:**
  - **High temperatures and pressures**
  - **Expensive catalysts in multiple process steps**
  - **High capital and operating costs**

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

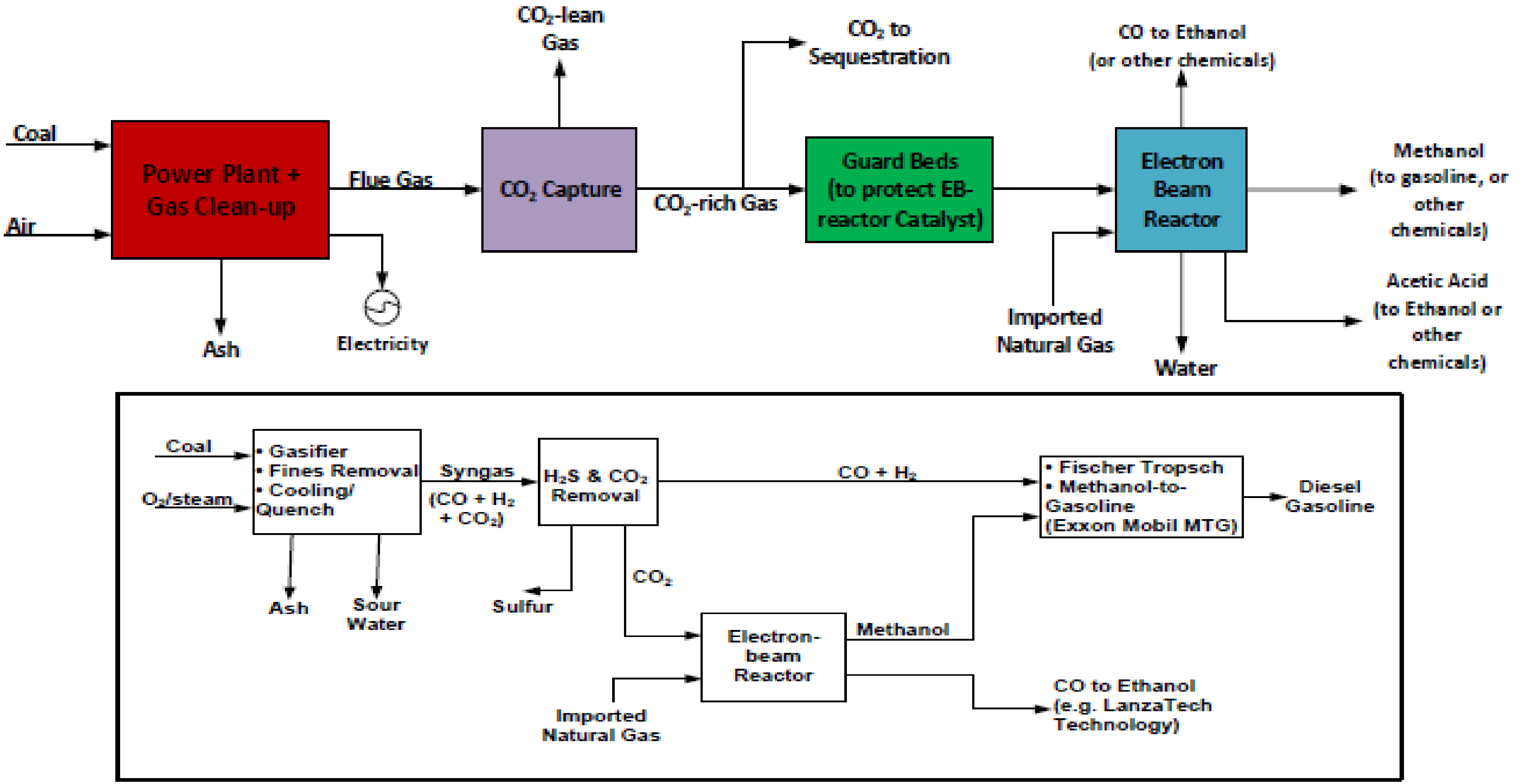
- Valuable chemical production by DEBS technology applied to CO_2 captured from coal-fired power plant:
  1. **Lower cost**
  2. **Low pressure / low temperature**
  3. **More energy-efficient**
  4. **Have reduced emissions**

DEBS - Direct Electron Beam Synthesis

Project Description



DEBS Process for Post- and Pre-combustion



Electron Beam Fundamentals

500keV & 15mA E-Beam:
E-Beam power = 7500 watt (7500 J/sec)

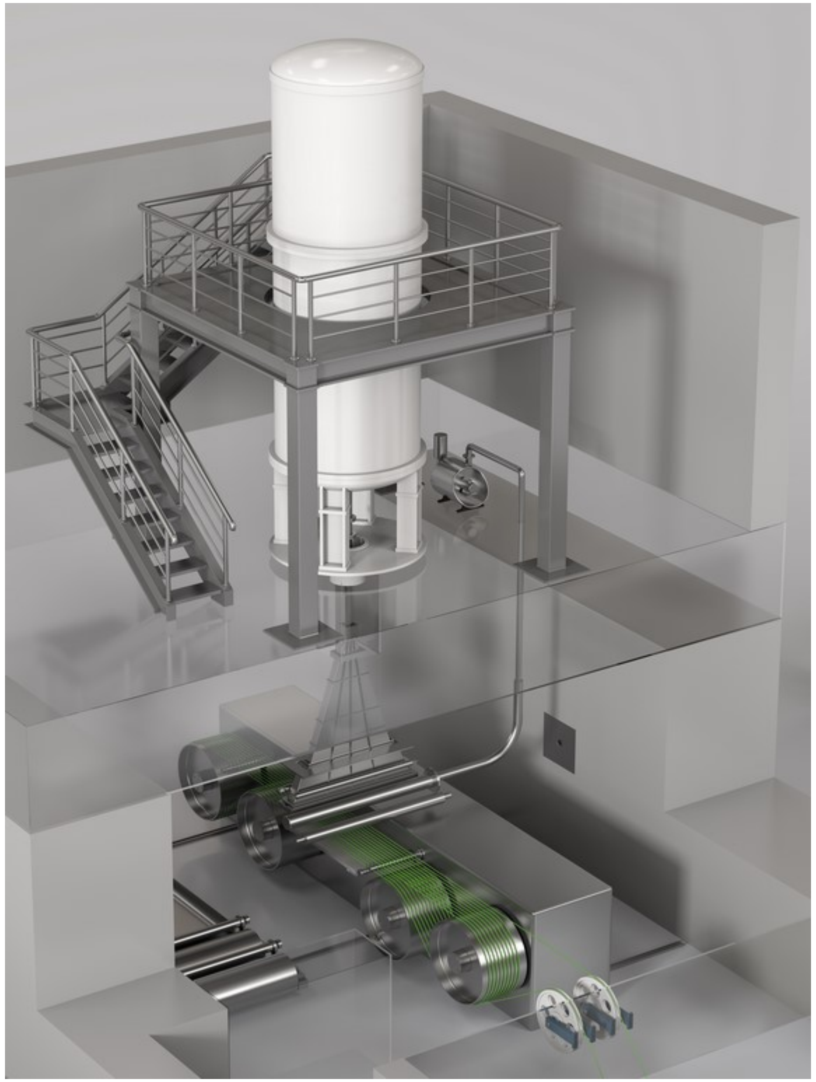
Each electron will have:
8 x 10^{-14} J of energy

E-Beam will have:
9.3633 x 10^{16} electrons per second

Bond dissociation energy (kJ/mol):

C-H	337.2
C-O	1076.5

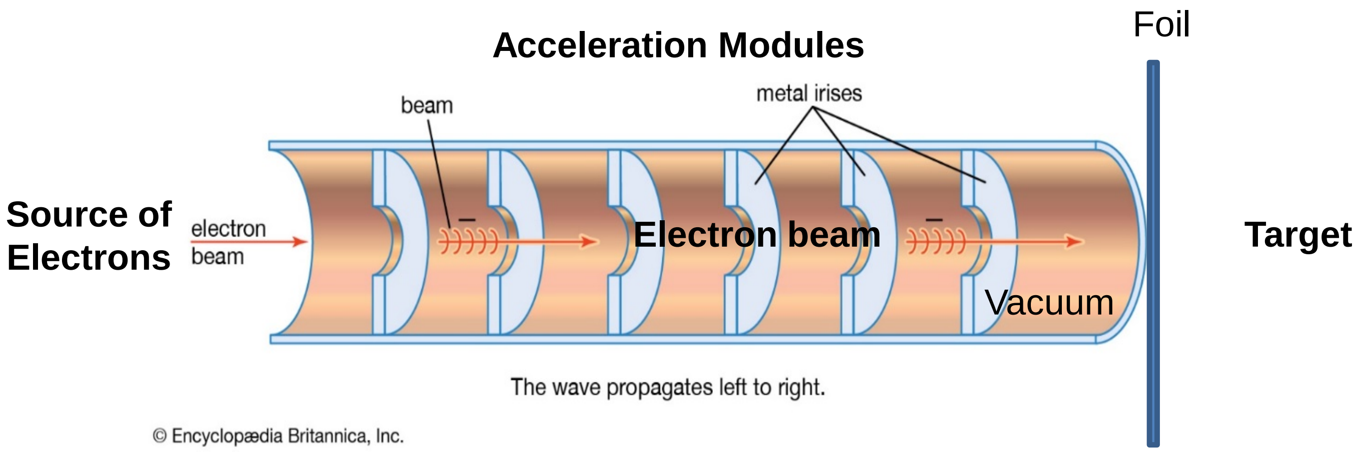
Each electron has the potential to achieve ~100,000 interactions



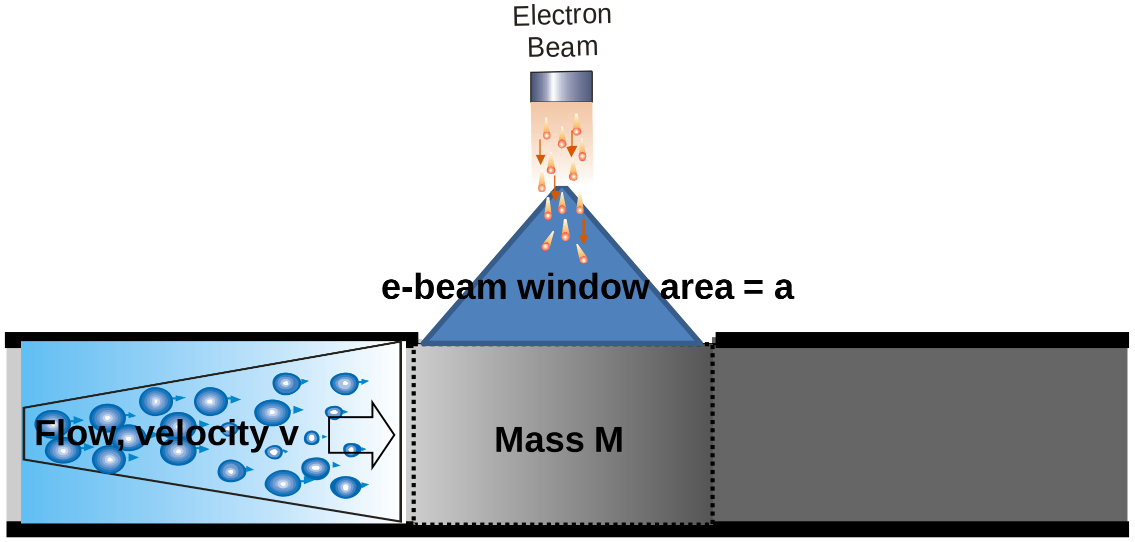
Industrial Accelerator Design (linear)

Voltage – Controls how FAR the electrons will go

Current – Controls how MANY electrons there will be

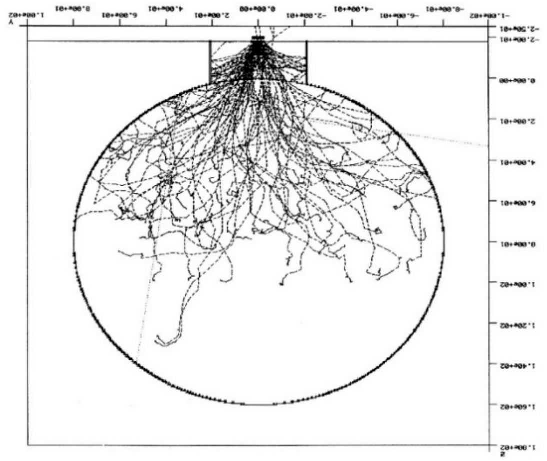


Maximum efficiency occurs when electron beam deposition depth is equal to reactor depth.

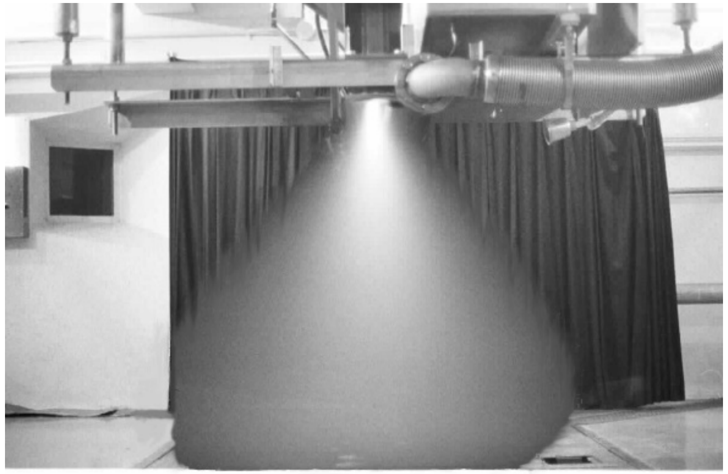


Monte Carlo Simulation of Electron Trajectories

- 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.
- Reactor should be sized to utilize the active electrons.



Electron trajectories in a reactor vessel



The luminance of nitrogen in air within radiation field area

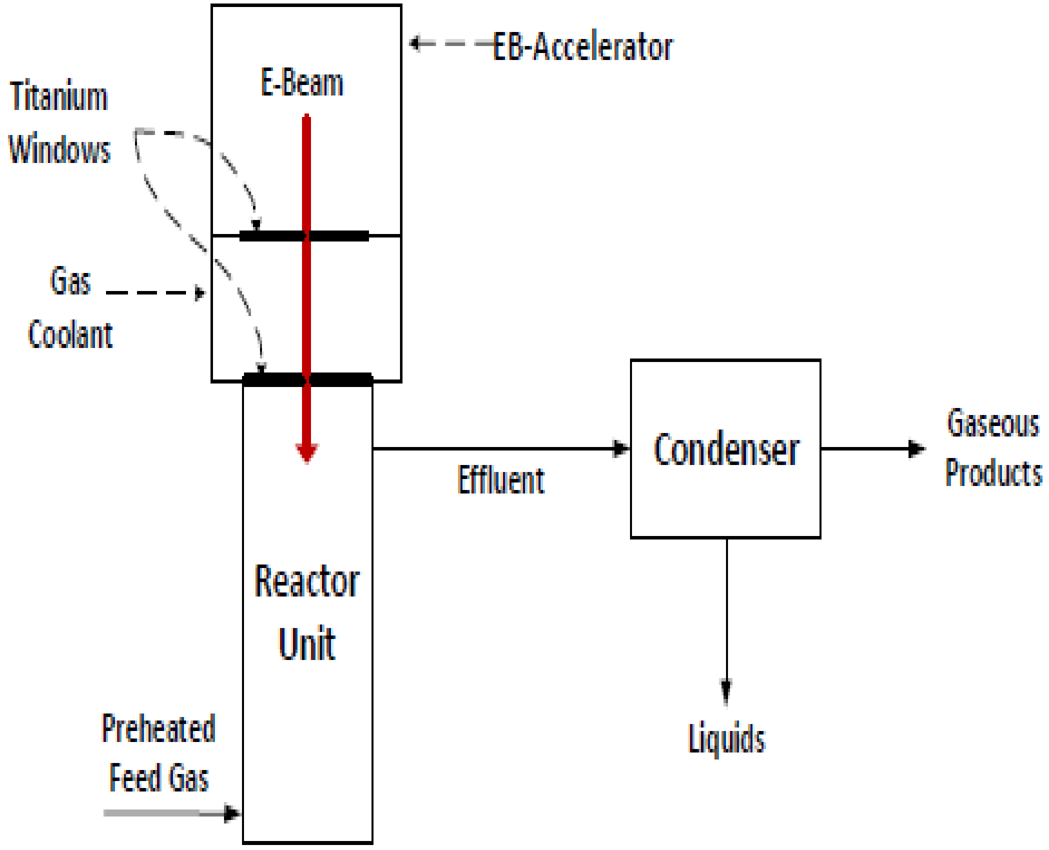
Ref. : Presentation by Sylwester Bułka et al. International Atomic Energy Agency Meeting on Electron Beam Flue Gas Treatment, Warsaw, Poland 14 – 18 May 2007

Technical and Economical Challenges

Technology Challenge: Delivering maximum e-beam dose while maintaining very short residence time
• Prepared multiple different reactor geometries • IBA performed Monte Carlo calculations • Reactor designed to maximize e-beam utilization inside the reactor

Technology Challenge: Determining which products are more probable
• SUNY developed a preliminary kinetic model to follow over 1600 reactions during irradiation • The model uses thermodynamic properties for over 200 compounds • Preliminary results are available for experimental design

Experimental Design & Key Experimental Parameters



- **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) to promote desired reactions**

Limitations of Experimental Approach

- Reactor size constraints:
  1. Size of Ti-window affects E-Beam dose in the reactor
  2. Volume of reactor affects residence time

- Duration of experiment to collect enough condensate

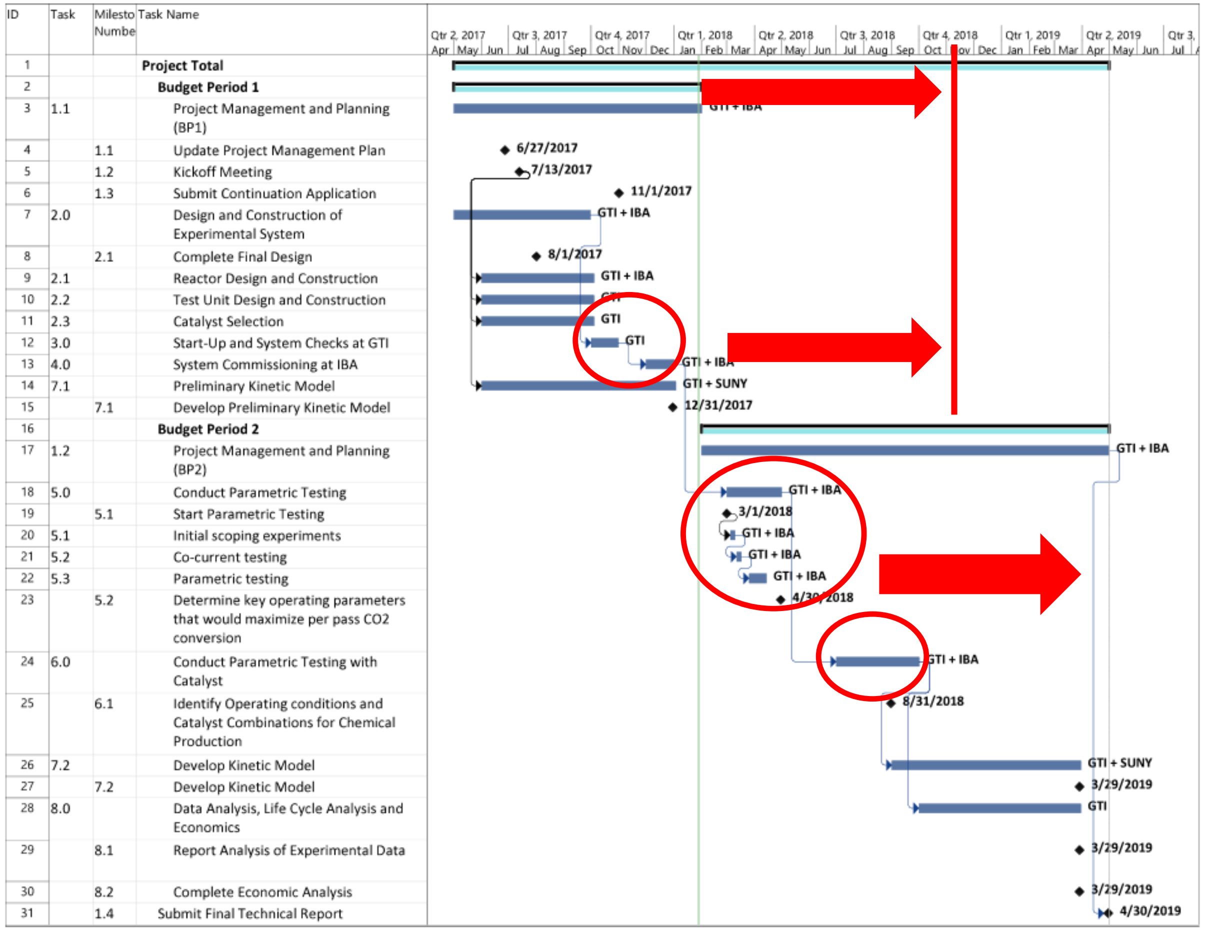
Project Task Plan and Schedule

BP1:

- 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



Period of Performance	Budget Period 1	Budget Period 2
05/17-04/19	05/17-10/18	11/18-04/19

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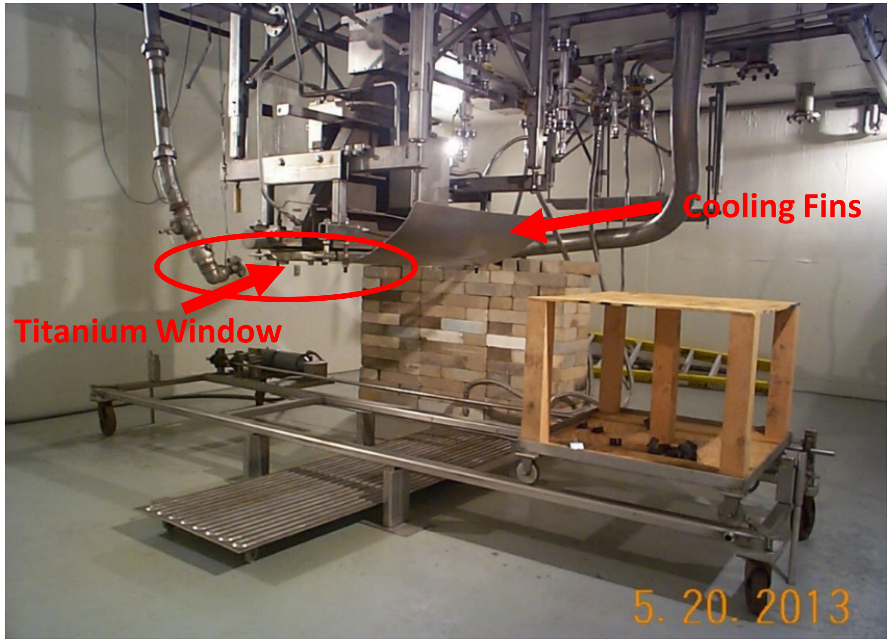
Progress and Current Status

- Based on availability of resources, IBA-Industrial decided not to participate in project
- Other particle accelerator facilities have been identified as alternatives
- BP1 is extended from 1/31/18 to 10/31/18

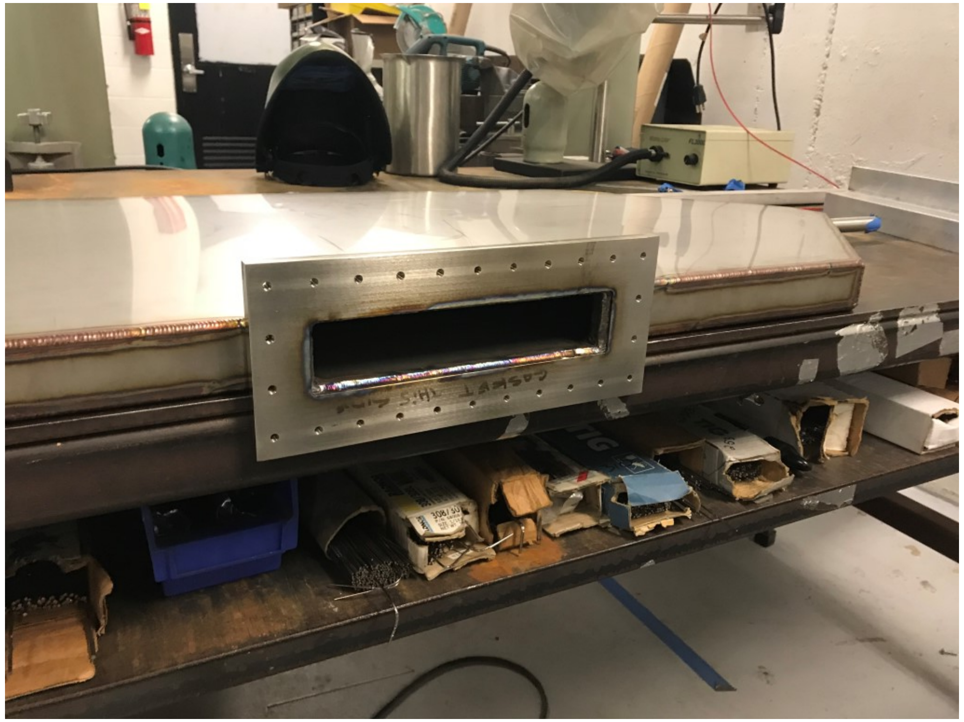


Progress and Current Status

- Worked with IBA to design the reactor to deliver enough beam energy with very short gas residence time
- Fabricated reactor based on final design
- Started test skid construction
- Work is on hold during new accelerator facility search

- Preliminary Kinetic model finished, ran initial conditions
- Model corrected based on an initial assessment of results

Electron Beam Reactor



Modeling

Goal: **predict** the best operating conditions

- Over 200 species, 1600 gas-phase reactions

By simulating all the reactions, **a kinetic model** could determine**:**

- Energy conversion efficiency (G value)
- Which reactions contribute most to production/loss of products

G value:

- is the number of specific molecules generated per 100 eV absorbed
- indicates how efficiently the electron beam energy has been used

Overview of the Model

Radiolysis Reactions:

$CH_4 \rightarrow CH_3^+ + H + eh^-$

$CO_2 \rightarrow CO_2^+ + eh^-$

$CO_2 \rightarrow C^+ + 2O + eh^-$

eh^- : high-energy electrons
et- : thermal electrons

$eh^- + X \rightarrow et^- + X$

Gas-phase reactions:

1. Electron attachment:

   ($et^- + H + M \rightarrow H^- + M$)

2. Ion-neutral reaction:

   ($CH^+ + CH_4 \rightarrow C_2H_3^+ + H_2$; $C^+ + CO_2 \rightarrow CO_2^+ + C$)

3. Neutral-neutral reaction:

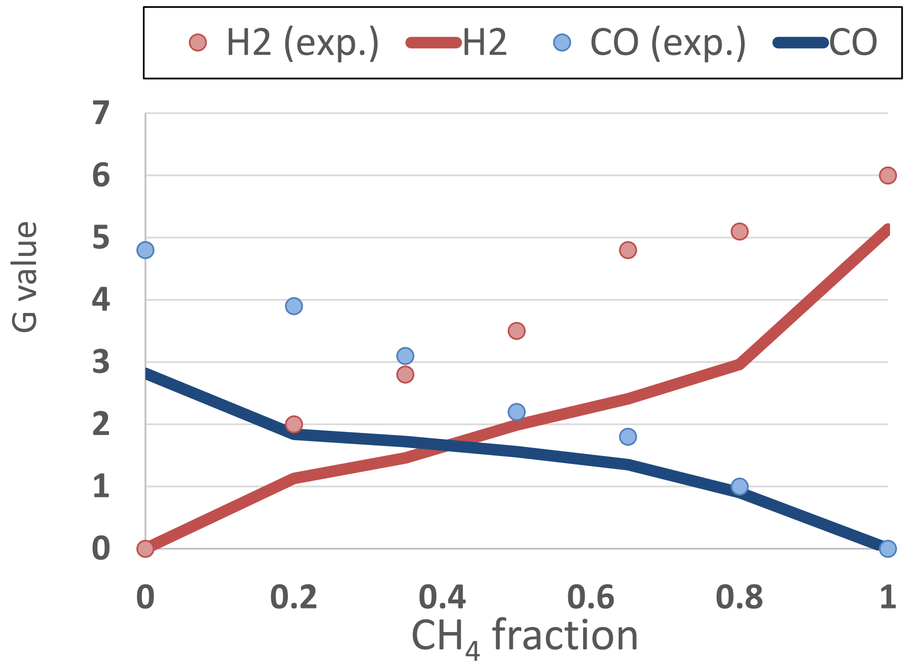
   ($H + CH_4 \rightarrow CH_3 + H_2$; $OH + CH_4 \rightarrow H_2O + CH_3$)

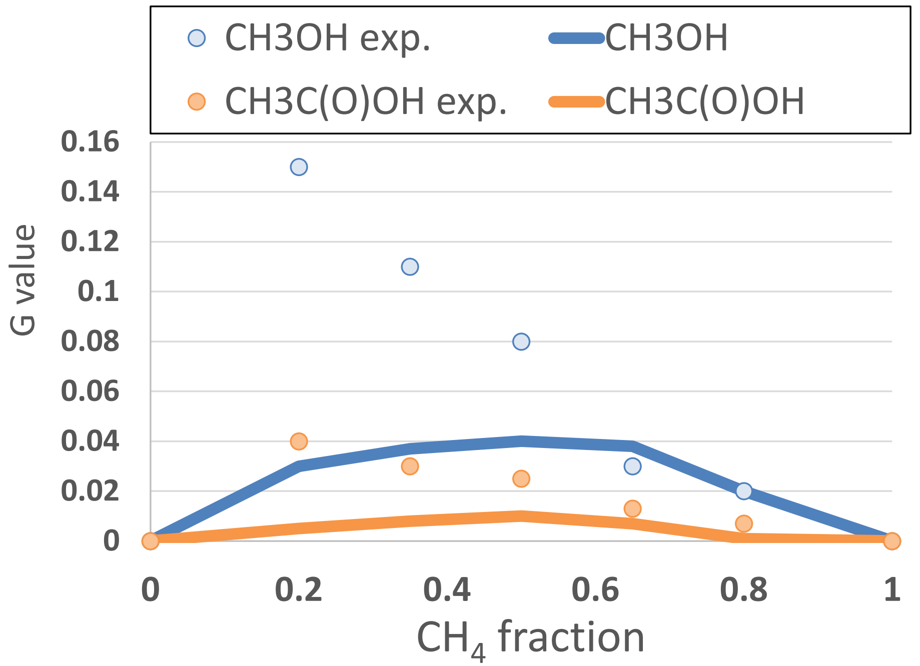
4. Cation-anion reaction:

   ($C^- + O^+ \rightarrow C + O$; $O^- + H_3O^+ \rightarrow H + O + H_2O$)

Energy Conversion Efficiency

G Values vs CH_4 fraction (Ambient, CO_2/CH_4 mix, constant dose rate 11.8 kGray/sec)





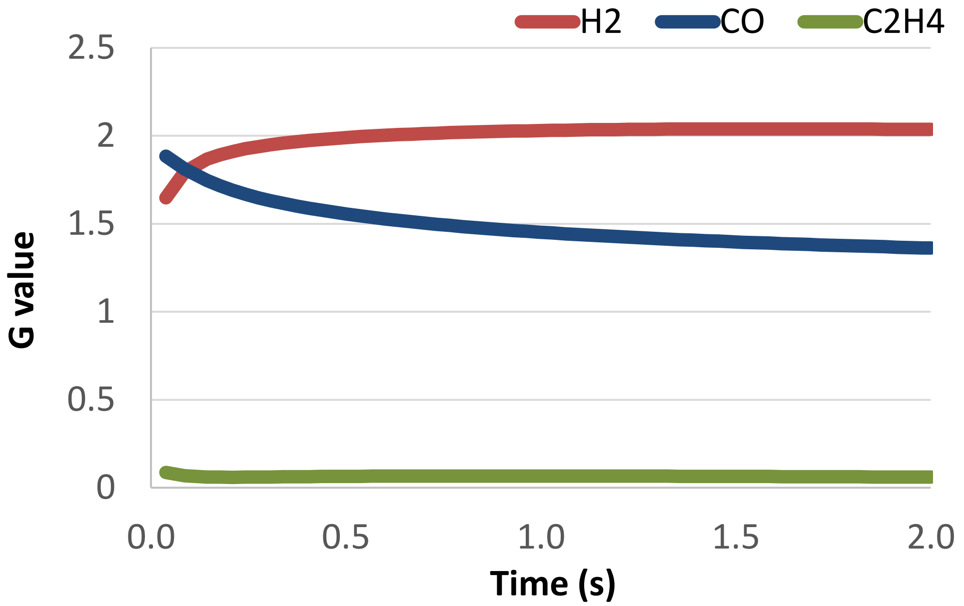
- **Initial gas composition influences G value**
- **Model discrepancy at low CH_4 fraction**

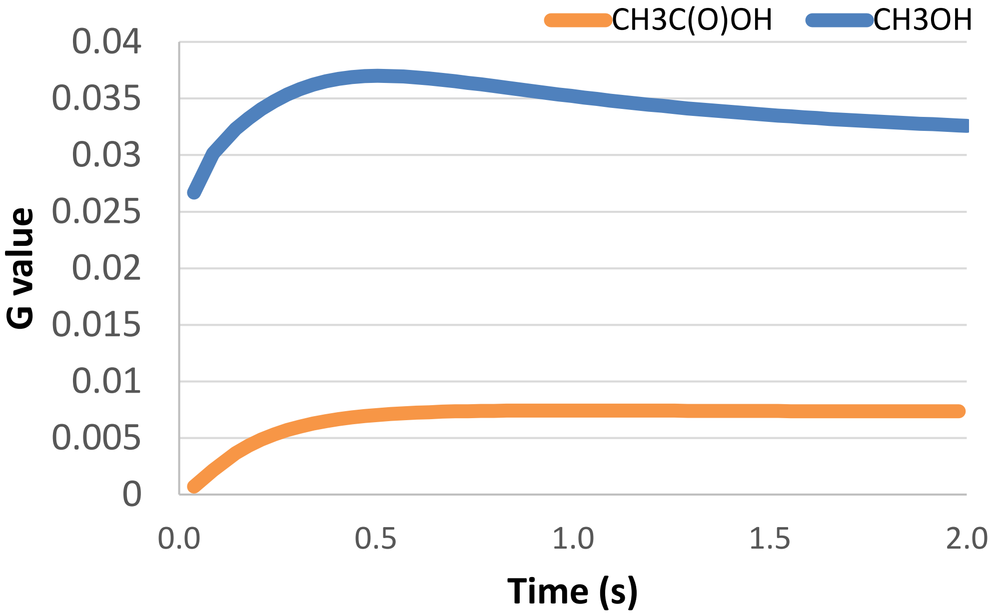
***   Experimental values are from *Arai H et al. 1982***

*Ref: Arai, H. et al., "Electron Beam Radiolysis of CH_4/CO_2 Mixtures,", Zeitschrift fur Physikalische Chemie Neue Folge, Bd. 131, S. 69-78 (1982)

Energy Conversion Efficiency (cont.)

G values at 1:1 CH_4/CO_2 ratio, 11.8 kGray/sec vs E-Beam residence time

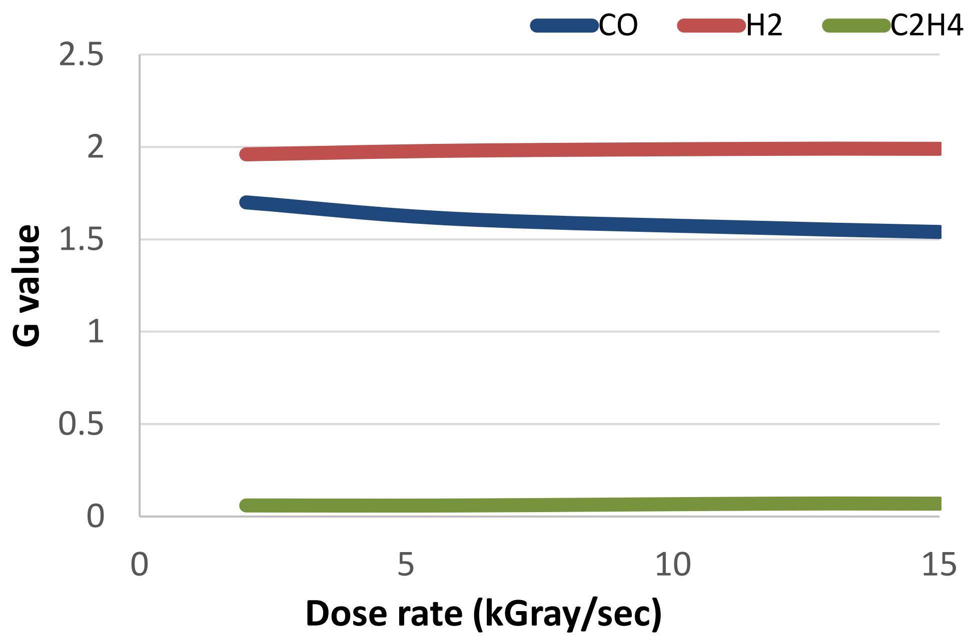


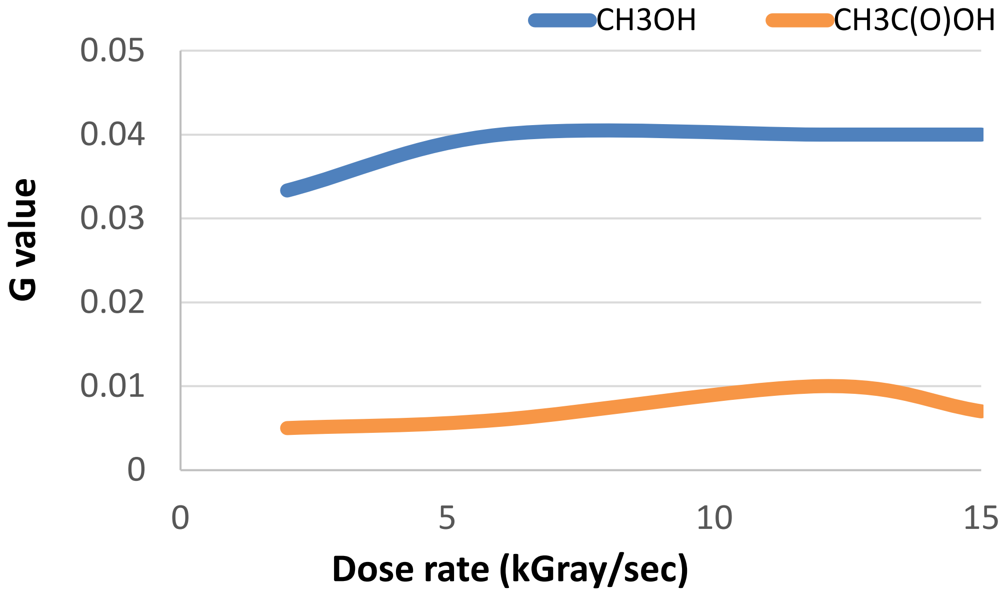


- **At certain point, G value no longer changes due to side-reactions**
- **The result shows G values of H_2, methanol and acetic acid peak at 0.5 sec.**
- **Model predicts low residence time**

Energy Conversion Efficiency (cont.)

G value at 1:1 CH_4/CO_2 ratio vs E-Beam dose rate





- **Variation in G value exists, but relative small**
- **Model predicts linear scale-up**

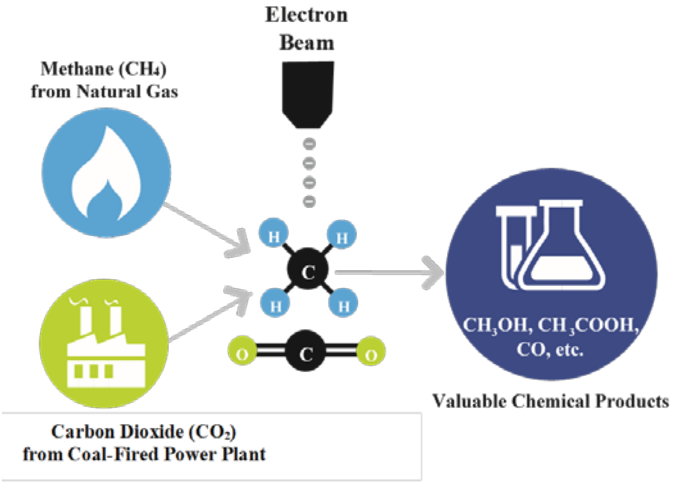
Plans for future testing/development

- Finish reactor and testing skid fabrication
- Begin testing with new accelerator facility
- Kinetic model verification
- Techno-economic analysis

- Scaling up accelerator and reactor is not expected to be an issue:
  1. Available beam coverage from existing equipment is large
  2. Multiple accelerators can be connected to increase beam coverage if necessary

Summary

- Objective is to develop a commercially viable non-equilibrium process that breaks bonds directly unlike conventional chemistry that requires heating the entire molecule
- E-Beam reactor designed and constructed to maximize e-beam utilization
- Irradiation of CH_4 and CO_2 mixture has been modeled for over 200 compounds with over 1600 reactions
- Conversion energy-efficiency peaks at 1:1 CH_4/CO_2 ratio for methane and acetic acid
- Model predicts low residence times and linear scale-up



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